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.

Keywords: *Natural fibre composites, Dynamic mechanical thermal analysis (DMTA), Differential scanning calorimetry (DSC), Extrusion, Injection moulding.*

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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]. 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 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 aureu*s (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 (Tab. 1). Detailed description of the modification method could be found in [23].

Table 1

The amount of ingredients in modifying solutions.

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

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

93 excessive fibres cutting. Extrusion took place in the following temperatures of
94 cylinder heating zones (I-IV): 180 ˚C, 182 ˚C, 184 ˚C, 186 ˚C and 185 ˚C (the
95 extrusion head temperature). The extruder screw was rotating with a speed of 120
96 rpm. The speed of materials feeding was 133.3 g/5 min for PLA and 33.3 g/5 min for
97 flax fibres. As a result, obtained biocomposites contained 80 wt% of PLA (1200 g)
98 and 20 wt% of flax fibres (300 g).
99 After extrusion, the injection moulding was conducted. The dumbbell-shaped
100 samples were prepared with an injection moulding machine (TRX 80 ECO 60,
101 Tederic Machinery Manufacture, Taiwan). Mentioned samples were used during the
102 mechanical and wettability tests. The injection moulding process was carried out at
103 170 ºC, 165 ºC, 165 ºC, 165 ºC, and 35 ºC. Mentioned temperatures are assigned to
104 the I-III zones of the moulding machine cylinder, its head, and mold. The pressure
105 during the process was 24.8 MPa. The mass of the single sample was approx. 11 g.
106 The films of 0.5 mm thickness for microbiological tests were prepared with a
107 vulcanization press (AW03M, Argenta, Poland). Extruded granules (0.7 g) were
108 pressed with a pressure of 0.7 MPa in 180 ºC for 10 s. Afterward, pressed samples
109 were cooled for 10 s with compressed air. The constant shape of samples was
110 ensured by cooling.
111 Tested samples were designated as P (for neat PLA sample), PF (for sample
112 containing non-modified fibres), PF1 (for sample contained fibres modified with 1%
113 of TA), PF5 (for sample contained fibres modified with 5% of TA), and PF10 (for
114 sample contained fibres modified with 10% of TA).

115 *2.3. Examination methods*

116 Mechanical properties were examined with DMA and tensile strength tests. DMA
117 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 the formula (1):

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

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

141 The contact angle values were evaluated using a goniometer (DSA100, Krüss GmbH,
142 Germany) with an automatic dosing drop system. As a test liquid, water has been
143 chosen. The contact angle measurements were carried out for six samples of each
144 material type. The 7 μl water drops were squeezed with the rate (Δv) of 50 μl/min.
145 Each sample was tested six times.
146 The biocidal properties evaluation was based on standard ISO 22196:2007 (E) [29]
147 According to the standard, the measurement is based on the evaluation of biocidal
148 activity against two reference bacterial strains – *E. coli* and *S. aureu*s. The strain
149 cultures were prepared in nutrient broth and used as a medium made. After the
150 medium inoculation, the cultures were left for 24 h at 37 ˚C. Further, the standard
151 method of optical density evaluation was used for the determination of the number of
152 cells present in a cell suspension. During this step, the densitometer (Densitometer II,
153 Pliva-Lachema, Czech Republic) with McFarland's scale [30] was used.
154 All the tested samples were covered with cell suspensions and left for the specified
155 time (0 h validation of recovery efficiency and 24 h). After this time, the cells
156 recovered from the surface of the material were suspended in a neutralizer (soybean
157 casein digest broth with lecithin) solution. Plates Count Agar (PCA) was used for
158 cell inoculation and its number evaluation. The examinations were conducted thrice
159 for each sample.
160 The antibacterial activity (R) is a difference in the logarithm of the number of viable
161 cells present on material containing biocides (PF1, PF5, and PF10 samples) and
162 reference material (sample PF). R coefficient has been calculated using formula (2):

163 $$R = (U_t - U_0) - (W - U_0) \quad (2)$$

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 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.

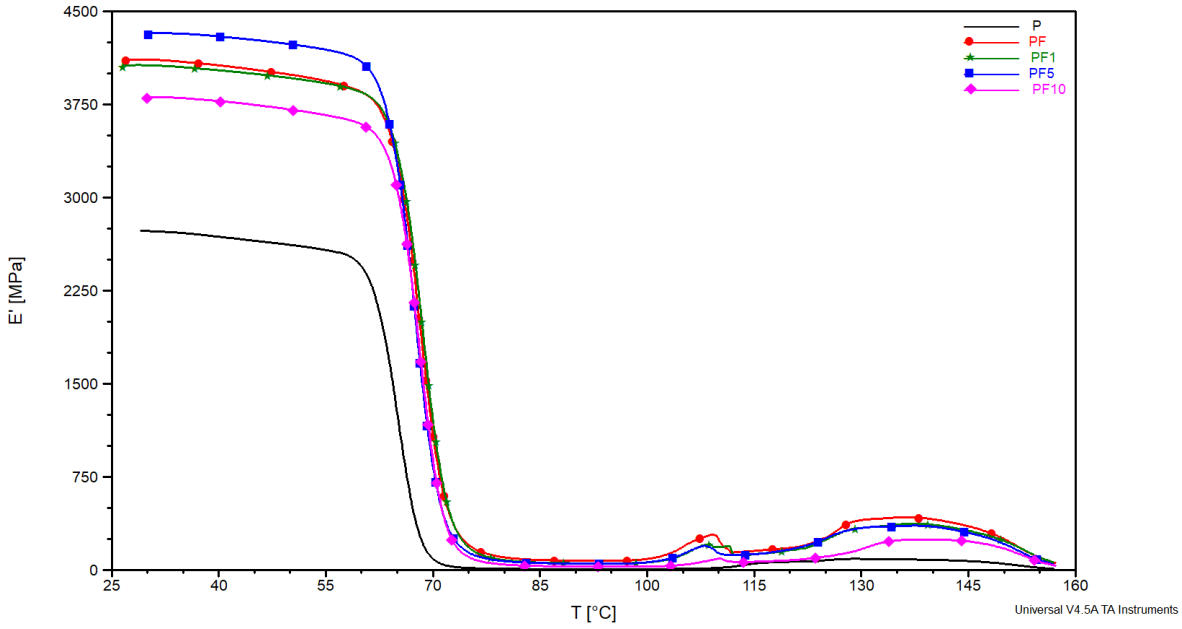


Fig. 1. The E′ dependence on the temperature (DMA curve) for the P, PF, PF1, PF5, and PF10 samples.

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.

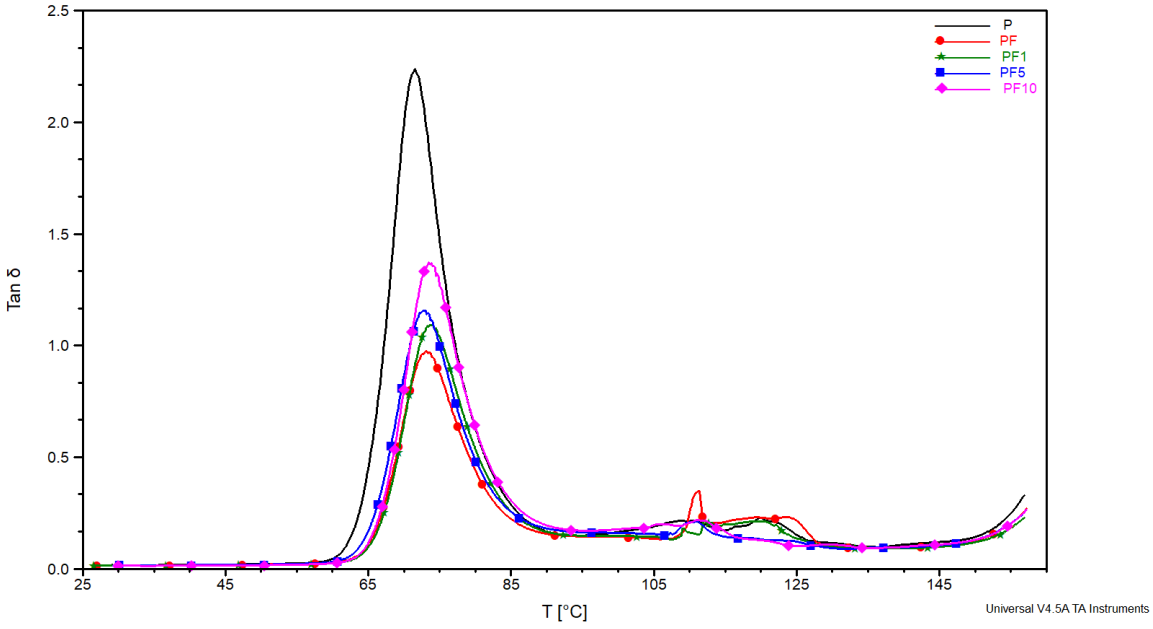


Fig. 2. The tan δ dependence on the temperature for the P, PF, PF1, PF5, and PF10 samples.

3.1.2. Tensile strength

Table 2 summarises the overage values of the tensile strength (σ), elongation to break (ε_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.

Table 2

The overage values of σ, ε_b, and E were obtained for P, PF, PF1, PF5, and PF10 samples during the tensile test.

Sample	σ [MPa]	ε_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

The dependence on TA concentration has also been noted among elongation to break (ε_b) values. The results show that ε_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 ε_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).

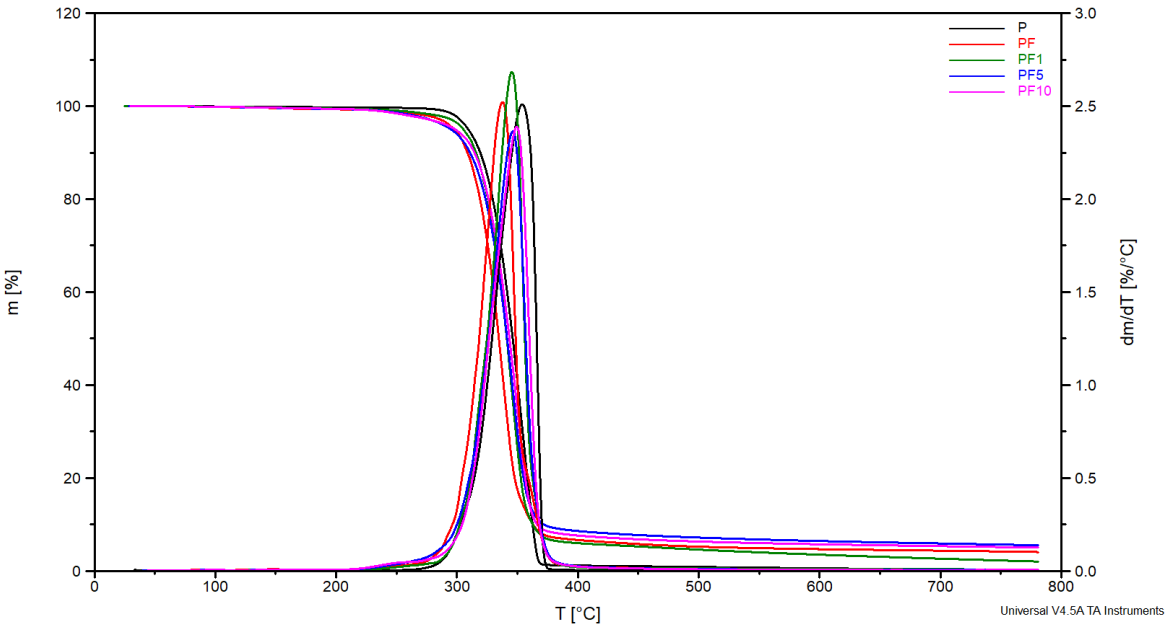


Fig. 3. TG and DTG curves obtained for P, PF, PF1, PF5, and PF10 samples.

Table 3 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.

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

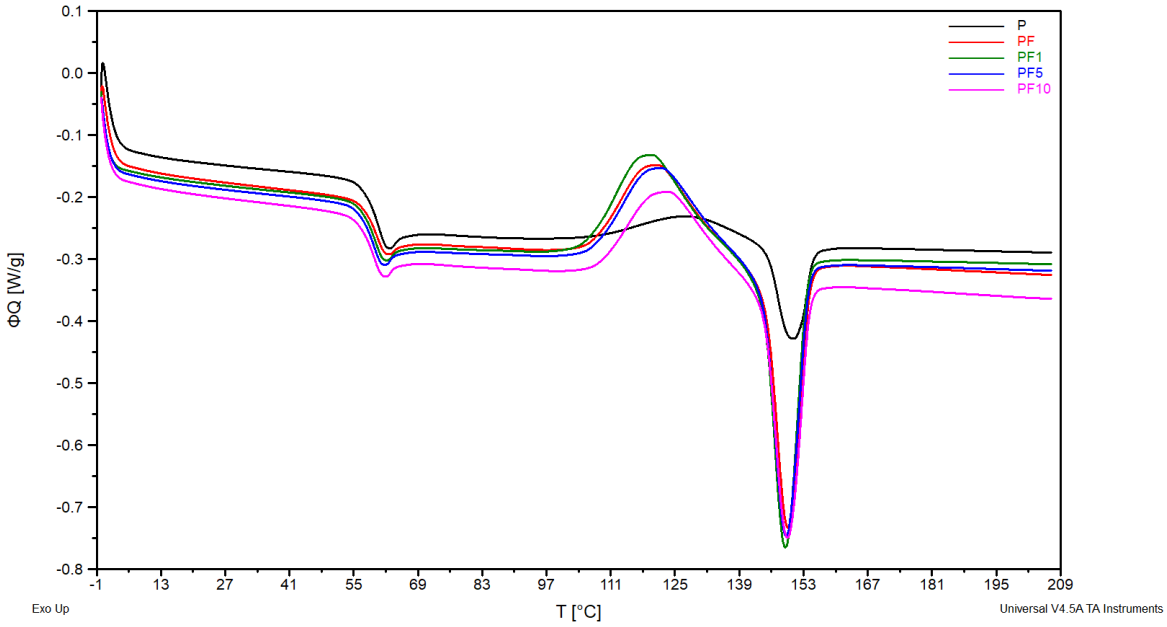
The comparison of degradation temperatures (T_d) showed their slight increase with the increase of TA concentration. It is known, that TA contained in the biocomposites retards their thermal decomposition. However, the increase of its concentration has a

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 (ΔH_{cc}) after the modification. This decrease progresses with TA concentration which confirms plasticizing properties of TA. The increase of ΔH_{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.



288

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

290 samples.

291 The highest differences between ΔH_{cc} and melting enthalpy (ΔH_m) for modified samples

292 were noted for the PF1. The migration of TA into the polymer and its effect on

293 properties depend on modifier concentration. Higher concentrations of TA decrease the

294 X_c of biocomposites (Table 3) and promote their plasticization.

295 Table 4

296 Parameters obtained during DSC measurement for P, PF, PF1, PF5, and PF10 samples.

Sample	T_g [˚C]	ΔH_{cc} [J/g]	T_{cc} [˚C]	ΔH_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

297

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 molecules by biocomposite. A comparison of water average contact angle ($\overline{\boldsymbol{\Theta_w}}$) values reveal, that flax fibres coated with TA increase the wettability of samples. The difference between PF and PF1 $\overline{\boldsymbol{\Theta_w}}$ 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 [23] and suggests, that higher increase in modifier concentration affects an increase in surface wettability.

Table 5

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

	P	PF	PF1	PF5	PF10
$\overline{\boldsymbol{\Theta_w}}$ [˚]	75.0	75.1	85.1	85.3	86.1

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.

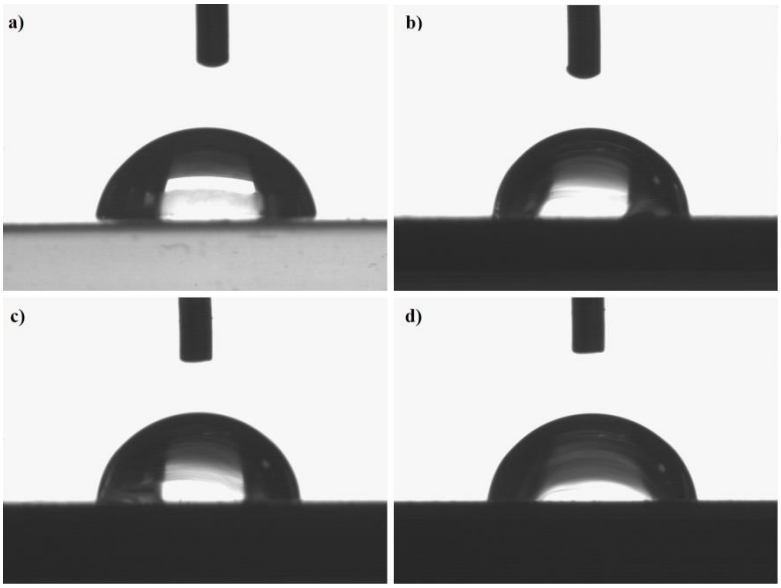


Fig. 5. Drop of water on the surface of: a) P, b) PF1, c) PF5 and d) PF10.

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

334 value was still too low for the material to be considered biocidal. The R-value for the
335 PF1 sample in the case of *S. aureus* was higher than in the case of *E. coli*. However,
336 TA in a concentration of 1% does not improve the ability of the material to combat the
337 microorganisms.

338 Table 6

339 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		3.8×10^6	0		9.8×10^6	0
PF		5.1×10^6	<0		10.2×10^6	<0
PF1	9.3×10^6	2.8×10^6	0.13	11.0×10^6	3.7×10^6	0.42
PF5		$<10^2$	>4.58		$<10^2$	>4.99
PF10		$<10^2$	>4.58		$<10^2$	>4.99

340

341 Different results have been obtained during the evaluation of the biocidal activity of
342 samples containing fibres modified in higher concentrations of TA (5% and 10%). The
343 reduction of 4 orders of magnitude from 10^6 to 10^2 has been achieved against both
344 bacterial strains. Computations revealed, that the R-value for PF5 and PF10 was higher
345 than 4.58 for *E. coli* and higher than 4.99 for *S. aureus*. It confirms the higher biocidal
346 activity of TA against *S. aureus* found in the previous study [23]. According to **[34]** TA
347 binds with the peptidoglycan layer of Gram-positive (*S. aureus*) bacteria in a direct way
348 which makes them more susceptible to TA than Gram-negative (*E. coli*) ones **[35–37]**.
349 Summarising, 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, Writing - original draft, Writing - review & editing, Investigation, Metodology. Magdalena Stepczyńska: Conceptualization, Formal analysis, Metodology, Writing - review & editing, Supervision, Validation.

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