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Insights into Compatibilization of Poly(ε-caprolactone)-based Biocomposites with Diisocyanates as Modifiers of Cellulose Fillers

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Abstract

This study aimed to analyze the impact of cellulose fillers' modification with diisocyanates on the performance of composites based on the poly(ε-caprolactone) (PCL) matrix. Four most commonly used diisocyantes (isophorone, hexamethylene, toluene, and methylene diphenyl) were applied as modifiers of cellulose fillers (5 and 15 wt% per mass of filler). Modified fillers were introduced in the amount of 30 wt% into the PCL matrix. Chemical structure, thermal, static and dynamic mechanical properties of composites were investigated using Fourier transform infrared spectroscopy, differential scanning calorimetry, tensile, hardness and rebound resilience tests, and dynamic mechanical analysis, respectively. Modifications of cellulosic fillers resulted in the decrease of matrix crystallinity and enhancement of interfacial interactions, causing even a two-fold increase of tensile strength and a 25% rise of modulus. These results indicate that through proper adjustment of type and content of diisocyanate modifier, composites' properties may be engineered.

***Keywords**:* compatibilization, filler modification, isocyanates, lignocellulosic fillers, wood polymer composites

1. Introduction

Research works associated with the wood polymer composites (WPCs) can be divided into two main trends – decreasing materials' costs and enhancement of their properties (Mysiukiewicz and Sterzyński, 2017). The first trend is realized by searching for new lignocellulosic fillers from different kinds of agriculture wastes or by applying recycled polymers as matrices (Lewandowski *et al*., 2016). The second one is mainly aimed to strengthen the interfacial interactions between polymer matrix and lignocellulosic filler. It is essential in the case of waste-based fillers when "conventional" fillers such as cellulose fibers or wood flour are applied (Barczewski *et al.*, 2018). For WPCs, lack of compatibility and weak interactions between phases are two of the major problems and challenges (Jiang *et al.*, 2020). Therefore, it is crucial to improve them, as strong interfacial interactions are necessary to achieve satisfactory mechanical properties of composites (Andrzejewski *et al.*, 2019). Such approach may be realized by matrix- or filler-based strategies. It is generally aimed at providing chemical bonding between phases or, at least, at the adjustment of the hydrophilicity of fillers' surface, simultaneously increasing their affinity towards polymer matrix (Wang *et al.*, 2017). Over the past years, numerous methods of enhancing the compatibility of WPCs have been developed (Matykiewicz *et al.*, 2019). Generally, the most popular compatibilizers for WPCs are anhydrides, namely maleic anhydride, succinic anhydride, dodecenyl succinic anhydride, or phthalic anhydride (Vaidya *et al.*, 2016). Slightly less known treatments are alkali treatment, silanization, acetylation, acrylation and permanganate treatment of fillers or matrix. Other less commonly used methods of modification, including fatty acid modification, sodium chloride treatment, benzoylation, and triazine or isocyanate treatment, were also described and analyzed. However, they were not analyzed as comprehensively as anhydrides.

A notable group of compounds used for the enhancement of interfacial interactions in WPCs are isocyanates. Their application is considered as highly beneficial due to their high reactivity and ability to create stable covalent bonds with functional groups present at the surface of lignocellulosic fillers and various polymers, particularly bio-based ones such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL) or thermoplastic starch, whose popularity in WPCs' production is growing (Jun, 2000; Abushammala and Mao, 2019). More importantly, isocyanates have been commonly used in the plastics industry for many years. Hence, they are well known and analyzed. The most popular ones are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), followed by hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), covering over 95% of the global market. They have been used as modifiers for WPCs in multiple works. However, only low contents, rarely reaching 10 wt%, were investigated, and modified fillers were applied mostly to prepare composites based on polyolefins (Geng and Simonsen, 2005; Qiu *et al.*, 2005).

Regarding PCL, diisocyanates were mainly applied as compatibilizers of its blends with thermoplastic starch or poly(butylene succinate) (Mani *et al*., 1998; Kweon *et al*., 2000; Ohkita and Lee, 2004). They were also used to modify lignocellulose fillers with PCL. Habibi and Dufresne (2008) grafted two types of PCL with differing molecular weight (M_n = 10,000 and 42,500 g/mol), on the surface of cellulose and starch nanocrystals. Nanocomposites were then prepared with different loadings of fillers. It was found out that modifications of lignocellulose fillers resulted in the enhancement of interfacial adhesion, simultaneously improving the strength and ductility of the composite. A similar process was investigated by Paquet *et al*. (2010), who performed grafting of the same types of PCL on the surface of two types of cellulose fillers. Grafting was successfully performed with the use of TDI as a binding agent. In the said work, it was indicated that only low quantities were grafted onto the surface, and further works should be performed to overcome this limitation. However, no further reports regarding this interesting approach were published. Therefore, the introduction of diisocyanates as compatibilizers of composites based on the PCL matrix, especially high-molecular-weight types, is still hardly analyzed topic.

As proven by Zhang *et al*. (2014), the structure of the modifier has a very significant influence on the properties of a modified filler. The most fundamental properties are molecular weight, functionality, and spatial structure. These properties of modifiers affect the structure of modified lignocellulosic fillers like crystallinity, which has an essential impact on the mechanical performance and ability to biodegradation. A proper selection of compatibilizers can be used to engineer the performance of the composite. Therefore, this work aimed to investigate the impact of type and content of diisocyanate modifiers on the thermal and mechanical performance of poly(ε-caprolactone)-based composites filled with commercially available cellulosic filler. At present, reports on the investigation concerning the introduction of more than two types of diisocyanates as compatibilizers for WPCs are scarce. Analysis related to two types of aromatic (MDI and TDI), and two types of aliphatic (HDI and IPDI) diisocyanates was also performed.

2. Methodology

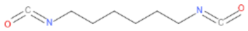
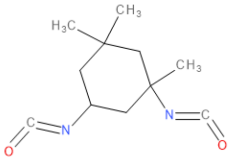
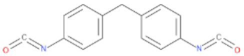
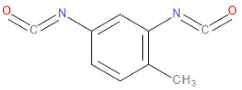
2.1 Materials

The commercially available poly(ε-caprolactone) (PCL) (Capa 6800, Mw = 80,000 g/mol) was purchased from Perstorp (Malmö, Sweden). It was selected as a matrix for investigated WPCs because of its excellent mechanical properties, potential biodegradability, and relatively low processing temperature, which enables the reduction of energy consumption, simultaneously preventing lignocellulosic fillers from decomposition and reducing potential emissions of volatile organic compounds (Hejna *et al.*, 2015).

Commercially available Arbocel® UFC100 filler from JRS J. Rettenmaier & Söhne GmbH (Germany) was used. The average particle size of this filler was 8 μm, while its bulk density was 160 g/l.

Modifications of cellulose filler were performed using four different diisocyanates (isophorone diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, and methylene diphenyl diisocyanate), which were acquired from Sigma Aldrich (Poland). Properties of applied modifiers are presented in Table 1.

Table 1. Chemical structure and properties of applied diisocyanate modifiers

Abbreviated name	Chemical structure	Molar mass (g/mol)	Density (g/cm^3)	Melting point (°C)	Vapor pressure, (Pa)
HDI		168.2	1.05	-67	7.0
IPDI		222.3	1.06	-60	$4.0 \cdot 10^{-2}$
MDI		250.3	1.18	40	$7.0 \cdot 10^{-4}$
TDI		174.2	1.21	22	1.3

2.2 Modification of Fillers

Fillers were modified using GMF 106/2 Brabender batch mixer at room temperature (21.1 to 23.1 °C) and rotor speed of 100 rpm. Room temperature was applied to reduce the possible emissions from applied diisocyanates, which at 20-25 °C show relatively low volatility. The values of vapor pressure can be seen in Table 1. At higher temperatures, their volatility is significantly increasing. For example, when the temperature is elevated to 50 °C, the vapor pressure of TDI, IPDI, and MDI increased 11.9, 22.5, and 33.5 times. Further rise of temperature to 100 °C increases TDI and MDI vapor pressure by 287 and 3,316 times.

The proper amount of filler was placed in an internal mixer with a calculated amount of diisocyanate to the mass of filler. Mixing was performed for 5 min, and then samples were put in zipper storage bags. Figure 1 presents possible interactions between cellulose filler and applied diisocyanates during modification, and further reactions of free isocyanate groups with moisture present in the atmosphere. According to Vilar (1998), reactions of isocyanate groups with primary hydroxyls and water show similar reaction rates when uncatalyzed at room temperature.

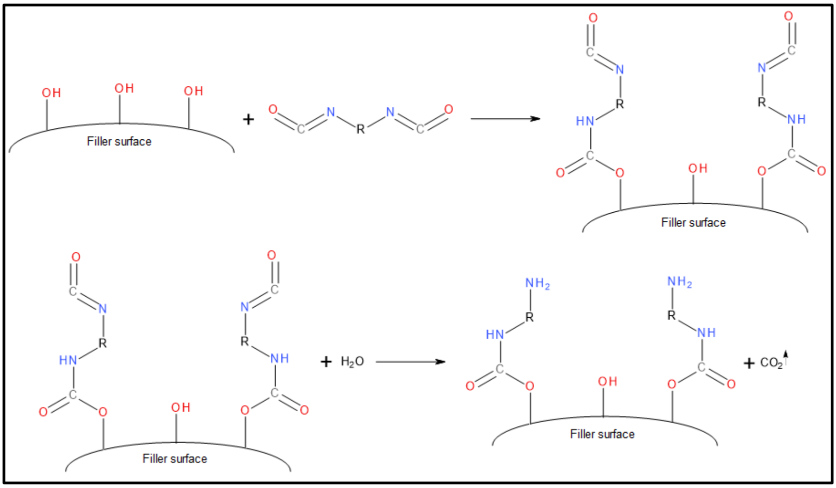


Figure 1. Interactions between cellulose fillers and diisocyanates used as modifiers

2.3 Preparation of Polymer Biocomposites

Analyzed WPCs were prepared in batch internal mixer (GMF 106/2 Brabender) at 70 °C and rotor speed of 100 rpm. Time of processing equalled

8 min, including the 3-min phase of PCL plasticization and 5 min of melt blending of polymer matrix with selected filler. Such conditions were based on the previous works of the present study' authors, and results published by other researchers (Soulestin *et al.*, 2007; Villmow *et al.*, 2010). Filler content in each sample was fixed at 30 wt%. The loading of filler enables a detailed analysis of its impact on the mechanical performance of resulting WPC, simultaneously not causing significant deterioration of its mechanical performance (Gironès *et al.*, 2007).

Prepared composites were compression molded at 100 °C and 4.9 MPa for 5 min and then kept under pressure at room temperature for another 5 min to enable solidification of the material. Obtained samples were coded as XY, where X stands for the abbreviated name of used diisocyanate modifier and Y for its content applied during modification. For proper evaluation of modifications' effects, the sample with unmodified UFC100 filler was also prepared and was named UFC. Figure 2 shows the photographs of obtained samples.

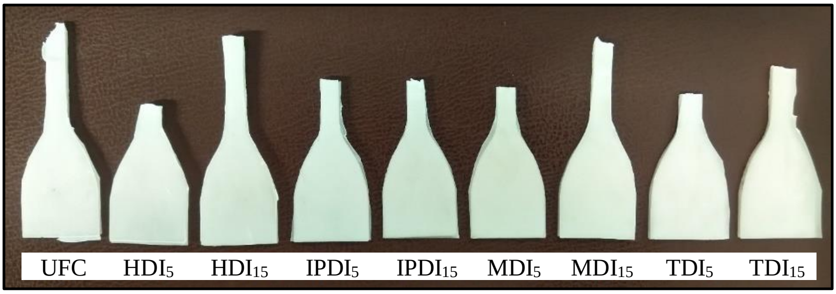


Figure 2. Appearance of prepared biocomposites

Schemes of the possible interactions between modified cellulose fillers and PCL applied as a matrix are presented in Figure 3. The schemes included two types of interactions. The first type comprised reactions between PCL end groups and free isocyanate groups resulting from the grafting of diisocyanates onto the surface of cellulose fillers (Gürtler and Danielmeier, 2004). The second type was associated with hydrogen bonds between PCL and functional groups generated on the surface of fillers during their modification.

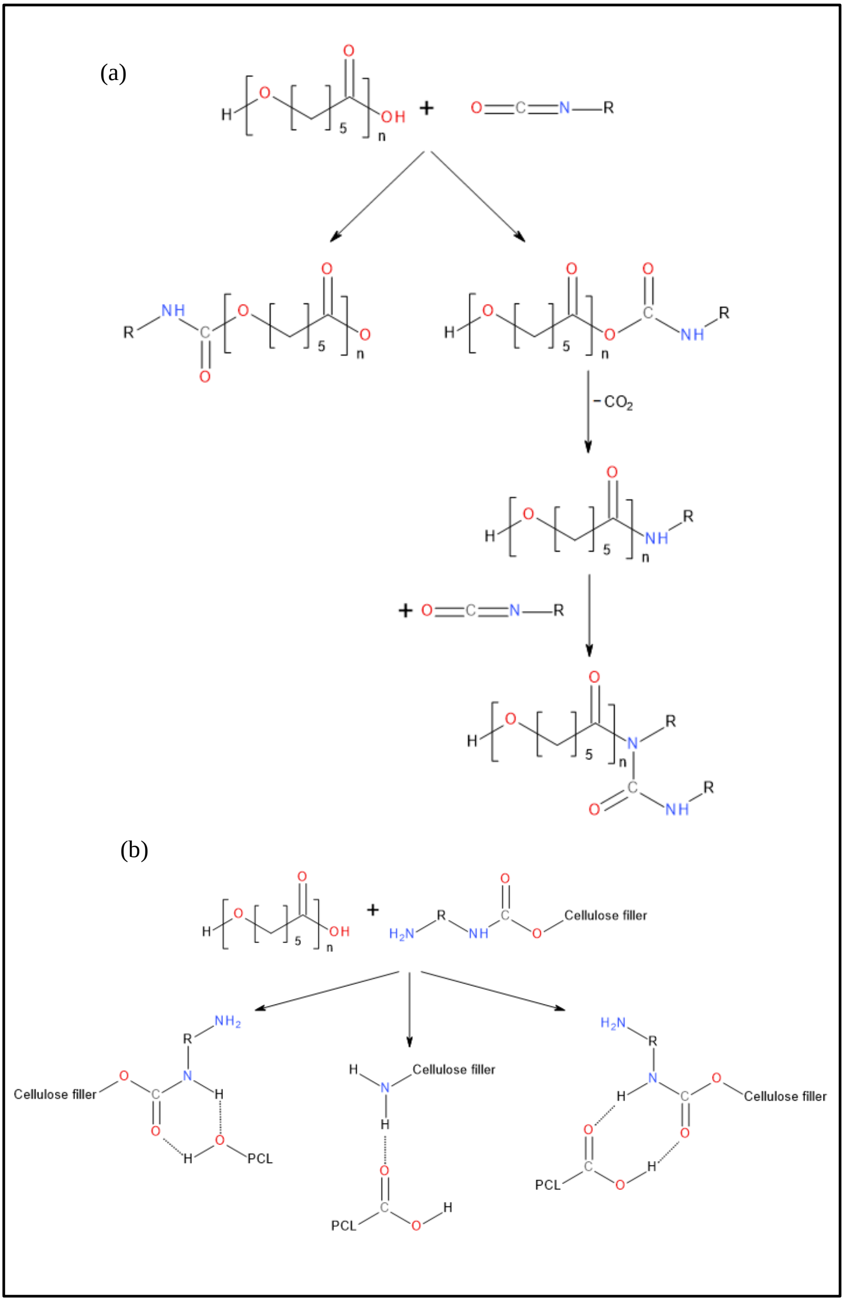


Figure 3. Schemes of possible covalent bonding (a) and hydrogen bonding (b) between PCL matrix and modified cellulose filler

2.4 Measurements

Chemical structure of lignocellulosic fillers' samples and biocomposites was determined using Fourier transform infrared spectroscopy (FTIR) analysis performed by a Nicolet Spectrometer IR200 (Thermo Scientific, USA). The device had attenuated total reflection (ATR) attachment with a diamond crystal. Measurements were performed with 1 cm^{-1} resolution in the range from 4000 to 400 cm^{-1} and 64 scans.

The thermal properties of the samples were measured by differential scanning calorimetry (DSC) carried out on a DSC 204 F1 Phoenix apparatus (Netzsch, Germany). Measurements were performed in the temperature range of -80 to 170 °C under N_2 atmosphere at a heating rate of 15 °C/min.

The tensile strength, elongation at break, and elastic modulus were estimated following PN-EN International Organization for Standardization (ISO) 527 standard through the Instron 4465 H 1937 (Instron, Colorado, USA) tensile testing machine with elongation head and an extensometer. Tensile tests were performed at a constant speed of 1 mm/min (for elastic modulus) and 50 mm/min (tensile strength and elongation at break). Five samples were analyzed for each specimen.

Shore hardness type D was estimated using Zwick 3131 durometer (Zwick Roell, Ulm, Germany) following PN-ISO 868. Each evaluation was prepared for seven test specimens. The rebound resilience was determined with a Schob type pendulum (Gibitre Rebound Check, Italy) using the ISO 4662 standard. Each evaluation was also prepared for seven test specimens.

The dynamic mechanical analysis was conducted on a Dynamic Mechanical Analyzer (DMA) Q800 apparatus (TA Instruments, Delaware, USA). Samples with dimensions of 40 x 10 x 2 mm were loaded with variable sinusoidal deformation forces in the single cantilever bending mode at the frequency of 1 Hz under the temperature rising rate of 4 °C/min, ranging the temperature from -100 to 100 °C.

3. Results and Discussion

3.1 Spectroscopic Analysis

Figure 4 shows the FTIR spectra of PCL-based composites containing unmodified and diisocyanate-treated cellulose fillers. Qualitatively, all spectra are very similar. Such effect is due to the overlapping of absorption bands attributed to the vibrations of bonds present in the unmodified sample with these related to generated urethane and urea groups. Lack of signals associated with the vibrations of N-H bonds in these groups is related to their low intensity compared to other signals as observed by other researchers (Mazurek and Rokicki, 2013). However, some differences in shape and magnitude of particular peaks were noted.

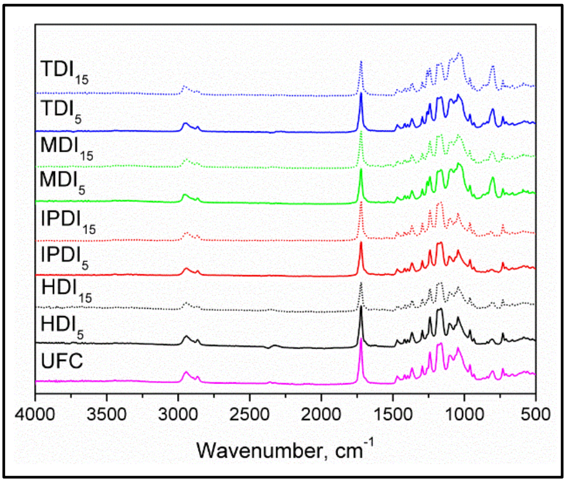


Figure 4. FTIR spectra of prepared composites

Signals observed in the range of 2860-2960 cm^{-1} were associated with the symmetric and asymmetric stretching vibrations of C-H bonds in methyl and methylene groups present in the structure of the PCL matrix and cellulose fillers. Peaks related to various deformation vibrations of these bonds were observed in the range of 1360-1470 cm^{-1}. Absorption band noted around 1720 cm^{-1} could be attributed to the stretching vibrations of carbonyl bonds, both in PCL structure and in potentially generated urethane bonds (Jiang *et al.*, 2020). In the range of 1160-1290 cm^{-1}, there were observed signals associated with the stretching vibrations of C-O and C-C bonds in crystalline and amorphous phases of PCL and in covalent bonds generated by the introduction of diisocyanate compatibilizers (Elzein *et al.*, 2004). Small differences between the samples were noted for these signals. This effect can be related to the differences in crystallinity of PCL-phase, and the generation of urethane bonds between matrix and filler. The same effect can be observed for bands in the range of 1040-1110 cm^{-1}, which are the characteristics for the stretching of C-O bonds. Also, it can be seen that the intensity of these bands is slightly higher for samples containing aromatic isocyanates. This is probably related to their higher reactivity compared to aliphatic ones, and generation of a higher amount of urethanes over ureas (Vilar, 1998). Peaks observed below 1000 cm^{-1} were attributed to the skeletal vibrations of C-C bonds and to the bending and deformation vibrations of C-H in poly(ε-caprolactone) backbone and cellulose filler (Hejna *et al.*, 2018). Changes in their intensity were related to the structural differences between applied diisocyanates – the presence of aromatic rings for instance.

3.2 Thermal Analysis

Table 2 shows the summarized results of DSC analysis for all samples. Associated with the melting and crystallization of semicrystalline phase of PCL, only one signal was observed both on heating and cooling. There are also presented values of the supercooling parameter, calculated according to Formula 1 (Qiu *et al.*, 2005).

$$\Delta T_{\alpha} = T_m - T_c \tag{1}$$

where:

T_m = melting temperature, °C
T_c = crystallization temperature, °C.

Table 2. Results of the DSC analysis of prepared composites

Sample	ΔH_m, J/g	T_m, °C	$W_{m1/2}$, °C	ΔH_c, J/g	T_c, °C	$W_{c1/2}$, °C	X_c, %	ΔT_{α}, °C
UFC	36.2	60.2	9.2	-41.6	30.8	7.1	37.1	29.4
HDI_5	32.4	59.2	10.3	-41.1	29.5	7.4	33.1	29.7
HDI_{15}	31.6	60.8	10.5	-40.8	28.3	7.6	32.4	32.5
$IPDI_5$	36.8	60.0	9.5	-43.3	30.2	6.8	37.7	29.8
$IPDI_{15}$	36.1	58.8	9.7	-42.7	29.1	7.3	37.0	29.7
MDI_5	30.2	58.3	9.2	-37.8	28.7	6.6	30.9	29.6
MDI_{15}	26.1	58.1	10.8	-36.1	27.2	7.9	26.7	30.9
TDI_5	31.3	58.4	8.7	-38.9	29.6	6.1	32.1	28.8
TDI_{15}	27.3	58.8	10.8	-37.5	27.6	7.9	27.9	31.2

The increase in the supercooling parameter for biocomposites containing modified fillers was observed. The decrease in crystallization and melting temperatures points to the reduction of nucleating activity of fillers after modification. Therefore, after performed modifications, cellulose fillers caused a slight reduction in the crystallinity of the PCL phase in investigated composites. Degree of crystallinity was calculated from the values of enthalpy of thermal transitions according to Formula 2.

$$X_c = \frac{\Delta H_m}{\Delta H_c} \cdot 100\% \tag{2}$$

where:

X_c = degree of crystallinity, %
ΔH_m = melting enthalpy, J/g
ΔH_c = melting enthalpy at 100% crystallinity, J/g

For the calculations, the heat of fusion of PCL at 100% crystallinity was assumed to be 139.5 J/g, according to Crescenzi *et al.* (1972).

As previously mentioned, the crystallinity of the PCL phase in investigated composites was decreased. This effect can also be attributed to the changes in polarity of fillers' surfaces and differences in the interfacial interactions with the matrix. These changes were caused by chemical reactions between applied diisocyanates and functional groups present on the surface of cellulose fillers, as shown in Figure 1.

Table 2 also shows the values of peaks' width at half of their height ($W_{1/2}$), which represent the purity and homogeneity of crystalline phase structure, e.g., distribution of crystallites size (Hejna *et al*., 2019). It can be seen that the increase in the isocyanate modifier content caused the rise of $W_{1/2}$ parameters. This effect is due to the generation of a less homogenous crystalline structure and corresponds with the values of the X_c parameter. Similar observations were made by other researchers investigating the modification of lignocellulosic fillers with isocyanates (Labet *et al*., 2007; Girouard *et al*., 2016).

3.3 Mechanical Performance

Figure 5 presents the impact of applied filler treatment on the tensile strength and elongation at break of resulting poly(ε-caprolactone)-based composites. It can be observed that the modification of cellulosic filler caused significant changes in composites' performance. The values of the tensile strength were significantly increased. However, the increase in isocyanate content did not result in the enhancement of mechanical performance.

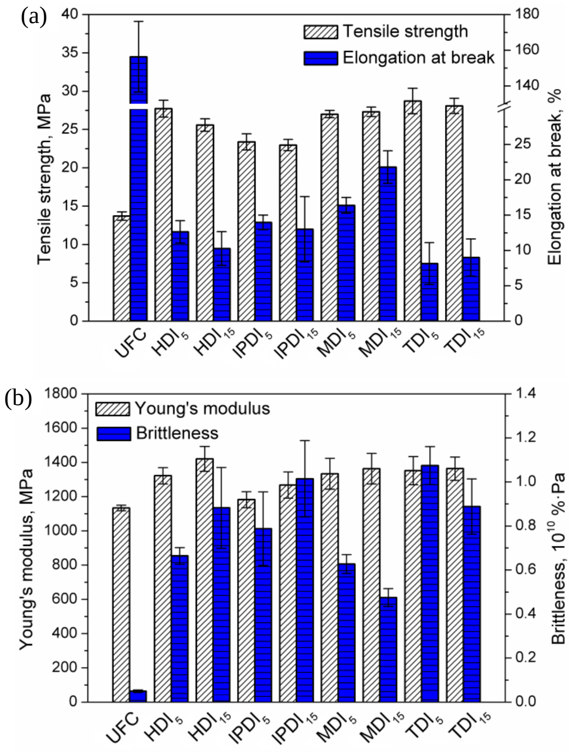


Figure 5. Impact of performed modifications on the mechanical performance of composites

On the other hand, the drastic reduction of elongation at break was noted. Such effect points to the reduced mobility of polymer chains in composites due to the enhancement of interfacial interactions between matrix and filler (Bello *et al.*, 2020). For composites containing neat UFC100 filler, these interactions were based mainly on hydrogen bonding, while isocyanate treatment provided the possibility for generation of significantly stronger covalent bonds. Therefore, at least part of filler particles was permanently bonded with polymer chains. This effect can be described as partial crosslinking of the structure. As a result, stiffening of composites was noted, which was expressed by the increase in Young's modulus and especially, the values of brittleness calculated from the results of static and dynamic mechanical tests by following Formula 3.

$$B = \frac{1}{(\varepsilon_b \cdot E')} \tag{3}$$

where:

B = brittleness, 10^{10} %·Pa
ε_b = elongation at break, %
E' = storage modulus at 25 °C, MPa

According to the presented formula, proposed by Brostow *et al.* (2006), to show the low value of brittleness, the material needs to withstand high stress for the wide range of strains; hence, the inclusion of storage modulus and elongation at break. For the analyzed composites, the most significant factor to determine the value of brittleness was elongation at break. Therefore, the lowest brittleness was noted significantly for the sample containing unmodified UFC100 filler, characterized by elongation at break exceeding 156%. Among modified samples, the lowest brittleness was observed when MDI was applied. This effect was associated with higher elongation and lower crystallinity as compared to other samples. When aromatic isocyanates (MDI and TDI) were applied, brittleness decreased with their content, which was related to the rise of elongation at break. Moreover, values of tensile strength for aromatic isocyanates were higher than aliphatic ones, which was also observed by Maldas *et al.* (1988).

Figure 6 presents the values of hardness and rebound resilience of prepared composites. Both parameters were strongly affected by the type and content of the applied modifier. It can be seen that in all modifications, the hardness of material was increased, while the opposite trend was noted for the rebound resilience. Both of these parameters are closely related to each other (Figure 6b), as previously confirmed by S. Moonchai and D. Moonchai (2013). The drop in rebound resilience may be associated with the stiffer structure and higher ability to dissipate the energy during tests. It can be achieved by breaking of urethane linkages between PCL matrix and modified fillers generated in reaction of unbound isocyanate groups with hydroxyls present in the backbone of PCL.

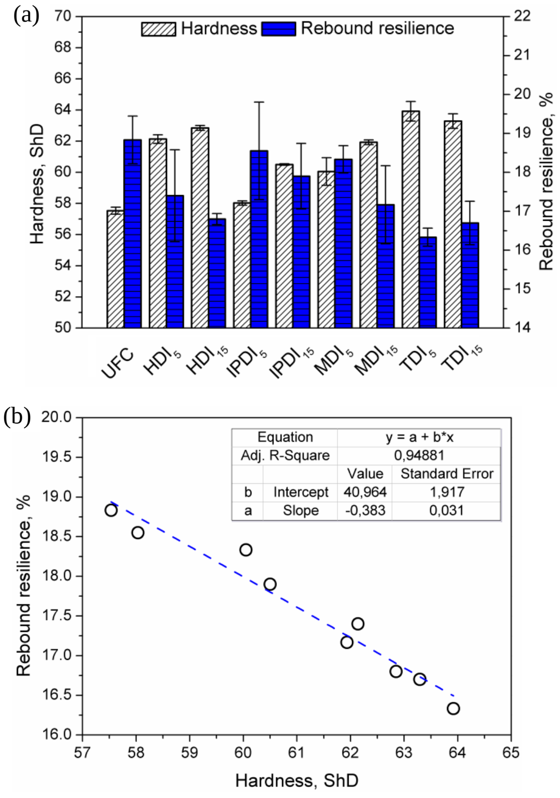


Figure 6. Hardness and rebound resilience of prepared PLA/cellulose composites

Prepared composites were also tested in terms of their dynamic mechanical performance. In Figure 5, values of brittleness, calculated from storage modulus, are presented. Another essential parameter obtained from DMA analysis is loss tangent, which is a ratio of storage and loss modulus, related to the elastic and viscous components of material (Meyers and Chawla, 2009). Changes in the position and the magnitude of the tan δ peak indicate changes in the viscoelastic characteristic of the material. Higher values of tan δ characterized the materials, which can dissipate the energy. Lower values are typical for more elastic materials and attributed to decreased mobility of the system. Figure 7 shows the temperature plots of tan δ.

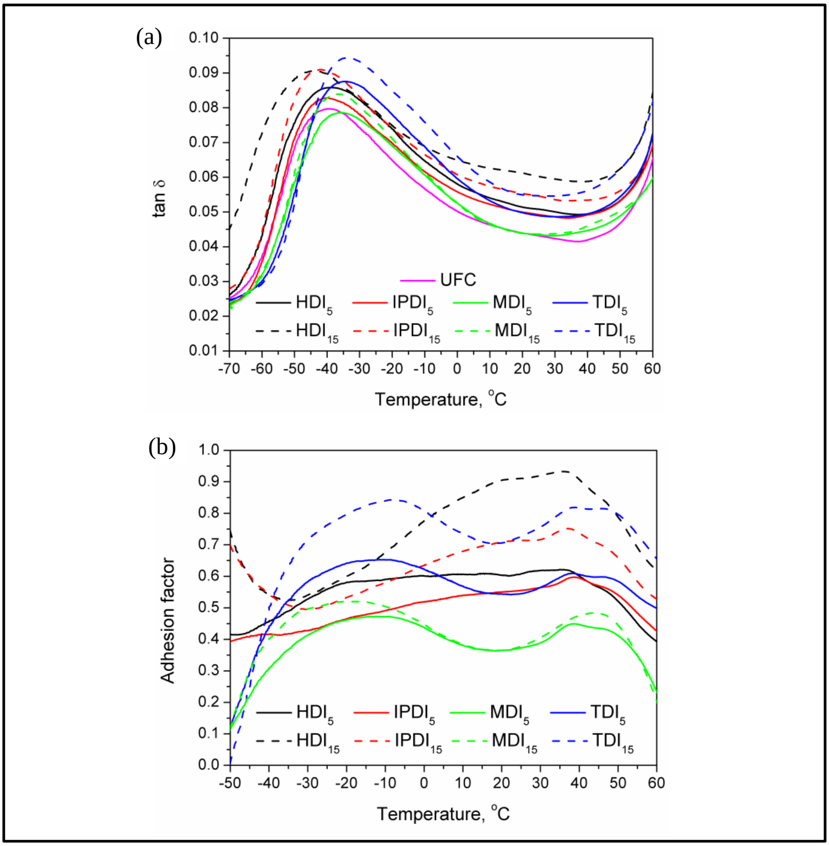


Figure 7. Plots of loss tangent (a) and adhesion factor (b) of composites as a function of temperature

It can be observed that the applied modifications of cellulose fillers had a relatively small influence on the glass transition temperature (T_g) of material, determined by the position of the tan δ peak. For a sample containing a neat filler, the value of T_g was -38.9 °C. Application of aliphatic isocyanates, HDI and IPDI resulted in a small drop of T_g. In contrast, modification with aromatic ones, MDI, and TDI caused its increase, which was associated with high rigidity of aromatic structures (Szycher, 2012). Nevertheless, for all materials, values of T_g were between -44.3 and -34.0 °C, which was noticeably lower than ambient temperature at which static mechanical tests were performed.

The magnitude of tan δ at ambient temperature was dependent on the applied treatment. It can be seen that modification with isocyanates caused a slight rise of tan δ values, suggesting a higher ability to dissipate the energy when stress is applied. Such effect may be associated with the potential breaking of relatively brittle urethane bonds between matrix and filler, and destruction of the “crosslinked” structure of composites (Szycher, 2012).

Moreover, the values of tan δ were used to calculate the adhesion factor (A), which describes the strength of interfacial interactions. Its values are presented in Figure 7b. Calculations of A factor are based on the concept that the tan δ value of the composite can be expressed as a combination of mechanical damping of filler, interphase, and matrix, as presented by Kubát *et al*. (1990). Compared to the PCL matrix, the rigidity of filler can be considered very low; its impact is neglected, similarly to the impact of interphase, due to its meager volume fraction. The detailed mathematical procedure in A factor was presented in the previous works of Hejna *et al*. (2015) and Formela *et al*. (2016). Generally, the adhesion factor can be calculated using the following Formula 4.

$$A = \left(\frac{1}{1-V_f}\right)\left(\frac{\tan\delta_c}{\tan\delta_m}\right) - 1 \tag{4}$$

where:

V_f = volume fraction of filler, %
$\tan\delta_c$ = loss tangent of composite
$\tan\delta_m$ = loss tangent of the matrix

Aimed at evaluating fillers’ modifications, this present work treated sample UFC as the matrix. Therefore, the values of A are only related to the efficiency of applied diisocyanate treatment of fillers. Generally, low values of adhesion factor is linked to a high level of interfacial adhesion (Wei *et al*., 2013). The best results were noted for composites containing MDI-treated fibers, which also confirms the lowest brittleness among modified samples. Moreover, the values of A for MDI_5 and MDI_{15} samples were very close, which was not observed in other modifiers. For other diisocyanates, the application of 5 wt% was enough. Higher loadings resulted in the rise of A parameter, indicating deterioration of interfacial adhesion. As can be seen in Figure 6, it did not cause further enhancement of mechanical performance. Therefore, it can be concluded that modification of cellulose fillers should be performed with the amounts of isocyanates lower than 15 wt% to limit unnecessary application and reduce the environmental impact of the process. Such observations confirm the results presented by other researchers; however, they presented results only for lower contents of isocyanates (George *et al.*, 1997; Geng and Simonsen, 2005; Qiu *et al.*, 2005).

4. Conclusion

This study performed a comparative analysis of the impact of four types of diisocyanates applied as compatibilizers on the performance of poly(ε-caprolactone)-based biocomposites filled with cellulose filler. Four most popular types of diisocyanates were investigated, two aromatics: MDI and TDI, and two aliphatics: HDI and IPDI. These compounds cover around 95% of the total isocyanate market. Therefore, considering their popularity, relatively low price compared to less common types, and the fact that they are well characterized, it is very beneficial to apply them as compatibilizers for wood polymer composites. None of the previously published reports related to this topic presented a comparative analysis of various types of diisocyanates.

Performed modifications of cellulosic fillers resulted in the significant enhancement of interfacial interactions between matrix and filler in the prepared composites, expressed by low values of adhesion factor. As a result, a significant increase in tensile strength from 13.7 to even 28.7 MPa was noted. Simultaneously, modulus and hardness increased even by 25 and 11%, comparing to a composite containing unmodified cellulose filler. Due to the drop in matrix crystallinity, the rebound resilience of the obtained composites did not significantly decrease. On the other hand, enhanced interfacial interactions resulted in higher brittleness of the composites, which were able to withstand a higher amount of stress, but in the lower range of strains. Therefore, the lower amount of energy was required to destroy them. These results indicate that by proper adjustment of type and content of diisocyanate modifier, composites' properties may be engineered.

5. Acknowledgement

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