UNIWERSYTET KAZIMIERZA WIELKIEGO W BYDGOSZCZY

**WYDZIAŁ INŻYNIERII MATERIAŁOWEJ**

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# Wybrane właściwości biokompozytów na osnowie polilaktydu zawierających włókna lniane modyfikowane za pomocą związków pochodzenia roślinnego

Rozprawa doktorska

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# Streszczenie

Rozwój biodegradowalnych materiałów kompozytowych wzmacnianych włóknami roślinnymi stanowi istotny kierunek badań w inżynierii materiałowej, wynikający z potrzeby ograniczenia wpływu materiałów polimerowych na środowisko naturalne. Szczególne znaczenie mają kompozyty o podwyższonym stopniu hydrofobowości oraz właściwościach biobójczych, które mogą znaleźć zastosowanie w obszarach wymagających polepszonej odporności na wilgoć i bezpieczeństwa użytkowania.

Teza rozprawy doktorskiej brzmiała następująco: „Zastosowanie naturalnych związków pochodzenia roślinnego takich jak kwas taninowy lub geraniol umożliwi skuteczne modyfikowanie włókien lnianych oraz korzystnie wpłynie na zmianę ich właściwości powierzchniowych, i przyczyni się do wytworzenia biokompozytów o właściwościach biobójczych w stosunku do drobnoustrojów oraz hydrofobowych, nie wpływając negatywnie w sposób znaczący na właściwości mechaniczne. Zastosowanie związków pochodzenia roślinnego będzie sprzyjać właściwościom użytkowym materiałów opakowaniowych i jednorazowego użytku.”

Celem naukowym było określenie wpływu naturalnych związków pochodzenia roślinnego, stosowanych jako modyfikatory włókien lnianych, na właściwości termiczne, mechaniczne, termomechaniczne, biobójcze i hydrofobowe, otrzymanych biokompozytów.

Biokompozyty wytworzono z polilaktydu (PLA), jako biodegradowalnej osnowy, oraz włókien lnianych, poddanych modyfikacji naturalnymi związkami pochodzenia roślinnego – kwasem taninowym lub geraniolem w stężeniach 1%, 5%, 10% oraz 20%. Badania obejmowały określenie właściwości biobójczych za pomocą badań mikrobiologicznych oraz stopnia hydrofobowości biokompozytów na podstawie pomiarów kątów zwilżania. Przeprowadzono analizę właściwości mechanicznych, termomechanicznych, termicznych, a także charakterystykę właściwości powierzchniowych za pomocą skaningowej mikroskopii elektronowej (SEM).

Wykonane badania wykazały, że zastosowanie naturalnych modyfikatorów pochodzenia roślinnego prowadzi do istotnej zmiany zachodzącej na powierzchni biokompozytów. W rezultacie uzyskano materiały o właściwościach biobójczych wobec bakterii *Staphylococcus aureus* oraz *Escherichia coli*, spowodowanych obecnością

bioaktywnych modyfikatorów pochodzenia roślinnego. Jednocześnie stwierdzono, że zmodyfikowane biokompozyty wykazują zwiększony stopień hydrofobowości dla próbek zawierających włókna modyfikowane w 20% roztworze kwasu taninowego jak i geraniolu. Biokompozyty te wykazują również ograniczoną podatność na absorpcję wody.

Oryginalnym wkładem Autorki jest opracowanie biodegradowalnych biokompozytów zawierających włókna lniane modyfikowane za pomocą naturalnych modyfikatorów pochodzenia roślinnego oraz kompleksowa ocena wpływu tej modyfikacji na właściwości biobójcze i hydrofobowe materiałów.

Opracowane biokompozyty stanowią alternatywę dla kompoztywów niebiodegradowalnych, bazujących na polimerach pochodzenia petrochemicznego wytwarzanych na masową skalę. Ze względu na charakterystyczne właściwości uzyskane w wyniku modyfikacji włókien związkami pochodzenia roślinnego, bezpiecznymi dla zdrowia ludzkiego, mogą one przyczynić się do postępu w dziedzinie materiałów jednorazowego użytku, których odpady aktualnie stanowią duże zagrożenie dla środowiska naturalnego. Uzyskane wyniki poszerzają aktualny stan wiedzy w zakresie funkcjonalizacji biokompozytów biodegradowalnych i wskazują na możliwość ich zastosowania w obszarach wymagających materiałów ekologicznych o podwyższonej trwałości i biobójczości. Dzięki interdyscyplinarnemu charakterowi pracy, opracowanie biokompozytów o właściwościach biobójczych oraz hydrofobowych wnosi znaczący wkład zarówno w inżynierię materiałową, jak i mikrobiologię oraz ochronę środowiska.

Rozprawa doktorska została przygotowana na podstawie cyklu artykułów naukowych opublikowanych w czasopismach indeksowanych na liście *Journal Citation Reports* (JCR).

# Abstract

The development of biodegradable composite materials reinforced with plant fibers is an important research direction in materials science, stemming from the need to reduce the environmental impact of polymeric materials. Composites with increased hydrophobicity and biocidal properties are of particular importance, as they can be used in areas requiring improved moisture resistance and safety of use.

The thesis of the doctoral dissertation was as follows: „The use of natural plant-derived compounds such as tannic acid or geraniol will enable the effective modification of flax fibers and favorably influence their surface properties, contributing to the production of biocomposites with biocidal and hydrophobic properties against microorganisms, without significantly negatively affecting mechanical properties. The use of plant-derived compounds will favor the functional properties of packaging and disposable materials."

The scientific goal was to determine the effect of natural plant-derived compounds used as flax fiber modifiers on the thermal, mechanical, thermomechanical, biocidal, and hydrophobic properties of the resulting biocomposites.

Biocomposites were made from polylactide (PLA) as a biodegradable matrix and flax fibers modified with natural plant-derived compounds – tannic acid or geraniol at concentrations of 1%, 5%, 10%, and 20%. The studies included determining biocidal properties through microbiological testing and determining the degree of hydrophobicity of the biocomposites based on contact angle measurements. Analysis of mechanical, thermomechanical, and thermal properties was conducted, as well as characterization of surface properties using scanning electron microscopy (SEM).

These studies demonstrated that the use of natural plant-derived modifiers led to significant changes on the surface of the biocomposites. As a result, the materials were obtained with biocidal properties against *Staphylococcus aureus* and *Escherichia coli*, due to the presence of bioactive plant-derived modifiers. At the same time, it was found that the modified biocomposites exhibited an increased degree of hydrophobicity for samples containing fibers modified with a 20% solution of tannic acid and geraniol. These biocomposites also exhibited limited susceptibility to water absorption.

The author's original contribution is the development of biodegradable biocomposites containing flax fibers modified with natural plant-derived modifiers and

a comprehensive assessment of the impact of this modification on the biocidal and hydrophobic properties of the materials.

The developed biocomposites represent an alternative to non-biodegradable composites based on petrochemical-derived polymers produced on a mass scale. Due to the characteristic properties obtained by modifying fibers with plant-derived compounds, safe for human health, they can contribute to progress in the field of disposable materials, the waste of which currently poses a significant threat to the natural environment. The obtained results expand the current state of knowledge regarding the functionalization of biodegradable biocomposites and indicate the possibility of their application in areas requiring ecological materials with increased durability and biocidal properties. Thanks to the interdisciplinary nature of this work, the development of biocomposites with biocidal and hydrophobic properties makes a significant contribution to both materials engineering, microbiology, and environmental protection.

This doctoral dissertation was prepared based on a series of scientific articles published in journals indexed in the *Journal Citation Reports* (JCR).

# Spis treści

# Spis symboli i akronimów

**BA** – kwas betulinowy (ang. betulinic acid)

**BE** – betulina (ang. betulin)

**$CH_2Cl_2$** – chlorek metylenu

**$CrO_3$** – tlenek chromu(VI)

**$C_3H_6O$** – aceton (propan-2-on)

**$C_4H_6O_3$** – bezwodnik octowy

**$C_5H_5N$** – pirydyna

**$C_5H_8O$** – 3,4-dihydro-2H-piran

**$CO_2$** – dwutlenek węgla

**DMA** – dynamiczna analiza mechaniczna (ang. dynamic mechanical analysis)

**DSC** – różnicowa kalorymetria skaningowa (ang. differential scanning calorimetry)

**DWW** – dwuślimakowa wytłaczarka współbieżna

**E** – moduł sprężystości wzdłużnej

**FDA** – Agencja ds. Żywności i Leków (ang. Food Drug Administartion)

**GR** – geraniol

**GRAS** – Powszechnie Uznawane za Bezpieczne (ang. Generally Recognized As Safe)

**$HNO_3$** – kwas azotowy (V)

**$H_2CrO_4$** – kwas chromowy

**$H_2O$** – woda

**$H_2SO_4$** – kwas siarkowy

**$KMnO_4$** – nadmanganian potasu

**$K_2CO_3$** – węglan potasu

**MeOH** – metanol

**MFR** – masowy wskaźnik szybkości płynięcia (ang. melt flow rate)

**$NaBH_4$** – borowodorek sodu

**NMR** – spektroskopia magnetycznego rezonansu jądrowego

**PE** – polietylen

**PLA** – polilaktyd

**PPTS** – pirydyniowy p-toluenosulfonian

**R** – współczynnik redukcji

**SEM** – skaningowa mikroskopia elektronowa (ang. scanning electron microscopy)

**TA** – kwas taninowy (ang. tannic acid)

**TG** – termograwimetria (ang. thermogravimetry)

**$U_t$** – średni logarytm liczby żywych bakterii odzyskanych z próbek kontrolnych po 24 h

**UV** – promieniowanie ultrafioletowe (ang. ultraviolet radiation)

**$U_0$** – średni logarytm liczby żywych bakterii odzyskanych z próbek kontrolnych bezpośrednio po szczepieniu

**v** – objętość kropli

**W** – średni logarytm liczby żywych bakterii odzyskanych z próbek badanych po 24 h

**$X_c$** – stopień krystaliczności

**ZnO** – tlenek cynku

$\mathbf{\Delta H_m}$ – zmiana entalpii procesu topnienia

$\mathbf{\Delta H_{cc}}$ – zmiana entalpii procesu zimnej krystalizacji

$\mathbf{\Delta H_{m100\%}}$ – zmiana entalpii procesu topnienia 100% krystalicznego PLA wynosząca 93,6 J/g

**Δv** – prędkość dozowania kropli

$\Theta_w$ – kąt zwilżania wodą

# Forma rozprawy doktorskiej i wkład doktorantki

Rozprawa doktorska pt. *Wybrane właściwości biokompozytów na osnowie polilaktydu zawierających włókna lniane modyfikowane za pomocą związków pochodzenia roślinnego* została opracowana na podstawie czterech oryginalnych artykułów opublikowanych w recenzowanych czasopismach naukowych indeksowanych w bazie Journal Citation Reports (JCR), uwzględnionych w wykazie czasopism przez Ministerstwo Nauki i Szkolnictwa Wyższego:

[A] **A. Pawłowska**, M. Stepczyńska, „Natural biocidal compounds of plant origin as biodegradable materials modifiers", *J Polym Environ* 2021, t. 30, nr 5, s. 1683–1708, doi: 10.1007/s10924-021-02315-y.

[B] **A. Pawłowska**, M. Stepczyńska, M. Walczak, „Flax fibres modified with a natural plant agent used as a reinforcement for the polylactide-based biocomposites", *Industrial Crops and Products* 2022, t. 184, s. 115061, doi: 10.1016/j.indcrop.2022.115061.

[C] **A. Pawłowska**, M. Stepczyńska, „The changes in selected properties of flax fibre-reinforced biocomposites affected by plant modifier concentration", *Composites Science and Technology* 2024, t. 257, s. 110829, doi: 10.1016/j.compscitech.2024.110829.

[D] **A. Pawłowska**, M. Stepczyńska, V. Krasinskyi, J. Pach, „Antibacterial and hydrophobic PLA biocomposites enabled by geraniol-modified flax fibres", *Polymers* 2026, t. 18, nr 2, s. 183, doi: 10.3390/polym18020183.

Oświadczenia współautorów publikacji, potwierdzają następujący wkład Doktorantki w ich powstanie:

Publikacja [A] – wkład Doktorantki polegał na zapoznaniu się z tematyką naturalnych związków biobójczych, opracowaniu struktury artykułu przeglądowego, przygotowaniu i edycji tekstu artykułu, rysunków oraz nanoszeniu poprawek wymaganych po otrzymanych recenzjach.

Publikacja [B] – wkład Doktorantki polegał na modyfikacji włókien lnianych w 20% roztworze kwasu taninowego (TA), przygotowaniu próbek do badań zawierających włókna modyfikowane, wykonaniu badań mechanicznych – statycznej próby rozciągania, termomechanicznych – dynamicznej analizy mechanicznej (DMA), termicznych – analizy termograwimetrycznej (TG) i różnicowej kalorymetrii skaningowej (DSC) oraz badań powierzchniowych – zwilżalności i skaningowej mikroskopii elektronowej (SEM). Ponadto, doktorantka wykonała niezbędne obliczenia, interpretację wyników i ich graficzne przedstawienie. Opracowała również strukturę artykułu, przygotowała i edytowała tekst artykułu oraz naniosła poprawki wymagane po otrzymaniu recenzji.

Publikacja [C] – wkład Doktorantki polegał na modyfikacji włókien lnianych w 1%, 5%, 10% i 20% w roztworze TA, przygotowaniu próbek do badań zawierających włókna modyfikowane, wykonaniu badań mechanicznych – statycznej próby rozciągania, termomechanicznych – DMA, termicznych – TG i DSC oraz badań powierzchniowych – zwilżalności. Ponadto, doktorantka wykonała niezbędne obliczenia, interpretację wyników i ich graficzne przedstawienie. Opracowała również strukturę artykułu, przygotowała i edytowała tekst artykułu oraz naniosła poprawki wymagane po otrzymaniu recenzji.

Publikacja [D] – wkład Doktorantki polegał na modyfikacji włókien lnianych w 1%, 5%, 10% i 20 % roztworze geraniolu (GR), przygotowaniu próbek do badań zawierających włókna modyfikowane, wykonaniu badań mechanicznych – statycznej próby rozciągania, termomechanicznych – DMA, termicznych – TG i DSC oraz badań powierzchniowych – zwilżalności i SEM. Ponadto, doktorantka wykonała niezbędne obliczenia, interpretację wyników i ich graficzne przedstawienie. Opracowała również strukturę artykułu, przygotowała i edytowała tekst artykułu.

# Teza badawcza i cele rozprawy doktorskiej

Na podstawie analizy literatury oraz wyników badań własnych sformułowano następującą ***tezę*** rozprawy:

*Zastosowanie naturalnych związków pochodzenia roślinnego takich jak kwas taninowy lub geraniol umożliwi skuteczne modyfikowanie włókien lnianych oraz korzystnie wpłynie na zmianę ich właściwości powierzchniowych, i przyczyni się do wytworzenia biokompozytów o właściwościach biobójczych w stosunku do drobnoustrojów oraz hydrofobowych, nie wpływając negatywnie w sposób znaczący na właściwości mechaniczne. Zastosowanie związków pochodzenia roślinnego będzie sprzyjać właściwościom użytkowym materiałów opakowaniowych i jednorazowego użytku.*

Na podstawie opracowanej tezy sformułowano następujące ***cele***:

***Cel naukowy***:

Określenie wpływu naturalnych związków pochodzenia roślinnego, stosowanych jako modyfikatory włókien lnianych, na wybrane właściwości otrzymanych biokompozytów takie jak termiczne, mechaniczne, termomechaniczne, biobójcze i hydrofobowe.

***Cele utylitarne***:

- Zmiana właściwości hydrofilowych na hydrofobowe włókien lnianych, poprzez ich modyfikacje naturalnymi związkami roślinnymi.
- Oszacowanie możliwości wykorzystania naturalnych związków roślinnych jako modyfikatorów włókien lnianych, w celu walki z mikroorganizmami.
- Scharakteryzowanie właściwości otrzymanych biokompozytów z różną zawartością naturalnych związków biobójczych, w celu określenia ich potencjału aplikacyjnego.
- Uzyskanie niezbędnego doświadczenia i wiedzy umożliwiających opracowanie wytycznych dotyczących modyfikowania włókien lnianych naturalnymi związkami

roślinnymi o właściwościach biobójczych przeznaczonych do wytworzenia biokompozytów polilaktydowych.

- Uzyskanie niezbędnego doświadczenia i wiedzy umożliwiających opracowanie wytycznych dotyczących wytwarzania całkowicie biodegradowalnych materiałów wykazujących właściwości biobójcze w stosunku do drobnoustrojów.

# 1. Wstęp

## *1.1. Uzasadnienie wyboru tematu*

Wraz z rozwojem gospodarczym oraz z ciągłym postępem technicznym rośnie zapotrzebowanie na materiały inżynieryjne o nowych właściwościach. Dotychczas stosowane tradycyjne materiały tj. szkło, papier, drewno i metale, są zastępowane przez materiały polimerowe, których wszechobecne zastosowanie w różnych dziedzinach życia i branżach przemysłu jest cechą charakterystyczną dzisiejszych czasów. Niestety ich odporność na czynniki środowiskowe stanowi poważny problem ekologiczny, gdyż nieustannie zwiększająca się ilość odpadów z materiałów polimerowych obciąża środowisko naturalne [1], [2].

Nieustające zainteresowanie materiałami polimerowymi spowodowane jest ich licznymi zaletami jak: łatwością kształtowania, stosunkowo niskim kosztem produkcji, niską masą i przewodnością cieplną oraz odpornością na korozję. Ze względu na niską cenę, materiały polimerowe cieszą się największym zainteresowaniem w przemyśle opakowaniowym, gdzie stanowią ponad 60% opakowań artykułów żywnościowych. Według United Nations Environment Programme, UNEP (Program Organizacji Narodów Zjednoczonych [ONZ] ds. Środowiska), aktualnie produkcja „plastiku" jest na poziomie ok. 400 mld t rocznie i zgodnie z przewidywaniami do 2050 roku zwiększy się ponad dwukrotnie. Tymczasem już w tej chwili nie jesteśmy w stanie poradzić sobie z przetworzeniem ogromnej ilości odpadów, które powstają po zakończeniu użytkowania produktów wykonanych z materiałów polimerowych. Na całym świecie co roku generowane jest około 350 milionów ton odpadów polimerowych, z których zaledwie 9% jest przetwarzana ponownie. Pozostała większość trafia na wysypiska, do spalarni lub w wyniku niewłaściwego zarządzania przedostaje się do środowiska naturalnego, w tym do oceanów. Odpady tego typu stanowią poważne zagrożenie dla natury i zdrowia ludzi [3]. Troska o środowisko naturalne i chęć rozwiązania kwestii zalegających odpadów z materiałów polimerowych spowodowała zainteresowanie biopolimerami zarówno w przemyśle jak i w nauce.

Również przepisy prawne, Dyrektywy Parlamentu Europejskiego i Rady UE (2018/851 z dnia 30 maja 2018 r. zmieniająca dyrektywę 2008/98/WE w sprawie odpadów) spowodowały, że polimery pochodzące z ropy naftowej coraz częściej zastępuje się polimerami pochodzenia naturalnego wytwarzanych z surowców

odnawialnych, np. kukurydzy, które ulegają rozkładowi na składniki mineralne, wodę i gazy.

Kolejną przyczyną opracowywania metod produkcji biopolimerów są ograniczone zasoby ropy naftowej, będącej surowcem do produkcji większości syntetycznych materiałów polimerowych. Materiały te stanowią przeważającą część obecnie produkowanych materiałów polimerowych [4]. Kończące się zasoby surowców kopalnych na świecie zapoczątkowały nowe trendy w zakresie inżynierii materiałowej, a mianowicie korzystanie z surowców z alternatywnych źródeł i materiałów. Dlatego podjęto próby stworzenia biopolimerów z surowców odnawialnych, dostępnych na całym świecie.

Wśród biopolimerów największym zainteresowaniem cieszy się polilaktyd (PLA) – całkowicie biodegradowalny polimer pozyskiwany między innymi ze skrobi kukurydzianej. Produkcja „zielonych" polimerów z surowców odnawialnych oparta jest głównie na PLA, którego udział stanowi około $\frac{2}{5}$ łącznej ilości wytwarzanych biopolimerów [5]. Od końca lat sześćdziesiątych XX wieku stosowany był głównie w medycynie (np. bioresorbowalne nici chirurgiczne), obecnie ze względu na swoje właściwości biodegradacyjne znalazł również zastosowanie w przemyśle opakowaniowym, jako materiał jednorazowego użytku (np. kubki, sztućce, talerzyki). Wyroby z PLA ulegają procesowi biodegradacji w warunkach kompostowania przemysłowego (rozkład pod wpływem mikroorganizmów, w odpowiedniej wilgotności i temperaturze powietrza) w ciągu około 2,5 miesiąca. Biodegradacja PLA jest kilkuetapowa. Końcowym etapem procesu biodegradacji jest całkowity rozpad materiału z wytworzeniem dwutlenku węgla ($CO_2$), $H_2O$ i biomasy. Dany proces jest ekologiczny i nie zanieczyszcza środowiska przy odpowiednim zarzadzaniu odpadami [6], [7].

PLA ma wiele zalet w porównaniu z konwencjonalnymi materiałami termoplastycznymi. Wykazuje dobre właściwości optyczne, mechaniczne i barierowe nawet w porównaniu z polimerami na bazie ropy naftowej. Pomimo wielu zalet PLA, wysoka kruchość, niska stabilność termiczna i udarność ograniczają niektóre jego zastosowania. Gotowe wyroby z PLA cechują się dobrymi właściwości eksploatacyjnymi, niemniej jednak przechowywanie gazowanych napojów w butelkach z PLA jest niemożliwe, ponieważ materiał ten jest niezdolny do utrzymania dwutlenku węgla obecnego w takiego rodzaju napojach. Dlatego w celu poprawy wybranych

parametrów PLA, a także w celu zwiększenia wytrzymałości mechanicznej gotowych wyrobów stosuje się różnego rodzaju dodatki w postaci napełniaczy lub środków pomocniczych, tworzących kompozyt o osnowie polimerowej.

Dotychczas najczęściej stosowanymi napełniaczami były włókna szklane, jednak zważywszy na potrzebę stosowania materiałów całkowicie biodegradowalnych, wiele projektów naukowych i przemysłowych skupia się na wykorzystaniu wypełniaczy pochodzenia roślinnego [8] do produkcji biodegradowalnych biokompozytów [9]. Coraz powszechniejsze staje się stosowanie kompozytów z włóknami naturalnymi, ze względu na ich stosunkowo niski koszt, niską gęstość, łatwość separacji, ulepszony odzysk energii, czy biodegradowalność. Są trwałe, niezawodne, lekkie i mają lepsze niż tradycyjne materiały właściwości mechaniczne. Dlatego w różnych gałęziach przemysłu, takich jak motoryzacja, budownictwo, opakowania, farmacja, biotechnologia czy ogrodnictwo rośnie zapotrzebowanie na włókna naturalne. Rosnące znaczenie kompozytów z włóknami naturalnymi znajduje odzwierciedlenie w rosnącej liczbie publikacji naukowych w ostatnich latach, w tym książkach i patentach.

W celu zwiększenia wytrzymałości mechanicznej gotowych wyrobów, jako napełniacze stosuje się włókna roślinne takie jak: włókna lniane, konopne, bambusowe, bawełniane, juta, sizal, kapok i inne [10]. Dzięki polepszonym właściwościom wzmocnione kompozyty mają szersze spektrum zastosowań w branżach, gdzie kompozyty są poddawane stałym obciążeniom mechanicznym. Jednak wydajność kompozytów polimerowych wzmocnionych włóknami naturalnymi zależy od kilku czynników m. in. od składu chemicznego włókien, wymiarów komórek krystalicznych, struktury, właściwości fizycznych i mechanicznych włókien, a także interakcji włókna z polimerem. Wysoki współczynnik kształtu (długość/szerokość) jest bardzo ważny w kompozytach włóknistych na bazie celulozy, ponieważ wskazuje na możliwe właściwości wytrzymałościowe. Wytrzymałość włókien jest ważnym czynnikiem przy wyborze konkretnego włókna naturalnego do określonego zastosowania.

Jednym z ważniejszych kryteriów doboru poszczególnych elementów kompozytu jest kompatybilność osnowy polimerowej i napełniaczy. Głównymi wadami włókien naturalnych w kompozytach jest słaba kompatybilność między włóknem a osnową oraz ich stosunkowo wysoka absorpcja wilgoci. Hydrofilowe włókna roślinne i względnie hydrofobowa osnowa polimerowa są termodynamicznie niemieszalne, co powoduje słabą adhezję międzyfazową i w efekcie małą wytrzymałość mechaniczną tych kompozytów.

Ta adhezja międzyfazowa znacząco wpływa na końcowe właściwości mechaniczne kompozytów, ponieważ przenoszenie naprężeń pomiędzy osnową a włóknami decyduje o skuteczności wzmocnienia.

Dotychczas włókna naturalne były często poddawane obróbce chemicznej poprzez merceryzację, silany, kwas maleinowy lub acetylację, w celu oczyszczenia i/lub modyfikacji energii powierzchniowej, żeby zwiększyć przyczepność międzyfazową z matrycą polimerową. Jednak te zabiegi są procesami czasochłonnymi i kosztownymi, niosącymi ze sobą również pewne ryzyko ekologiczne. Z uwagi na przedstawione problemy, opracowanie nowych metod poprawy adhezji między włóknami roślinnymi a makrocząsteczkami PLA jest niezmiernie istotne ze względów naukowych, ekonomicznych i społecznych.

Pomimo postępów w dziedzinie biokompozytów na bazie surowców roślinnych, wciąż istnieje brak szczegółowych informacji na temat wpływu modyfikacji związkami roślinnymi na właściwości tych materiałów. Badania w tej dziedzinie mogą przyczynić się do lepszego zrozumienia mechanizmów interakcji między poszczególnymi fazami biokompozytu oraz identyfikacji optymalnych warunków modyfikacji włókien w celu uzyskania pożądanych właściwości biokompozytów. Jest to istotne nie tylko dla rozwoju nowych materiałów, ale także dla zwiększenia efektywności produkcji i ograniczenia negatywnego wpływu na środowisko.

Wielofunkcyjne materiały i kompozyty o zaawansowanych właściwościach to przyszłość. Społeczeństwo oczekuje, że stosowane przez nich materiały będą pełnić kilka funkcji na raz. Będą trwałe, wytrzymałe, nietoksyczne, biodegradowalne i będą przeciwdrobnoustrojowe.

W dzisiejszych czasach istnieje konieczność ciągłej i powtarzającej się sterylizacji różnego typu produktów, w tym powierzchni (siedziska, w czasie pandemii w szczególności), tacek opakowań, czy też instrumentarium medycznego. Najczęściej do sterylizacji sprzętu medycznego, jak również różnych opakowań (w tym produktów spożywczych) stosowane są promienie gamma oraz metody dezynfekcji za pomocą środków chemicznych. Niestety często materiały biodegradowalne, biokompozyty, nie są odporne na działanie powyższych czynników, a stosowane związki chemiczne często zmieniają ich właściwości i trwałość. Ponadto pozostałości związków dezynfekcyjnych na powierzchniach urządzeń stosowanych w medycynie (np. instrumentarium) czy w opakowalnictwie mają istotny wpływ na zdrowie ludzi.

Natomiast sterylizowanie promieniami gamma jest techniką wymagającą dużego nakładu finansowego oraz czasu. Z tych względów uzasadnione jest zastosowanie naturalnych związków roślinnych, które wykazują działanie biobójcze, jednocześnie nie wpływając negatywnie na właściwości fizykochemiczne materiałów oraz zdrowie konsumentów.

Modyfikacja włókien roślinnych w celu zmiany ich właściwości i kształtowania nowych, stosując do tego naturalne związki roślinne o właściwościach biobójczych jest elementem innowacyjności i będzie działaniem na rzecz rozwoju cywilizacyjnego naszego kraju i świata oraz przyczyni się do rozwoju inżynierii materiałowej. Połączenie odpowiednio zmodyfikowanych włókien z PLA i wytworzenie bioproduktu, który łączy cechy użytkowe – praktyczne (dla społeczeństwa) z dodatkowymi, jak ochrona przed mikroorganizmami, jest w dzisiejszych czasach mocno poszukiwanymi rozwiązaniami.

Podsumowując, przedmiotem niniejszej pracy było opracowanie biokompozytów zawierających włókna modyfikowane naturalnymi związkami pochodzenia roślinnego w celu poprawy wybranych właściwości gotowych materiałów. Zagadnienia związane z opracowaniem nowoczesnych materiałów biodegradowalnych, biokompozytów, których znaczenie użytkowe gwałtownie wzrasta i które wykazywać będą działanie biobójcze w stosunku do drobnoustrojów, a także zwiększoną hydrofobowość.

### *1.2. Sposób realizacji celów rozprawy*

Weryfikacja tezy rozprawy wymagała wykonania wielu badań, dlatego zostały podzielone na dwie części: rozpoznawczą i zasadniczą. Głównym celem badań rozpoznawczych było ustalenie odpowiedniej metodyki i zakresu badań zasadniczych. Natomiast celem badań zasadniczych była weryfikacja tezy rozprawy oraz osiągnięcie jej celów poznawczych i utylitarnych. Poszczególne rodzaje badań zrealizowano w następujących jednostkach naukowych:

- Próbki do badań rozpoznawczych wytworzono w Instytucie Inżynierii Materiałów Polimerowych i Barwników w Toruniu.
- Próbki do części badań zasadniczych wytworzono na Wydziale Mechanicznym Politechniki Wrocławskiej, a w późniejszym okresie na Wydziale Inżynierii Materiałowej Uniwersytetu Kazimierza Wielkiego w Bydgoszczy. Jest to

związane z zakupem przez Katedrę Materiałów Polimerowych wytłaczarki dwuślimakowej.

- Określenie odpowiednich stężeń wybranych środków biobójczych, a także badania mikrobiologiczne biokompozytów wykonano przy współpracy z Wydziałem Nauk Biologicznych i Weterynaryjnych Uniwersytetu Mikołaja Kopernika w Toruniu.
- Badania termiczne, mechaniczne, termo-mechaniczne, zwilżalności, powierzchniowe wykonane zostały w Katedrze Materiałów Polimerowych na Wydziale Inżynierii Materiałowej Uniwersytetu Kazimierza Wielkiego w Bydgoszczy.

### *1.3. Wybrane dodatki pochodzenia roślinnego*

Modyfikacje materiałów polimerowych są wykonywane w celu poprawy właściwości użytkowych lub nadania pożądanych cech gotowym wyrobom. Cechy te różnią się i zmieniają w zależności od branży, w której materiały polimerowe zostaną wykorzystane i funkcji jaką będą pełnić. Modyfikacja struktury materiałów polimerowych jest najbardziej powszechnym sposobem nadania gotowym wyrobom unikatowych cech oraz polepszenia wybranych parametrów. Jedną z metod zmiany struktury materiałów jest stosowanie dodatków modyfikujących, wprowadzanych w materiał w procesie wytwarzania. Dążenie do zminimalizowania ilości wprowadzanych dodatków przyczyniło się do opracowywania modyfikatorów, które nadawać będą więcej niż jedną nową funkcję materiału.

Ponieważ w artykule przeglądowym [A] przedstawiono obszerną analizę dodatków stosowanych w przetwórstwie materiałów polimerowych, zdecydowano, że w danym rozdziale, w celu otrzymania spójności pracy, omówione zostaną pokrótce tylko te, które stosowane były w pracy badawczej, zasadniczej.

Istnieją grupy dodatków, które stosowane w przetwórstwie materiałów polimerowych, poprawiają ich właściwości mechaniczne, a także nadają zupełnie nowe – biobójcze. Jak już wspomniano, ze względu na panującą sytuację epidemiologiczną i konieczność sterylizacji różnego typu powierzchni wytwarzanych z materiałów biodegradowalnych, rośnie zainteresowanie w świecie naukowym i przemyśle dodatkami pochodzenia roślinnego i o działaniu biobójczym.

Zgodnie z normą ISO 22196 [11] za materiały biobójcze uznaje się takie, które powodują zmniejszenie liczebności żywych i zdolnych do wzrostu komórek bakteryjnych *Escherichia coli* oraz *Staphylococcus aureus* o dwa rzędy wielkości. W języku potocznym jest rozumiane jako cecha, powodująca zatrzymanie namnażania się bakterii mających kontakt z materiałem [12].

Wzrost świadomości społeczeństwa na temat zanieczyszczeń środowiska oraz chęć troski o stan Planety i własne zdrowie spowodował, że w dzisiejszych czasach dodatkom modyfikującym postawiono więcej kryteriów, które muszą spełniać. Nie tylko powinny być trwałe i nie zmieniać właściwości materiałów, ale przede wszystkim muszą być nietoksyczne dla ludzkiego zdrowia i środowiska [13]. Branże (medyczna, spożywcza, przemysł opakowaniowy), w których jest rozpowszechnione stosowanie materiałów polimerowych, znajdują się w ścisłym kontakcie z organizmem ludzkim. Zastosowania materiałów polimerowych w danych branżach jest zależne między innymi od składników, wchodzących w ich skład – wszystkie dodatki obecne w materiale muszą być nie tylko nietoksyczne, ale również naturalne. Dlatego tak ważne jest poszukiwanie nowych rozwiązań, które będą spełniały wszystkie stawiane im wymagania.

Tworzenie biokompozytów o osnowie polimerowej z PLA i dodatkami pochodzenia naturalnego stanowi obiecujący nurt w dziedzinie inżynierii materiałowej. Nowy obszar w tworzeniu biodegradowalnych biokompozytów intensywnie się rozwija i ma potencjał do bycia materiałem, który zostanie wprowadzony do użytku codziennego.

Analiza literatury [14], [15], [16], [17], [18], [19], [20] pozwoliła na zaobserwowanie panujących trendów w przemyśle materiałów polimerowych i stworzenie klasyfikacji stosowanych dodatków pochodzenia naturalnego na podgrupy, zawierające substancje organiczne [21]. Podczas wyboru dodatków roślinnych jak kwas taninowy lub geraniol, kierowano się kilkoma kryteriami: przede wszystkim muszą być naturalne (roślinne), muszą rozpuszczać się w wodzie (brak pozostałości związków chemicznych), wykazywać właściwości biobójcze oraz sieciujące, muszą być bezpieczne, nietoksyczne oraz biodegradowalne.

### *1.3.1. Kwas taninowy*

Kwas taninowy jest substancją występującą powszechnie w środowisku naturalnym, a mianowicie w roślinach. Zauważono, że substancja ta występuje prawie we wszystkich częściach naziemnych roślin [22]. Najbogatszym źródłem kwasu taninowego są galasy, czyli stwardniałe struktury w formie narośli na liściach dębu, będące skutkiem żerowania niektórych rodzajów owadów, a także produktami ubocznymi wytwarzanymi przez roztocza, grzyby, bakterie. Galasy występują nie tylko na dębach, ale również na różach, jabłoniach, wierzbach, topolach, bukach, akacjach, sekwojach i drzewach pistacjowych [23], [24], [25]. Ponadto, kwas taninowy występuje również w korze orzecha (powszechnie występującego w naszym regionie), a także sosny i mahoniowca. Jest również składnikiem truskawek i pokrzywy [25].

Charakterystyczny cierpki smak niektórych owoców: czarnych jagód, winogron, jeżyn, żurawiny, jest zasługą danej substancji. Właściwość ta chroni owoce przed zniszczeniem przez szkodniki, dla których cierpki smak jest nieodpowiedni [25].

Kwas taninowy występuje w postaci bezzapachowego krystalicznego proszku o kolorze beżowym i masie molowej 1701,20 $g/mol^{-1}$ [26]. Rozpuszcza się w wodzie i rozpuszczalnikach organicznych. W kontakcie z $H_2O$ nabiera lepkości i ciągliwości podobnej do karmelu. Podczas rozpuszczania w rozpuszczalnikach organicznych tworzy silnie barwiący roztwór o ciemnobrązowym kolorze. Zapach takiego roztworu może być skojarzony z przyjemnym zapachem herbaty ziołowej. Jest również substancją mocno ściągającą i wysuszającą skórę [27].

Temperatura rozkładu kwasu taninowego przekracza 210°C, co sprawia, że nadaje się do modyfikowania włókien i stosowania w biokompoztach PLA ze względu na niższe temperatury jego przetwórstwa. Kwas taninowy jest substancją bezpieczną. Został umieszczony przez Amerykańską Agencję ds. Żywności i Leków (FDA – *ang. Food Drug Administartion*) na liście GRAS (*ang. Generally Recognized As Safe*), co oznacza substancje powszechnie uznawaną za bezpieczną i odnosi się do składników dodawanych do żywności lub substancji chemicznych uznawanych przez ekspertów za bezpieczne [28].

Substancja charakteryzuje się właściwościami bakteriostatycznymi w stosunku do niektórych szczepów bakterii Gram-ujemnych (*Cytophaga columnaris, Helicobacter pylori, Escherichia coli i Klebsiella pneumoniae*) i Gram-dodatnich (*Staphylococcus*

*aureus, Listeria monocytogenes i Bacillus subtilis*) [29], [30], [31]. Obróbka termiczna kwasu taninowego wzmacnia właściwości bioaktywne, co zostało udowodnione w [30].

Kwas taninowy należy do substancji o szerokim spektrum zastosowań. w przemyśle spożywczym wykorzystywany jest jako środek klarujący wina i piwa [22] w celu zapobiegania powstania i rozwoju drobnoustrojów. Substancja ta, wykazująca wpływ ściągający na skórę może zostać wykorzystana w branży farmakologicznej, jako potencjalny składnik preparatów tamujących krwawienie [27]. Właściwości ściągające kwasu taninowego oddziaływują również na błonę komórkową bakterii, hamując procesy metaboliczne zachodzące w bakteriach.

Kwas taninowy od wieków znajduje zastosowanie w garbowaniu skóry zwierząt. Dzięki temu chroni ją przed procesami gnilnymi oraz zwiększa jej odporność termiczną. Warto zauważyć, że wyrabianie skóry z wykorzystaniem garbników jest naturalne i nie prowadzi do produkcji toksycznych substancji. Kwas taninowy stosuje się jako warstwę ochronną, którą powlekane są owoce. Taka osłona ogranicza ich dojrzewanie i wydłuża czas na ich spożycie.

Kwas taninowy jest również środkiem sieciującym, zwiększającym adhezję pomiędzy osnową polimerową i włóknami, co sprawia, że kompozyty te są bardziej odporne na obciążenia mechaniczne [32], [33]. Kwas taninowy jest obiecującym związkiem bioaktywnym stosowanym w przemyśle opakowaniowym ze względu na brak toksyczności. Opakowania biodegradowalne domieszkowane tą substancją wykazującą właściwości zarówno bioaktywne jak i przeciwutleniające [31].

### *1.3.2. Geraniol*

Geraniol, podobnie jak kwas taninowy, jest związkiem powszechnie występującym w świecie roślin. Jest to naturalny związek biobójczy stanowiący jeden ze składników wielu olejków eterycznych (różanego, pelargoniowego, lawendowego, cytrynowego, imbirowego i pomarańczowego), odpowiadający za ich charakterystyczny, przyjemny zapach [34]. Jego najbogatszymi i najbardziej znanymi źródłami są olejek różany, pozyskiwany z płatków róży damasceńskiej, oraz olejek palmarozowy z trawy palczatki imbirowej, w którym jego stężenie może przekraczać 70% [35], [36]. W znaczących ilościach występuje również w olejku z geranium, trawy cytrynowej oraz cytroneli. Ponadto, geraniol jest obecny w mniejszych stężeniach w ponad 250 różnych

olejkach eterycznych [37]. Jego najbardziej charakterystyczną cechą jest intensywny, słodki zapach, powszechnie kojarzony z różą.

Geraniol w warunkach standardowych występuje jako bezbarwna lub bladożółta, oleista ciecz o masie molowej 154,25 g/mol$^{-1}$ [38]. Proces rozkładu geraniolu zaczyna się w temperaturze ok. 200°C, co sprawia ze jego przetwarzanie termiczne w celu uzyskania biokompozytów jest możliwe [39].

Geraniol wykazuje szerokie spektrum działania biobójczego zarówno wobec bakterii Gram-ujemnych, takich jak *Escherichia coli*, *Salmonella Typhimurium*, *Pseudomonas aeruginosa* i *Helicobacter pylori*, jak również wobec bakterii Gram-dodatnich, w tym *Staphylococcus aureus*, *Listeria monocytogenes*, *Bacillus subtilis* oraz *Enterococcus faecalis* [40], [41].

Oprócz silnych właściwości biobójczych, geraniol jest znany ze swojej nietoksyczności (zgodnie z 21 Kodeksem Przepisów Federalnych, Agencji ds. Żywności i Leków [42]), właściwości przeciwutleniających i kojących, co sprawiło, że jest szeroko stosowany w przemyśle kosmetycznym [43], [44]. Jednak jego interakcja z polimerami nie została w pełni zbadana, co czyni ten naturalny środek biobójczy interesującym przedmiotem badań.

# 2. Metodyka badań

## *2.1. Materiały*

Przygotowane biokompozyty składały się z osnowy, wzmocnienia oraz modyfikatora poprawiającego wybrane właściwości gotowych biokompozytów. Jako osnowę zastosowano PLA typu 2003D firmy Cargill Down LLC (Stany Zjednoczone) o następującej zawartości merów: D - 3,5%, L - 96,5% [45]. Masowy wskaźnik szybkości płynięcia (MFR, ang. melt flow rate) PLA został zbadany przy temperaturze 190°C oraz masie obciążnika równej – 2,16 kg. Wartość MFR wyniosła 4,2 g/10 min. Wykorzystany PLA charakteryzował się gęstością (ρ) na poziomie 1,24 g/cm$^3$. Ilość PLA zawartego w próbkach wynosiła 80% wag. (w/w).

Jako wzmocnienie zastosowano cięte włókna lniane (*Linum usitatissimum*) o długości 5 mm. Włókna te zostały wyprodukowane w Polsce przez firmę Ekotex. Na podstawie obszernej analizy literatury, dotyczącej ilości włókien roślinnych zawartych w biopolimerze, wybrano optymalną ilość wzmocnienia wynoszącą 20% w/w. Jednocześnie jest to maksymalna ilość włókien lnianych, która może być zawarta w biokompozycie, ponieważ przekroczenie tej wartości skutkuje pogorszeniem właściwości mechanicznych materiału, a mianowicie obniżeniem wytrzymałości na rozciąganie biokompozytu [9], [45].

Jako modyfikatory wybrano związki pochodzenia roślinnego, które naturalnie występują w niektórych roślinach, są bezpieczne (nietoksyczne) i nie wpływają negatywnie na środowisko naturalne:

- Kwas taninowy (TA) o wzorze chemicznym $C_{76}H_{52}O_{46}$ wyprodukowany przez firmę Sigma-Aldrich w Polsce.
- Geraniol (GR) o wzorze chemicznym $C_{10}H_{18}O$ wyprodukowany przez firmę Thermo Scientific w Stanach Zjednoczonych.

## *2.2. Przygotowanie roztworu*

Pierwszym etapem przygotowania próbek było sporządzenie roztworu modyfikującego (wodnego roztworu kwasu taninowego oraz wodnego roztworu geraniolu). Ze względu na różne postacie tych modyfikatorów (kwas taninowy – proszek,

geraniol – ciecz) ich ilość została zmierzona w odpowiednio – gramach lub mililitrach. Roztwory te przygotowano w następujących stężeniach (tabela 1).

*Tabela 1. Poszczególne składniki roztworu modyfikującego wraz ze stężeniami.*

| **Stężenie roztworu [%]** | **$H_2O$ [ml]** | **Modyfikator [ml/g]** |
|---|---|---|
| 1 | 1782 | 18 |
| 5 | 1710 | 90 |
| 10 | 1620 | 180 |
| 20 | 1440 | 360 |

Do szklanej zlewki z wodą destylowaną podgrzaną do 80°C wprowadzono modyfikator (TA lub GE) i mieszano z prędkością obrotową 1500 obr/min. Mieszanie wykonano przy użyciu mieszadła magnetycznego z grzaniem i czujnikiem temperatury (LLG-uniSTIRRER 3, LLG-Labware, Niemcy). Podwyższona temperatura roztworu ułatwiła rozpuszczenie modyfikatora. Po jego wstępnym rozpuszczeniu w wodzie, temperaturę roztworu obniżono do 50°C i kontynuowano mieszanie przez 1h.

### *2.3. Przygotowanie matrycy*

W celu dokładnego wysuszenia osnowy polimerowej z PLA zastosowano suszarkę laboratoryjną (SUP-100 G, Wamed, Polska). PLA suszono przez 12h w temperaturze 50°C. Wstępne suszenie matrycy miało zapobiec powstaniu pustych przestrzeni (pęcherzy), które zwiększają stopień porowatości materiałów. Zwiększona porowatość próbek najczęściej skutkuje pogorszeniem się właściwości mechanicznych biokompozytów.

### *2.4. Przygotowanie włókien*

Następnym etapem prac było odpowiednie przygotowanie włókien lnianych oraz ich modyfikacja. Włókna te poddano suszeniu w suszarce laboratoryjnej w temperaturze 60°C przez 12h. Usunięcie nadmiaru wilgoci z poszczególnych części biokompozytu zapewniło większą przyczepność wzmocnienia do osnowy.

W uprzednio przygotowanym roztworze zanurzono włókna lniane na czas 12h. Po upływie 12h przebywania włókien w roztworze modyfikującym, nadmiar roztworu usunięto (odsączono za pomocą sita), a zmodyfikowane włókna pozostawiono do powolnego odsączania na kolejne 12h. Następnie, zmodyfikowane włókna poddano suszeniu w suszarce laboratoryjnej przez 30h w temperaturze 60°C. w celu zapewnienia równomiernego suszenia się włókien zastosowano mieszanie ręczne. w ciągu pierwszych 4h suszenia wykonano 2 mieszania (co drugą godzinę). Następne mieszanie, będące ostatnim, nastąpiło po 20h od rozpoczęcia suszenia. Opisana metoda modyfikacji włókien została objęta ochroną patentową [46].

### *2.5. Przygotowanie biokompozytu*

Proces przygotowania próbek polegał na połączeniu osnowy polimerowej i jej wzmocnienia w postaci zmodyfikowanych włókien lnianych oraz włókien niezmodyfikowanych (próbki kontrolne). Przygotowanie próbek wykonano w dwóch etapach. Pierwszym etapem było wytłaczanie z granulowaniem, a drugim i ostatnim wtryskiwanie lub prasowanie.

Biokompozyty zostały wytłoczone na dwuślimakowej wytłaczarce współbieżnej (DWW) (BTSK 20/40D, Bühler, Niemcy). Zastosowano specjalny kształt ślimaków ograniczający degradację fazy rozproszonej (włókien) oraz ich cięcie na krótsze fragmenty. Ślimak nie zawierał elementów cofających, intensywnie mieszających oraz istotnie ścinających. Zamiast nich zastosowano elementy: a) ugniatające o długości 15 mm; b) ugniatające o długości 20 mm; c) transportujące o długości 20 mm – 40 mm oraz d) z naciętymi ostrzami o długości 30 mm. Wytłaczanie przeprowadzono w następujących temperaturach poszczególnych stref cylindra: 180°C, 182°C, 184°C, 186°C i głowicy: 185°C. Obroty ślimaków wynosiły 120 rpm. PLA i włókna podawano za pomocą dozowników w proporcji 80:20 (1200 g PLA i 300 g włókien). Prędkość dozowania wynosiła 266,6 g/10 min dla PLA i 66,6 g/10 min dla włókien. Zawartość włókien lnianych, zarówno modyfikowanych jak i niemodyfikowanych, wynosiła 20% wag. biokompozytu.

Próbki w postaci beleczek lub wiosełek do badań mechanicznych zostały przygotowane metodą formowania wtryskowego z wytworzonych granulatów biokompozytowych. Wtryskarka (TRX 80 ECO 60, Tederic Machinery Manufacture,

Taiwan) wyposażona była w formy do formowania beleczek i wioseł, z ujściem na nadmiar wtryśniętego materiału. Forma ta zapełniła powtarzalny kształt próbek jak i ich stałą masę (ok. 11 g). Proces wtryskiwania przeprowadzono w następujących temperaturach poszczególnych stref cylindra wtryskarki: 170°C, 165°C, 165°C, 165°C, i głowicy: 35°C. Ciśnienie osiągnięte podczas wtrysku wynosiło 24,8 MPa.

Do badań mikrobiologicznych wytworzono folie biokompozytowe o grubości 0,5 mm.W tym celu użyto prasę wulkanizacyjną (AW03M, Argenta, Polska). Wstępnie wysuszony granulat o wadze 0,7 g poddano prasowaniu w temperaturze 180°C przez 10 s. Ciśnienie panujące podczas prasowania wynosiło 0,7 MPa.

W celu uproszenia nazewnictwa i lepszego zrozumienia interpretacji przedstawionych wyników przyjęto następujące oznaczenia badanych próbek (tabela 2):

*Tabela 2. Oznaczenia próbek.*

| **Oznaczenie** | **Opis** |
|---|---|
| P | Czysty PLA |
| N | PLA + włókna niemodyfikowane |
| T1 | PLA + włókna modyfikowane kwasem taninowym o stężeniu od 1% do 20% |
| T5 | |
| T10 | |
| T20 | |
| G1 | PLA + włókna modyfikowane geraniolem o stężeniu od 1% do 20% |
| G5 | |
| G10 | |
| G20 | |

### *2.6. Metody badawcze*

#### *2.6.1. Badania właściwości termomechanicznych*

Dynamiczno-mechaniczna analiza termiczna (DMA) jest techniką polegającą na oscylacyjnym odkształcaniu badanego materiału wraz ze zmianą jej temperatury w funkcji czasu. w trakcie badania rejestrowane są temperatura, czas, siła wywierana na próbkę oraz jej odkształcenie.

Do określenia właściwości termomechanicznych przygotowanych biokompozytów użyto analizatora DMA (Q 800, TA Instruments, Stany Zjednoczone) wyposażonego w uchwyty zginające typu dual-cantilever. w trakcie badania rejestrowane były temperatura, czas, siła wywierana na próbkę oraz jej odkształcenie. Badania prowadzono zgodnie z normą ISO 6721-1:2019 [47]. Badania biokompozytów w kształcie beleczek przeprowadzono w zakresie temperatur od 25°C do 160°C z prędkością ogrzewania 3°C/min. Amplituda odkształceń zginających była stała i wynosiła 1 Hz, a częstotliwość – 15 μm.

#### *2.6.2. Wytrzymałość na rozciąganie*

Próbki badane zostały poddane statycznej próbie rozciągania, będącej jedną z podstawowych technik dostarczających informacji o właściwościach mechanicznych biokompozytów. Badanie to polegało na jednoosiowym odkształceniu próbki ze stałą prędkością wynoszącą 2 mm/min. Do przeprowadzenia badań użyto maszynę wytrzymałościową Instron 3367 (Instron, Stany Zjednoczone) rejestrującą między innymi siłę odkształcenia i wydłużenie próbki. Badania wykonano zgodnie z normami ISO 527-1:2019 [47] i ISO 527-2:2025 [48].

Statycznej próbie rozciągania poddano po 12 próbek z każdego materiału. Aby osiągnąć wyniki najbardziej zbliżone do średnich, przed przeprowadzeniem analizy zaniedbano ekstremalne wartości w każdej próbie uzyskane podczas badania.

### *2.6.3. Badania właściwości termicznych*

Badania termograwimetryczne przeprowadzane są w celu określenia odporności materiałów na degradację termiczną. Technika ta polega na rejestrowaniu gradientu masy próbki w trakcie jej ogrzewania w funkcji temperatury bądź czasu. Badania zostały przeprowadzone według normy ISO 11358-1:2022 [50].

Degradację termiczną badanych biokompozytów przeprowadzono za pomocą termograwimetru Q500 (TA Instruments, Stany Zjednoczone). Próbkę w postaci granulatu umieszczano na szalce z platyny charakteryzującą się odpornością na wysokie temperatury. Do uzyskania porównywalnych wyników, masa próbek z poszczególnych rodzajów materiałów powinna być zbliżona. Próbki o masie od 19,7 do 20,3 mg ogrzewano od 25°C do 800°C z szybkością 10°C/min w atmosferze azotu.

Identyfikacja przejść fazowych zachodzących podczas ogrzewania badanych bikompozytów jak i określenie stopnia ich krystaliczności analizowano przy użyciu różnicowego kalorymetru skaningowego Q200 (TA Instruments, Stany Zjednoczone). Badania wykonano zgodnie z normą ISO 1135-1:2023 [51].

Próbki do badań w postaci granulek o wadze od 7,8 mg do 8,2 mg umieszczano w aluminiowych tygielkach zamkniętych pokrywkami. Badania prowadzono w atmosferze azotu. Próbki zostały poddane trzystopniowemu procesowi termicznemu składającego się z następujących cykli: pierwsze grzanie, chłodzenie oraz drugie grzanie. Podczas grzania temperatura wynosiła od 20°C do 210°C, natomiast minimalna temperatura przy chłodzeniu próbek wynosiła -80°C. Zarówno szybkość grzania jak i chłodzenia wynosiła 10°C/min. Analizie poddano krzywą drugiego grzania, niezawierającą historii termicznej próbki.

Stopień krystaliczności ($X_c$) badanych biokompozytów obliczono według następującego równania:

$$X_c = \left(\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m100\%}}\right) \cdot 100\% \quad (1)$$

gdzie:

$\Delta H_m$ – zmiana entalpii procesu topnienia [J/g],

$\Delta H_{cc}$ – zmiana entalpii procesu zimnej krystalizacji [J/g],

$\Delta H_{m100\%}$ – zmiana entalpii procesu topnienia 100% krystalicznego PLA wynosząca 93,6 [J/g] [52].

### *2.6.4. Badania strukturalne*

W celu analizy charakteru pęknięć powstałych w biokompozytach podczas statycznej próby rozciągania, zastosowano skaningową mikroskopię elektronową (SEM). Przekroje badanych próbek obejmujące miejsca pęknięć zbadano za pomocą skaningowego mikroskopu elektronowego SU8010 (Hitachi Ltd, Japonia). Przed wykonaniem mikrofotografii, próbki zostały powleczone cienką warstwą (2 nm) złota zapewniającą odpowiednią przewodność biokompozytów.

### *2.6.5. Zwilżalność*

Miarą zwilżalności materiału przez ciecz pomiarową jest kąt (θ) zwilżania, jaki tworzy styczna do powierzchni kropli cieczy w punkcie jej styku z płaską powierzchnią badanego materiału [53]. Zgodnie z powszechnie przyjętą definicją wraz ze zmniejszeniem się wartości kąta θ zwiększa się zwilżalność badanego materiału.

Do pomiarów kąta zwilżania użyto goniometr DSA 100 (Krüss GmbH, Niemcy) wyposażony w automatyczny system dozujący ciecz pomiarową. Do badań zastosowano wodę jako ciecz polarną. Każdorazowo kropla cieczy pomiarowej o objętości (v) 7 µl została sześciokrotnie osadzona na różnych częściach próbki. Prędkość dozowania (Δv) wynosiła 5 µl/min. Sześć próbek z każdego rodzaju biokompozytu poddano badaniom zwilżalności.

### *2.6.6. Badania mikrobiologiczne*

Ocenę właściwości biobójczych przygotowanych biokompozytów przeprowadzono zgodnie z normą ISO 22196:2024 [54]. w badaniu zostały użyte dwa szczepy bakterii uważane za wzorcowe dla tego typu badań – *Staphylococcus aureus* (*S. aureus*) (ATCC 6538 P) i *Escherichia coli* (*E. coli*) (ATCC 8739). Bakterie *S. aureus* należą do grupy bakterii Gram-dodatnich, natomiast *E. coli* – do Gram-ujemnych. Zasadniczą różnicą pomiędzy tymi grupami bakteryjnymi jest obecność lub brak zewnętrznej błony komórkowej. Występowanie błony komórkowej definiuje ich podatność na wpływ czynników zewnętrznych oraz mechanizm przenikania substancji do jądra komórki. Bakterie te są najczęstszą przyczyną skażenia mikrobiologicznego

żywności. Metody przygotowania zawiesiny komórek bakterii, sposób inkubacji oraz proces oznaczania aktywności biobójczej badanych biokompozytów opisano szczegółowo w publikacji [B].

Zgodnie z normą [54], aby dany czynnik można było uznać za biobójczy, stopień redukcji (R) musi wynieść co najmniej 2. a zatem, działanie bakteriobójcze materiału biokompozytowego można osiągnąć, jeśli liczba komórek bakterii zdolnych do wzrostu zostanie zmniejszona o dwa rzędy wielkości lub więcej ($R \geq 2$). Redukcję liczebności komórek bakterii po kontakcie z materiałem badanym w stosunku do próbki kontrolnej obliczono z następującego równania:

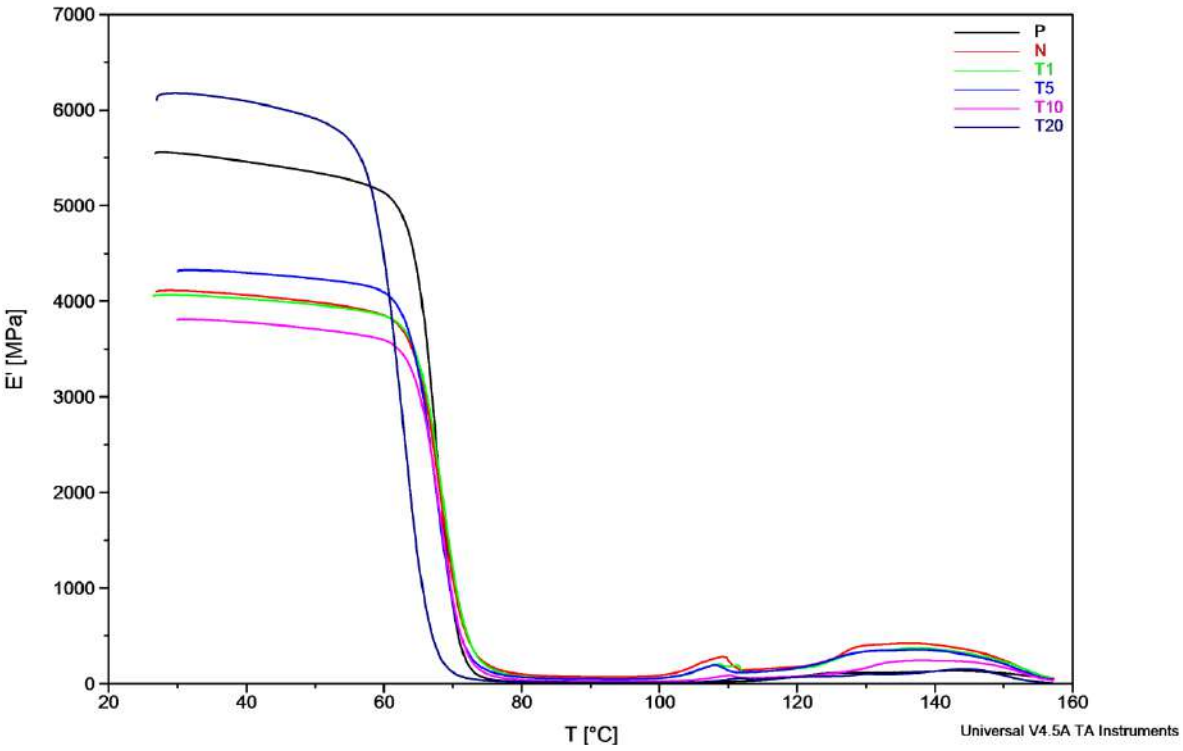
$$R = (U_t - U_0) - (W - U_0) \quad (2)$$

gdzie: $U_t$ – średni logarytm liczby żywych bakterii (jtk/cm$^3$) odzyskanych z próbek kontrolnych po 24 h, $U_0$ – średni logarytm liczby żywych bakterii (jtk/cm$^3$) odzyskanych z próbek kontrolnych bezpośrednio po szczepieniu ($t_0$) i w – średni logarytm liczby żywych bakterii (jtk/cm$^3$) odzyskanych z próbek badanych po 24 h.

# 3. Wyniki badań

## *3.1. Właściwości termomechaniczne*

Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

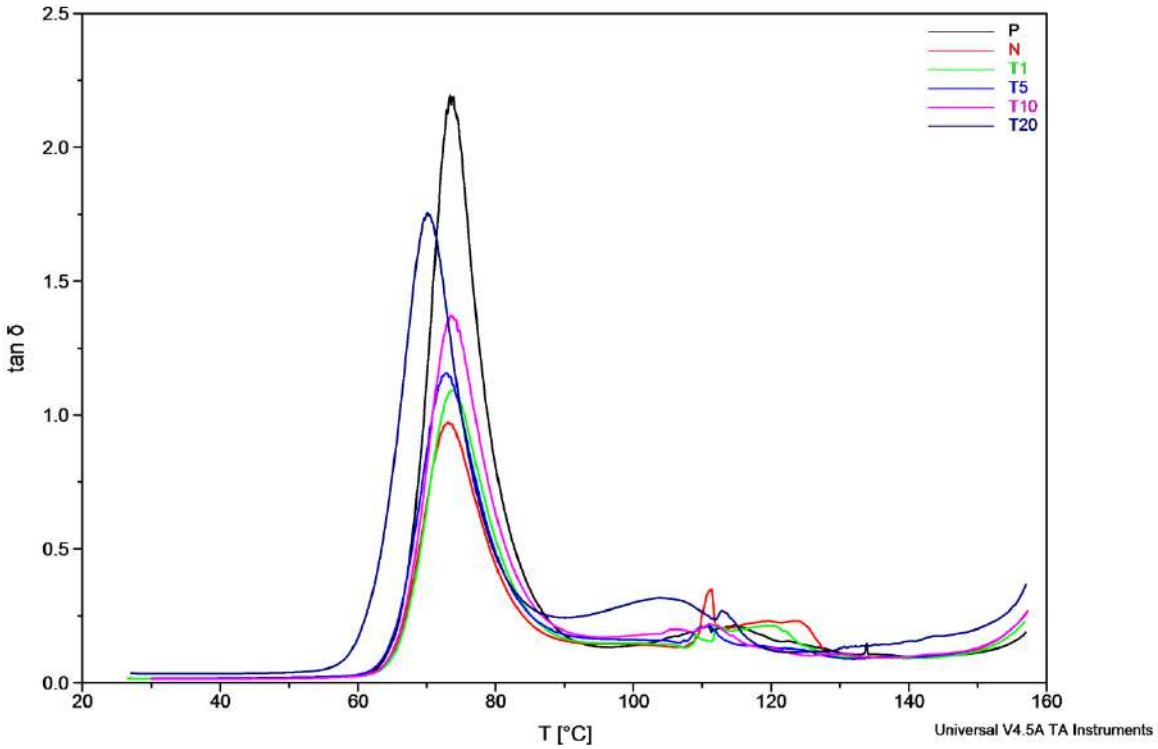



*Rysunek 1. Krzywe DMA opisujące zależność modułu zachowawczego od temperatury otrzymane dla próbek zawierających TA.*

Na rysunku 1 przedstawiono zależność E' od temperatury próbek modyfikowanych TA. Porównanie modułu zachowawczego w stanie szklistym (do 60°C) próbek N i P wskazuje na lepszą wytrzymałość mechaniczną N. Włókna lniane użyte jako wzmocnienie zwiększyły E' próbki N w podanym zakresie o prawie o 1100 MPa. Analiza wartości E' w stanie szklistym wskazuje na brak istotnej różnicy w wytrzymałości mechanicznej pomiędzy N i T1. Dana obserwacja pozwala stwierdzić, że włókna lniane modyfikowane niskim stężeniem TA (1%) nie poprawiają przenoszenia obciążeń międzyfazowych w biokompozycie. Odwrotny efekt uzyskano przy niewielkim

zwiększeniu stężenia modyfikatora z 1% do 5%. w porównaniu z próbką N wartość E' próbki T5 wzrosła o ok. 200 MPa w zakresie temperatur stanu szklistego. Dalsze zwiększanie stężenia modyfikatora doprowadziło do redukcji E' o około 200 MPa. Wartość E' dla próbki T5 jest o 400 MPa wyższa w porównaniu z T10. Można zatem stwierdzić, że T5 ma lepszą odporność na zginanie niż N w zakresie temperaturowym związanym ze stanem szklistym. Badania wykazały, że wartość E' dla próbki T20 jest wyższa od E' dla próbki P. Włókna zawarte w T20 zostały dostarczone w osobnej partii i najprawdopodobniej miały nieco odmienne właściwości mechaniczne niż włókna zawarte w pozostałych próbkach.

Dalsze zmiany krzywej pojawiają się w zakresie zimnej krystalizacji. Wzrost E' w podanym zakresie wskazuje na rozpoczęcie procesu zimnej krystalizacji. Znaczący wzrost E' dla próbki N można wytłumaczyć obecnością włókien lnianych, które wykazują właściwości zarodkujące. Migracja TA do matrycy polimerowej w modyfikowanych próbkach spowodowała zmniejszenie ich E' co wskazuje na plastyfikację objętościową biokompozytu. Największy efekt plastyfikujący uzyskano przy stężeniu TA 20%. Dalsze wyniki DSC potwierdzają plastyfikację materiałów i zmniejszenie ich stopnia krystaliczności ($X_c$) wraz ze wzrostem stężenia TA.

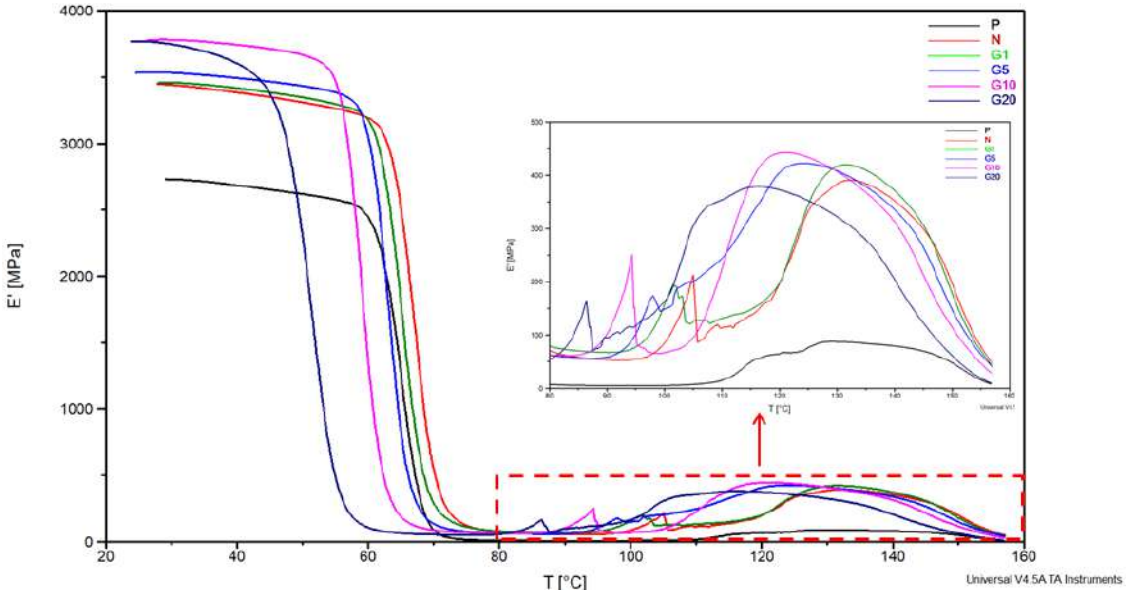



*Rysunek 2. Krzywe odwzorowujące zależność tan δ od temperatury otrzymane dla próbek zawierających TA.*

Na rysunku 2 przedstawiono zależność tan δ od temperatury dla próbek modyfikowanych TA. Najwyższe wartości tan δ charakteryzują się pikami, znajdującymi się między 71 a 74°C. Dla wszystkich próbek odnotowano wzrost tan δ w zakresie zeszklenia – od ok. 60°C do ok. 80°C. Najwyższy pik zauważono dla krzywej próbki P co wskazuje na największą ilość amorficznej fazy polimerowej, która spowodowała wzrost tan δ. Najniższą wartość tan δ zaobserwowano dla próbki N, co sugeruje wyższą wytrzymałość mechaniczną próbki w porównaniu z T1, T5, T10 i T20. Prawdopodobną przyczyną wzrostu tan δ dla próbek modyfikowanych jest migracja TA do osnowy polimerowej i jej uplastycznienie. Krzywe przedstawione na rysunku 4 ilustrują stopniowy wzrost tan δ wraz ze wzrostem zawartości modyfikatora. Wraz ze zwiększeniem ilości modyfikatora obecnego na powierzchni włókien, zwiększa się jego ilość w matrycy polimerowej co powoduje większą plastyfikację próbek.

Na rysunku 3 przedstawiono krzywe DMA próbek P, N, G1, G5, G10 i G20 ukazujące korelację między modułem zachowawczym (E′) a zawartością GR. Porównanie wartości E′ dla próbki N i P w temperaturze 30°C wykazało zwiększenie tej

wartości o ponad 700 MPa (z 2730 MPa do 3441 MPa) dla próbki zawierającej włókna. Obserwacja ta jest zgodna z założeniem, że wprowadzenie włókien lnianych będzie miało pozytywny wpływ na właściwości mechaniczne biokompozytów, a mianowicie na poprawę sztywności [55].




*Rysunek 3. Krzywe DMA opisujące zależność modułu zachowawczego od temperatury otrzymane dla próbek zawierających GR.*

Sztywność próbki G1, nie uległa zmianie na co wskazuje wartość jej E′ (3459 MPa). Wprowadzenie do osnowy polimerowej włókien modyfikowanych GR, spowodowało obniżenie temperatury przejścia szklistego, którego początek zaobserwowano w temperaturze ok. 62°C. Spadek tej temperatury wskazuje na to, że nawet niewielkie ilości GR zawarte w biokompozycie, sprzyjają jego uplastycznieniu.

Próbka G5 charakteryzowała się nieco większą wartością E′ (3533 MPa), z jednoczesnym początkiem zeszklenia w temperaturze około 60°C. Podobne zależności odnotowano w przypadku próbki G10 – wzrost wartości E′ (3781 MPa) oraz spadek temperatury początku przejścia szklistego (56°C). Zarówno w przypadku próbki G5 jak i G10 zauważono wyraźną poprawę E′, który zwiększył się o ponad 10% w porównaniu do próbki N. Wzrost ten związany jest z większą zawartością GR, a tym samym większą ilością łańcuchów alkilowych.

Łańcuchy te znane są ze swoich właściwości hydrofobowych, które poprawiają wewnętrzną hydrofobowość biokompozytu, co skutkuje wyższym E′ [56].

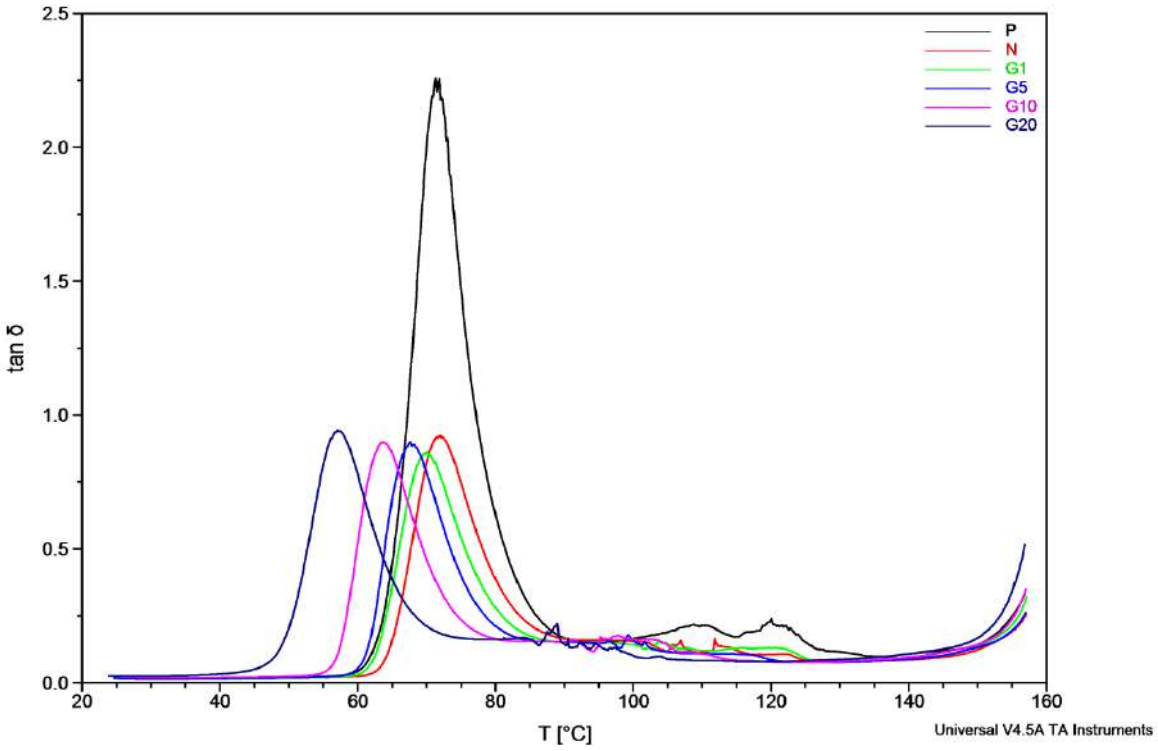
Geraniol w stężeniu 20% (próbka G20) przyśpieszył proces zeszklenia, który rozpoczął się w ok. 47°C. Obniżenie tej temperatury o 7°C w porównaniu z próbką N wskazuje na wzmocniony efekt plastykujący i zwiększoną ruchliwość cząsteczek matrycy spowodowaną wysoką zawartością modyfikatora.

Podsumowując, zwiększona odporność na zginanie próbek G5 oraz G10 w zakresie temperaturowym poprzedzającym zeszklenie, spowodowana była obecnością grup alkilowych zawartych w geraniolu. Grupy te, w umiarkowanej ilości poprawiają sztywność biokompozytu. Można stwierdzić, że najbardziej pozytywny wpływ modyfikacji na właściwości mechaniczne biokompozytów w zakresie temperatur stanu szklistego uzyskano w przypadku próbki G10, w której E′ było o ponad 300 MPa wyższe w porównaniu do E′ próbki N.

Krzywe próbek N oraz G1, G5, G10 i G20 znajdujące się w zakresie temperaturowym od 80°C do 150°C (zakres zimnej krystalizacji) charakteryzują się dwuetapową krystalizacją. w przypadku próbki P krystalizacja przebiega w jednym etapie. Obserwując dwuetapową krystalizację można stwierdzić, że pierwszy etap jest wyrażony pikiem ze znacznym wzrostem wartości E′. Najprawdopodobniej, pik ten jest spowodowany zwiększeniem ruchliwości cząsteczek polimeru w wyniku uplastycznienia osnowy [57]. Ruchliwość cząsteczek próbki N, charakteryzującej się pikiem występującym w temperaturze 105°C, spowodowana była topnieniem naturalnie występujących we włóknach lnianych wosków i tłuszczy. Podobny pik odnotował Aliotta et al. [58], badający PLA zawierający 20% włókien lnianych. Dla próbek G1, G5, G10 i G20 wspomniany pik zaobserwowano w około 102°C, 98°C, 94°C i 86°C. Przesunięcie piku dla próbek modyfikowanych może wskazywać na zwiększenie ruchliwości cząsteczek polimeru. Podsumowując, wraz ze wzrostem stężenia GR, odnotowano wzmacniającą się plastyfikację biokompozytów.

Włókna naturalne posiadają właściowści zarodkujące, poprawiając stopień krystaliczności matrycy polimerowej [59]. Wzrost wartości E′ odnotowany w zakresie temperaturowym od 100°C do 150°C dowodzi nukleacyjnej natury włókien lnianych. Wzrost E′ dla próbki N pokrywa się z krzywą próbki G1, natomiast w przypadku próbek G5, G10 i G20 wzrost wspomnianej wartości odnotowano w niższych temperaturach.

Obserwacje te potwierdzają wzrost uplastycznienia biokompozytów wraz ze wzrostem stężenia zawartego w nich modyfikatora.




*Rysunek 4. Krzywe odwzorowujące zależność tan δ od temperatury otrzymane dla próbek zawierających GR.*

Obniżenie wartości tan δ dla próbek zawierających włókna lniane (N, G1, G5, G10 i G20) w porównaniu do próbki P (rysunek 4) potwierdza zwiększenie sztywności biokompozytów. Pik tan δ odwzorowuje przejście szkliste, które w przypadku próbek zawierających włókna modyfikowane występuje w niższych temperaturach (w porównaniu z próbką N). Przesunięcie piku w kierunku niższych temperatur wzrasta wraz ze wzrostem stężenia GR, co wskazuje na wzmocnioną plastyfikację osnowy polimerowej. Można zaobserwować, że temperatura $T_g$ maleje wraz ze wzrostem stężenia modyfikatora, ponieważ geraniol zwiększa ruchliwość łańcuchów polimerowych, co prowadzi do zmniejszenia kohezji i naprężeń międzycząsteczkowych. Zatem przy niskich stężeniach modyfikatora występuje wyższa sztywność. Obserwacja ta potwierdza wzmocnienie efektu plastyfikacji wraz ze wzrostem stężenia modyfikatora.

### *3.2. Właściwości mechaniczne*

Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

Wartości przedstawione w tabeli 3 pokazują, że wprowadzenie włókien modyfikowanych do osnowy polimerowej miało wpływ na obniżenie σ. Wraz ze zwiększeniem stężenia modyfikatora wartość σ spadała. Wartości σ dla próbek P, N i N1 są porównywalne, natomiast wzrost stężenia TA (od 1% do 10%) powoduje zmniejszenie σ o ponad 4 MPa. Najniższą wartość σ zaobserwowano dla próbki o największym stężeniu modyfikatora – T20. Fakt ten potwierdza przypuszczenia opisane w trakcie analizy DMA. Migracja TA w wyższej zawartości (20%) poprawia elastyczność i zmniejsza σ modyfikowanych biokompozytów.

*Tabela 3. Średnie wartości σ, εb, i E otrzymane dla próbek zawierających TA.*

| **Próbka** | **σ [MPa]** | **$\varepsilon_b$ [%]** | **E [GPa]** |
|---|---|---|---|
| P | 70,0 ± 0,7 | 4,1 ± 0,1 | 2,2 ± 0,1 |
| N | 70,7 ± 0,7 | 3,4 ± 0,1 | 3,7 ± 0,1 |
| T1 | 69,0 ± 0.2 | 3,3 ± 0,1 | 3,5 ± 0,1 |
| T5 | 67,8 ± 0,4 | 2,9 ± 0,1 | 3,6 ± 0,1 |
| T10 | 64,4 ± 1,0 | 2,9 ± 0,1 | 3,3 ± 0,1 |
| T20 | 59,2 ± 3,5 | 1,3 ± 0,1 | 5,9 ± 0,2 |

Zaobserwowano również zmiany wartości $\varepsilon_b$ w zależności od stężenia TA. Wyniki pokazują, że $\varepsilon_b$ dla N i T1 są zbliżone, zatem 1% stężenia TA nie zmienia w istotny sposób właściwości mechanicznych biokompozytów. Porównanie T1 i T10 wykazało spadek zarówno $\varepsilon_b$ jak i σ. Niemniej jednak, największy spadek wspomnianych wartości zaobserwowano dla próbki T20. Obserwację tą można wytłumaczyć migracją TA w wysokich stężeniach, która zmniejsza sztywność biokompozytów.

Podobne zmiany można było zaobserwować w wartościach E próbek T1 i T10 (tabela 3). Niższe wartości E są charakterystyczne dla materiałów o większej elastyczności. Stąd redukcja E dla próbki T10 w porównaniu z próbką T1 może być

spowodowana działaniem uplastyczniającym 10% roztworu TA zastosowanego podczas modyfikacji. Wyniki wykazały niewielką poprawę E dla T5 w porównaniu z T1, jednakże odchylenia standardowe nie wykazały różnicy pomiędzy sprężystościami wspomnianych próbek. Próbka T20 charakteryzowała się wartością E o ponad 2 GPa większą niż reszta próbek modyfikowanych. Zwiększona wytrzymałość mechaniczna próbki T20 została również potwierdzona wynikami DMA, gdzie wartość E'dla tego materiału była najwyższa ze wszystkich badanych próbek.

Tabela 4 przedstawia wyniki otrzymane podczas badań wytrzymałości na rozciąganie. Badania zostały przeprowadzone w warunkach normalnych [60]. Zgodnie z przewidywaniami, największą wartość wytrzymałości na rozciąganie (σ) odnotowano dla próbki P. Badania wykazały spadek σ po wprowadzeniu włókien lnianych, co potwierdza wzrost sztywności próbki N odnotowany podczas analizy wyników DMA. Stopniowy spadek σ następował wraz ze wzrostem stężenia modyfikatora. Podobne wartości σ dla próbek N i G1 wskazują na znikomy wpływ modyfikatora w stężeniu 1% na właściwości mechaniczne biokompozytu. Jednakże, dalszy wzrost stężenia modyfikatora spowodował obniżenie σ. Spadek ten może być spowodowany pogorszeniem wytrzymałości mechanicznej próbek G5, G10 i G20 oraz ich małą odpornością na odkształcenia. Można przypuszczać, że zastosowany modyfikator, będący terpenem, migrował do matrycy polimerowej i wywołał efekt plastyfikujący polegający na osłabieniu oddziaływań łańcuchów polimeru [57], [61], [62].

*Tabela 4. Średnie wartości σ, $\varepsilon_b$, i E otrzymane podczas badania próbek zawierających GR.*

| **Próbka** | **σ [MPa]** | **$\varepsilon_b$ [%]** | **E [GPa]** |
|---|---|---|---|
| P | 69,99±0,73 | 4,07±0,07 | 2,25±0,05 |
| N | 59,86±0,74 | 2,91±0,12 | 3,34±0,12 |
| G1 | 60,33±0,70 | 2,77±0,12 | 3,49±0,14 |
| G5 | 54,33±0,32 | 2,51±0,10 | 3,45±0,04 |
| G10 | 47,93±0,58 | 2,32±0,09 | 3,31±0,15 |
| G20 | 41,07±0,84 | 2,25±0,11 | 3,10±0,07 |

Odnotowano również zmniejszenie wydłużenia przy zerwaniu ($\varepsilon_b$) dla próbek niemodyfikowanych, jak i modyfikowanych w porównaniu z próbką P. Obserwacja ta potwierdza wzrost sztywności próbki N w porównaniu z próbką P. Nieznaczny spadek wartości $\varepsilon_b$ występuje po wprowadzeniu włókien modyfikowanych do matrycy polimerowej. Obniżenie wartości $\varepsilon_b$ następuje wraz ze zwiększeniem stężenia GR. Niemniej jednak, spadek wartości $\varepsilon_b$ nie przekracza 1%, co można potraktować jako zmianę nieistotną.

Wartość modułu Younga (E) wzrosła po wprowadzeniu włókien niemodyfikowanych o ponad 1 GPa, co wskazuje na poprawę sztywności próbki N. Zastosowanie modyfikatora w stężeniu 1% i 5% miało nieznaczny wpływ na sztywność G1 i G5. Jednakże, wspomniany efekt został zaburzony przy wyższych stężeniach modyfikatora (G10 i G20). Duże ilości związków pochodzenia roślinnego w biokompozytach prowadzą do obniżenia interakcji pomiędzy łańcuchami polimerowymi [63]. Redukcja ruchliwości cząsteczek w konsekwencji prowadzi do pogorszenia właściwości mechanicznych biokompozytów polimerowych. Podsumowując, zastosowanie 1% i 5% stężenia modyfikatora z jednej strony poprawiło sztywność biokompozytu, ale z drugiej strony doprowadziło do pogorszenia odporności na odkształcenia.

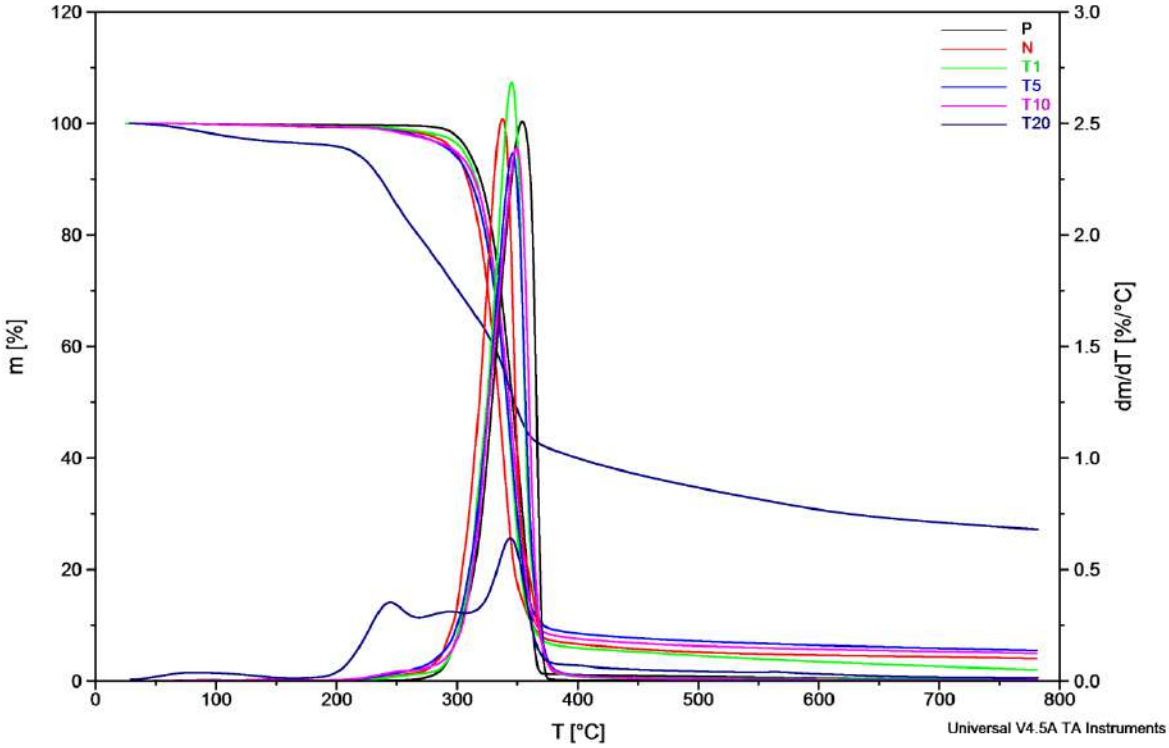
### *3.3. Właściwości termiczne*

#### *3.3.1. Proces degradacji termicznej*

Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

Degradacja termiczna próbek modyfikowanych TA przedstawiona została na rysunku 5. Krzywe TG ilustrują nieznaczne ubytki masy przy ok. 240°C, przy czym ubytek masy dla próbek zawierających modyfikator rośnie wraz ze zwiększeniem zawartości modyfikatora. Gwałtowne zmiany masy badanych próbek zarejestrowano w zakresie temperatur od 290°C do 300°C. Ze względu na właściwości termiczne PLA, proces jego degradacji zazwyczaj zachodzi w około 330°C [64]. Porównanie krzywych próbek zawierających włókna modyfikowane wykazało, że zmiana masy próbki T20 została zainicjowana w niższej temperaturze (ok. 205°C)

niż w przypadku pozostałych próbek modyfikowanych (ok. 290°C). Pomimo polepszonych właściwości mechanicznych tej próbki, charakteryzowała się ona obniżoną odpornością termiczną.




*Rysunek 5. Krzywe TG i DTG przedstawiające próbki zawierające TA.*

W tabeli 5 przestawiono $T_d$, $T_{d/dt}$, $T_{5\%}$, $T_{50\%}$, oraz $T_{95\%}$ dla badanych próbek. Próbka T1 straciła 5% swojej masy w nieco wyższych temperaturach w porównaniu z T5 i T10. Temperatura $T_{5\%}$ dla próbek T5 i T10 nastąpił w podobnych temperaturach. Strata 5% masy odnotowana w wyższych temperaturach może być spowodowana głównie zmniejszoną zawartością TA, który dekarboksyluje w temperaturze od 240°C do 340°C [65]. Nie zaobserwowano istotnej różnicy pomiędzy $T_{50\%}$ modyfikowanych próbek, pomimo że $T_{95\%}$ różniły się znacznie. Najbardziej znaczącą różnicę zaobserwowano pomiędzy T10 i T20. Strata 95% masy próbek T5, T10 i T20 nastąpiła w temperaturach prawie 2 razy wyższych niż w przypadku T1. Najprawdopodobniej, przyczyną tego jest zwęglenie się TA pod wpływem wysokiej temperatury w wyniku czego powstaje warstwa węglowa, która działa jak izolator

termiczny [66]. W próbkach T5, T10 i T20 zawartość modyfikatora jest większa niż w próbce T1. Ze względu na to, warstwa węglowa jest większa co najprawdopodobniej miało wpływ na wzrost $T_{95}$% dla próbek T5, T10 i T20.

*Tabela 5. Wybrane temperatury otrzymane podczas badania próbek zawierających TA.*

| **Próbka** | **$T_{onset}$** | **$T_{d/dt}$[°C]** | **$T_{5\%}$ [°C]** | **$T_{50\%}$ [°C]** | **$T_{95\%}$ [°C]** |
|---|---|---|---|---|---|
| P | 326,59 | 354,01 | 309,33 | 346,10 | 365,09 |
| N | 330,15 | 337,76 | 297,82 | 334,62 | 526,64 |
| T1 | 322,90 | 345,46 | 305,30 | 341,20 | 466,89 |
| T5 | 320,71 | 346,10 | 294,99 | 341,46 | 781,14 |
| T10 | 322,97 | 349,42 | 298,60 | 343,43 | 774,86 |
| T20 | 322,62 | 359,80 | 268,31 | 353,62 | 781,71 |

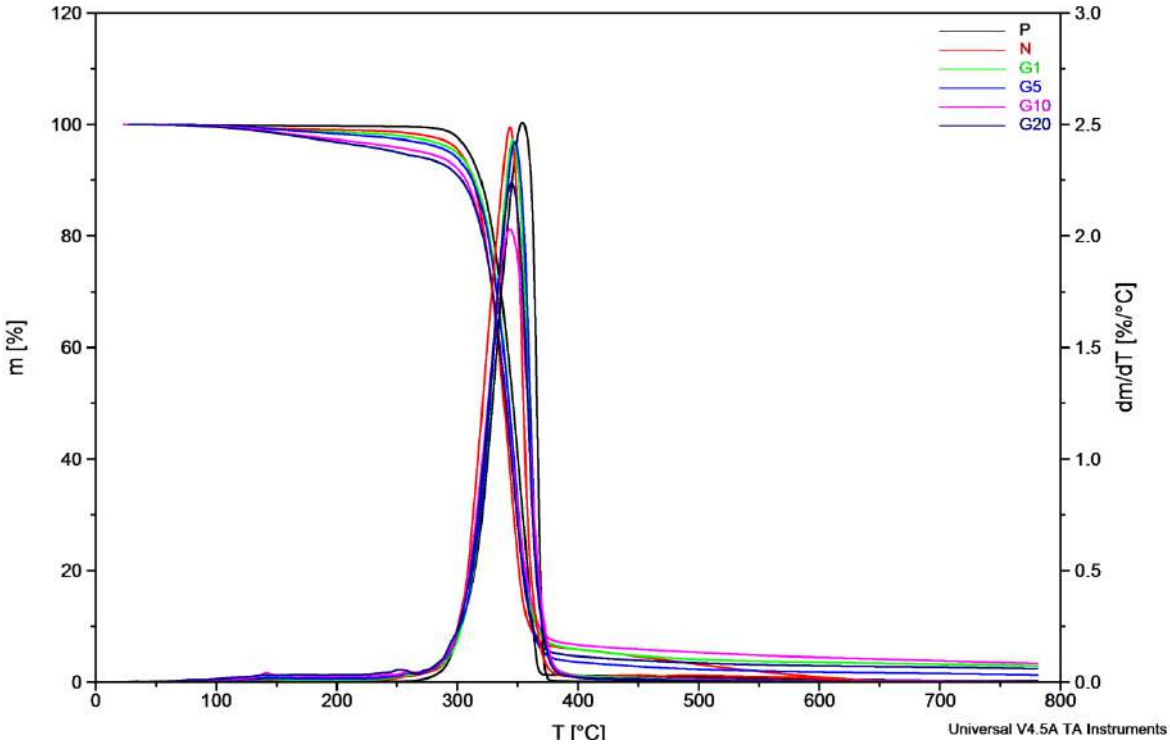
Wraz ze wzrostem stężenia TA obserwuje się niewielki wzrost wartości $T_{d/dt}$, co można wiązać z opóźnieniem degradacji termicznej biokompozytów na skutek tworzenia się warstwy węglowej [66]. Różnica w $T_{d/dt}$ pomiędzy próbkami T20 i T1 wynosi jedynie ok. 14°C, co wskazuje na ograniczony wpływ TA na przebieg procesów degradacji. Może to wynikać z niskiej zawartości wagowej modyfikatora oraz jego znikomego wpływu na właściwości termiczne materiału.

Na rysunku 6 przedstawiono krzywe ubytku masy badanych próbek funkcji temperatury (TG) oraz pierwszej pochodnej (DTG), zarówno dla próbek modyfikowanych, niemodyfikowanych, jak i referencyjnej.

W przypadku próbki P szybki ubytek masy zaobserwowano przy ok. 200°C co wskazuje na spadek jej stabilności termicznej. Początkowy ubytek masy próbek zawierających włókna (zarówno modyfikowane jak i niemodyfikowane) odnotowano w zakresie temperatur nie przekraczających 100°C, co odpowiada odparowaniu wody zawartej we włóknach lnianych. Wprowadzenie do matrycy włókien niemodyfikowanych (próbka N) skutkowało obniżeniem stabilności termicznej (w zakresie od 200°C do 300°C, co wynika z naturalnych właściwości termicznych włókien pochodzenia roślinnego.

Biokompozyty z niską zawartością modyfikatora (G1 i G5) wykazywały zachowanie bardzo zbliżone do próbki niemodyfikowanej N. Ich ubytek masy również

następował w zakresie od 200°C do 300°C, co sugeruje, że dodatek modyfikatora w stężeniach 1% i 5% nie wywarł znaczącego wpływu na stabilność termiczną materiału na tym etapie rozkładu. Badania wykazały, że ubytek masy we wspomnianym zakresie temperatur dla próbek zawierających 10% i 20% modyfikatora (G10 i G20) był większy. Można to wytłumaczyć większą ilością GR, który ulega przemianie termicznej przebiegającej w następnych etapach: a) parowanie w zakresie temperaturowym do 230°C oraz b) rozkład w temperaturze od 230°C do 291°C [67].




*Rysunek 6. Krzywe TG i DTG przedstawiające próbki zawierające GR.*

Tabela 6 przedstawia procentowy ubytek masy i temperatury degradacji dla badanych próbek. Nieznaczny spadek 5% temperatury ubytku masy ($T_{5\%}$) próbki N w porównaniu do próbki P wynika z obecności zawartych w niej włókien lnianych, które są podatne na degradację termiczną. Dalszy spadek $T_{5\%}$ dla modyfikowanych próbek w porównaniu z próbką N wskazuje na obecność GR. Związek ten w temperaturze 230°C zaczyna wrzeć, co w konsekwencji prowadzi do jego rozkładu [68]. Wyniki wykazały, że temperatura 5% ubytku masy ulegała obniżeniu wraz ze wzrostem stężenia

modyfikatora. Porównanie próbek G5, G10 i G20 pokazało najbardziej znaczące różnice w $T_{5\%}$. Temperatura 5% ubytku masy dla próbki G10 zmalała o ponad 22°C w porównaniu z próbką G5. Zwiększenie stężenia modyfikatora (G20) doprowadziło do dalszego obniżenia $T_{5\%}$ o kolejne 22°C.

*Tabela 6. Wybrane temperatury otrzymane dla próbek zawierających GR.*

| **Próbka** | **$T_d$** | **$T_{d/dt}$ [°C]** | **$T_{5\%}$ [°C]** | **$T_{50\%}$ [°C]** | **$T_{95\%}$ [°C]** |
|---|---|---|---|---|---|
| P | 326,59 | 354,01 | 309,33 | 346,10 | 365,09 |
| N | 319,36 | 343,47 | 302,16 | 338,58 | 434,52 |
| G1 | 322,82 | 345,87 | 299,16 | 342,94 | 435,05 |
| G5 | 323,64 | 347,58 | 293,74 | 342,63 | 372,85 |
| G10 | 316,67 | 343,50 | 271,72 | 340,61 | 527,89 |
| G20 | 321,07 | 344,82 | 250,36 | 340,20 | 384,87 |

Porównanie temperatur, w których nastąpił 50% ubytek masy ($T_{50\%}$) próbek N i P, pozwala na zaobserwowanie podobnych tendencji jak w przypadku $T_{5\%}$. Dodatkowo, spadek temperatury rozkładu ($T_{d/dt}$) dla próbki N odnotowano w temperaturze niższej o 11°C niż dla próbki P. Zmiana ta może być spowodowana obecnością włókien lnianych w próbce N, które ulegają degradacji termicznej w niższej temperaturze niż czysty PLA (P). Dla wszystkich modyfikowanych próbek zaobserwowano nieistotne zmiany wartości $T_{50\%}$ jak i $T_d$. Zaobserwowano również wzrost $T_{50\%}$ i $T_{d/dt}$ dla G1 i G5 w porównaniu do próbki N. Jednakże, przy zwiększonym stężeniu modyfikatora (10% i 20%) temperatury $T_{50\%}$ i $T_{d/dt}$ obniżyły się. Dana obserwacja najprawdopodobniej wskazuje na to, że geraniol migrował do matrycy co spowodowało zmiany struktury molekularnej PLA. Obniżenie wartości $T_{d/dt}$, pod wpływem GR w wysokich stężeniach, zostały odnotowało także w pracy [69].

Zmiany wartości temperatury 95% ubytku masy ($T_{95\%}$) odbiegają od zaobserwowanej zależności i nie są zgodne z oczekiwanym wzorcem. Wysokie wartości T95% można prawdopodobnie przypisać dwóm głównym zjawiskom: tworzeniu się tzw. węgla zwęglonego (karbonizacji) oraz sieciowaniu, wraz ze stabilizacją termiczną dzięki wysokiej zawartości geraniolu (GR). w warunkach ograniczonej dostępności tlenu niepełne spalanie może prowadzić do tworzenia się węgla zwęglonego. Powstała warstwa

węgla zwęglonego działa jak izolator termiczny, potencjalnie tworząc lokalne punkty zapalne, w których temperatura może znacznie przekroczyć średnią. Geraniol zawiera reaktywne grupy funkcyjne, które mogą ulegać sieciowaniu termicznemu z PLA lub produktami jego degradacji. Przy wyższych stężeniach GR może utworzyć się usieciowana, termicznie stabilna sieć. Sieć ta jest odporna na topnienie i zamiast tego ma tendencję do powolnej degradacji lub karbonizacji, co może dodatkowo sprzyjać wysokim temperaturom lokalnym. Połączenie spowolnionego rozkładu i zatrzymywaniu ciepła przyczynia się do wysokich wartości w T95%. Niemniej jednak, na dalszych etapach kariery naukowej zaplanowane jest przeprowadzenie bardziej szczegółowych badań w celu ustalenia przyczyny takiego zachowania.

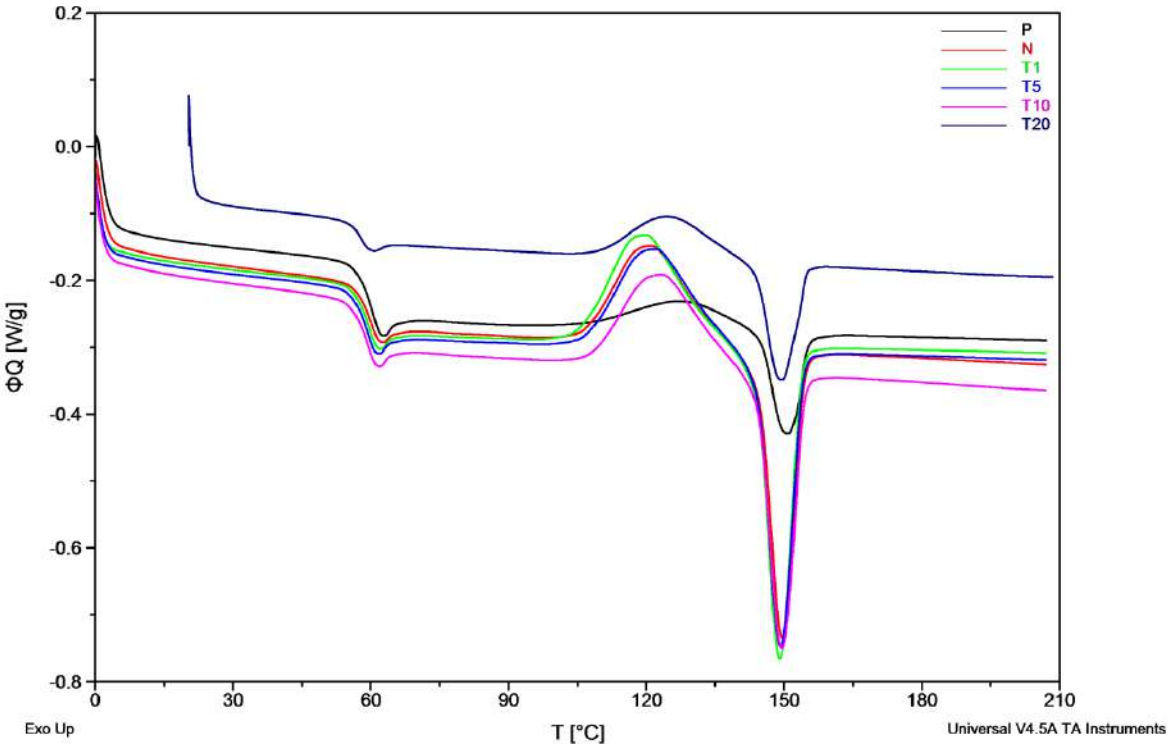
Na podstawie analizy przeprowadzonych badań, można stwierdzić, że GR w małych stężeniach (1% i 5%) w niewielkim stopniu hamuje tempo degradacji biokompozytu. Modyfikator w dużych stężeniach (10% i 20%), najprawdopodobniej migrował do matrycy polimerowej, co spowodowało pogorszenie stabilności termicznej próbek G10 i G20. Najbardziej prawdopodobną przyczyną tego typu zjawisk jest duża ilość grup hydroksylowych zawartych w GR, przyspieszających proces degradacji [70], [71], [72], [73]. Niemniej jednak, biokompozyty badane w danej pracy przeznaczone są do stosowania w znacznie niższych zakresach temperaturowych, które zapewniają stabilność termiczną ich składników, w tym GR.

### *3.3.2. Przejścia fazowe i stopień krystaliczności*

Rysunek 7 przedstawia zależność pomiędzy stężeniem modyfikatora a przepływem ciepła. Analiza krzywych wykazała, że stężenie TA w próbce jest dodatnio skorelowane z energią potrzebną do inicjacji procesu zeszklenia. Obniżenie $T_g$ wraz z wprowadzaniem włókien modyfikowanych potwierdza, że TA powoduje plastyfikację biokompozytów. Nie odnotowano jednak znaczących różnic pomiędzy $T_g$ przypisaną do T1, T5 i T10 (tabela 7). Niemniej jednak, w przypadku próbki T20 zaobserwowano obniżenie $T_g$ o prawie 3°C. Obserwacja ta sugeruje zwiększony efekt plastyfikujący modyfikatora o stężeniu 20%.

Obserwując kolejny pik, należący do pików egzotermicznych, można zauważyć spadek $\Delta H_{cc}$ po modyfikacji. Intensywność zimnej krystalizacji maleje wraz ze wzrostem stężenia modyfikatora, co potwierdza właściwości uplastyczniające TA. Wzrost $\Delta H_{cc}$ dla

próbki N w porównaniu z próbką P potwierdza, że wprowadzone włókna działały jako zarodki krystalizacji. Wzrost temperatury $T_{cc}$ w próbkach modyfikowanych sugeruje, że energia potrzebna do zapoczątkowania zimnej krystalizacji wzrasta wraz ze wzrostem stężenia TA. Może to być spowodowane większą ilością fazy amorficznej w T10 i T20 w porównaniu z T1 i T5.



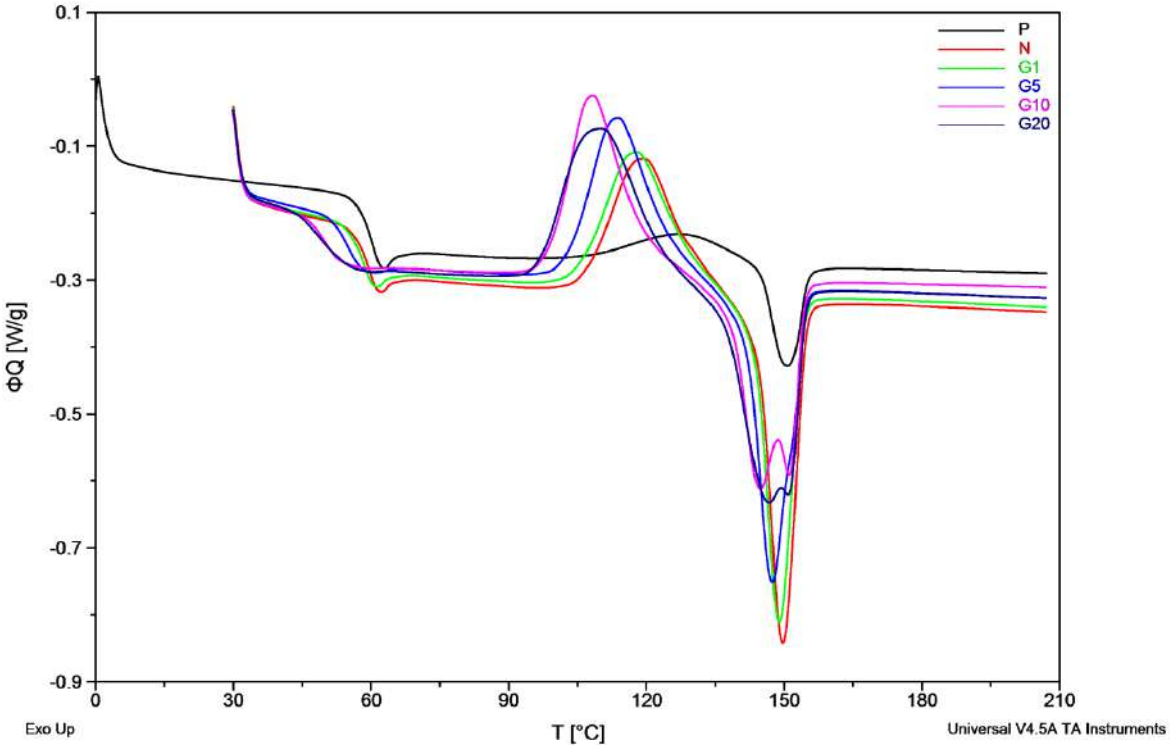

*Rysunek 7. Krzywe DSC opisujące zależność ΦQ od temperatury otrzymane dla próbek zawierających TA.*

Największe różnice pomiędzy $\Delta H_{cc}$ i $\Delta H_m$ dla próbek modyfikowanych odnotowano w przypadku próbki T1 i T20. Migracja TA do polimeru i jej wpływ na właściwości zależą od stężenia modyfikatora. Obniżenie wartości $X_c$ dla próbek modyfikowanych w porównaniu z próbką N (tabela 7) potwierdza plastykujący efekt TA.

*Tabela 7. Wybrane parametry otrzymane dla próbek zawierających TA.*

| **Próbka** | **$T_g$ [°C]** | **$\Delta H_{cc}$ [J/g]** | **$T_{cc}$ [°C]** | **$\Delta H_m$ [J/g]** | **$T_m$ [°C]** | **$X_c$ [%]** |
|---|---|---|---|---|---|---|
| P | 60,52 | 5,38 | 127,42 | 6,30 | 150,73 | 0,98 |
| N | 60,36 | 15,67 | 121,17 | 16,62 | 149,60 | 1,01 |
| T1 | 59,78 | 17,21 | 119,98 | 17,94 | 149,00 | 0,78 |
| T5 | 59,56 | 16,40 | 121,94 | 16,81 | 149,13 | 0,44 |
| T10 | 59,62 | 15,74 | 123,47 | 15,89 | 149,54 | 0,16 |
| T20 | 57,71 | 13,72 | 124,70 | 14,36 | 149,52 | 0,68 |

Zmiany przepływu ciepła (ΦQ) w funkcji temperatury dla próbek modyfikowanych geraniolem przedstawiono na rysunku 8. Można zauważyć, że każda krzywa ma 3 piki – 2 endotermiczne i 1 egzotermiczny. Pierwszy pik endotermiczny jest przypisany procesowi zeszklenia. Pik ten w przypadku próbki N jest nieznacznie przesunięty w stronę niższych temperatur (w porównaniu z próbką P). Może to być spowodowane obecnością wosków zawartych we włóknach lnu, które zachowują się jako naturalne plastyfikatory matrycy polimerowej. Podobną tendencję zaobserwowano dla próbki G1, gdzie wspomniany pik jest dość podobny do piku endotermicznego na krzywej dla próbki N. Wraz ze wzrostem ilości GR zaobserwowano spadek energii potrzebnej do zapoczątkowania zeszklenia. Na krzywych dla próbek G5, G10 i G20 nie występuje charakterystyczny pik endotermiczny. Krzywe tych próbek zaczęły przesuwać się w kierunku endotermicznym wraz z dalszym łagodnym przejściem do linii bazowej. Dodatkowo temperatura zeszklenia ($T_g$) badanych próbek (tabela 8) stopniowo spadała wraz ze wzrostem stężenia GR. Wspomniane zmiany są charakterystyczne dla plastyfikatorów, które pełnią w polimerach funkcję smarów [74]. Obserwacje te potwierdzają wcześniejsze założenia dotyczące właściwości uplastyczniających zastosowanego modyfikatora.




*Rysunek 8. Krzywe DSC opisujące zależność ΦQ od temperatury otrzymane dla próbek zawierających GR.*

Zgodnie z przypuszczeniami, zmiana entalpii zimnej krystalizacji ($\Delta H_{cc}$) wzrosła po wprowadzeniu włókien lnianych do matrycy polimerowej (próbka N). Włókna lniane pełnią rolę czynników nukleacyjnych, przyspieszających krystalizację PLA (tabela 8). Dalszy wzrost $\Delta H_{cc}$ próbek zawierających GR jest spowodowany zwiększoną ruchliwością łańcuchów uplastycznionej matrycy [75]. Największą wartość $\Delta H_{cc}$ zaobserwowano w przypadku próbki G20 co potwierdza, że GR w stężeniu 20% ma najsilniejsze działanie uplastyczniające. Wprowadzenie do matrycy niemodyfikowanych włókien lnianych spowodowało przesunięcie piku egzotermicznego (piku zimnej krystalizacji) w stronę niższych temperatur. Dla wszystkich modyfikowanych próbek zaobserwowano także obniżenie maksymalnej temperatury piku zimnej krystalizacji ($T_{cc}$). Obserwacja ta jest zgodna z wcześniej omówionymi wynikami dotyczącymi właściwości uplastyczniających GR.

*Tabela 8. Wybrane parametry otrzymane podczas badania próbek zawierających GR.*

| **Próbka** | **$T_g$ [°C]** | **$\Delta H_{cc}$ [J/g]** | **$T_{cc}$ [°C]** | **$\Delta H_m$ [J/g]** | **$T_m$ [°C]** | **$X_c$ [%]** |
|---|---|---|---|---|---|---|
| P | 60,43 | 5,86 | 127,49 | 6,22 | 150,70 | 0,38 |
| N | 59,71 | 20,38 | 119,52 | 21,48 | 149,69 | 1,18 |
| G1 | 58,60 | 20,53 | 117,96 | 20,82 | 148,92 | 0,31 |
| G5 | 55,02 | 22,59 | 113,85 | 22,77 | 147,41 | 0,19 |
| G10 | 49,95 | 22,69 | 108,35 | 23,27 | 144,82 | 0,62 |
| G20 | 48,96 | 24,99 | 110,26 | 25,29 | 146,77 | 0,32 |

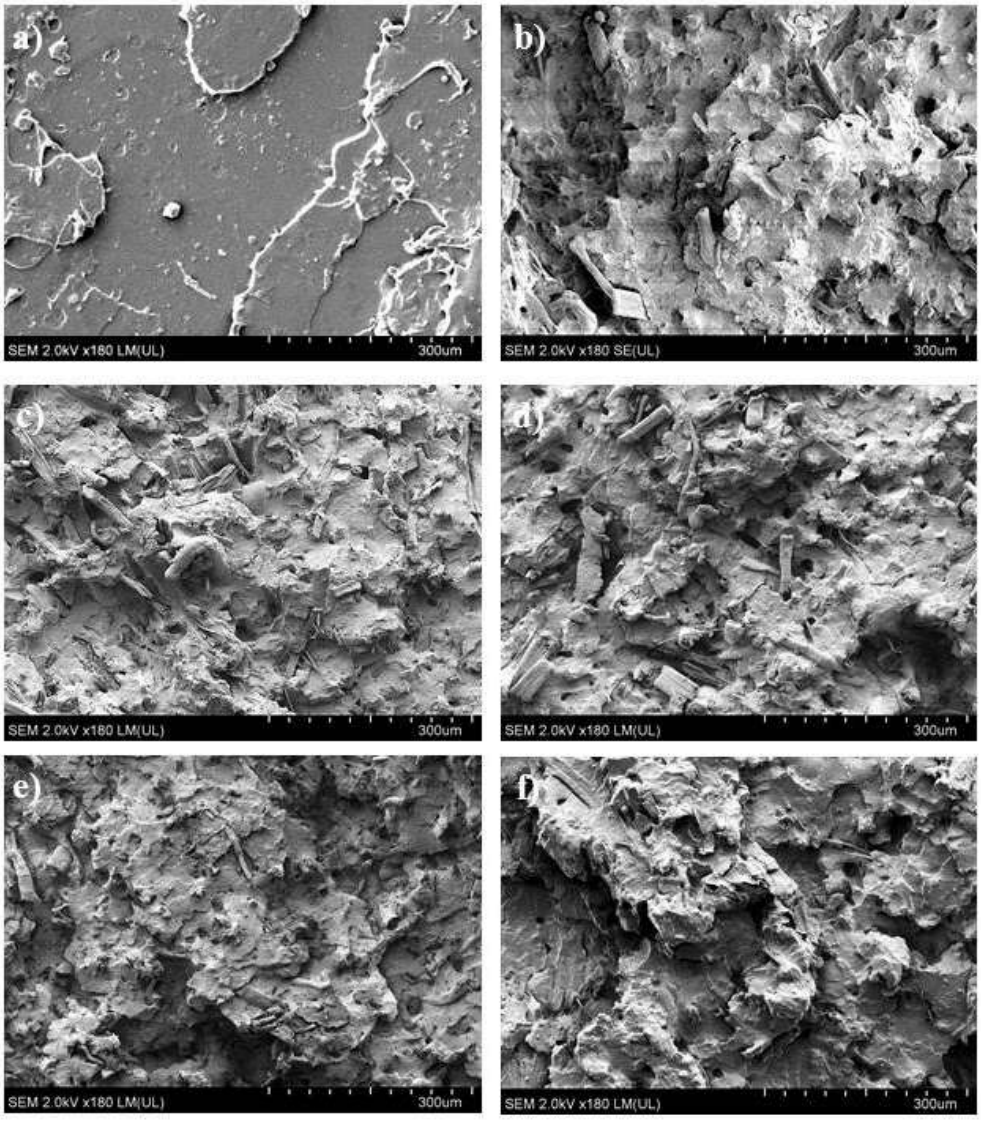
Dygresję wartości zaobserwowano również w przypadku $\Delta H_m$ i $T_m$. Drugi pik endotermiczny (pik topnienia) przedstawia jednoetapowe topienie w przypadku próbek P, N, G1 i G5. Natomiast próbki zawierające 10% i 20% GR topiły się w dwóch etapach. Proces parowania GR może wystąpić w 150°C, co odpowiada pikowi topnienia [76]. Niemniej jednak, parowanie to powierzchniowy proces fizyczny, który nie powoduje degradacji modyfikatora którego maksymalna temperatura przetwarzania nie powinna przekroczyć 200°C [77]. Można stąd wywnioskować, że pierwszy etap topienia odpowiada za topnienie fazy krystalicznej utworzonej przez zarodki zawarte we włóknach lnianych, natomiast drugi etap to topienie się modyfikatora. Prawdopodobnie, ze względu na małą ilość modyfikatora w próbkach G1 i G5, omówione stadia topnienia nałożyły się na siebie, w wyniku czego nie można było wyróżnić poszczególnych faz procesu.

Oprócz przyśpieszonej krystalizacji wraz ze wzrostem stężeń GR, stopień krystaliczności $X_c$ ulegał zmniejszeniu. Może to być spowodowane defektami w strukturze PLA wywołanymi obecnością modyfikatora [75]. Tłumaczyłoby to również zaobserwowane pogorszenie właściwości mechanicznych próbek zawierających włókna modyfikowane.

### *3.4. SEM*

Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

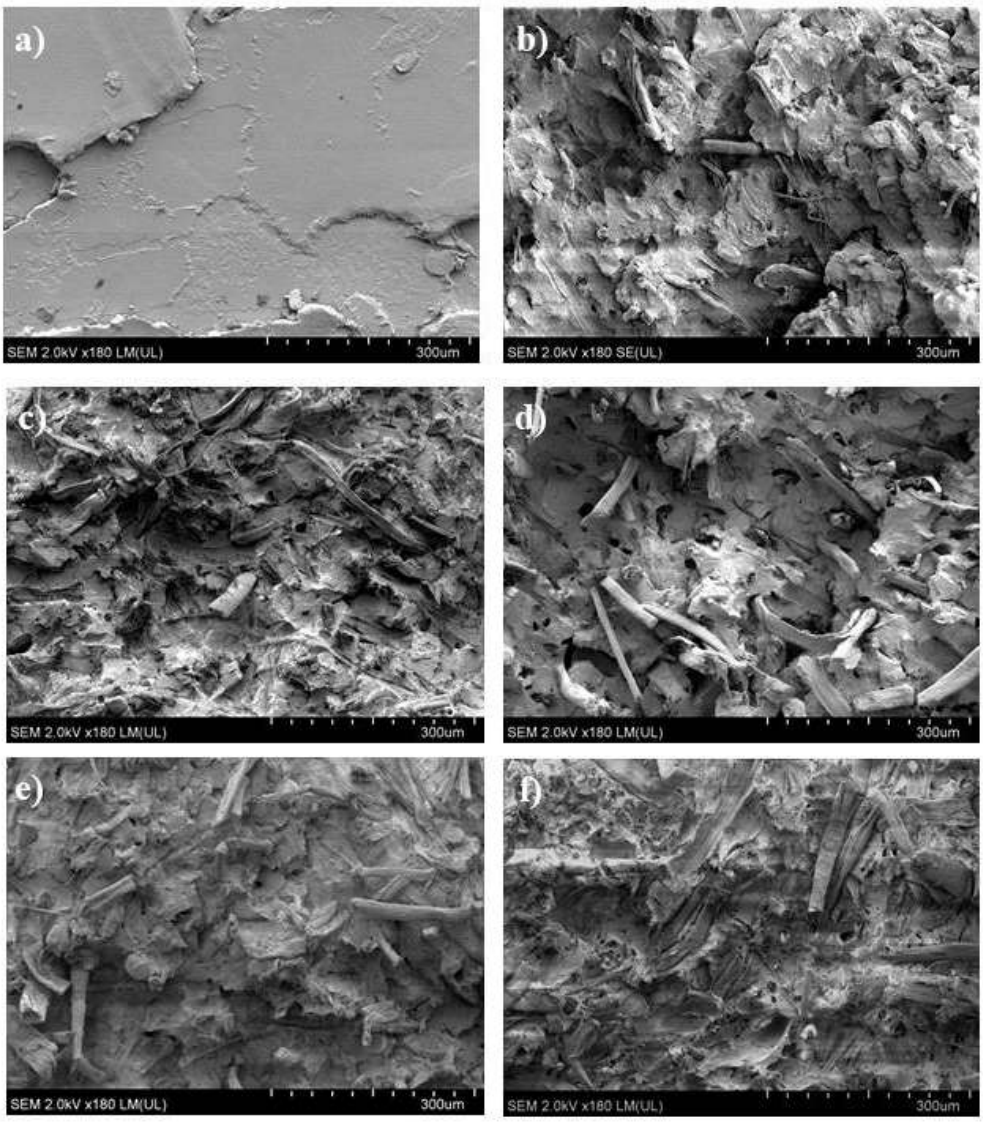
Obrazy SEM (rysunek 9) przedstawiają przekroje pęknięć po statycznej próbie rozciągania próbek zawierających włókna modyfikowane TA. Przekrój próbki N (rysunek 9b) charakteryzuje się mniejszą ilością wyrwanych włókien w porównaniu do próbki T1 (rysunek 9c). Niemniej jednak, wyniki badań statycznej próby rozciągania wykazały podobne właściwości mechaniczne próbek N i T1.




*Rysunek 9. Mikrofotografie SEM otrzymane dla próbek zawierających TA.*

Mikrofotografia przekroju próbki T5 jest podobna do T1 z widoczną niewielką ilością wystających włókien. Rysunek 9e – mikrofotografia próbki T10 przedstawia pojedyncze nitki lnu, które zostały w osnowie polimerowej po wyrwaniu włókien. w przypadku próbki T20 struktura pęknięcia jest znacznie bardziej pofałdowana. Omówiona obserwacja potwierdza wyniki badań mechanicznych i migrację TA w głąb matrycy, który w stężeniu 10% i 20% zmniejszył sztywność kompozytu.

Mikrofotografia na rysunku 10a przedstawia próbkę P z charakterystycznym pęknięciem warstwowym [78]. Wprowadzenie do osnowy polimerowej włókien niemodyfikowanych (rysunek 10b) znacząco zmieniło morfologię pęknięcia. Włókna są mocno osadzone w matrycy polimerowej, co świadczy o dobrej adhezji międzyfazowej. Lepsza przyczepność międzyfazowa zapewniła polepszone przenoszenie obciążeń rozciągających z osnowy na włókna. w przypadku próbek G1 i G5 morfologia struktur przedstawionych na rysunkach 10b i 10c jest podobna. Widoczna jest niewielka ilość pustych przestrzeni, większość włókien jest złamana, a niektóre powyciągane. Jest to spójne z wynikami wcześniej przedstawionych badań wskazujących na umiarkowanym wpływie modyfikatora w małych ilościach (1% i 5%) na właściwości mechaniczne kompozytów.




*Rysunek 10. Mikrofotografie SEM otrzymane dla próbek zawierających GR.*

Bardziej postrzępioną strukturę zaobserwowano dla próbek zawierających włókna modyfikowane w 10% i 20% roztworach GR (rysunek 10e-f). Ilość wyrwanych włókien zwiększała się wraz ze zmianami struktury. Wspomniane obserwacje potwierdzają migrację GR do osnowy polimerowej i jej wpływ na adhezję międzyfazową biokompozytu.

### *3.5. Zwilżalność*

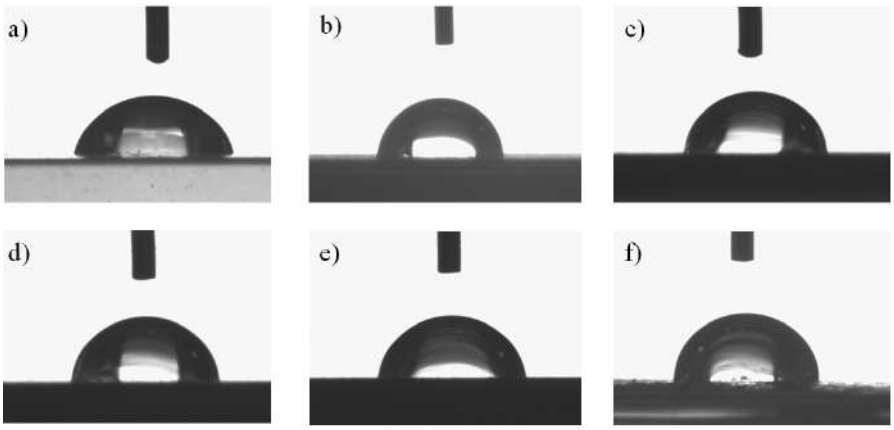
Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

Wyniki uzyskane podczas badania zwilżalności biokompozytów zawierających włókna modyfikowane TA przedstawiono w tabeli 9.

*Tabela 9. Wartości $\overline{\Theta}_w$ otrzymane dla próbek zawierających TA.*

| | **P** | **N** | **T1** | **T5** | **T10** | **T20** |
|---|---|---|---|---|---|---|
| $\overline{\Theta}_w$ [°] | 75,0 | 75,1 | 85,1 | 85,3 | 86,1 | 91,8 |

Porównanie wartości $\overline{\Theta}_w$ wykazało, że włókna lniane pokryte TA obniżają zwilżalność próbek. Różnica pomiędzy wartościami $\overline{\Theta}_w$ dla N i T1 wynosi 10°, co sugeruje, że TA we wspomnianym stężeniu sprzyja zdolności powierzchni biokompozytów do odpychania cząsteczek wody. Podobne tendencje zaobserwowano dla T5 w porównaniu z T1. Nieznaczny wzrost odnotowano także w przypadku T10. Niemniej jednak, właściwości hydrofobowe osiągnięto wyłącznie w przypadku T20. Porównanie kształtów kropli wody (rysunek 11) przedstawia ich kulisty kształt dla próbek modyfikowanych. Wyniki omówionych badań sugerują, że wzrost stężenia modyfikatora jest ujemnie skorelowany ze zwilżalnością powierzchni.



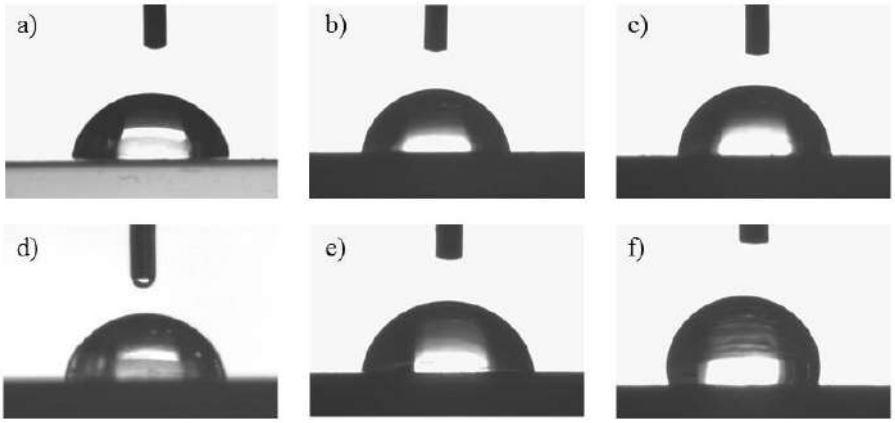

*Rysunek 11. Fotografia kropli wody osadzonej na powierzchni próbek zawierających TA.*

W tabeli 10 przedstawiono średnie wartości kąta zwilżania ($\overline{\Theta}_w$) wodą dla próbek modyfikowanych GR. Zwilżalność materiałów po wprowadzeniu niemodyfikowanych włókien lnianych do osnowy polimerowej nie uległa zmianie. Geraniol zawarty w małych stężeniach w próbkach G1 i G5 obniżał zwilżalność, jednakże wartości $\overline{\Theta}_w$ nadal były zbliżone do próbki N. Modyfikator w 10% stężeniu zwiększył wartość $\overline{\Theta}_w$ o prawie 8° w porównaniu do próbki N, jednakże wzrost ten nadal jest niewystarczający, aby stwierdzić, że nadał on właściwości hydrofobowe próbce G10. Materiał można uznać za hydrofobowy, jeżeli wartość jego $\overline{\Theta}_w$ jest większa niż 90° [79]. Materiały przeznaczone do zastosowań w przemyśle opakowaniowym znajdują się w stałym kontakcie z żywnością, dlatego hydrofobowość ich powierzchni jest pożądana (brak wycieków płynów, zmniejszona ilość namnażanych drobnoustrojów).

*Tabela 10. Wartości $\overline{\Theta}_w$ próbek zawierających GR.*

| | **P** | **N** | **G1** | **G5** | **G10** | **G20** |
|---|---|---|---|---|---|---|
| $\overline{\Theta}_w$ [°] | 75,0 | 75,1 | 76,3 | 77,3 | 83,0 | 96,3 |

Warunek ten jest spełniony w przypadku próbki G20 zawierającej 20% modyfikatora, gdzie wartość $\overline{\Theta}_w$ przekracza 90°, co wskazuje na hydrofobowy charakter powierzchni G20. Zaobserwowany po modyfikacji stopniowy spadek zwilżalności biokompozytów może być spowodowany migracją GR do osnowy polimerowej. Modyfikator w stężeniu 20% zawierający dużą ilość hydrofobowych łańcuchów alkilowych stworzył naturalną barierę hydrofobową na powierzchni próbki G20. Na rysunku 12 przedstawiono zmianę kształtu kropli wraz ze wzrostem stężenia modyfikatora. Można zauważyć, że kształt próbki G20 znacznie różni się od kropli osadzonych na powierzchni pozostałych próbek.




*Rysunek 12. Zdjęcia kropli wody osadzonej na powierzchni próbek zawierających GR.*

Hydrofobowość powierzchni jest niezwykle ważnym parametrem biokompozytów dedykowanych do zastosowań przemysłowych, a mianowicie w branży żywnościowej i opakowaniowej. Materiały biodegradowalne o zwiększonej hydrofobowości są bardzo pożądane w wielu gałęziach przemysłu. Bliski kontakt z żywnością materiałów stosowanych w wymienionym przemyśle wymaga zwiększonej kontroli ich higieny mikrobiologicznej. Właściwości hydrofobowe są kluczowe, ponieważ ograniczają namnażanie się mikroorganizmów na powierzchni wyrobu i pozwalają na dłuższe przechowywanie żywności w opakowaniach. Dzięki temu, zmniejszają straty finansowe związane z przedwczesnym psuciem się produktów.

### *3.6. Biobójczość*

Poniższe wyniki badań wraz z dyskusją zostały opublikowane w artykułach [B], [C] i [D].

Biobójczość próbek określono na podstawie dwóch szczepów bakterii – *E. coli i S. aureus* (tabela 11). Bakterie te są najczęstszą przyczyną skażeń mikrobiologicznych żywności. Wyniki badań biobójczości dla próbek modyfikowanych TA przedstawiono w tabeli 12. Analiza porównawcza $T_0$ i $T_1$ dla bakterii *E. coli i S. aureus* wykazała brak spadku rzędu wielkości $T_1$ dla próbek P, N i T1. Brak redukcji jest również zauważalny przy wartościach R, zbliżonych do 0. Najwyższa wartość R dla wymienionych próbek była odnotowana dla próbki T1. Niemniej jednak, jej wartość była wciąż zbyt niska, by stwierdzić aktywność biobójczą danej próbki.

Wartość R dla próbki T1 wobec *S. aureus* była nieco większa niż wobec *E. coli,* niemniej jednak modyfikacja włókien w 1% roztworze TA nie przyniosła oczekiwanych rezultatów w postaci właściwości biobójczych.

*Tabela 11. Wyniki otrzymane podczas badań biobójczości próbek zawierających TA.*

| **Próbka** | ***E. coli* [jtk/ml]** | | | ***S. aureus* [jtk/ml]** | | |
|---|---|---|---|---|---|---|
| | $T_0$ | $T_1$ | R | $T_0$ | $T_1$ | R |
| P | $9{,}30 \times 10^6$ | $3{,}80 \times 10^6$ | 0,00 | $11{,}00 \times 10^6$ | $9{,}80 \times 10^6$ | 0,00 |
| N | | $5{,}10 \times 10^6$ | <0,00 | | $10{,}20 \times 10^6$ | <0,00 |
| T1 | | $2{,}80 \times 10^6$ | 0,13 | | $3{,}70 \times 10^6$ | 0,42 |
| T5 | | $<10^2$ | >4,58 | | $<10^2$ | >4,99 |
| T10 | | $<10^2$ | >4,58 | | $<10^2$ | >4,99 |
| T20 | $1{,}50 \times 10^8$ | $\leq 0{,}40 \times 10^6$ | 3,00 | $1{,}40 \times 10^8$ | $< 1{,}00 \times 10^3$ | 5,00 |

W przypadku próbek zawierających włókna modyfikowane w 5% i 10% stężeniach TA odnotowano wyraźny spadek $T_1$, czyli wzrost wartości R. $T_1$ zmalała o 4rzędy wielkości dla obu szczepów bakterii. Wartości R przekraczały 4,58 w przypadku *E. coli* i 4,99 w przypadku *S. aureus*. Według [80] silniejsza biobójczość TA wobec *S. aureus*. może być spowodowana tym, że TA wiąże się w sposób bezpośredni z warstwą peptydoglikanu bakterii Gram-dodatnich (*S. aureus*), co zwiększa ich podatność na działanie mikrobiologiczne modyfikatora, niż bakterii Gram-ujemnych (*E. coli*) [81], [82], [83]. Próbka T20 wykazała te same tendencje, niemniej jednak jej wartość R w stosunku do *E. coli* była mniejsza niż R dla T10. Podsumowując, wartość Rdla T5 i T10 jest ponad dwa razy większa niż minimalna wartość R uznana dla materiałów biobójczych. Należy również zauważyć, że odporność TA na bakterie Gram-ujemne spada z biegiem czasu. Podsumowując, modyfikacja włókien TA w stężeniu 5%, 10% oraz 20% znacznie wpłynęła na właściwości biobójcze próbek T5, T10 i T20 co było zgodne z początkowymi założeniami rozprawy doktorskiej, bazującymi na przeglądzie literatury.

Tabela 12 przedstawia wyniki badań biobójczości dla próbek zawierających włókna lniane modyfikowane w GR. Wraz z wprowadzeniem włókien modyfikowanych

do osnowy polimerowej zauważono spadek liczby bakterii na powierzchni materiału odnotowanych po 24 h od ich osadzenia ($T_1$). w porównaniu do początkowej ilości bakterii tworzących kolonie ($T_0$) wartość $T_1$ zmalała o 2 rzędy wielkości dla próbki G1. Jednocześnie, wartość R wyniosła 1,00 w stosunku do *E. coli* i do *S. aureus*. Można wnioskować, że GR w stężeniu 1% wykazuje aktywność mikrobiologiczną w stosunku do badanych szczepów bakterii, niemniej jednak nie wykazuje właściwości biobójczych.

*Tabela 12. Wyniki otrzymane podczas badań biobójczości próbek zawierających GR.*

| **Próbka** | ***E. coli* [jtk/ml]** | | | ***S. aureus* [jtk/ml]** | | |
|---|---|---|---|---|---|---|
| | $T_0$ | $T_1$ | R | $T_0$ | $T_1$ | R |
| P | $1{,}50 \times 10^8$ | $1{,}50 \times 10^7$ | 0,00 | $1{,}50 \times 10^8$ | $2{,}00 \times 10^7$ | 0,00 |
| N | | $1{,}50 \times 10^7$ | 0,00 | | $1{,}50 \times 10^7$ | 0,00 |
| G1 | | $1{,}50 \times 10^6$ | 1,00 | | $2{,}00 \times 10^6$ | 1,00 |
| G5 | | $2{,}00 \times 10^5$ | 2,00 | | $3{,}00 \times 10^6$ | 1,00 |
| G10 | | $1{,}50 \times 10^2$ | 5,00 | | $1{,}50 \times 10^2$ | 5,00 |
| G20 | | $\leq 1{,}00 \times 10^1$ | $\geq 6{,}00$ | | $1{,}20 \times 10^1$ | 6,00 |

Działanie biobójcze GR zaobserwowano w przypadku próbki G5 zawierającej włókna modyfikowane w 5% roztworem TA. Wartość R dla *E. coli* była równa 2,00, a dla *S. aureus* wynosiła 1,00, co sugeruje że GR w małych stężeniach jest mniej skuteczny przeciwko szczepom bakterii Gram-dodatnich. Bakterie Gram-dodatnie (*S. aureus*) i Gram-ujemne (*E. coli*) różnią się budową komórki. Pierwsze nie mają zewnętrznej błony komórkowej, ale otoczone są grubszą ścianą peptydoglikanowa. Natomiast drugie dodatkowo wyposażone są w zewnętrzną błonę komórkową. Najprawdopodobniej grubsza ściana peptydoglikanowa bakterii *S. aureus* składająca się z wielu warstw stanowi bardziej efektywną barierę spowalniającą działanie GR. Natomiast większe stężenie modyfikatora (5%) skutecznie przebija zewnętrzną błonę komórkową, na skutek czego następuje szybsza śmierć komórki *E. coli w* porównaniu do *S. aureus*, którego grubsza ściana peptydoglikanowa hamuje przenikanie GR do jądra komórki [84].

Znaczące obniżenie rzędów wielkości $T_1$ (o 6 i 7) stwierdzono dla próbek G10 i G20. Próbki te, zawierające modyfikator w większych stężeniach wykazały silne działanie biobójcze wobec obu szczepów bakterii. Najprawdopodobniej, działanie to jest na tyle silne, że pokonuje mechanizmy obronne obu typów bakterii. Podsumowując, GR charakteryzował się biobójczością w stosunku do *E. coli* w stężeniach 5%, 10% i 20% oraz w stosunku do *S. aureus* w stężeniach 10% i 20%.

# 4. Podsumowanie i wnioski

Przeprowadzone badania pozwoliły na porównanie wpływu dwóch modyfikatorów pochodzenia roślinnego, kwasu taninowego oraz geranioliu, na wybrane właściwości biokompozytów na osnowie polilaktydu wzmocnionych włóknami lnianymi. Uzyskane wyniki badań potwierdziły zarówno cel naukowy jak i cele utylitarne rozprawy doktorskiej. Wprowadzenie do osnowy włókien modyfikowanych zarówno kwasem taninowym jak i geraniolem spowodowało oddziaływania pomiędzy materiałem osnowy a modyfikatorem na poziomie makrocząsteczkowym. Ze względu na brak zastosowanych technik modyfikacji polegających na chemicznej obróbce włókien, i jej zastąpienie zrównoważonym powlekaniem wzmocnienia, zaobserwowano słabszą adhezję modyfikatora na ich powierzchni. Dzięki temu, modyfikator pod wpływem temperatury mógł migrować do matrycy, a zwiększona ruchliwość łańcuchów polimerowych poskutkowała zwiększeniem plastyfikacji biokompozytu.

Badania termomechaniczne wykazały, że nawet niewielkie ilości modyfikatora sprzyjają procesom plastyfikującym zachodzącym w materiale. Wraz ze wzrostem stężenia modyfikatorów zwiększała się jego plastyfikacja. Potwierdza to fakt, że zarówno kwas taninowy jak i geraniol przyśpieszyły proces zeszklenia badanych kompozytów z jednoczesnym obniżeniem stopnia krystaliczności materiałów. Jest to proces naturalny charakterystyczny dla modyfikatorów pochodzenia roślinnego. Obniżona odporność na odkształcenia została zaobserwowana również podczas analizy badań mechanicznych zarówno dla próbek modyfikowanych kwasem taninowym jak i geraniolem. Jej zwiększenie następowało wraz ze wzrostem stężenia modyfikatorów. Niemniej jednak, ze względu na docelowe przeznaczenie opracowywanych materiałów (głównie branża opakowaniowa i opakowania jednorazowego użytku) właściwości mechaniczne gotowych wyrobów nie są kluczowe.

Badania termiczne potwierdziły porównywalne temperatury degradacji w przypadku obu modyfikatorów i ich stabilność termiczną w zakresie temperaturowym do 240°C dla kwasu taninowego i do 200°C dla geraniolu.

Badania strukturalne przeprowadzone przy użyciu SEM pozwoliły na głębsze zrozumienie oraz potwierdzenie badań mechanicznych, a mianowicie statycznej próby rozciągania. Obserwacja pęknięć próbek wykazała zmiany w mikrostrukturze biokompozytów związane z migracją modyfikatora w głąb matrycy, co spowodowało obniżenie adhezji na granicy faz materiałów.

Niemniej jednak, migracja modyfikatora w głąb matrycy jest niewątpliwie pozytywnym zjawiskiem, biorąc pod uwagę zmiany, które zaszły na powierzchni materiałów zawierające włókna modyfikowane. Badania zwilżalności wykazały, że zwilżalność badanych materiałów uzależniona jest od stężenia modyfikatora wprowadzonego wraz z włóknami do matrycy polimerowej. w przypadku stężeń od 1% do 10% odnotowano obniżenie zwilżalności, natomiast materiały zawierające modyfikator w stężeniu 20% charakteryzowały się właściwościami hydrofobowymi. Tendencje te były wspólne dla kwasu taninowego jak i dla geraniolu.

Nieco różne wyniki dla kwasu taninowego i geraniolu otrzymano w wyniku przeprowadzenia badań biobójczości. Dla biokompozytu zawierającego 1% kwasu taninowego współczynnik redukcji był również większy w stosunku do szczepu *Staphylococcus aureus* (0,42) niż do *Escherichia coli* (0,13). Szczep *Staphylococcus aureus* zaliczany jest do bakterii Gram-dodatnich charakteryzujących się brakiem zewnętrznej błony komórkowej co ułatwia przenikanie modyfikatora w głąb komórki bakteryjnej oraz jej bardziej skuteczną destrukcję. Współczynnik redukcji dla materiału zawierającego 1% geraniolu wynosił 0 w stosunku do *Escherichia coli* i 1 w stosunku do *Staphylococcus aureus*. Materiały z współczynnikiem redukcji poniżej 2 nie są uważane za materiały biobójcze, niemniej jednak wartość 1 sugeruje zachodzące zmiany ograniczające proliferację komórek bakteryjnych na powierzchni materiału. Kompozyt zawierający 5% kwasu taninowego wykazywał właściwości biobójcze zarówno do *Escherichia coli* jak i *Staphylococcus aureus*, natomiast materiał zawierający geraniol o tym samym stężeniu, był biobójczy wyłącznie w stosunku do *Escherichia coli.* Biobojczość w stosunku do obu bakterii była zaobserwowana w przypadku próbek zawierającym większe stężenie kwasu taninowego jak i geraniolu – 10% i 20%. Współczynnik redukcji próbki modyfikowanej kwasem taninowym o stężeniu 20% w stosunku do *E. coli* wynosił 3. Oprócz właściwości biobójczych, zauważono, że kwas taninowy wykazuje działanie bakteriostatyczne polegające na hamowaniu proliferacji żywych mikroorganizmów, które były odporne na jego biobójcze działanie [85].

Przeprowadzone badania pozwoliły oszacować możliwości wykorzystania związków pochodzenia roślinnego w postaci modyfikatorów włókien lnianych w celu skutecznej walki z mikroorganizmami. Jednocześnie, przedstawione wyniki badań potwierdziły potencjał aplikacyjny modyfikowanych materiałów w branżach, gdzie

wymagana jest ochrona mikrobiologiczna oraz obniżona zwilżalność materiałów. Takimi branżami są między innymi branża kosmetyczna, opakowaniowa, gastronomiczna. w branży gastronomicznej, materiały narażone są na stały kontakt z żywnością oraz działanie mikroorganizmów, co sprawia że odporność mikrobiologiczna powierzchni stosowanych materiałów jest niezwykle ważna. Interdyscyplinarność pracy pozwala na rozwój w dziedzinie inżynierii materiałowej jak i mikrobiologii.

Przedstawione wyniki badań nie tylko potwierdziły wysoki potencjał aplikacyjny opracowanych biokompozytów, ale również wypełniły istotną lukę w dotychczasowej wiedzy. Dodatkowo, szczegółowo wskazały na mechanizmy interakcji między modyfikatorami roślinnymi, włóknami lnianymi a osnową polimerową PLA, umożliwiając optymalizację warunków modyfikacji dla uzyskania stabilnych, powtarzalnych właściwości końcowych materiałów. Dodatkowo, interdyscyplinarność podejścia (łączące inżynierię materiałową, mikrobiologię oraz ochronę środowiska) przyczynia się do rozwoju nowych kierunków w naukowych badaniach i przemysłowych rozwiązaniach, które łączą korzyści ekologiczne (biodegradowalność, brak negatywnego wpływu na środowisko i zdrowie ludzi) z funkcjonalnością użytkową (odporność mikrobiologiczna oraz obniżona zwilżalność).

Opracowane materiały stanowią innowacyjne, dostosowane do współczesnych potrzeb rozwiązanie – łączą biodegradowalność, bezpieczeństwo dla zdrowia oraz multifunkcyjność, przyczyniając się do zrównoważonego rozwoju oraz ograniczenia negatywnego wpływu przemysłu polimerowego na środowisko naturalne.

Dodatkowo, przygotowanie materiałów, biokompozytów pozwoliło na uzyskanie niezbędnego doświadczenia i wiedzy w obszarze modyfikacji włókien lnianych modyfikatorami pochodzenia roślinnego oraz przetwarzania kompozytów na osnowie polilaktydowej. Badane materiały, w pełni składające się z surowców roślinnych, charakteryzowały się wysoką biodegradowalnością. Rozwój i opracowanie materiałów nieobciążających środowiska i zastąpienie nimi materiałów pochodzenia petrochemicznego, stosowanych obecnie na szeroką skalę, w przyszłości przyczyni się do postępu nie tylko w inżynierii materiałowej, jak i również w ekologii i ochronie środowiska.

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# Załączniki

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REVIEW

# Natural Biocidal Compounds of Plant Origin as Biodegradable Materials Modifiers

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**Abstract**
The article presents a literature review of the plant origin natural compounds with biocidal properties. These compounds could be used as modifiers of biodegradable materials. Modification of polymer material is one of the basic steps in its manufacturing process. Biodegradable materials play a key role in the current development of materials engineering. Natural modifiers are non-toxic, environmentally friendly, and renewable. The substances contained in natural modifiers exhibit biocidal properties against bacteria and/or fungi. The article discusses polyphenols, selected phenols, naphthoquinones, triterpenoids, and phytoncides that are natural antibiotics. Due to the increasing demand for biodegradable materials and the protection of the natural environment against the negative effects of toxic substances, it is crucial to replace synthetic modifiers with plant ones. This work mentions industries where materials containing natural modifying additives could find potential applications. Moreover, the probable examples of the final products are presented. Additionally, the article points out the current world's pandemic state and the use of materials with biocidal properties considering the epidemiological conditions.

**Keywords** Biodegradable polymers · Natural origin modifiers · Biocidal additives · Polyphenols · Phytoncides

## Introduction

Modification of polymer materials is carried out to give the desired characteristics to the final products. These features depend on the application. For example, the industry in which the polymer materials will be used or the function they will perform. Modification is the most common way to give unique features and improve selected parameters of finished goods made from polymer materials. The modification changes their properties and internal structure. One of the methods of changing the internal structure of materials is the insertion of modifying additives. In general, it is carried out during the production process. The aspiration to reduce the number of additives gave rise to the search for modifiers that would give more than one new feature to the biodegradable material. Due to the current epidemiological situation, the research of compounds with biocidal properties added to polymer materials is in more dynamic progress than ever before. The biocidal properties of the material are understood as the capability to reduce the number of pathogenic microorganisms under defined conditions [1–4]. The increase of public awareness of environmental pollution, the constant growth of the number of post-consumer waste, and care for human health are observed nowadays. Thus additives should meet the modern criteria and conditions. First of all, they should be non-toxic to human health and the environment [5]. Polymer materials used in the medical, pharmaceutical, and packaging industries are in close contact with the human body or food [6, 7]. The application of polymer materials in mentioned industries may depend on the substances they contain. The additives contained in the material cannot interact with other materials. All of the mentioned conditions concern both modifying additives and polymer matrices.

Biopolymers are the polymers that naturally occur in flora and fauna [8]. They cause no environmental pollution and are completely harmless for the inhabitants of the earth. Moreover, this kind of polymers is obtained from renewable resources which do not destroy our planet. The natural origin of this type of materials makes them biodegradable—susceptible to chemical processes that lead to the decomposition of biochemical substances. The decomposition is done by

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microorganisms [9]. The biopolymers are well suited for biocomposites (composites that are produced from renewable raw materials) manufacturing due to their biodegradability, no-toxicity, and natural origin.

Biocomposites are promising materials that may be implemented into everyday use. The processing of biocomposites with biopolymer matrix doped with natural-origin modifying additives is a promising field of biodegradable biocomposites. Biocomposites like this are the present development trend in polymer materials. The current literature state helps to create a classification of modifying additives of natural origin which contain organic substances.

This article presents already used modifiers and those having the potential to be used in the production of polymer materials that exhibit biocidal properties. The synthesis, properties, and application of natural modifiers of plant origin are discussed. The basic groups of polyphenols and selected compounds of natural origin such as some phenols, naphthoquinones, triterpenoids, or phytoncides are presented.

## Biopolymer Matrices

Polymer might be called biopolymer if it is biobased (produced by the living organism) or/and biodegradable. They are divided into two groups. The first group of biopolymers (natural) is obtained from living organisms, while the second one (synthetic) is produced during the polymerization of selected compounds contained in renewable resources [10–12]. Moreover, the natural biopolymers group consists of two subgroups: polysaccharides and proteins, while the synthetic biopolymers group is divided into degradable and non-degradable biopolymers [10]. Most of the representatives of mentioned groups are used as materials for biocomposite matrices. Due to the current ecological threat resulted from residual plastic waste the creation of completely biodegradable composites is crucial. It is possible, however, every part of the composite should be biodegradable. Therefore, the application of natural plant modifiers in biocomposites is an excellent solution for environment-friendly materials.

### Chitosan

Chitosan belongs to polysaccharides. This biopolymer is sourced from chitin—one of the most common polysaccharides in the world. It occurs in marine shellfish, insects, mushrooms, and yeast. The highest percentage content of chitin has been observed in shells and tails of crabs, shrimps, and lobsters. Hence, chitosan could be "recycled" from seafood waste. This method of chitosan extraction could improve current environmental conditions [13–15].

Chitosan is known as a semicrystalline polymer material with various types of crystal structures (polymorphism). It is a biodegradable, biocompatible, and renewable polymer material with antioxidant properties. Moreover, chitosan is non-toxic for humans and bioactive against selected microorganisms and viruses [15, 16]. Material is soluble in acid solution and non-soluble in the majority of solvents. Its hydrophilic properties promote the ability to create films. However, the hydrophilicity of this material has its drawback: it leads to material swelling in water. Hence, material modification is advised. Furthermore, it is known that chitosan is susceptible to modification [17].

This biopolymer is used for environmental protection purposes (e.g. water purification) [17]. In the agricultural industry, chitosan is applied as a biostimulator that promotes plants growth and their defense mechanisms. As a seed coating material chitosan improves its germination rate [18]. Due to its biological activity, it is used in the food and food packing industries as a biopreservative that extends the shelf life of products [19, 20]. Material has potential application in the medical industry due to its unique (e.g. wound healing) properties. Chitosan could be applied as surgical sutures or in bones and dental prosthetics. According to the hydrating properties of the compound, it is could be used as a material for contact lenses [15, 21].

### Starch

Starch is another natural polymer that belongs to polysaccharides [22]. It occurs in plant roots, tubers, and fruits. The main sources of starch are cereals and potatoes. Although it could be extracted from certain varieties of pea and lily [23, 24]. Starch consists of homopolymers—amylase and amylopectin. Amylase is soluble, while amylopectin is non-soluble [8, 22]. Wet grinding, drying, and sieving are the main ways to obtain starch [24].

Energy storage is the main function performed by starch in various plants [25]. Starch is a hydrophilic biodegradable polymer that is non-soluble in cold water and soluble in diluted solutions of acids and bases. It is known that the mechanical treatment (milling) of starch improves its solubility [22, 26, 27]. This polymer is renewable, biocompatible, and biodegradable [24]. Its presence in polymer materials increases their biodegradability [25]. According to Syafiq et al. [28], the mechanical properties of the starch-based films are comparable to currently used plastics. Besides this, the starch films have an advantage—they are edible. Moreover, starch is a low-price polymer [24].

According to the non-toxicity of starch and its unique polymer properties, it is applied in many industries [24]. However this polymer is mainly used in textile [29], pharmaceutical [24], paper [30], printing [31], and cosmetic [32] industries. This polymer would be an excellent material for

the production of biodegradable disposables if it exhibited hydrophobic properties [25]. The wide range of starch modification methods enables its application in the food industry [33].

## Zein

Zein which belongs to proteins is one of the most frequently used biopolymers from renewable sources [34]. It is obtained only from maize: corn gluten meal (CGM), distillers dried grains (DDG), and dried milled corn [35, 36]. It is the main protein that occurs in corn endosperm cells and its percentage content varies from 35 to 65% [35, 37].

It is a biodegradable and biocompatible material that exhibits hydrophobic, antioxidant, and mucoadhesive properties [38–41]. The solubility of zein depends on the solvent: it is insoluble in water, while anionic detergents, alcohols, and urea (only in high concentration) dissolve it [35]. Solvent parameters (such as pH and temperature) affect zein structure [42]. According to Arvanitoyannis et al. [43] zein is a brittle material and this characteristic has a negative effect on its structural properties.

Zein is used in the textile, food, and biomedical industries [35]. According to Gonçalves et al. [44], zein-coatings improve the hydrophobic properties of cotton. Due to the United States Food and Drug Administration (FDA) zein is generally recognized as safe (GRAS) [38]. Hence, it is widely used in industries where this polymer could have close contact with the human body. Zein-based edible coatings which contain various antioxidant modifiers are used as food biopreservatives. Zein is applied as a component of adhesives [35]. It is known that the bioactive agents could be encapsulated with this biopolymer [38, 45]. Zein is applied as a material for gene, drug, and vaccine delivery. Tissue engineering is another industry where zein could be potentially used [41]. It could be also implemented as a film and coating material for materials engineering uses. According to the unique properties of zein, it has the potential to replace currently used polymers with the petrochemical origin [42].

## Gelatin

Gelatin is another protein biopolymer [46, 47]. It is obtained from animal skin, bones, cartilages, connective tissues, and fish scales. All the mentioned sources contain collagen [8, 46, 48]. Nowadays, the main source of gelatin is cattle and a pig skin. However, these kinds of animals are suffering from various infectious diseases. Therefore, the alternative sources of gelatin are in constant search. For example, almost one-third of fish waste is skin, scales, and bones which could be used for protein extraction and further gelatin production [25]. It is one of the sustainable ways of waste management which could improve the current ecological state.

According to the natural origin of this polymer, it is completely biodegradable and biocompatible. Gelatin exhibits bioactive (especially antimicrobic), antioxidant, and crosslinking properties [46]. The organic solvents dissolve this material [49]. Gelatin prevents recrystallization and promotes adhesion. However, its adhesive properties depending on the viscosity of the solution. Gelatin is a promising biopolymer for materials engineering applications because of its ability to form films and foams [50]. The fish gelatin is a strong rival to mammal one due to their similar properties. However, the characteristics of fish gelatin depend on the species of fish and the extraction conditions [51].

This biopolymer is widely used in the pharmaceutical, medical, cosmetic, and food industries due to its biocompatible properties [8, 25]. Gelatin is a feedstock for capsules production [49]. Medical applications of material cover mainly tissue engineering (especially tissue regeneration) [52]. Gelatin-based face masks are widely used by consumers [53]. It is known that this polymer is applied as a compound of lotions and creams [54]. The tasteless edible films and encapsulating materials made from gelatin are used in the food industry [49, 55]. Gelatin-based biofilms with improved mechanical properties and water resistance are in current research [55]. Moreover, it is applied as a photographic emulsion and surface modifier [46, 55–58].

## Polylactide (PLA)

PLA is classified as a synthetic degradable polymer [10]. PLA is obtained from lactic acid which is mainly isolated from sugar beets, potatoes, and corn [59–61]. There are two main methods of PLA production: polycondensation of lactic acid and ring-opening polymerization of lactide (extracted from lactic acid) [62, 63]. According to Su et al.'s [64] predictions, the amount of produced PLA will increase in the next 2 years.

PLA is a thermoplastic polymer, its properties (clarity and rigidity) are similar to polystyrene (PS) [65]. However, the melting temperature ($T_m$) of PLA is higher and riches 180 °C [61]. Another advantage of PLA is a lower greenhouse gas emission compared to PS [66]. It is completely biodegradable, dissolves in organic solvents, and swells in a wide range of solvents. The water absorption tendency of PLA affects negatively its degree of crystallinity [61, 67]. The toxicity of polymer is low [68].

According to the biocompatibility of PLA it is widely used in healthcare (e.g. medical and drug) and cosmetic industries. Material is used in prosthetics, orthopedics, reconstructive surgery, tissue engineering and so forth. The PLA microcapsules and microspheres are used to reach the effect of prolonged drug release. Cosmetic application

of material includes microbeads, face masks, and tissues [68–72]. Due to its relatively high mechanical strength, it is used in the food-packing industry as a vegetable packaging, shrink films, and food trays material. Moreover this it is used for paper bags lamination [73]. The PLA-based packing materials are an environmentally friendly solution that could replace the packaging with petrochemical and non-degradable origin [74, 75]. Another industry of PLA application is the textile industry. PLA fibers are similar to PET fibers, however, the first ones have several advantages: they are more hydrophilic, have better self-extinguishing parameters, and prevent the multiplication of bacteria. Hence, it is used in clothing, towels, wipes, and filters. Due to sustainability and environmental friendliness, PLA is applied in geotextiles [76]. Moreover, PLA is used for environmental purposes as a sorbent that disposes harmful contaminants contained in water. Additionally, PLA takes part in bioremediation—a technique that uses microorganisms to remove environmental impurities [77].

### Polyhydroxybutyrate (PHB)

PHB is another biopolymer that belongs to the degradable biopolymers subgroup [10]. It is produced by various bacteria and microalgae under certain stress conditions (e.g. carbon excess; oxygen, nitrogen, or phosphate deficiency) and performs a storage function [12, 78, 79]. Bacteria and microalgae are the most common forms of life in the world. However, the cultivation and harvesting of these microorganisms is limited due to the expensive equipment used in these processes [12]. According to Sirohi et al. [80], PHB could be isolated from by-products created during production processes in agricultural, dairy, and food industries.

Certain properties (e.g. physicochemical) of PHB are comparable to fossil fuel-based polymer materials. Despite this, the high biodegradability and biocompatibility of this polymer are known. This fact makes PHB a potential alternative to currently used petroleum-based polymers. However, the high production costs of biopolymer are the main obstacle for its implementation into the industry for commercial purposes. It creates no environmental pollution due to the no-toxicity of its degradation products [78–82]. PLA is characterized as a high crystallinity (degree of its crystallinity rages from 50 to 70%) polymer with low water vapour permeability [79, 83–85].

PHB is used in aquacultural, medical, and tissue engineering industries. Moreover, biopolymer is used for equipment production [79, 85]. PHB is applied as a material for the wound dressings and microspheres used in drug delivery systems. Tissue engineering applications of biopolymer and its composites cover sutures, screws, bone plates, staples, rivets, tacks, etc. In the aquacultural industry, it is used as an anti-adhesive agent against shellfish pathogens. While in the agricultural industry it could be applied as an antifouling compound [85]. Also, it is used as an additive for paints and coatings that cause no environmental pollution [86]. It hardly interacts with food, hence it has potential application in the food packing industry [87].

## Classification of Polyphenols

Polyphenols are organic compounds and plant secondary metabolites i.e. final products of enzymatic reactions which occur as a result of metabolism in plants [8, 88]. Polyphenols are present in fruits, seeds, roots, bark, stalk, timber, and leaves of numerous plants. They are divided into phenolic acids, lignans, stilbenes, and flavonoids [89]. This classification is based on the number of phenolic groups contained in the phenolic ring and also on the method of aromatic rings combining. Each group additionally includes over a dozen subgroups. More than 8000 polyphenol compounds have been discovered [90, 91]. The majority of polyphenols are compounds of products that play an essential part in the basic human diet. The well-known properties of polyphenols make them interesting modifying additives of biocomposites [92–94]. The next parts of the article perform a detailed analysis of mentioned groups of polyphenols.

### Flavonoids

The best-known group of polyphenols is flavonoids (Fig. 1)—compounds that dye flowers, fruits, and drupes of plants. Flavonoids are the biggest group of polyphenols that includes over 8000 compounds [95, 96]. The number of discovered compounds is constantly increasing [97]. These compounds perform plenty of functions: protecting plants from ultraviolet radiation (UV) damage, creating a biological protective barrier, and exhibit biocidal functions against microorganisms. Furthermore, flavonoids are known as natural antioxidant compounds [98]. Representatives of flavonoids such as flavanones, flavones, flavonols, and isoflavonoids are also well-known for their biocidal properties.

Flavonoids are the promising modifiers of polymer materials due to mentioned properties. These modifiers can be used in the building industry as compounds of products that are exposed to UV radiation (windows, gutters, and other

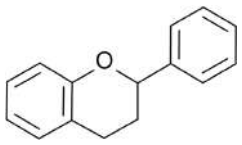


**Fig. 1** Chemical structure of flavonoids [99]

elements manufactured from polymer materials). Increased resistance to UV radiation may improve the aesthetic values which getting worse over time. Window or door elements such as handles doped with biocidal modifiers compounds like flavonoids are necessary in public spaces, especially in current epidemiological conditions. This solution may decrease the number of microorganisms embedded in elements of public usage. In the future, it may reduce the number of infections with various diseases. This group of compounds and their applications are discussed in section 'Classification of Flavonoids'.

## Phenolic Acids

Phenolic acids are the subgroup of polyphenols that contains carboxyl and hydroxyl groups. Phenolic acids can be divided into two groups: the first group contains hydroxybenzoic structures (Fig. 2a) and the second group—hydroxycinnamic (Fig. 2b). Phenolic acids naturally occur in fruits, vegetables, and grains. They are found as compounds in free form (not connected with other compounds) and as connected form. The last form is connected by ether, ester, and acetal bonds with molecules that perform building functions in plants [100]. Proteins, cellulose, and lignin are responsible for these kinds of functions in plants. Phenolic acids also occur in the form that is connected with polysaccharides (starch). They take part in the synthesis of proteins, nutritional and allelopathic processes. During the allelopathic processes, the toxic substances produced by plants are releasing into the environment. The research confirms that substances performing allelopathic functions are also natural bio-stabilizers—substances that inhibit cell division processes (multiplication) of pathogenic microorganisms [2]. These compounds are contained in cucumber and onion [101–105]. Phenolic acids as modifiers of polymer materials may be potentially applied in conditions with a high risk of microorganisms invasion. Products that are used in humid conditions should perform both exploitative and biocidal functions since humidity promotes the multiplication of microorganisms. Phenolic acids fulfill these conditions and can be used as modifying additives of materials used in water transport systems.

The caffeic, gallic, vanillic acids are the representatives of this group [106]. Caffeic acid connected with chitosan exhibits anti-tumor properties what makes it a potential anti-cancer agent [107]. Zein-based and PLA-based coatings which contain caffeic acid can be used in the food packing industry. PHB/gallic acid nanofibers with antibacterial properties are a novel material for the food packing industry. Chitosan-based mats doped with gallic acid and vanillic acid grafted chitosan (as a wall material) are used for food encapsulation. These materials exhibit antioxidant properties [108–112]. In materials engineering, phenolic acids are used as UV stabilizers in biopolymers (PLA + vanillic acid) [113]. Completely degradable nanoparticles made from PLA which contains caffeic acid could be potentially applied in various industries [114].

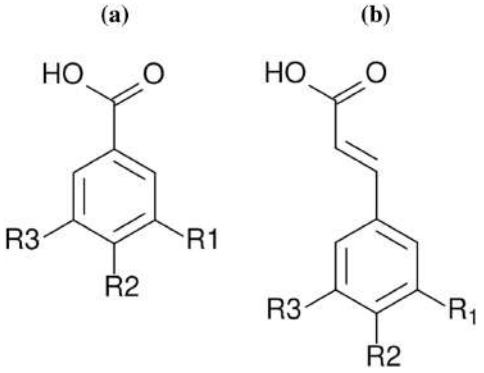


**Fig. 2** Chemical structures: hydroxybenzoic (**a**) and hydroxycinnamic (**b**) [115]

## Lignans

Lignans (Fig. 3) are the phenylpropane dimers that are classified as phytoestrogens—the plant origin hormones. Linseed is one of the richest sources of lignans. These phytoestrogens control the growth and development of linseed and also take part in its protection against the harmful effect of UV radiation. They exhibit antifungal and antiparasitic activity. Moreover, lignans are known for their strong antioxidant properties. The solubility of these compounds in the essential oils and resins is high [98, 116]. This property can be used in the field of materials engineering during resin-based materials processing. The biocidal and antioxidant properties of these materials would be increased. The

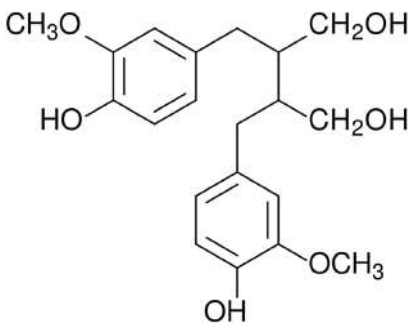


**Fig. 3** Chemical structure of lignans [120]

additives that improve more than one property of the biodegradable materials (e.g. mechanical strength and microbiological resistance) are currently searched.

Certain lignans (phyllanthin and silymarin) are implemented into biopolymers. Chitosan-based microcapsules with phyllanthin have a potential application in the pharmaceutical industry [117]. Cellulose biocomposites containing zein/silymarin nanoparticles could be used in food packing. The strong antioxidant properties of this packaging elongate the shelf life of products packed in it [118]. Silymarin improves the resistance of biopolymer blends (PLA/PHB) on thermo-oxidative degradation. Therefore it could be applied as a thermooxidative stabilizer in materials engineering [119].

### Stilbenes

Stilbenes (Fig. 4) are the organic compounds contained i.a. in berries, grapes, and nuts. These substances have a complicated structure. They exhibit antioxidant and antimicrobic properties and have the ability to polymerization. The antioxidant mechanism of stilbenes is based on the stimulation of proteins and enzymes contained in plant cells. Stilbenes are not widely spread and occur only in 30 plant species. In the years 1995–2008 approximately 400 new stilbenes were discovered [98, 121]. This group of substances exhibits both biocidal and antioxidant properties. The presence of these modifying additives could increase the service life of final products which could be exposed to pathogenic microorganisms and adverse climatic conditions (e.g. UV oxidation).

The resveratrol and piceatannol belong to stilbenes. Biopolymer-based nanoparticles loaded with resveratrol have a potential application in the drug industry. The delivery of resveratrol in nanoparticles improves its solubility in the human body [122, 123]. Biopolymers/resveratrol materials are used as repairing scaffolds in tissue engineering [124]. The gelatin/zein mats and pectin/gelatine films containing resveratrol are used as an active packaging material that elongates the shelf life of food [125, 126].

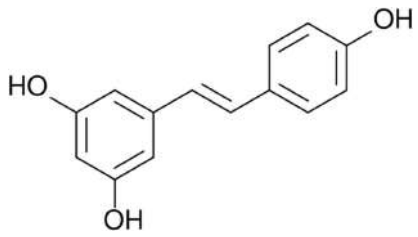


**Fig. 4** Chemical structure of stilbenes [120]

It is known that resveratrol improves the photo-oxidative and thermal stability of PLA and could be applied in materials engineering [127]. Piceatannol is a stilbene with strong anti-cancer, anti-viral, anti-inflammatory, and antioxidant activity which is used in the pharmaceutical industry. The chitosan-PLA nanoparticles and zein nanospheres have a potential application as drug carriers for the piceatannol [128, 129].

## Classification of Flavonoids

### Flavanones

Flavanones is a small subgroup of flavonoids that takes a big part in medicine. Citrus fruits are the richest source of flavanones. Citrus peel has the greatest concentration of these active substances. Due to their bioactive properties (effecting on human health), citrus fruits extracts are used as well as immunostimulants, preservatives and cleaning agents [130]. Pinostrobin, naringenin, and hesperidin are the most known flavonoids (Fig. 5).

Pinostrobin is obtained from plants *Renealmia alpinia* and *Alpinia zerumbet* [131, 132]. It is the dominant polyphenol contained in certain propolis species [133]. Due to the research described in [134], this substance has a biostatic effect against *Helicobacter pylori* and *Herpes simplex virus* type I.

Chitosan/sodium alginate nanoparticles doped with pinostrobin could be used in the pharmaceutical industry as an anticancer drug [135]. Biopolymer films doped with propolis extract have a potential application as an active packaging material [133].

Naringenin contained in pomegranate juice is a naringin derivative. This compound caused the characteristic bitter taste of pomegranate [136, 137]. Naringenin is also contained in peach drupels, citrus fruits, and tomatoes. Apart from many anticancer properties, naringenin exhibits biostatic activity against *H. pylori* strain and inhibits the enzymes secreted by it [138]. Moreover, this compound exhibits antioxidant and anti-inflammatory properties and also can be used as the agent that inhibits the development of the SARS-CoV-2 virus [139].

Chitosan nanoparticles loaded with naringenin are used in the pharmaceutical industry due to the anti-cancer properties of naringenin [140]. Biopolymer nanoparticles doped with naringenin increase the water solubility of flavanone. This solution has potential application in drug delivery systems [141]. The effectiveness of chitosan-based nanoemulsions doped with naringenin in skin injuries treatment has been proved [142].

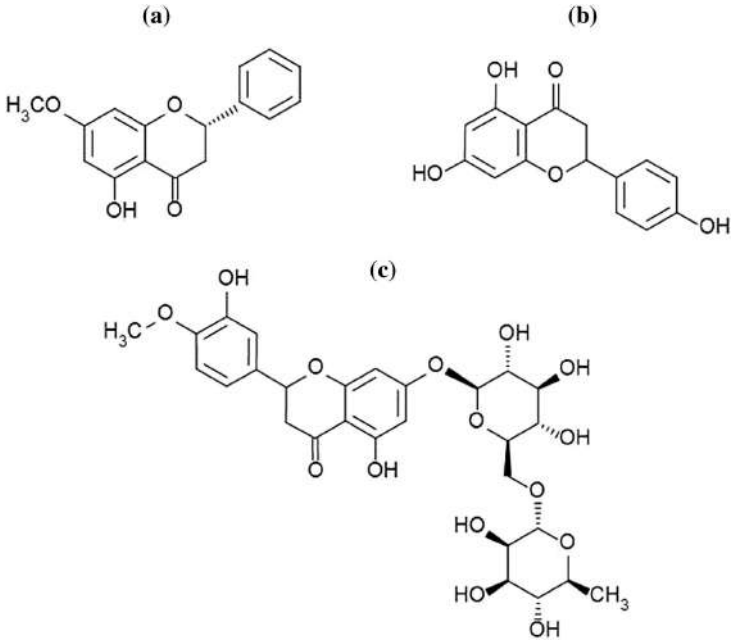


**Fig. 5** Chemical structure of: pinostrobin (**a**) [131], naringenin (**b**) [149], and hesperidin (**c**) [150]

Hesperidin like naringenin is contained in citrus fruits and is active against some types of viruses such as *Herpes*, *Poliomyelitis*, and *Paramyxovirus.* Due to the latest research that shows low cytotoxicity of hesperidin, it can be used as an active compound of antivirals against coronaviruses [143–145].

The biopolymer-based hydrogels containing hesperidin in the concentration of 10% could be used as a wound healer agent [146]. Gelatin films with chitosan nanoparticles doped with hesperidin have been considered as an active packaging material [147]. Biopolymer-based materials with hesperidin have a potential application in the food packing industry due to their antioxidant properties and environmental friendliness [148].

## Flavones

As well as previous group flavones are contained in citrus fruits and their juices [151]. The biological activity was observed in luteolin and apigenin which are classified as flavones (Fig. 6). Luteolin is contained in red onion, kohlrabi, lettuce, arugula, carrots, red and yellow peppers, beetroot, green beans, and spinach. The mechanism of biocidal activity is based on the inhibition process of DNA (nucleic acids are built of nucleotides connected with phosphodiester bond) polymerase [8]. Luteolin exhibits its biological activity against the flu virus, *Herpes* virus, and some *Propionibacterium* and *Staphylococcus* bacteria [152, 153]. It is biostatic against *Chlamydia pneumoniaem*,

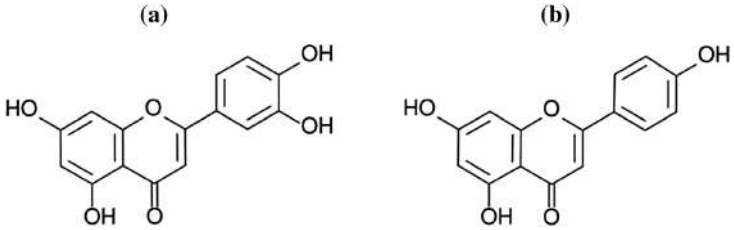


**Fig. 6** Chemical structure of: luteolin (**a**) [159], apigenin (**b**) [149]

*Trichophyton rubrum*, and *T. mentagraphytes* bacterias. The effectiveness of luteolin against some fungi is comparable to the effectiveness of ketoconazole which is classified as an antifungal drug [152].

Luteolin is used in the pharmaceutical industry, however, the low absorption (bioavailability) in the human body is one of its disadvantages. The biopolymer drug carriers (zein, chitosan, etc.) make it more bioavailable [154–156]. The elongated antioxidant activity of luteolin encapsulated with starch nanoparticles is proved. This kind of nanoparticles could be used in both the drug and food industries [157]. The antioxidant and biocidal properties of luteolin make it an interesting additive for chitosan-based active packing films [158].

Apigenin is contained in i.a. the chicory, pak choi cabbage, and red onion [160]. Clinical trials prove the biostatic activity of apigenin against SARS-CoV-2 and its anti-HIV effect that was similar to the effect of the nelfinavir—the HIV drug [139]. Due to this observation, the substances used in the treatment of HIV can also be applied in cases of coronavirus infection. Apigenin is a natural antioxidant and this property can increase the service life of polymer materials. The cosmetics with an antioxidant effect are in high demand, therefore the apigenin can be potentially implemented in this industry [149]. Luteolin and apigenin constitute a new interesting application—as active ingredients of polymer materials with biocidal properties.

As well as luteolin, apigenin is a flavone with low bioavailability. This property could be improved with its introduction into zein/lecithin nanocomposite. This material has a potential application in the pharmaceutical, cosmetic, and food industries [161]. Chitosan also enhances the solubility of apigenin and could be used as its carrier in drug delivery systems [162]. The apigenin hydrogels based on biopolymers [gelatin, chitosan, and polyethylene glycol (PEG)] promote diabetic wound treatment. Hence, its prospects in diabetic skin injuries therapy is huge [163]. Chitosan-based nanogels loaded with apigenin stop the cancer cells proliferation, therefore the potential application of these materials in oncology is justified [164]. Starch-apigenin complex has a potential application as a supplement supporting stable glucose level in blood. In materials engineering, apigenin could be used as a thermal stabilizer of starch [165].

## Flavonols

Kaempferol, quercetin, and myricetin are the best known and the most common flavonols (Fig. 7) [160, 166]. This group performs different functions such as photoprotection, i.e. protects plants against the harmful effects of UV and parasites, gives plants colour, and also prevents oxidation processes [167]. The biological activity of flavonols depends on their chemical structure and the presence of hydroxyl groups [166].

Kaempferol occurs in many plant species, however the highest content of this substance is found in several plant species: acacia, saffron, aloe, ginkgo, goatweed, leaf flower, and rosemary [170, 171]. Among berries, kaempferol occurs in blackcurrants, gooseberries, and strawberries [160, 172]. This substance also exhibits antioxidant and antimicrobial properties [170]. Kaempferol is a nontoxic substance and has the ability to inhibit inflammatory processes caused by *H. pylori* which take place in the human body [172, 173].

Zein nanoparticles coated with alginate and chitosan are used for kaempferol encapsulation in order to increase its absorption in the blood. This form of kaempferol administration is a prospective solution for drug delivery systems [174]. Zein-kaempferol coatings improve the mechanical and bioactive properties of scaffolds, thus their tissue engineering application is justified [175]. The biopolymer-based membrane doped with kaempferol could be potentially applied as an infected wound dressing [176]. The study of gelatin nanoparticles doped with kaempferol confirms that it could be used as an eye drops for certain eye diseases [177]. The lecithin/chitosan nanoparticles loaded with kaempferol has a potential application as an antifungal agent [178].

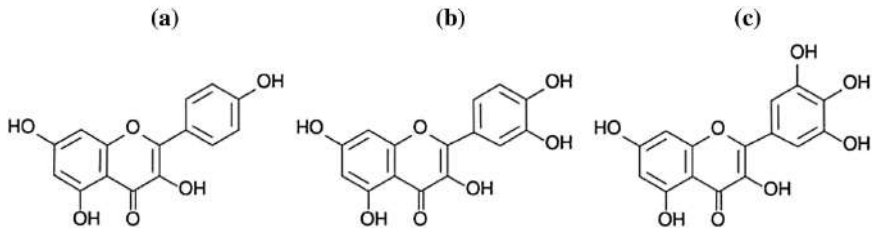


**Fig. 7** Chemical structure of: kaempferol (**a**), quercetin (**b**) [168], and myricetin (**c**) [169]

Quercetin is a substance with antioxidant properties. It stimulates the human enzyme system which is responsible for metabolic processes [96]. This substance has been applied in silver nanoparticles processing and replaced widely used reducing agents which pollute the environment. Silver nanoparticles with biocidal properties that are obtained with quercetin are called "green" due to the ecological method of their production [179, 180]. Quercetin exhibits biostatic properties and the activity of these properties depends on the type of bacteria. It is a strong agent that inhibits Gram-positive bacteria, however, its activity against Gram-negative bacteria is weak. Research proved that quercetin inhibits the growth of several bacterial strains: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Salmonella enterica* [181]. The literature overview reveals that both quercetin and kaempferol are bioactive against *SARS-CoV-2* and inhibit metabolic processes of this virus type [139]. This property is crucial in the current pandemic situation. Previously mentioned modifiers have a potential application as biocomposites additives. These modifiers could limit the spread of the pathogenic virus on the surface of materials. Due to their properties, the biocomposites that contain this type of modifying additives could be applied in the public spaces and medical industry.

Zein is used for quercetin encapsulation and as a drug carrier. Due to the bioactive and antioxidant properties of the material, it could be applied in the pharmaceutical, healthcare, food, and food packing industries [182–185]. The potential biomedical applications are based on the implementation of quercetin encapsulated with biopolymers [186, 187]. It has been proved that biopolymer-based hydrogels containing quercetin regenerate bones. Therefore, these hydrogels could be applied as scaffolds in tissue engineering [188]. Chitosan, chitosan/gelatin, and starch/gelatin films loaded with quercetin elongate the shelf life of food due to the above-mentioned properties. Hence, it is well-suited for food packaging applications. Additionally, these films are edible, which makes them even safer for humans [189–193]. The presence of quercetin in PLA-based films makes them interesting materials for active packaging due to the antibacterial activity [194]. Lecithin/chitosan nanoparticles doped with quercetin have a potential application in functional food (food that besides its nutritional value prevents diseases or supports health) production [195]. The thermal stability of starch doped with quercetin was greater than the pure starch one. This fact suggests that quercetin could be potentially used during polymer processing [196].

Another flavonol is myricetin that occurs in parsley, marigold, berries, grapes, oranges, broad beans, herbs, wine, and tea [197–200]. The characteristic feature of this compound is the high melting point—357 °C. The activity of myricetin against *S. aureus* has been reported in [153]. It is a natural antioxidant compound that neutralizes free radicals. The application of this substance in various industries is complicated due to its physicochemical properties, which are poorly understood so far [198].

Chitosan, chitosan-based, and starch materials could be applied as myricetin carriers used in the therapy of various diseases [201–203]. Certain biopolymers improve the bioavailability of myricetin [204]. Chitosan loaded with flavonols (myricetin, kaempferol, and quercetin) is considered to be an excellent active packaging material due to its modified properties (antimicrobial, antioxidant, etc.) of chitosan [205].

## Isoflavonoids

Isoflavonoids occur in various plants: red clover, lentil, spinach, some species of burclover, meadow-grass, coffee beans, plants as the broad bean, and white kwao krua which belong to the bean family [206]. However, soybeans have the highest concentration of isoflavonoids. In the medical industry, the most commonly used isoflavonoids are genistein, daidzein (Fig. 8), and glycitein (Fig. 9) due to their biological activity [207].

Genistein naturally occurs in beans, potatoes, coffee beans, babchi plant, and red clover [208]. This substance inhibits the development of several types of bacteria: *S. aureus*, *H. pylori*, *Bacillus anthracis*, and *Vibrio vulnificus*. Further research does not confirm a similar effect of genistein on *E. coli*, *Lactobacillus reuteri*, *Shigella sonnei*, and *Klebsiella pneumoniae*. It suggests that the biocidal properties of genistein depend on the properties of selected bacteria

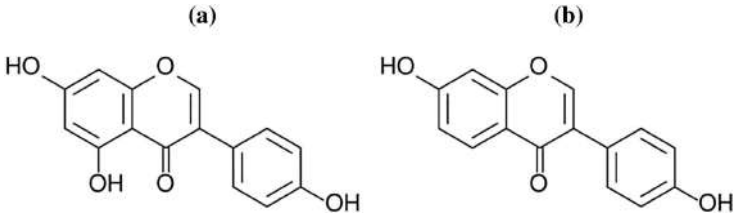


**Fig. 8** Chemical structure of: genistein (**a**) [230], daidzein (**b**) [220]

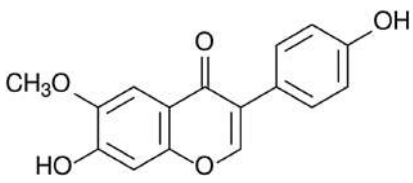


**Fig. 9** Chemical structure of glycitein [235]

[209]. Genistein is a natural antioxidant and also antiallergic and anti-inflammatory agent [210, 211].

Genistein encapsulated with biopolymer nanoparticles is a promising material for food and pharmaceutical applications [212–214]. Gelatin and starch could be used as genistein carriers. A high possibility of commercialization of these drug carriers is caused by the low manufacture costs [215, 216]. PLA improves the solubility of genistein. Due to the non-toxicity of PLA and therapeutic properties of isoflavonoid, the pharmaceutical application of their blend is justified [217]. It has been proved that the bioactive properties of genistein contained in gelatin do not change within 3 months. This suggests, that gelatin is an excellent matrix for genistein storage [215]. Chitosan-based nanofibers loaded with genistein could be used for biomedical purposes [218]. Chitosan doped with antioxidant genistein can be potentially used as a functional food additive [219].

Daidzein is another substance that belongs to isoflavonoids. This isoflavonoid occurs in various subspecies of the bean family, red clover, and kudzu roots [220, 221]. The substance exhibits antibacterial and fungicidal properties [222]. The conducted research proved, that daidzein is an auxiliary substance of several antibiotics. *S. aureus* is resistant to methicillin, but its combination with daidzein makes it active against this type of bacteria [223]. The activity of daidzein against *P. aeruginosa* has been proved. Moreover, it exhibits antioxidant, anti-inflammatory, and anti-aging properties [220, 224].

Daidzein is a natural adhesive agent which could be applied in certain non-metallic coatings which are widely used in the automotive, furniture, and cosmetic industries [222]. The possibility to improve the adhesion of this type of coatings is crucial due to their low durability and exposure to abrasion during their exploitation. The main reason of the paint coatings chipping is the disruption of their integrity caused by low adhesion between the coating and coated material. The search for an agent which increases adhesion is in the constant process due to the needs of coated products users. The non-toxicity and the renewability are extremely desired in modern materials engineering. Therefore these features of daidzein make it even more attractive as a modern adhesive agent.

Chitosan, starch, gelatin, poly(lactic-co-glycolic) acid (PLGA), and PHB could be used as daidzein carriers which improve its bioavailability [225–229]. This fact shows the pharmacological value of these material blends and daidzein in particular.

Glycitein occurs in soybean and it is responsible for the characteristic taste of products made of soybean [206, 231]. The substance exhibits antibacterial and fungicidal properties against *Colletotrichum gloeosporioides* [232, 233]. It is an antioxidant compound [234]. According to the above-mentioned properties of this isoflavonoid, it has potential applications in various industries (cosmetic, medical, pharmaceutical, and polymer). However, the current literature analysis suggests that glycitein is not well-exanimated yet. Therefore its potential applications as a biopolymer-modifier are poorly studied.

## Blackcurrant Extract

One of the richest sources of polyphenols is a blackcurrant bush. Although the extract obtained from each part of the plant exhibits biocidal properties. The comparison of the amount of the polyphenols in various fruits shows their greater content in the blackcurrant. The content of polyphenols in this plant is 340 mg in 100 g of blackcurrant seeds.

The high content of polyphenols in blackcurrant extract made it a promising modifier of polymer materials due to its non-toxicity and easy cultivation in the middle European climate. Blackcurrant extract is obtained from various parts of the plant such as fruits, leaves, seeds, and buds. However, it has been proved that the blackcurrant buds are the richest source of biocidal substances contained in blackcurrant [236].

There is a wide spectrum of biocidal properties of this extract. It exhibits biocidal activity against *Candida albicans* which belongs to fungi. The mechanism of fungicidal activity is based on fungi cell wall deformation which leads to the leak of the internal substance. This process initiates the inevitable death of the microorganisms [237]. Blackcurrant buds exhibit antimicrobic properties owed to kaempferol, quercetin, rutin, and myricetin contained in them [238]. According to the literature review extract from the blackcurrant buds exhibits biological activity against several bacterial strains: *B. subtilis*, *Listeria monocytogenes*, *S. aureus*, *E. coli*, *P. aeruginosa*, and *Acinetobacter bacteria*. The biostatic activity of blackcurrant extract on *C. albicans*, *Alternaria alternata*, and *Aspergillus niger* depends on blackcurrant variety [236, 239]. The effect of the extract on certain fungi strains has been compared to the effect of fluconazole (antibiotic). According to the conducted research, the plant extract is

more effective against microorganisms than certain antibiotics [239]. The extract exhibits anti-inflammatory and antioxidant properties due to the content of ascorbic acid which is a natural antioxidant [236, 240]. The blackcurrant berries contain calcium, aluminium, magnesium, and iron which give them their characteristic navy blue colour. The red shade of blackcurrant pulp is caused by the presence of potassium [240]. The pigment substances contained in the blackcurrant berries extract limit its application as modifying additive of biodegradable polymer materials. However, this property can also be an advantage of this modifier in cases where the colour of products is desired. Besides biocidal and antioxidant properties, the extract performs pigment functions which could reduce the number of additives contained in polymer biocomposites. It is another advantage of this extract.

The influence of the blackcurrant extract encapsulated with gelatin on the blood flow has been confirmed. Therefore it can be used for pharmaceutical purposes [241]. The effect of blackcurrant extract on the biopolymer mixtures was investigated. It was founded, that certain blackcurrant concentrations improve the crosslinking, hydrophilic, and optical properties of materials. Hence, this fact makes these materials an interesting solution that could be implemented in the optoelectronic industry [242]. The colouring properties of the blackcurrant anthocyanins are known. The biopolymer-blackcurrant anthocyanins mix is an excellent substitute for the currently used dyes with the synthetic origin [243]. Due to the unique properties (bioactive and antioxidant) of blackcurrant, its complexes with proteins could be applied as an additive in functional food [244]. The starch-blackcurrant complexes have the same application. It has been founded that blackcurrant modifies the physicochemical properties and colour features of the biopolymer [245]. The presence of blackcurrant in gelatin increases its hardness and brittleness which are desired in the food industry [246].

## Tannic Acid

Tannic acid (Fig. 10) is a substance that occurs commonly in the natural environment as a plant compound [247] This substance is classified as phenol—the organic compound which includes one or more hydroxyl groups connected with the aromatic ring [8]. It is noticed that this substance occurs in almost all aerial parts of plants [247]. The richest source of tannic acid is galls—growths with hardened structures. The galls are appearing as a result of certain insect spices preying and also as by-products produced by mites, fungi, and bacteria. Oak galls, also known as oak apples, are created by two insects that belong to the *Cynipidae* family. One of these insects called the gall-fly is probably the main reason of the galls creation [248]. Besides oaks, galls occur in roses, apples, willows, poplars, beeches, acacias, redwoods, and pistachio trees [249–251]. Tannic acid also occurs in other plants—in the walnut tree bark which is common in middle Europe, in pine and mahogany which grows in Central America. It is the ingredient of strawberries and nettle [251].

Tannic acid exhibits antioxidant properties and is active against viruses, bacteria, and fungi [254–260]. Flu virus and HIV are susceptible to tannic acid. This substance exhibits a bacteriostatic effect against several Gram-negative bacterial strains (*Cytophaga columnaris*, *H. pylori*, *E. coli*, and *K. pneumoniae*) and Gram-positive bacterial strains (*S. aureus* and *L. monocytogenes*, *B. subtilis*) [254–256]. The antimicrobial activity depends on the type of bacteria—the inhibiting effect was stronger against Gram-positive bacterial strains. The tannic acid is also antimicrobic against *C. albicans* which belongs to fungi [254]. Kim [255] proved that the thermal treatment of tannic acid increases its antimicrobic properties.

The combination of several properties (biocidal, antioxidant, and crosslinking) in one additive makes tannic acid a potential modifier that could be applied in polymer biocomposites. When the tannic acid contacts with a solvent, it releases dyes which makes it a natural colouring agent. According to this, tannic acid could replace synthetic dyes which are currently used. The main disadvantage of polymer biocomposites is a low adhesion between phases which could be improved with tannic acid introduction. It increases the mechanical strength of the biocomposite and expands the area of the final product application. The application of tannic acid in biocomposites could probably increase the service life of material due to the reduced amount of microorganisms present on their surface. Moreover, tannic acid could inhibit internal and external antioxidant processes.

This type of biocomposites has a potential application in the medical, catering, and other industries where microbiological hygiene is required. Tannic acid is a promising

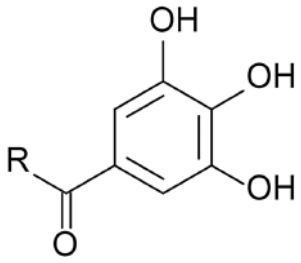


**Fig. 10** Chemical structure of tannic acid [252, 253]

modifier with biocidal properties which could be applied in the packaging industry due to its non-toxicity. The antimicrobic and antioxidant properties of tannic acid are confirmed with research conducted on the biodegradable packaging made of starch doped with this substance [256]. This type of packaging can certainly be implemented in the industry and have the potential to replace the currently used packaging made of crude oil. Polymer biocomposites made of chitosan containing tannic acid are interesting materials with potential application in cosmetology as acne patches [257]. The colonization of the sebaceous glands by the bacteria *Propionibacterium acnes* is one of the reasons of acne [261]. The biocomposites with tannic acid probably could lead to the death of these pathogenic microorganisms. However, this type of research is not done so far and the effect of tannic acid on these bacterial strains is not investigated yet.

These complexes could be applied in drug or supplement delivery systems as a carrier due to the non-toxicity and ability to controlled supplement/drug release [262]. Gelatin microspheres containing tannic acid could be applied for nutraceutical purposes [263]. Gelatin/tannic acid films exhibit antibacterial properties which are desired in biomedical materials [264]. Gelatin/tannic acid hydrogels with shape memory are interesting materials for potential biomedical and robotic applications [265]. Biocomposite nanofibers with tannic acid could be used as a biocompatible wound dressing material with an antibacterial effect [266]. The zein/tannic acid complexes acid have a wide range of applications in food and cosmetic industries due to their stabilizing and crosslinking properties [267, 268]. Zein/tannic acid coatings elongate the shelf life of fruits, therefore this kind of edible layers could be used as nontoxic biopreservatives in the food industry [269]. Zein particles modified with tannic acid improve mechanical properties and hydrophobicity of gelatin-based composites for food packing [270]. The gelatin doped with silver nanoparticles and tannic acid is another material for potential food packing application [271]. The chitosan films containing tannic acid could have the same application [272]. Tannic acid improves interfacial adhesion in composites and as a result—mechanical properties of ones. Therefore, it could be used in polymer biocomposites production [273, 274]. Chitosan/tannic acid coatings applied on biocomposites fillers increase the fire resistance of biocomposites. This kind of coatings has a potential application in materials engineering [275].

## Betulinic Acid

Betulinic acid belongs to triterpenoids which are the triterpenes derivates. The source of the betulinic acid is i.a. varied birch species [276, 277]. This substance is obtained from betulin (BE) shown in Fig. 11. The betulin occurs in plants such a birch, London plane tree, jujube, Caucasian alder, thistle, and rosemary [278, 279]. Among mentioned plants, the highest concentration of betulin is found in birch bark which consists of inner and outer parts. It has been proved, that the content of betulin in the outer bark ranges from 30 to 35% and this value depends on the birch variety [276, 280]. The white colour of the tree is caused by the presence of betulin, which is a natural dye. This substance was discovered in 1788 by a pharmacist and chemist Tobias Lowitz [281].

Betulinic acid exhibits antiviral properties against HIV due to the functional groups that occur in it at carbon atoms C-23 and C-28. Betulinic acid is biocidal against the *Herpes simplex* virus (type 1 and type 4) and several *Enterovirus* viruses [284–286]. Some of the betulin derivatives are also exhibiting antiviral activity. Bevirimat which is produced by the chemical modification of betulinic acid exhibits the highest activity against HIV and inhibits HIV-1 and HIV-2 [287]. This substance also inhibits the advanced stage of HIV-1. Due to the mentioned properties of bevirimat, it is a promising compound that could be used as an anti-HIV drug [279, 288].

Antibacterial property is another advantage of betulinic acid. According to conducted research, the tannic acid is the only betulin derivate with biostatic activity against *E. coli*,

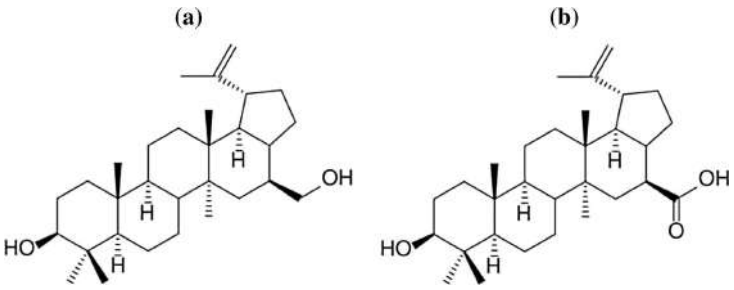


**Fig. 11** Chemical structure of: betulinic acid (**a**) and betulin (**b**) [282, 283]

*P. aeruginosa*, and *Enterobacter aerogenes*. It is probably caused by the structure of mentioned bacteria which belong to Gram-negative bacteria. They have an extracellular membrane which could be an obstacle during the penetration of active compounds—betulin derivatives. Furthermore, betulinic acid exhibits biostatic activity against *E. faecalis* bacterial strain and inhibits the growth of these bacterial colonies by 56% [289]. The antibacterial activity of betulinic acid against bacteria *P. aeruginosa*, *E. coli*, and *S. aureus* bacterial strains is caused by increased production of superoxide anion radicals which cause oxidative stress in bacterial cells. This process is unfavorable for bacterial cells and most often leads to their death. The oxidation process of bacterial cells has been proved by increased concentration of malondialdehyde which is an indicator of oxidative stress and cell destruction [290]. According to the current literature state, the substance also inhibits the SARS-CoV virus [291]. The inhibiting mechanisms of viruses can be divided into two groups which are implemented at different stages of viral development. The processes which belong to the first group are activated during the cell penetration by the virus. These processes make it difficult for the virus to cross the cell membrane. The second group is based on inhibiting the process of viral replication caused by the effect of betulinic acid on SARS-CoV 3CL protease [291]. Ascorbic acid is a substance that has a synergistic effect on betulinic acid.

The literature overview allowed us to estimate the validity of betulinic acid application as a modifier of biodegradable polymer materials. The estimation was based on the previously described properties of the substances. Betulinic acid is a new substance in the polymer industry, therefore the information about its behavior and effects on the polymer matrix is very limited. However, there is a reliable report—a patent invented by scientists from the University of Silesia in Katowice, Poland, and the Medical University of Silesia in Katowice. The method of obtaining betulin-modified thermoplastic polymers is the subject of this patent. The characteristic features of this polymer are antibacterial and anti-inflammatory properties [292]. This is a breakthrough discovery because betulin and betulinic acid have similar properties. This fact suggests that polymer materials containing betulinic acid would probably exhibit antibacterial properties as well. This will undoubtedly extend the service life of final products and increase the area of their potential application. Such areas may be industries where sterile conditions are desired.

The effectiveness of betulinic acid against parasites has been proved via testing chitosan nanoparticles loaded with betulinic acid [293, 294]. Certain biopolymer coatings containing betulinic acid exhibit anticancer properties [295–297]. The same properties were noticed in biopolymer-based nanoparticles loaded with betulinic acid [298, 299]. Therefore, the pharmaceutical potential of betulinic acid is huge. From the literature overview, it could be concluded, that the applications of betulinic acid as a biopolymer-additive in other industries have not been described yet.

## Lapachol

Lapachol is a compound that occurs both in the inner part of the bark and in the heartwood of *Tabebuia* trees, commonly found in South and Central America [300]. In the colloquial language of Brazilians, this tree species is also called taheebo, pau d'Arco, or lapacho which probably gives the name to the active substance contained in the tree bark [301, 302]. According to the literature reports, the other plants which belong to the *Bignoniaceae* family (as well as *Tabebuia* does) also include lapachol in their timber [303, 304]. The *Tabebuia* bark has been already used by Incas in ancient times—the infusion of chopped tree bark was applied for medicinal purposes. In 1882 lapachol was extracted by Italian phytochemist—Emanuel Paterno for the first time [301, 302, 306, 305]. Lapachol (2-Hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone) is classified as naphthoquinone [303]. Naphthoquinones are organic compounds derived from naphthalene. The presence of ketone groups (C=O) in the naphthoquinones structure is known [8, 307]. The chemical structure of lapachol is illustrated in Fig. 12.

Lapachol exhibits biological activity against microorganisms. Its biocidal mechanism is based on the initiation of oxidation processes and enzyme inhibition. Both reactions occur in cells [300]. It has been proved that the biological activity of naphthoquinones depends on their structure [308]. The biological effect of this substance is similar to the effect of antibiotic amphotericin B. Lapachol is effective against the following bacterial strains: *H. pylori*, *Streptococcus*, *Enterococcus*, *Clostridium*, *Staphylococcus*, and *Bacillus* which are hazardous for human health. The antifungal activity extends to *Candida* species and *Cryptococcus neoformans* [300]. Lapachol like the majority of naphthoquinones exhibits colouring properties and could be used as the yellow pigment [301, 303, 304]. It is also a natural antioxidant agent [309].

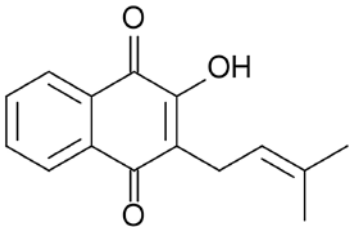


**Fig. 12** Chemical structure of lapachol

The unique properties of lapachol and its toxicity against microorganisms are advantages. The resistance of polymer materials on the microorganisms is crucial due to their common exposure to the microorganisms. Hence, the bark of *Tabebuia* which contents lapachol is a promising material that could be introduced in biodegradable polymer biocomposites. The modification of biocidal and mechanical properties of biocomposites with the lapachol does not pollute the environment. The biocomposite that consists of the biodegradable PLA matrix and the reinforcement such a *Tabebuia* bark is completely biodegradable. This type of biocomposite has been examined by authors. The manufacturing of the biocomposite was carried out in several stages—by extrusion with granulation and injection. The enzymatic biodegradation studies were performed according to the method contained in the article [310]. These studies lasted 8 weeks. Due to our studies [311], the increase of bark content in biocomposite leads to the increase of the percent mass loss which proves higher biodegradability of biocomposite. The same dependence has been noticed during the mechanical studies. The increased content of *Tabebuia* bark in the biocomposites increases the tensile modulus of materials. The presence of lapachol contained in the *Tabebuia* bark improved the thermal durability of the biocomposites. However, more detailed research of lapachol influence on the thermal properties of PLA is recommended. According to biocidal studies, the antimicrobic activity of biocomposites was lower than the one mentioned in [301]. The decrease of biocidal activity of the biocomposites is caused by the high processing temperatures (e.g. extrusion and injection molding) applied.

The lapachol derivative—lapachol sodium salt exhibits biological activity and could be used as a drug. The chitosan flakes/lapachol sodium salt complex increases the bioavailability of the latter [312]. The lapachol derivative lapazine has a potential application as a drug used in infectious diseases treatment. The studies of alginate/chitosan microparticles loaded with lapazine prove it. β-Lapachone is another lapachol derivative with a wide range of therapeutic properties. However, the high toxicity of β-lapachone is an obstacle to its implementation into the pharmaceutical industry. The studies on the β-lapachone connected with chitosan confirms the decrease of agent toxicity. This fact increases the probability of its application in the pharmaceutical industry [313, 314]. According to Pereira et al. [315], starch could be used as a lapachol carrier in drug delivery systems.

## Allicin

Allicin (diallyl thiosulfonate) (Fig. 13) is the main ingredient of garlic, onion, and clove extracts which exhibits biocidal properties [8, 316]. It creates during garlic or onion crushing [317]. This compound belongs to phytoncides—the bioactive compounds that are produced by selected plants. Phytoncides are defined as natural antibiotics. The biocidal properties of garlic extract were observed at the end of the nineteenth century by Louis Pasteur. The isolation of allicin from cloves was carried out by Chester John Cavallito and John Hays Bailey in 1944 for the first time [318]. The highest concentration of allicin is found in the garlic extract. For this reason, the plant is applied in traditional medicine. Moreover, due to its high taste attributes it is used in almost every cuisine of the world. The wide spectrum of garlic biocidal properties has caused a growing interest in the modern scientific world including materials engineering.

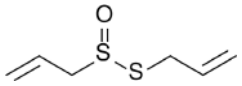


**Fig. 13** Chemical structure of allicin [319]

Allicin is a substance that exhibits a strong antioxidant effect based on free radicals inhibiting [318, 320]. It has antifungal and antimicrobic (the antibacterial activity against several Gram-positive and Gram-negative bacterial strains was noticed) properties [319, 321, 322]. The mechanisms of the biocidal action of the substance are not well known so far, but literature reports show that the formation of allylsulfide compounds changes L-cysteine, which is a free amino acid [318]. Allicin has a cytotoxic effect on proteins contained in microbes cells. The penetration of parasitic cells by allicin leads to their death [323].

According to the conducted research, the highest activity of allicin (more than 86%) was noticed on the 3rd day of studies while this percentage value changed over time. The last measurement has been done on the 11th day of studies and the percentage value of substance activity decreased by almost 1/3 compared to the 3rd day of studies. It was probably caused by the high volatility of allicin. However, the substance had high biological activity even after 11 days of exposure to the bacteria [324]. The allicin is also bioactive against several fungi and protozoa [325].

Due to the wide spectrum of biocidal properties of allicin, it can replace currently used additives which give the resistance of the biodegradable material to the adverse effects of pathogenic microorganisms. However, one of the main disadvantages of this compound is the characteristic sulfuric smell which is associated with the garlic smell. According to this, allicin can be applied in biodegradable materials which have limited contact with humans. It can also be used in conditions where the controlled development of microorganisms on the surface of the material is desired.

Cellulose nanoparticles doped with allicin exhibit antimicrobial properties which suggest that this complex could

be used in food, food packing, and textile industries to limit microbial proliferation [326]. The starch-based wall material is used to produce allicin microcapsules which can be used as a biopreservative in the food industry [327]. The chitosan/allicin complex exhibits grown antimicrobial activity, therefore this material is suitable for the food industry applications [328–330]. Allicin encapsulated in chitosan/starch could be used as a nitrogen fertilizers additive. The presence of allicin elongates the release of the nutrients in the soil which is desired in perennial plants cultivation [331]. Gelatin nanoparticles loaded with allicin could be used in cancer therapy due to the anticancer activity of allicin [332]. The strong antibacterial activity of biocomposites [chitosan/polyvinyl alcohol (PVA)] doped with allicin has been noticed. The long-term antibacterial impact makes allicin a perspective material for medical purposes as a tissue engineering and wound dressing material [333, 334].

## The Effect of Modifiers on Certain Biopolymers

The modification of biopolymers is one of the basic steps in their processing. It helps to suit the biopolymers to certain applications. The aim of the modification is based on changing, improving, or/and creating new properties of the materials. The below table summarizes the modification effects of biopolymers caused by plant-based modifiers (Table 1).

## Conclusions

This literature overview shows a new direction in the development of natural modifying substances with biocidal properties. The compounds contained in plants are an undoubtedly competitive group of natural modifiers because the

**Table 1** The effectiveness of the biopolymers modification by certain natural additives

| Modifier | Material | Modification effects |
|---|---|---|
| Lignin | PLA | Enhanced thermal resistance [335] |
| Caffeic acid, gallic acid | Gelatin | Increased mechanical and antioxidant properties [336] |
| Vanillic acid | PLA | Improved resistance on the photooxidative degradation [113, 337] |
| Silymarin | PLA/PHB blends | Enhanced resistance on thermo-oxidative degradation [119] |
| Resveratrol | PLA | Improved photo-oxidative and thermal stability [127] |
| Hesperidin | PLA, PHA | Improved oxidation resistance [148] |
| Apigenin | Starch | Decreased digestion rate of and improved thermal stability [165] |
| Kaempferol, myricetin, quercetin | Chitosan | Improved mechanical properties, reduced oxygen and water vapor permeability, decreased UV light transmittance [205] |
| Quercetin | Gelatin | Increased mechanical properties and decreased swelling degree, improved the UV-light absorption [336, 338] |
| | Chitosan | Reduced transparency and altered tint (to green one) [189] |
| | Starch | Elevated thermal stability [196] |
| | PLA/PEG blends | Enhanced mechanical and thermal properties, changed colour and reduced transparency [194] |
| | PLA | Improved resistance on the photooxidative degradation [337] |
| Blackcurrant | Starch | Altered colour and physicochemical characteristics [245] |
| | Gelatin | Increased hardness and brittleness of polymer [246] |
| Tannic acid | Zein | Changed shape of zein molecule which affects wettability changes [267] |
| | Gelatin | Improved mechanical properties, increased compatibility between polymer matrix and additives modified with tannic acid, improved antioxidant activity, stability, transparency, and antibacterial properties [263, 270, 339] |
| | Gelatin/silver nanoparticles | Synergistically increased antibacterial properties [271] |
| | Chitosan | Improved transparency, antibacterial properties; increased tensile strength and decreased solubility of the material, affected synergistically on plasticizer contained in the material [272, 340] |
| | PLA/filler | Improved adhesion between polymer matrix and filler and greater dispersion of filler in the matrix [273, 274] |
| Betulinic acid | PEG | Changed physical structure [341] |
| Lapachol | PLA | Increased thermal durability and biodegradability [311] |
| Allicin | Chitosan | Increased water solubility and changed colour [328] |
| | Chitosan/PVA blend | Decreased hydrophilicity, increased porosity and changed microstructure [333] |

effects of their antimicrobial activities are comparable to those of some synthetic biocides. In some cases, the natural compounds exhibit stronger biocidal activity. This fact makes them an interesting alternative for synthetic modifiers. Non-toxicity and complete biodegradability are some of their unquestionable advantages. Further development of natural modifiers and focus on biocidal properties of polymer materials are expected. Those expectations are justified due to the current pandemic conditions and the necessity of the elongated service life of the biocomposites. The biodegradability of polymer materials and their modifiers is crucial. Hence, the environmentally friendly and non-toxic modifiers are in constant search.

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**Data Availability** Data is contained within the article.

## Declarations

**Conflict of interest** The authors have no conflicts of interest to declare that are relevant to the content of this article.



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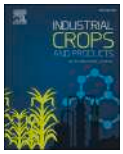

# Flax fibres modified with a natural plant agent used as a reinforcement for the polylactide-based biocomposites

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ABSTRACT

The purpose of this study was to create "green" biocomposite consisting of natural components which will exhibit biocidal properties against microorganisms and would have positive effect on mechanical properties. The authors assumed that the application of natural plant compound will reduce the hydrophilicity of natural fibres. Polylactide (PLA) biocomposites containing flax (*Linum usitatissimum)* fibres (20 wt%) were prepared by extrusion and injection molding processes. The samples containing fibres modified with the tannic acid (TA) used as biocidal and crosslinking agent as well as the control samples (with non-modified fibres) were prepared. The TA-treatment effects on the mechanical and structural properties of the biocomposites were studied using dynamic mechanical analysis (DMA) and tensile tests, differential scanning calorimetry (DSC), and thermogravimetry (TG). The flax fibres and biocomposites were examined with scanning electron microscopy (SEM): the analysis of samples fractures was performed in order to evaluate the influence of TA modification on interfacial adhesion properties. We investigated the biocidal and wettability properties of the materials. Application of the TA-modified fibres led to the deterioration of mechanical properties. TA decreased interphase adhesion and led to plasticization of PLA phase in the biocomposite. The migration of TA into PLA matrix caused its volume plasticization which lowered stiffness of the biocomposites with modified fibres. According to the thermal studies, the higher degradation temperature ($T_d$ = 352.72 ℃) of materials containing modified fibres has been noted. Moreover, the hydrophobic ($\Theta_w$ = 91.82) and biocidal (against *Escherichia coli* and *Staphylococcus aureus)* properties of the TA-treated biocomposites have been observed. The modification of the biocomposites plant reinforcements with a natural agent is an eco-friendly method that allows to change its properties in a safe way. However, it should be conducted with caution and consideration of the intended use of the finished material.

## 1. Introduction

The constantly growing demand for "green" products causes their higher popularity in both global industry and science. Hence, the increasing interest of companies and researchers in natural fibre composite materials is observed. The relatively low cost of natural fibres, their lowered density (compared with the glass fibres which are almost 50% heavier than plant ones), biodegradability, ease of separation, enhanced energy recovery, and environmental sustainability, are the main driving forces which accelerate the new biocomposite materials development. Therefore, the growing demand for natural fibre in various industries such as packaging, automotive, construction, pharmaceutical, biotechnology, or horticulture is noted (Armentano et al., 2010; Faruk et al., 2014; Lau et al., 2018; Perumal et al., 2022b; Rytlewski et al., 2017).

Biocomposite performance depends on the structure and chemical composition of the fibres, their physical and mechanical properties, as well as the interaction between fibre and the polymer. Fibre strength can be crucial in selecting a specific natural fibre for the desired application. Besides fibre strength, its dimensions, defects, crystallinity, and structure should be also taken into account during fibre selection (Faruk et al., 2014). Starch, woodflour, and plant fibres such as hemp, flax, kenaf, bamboo, sisal, coir, or ramie are examples of natural materials which are commonly used as reinforcements in biocomposites (Sanjay et al., 2015, 2018). The main disadvantages of using natural fibres as reinforcements in biocomposites are: poor compatibility between

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natural fibre and biodegradable matrix (such as PLA) and high susceptibility of the natural fibres to moisture absorption. The latter is caused by the hydrophilic nature of the fibre compounds (cellulose and hemicellulose) (Antti Sirviö et al., 2020). Therefore, natural fibre modifications that change the fibre surface properties are crucial element, since they lead to improved adhesion between fibres and the biodegradable matrices (Jagadeesh et al., 2021; Abd Manaf et al., 2007; Li et al., 2007; Rytlewski et al., 2014, 2017, 2018a; Sepe et al., 2018; Zhou et al., 2016). The issue of the plant fibre modification and its application as a reinforcement in biocomposites has been discussed in (Perumal et al., 2018b). The results revealed an increase in the mechanical and thermal properties.

The control of microorganisms number on the surface of the biocomposites is extremely important due to the growing demand for this type of materials in different industries. The willingness to create materials that are free of microorganisms stimulates the development of new methods of microorganisms combating. A growing interest in the natural plant origin compounds, which exhibit antimicrobial activity, is observed due to the necessity of various types of equipment sterilization. Examples of the mentioned equipment are e.g. public space items such as seats, handles, tables, medical instruments, and packaging. The everyday items resistance to the deposition of the microbes is particularly important during the pandemic. The sterilization of these articles could be omitted, if only they are manufactured from biocidal materials. The additional, but not less crucial, advantage of natural fibres and plant-origin biocidal compounds concerns their zero environmental pollution. Biocidal compounds are compounds that are capable to reduce the number of pathogenic microorganisms under defined conditions (Pawłowska and Stepczyńska, 2021). The materials created with "green" polymers, natural fibres, and plant-origin biocidal compounds are completely biodegradable (Praveena et al., 2022; Stepczyńska et al., 2021; Stepczyńska and Rytlewski, 2018).

TA is a natural polyphenol that occurs in various plants and their fruits, red wine, and tea leaves (Kharouf et al., 2020, 2021; Türkan et al., 2019). This substance is a promising polymer biocomposites modifier that combines biocidal, antioxidant, anticancer, antibacterial, and crosslinking properties (Le et al., 2018; Pawłowska and Stepczyńska, 2021; Tintino et al., 2017). The wide application range of the TA is caused by its numerous advantages, such as biodegradability, high adhesion, non-toxicity, inexpensiveness, and high availability (Bacelo et al., 2016). TA is widely used in the pharmaceutical, medicinal, and food industries. Moreover, it is applied during leather processing, as a natural adhesive and a coatings component. Additionally, it is known that the TA is used for wood protection and paper impregnation (Shirmohammadli et al., 2018). The enhanced mechanical and functional properties of food packaging materials containing TA have been noted in several pieces of research (Hazer and Ashby, 2021; Roy et al., 2021). The large number of phenolic hydroxyl groups contained in TA is responsible for its antibacterial activity.

However, the natural biocidal compounds may impair the interaction between polymer molecules, which leads to mechanical properties deterioration (Chu et al., 2020; Filipini et al., 2020; Han and Song, 2021; Stepczyńska et al., 2021; Yuan et al., 2021). The modification of the natural plant fibres is a crucial step that changes their properties and provides higher interfacial adhesion between fibres and the matrix. In the current work, the effect of TA on the mechanical, thermal, surface, and microbiological properties of materials has been evaluated. The natural plant origin compounds are safe for humans and cause no environmental pollution which is extremely important in current environmental conditions (Perumal et al., 2022a).

The scientific purpose of this paper was based on the development of novel biocomposites made of "green" components exclusively. The hydrophilic nature of fibres is a major problem of natural fibres used as reinforcement in plastics. The modification of the flax fibres has been applied in order to evaluate the effects of TA on the interfacial adhesion between hydrophilic fibres and the hydrophobic matrix. The aim of the study was based on the natural plant compound implementation and the examination of the mechanical, biocidal, surface wettability, and microbiological properties of finished biocomposite. It was expected that the natural plant compound will promote the biocidal activity of biocomposites and positively affected the mechanical strength of the materials.

The novelty of the work is based on the development of biocidal biocomposite material made from natural, fully-biodegradable, and non-toxic compounds (matrix, reinforcement, and modifiers). Chemical modification of plant fibres (Ahmad et al., 2019; Asyraf et al., 2021; Khalil, 2018; López Durán et al., 2018; Madhu et al., 2020; Mukesh and Godara, 2019) has been replaced with the "green" modification with TA. The method of modification of flax fibres described in the current paper did not attempt in the literature and is based on a patent application (P.440287) made by the authors. TA does not burden the environment and it is completely safe for human health. Non-toxicity, enhanced surface hydrophobicity, and biocidal properties of produced materials make them interesting for consumers which care about both environment and their health.

## 2. Materials and methods

### 2.1. Materials

- PLA type 2003D (Cargill Down LLC, USA) with a melt flow rate of 4.2 g/10 min (2.16 kg, 190 °C) and density $\rho = 1.24$ g/cm$^3$ was used as a material matrix.
- The reinforcing flax 5 mm fibres (Ekotex, Poland) in the amount of 20% (w/w) were melt-compounded with the PLA matrix.
- TA $C_{76}H_{52}O_{46}$ (Sigma-Aldrich, Poland) with a molecular weight of 1701.20 g/mol was used as a biocidal and modifier.
- *Staphylococcus aureus* (6538 P, ATCC, USA) and *Escherichia coli* (8739, ATCC, USA) bacterial strains were used for the microbiological examination.
- Propidium iodide and CYTO Green (Invitrogen, USA) were used for the biocidal activity examination.

### 2.2. Processing methods

The modification of the flax fibres has been preceded by the fibres drying for 12 h at 60 °C. This process has been conducted in the laboratory dryer (SUP-100 G, Wamed, Poland). The modification took place in three steps. The first one was based on the preparation of the 20% (wt %) aqueous solution of TA with the magnetic stirrer (LLG-uniSTIRRER 3, LLG-Labware, Germany). The distilled water (1440 mL) has been heated up to 80 °C, then the TA (360 g) has been added and intensively mixed at 1500 rpm. The high temperature of the solution has been kept for 15 min to provide a better dissolution of the TA. Subsequently, the temperature of the solution has been decreased to 50 °C, however, the mixing has not been stopped – it has been continued for one hour more in order to make the solution even more homogeneous. The next step was based on the flax fibres coating with the TA solution. The already dried fibres (300 g) have been placed in the TA solution for 12 h. After that time, the fibres have been taken out from the solution and placed in the sieve for the next 12 h. During this stage, the TA solution excess has been slowly removed. In the final stage, the fibres have been dried for 30 h at 60 °C. The even fibres drying has been ensured by their mixing. During the first 4 h of drying, 2 mixes were carried out (every other hour). The next mixing, which was the last, took place 20 h after drying has started. Non-modified fibres have been dried for 24 h at 60 °C before extrusion. Polymer matrix – PLA granulate has been dried for 20 h at 80 °C. After the drying process, the materials have been weighted with the laboratory scale (WPS 2100/C/2, Radwag, Poland). The described method of the fibre treatment was based on the description of the patent application (P.440287).

All composites were prepared using a co-rotating twin-screw

extruder (BTSK 20/40D, Bűhler, Germany). In order to limit the cutting of the flax fibres into shorter pieces, special-shaped screws have been applied. The screws were made of several parts: (a) transporting with lengths raging between 20 mm and 40 mm; (b) parts with incised cutters with 30 mm length; (c) kneading parts with 15 mm length; (d) mixing part with 20 mm length. The temperatures of the cylinder heating zones (I-IV) were 180 °C, 182 °C, 184 °C, 186 °C, respectively. The temperature of the extruder head was 185 °C. The rotational speed of the extruder screw was 120 rpm. The dried materials – flax fibres (300 g) and PLA (1200 g) were added to the extruder feeding zone to achieve the 20 wt% of fibres content. The feeding speed of the PLA and flax fibres were 133.3 g/5 min and 33.3 g/5 min respectively.

The dumbbell-shaped samples for mechanical testing (dumbbell- and bar-shaped) were prepared using an injection molding machine (TRX 80 ECO 60, Tederic Machinery Manufacture, Taiwan). The temperatures of the I, II, and III zones of the injection molding machine cylinder, head, and mold were 170 ºC, 165 ºC, 165 ºC, 165 °C, and 35 °C respectively. The injection molding pressure was 24.8 MPa. The single sample mass was about 11 g.

The 0.5 mm films used for the microbiological examination were prepared from the extruded granules using the vulcanization press (AW03M, Argenta, Poland). The 0.7 g of granules, containing both PLA and fibres, were placed in a hot press (180 °C) and pressed for 10 s with a pressure of 0.7 MPa. After the pressure process have been completed, samples were cooled with compressed air for 10 s and removed from the press. The cooling stage ensures the constant shape of films.

The samples are denoted as follows: P, N, M, NF, and MF, where P indicates neat PLA, N –PLA containing non-modified flax fibres, M – PLA containing modified flax fibres by TA, NF – non-modified flax fibres, MF – modified flax fibres.

### 2.3. Examination methods

Dynamic mechanical analysis (DMA) has been performed with the DMA analyzer (Q 800, TA Instruments, USA). The dual cantilever mode has been applied for the examination of the one bar-shaped sample of each material (P, N, and M). The examination took place at a constant frequency of 1 Hz and amplitude of 15 μm as a function of temperature ranging from 25 °C to 160 °C.

Tensile strength and Young modulus have been examined using a tensile testing machine, (3367 Instron, USA). The examination has been conducted according to the PN-EN ISO 527–1 standard. During the test, the twelve samples of each material (P, N, and M) have been tested. The lowest and the highest values obtained during the test were rejected.

The TG measurements have been performed in a nitrogen atmosphere, using a thermogravimetric analyzer (Q500, TA Instruments, USA). One sample of each material (P, N, and M) has been examined. The masses of samples ranged from 19.7 mg to 20.3 mg. The TGA measurements were carried out in a temperature range from 25 °C to 800 °C and a heating rate of 10 °C/min.

The DSC measurements have been carried out in a nitrogen atmosphere using a differential scanning calorimeter (Q200, TA Instruments, USA). One sample of each material (P, N, and M) has been tested. The weight of samples ranged from 7.8 mg to 8.2 mg. The measurement temperatures ranged between 20 °C and 210 °C. The DSC curves were recorded in three stages: first heating, cooling, and second heating. The change of the temperature rate was 10 °C/min. In order to eliminate the thermal history of the tested samples, the measurement results analysis was based on the data obtained from the second heating stage. The degree of crystallinity ($X_c$) has been calculated using the following formula:

$$X_c = \left(\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m100\%}}\right)\cdot 100\% \quad (1)$$

Where $\Delta H_m$ is the change of melting enthalpy, $\Delta H_{cc}$ is the change of cold crystallization enthalpy, $\Delta H_{m100\%}$ is the change of the melting enthalpy evaluated for the neat PLA which has a maximum $X_c$. The value of this parameter is 93.6 J/g (Fambri and Migliaresi, 2010).

The contact angles were measured by a goniometer (DSA100, Krüss GmbH, Germany) equipped with an automated dosing drops system. The measurements of the contact angle have been performed using water as a test liquid. Six samples of each material have been tested. The biocomposites used in everyday life are in constant contact with water, hence the interactions between polar liquid and biocomposite surface are more important than non-polar ones. The test liquid drops (with a volume (v) 7 μl) were placed on the central part of the specimen surface at the rate of Δv= 5 μl/min. The determination of the contact angle of each sample was made 6 times.

Micrographs reflecting changes in the surface structure of fibres and fracture morphology of biocomposites were taken using a scanning electron microscope (SEM) (Quanta 3D FEG, Fei, USA). The samples were covered with a 2 nm layer of gold before measurement.

The evaluation of the biocidal properties of the prepared biocomposites has been performed according to standard ISO 22196:2011 (ISO 22196:2011Measurement of antibacterial activity on plastics and other non-porous surfaces). The study was based on reference bacterial strains, i.e. *Staphylococcus aureus* (ATCC 6538 P) and *Escherichia coli* (ATCC 8739). Each culture of a strain was prepared in the medium made up of a nutrient broth. Having the medium inoculated, the cultures were maintained at 37 °C for 24 h. Then, the count of cells was determined by a standard method of evaluation of optical density of the prepared cell suspension with the use of a densitometer (Densitometer II, Pliva-Lachema, Czech Republic) based on the McFarland's scale (McFarland, 1907). The determined optical density of the studied suspension was on the order of magnitude of 0.5, which corresponded to $1.5 \times 10^8$ CFU/mL of the suspension, according to the McFarland scale.

Antibacterial activity (R) of each biocomposite was determined in relation to the control sample as the difference in the logarithm of the viable cell counts found on an antibacterial-treated product and an untreated product after inoculation. The analysis was performed in triplicate. The film samples were produced using a vulcanization press (as described above). The N sample has been used as a control sample.

The control and all tested samples were covered with the suspensions of bacterial strains investigated in the research with a specified number of cells having been left for a specified time (0 h validation of recovery efficiency and 24 h). After this time, bacterial cells were recovered from the surface and suspended in a solution containing a neutralizer (Soybean casein digest broth with leticin). Subsequently, the number of cells viable and capable of growing was determined by the inoculation on Plate Count Agar in triplicate. The plates were incubated for 24 h at 37 °C. The reduction of the number of living and viable cells of tested bacteria was calculated using the following Eq. (2):

$$R = (U_t\text{-}U_0) - (W\text{-}U_0) \quad (2)$$

where: $U_0$ is the average of the common logarithm of the number of viable bacteria recovered from the control samples immediately after inoculation (validation of recovery efficiency), $U_t$ is the average of the common logarithm of the number of viable bacteria recovered from the control samples after 24 h (controls of survival in time), W is the average value of the common logarithm of the number of viable bacteria recovered from the test samples after 24 h.

According to standard ISO 22196:2011 the reduction of the number of cells capable of growing by two orders of magnitude ($R \geq 2$) was interpreted as a bactericidal effect of the investigated composite.

The epifluorescence micrographs of the bacterial cells stained using the LIVE/DEAD test (Invitrogen Molecular Probes, Eugene, USA), enabled us to differentiate between the living and dead cells. The microscope (Eclipse E-200, Nikon, Japan) was equipped with the excitation filter with a wavelength of λ = 470–490 nm and an emission range of 5000-∞ nm. During the experiment, the surface of the specimens

inoculated with microorganisms was treated with CYTO Green. The properly prepared samples were left for 15 min in the dark. Subsequently, the reagents excess was removed by pouring them out and the samples were dried. The surface of the dried samples was coated with immersion oil and observed under the microscope lens of × 10.000 magnification. Colour micrographs were taken with the colour camera (Digital Sight, Nikon, Japan) using a software package (NIS-F, Nikon, Japan). The amount of the bacteria was determined using the Multi-ScanBase software. During this process, the living bacteria cells turned green, while the dead ones got red or orange (Stepczyńska, 2014, 2016).

## 3. Results and discussion

### 3.1. Mechanical properties

#### 3.1.1. DMA

The results concerning the damping coefficient (tan δ) and storage modulus (E′) in the function of temperature are shown in Fig. 1. The application of flax fibres caused a significant increase in E′ from about 2731–7141 MPa. This increase proves a relatively good transfer of tension from the PLA matrix to flax fibres. However, after fibres modification with TA, the value of E′ decreased to about 6012 MPa, as compared to the N sample. This can indicate that TA decreased interphase adhesion and/or led to plasticization of the PLA phase in the M sample.

In the glass transition temperature range (from about 60–90 °C), no significant changes were detected. The maximum values of tan δ were around 72 °C. The highest maximum of tan δ was observed for the P sample. It may result from the highest content of PLA, thus tan δ of that phase was the largest. However, in the M sample, although less PLA phase was present, the value of tan δ was higher as compared to that for N sample. It can result from the migration of TA into the PLA matrix causing its volume plasticization, which would be also in line with lower stiffness of M compared to N sample. Also, in the case of the M sample, the maximum value of tan δ is shifted toward lower temperatures, which means that TA act as a plasticizer for the matrix.

In the cold crystallization temperature range (from about 90 °C to about 140 °C), an increase in the E′ of all samples can be seen, especially for the M sample. On the other hand, DSC results indicate that crystallization for composite N occurred at lower temperature and was much more intensive as compared to composite M. Therefore, higher strengthening of M samples in the cold crystallization range of DMA analysis as compared to N sample can additionally confirm that TA acted as a nucleating agent in the whole volume of PLA, whereas in N sample fibres were nucleating PLA mainly at their interfaces.

#### 3.1.2. Tensile strength

The conducted research shows that the average value of the tensile strength (σ) is about 68 MPa for the N sample which is almost 10 MPa higher than in the case of the M sample (Table 1). The σ values of P and N samples are comparable. The reason for the M sample σ decrease is the higher content of the plant additives (Colomer-Romero et al., 2020). According to the DMA test TA may migrate into the PLA matrix which changed the mechanical properties of the M sample compared to N.

The overage values of the elongation at break ($\varepsilon_b$) of the N and M samples are similar (Table 1). However, the N sample has a higher value of $\varepsilon_b$. The modification of flax fibres with TA had no significant effect on the $\varepsilon_b$ of the sample. The decrease of the σ along with $\varepsilon_b$ for the M sample compared to the N sample reveals deterioration of mechanical strength after the modification.

The increase in the Young modulus (E) of the N sample was caused by the presence of the fibres (Table 1). It is known that the cellulose contained in fibres increases the E value of the materials (Stepczyńska et al., 2021). The modification with the TA creates the opposite effect. The comparison of the E values for the N and M samples shows the decrease of the E value of the M sample by almost 0.6 GPa. Sumarizing, the deterioration of σ, $\varepsilon_b$, E after TA modification confirms DMA results which show that the TA modification decreased the stiffness of the material.

### 3.2. TG

Fig. 2 presents the mass (m) dependence on the temperature (T)

**Table 1**
The σ, $\varepsilon_b$ and E for the P, N and M samples.

| Sample | σ [MPa] | $\varepsilon_b$ [%] | E [GPa] |
|---|---|---|---|
| P | 66.1 ± 0.5 | 4.2 ± 0.1 | 2.1 ± 0.1 |
| N | 67.8 ± 0.3 | 1.8 ± 0.1 | 6.6 ± 0.1 |
| M | 59.2 ± 3.5 | 1.3 ± 0.1 | 5.9 ± 0.2 |

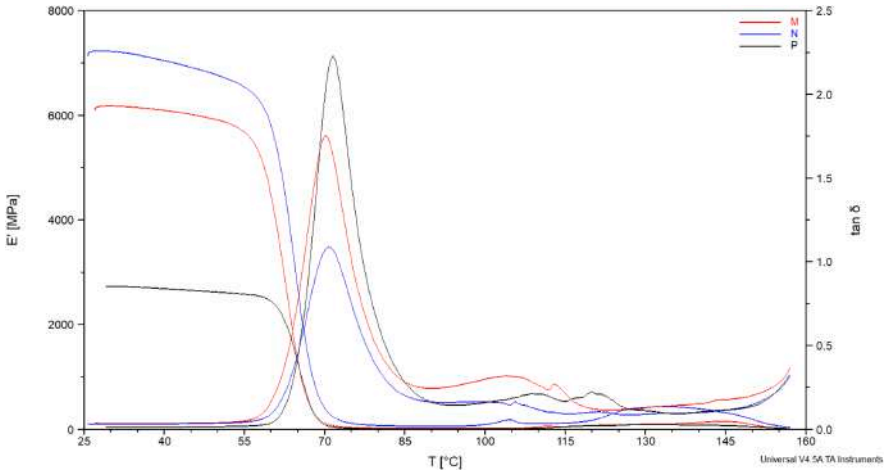


**Fig. 1.** The E′ dependence on the temperature (DMA curve) and the tan δ dependence on the temperature for the P, N, and M samples.

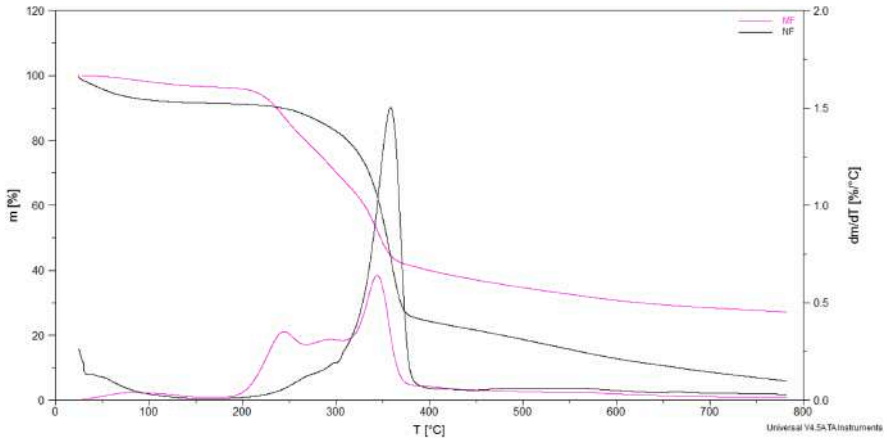


**Fig. 2.** The TG curve and DTG curve for the modified and non-modified flax fibre.

called TG curve and DTG curve – the first derivative (dm/dT) of the TG curve. The TG curves (Fig. 2) show a slight weight loss at about 100 °C related to the evaporation of water present in fibres. A greater amount of weight loss has been noted in the case of the MF sample. Fibre modification took place in an aqueous solution, hence a higher amount of water has been preserved. Moreover, the temperature influence causes TA dehydration (Wen et al., 2019). The rapid weight change of the NF sample observed between 250 °C and 380 °C is caused by the fibre decomposition during the pyrolysis process initiated in mentioned range. The sudden weight loss of the MF sample started at 205 °C. Plant pyrolysis leads to the solid phase (carbon) and gas creation (Shinogi and Kanri, 2003). The gradual loss of the carbon amount is noticed on the TG curve above 380 °C. The different percent weight loss of the NF (74%) and MF (59%) samples has been noted at the mentioned temperature. It shows that TA modification caused no significant changes in the thermal stability of fibres.

The analysis of the DTG curve shows that the tested fibres (both N and M) exhibit thermal stability to about 197 °C. It also has been confirmed by several pieces of research (Aliotta et al., 2019; Rytlewski et al., 2018b). The thermal stability of plant fibres was one of the basic requirements of their selection. The temperatures of the biocomposites processing were adjusted to the thermal properties of both flax fibres, TA, and polymer matrix.

Flax fibres, like all plant fibres, mainly contain cellulose, hemicellulose, and lignin which are classified as polymers (Celino et al., 2014; Perumal et al., 2018a). Their presence may be noticeable at the DTG curve of the NF sample which illustrates the decomposition of the flax fibres. This process took place in several stages. The thermal degradation was initiated only at 210 °C where the increased weight loss has been noticed. According to Gröndahl et al. (Gröndahl et al., 2003), the decomposition of the hemicellulose takes place at lower temperatures than lignin and cellulose. The weight loss observed between 235 °C and 285 °C could describe the thermal decomposition of the hemicellulose and pectins. Their content in flax fibres is 19% (Kozłowski et al., 2012). The slight peak observed at almost 298 °C could be interpreted as the start of the decomposition process of lignin (Nassar and MacKay, 1984). The small size of the mentioned peak is caused by the low lignin content in fibre (Kozłowski et al., 2012). The main peak noted at approximately 359 °C describes cellulose decomposition. It is narrow, hence there is only one component attributed to this peak. According to Dorez et al. (Dorez et al., 2014), the pyrolysis of the cellulose takes place in a similar temperature range. Cellulose is the dominant compound of the flax fibres and its content ranges from almost 65% to near 76% (Celino et al., 2014; Dorez et al., 2014; Zommere et al., 2014). The height of mentioned peak confirms rapid mass loss caused by the cellulose decomposition.

The presence of the TA is visible on the DTG curve of the MF sample. Its thermal decomposition consists of the three main stages: (a) the water evaporation and dehydration of TA (below 150 °C); (b) the decarboxylation of the galloyl groups in the external layer (between 240 °C and 340 °C); (c) the degradation of the glucose group and the galloyl groups in the internal layer (above 340 °C) (Wen et al., 2019). The slight weight loss noticed on the DTG curve belongs to stage (a), while the second peak (245 °C) combines both – the (b) stage and decomposition of the hemicellulose and pectins. However, the indistinct shape of the next peak (about 294 °C) suggests that stage b overlaps with the lignin decomposition process. The main peak (about 344 °C) describes the c stage and the cellulose decomposition.

Fig. 3 shows the changes in the weights of samples. Table 2 summarizes the percent weight loss (5%, 50%, and 95%) temperatures and the decomposition temperatures obtained from the TG and DTG curves respectively.

The slight weight changes of the samples have been noticed from approx. 200 °C. The weight loss of the M sample between 240 °C and 305 °C is caused by the decarboxylation of TA. The rapid weight losses of the N and M samples started at 305 °C. These changes are caused by the depolymerization process of the PLA which is thermally stable up to 300 °C (Stepczyńska et al., 2021).

The $T_{5\%}$ of the M sample was lower than the $T_{5\%}$ of the N sample. This difference is caused by the degradation process of the TA that took place in the previously mentioned temperature range. The opposite tendency has been noted at the 50% sample weight loss which has been recorded at 347.88 °C and 353.62 °C for the N and M samples respectively. The degradation of cellulose takes place in mentioned temperatures. The comparison of the $T_{95\%}$ values of the N and M samples demonstrates that the $T_{95\%}$ value increased more than twice in the case of M.

The presence of the TA in the M sample also affects the decomposition temperature ($T_d$) which was more than 7 °C higher than the $T_d$ of the N sample. It shows, that the thermal decomposition of the biocomposites has been slightly inhibited by the TA contained in them. However, the thermal resistance of the biocomposites containing modified fibres has not changed in the temperature range of PLA use.

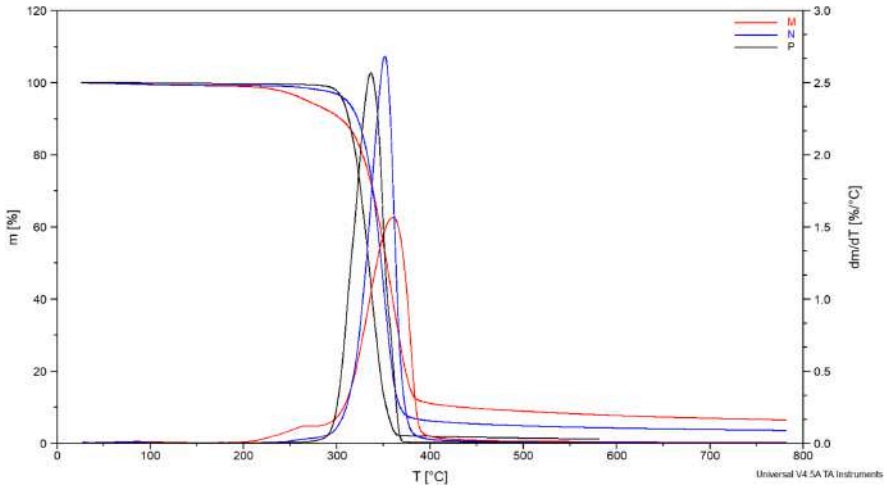


**Fig. 3.** The TG curve and DTG curve for the P, N, and M samples.

**Table 2**
The parameters of the studied samples obtained during the TG.

| Sample | $T_{5\%}$ [ °C] | $T_{50\%}$ [°C] | $T_{95\%}$ [°C] | $T_d$ [°C] |
|---|---|---|---|---|
| P | 306.94 | 334.36 | 358.78 | 337.72 |
| N | 310.78 | 347.88 | 479.44 | 352.72 |
| M | 268.31 | 353.62 | 781.71 | 359.80 |

### 3.3. DSC

Phase transitions of polymers are affected by the temperatures. Polymer properties (such as mechanical or physical) are changing during these transitions. Therefore the investigation of mentioned thermal transformations, which clears their relationship with other functional properties, is crucial.

where: $T_g$ is the glass transition temperature, $T_{cc}$ is the maximum temperature of the cold crystallization peak, $T_m$ is the maximum temperature of the melting peak.

The DSC peaks (exothermal and endothermal) are caused by the amount of heat released by the sample. The analysis of the first endothermal peak (Fig. 4) which relates to the glass transition shows that the heat flow of the N sample was lower than the M sample. The energy needed for the initiation of the M sample glass transition was greater. It suggests that the TA affected the crystal structure of the sample. The comparison of the $T_g$ shows that the P sample has the highest $T_g$ value (Table 3). A slight decrease of $T_g$ in the case of N and M samples is caused by the additives contained in them that act as plasticizers. The waxes

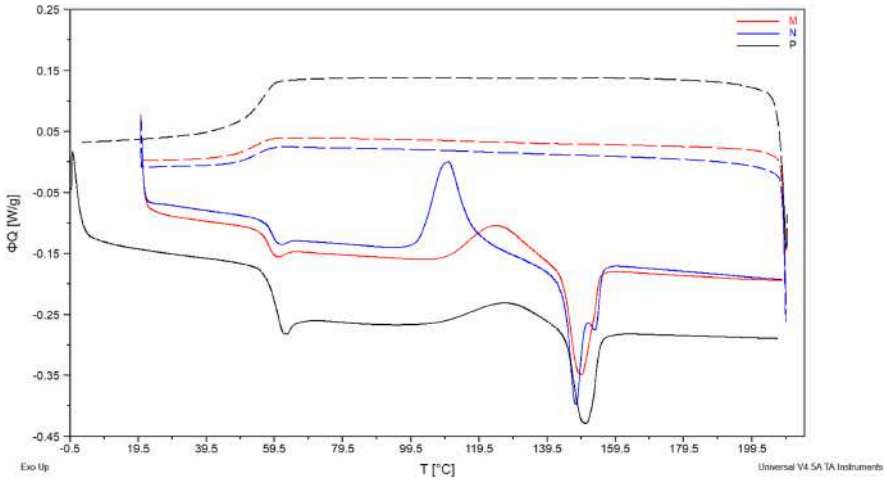


**Fig. 4.** The temperature dependence on the heat flow (DSC solid curve - second heating cycle and DSC dashed curve - cooling cycle) for the P, N, and M, where ΦQ is a heat flow.

**Table 3**
The parameters of the studied samples obtained during the DSC.

| Sample | $T_g$ [°C] | $\Delta H_{cc}$ [J/g] | $T_{cc}$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] | $X_c$ [%] |
|---|---|---|---|---|---|---|
| P | 60.90 | 4.94 | 127.10 | 5.35 | 149.50 | 0.44 |
| N | 58.80 | 20.26 | 110.50 | 20.48 | 147.98 | 0.24 |
| M | 57.71 | 13.72 | 124.70 | 14.36 | 149.52 | 0.68 |

and fats (Kozłowski et al., 2012) contained in flax fibres plasticize the biocomposites. Additionally, TA migration, discussed in the DMA results analysis, into polymer matrix causes its plasticization. According to (Santos et al., 2017) TA could be both a crosslinker and plasticizer. TA effect on the materials depends on its content in materials. TA in lower contents acts as a crosslinker (enhances mechanical properties) and in higher contents as a plasticizer (deteriorates mechanical properties). In this work, the high content of TA has been applied which resulted in plasticizing of sample M.

The next peak belongs to the exothermal ones and describes the cold crystallization of the samples. The comparison of the $\Delta H_{cc}$ values (Table 3) of the P and N samples reveals that the flax fibres increase the intensity of the cold crystallization. The cold crystallization peak of the N sample indicates the nuclear properties of the flax fibres. The $\Delta H_{cc}$ of the M sample was lower than the $\Delta H_{cc}$ of the N sample. The cold crystallization of the M sample took place at higher temperatures than the N sample which positively affected the crystallization degree of the M sample (Table 3) (Huda et al., 2008). This fact confirms the nucleating properties of TA in the whole volume of PLA mentioned in the DMA analysis.

Furthermore, the comparison of the $\Delta H_{cc}$ and $\Delta H_m$ values that refer to the N and M samples clearly indicates greater differences in these parameters in the case of the M sample. The higher differences between $\Delta H_{cc}$ and $\Delta H_m$ of sample M suggest that this sample has a higher degree of crystallinity. The higher content of the amorphous phase has been noted in sample N. The amount of heat that was absorbed during the melting process was slightly different for both N and M samples. The sample N absorbed more heat than sample M.

The $T_m$ of the M sample was about 2 °C higher than in the case of the N sample and the same as the $T_m$ of the P sample. The double melting peak of the N sample is caused by the presence of flax fibres which promote the recrystallization of PLA in higher temperatures. (Du et al., 2014; Gracia-Fernández et al., 2012; Mapossa et al., 2021). The melting process of the M sample took place at slightly higher temperatures. It could result from the migration of TA into the PLA which delayed the matrix meling process.

### 3.4. Wettability

The water contact angle ($\Theta_d$) values of the N and M samples are summarized in Table 4. The comparison of the $\Theta_d$ values of the P (74.5°) and N (75.1°) shows that the flax fibres create no significant changes in the polarity of sample N. However, the great differences between N and M samples have been noted (Table 4). The $\Theta_d$ clearly indicates the improved hydrophobicity of the M sample. TA increases the $\Theta_d$ of the M sample by almost 17°. The material could be considered hydrophobic if its water contact angle is higher than 90° (de Deus et al., 2021; Spada et al., 2021; Torres et al., 2021). From Fig. 5 it can be seen that the drop shape on the M sample surface is more spherical than the ones on the N sample surface.

**Table 4**
The $\Theta_w$ values of the studied samples.

| | P | N | M |
|---|---|---|---|
| $\Theta_w$ [°] | 74.4 | 74.7 | 93.0 |
| | 74.0 | 73.5 | 91.8 |
| | 74.9 | 75.6 | 91.5 |
| | 74.6 | 78.2 | 91.7 |
| | 75.0 | 72.9 | 92.3 |
| | 74.2 | 75.5 | 90.7 |
| $\overline{\Theta_w}$ [°] | 74.5 | 75.1 | 91.8 |

The presence of TA, which is a natural biocidal agent, has a positive effect on the hydrophobicity tested samples. On the one hand, the polarity difference between hydrophilic flax fibres and hydrophobic polymer decreases interfacial adhesion, but on the other hand surface hydrophobicity after TA modification increases. Hydrophobicity is extremely important in the case of materials that are exposed to pathogens. The higher degree of the surface hydrophobicity decreases the probability of its colonization by the microorganisms. Due to this, the service life of the finished products automatically extends.

### 3.5. SEM

The hydrophilic properties of the plant fibres are the main reason of the decreased interfacial adhesion in biocomposites. Low adhesion between matrix and fillers creates a noncontinuous structure of the biocomposite which has a negative effect on the transfer of biocomposite loads. Hence, the application of the plant fibres in the biocomposite leads to the inevitable deterioration of its mechanical properties. Plant fibres modifications are mainly done in order to improve the mechanical parameters of the biocomposites (Amiandamhen et al., 2020; Asyraf et al., 2021; Fogorasi and Barbu, 2017; Lee et al., 2021). However, natural plant modifiers used for other properties (such as hydrophobicity and antimicrobial properties) enhancement could be a sustainable replacement for chemical ones. (Jagadeesh et al., 2021) have discussed the necessity of modification of plant fibres which are used as reinforcement in biocomposites.

Fig. 6 presents the NF and MF samples micrographs that were taken on an SEM. The TA creates a characteristic coating of the modified fibres (Fig. 6b). The TA coating seemed to protect the fibres from thermal decomposition. However, the TA modification did not improve the thermal resistance of lignocellulosic materials. Non-modified are shown in Fig. 6a.

The surface analysis of fractured samples was conducted in order to compare the influence of TA on the interfacial adhesion between PLA and flax fibres. The fracture morphologies of samples P, N, and M are presented in Fig. 7. It can be seen, that the M sample (Fig. 7c) micrograph indicates a higher amount of visible holes and their greater depth compared to N. The fracture of the N sample (Fig. 7b) is more homogeneous that the M sample. The non-modified fibres (N sample) broke along with the matrix, while modified fibres (M sample) protrude from the matrix. During the tensile tests, the modified fibres were pulled out due to the weak interfacial adhesion. This fact suggests that TA migrated into the matrix which created a negative effect on the mechanical strength of the sample M. The SEM analysis proves the correctness of mechanical results interpretation.

### 3.6. The biocidal properties

The biocidal activity of materials against *Escherichia coli* and *Staphylococcus aureus* bacterial strains was evaluated. The bacteria selection was based on the frequency of bacteria occurrence and its range of negative effects on human health (Cheung et al., 2021; Loyola et al., 2021). The biocidal activity depends on the R which should be greater or equal to 2 due to the standard ISO 22196:2011. If this condition is fulfilled, the material could be called biocidal. The results of the biocidal activity of the tested material are presented in Table 5.

In a study with the *Escherichia coli* strain, the cell suspension at $T_0$ contained $150 \times 10^6$ CFU/mL. After 24 h of contact with the M sample, the number decreased to $0.4 \times 10^6$, which means a decrease by 3 orders of magnitude. According to the applied methodology, the material could be called biocidal when its R is equal to or higher than 2. This means that the M sample exhibits biocidal activity against the tested *Escherichia coli* strain. The comparative study of the N sample showed no biocidal

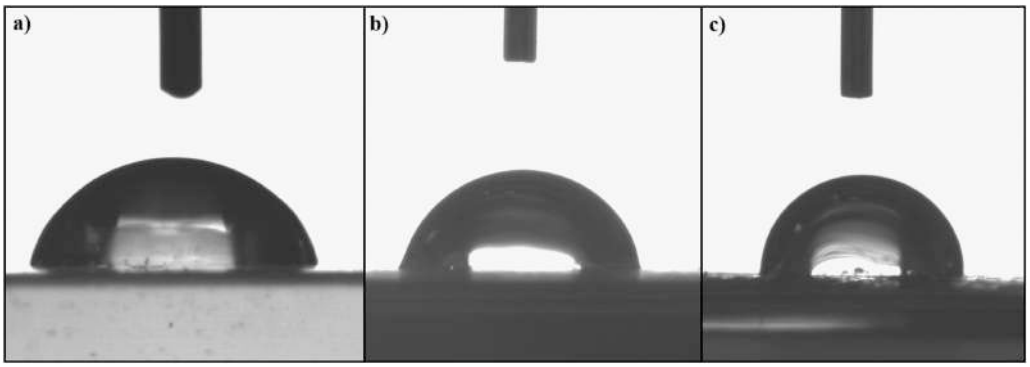


**Fig. 5.** The water drop placed on the sample: a) P, b) N, and c) M.

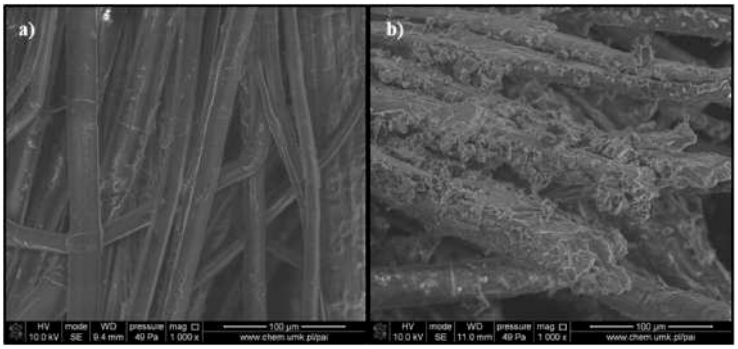


**Fig. 6.** The SEM micrographs of the: a) NF and b) MF.

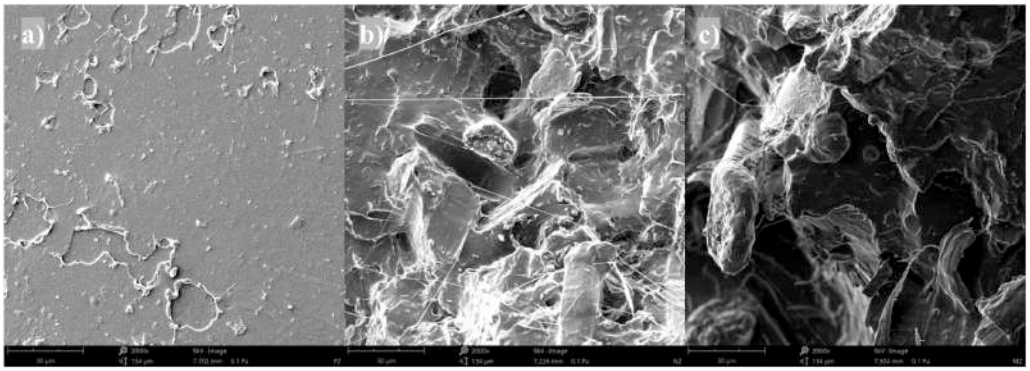


**Fig. 7.** The SEM micrographs of the: a) P, b) N and c) M.

activity against mentioned strain (R was equal to 1).

In a study with the *Staphylococcus aureus* strain, the suspension at $T_0$ contained $140 \times 10^6$ CFU/mL. After 24 h of contact of cells with the sample, the number of cells capable for growing fell below $0.001 \times 10^6$. This means that the number of cells capable for growing was reduced by at least 5 orders of magnitude. Therefore, the tested film has a biocidal effect on the cells of the tested *Staphylococcus aureus*. The evaluation of the effects of the sample N on this stain reveals no biocidal activity of the tested material (R was lower than 2).

Evaluation of the influence of the biocomposites on the bacterial cell

**Table 5**
The biocidal efficacy of the N and M sample.

| | N | | | M | | | |
|---|---|---|---|---|---|---|---|
| Tested bacterial strain | $T_0$ | $T_1$ | R | $T_0$ | $T_1$ | R | Unit |
| *Escherichia coli* | 150 | 5 | 1 | 150 | 0.4 | 3 | [CFU/mL] |
| *Staphylococcus aureus* | 140 | 15.7 | 1 | 140 | $< 0.001$ | 5 | $\times 10^6$ |

where: $T_0$ is the initial amount of bacteria that create the colony, T1 is the number of bacteria that create the colony noted after 24 h from start, and R is explained in the above text.

membrane integrity has been performed using a LIVE/DEAD BacLight kit which indicates the viability of the bacterial cell. During the mentioned test the bacterial cells have been dyed with two fluorescent dyes. One of the dyes penetrates the cells which leads to cell membrane damage. As a result, the dead bacterial cells turn red or orange while the living ones are green (Robertson et al., 2021). The cell viability has been determined with an epifluorescence microscope (Fig. 8).

Cell viability examination done with the LIVE/DEAD test showed that after 24 h of contact with the N sample all cells were live (green). This result was obtained for both *Escherichia coli* (Fig. 8a) and *Staphylococcus aureus* strains (Fig. 8b). Virtually no dead cells (orange) were found. The opposite effect was obtained in the case of the M sample. The majority of cells were dead (orange) which indicates the biocidal properties of this sample. The comparison of the effects of *Escherichia coli* (Fig. 8c) and *Staphylococcus aureus* (Fig. 8d) strains reveals the different amounts of dead cells. Mentioned observations confirm the results of the previous test. It showed no biocidal activity against both strains in the case of the N sample and different degrees of the biocidal activity (R=3 for the *Escherichia coli* strain and R=5 for the *Staphylococcus aureus* strain) for the M sample. Similar results of the LIVE/DEAD test were obtained by (Meng et al., 2021). The author applied the TA treatment and proved that with the increase in TA concentration the number of live cells on the surface of samples decrease.

Due to this, the biocidal properties of the TA in biodegradable materials are verified. Moreover, the application of TA in polymer biocomposites is recommended according to the current epidemiological state.

## 4. Conclusions

The modification the biocomposite reinforcement with the TA decreased the mechanical properties of the material. Due to the DMA studies, the stiffness of the material containing modified fibres was lower compared to the material with non-modified fibres. The probable reason for the lower mechanical strength noticed after the fibre modification was the migration of the TA into the PLA matrix. The plasticizing properties of the TA have been also confirmed by the tensile test.

The decreased stiffness of material containing modified fibres has been additionaly confirmed by the analysis of SEM fracture micrographs which reveals holes in material and protruded flax fibres from matrix. The fracture surface of the material with non-modified fibres was more homogeneous. This observation suggests that adhesion between modified fibres and matrix after modification was weaker than before.

The thermal properties of the materials containing modified fibres have not changed due to the TG. However, the $T_d$ increased slightly after the modification. Thus the TA retards the decomposition of the material.

Due to the DSC studies, the decrease of $T_g$ resulted from the plasticizing properties of the TA. However, the crystallinity of the biocomposite containing modified fibres increased. The higher degree of

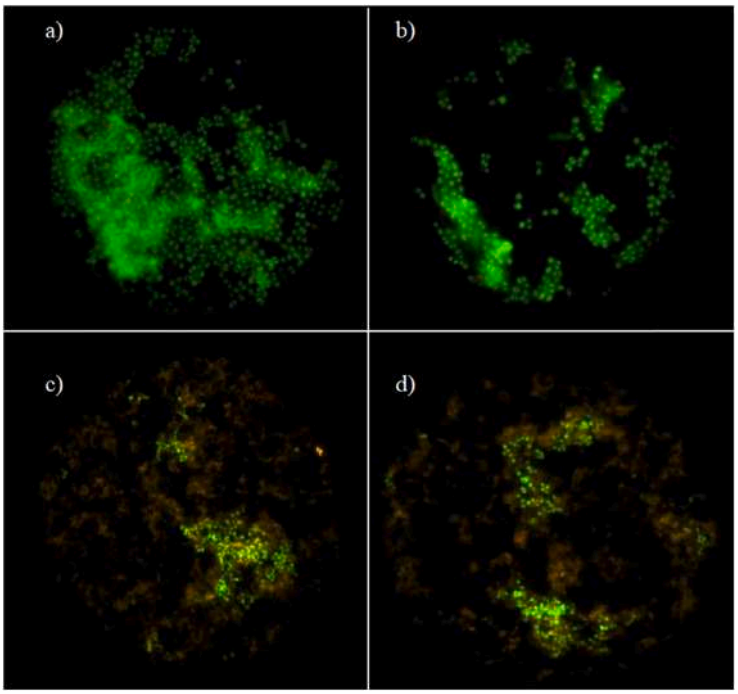


**Fig. 8.** The results of the LIVE/ DEAD test of: the N sample (a,b) and the M sample (c,d).

crystallinity is caused by the nucleating effect of TA on the material.

The hydrophobic properties of the modified sample were improved. The increased degree of hydrophobicity of materials is desired in the industries where microbiological hygiene or sterility is required. The hydrophobic surface limits its susceptibility to colonization by the bacteria and inhibits the growth of pathogens. This type of biocomposite could be potentially applied in the medical, beauty, and tattoo industries. Moreover, the hydrophobicity of materials is highly desired in the packaging and disposable products industry.

According to the biocidal activity study, the modified biocomposite was biocidal against both *Staphylococcus aureus* and *Escherichia coli* bacteria strains. However, stronger biocidal activity against *Staphylococcus aureus* has been noted. Due to the non-toxicity of the TA, the mentioned biocomposite could be applied in the industries where the materials have contact with the food. Such industries include the catering and packaging industries.

## CRediT authorship contribution statement

**Alona Pawłowska**: Methodology, Verification, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **Magdalena Stepczyńska**: Conceptualization, Methodology, Verification, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration. **Maciej Walczak**: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# The changes in selected properties of flax fibre-reinforced biocomposites affected by plant modifier concentration

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ABSTRACT

The application of the sustainable materials is one of the basic steps towards environmentally friendly and resource-efficient society. The aim of the study was to characterise the effects of the natural plant modifier concentration on properties of the biocomposites. The paper describes the influence of tannic acid (TA) concentration on flax fibre-reinforced biocomposites. The prepared biocomposites contained polylactide in 20 wt% and flax fibres (*Linum usitatissimum*) in 80 wt%, while the modifier concentrations varied from 1 % to 10 %. The manufacturing methods included extrusion and injection moulding of the biocomposites. The evaluation of the effects of modifier concentration on selected parameters of biocomposites was conducted using mechanical tests - tensile tests, thermomechanical - dynamic mechanical analysis (DMA), and thermal tests - differential scanning calorimetry (DSC) and thermogravimetry (TG). Additionally, biocidal and wettability studies were conducted. The examination results revealed, that 5 % is an optimum concentration of modifier which positively affected both mechanical and biocidal properties. The efficient use of modifiers can help in natural resources conversion and minimization of environmental impacts.

## 1. Introduction

The production of non-biodegradable materials on the large scale caused a serious escalation of the residual waste problem observed during the last decades [1]. Materials with petrochemical origin left in landfills have a huge impact on the inhabitants of the Earth. Non-degradable materials which cause microplastic generation have a huge impact on global environmental pollution. According to World Health Organisation, environmental pollution causes 1.7 million annual deaths among children under the age of 5 [2]. Smart waste management is not enough, therefore significant worldwide attention is drawn toward biodegradable materials. The growing demand for biodegradable materials observed during the last years in both science and industry is caused by increased public awareness and readiness for environmental protection [3].

Petrochemical plastic replacement with „green" ones is one of the basic steps in the solution of the residual waste problem [4]. According to statistics on plastic waste production, the packaging industry is the unquestionable leader which generates 40 % of plastic waste [5]. Therefore, the implementation of biodegradable packaging materials is extremely important.

Nowadays, biopolymers (polymers obtained from natural sources) are used in multiple industries all over the world [6–10]. Their popularity is gained by non-toxicity, biodegradability, and ecological sustainability [11,12]. It is known, that biopolymers (such as PLA) are widely used as a matrix for biocomposites, especially for biocomposites containing plant fillers [13–15]. One of such fillers are plant fibers [16,17]. Compared with glass fibres, plant fibres have several advantages as lower price, lighter weight, and higher specific strength [18,19,38]. However, the difference in electronegativity of hydrophobic polymer matrix and hydrophilic plant fibres decreases the interfacial adhesion of biocomposite which led to mechanical properties deterioration [20]. To predict this, different modification techniques are applied. Unfortunately, most of them are using chemicals that are toxic to humans and harmful to the environment [21]. The application of "green" modifiers is an essential step in biocomposites development which would increase the probability of petrochemical materials replacement over the world [22].

This paper describes a sustainable technique of flax fibres modification. The purpose of current studies was based on the evaluation of the influence of modifier content on some properties of biocomposites. TA has been chosen as a "green" modifier. The selection was based on the

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**Table 1**
The amount of ingredients in modifying solutions.

| Solution [%] | Water [mL] | TA [g] |
|---|---|---|
| 1 | 1782 | 18 |
| 5 | 1710 | 90 |
| 10 | 1620 | 180 |

origin of the modifier and its properties. TA is a natural polyphenol that widely occurs in various plants and combines crosslinking and plasticizing properties. Additionally, TA is a plant biocidal agent with strong antioxidant properties [23,24].

In everyday life, humans are surrounded by multiple pathogenic microorganisms which are present on almost every solid surface [25]. Pathogens are dangerous for human health and life. It is known, that pathogens cause 670 hundred annual infections in European Union only [26]. To predict microorganisms spreading, sterilization has been applied. However, sterilization uses strong chemicals which are not "green". Hence, the sterilization step could only be omitted in the case of biocidal materials.

## 2. Materials and methods

### 2.1. Materials

- Matrix – PLA type 2003D (Cargill Down LLC, USA) with density (ρ) of 1.24 g/cm$^3$, and melting flow rate of 4.2 g/10 min (2.16 kg, 190 °C). Biocomposites contained 80 wt% of PLA.
- Reinforcement – 5 mm flax fibres (Ecotex, Poland). Materials contained 20 wt% of fibres.
- Natural modifier – TA $C_{76}H_{52}O_{46}$ (Sigma-Aldrich, Poland) with a molecular weight of 1701.20 g/mol. Modifier content was 1 %, 5 %, and 10 %.
- *Escherichia coli* (ATCC 8739) and *Staphylococcus aureus* (6538 P, ATCC, USA)

### 2.2. Processing methods

The initial step of materials processing was based on their pre-drying with laboratory dryer type SUP-100 G (WAMED, Poland). Flax fibres were dried at a temperature of 60 °C, while PLA – was in 50 °C. Afterward, the modification with TA took place. The solutions of water and TA in concentrations of 1 %, 5 %, and 10 % were prepared (Table 1). Detailed description of the modification method could be found in Ref. [23].

The next step of processing was based on the weighting of pre-dryed compotents of biocomposites (PLA, non-modified flax fibres, and modified flax fibres). The laboratory scale (WPS 2100/C/2, Radwag, Poland) was used. Biocomposites were extruded and granulated with a co-rotating twin-screw extruder (BTSK 20/40D, Buhler, Germany). The special-shaped extruder screws were applied to prevent excessive fibres cutting. Extrusion took place in the following temperatures of cylinder heating zones (I-IV): 180 °C, 182 °C, 184 °C, 186 °C and 185 °C (the extrusion head temperature). The extruder screw was rotating with a speed of 120 rpm. The speed of materials feeding was 133.3 g/5 min for PLA and 33.3 g/5 min for flax fibres. As a result, obtained biocomposites contained 80 wt% of PLA (1200 g) and 20 wt% of flax fibres (300 g).

After extrusion, the injection moulding was conducted. The dumbbell-shaped samples were prepared with an injection moulding machine (TRX 80 ECO 60, Tederic Machinery Manufacture, Taiwan). Mentioned samples were used during the mechanical and wettability tests. The injection moulding process was carried out at 170 °C, 165 °C, 165 °C, 165 °C, and 35 °C. Mentioned temperatures are assigned to the I-III zones of the moulding machine cylinder, its head, and mold. The pressure during the process was 24.8 MPa. The mass of the single sample was approx. 11 g.

The films of 0.5 mm thickness for microbiological tests were prepared with a vulcanization press (AW03 M, Argenta, Poland). Extruded granules (0.7 g) were pressed with a pressure of 0.7 MPa in 180 °C for 10 s. Afterward, pressed samples were cooled for 10 s with compressed air. The constant shape of samples was ensured by cooling.

Tested samples were designated as P (for neat PLA sample), PF (for sample containing non-modified fibres), PF1 (for sample contained fibres modified with 1 % of TA), PF5 (for sample contained fibres modified with 5 % of TA), and PF10 (for sample contained fibres modified with 10 % of TA).

### 2.3. Examination methods

Mechanical properties were examined with DMA and tensile strength tests. DMA was conducted using a DMA analyzer (Q 800, TA Instruments, USA) with a dual cantilever. The evaluation was conducted on one sample from each material. The temperature range varies from approx. 28 °C to 160 °C, the applied amplitude was 15 μm and the frequency - 1 Hz. During the tensile strength tests, the tensile machine (3367 Instron, USA) has been used. Tensile tests were performed according to the PN-EN ISO 527–1 [27] standard which requires twelve samples from each material. After the examination, the extreme values were neglected.

The TG examination took place in inert gas (nitrogen) atmosphere using a thermogravimetric analyzer (Q500, TA Instruments, USA). One sample from each biocomposite was tested. The weight of mentioned samples varied from 19.7 mg to 20.3 mg. The temperature ranged from 25 °C to 800 °C with a heating range of 10 °C/min.

Same as TG, the DSC analysis has been performed in a nitrogen atmosphere. One sample from each material was examined with a differential scanning calorimeter (Q200, TA Instruments, USA). Samples weight varied from 7.8 mg to 8.2 mg. The three-cycle analysis (first heating, cooling, and second heating) has been carried out in temperatures from 20 °C to 200 °C and a heating range of 10 °C/min. To erase the thermal history of samples, the analysis was based on the curves obtained from the second heating cycle. The calculation of the degree of crystallinity ($X_c$) was based on formula (1):

$$\mathbf{X_c} = (\mathbf{\Delta H_m} - \mathbf{\Delta H_{cc}}) / \mathbf{\Delta H_{m100\%}} \quad (1)$$

where $\Delta H_m$ is melting enthalpy change, $\Delta H_{cc}$ – is cold crystallization enthalpy change, and $\Delta H_{m100\ \%}$ – is melting enthalpy change for neat PLA with maximum $X_c$. According to Ref. [28] the $\Delta H_{m100\ \%} = 93.6$ J/g.

The contact angle values were evaluated using a goniometer (DSA100, Krüss GmbH, Germany) with an automatic dosing drop system. As a test liquid, water has been chosen. The contact angle measurements were carried out for six samples of each material type. The 7 μl water drops were placed on the surface of the material. Each sample was tested six times.

The biocidal properties evaluation was based on standard ISO 22196:2007 (E) [29] According to the standard, the measurement is based on the evaluation of biocidal activity against two reference bacterial strains – *E. coli* and *S. aureus*. The strain cultures were prepared in nutrient broth and used as a medium made. After the medium inoculation, the cultures were left for 24 h at 37 °C. Further, the standard method of optical density evaluation was used for the determination of the number of cells present in a cell suspension. During this step, the densitometer (Densitometer II, Pliva-Lachema, Czech Republic) with McFarland's scale [30] was used.

All the tested samples were covered with cell suspensions and left for the specified time (0 h validation of recovery efficiency and 24 h). After this time, the cells recovered from the surface of the material were suspended in a neutralizer (soybean casein digest broth with lecithin) solution. Plates Count Agar (PCA) was used for cell inoculation and its number evaluation. The examinations were conducted thrice for each sample.

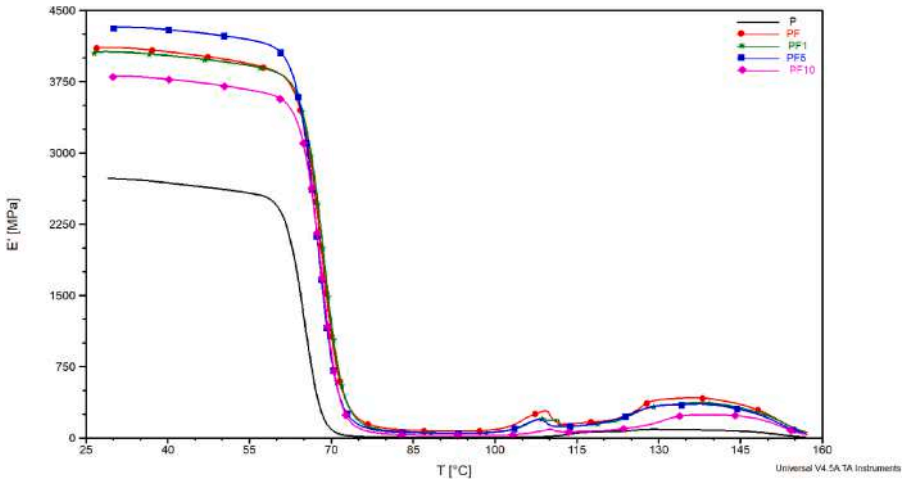


**Fig. 1.** The E′ dependence on the temperature (DMA curve) for the P, PF, PF1, PF5, and PF10 samples.

The antibacterial activity (R) is a difference in the logarithm of the number of viable cells present on material containing biocides (PF1, PF5, and PF10 samples) and reference material (sample PF). R coefficient has been calculated using formula (2):

$$R = (U_t - U_0) - (W - U_0) \quad (2)$$

Where $U_t$ is the average of the common logarithm of the number of viable cells recovered from the reference samples after 24 h, $U_0$ is the average of the common logarithm of the number of viable cells recovered immediately after the inoculation, W is the average of the common logarithm of the number of viable cells recovered from the test samples after 24 h.

## 3. Results and discussion

### 3.1. Mechanical properties

#### 3.1.1. DMA

Fig. 1 presents storage modulus (E′) dependence on the temperature. The E′ comparison in the glassy state (up to 60 °C) of P and PF samples reveals the increase of E′ of the PF sample by almost 1100 MPa. It can be understood as a quite good tension transfer between the matrix and non-modified fibres used as reinforcement in the PF sample [31]. The analysis of the E′ values in the glassy state temperature range indicates no significant difference in matrix-reinforcement interactions between the PF sample and PF1 sample. It can be concluded that flax fibres modified with a low concentration of TA (1 %) do not improve interfacial tension transfer in biocomposite. The opposite effect has been achieved with a

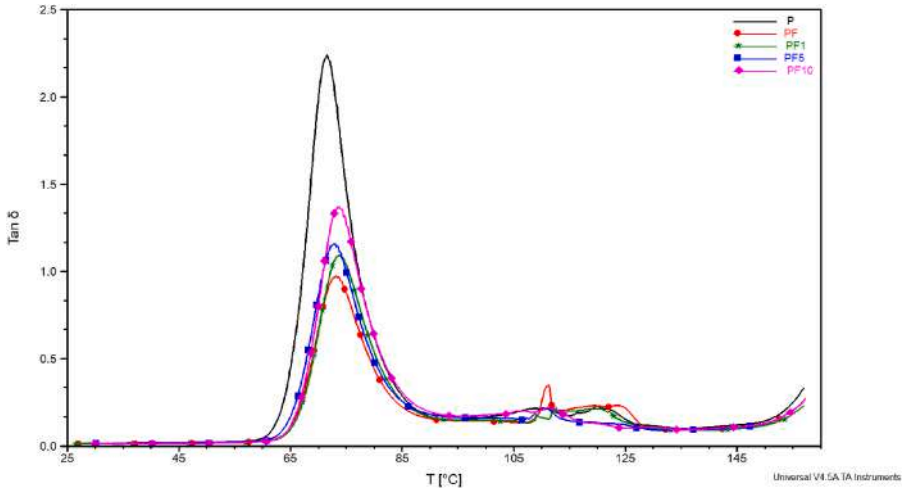


**Fig. 2.** The tan δ dependence on the temperature for the P, PF, PF1, PF5, and PF10 samples.

**Table 2**
The overage values of σ, $\varepsilon_b$, and E were obtained for P, PF, PF1, PF5, and PF10 samples during the tensile test.

| Sample | σ [MPa] | $\varepsilon_b$ [%] | E [GPa] |
|---|---|---|---|
| P | 70.0 ± 0.7 | 4.1 ± 0.1 | 2.2 ± 0.1 |
| PF | 70.7 ± 0.7 | 3.4 ± 0.1 | 3.7 ± 0.1 |
| PF1 | 69.0 ± 0.2 | 3.3 ± 0.1 | 3.5 ± 0.1 |
| PF5 | 67.8 ± 0.4 | 2.9 ± 0.1 | 3.6 ± 0.1 |
| PF10 | 64.4 ± 1.0 | 2.9 ± 0.1 | 3.3 ± 0.1 |

slight increase of modifier concentration from 1 % to 5 %. Compared with the PF sample the E′ of the PF5 has increased by approx. 200 MPa in the temperature range of glassy state. Further increase of modifier concentration led to E′ reduction. It decreases by about 200 MPa. The value of E′ for the PF5 sample is 400 MPa higher compared with PF10. Thus, it can be concluded, that PF5 has a better bending resistance than PF in the glassy state temperature range.

The further curve changes appear in the cold crystallization range. The increase of E′ in mentioned range indicates the initiation of the cold crystallization process. A significant increase of E′ for the PF sample could be explained by the presence of flax fibres which acted as nucleating agents. Migration of TA into the polymer matrix in modified samples decreased their E′ and caused its volume plasticization. The highest plasticization effect has been achieved with TA in a concentration of 10 %. Further DSC results confirm the plasticization of materials and reduction of their degree of crystallinity ($X_c$) with an increase of TA.

Fig. 2 shows the dependence of the damping coefficient (tan δ) on the temperature. The highest values of tan δ are presented by peaks that appear between 71 and 74 °C. The increase of tan δ for all samples has been recorded in the glass transition range – between approx. 60 °C and 80 °C. The highest peak is assigned to the P sample and connected with the highest amount of amorphous polymer phase which caused the increase of tan δ. The lowest value of tan δ was recorded for the PF sample. The mentioned behaviour is characteristic for materials that absorb less energy. Energy absorption depends on their rigidity properties, therefore PF sample tends to be more rigid compared with PF1, PF5, and PF10. The probable reason of the increase of tan δ for modified samples is TA migration into the polymer phase and its plasticization. It can be seen in Fig. 2 illustrating a gradual increase of tan δ with an increase of modifier content. The higher amount of TA applied, the more modifier enters the polymer matrix which results in higher plasticization of samples.

### 3.1.2. Tensile strength

Table 2 summarises the overage values of the tensile strength (σ), elongation to break ($\varepsilon_b$), and Young modulus (E). The comparison of σ values reveals their slight decrease after the modification. The decrease progresses with the increase of modifier content. The σ values of P, PF, and PF1 are comparable, while the increase of TA concentration (from 1 % to 10 %) decreases σ by more than 4 MPa. This fact confirms the suppositions described during the DMA analysis. The migration of TA in higher content (10 %) improves the elasticity and decreases σ of modified biocomposites.

The dependence on TA concentration has also been noted among elongation to break ($\varepsilon_b$) values. The results show that $\varepsilon_b$ for PF and PF1 are quite similar, thus 1 % of TA concentration does not change the mechanical properties of biocomposites in a significant way. A comparison of PF1 and PF10 reveals the decrease of $\varepsilon_b$ as well as σ. It could be explained by the migration of TA in high concentrations which decreased the stiffness of biocomposites.

Similar changes could be seen in the E results of PF1 and PF10 samples (Table 1). Lower E values are characteristic for materials with higher elasticity. Hence, the reduction of E for the PF10 sample compared with the PF1 sample could be caused by the plasticizing effect of the 10 % TA solution applied during the modification. Results showed a slight improvement of E for PF5 compared with PF1, however, the standard deviations reveal no difference between the elasticity of mentioned samples.

## 3.2. TG

According to Fig. 3 showing TG and DTG curves, the slight weight losses for all the samples have been registered at approx. 240 °C. Rapid weight changes for all the samples took place in the temperature range between 290 °C and 300 °C. Due to the thermal properties of PLA, its degradation processes usually occur in mentioned range [32]. A comparison of curves assigned to PF and modified samples revealed, that PF weight changes have been initiated in lower temperatures (290 °C). It can be explained by the higher amount of polymer phase in the non-modified sample (PF sample).

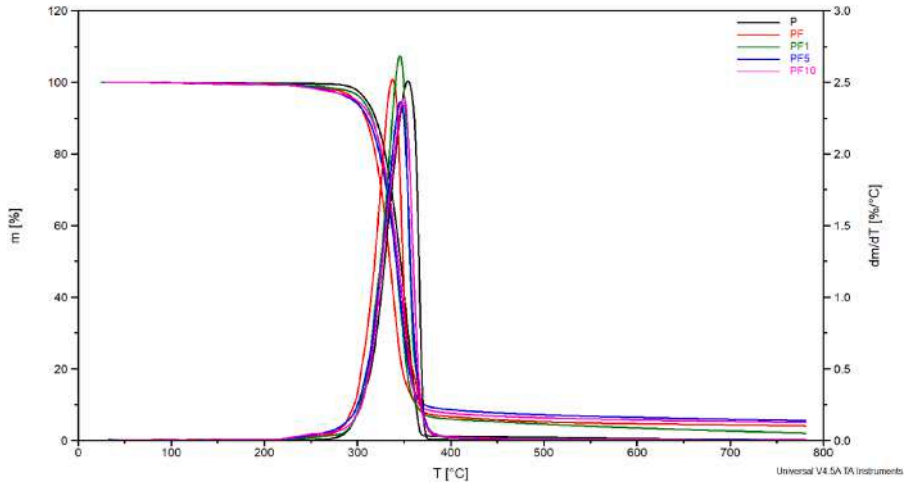


**Fig. 3.** TG and DTG curves obtained for P, PF, PF1, PF5, and PF10 samples.

**Table 3**
Selected temperatures registered for P, PF, PF1, PF5, and PF10 samples during the TG.

| Sample | $T_{5\%}$ [°C] | $T_{50\ \%}$ [°C] | $T_{95\ \%}$ [°C] | $T_d$ [°C] |
|---|---|---|---|---|
| P | 309.33 | 346.10 | 365.09 | 354.01 |
| PF | 297.82 | 334.62 | 526.64 | 337.76 |
| PF1 | 305.30 | 341.20 | 466.89 | 345.46 |
| PF5 | 294.99 | 341.46 | 781.14 | 346.10 |
| PF10 | 298.60 | 343.43 | 774.86 | 349.42 |

Table 3 summarises temperatures assigned to selected percentage weight losses and degradation temperatures for tested samples. The comparison of 5 % percentage loss temperatures ($T_{5\%}$) of modified samples showed, that weight loss for PF5 and PF10 took place in similar temperatures. While PF1 lost 5 % in slightly higher temperatures. The 5 % weight losses recorded in higher temperatures could be mainly caused by the lower presence of TA which decarboxylates between 240 °C and 340 °C [33]. No significant difference was noted between 50 % weight loss temperatures ($T_{50\ \%}$) of modified samples, while 95 % weight loss temperatures ($T_{95\ \%}$) differ. The most significant difference has been noted between PF1 and PF5. The 95 % weight loss for samples with higher concentrations of TA (PF5 and PF10) occurred in almost 2 times higher temperatures than for PF1.

The comparison of degradation temperatures ($T_d$) showed their slight increase with the increase of TA concentration. It is known, that TA contained in the biocomposites retards their thermal decomposition. However, the increase of its concentration has a moderate impact on degradation processes, which confirms the $T_d$ value of PF10 which is almost 4 °C higher that $T_d$ for PF1.

### 3.3. DSC

Fig. 4 illustrates changes in heat flow (ΦQ) with the temperature. It can be seen, that each curve has its 3 peaks – 2 endothermal and 1 exothermal. The first endothermal peak is assigned to the glass transition process. It reveals the relationship between modifier concentration and heat flow. The higher the amount of TA applied, the greater the energy needed for glass transition initiation. According to glass transition temperatures ($T_g$) it can be seen, that TA caused the plasticization of biocomposites. However, no significant differences between $T_g$ assigned to PF1, PF5, and PF10 have been noted (Table 4).

The next peak describing cold crystallization belongs to the exothermal ones. It reveals a decrease in crystallization enthalpy ($\Delta H_{cc}$) after the modification. This decrease progresses with TA concentration which confirms plasticizing properties of TA. The increase of $\Delta H_{cc}$ of PF compared with the P sample confirms, that fibres applied acted as nucleants. The increase of cold crystallization temperature ($T_{cc}$) in PF1-PF10 suggests, that energy needed for the initiation of cold crystallization increases with higher TA concentration. It might be caused by the higher amount of amorphous phase in PF5 and PF10 compared with PF1.

The highest differences between $\Delta H_{cc}$ and melting enthalpy ($\Delta H_m$) for modified samples were noted for the PF1. The migration of TA into the polymer and its effect on properties depend on modifier concentration. Higher concentrations of TA decrease the $X_c$ of biocomposites (Table 3) and promote their plasticization.

### 3.4. Wettability

The results obtained during the wettability examination of biocomposites are presented in Table 5. The hydrophilic nature of flax fibres contained in PF causes a decrease in the ability to repel the water

**Table 4**
Parameters obtained during DSC measurement for P, PF, PF1, PF5, and PF10 samples.

| Sample | $T_g$ [°C] | $\Delta H_{cc}$ [J/g] | $T_{cc}$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] | $X_c$ [%] |
|---|---|---|---|---|---|---|
| P | 60.52 | 5.38 | 127.42 | 6.30 | 150.73 | 0.98 |
| PF | 60.36 | 15.67 | 121.17 | 16.62 | 149.60 | 1.01 |
| PF1 | 59.78 | 17.21 | 119.98 | 17.94 | 149.00 | 0.78 |
| PF5 | 59.56 | 16.40 | 121.94 | 16.81 | 149.13 | 0.44 |
| PF10 | 59.62 | 15.74 | 123.47 | 15.89 | 149.54 | 0.16 |

**Table 5**
The $\overline{\Theta_w}$ values for P, PF, PF1. PF5, and PF10.

| | P | PF | PF1 | PF5 | PF10 |
|---|---|---|---|---|---|
| $\overline{\Theta_w}$ [°] | 75.0 | 75.1 | 85.1 | 85.3 | 86.1 |

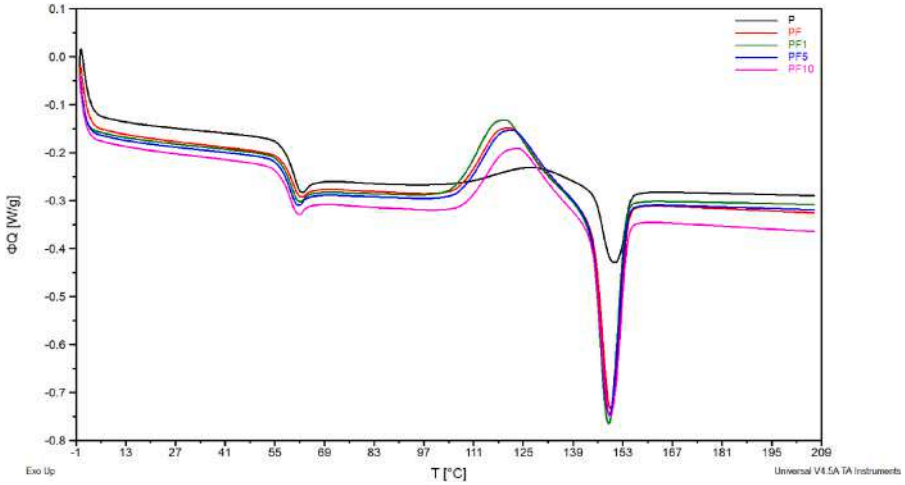


**Fig. 4.** The ΦQ dependence on the temperature for the P, PF, PF1, PF5, and PF10 samples.

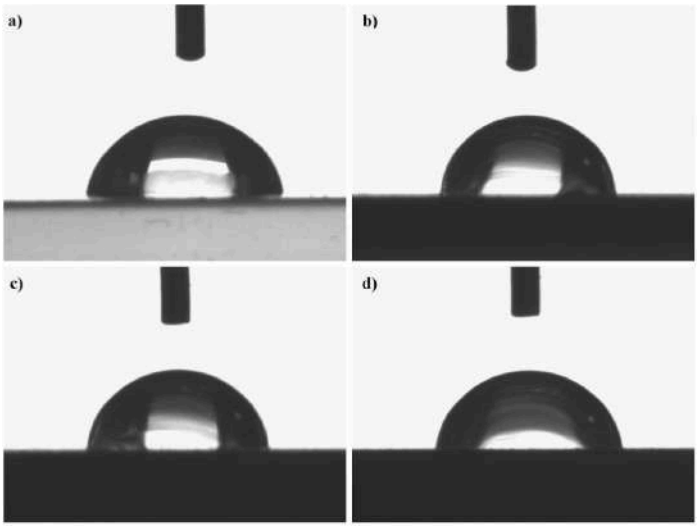


**Fig. 5.** Drop of water on the surface of: a) P, b) PF1, c) PF5 and d) PF10.

**Table 6**
Results obtained during the biocidal efficacy test.

| Sample | *Escherichia coli* [CFU/mL] | | | *Staphylococcus aureus* [CFU/mL] | | |
|---|---|---|---|---|---|---|
| | $T_0$ | $T_1$ | R | $T_0$ | $T_1$ | R |
| P | $9.3 \times 10^6$ | $3.8 \times 10^6$ | 0 | $11.0 \times 10^6$ | $9.8 \times 10^6$ | 0 |
| PF | | $5.1 \times 10^6$ | <0 | | $10.2 \times 10^6$ | <0 |
| PF1 | | $2.8 \times 10^6$ | 0.13 | | $3.7 \times 10^6$ | 0.42 |
| PF5 | | $<10^2$ | >4.58 | | $<10^2$ | >4.99 |
| PF10 | | $<10^2$ | >4.58 | | $<10^2$ | >4.99 |

molecules by biocomposite. A comparison of water average contact angle ($\overline{\Theta_w}$) values reveal, that flax fibres coated with TA increase the wettability of samples (Fig. 5). The difference between PF and PF1 $\overline{\Theta_w}$ values is 10°, which suggests that TA in mentioned concentration promotes the ability of biocomposite surfaces to repel the water molecules. Similar wettability properties have been noted for PF5 compared with PF1. Slight increase has also been noted for PF10. Current study confirms the results described in Ref. [23] and suggests, that higher increase in modifier concentration affects an increase in surface wettability.

Hydrophobicity is an extremely important parameter of biocomposites which is taken into account during the preparation of materials for industrial implementation. Biodegradable materials with improved water resistance are highly desired in many industries. The packaging industry belongs to such industries. Close food contact of materials used in the mentioned industry requires increased control level of their microbiological hygiene. Materials with increased hydrophobic properties limit the multiplication of microorganisms on their surface and protect them from further biodeterioration. As a result, materials service life elongates which decreases exploitation costs.

### 3.5. Biocidal properties

Biocidal activity against the most common bacteria strains - *Escherichia coli* and *Staphylococcus aureus* has been examined. Due to the standard [29], the antibacterial activity is quantified by R. Material could be called biocidal, if the R-value is greater than 2 or equal to 2.

The biocidal activity evaluation was based on the results presented in Table 6. A comparison of the initial number of bacteria needed to create a colony ($T_0$) and the amount of bacteria noted after 24 h from the beginning of the experiment ($T_1$) has been conducted. It revealed no reduction of magnitude orders for P, F, and PF1 for both *E. coli* and *S. aureus*. Consequently, their R values were close to zero. The highest R value among mentioned samples has been noted for the PF1 sample. However, the mentioned value was still too low for the material to be considered biocidal. The R-value for the PF1 sample in the case of *S. aureus* was higher than in the case of *E. coli*. However, TA in a concentration of 1 % does not improve the ability of the material to combat the microorganisms.

Different results have been obtained during the evaluation of the biocidal activity of samples containing fibres modified in higher concentrations of TA (5 % and 10 %). The reduction of 4 orders of magnitude from $10^6$ to $10^2$ has been achieved against both bacterial strains. Computations revealed, that the R-value for PF5 and PF10 was higher than 4.58 for *E. coli* and higher than 4.99 for *S. aureus*. It confirms the higher biocidal activity of TA against *S. aureus* found in the previous study [23]. According to Ref. [34] TA binds with the peptidoglycan layer of Gram-positive (*S. aureus*) bacteria in a direct way which makes them more susceptible to TA than Gram-negative (*E. coli*) ones [35–37]. Summarizing, the R value of PF5 and PF10 is more than two times greater than the minimum R for biocidal materials. It can be concluded, that modification with 5 % and 10 % of TA significantly affected the biocidal properties of tested materials.

## 4. Conclusions

DMA analysis revealed, that TA applied as a fibres modifier migrates into the polymer matrix and acted as a plasticizer in the whole volume. The increase of TA concentration and ambient temperature promotes plasticization and decreases the E′ of modified samples. However, in the glassy state temperature range the highest value of E′ was assigned to a sample containing fibres modified with 5 % of TA. It can be concluded, that modification positively affected its bending resistance in the mentioned temperature range. The tensile strength test confirms the DMA analysis. The highest E value among the modified samples was noted for the sample containing fibres modified with 5 % of TA which

suggests its highest stiffness. Mentioned stiffness is comparable to the stiffness of the non-modified sample.

TG analysis revealed no significant changes in the thermal properties of biocomposites after the modification. However, a slight increase of $T_d$ with the increase of TA concentration was noted. It confirms the ability of TA to inhibit thermal degradation. Moreover, mentioned ability enhances with an increase of TA concentration.

Plasticizing properties of TA have been confirmed by the DSC results. The decrease in $T_g$ has been noted for all modified samples. Moreover, changes in $X_c$ have also been observed. Its decline with the increase of TA content confirms the migration of modifier into the polymer matrix which resulted in higher plasticity of biocomposites.

The increase in wettability after the modification has been observed. The highest values of $\overline{\Theta_w}$ was noted for samples containing fibres modified with 10 % of TA. However, no significant difference in wettability between samples with 1 %, 5 %, and 10 % TA concentration has been noted. It can be concluded, that application of TA in mentioned concentrations slightly enhance the hydrophobic properties of materials. The findings of the study suggests that effects of TA modification on the surface wettability of the biocomposites could be a promising area of research.

Evaluation of biocidal efficacy of modified biocomposites showed no biocidal activity of samples containing 1 % of TA. However, the opposite effects were obtained for samples containing higher TA concentrations (5 % and 10 %). Mentioned samples were active against both bacterial strains - *Escherichia coli* and *Staphylococcus aureus*. Although, stronger biocidal activity against *Staphylococcus aureus* was noticed.

Summarizing, the most effective influence on mechanical (in glassy state temperature range) properties has been achieved after the modification of flax fibres with 5 % of TA. Additionally, 5 % of TA was the lowest concentration which created biocidal activity of samples. Hence, 5 % of this modifier is an optimum and the lowest concentration which positively affected mentioned properties. Due to the limited amounts of natural resources, the application of minimum allowable amounts of modifiers is extremely important.

## CRediT authorship contribution statement

**Alona Pawłowska:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Magdalena Stepczyńska:** Conceptualization, Formal analysis, Methodology, Supervision, Validation, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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# Antibacterial and Hydrophobic PLA Biocomposites Enabled by Geraniol-Modified Flax Fibres

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**Abstract**

In the medical industry, strong disinfectants are used to limit bacterial proliferation on the surface of polymer-based materials; however, they may leave hazardous residues. To prevent potential harm to human health, safer disinfection substitutes are continuously searched. This study evaluates the effect of a natural biocidal modifier, geraniol (GR), on the properties of flax-reinforced biocomposites. Biocomposites containing 80 wt% polylactide (PLA) and 20 wt% flax fibres were prepared, and fibres were modified with 1%, 5%, 10%, or 20% GR. The materials were examined using tensile tests, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetry (TG), contact angle measurements, scanning electron microscopy (SEM), and antibacterial activity tests. The incorporation of flax fibres increased the storage modulus from 2730 MPa (PLA) to 3447 MPa, while GR-modified fibres further enhanced stiffness up to 3769 MPa for the 20% GR sample. Strong antibacterial activity against Escherichia coli and Staphylococcus aureus was achieved in biocomposites containing $\geq$10% GR, with R = 5 and R $\geq$ 6, respectively. Surface hydrophobicity also improved progressively, and a water contact angle of 92° was obtained at 20% GR. These results demonstrate that geraniol-modified flax fibres effectively impart antibacterial activity and hydrophobicity to PLA biocomposites, indicating their potential for use in sustainable packaging applications and materials for the medical sector.

**Keywords:** biocomposites; natural fibres; plant fibres modification; natural origin modifiers; plant biocidal compounds; geraniol



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## 1. Introduction

The problem of residual waste is one of the biggest threats to the current ecological state, and it has already caused irreversible effects. The majority of currently used polymer materials are produced from petrochemical resources and their recycling is difficult. Statistics on polymer waste generation clearly indicate that the packaging industry holds the top position, being responsible for approximately 40% of the total annual waste generated [1]. The waste management issue could be improved by replacing petrochemical polymers with biodegradable polymers in the industries where polymers are commonly used (e.g., medical industry—medical equipment, etc.). For example, polylactide (PLA) is one of the best-known plant-based biodegradable polymers processed from renewable resources.

PLA is a thermoplastic material with rigidity and clarity similar to PS or PET and shows high strength and modulus comparable to those of PP and PS [2]. However, biodegradable polymers cause no environmental pollution, unlike petrochemical polymers, because they are biodegradable under industrial composting conditions.

To enhance the mechanical properties of the polymers, different reinforcements are applied. For example, fibres are among the most commonly used reinforcements. The biocomposites that include fibres are more resistant to mechanical stress [3]. A comparison of plant fibres with synthetic ones shows that plant fibres have some undoubted advantages. They are lightweight (unlike glass fibres), cost less, and they are completely biodegradable and processed from renewable resources [4]. Therefore, the development of plant-fibre biocomposites is a huge step for materials engineering with potential applications in everyday life, including food-contact packaging (e.g., trays, disposable cutlery, fresh-produce containers), horticultural items (seedling pots), single-use medical accessories, and touch surfaces in public or clinical environments, where the reduction in microbial load is essential. In such applications, materials must not only exhibit good mechanical performance but also possess inherent biocidal activity, reducing the need for chemical disinfectants [5,6].

Fibre selection was based on their availability in Europe and their physical properties. Flax and hemp are widely cultivated across Europe and represent major sources of natural technical fibres. Comparative studies [7] indicate that flax fibres show greater mechanical characteristics compared with hemp, including higher tensile strength and greater elongation at break.

Besides mechanical strength, materials used in the medical industry must meet other requirements. Due to their close contact with bacteria, materials used in the medical industry (e.g., equipment, elements of public space, etc.) should be pathogen-free. To limit the pathogen proliferation, the densification of the material surfaces is applied. Unfortunately, most disinfectants contain strong chemicals which are harmful to the environment. The toxic residues of these chemicals that remain on the surface have a negative impact on the human health. The application of biocidal modifiers is one of the ways to avoid harmful disinfections. However, most of the currently used biocidal modifiers are also synthetic and hazardous to human health. Therefore, natural and non-toxic modifiers are constantly being sought in both science and industry [6]. Sustainable biocomposites which contain natural biocides are an excellent alternative to petrochemical ones that need to be constantly disinfected with unsafe disinfectants.

Geraniol is a naturally occurring biocidal agent, derived from various plants, including roses, wild roses, geraniums, lavender, lemon, ginger, and orange [8–10]. In addition to its strong biocidal properties, geraniol is known for its non-toxic—according to 21 Code of Federal Regulations, Food Drug Administration—antioxidant, and soothing properties, which have made it widely used in the cosmetics industry [11–13]. In recent years, geraniol has also gained attention in biomedical systems, including geraniol-loaded nanoparticles for anti-inflammatory or anticancer therapies [14,15] geraniol–cyclodextrin inclusion complexes improving compound stability [16,17], and geraniol-functionalized chitosan derivatives showing promising antimicrobial behaviour suitable for wound-care materials or antimicrobial surface coatings [18]. Geraniol has additionally been incorporated into biopolymer films and hydrogels to enhance antibacterial effectiveness and prolong shelf life in biomedical and food-related applications [19]. However, its interaction with polymer matrices has not been fully explored, making this natural biocidal agent an interesting subject of study.

As well as biocidal activity, hydrophobic properties of the packaging materials are also highly desired. Hydrophilic surfaces are more susceptible to bacterial colonization

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than hydrophobic ones [20]. The colonization of the surfaces by bacteria leads to a gradual decrease in their properties and, eventually, their biodeterioration (material breakdown). Research shows that the damage caused by microorganisms reduces the lifespan of materials and leads to significant financial losses each year [21].

Flax fibres are plant fibres with a hydrophilic nature. To increase its hydrophobicity, various modification methods are applied [22]. They are often not sustainable and can be harmful for the environment and human health. Additionally, many chemical modifications cause irreversible changes in fibre surface structure, reducing their mechanical properties. Hence, the research focuses on the application of natural, plant-derived modifiers that effectively modify flax fibres and positively affect their surface properties [23]. The introduction of modified fibres into the polymer matrix will contribute to the development of novel biocomposites with biocidal properties and increased hydrophobicity.

Recent studies have extensively explored methods to improve the interface between hydrophilic natural fibres and hydrophobic polymer matrices like PLA. For example, a plasma-enhanced chemical vapour deposition significantly improves the thermo-mechanical properties of flax/PLA composites [24], while their ageing resulted in the deterioration of mechanical properties [25]. There is a growing interest in utilizing natural, bioactive compounds as alternatives to synthetic additives [26]. However, the application of essential oil derivatives, especifically geraniol, as a dual-functional modifier for flax fibres has received limited attention.

## 2. Materials and Methods

### *2.1. Materials*

Biocomposite matrix—PLA type 2003D (Cargill Dow LLC, Minnetonka, MN, USA) with a density of $\rho = 1.24$ g/cm$^3$ and a melt flow rate of 4.2 g/10 min (measured at 2.16 kg, 190 °C). The matrix constituted 80% of biocomposite.

Reinforcement—5 mm flax fibres' length (Ekotex, Namysłów, Poland) which constituted 20% of the biocomposite.

Biocidal modifier—GR C10H18O (Thermo Scientific, Waltham, MA, USA) with a molecular weight of 154.25 g/mol.

Bacterial strains—*E. coli* 8739 and *S. aureus* 6538 P (ATCC, Manassas, VA, USA), needed during the microbiological studies.

### *2.2. Processing Methods*

Processing was carried out in a five-step procedure (Figure 1). Stages I and II involved the preliminary preparation of the matrix and fibres, while stage III was used to combine these components to form the composite. The final stage (IV) comprised the preparation of two types of samples. A detailed description of each stage is provided in below subsections.

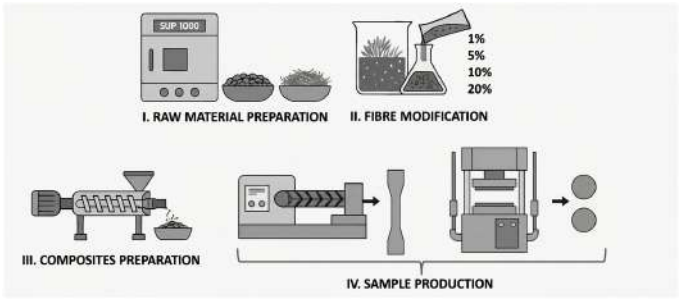


**Figure 1.** Processing procedure.

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2.2.1. Raw Material Preparation and Fibre Modification

Before processing, all the used materials were dried using laboratory dryer type SUP-100 G (WAMED, Warszawa, Poland). The temperature differed based on specific properties of dried materials: the matrix was dried at 50 °C, while the reinforcement was dried at 60 °C for 12 h. Prepared fibres were modified with GR in concentrations of 1%, 5%, 10%, and 20% (wt%). Table 1 presents the amounts of components contained in the modifying solutions used. The mentioned concentrations were chosen in accordance with our previous research [27] to compare the effects of different modifiers (tannic acid and geraniol) at the same concentrations. The modification technique has been described in detail in [27,28].

**Table 1.** Compositions of different GR solutions.

| Solution [1%] | Water [mL] | GR [mL] |
|---|---|---|
| 1 | 1782 | 18 |
| 5 | 1710 | 90 |
| 10 | 1620 | 180 |
| 20 | 1440 | 360 |

2.2.2. Composites Preparation

Further processing includes thermal methods such extrusion and injection moulding. The co-rotating twin-screw extruder FI = 24 mm, L/D = 40, (Zamak Mercator, Skawina, Poland) ensured better mixing of reinforcement and polymer matrix and improved dispersion of flax fibres in PLA. A special configuration and shape of the screws was applied, intended to minimize the cutting of the fibres into shorter fragments (Figure 2) [28,29]. It did not involve the elements returning and intensively mixing the polymer melt but they were replaced by the elements mainly transporting the melt. The extruder was equipped with a granulator making the extrusion process continuous. The temperature of the extruder head was 185 °C, while the temperatures of the cylinder heating zones (IV–I) were 186 °C, 184 °C, 182 °C, and 180 °C. The speed of the extruder screw was 100 rpm. The polymer matrix was fed at a speed of 133.3 g/5 min, while the reinforcement was fed at a speed of 33.3 g/5 min. The prepared biocomposites contained 80 wt% of the polymer matrix and 20 wt% of the reinforcement.


**Figure 2.** Elements of extruder screw configuration.

2.2.3. Sample Production

To produce the paddle-shaped samples needed for mechanical and wettability examinations, an injection moulding machine (TRX 80 ECO 60, Tederic Machinery Manufacture, Hangzhou, China) was used. The process was carried out at 170 °C, 165 °C, 165 °C, 165 °C,

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and 35 °C assigned to the heating zones (I–III) of the moulding machine cylinder, its head, and mould. Samples were moulded at 24.8 MPa.

A vulcanization press was used to prepare the films needed for the microbiological studies. To prepare 0.5 mm thick samples, 0.7 g of extruded granulate was pressed at 180 °C and 0.7 MPa for 10 s. To prevent deformations, hot films were cooled with compressed air for the next 10 s. Prepared samples were labelled as follows (Table 2).

**Table 2.** The description of the sample labels.

| Sample Label | PLA Content [%] | Flax Fibres Content [%] | GR Solution Used [%] |
|---|---|---|---|
| P | 100 | 0 | 0 |
| N | 80 | 20 | 0 |
| M1 | 80 | 20 | 1 |
| M5 | 80 | 20 | 5 |
| M10 | 80 | 20 | 10 |
| M20 | 80 | 20 | 20 |

The samples are indicated as follows: P, N, and MX, where P and N are reference samples, MX indicates samples containing flax fibres that have been modified using geraniol, and X stands for wt%GR.

### *2.3. Examination Methods*

#### 2.3.1. Dynamic Mechanical Analysis

The dynamic mechanical analyzer (Q 800, TA Instruments, New Castle, DE, USA) was used to conduct dynamic mechanical analysis (DMA). In this study, the dual cantilever mode was employed to investigate the mechanical properties of the reference sample as well as samples containing non-modified and modified fibres. The experiment was conducted by subjecting bar-shaped samples (35 × 10 × 4 mm) to a consistent frequency of 1 Hz and a deformation amplitude of 15 µm. This evaluation was performed while varying the temperature from 25 °C to 160 °C.

#### 2.3.2. Static Tensile Test

A tensile testing machine (3367 Instron, Norwood, MA, USA) was employed to analyze the tensile strength and Young's modulus [30,31]. The analysis was carried out following the standard with a strain speed of 20 mm/min. According to ISO 527-2 [31], during the mechanical tests, specimen type 1A (115 × 20/10 × 4 mm) was used. Within this test, twelve samples in the shape of a paddle of each material (reference, containing non-modified and modified fibres) underwent examination. Extreme values recorded during the test were excluded from the analysis.

#### 2.3.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted using a thermogravimetric analyzer (Q500, TA Instruments, New Castle, DE, USA) under a nitrogen atmosphere. A single specimen of each material (reference, containing non-modified and modified fibres) was subjected to examination. The sample masses ranged from 19.7 mg to 20.3 mg. The TGA measurements were conducted over a temperature range from 25 °C to 800 °C with a heating rate of 10 °C/min.

#### 2.3.4. Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) measurements were conducted within a nitrogen atmosphere using a differential scanning calorimeter (Q200, TA Instruments, USA). Each material (reference, containing non-modified and modified fibres) was studied

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using a single sample. The sample weights varied from 7.8 mg to 8.2 mg. The measurement temperatures ranged from 20 °C to 210 °C. The DSC curves were captured across three cycles: first heating, cooling, and second heating. A temperature change rate of 10 °C/min was maintained. To ensure the removal of any prior thermal history of the samples, the analysis focused on data derived from the second heating phase. The degree of crystallinity ($X_c$) for modified samples was calculated based on total composite mass, including PLA, flax fibres, and geraniol. The below formula was used:

$$X_c = \frac{(\Delta H_m - \Delta H_{CC})}{\Delta H_{m100\%}} \cdot 100\% \quad (1)$$

where $\Delta H_m$ refers to the alteration in the melting enthalpy, $\Delta H_{cc}$ to the alteration in cold crystallization enthalpy, and $\Delta H_{m100\%}$ the to the alteration in melting enthalpy calculated for the pure PLA with maximum $X_c$ (for pure 100% crystalline PLA $\Delta H_{m100\%}$ = 93.6 J/g [32]).

An automated dosing drops system was used during the contact angle measurements, which were performed with a goniometer (DSA100, Krüss GmbH, Hamburg, Germany). During the analysis, water was used as a test liquid for the evaluation of surface wettability of six samples of each biocomposite (reference, containing non-modified and modified fibres). To conduct the studies, drops of the test liquid (with a volume (v) of 7 µL) were placed on the surface of samples at a controlled rate of $\Delta v$ = 50 µL/min.

#### 2.3.5. Electron Microscope Analysis

Micrographs depicting fractures of the biocomposites after the tensile strength tests were captured using a scanning electron microscope (SEM) (SU8010, Hitachi Ltd., Tokio, Japan). The samples were previously dried at 50 °C using a laboratory dryer type SUP-100 G (WAMED, Warszawa, Poland) to decrease their moisture content, which can deteriorate the quality of the micrographs. To ensure the proper conductivity of tested biocomposites, a thin layer (5 nm) of gold was applied on the surface of the samples using a sputter coater before examination.

#### 2.3.6. Microbiological Testing

The assessment of biocidal properties was carried out following the ("ISO 22196:2024" [33]) standard. According to this standard, the evaluation of biocidal activity was performed against two reference bacterial strains: *E. coli* and *S. aureus.* The strains were cultivated in nutrient broth which served as the growth medium. After the inoculation, the cultures were incubated for 24 h at 37 °C. Subsequently, the optical density assessment method outlined in the standard was used to determine the cell count within a cell suspension. For this purpose, a densitometer (Densitometer II, Pliva-Lachema, Czech Republic) with McFarland's scale was used [34].

The antibacterial activity (R) is defined as the difference in the logarithm of the number of viable cells found on materials containing biocides (samples containing modified fibres) compared to the reference material (sample containing non-modified fibres). The R coefficient is determined using the following Equation (2):

$$R = (U_t - U_0) - (W - U_0) \quad (2)$$

where $U_t$ refers to the average of the common logarithm of the number of viable cells recovered from the reference samples after 24 h, $U_0$ refers to the average of the common logarithm of the number of viable cells recovered immediately after inoculation, and W refers to the average of the common logarithm of the number of viable cells recovered from the test samples after 24 h. For each of the tested materials, three tests were performed.

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2.3.7. Statistical Analysis

Statistical analysis for mechanical and wettability tests was performed using a one-way analysis of variance (ANOVA) and Tukey's post hoc test to determine the statistical significance (level $\alpha = 0.05$) of the effect of fibre and GE content.

## 3. Results and Discussion

### *3.1. DMA*

A comparison of DMA curves illustrated in Figure 3 revealed the dependence of storage modulus (E′) on GR concentrations. The introduction of flax fibres into the polymer matrix resulted in an increase in E′ from 2730 MPa (P sample) to 3447 MPa (N sample) at ambient temperature (25 °C). Table 3 sumarizes storage modulus (E′) at ambient temperature. The more than 20% increase in E′ confirms an efficient increase in the biocomposite stiffness after the incorporation of flax fibres into the polymer matrix.

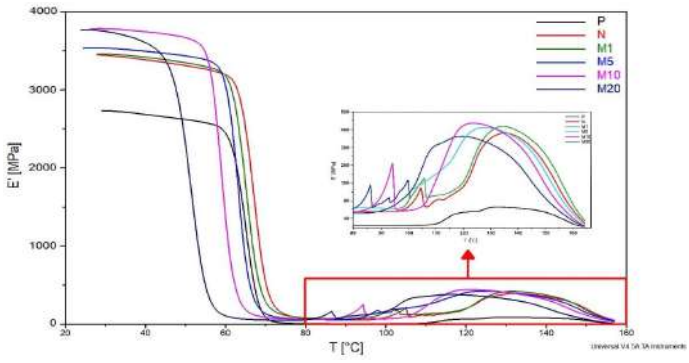


**Figure 3.** The E′ dependence on the temperature (T) (DMA curve) for the P, N, M1, M5, M10, and M20 samples.

**Table 3.** Storage modulus (E′) at ambient temperature.

| Sample | E′ [MPa] at 25 °C |
|---|---|
| P | 2730 |
| N | 3447 |
| M1 | 3456 |
| M5 | 3369 |
| M10 | 3568 |
| M20 | 3769 |

The onset point of glass transition for the N sample is approx. 64 °C. Application of 1% of GR does not affect further stiffness increase—E′ value was 3459 MPa which is similar to E′ of N sample. However, the glass transition of the M1 sample was initiated at a slightly lower temperature (about 62 °C). GR is known for its plasticizing properties [19], which are confirmed by the shifting of the glass transition range for M1. The higher increase in E′ (3533 MPa) was noted for the M5 sample. Also, the beginning of the glass transition was initiated at approx. 60 °C. The same tendencies have been noted in the case of M10 where E′ was approx. 3781 MPa and glass transition started at near 56 °C. The improvement of E′ by more than 300 MPa (compared to the N sample) could be explained by the higher amount of GR, which contains more alkyl chains. The mentioned chains are known for their hydrophobic properties which improve the internal hydrophobicity of biocomposite,

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resulting in higher E′. A double increase in modifier concentration (M20) caused the glass transition to start at about 47 °C. The increase in GR concentration led to a greater mobility of polymer molecules, which enhances the plasticization effect. In summary, the increase in bending resistance for the M5 and M10 samples in the glassy state temperature range could be explained by alkyl groups contained in GR, which improved the stiffness of the biocomposites. It can be concluded that the most positive effect of modification on the mechanical properties of biocomposites in the glassy state temperature range was achieved in the case of the M10 sample, where E′ was more than 300 MPa higher compared to E′ of the N sample.

A zoomed-in fragment of the curves (Figure 3) in the cold crystallization range (from 80 °C to 150 °C) shows one-step crystallization for the P sample and two-step crystallization for fibre-reinforced samples (both modified and non-modified). The cold crystallization peak of the P sample occurs at around 110 °C, which indicates typical recrystallization for PLA. The first step of the fibre-reinforced sample crystallization occurs as a single peak with a rapid increase in E′. These changes can be explained by the plasticization of the polymer and the rapid increase mobility of chains in both modified and non-modified samples. The mobility of chains in the N sample with a peak at 105 °C could be caused by the melting of fats and waxes which naturally present in flax fibres [35]. A similar peak in the cold crystallization area for PLA reinforced with 20% flax fibres was obtained by Aliotta et al. [36]. The introduction of modified fibres increases the mobility of polymer chains which was confirmed by the shifting of peaks to the lower temperatures (Table 4). These peaks appear at approx. 102 °C, 98 °C, 94 °C and 86 °C for M1, M5, M10 and M20, respectively. It can be concluded that the degree of plasticization increases with the increase of the concentration of the modifier.

**Table 4.** The glass transition ($T_g$) temperature and damping coefficient (tan δ) peak temperature for P, N, M1, M5, M10, and M20 samples.

| Sample | $T_g$ [°C] | tan δ |
|---|---|---|
| P | 71.34 | 2.2585 |
| N | 71.96 | 0.9239 |
| M1 | 70.15 | 0.8626 |
| M5 | 62.27 | 0.9097 |
| M10 | 60.79 | 0.8951 |
| M20 | 57.13 | 0.9431 |

It is known that fibres improve the degree of matrix crystallization due to their nucleating properties. The increase in E′ after the previously discussed peaks proves the nucleating nature of flax fibres. The E′ increase for the M1 sample overlaps with that of the N sample. The increase for the M5, M10, and M20 samples begins at lower temperatures. This shift confirms the plasticizing effect of the modifier which intensifies with increasing modifier concentration.

The damping coefficient (tan δ) can indicate the mechanical energy macromolecular segments absorb in their translational movements. Figure 4 illustrates the decrease in tan δ values of samples N, M1, M5, M10, and M20 compared to the tan δ value of the P sample. This change confirms the increased stiffness of the biocomposites due to the presence of flax fibres [37]. The tan δ peak is associated with the glass transition ($T_g$) temperature range, which is shifted towards lower temperatures for all of the modified samples [38]. It can be observed that $T_g$ temperature decreases with the increase in modifier concentration, because geraniol increases the mobility of polymer chains, resulting in reduced intermolecular cohesion and stress. So, at low modifier levels, we have higher

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stiffness. This observation confirms the enhancement of the plasticization effect with an increasing modifier concentration.

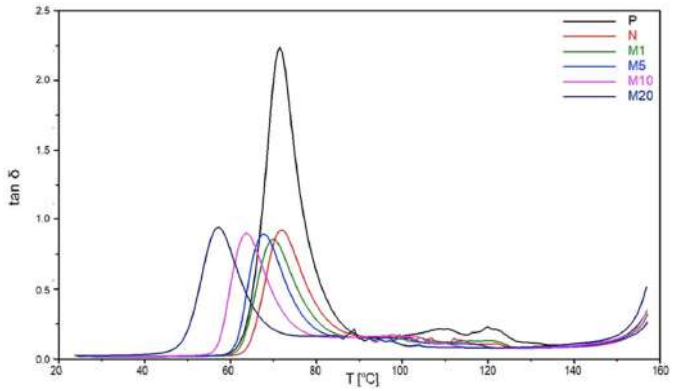


**Figure 4.** The damping coefficient (tan δ) dependence on the T for the P, N, M1, M5, M10, and M20 samples.

### *3.2. Static Tensile Test*

The results obtained during the tensile strength examination, conducted under normal temperature conditions [39], are presented in Table 5. Graphical interpretation of obtained results is showed in Figure 5. As expected, the highest tensile strength ($\sigma_m$) value was noted for the P sample. Examination revealed the decrease in σ after the introduction of flax fibres which confirms an increase in stiffness of the N sample noted in the DMA section. The gradual decrease in σ occurred with an increase in modifier concentration. The $\sigma_m$ values for the N and M1 samples are similar, which indicates an insignificant effect of such a concentration of modifier. However, further increases in modifier concentration leads to a greater decrease in σ. This decrease could be caused due to the deterioration in durability of M5, M10, and M20 samples and their low resistance to deformation. Initially, it was considered that the applied modifier might migrate into the polymer matrix, and terpenoid esters in GR could create a plasticization effect by weakening polymer chain interactions [40,41]. However, analysis of mechanical properties (increase in Young's modulus and decrease in elongation at break) suggests that the modifier acts as a stiffening agent rather than a classic plasticizer.

**Table 5.** The tensile strength studies results obtained for P, N, M1, M5, M10, and M20 samples.

| Sample | $\sigma_m$ [MPa] | $\varepsilon_b$ [%] | E [GPa] |
|---|---|---|---|
| P | 69.99 ± 0.73 | 4.07 ± 0.07 | 2.25 ± 0.05 |
| N | 59.86 ± 0.74 | 2.91 ± 0.12 | 3.34 ± 0.10 |
| M1 | 60.33 ± 0.70 | 2.77 ± 0.12 | 3.49 ± 0.14 |
| M5 | 54.33 ± 0.32 | 2.51 ± 0.10 | 3.45 ± 0.04 |
| M10 | 47.93 ± 0.58 | 2.32 ± 0.09 | 3.31 ± 0.15 |
| M20 | 41.07 ± 0.84 | 2.25 ± 0.11 | 3.10 ± 0.07 |

The observed reduction in elongation at break ($\varepsilon_b$) for non-modified and modified samples compared to the P sample indicates increased brittleness of the N sample. The modifier slightly promotes the decrease in $\varepsilon_b$ values; although the decrease is less than 1 percentage point, due to low baseline values (~4%), this corresponds to approximately a 25% relative reduction in elongation, which is significant. Similar observations have

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been made in previous studies concerning the effect of tannic acid used as a flax fibre modifier [27].

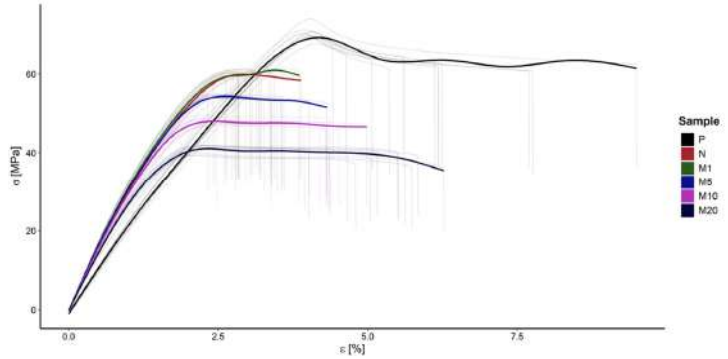


**Figure 5.** Stress–strain curves for the P, N, M1, M5, M10, and M20 samples. Grey lines represent raw data while bold lines are obtained by averaging the measurements of the same material.

Young's modulus (E) value increased by more than 1 GPa after the introduction of fibre, which indicates an improvement in biocomposite stiffness. An increase in Young's modulus with a simultaneous decrease in tensile strength means an increase in the stiffness of the material, but also its greater susceptibility to brittle fracture. The application of the modifier in concentrations of 1% and 5% slightly enhanced stiffness. However, this effect was disturbed at higher modifier concentrations (M10 and M20). The high amounts of plant agents in biocomposites led to a decrease in polymer chain interactions and deterioration of mechanical properties [42]. In summary, while the application of 1% and 5% modifier concentration improved biocomposite stiffness, it also led to deterioration in resistance to deformation.

The statistical analysis reveals consistent trends between $\sigma_m$, $\varepsilon_b$, and E across the material variants. For all three mechanical properties tested, $\sigma_m$, $\varepsilon_b$, and E, the $p$ value was <0.001 (statistically significant differences). The results allow us to reject the null hypothesis of equality of means in all groups. To identify specific pairs of groups that differed significantly, Tukey's test was performed at a significance level of $\alpha = 0.05$. No significant differences were observed for the following: N vs. M1 in tensile strength ($p = 0.430$); M10 vs. M20 in elongation at break ($p = 0.149$); and M1 vs. M5 (0.479), M5 vs. M10 ($p = 0.803$) in Young's modulus.

Because GE modification causes significant changes in properties, with higher concentrations (20%) additionally worsening the strength and stiffness compared to 10% modification, a direct comparison of M10 vs. M20 was performed (using Welch's *t*-test). The statistical analysis reveals that an increase in GE concentration from 10% to 20% significantly reduces $\sigma_m$ by 14.3% ($p < 0.001$), does not significantly affect $\varepsilon_b$ ($p = 0.103$), and significantly reduces Young's modulus by 6.3% ($p < 0.001$).

### *3.3. TG*

Figure 6 illustrates mass loss (m) in the function of temperature (T) known as the TG curve for both modified, non-modified, and neat samples. Moreover, its first derivative (DTG curve) is also shown. The initial mass loss of fibre-reinforced samples (both modified and non-modified) has been noted before 100 °C, which corresponds to the evaporation of water contained in flax fibres as well as in GR. The P sample began to rapidly lose weight at approx. 300 °C, indicating a decrease in its thermal stability. Similar behaviour from 200 °C

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to about 300 °C was observed for the N, M1, and M5. The modifier in concentrations of 1% and 5% had an insignificant impact on the thermal properties of biocomposites. However, the mass loss rate in this temperature range was higher for samples containing 10% and 20% of modifier (M10 and M20). This can be explained by higher amounts of GR which undergoes a two-step thermal transition: a) evaporation up to 230 °C, and b) decomposition between 230 °C and 291 °C [16].

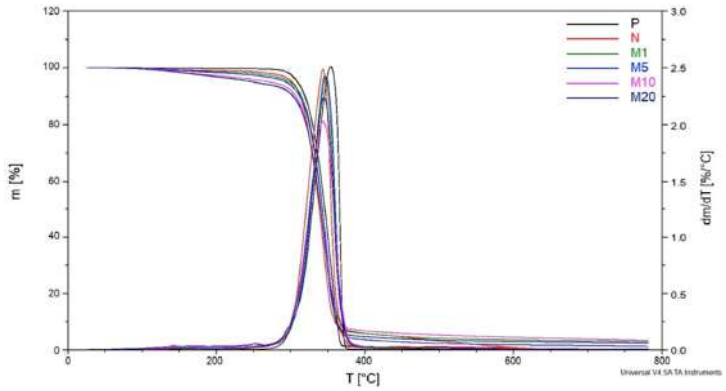


**Figure 6.** TG and DTG curves for P, N, M1, M5, M10, and M20 samples.

Table 6 summarizes mass loss and degradation temperatures for each sample. A slight decrease in the 5% mass loss temperature (T5%) of the N sample compared to the P sample is attributed to the presence of flax fibres which are susceptible to thermal degradation. A further decrease in T5% for modified samples compared to the N sample indicates the presence of GR. The modifier loses its thermal stability after it exceeds 200 °C. The results show that T5% decreased with the increase in modifier concentration. Comparison of M5, M10, and M20 samples revealed the most significant differences in T5%. The T5% of M10 decreased by more than 22 °C compared to the M5 sample. The doubling of the modifier concentration in the M20 sample led to a further decrease in T5% by another 22 °C.

**Table 6.** Results obtained during the thermogravimetric studies for P, N, M1, M5, M10, and M20 samples.

| Sample | $T_{5\%}$ [°C] | $T_{50\%}$ [°C] | $T_{95\%}$ [°C] | $T_d$ [°C] |
|---|---|---|---|---|
| P | 309.33 | 346.10 | 365.09 | 354.01 |
| N | 302.16 | 338.58 | 434.52 | 343.47 |
| M1 | 299.16 | 342.94 | 435.05 | 345.87 |
| M5 | 293.74 | 342.63 | 372.85 | 347.58 |
| M10 | 271.72 | 340.61 | 527.89 | 343.50 |
| M20 | 250.36 | 340.20 | 384.87 | 344.82 |

The comparison of 50% mass loss temperatures (T50%) between the N sample and P sample shows similar tendencies as in T5%. Additionally, a decrease of 11 °C was noted in the decomposition temperature (Td). Insignificant changes in T50% and Td were noted for all of the modified samples. The increase in T50% and Td for M1 and M5 compared to the N sample was noted. However, decreased T50% and Td temperatures were noted within increased modifier concentration (10% and 20%). Lower Td values affected by GR in high concentrations were also noted by [18].

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Changes in 95% mass loss temperature (T95%) values deviate from the observed dependency. Changes in the temperatures associated with 95% mass loss (T95%) do not align with the expected pattern. The unusually high T95% values can likely be attributed to two main phenomena: char formation (carbonization) and crosslinking, along with thermal stabilization due to high geraniol (GR) content. These factors can lead to rare but extreme temperature peaks. In conditions with limited oxygen, incomplete combustion may result in the formation of carbonaceous char. This char layer acts as a thermal insulator, potentially creating localized hotspots where temperatures can rise significantly above the average. Geraniol contains reactive functional groups that can undergo thermal crosslinking with PLA or its degradation products. At higher concentrations of GR, a crosslinked, thermally stable network may form. This network resists melting and instead tends to undergo slow degradation or carbonization, which can further promote high local temperatures. The combination of slowed decomposition and heat retention contributes to the extreme temperatures recorded in the T95% values. Nevertheless, it is recommended to conduct more detailed studies to determine the reason for such behaviour. Based on the observations, it can be concluded, that GR in low concentrations (1%, 5%) slightly inhibits the degradation rate of biocomposite. Oppositely, high amounts of GR (10% and 20%), which presumably migrated into the polymer matrix, resulted in the deterioration of the thermal stability of M10 and M20. This could be caused by the high amount of hydroxyl group contained in GR, accelerating the degradation process [14,19,43,44]. However, the biocomposites are designed for application within specific temperature ranges, ensuring the thermal stability of their components, including GR. This precautionary measure aims to prevent decomposition or any undesirable reactions.

### *3.4. DSC*

The changes in heat flow (ΦQ) in the function of temperature are demonstrated in Figure 7. The first endothermic peak assigned to the N sample slightly shifts towards lower temperatures compared to the P sample. It could be caused by the waxes contained in the flax fibres, which act as natural plasticizers in polymer matrix. A similar tendency was noted for the M1 sample, where the mentioned peak is quite similar to the ones of the N sample. With the increase in GR amount, a decrease in the energy needed for the initiation of glass transition was observed. The M5, M10, and M20 samples have no characteristic endothermic peak, their curves started to shift in the endothermic direction with the further soft transition into the baseline. Additionally, the glass transition temperature ($T_g$) (Table 7) gradually decreased with the increase in GR concentration. These changes are characteristic for plasticizers, which act as lubricants in polymers [37]. These observations confirm our previous assumptions concerning the plasticizing properties of the applied modifier.

**Table 7.** Results obtained during DSC studies for P, N, M1, M5, M10, and M20 samples.

| Sample | $T_g$ [°C] | $\Delta H_{cc}$ [J/g] | $T_{cc}$ [°C] | $\Delta H_m$ [J/g] | $T_m$ [°C] | $X_c$ [%] |
|---|---|---|---|---|---|---|
| P | 60.43 | 5.86 | 127.49 | 6.22 | 150.70 | 0.38 |
| N | 59.71 | 20.38 | 119.52 | 21.48 | 149.69 | 1.18 |
| M1 | 58.60 | 20.53 | 117.96 | 20.82 | 148.92 | 0.31 |
| M5 | 55.02 | 22.59 | 113.85 | 22.77 | 147.41 | 0.19 |
| M10 | 49.95 | 22.69 | 108.35 | 23.27 | 144.82 | 0.62 |
| M20 | 48.96 | 24.99 | 110.26 | 25.29 | 146.77 | 0.32 |

The cold crystallization enthalpy increased after the introduction of flax fibres into the polymer matrix (N sample). Flax fibres are known for their nucleating properties, which increase the PLA crystallization rate (Table 7). Further increases in cold crystallization enthalpy ($\Delta H_{cc}$) of samples containing GR are caused by improved chain mobility of

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plasticized PLA [45]. The highest $\Delta H_{cc}$ value was observed in the case of the M20 sample. The 20% GR concentration has the strongest plasticizing effect. The application of non-modified flax fibres led to a shift in the exothermal peak (cold crystallization peak) towards lower temperatures. The decrease in the maximum temperature of the cold crystallization peak ($T_{cc}$) was also noted for all the modified samples. This observation is consistent with previously discussed results concerning the plasticizing properties of GR.

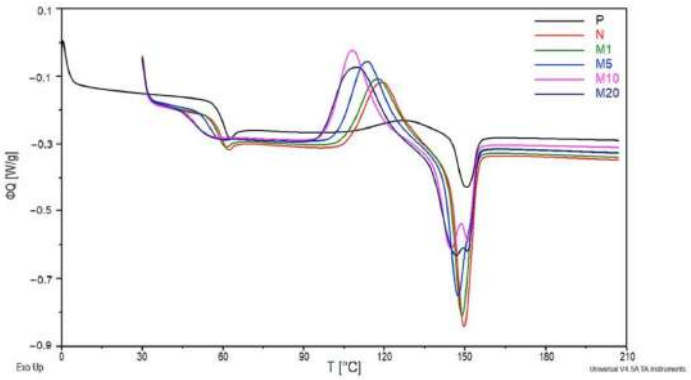


**Figure 7.** The dependence of ΦQ on T for P, N, M1, M5, M10, and M20 samples.

The same trends for $\Delta H_m$ and Tm were observed. Analysis of the second endothermic peaks (melting peaks) revealed ordinary one-stage melting in the case of P, N, M1 and M5. However, the samples containing 10% and 20% of GR concentration melted in two stages. The volatilization of GR begins at approx. 150 °C, which corresponds to the melting peak. Hence, it can be deduced, that the first stage of melting is associated with the melting of the crystalline phase created by nucleates contained in flax fibres, while the second stage correspondes to the volatilization of the modifier. Presumably, due to the low amounts of modifier in the samples M1 and M5, the two melting stages overlapped into one. In addition to the enhanced crystallization rate with an increase in GR concentrations, the $X_c$ degree of crystallinity decreased. This could be attributed to defects in PLA structure caused by GR [45]. Therefore, the deterioration of the mechanical properties of samples containing modified fibres is justified.

### *3.5. Wettability*

Table 8 presents the average contact angle ($\overline{\Theta}_w$) values. The introduction of flax fibres into the polymer matrix does not signifficantly affect the wettability of the biocomposites. However, a slight improvement in $\overline{\Theta}_w$ was noted after the modification of flax fibres. Low amounts of modifier contained in M1 and M5 samples slightly increased the $\overline{\Theta}_w$ values. The application of a 10% modifier concentration increased the $\overline{\Theta}_w$ value by almost 8° compared to N. Materials used in the packaging industry are expected to be hydrophobic due to close contact with food. A material can be considered hydrophobic if its $\overline{\Theta}_w$ value is greater than 90° [27,46,47].

**Table 8.** The results were obtained during the wettability studies for samples P, N, M1, M5, M10, and M20.

| | **P** | **N** | **M1** | **M5** | **M10** | **M20** |
|---|---|---|---|---|---|---|
| $\overline{\Theta}_w$ [°] | 75.0 | 75.1 | 76.3 | 77.3 | 83.0 | 96.3 |

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The observed effect was achived after modifying the flax fibres with 20% GR. The $\overline{\Theta}_w$ value of the M20 sample exceeded 90°, making it hydrophobic. The gradual decrease in the wettability of the biocomposites, noted after modification, could be attributed to the migration of GR into the polymer matrix. The 20% modifier concentration, which contains a high amount of hydrophobic alkyl chains, created a natural hydrophobic barrier on the surface of the M20 sample. Figure 8 illustrates the changes in drop shape with increasing modifier concentration. It can be seen that the shape of the M20 sample significantly differs from that of the other samples.

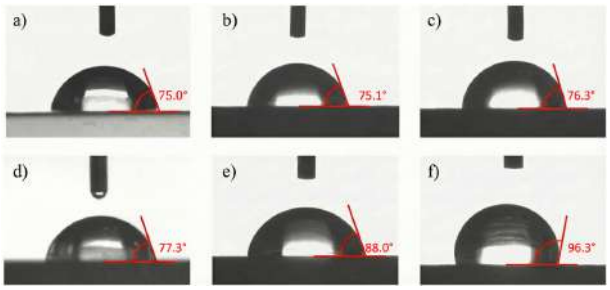


**Figure 8.** The drops of water placed on the surface of (**a**) P, (**b**) N, (**c**) M1, (**d**) M5, (**e**) M10, and (**f**) M20 samples.

The ANOVA test showed statistically significant differences between the tested samples ($p < 0.001$). Post hoc analysis (Tukey's HSD test) revealed no significant differences between samples P, N, M1, and M5 (all pairwise comparisons yielded $p > 0.05$). GE modification at low concentrations (1% and 5%) does not significantly affect the surface wetting properties. On the other hand, the GE modification of flax fibres at concentrations of 10% and 20% results in a statistically significant increase in the hydrophobicity of the biocomposites, with the strongest effect observed at the 20% concentration. Statistical analysis of M10 vs. M20 showed that increasing the geraniol concentration from 10% to 20% leads to a highly statistically significant ($p = 0.0003$) increase in the hydrophobicity of the biocomposite surface.

### *3.6. SEM*

The micrograph shown in Figure 9a presents the P sample with a characteristic layered fracture, whereas the micrograph of the N sample fracture shows a lower number of protruding fibres compared to modified samples. This observation indicates better adhesion between the matrix and non-modified fibres than in the case of modified ones. The greater interfacial adhesion resulted in better transfer of tensile loads from the matrix to the fibres. A similar structure was observed in the M1 sample, where 1% GR concentration did not affect the fibre–matrix interaction (Figure 9c). Protruded fibres were highlighted with circles, while holes with arrows.

The introduction of fibres modified with 5% of the modifier led to the deterioration of interfacial adhesion in M5. The holes seen in Figure 9d remained after the fibres were pulled out. A further increase in modifier concentration (10% and 20%) resulted in a much more debonding structure of M10 and M20 (Figure 9e,f). Along with the structure changes, the number of pulled-out fibres increased. A number of protruded fibres visible in Figure 9f is big, hence no highlights were added. These observations suggest the migration of GR into the polymer matrix, affecting the interfacial adhesion of the biocomposite.

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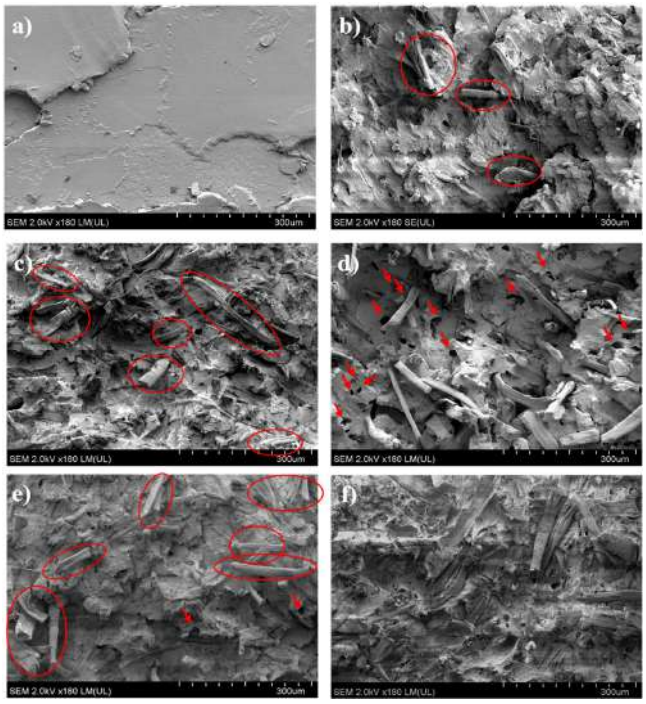


**Figure 9.** The SEM micrographs of the (**a**) P, (**b**) N, (**c**) M1, (**d**) M5, (**e**) M10, and (**f**) M20 samples. Prostruded fibres highlighted with red circles. Holes in materials indicated with red arrows.

### *3.7. The Biocidal Properties*

The biocidal activity of the samples was determined against two bacterial strains—*E. coli* and *S. aureus*. A material is considered biocidal if the R-value is >2 (Table 9). No biocidal activity was observed in the P and N samples. In the case of the M1 sample, the R-value was 0 against *E. coli* and 1 against *S. aureus*. *S. aureus* is a Gram-positive bacterium with no outer membrane, making it more susceptible to modifier penetration. However, the antibacterial effect of GR was noted only at a 5% modifier concentration. It was effective against *E. coli* but not against *S. aureus*, suggesting lower efficiency of low amounts of GR against Gram-positive bacterial strains. To confirm the mentioned assumption, more detailed research is needed. Tests on samples with higher modifier concentrations (M10 and M20) revealed strong biocidal activity against both bacterial strains. In summary, GR exhibited biocidal activity against *E. coli* in the M5, M10, and M20 samples, and against *S. aureus* in the M10 and M20 samples. Determining the biocidal activity of a material is essential for predicting which microorganisms it can effectively combat and what potential applications it may have. Because of its non-toxic nature and enhanced hydrophobicity, the biocomposite is suitable for use in food-contact applications, such as food packaging or disposable packaging.

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**Table 9.** Biocidal activity of P, N, M1, M5, M10, and M20 against *E. coli* and *S. aureus*.

| Sample | *E. coli* [CFU/mL] | | *S. aureus* [CFU/mL] | |
|---|---|---|---|---|
| | $T_1$ | R | $T_1$ | R |
| P | $1.5 \times 10^7$ | 0 | $2.0 \times 10^7$ | 0 |
| N | $1.5 \times 10^7$ | 0 | $1.5 \times 10^7$ | 0 |
| M1 | $1.5 \times 10^6$ | 0 | $2.0 \times 10^6$ | 1 |
| M5 | $2.0 \times 10^5$ | 2 | $3.0 \times 10^6$ | 1 |
| M10 | $1.5 \times 10^2$ | 5 | $1.5 \times 10^2$ | 5 |
| M20 | $\leq 1.0 \times 10^1$ | $\geq 6$ | $1.2 \times 10^1$ | 6 |

$T_0$—the numbers of cells of the tested strains ($1.5 \times 10^8$ jtk); $T_1$—number of bacterial cells after contact time. The time of the contact of bacteria with the tested foil was 24 h.

## 4. Conclusions

This study was carried out to investigate the use of natural, plant-derived modifiers that effectively modify flax fibres and positively affect their surface properties. The introduction of modified fibres into the polymer matrix contributed to the development of novel biocomposites with biocidal properties and increased hydrophobicity. The key findings are as follows:

Mechanical and thermal properties: While low concentrations of geraniol (1–5%) slightly improved stiffness (Young's modulus), higher concentrations acted as plasticizers, lowering the glass transition temperature ($T_g$) and reducing tensile strength. Thermal analysis (TG/DTG) indicated that high geraniol concentrations ($\geq$10%) accelerate thermal degradation.

Antibacterial efficacy: The modification imparted significant biocidal activity to the biocomposites. Samples with 10% and 20% geraniol content achieved a coefficient reduction in R $\geq$ 5 against *E. coli* and *S. aureus*, effectively inhibiting bacterial proliferation.

Hydrophobicity: A transition from hydrophilic to hydrophobic surface properties was observed. The water contact angle increased progressively with modifier content, exceeding 90° for the composite containing 20% geraniol.

Based on these outcomes, future research will focus on assessing the long-term stability of these biocomposites. Specifically, the plan is to investigate the influence of ageing on selected properties of biocomposites containing geraniol.

**Author Contributions:** A.P.: Data curation, Formal analysis, Writing—original draft, Writing—review and editing, Investigation, Metodology. M.S.: Conceptualization, Formal analysis, Metodology, Writing—review and editing, Supervision, Validation. V.K.: Investigation. J.P.: Methodolody. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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