Influence of accelerated weathering on mechanical and thermomechanical properties of poly(lactic acid) composites with natural waste filler

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Abstract: In this study we investigated the impact of accelerated weathering on selected mechanical and thermomechanical properties of poly(lactic acid) (PLA) composites filled with ground chestnut shell (CN). The mechanical properties were evaluated through static tensile test and Dynstat impact test, which were conducted for pure PLA and composites containing various amounts of the lignocellulosic organic filler (2.5–30 wt %). The results of the dynamic thermomechanical analysis (DMTA) are discussed in reference to structural changes obtained by differential scanning calorimetry (DSC), and they confirm changes in crystalline structure of PLA and its composites induced by cyclic temperature changes and UV light exposure. Scanning electron microscopy (SEM) images showed presence of microcracks and erosion of the PLA and composite surface after the aging process.

Keywords: poly(lactic acid), composite, accelerated weathering, waste management, chestnut, mechanical properties.

Wpływ przyspieszonego starzenia na mechaniczne i termomechaniczne właściwości kompozytów poli(kwasu mlekowego) z napełniaczem z odpadów naturalnych

Streszczenie: Przedstawiono wpływ przyspieszonego starzenia na wybrane właściwości mechaniczne oraz termomechaniczne kompozytów na osnowie polilaktydu (PLA) modyfikowanego rozdrobnionymi łupinami kasztana (CN). Właściwości mechaniczne kompozytów zawierających 2,5–30 % mas. napełniacza naturalnego oceniano w próbie statycznego rozciągania oraz na podstawie pomiarów udarności metodą Dynstat. Zmiany właściwości niemodyfikowanego PLA oraz jego kompozytów odniesiono do właściwości termomechanicznych ocenianych metodą dynamiczno-mechanicznej analizy termicznej (DMTA) oraz różnicowej kalorymetrii skaningowej (DSC). Zastosowanie wielokryterialnej oceny zmiany właściwości kompozytów, spowodowanej przyspieszonym starzeniem, pozwoliło na stwierdzenie istotnych modyfikacji struktury krystalicznej osnowy polimerowej pod wpływem ekspozycji na światło UV oraz dynamicznych zmian temperatury i wilgotności powietrza. Powierzchnie starzonych próbek materiałowych obserwowano z zastosowaniem skaningowej mikroskopii elektronowej (SEM).

Słowa kluczowe: polilaktyd, kompozyt, przyspieszone starzenie, gospodarka odpadami, kasztan, właściwości mechaniczne.

In recent years, the use of biomass solid waste as a material for development of polymeric composites has attracted much interest. The possibility of biomass utilization and application as a filler for polymeric composites' manufacturing has become an intensively explored field [1, 2]. Waste parts of plants such as: stalks [3], husks, shells [4–6], seeds [7], leaves [8, 9] and others [10] have been attracting attention of researchers as potential materials for production of both fibrous and particle-shaped fillers, which allow to modify the properties of thermoplastic and thermoset polymers as well as significantly decrease the price of the final composite product. Poly(lactic acid) (PLA) is a biodegradable material with the greatest opportunities for industrial application. Thanks to its good mechanical properties, possibility of utilization by com-

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posting as well as high availability in form of ready-to-use commercial grades, modified for different melt processing technologies, may in future compete with petroleum-based polymers, such as polypropylene or polyoxymethylene. However, the low glass transition temperature and the resulting low thermomechanical stability of PLA, as well as its high price, cause its still limited application in comparison to petroleum-based non-biodegradable polymers [11]. One of the strategies which may extend the application range of biodegradable polyesters is the incorporation of low-cost waste fillers, which allow to decrease final products price. Moreover, chemical composition of lignocellulosic fillers will not limit the biodegradation ability of the matrix [1]. The main advantage of biodegradable composites is that they can be composted as solid waste. On the other hand, this factor may also deteriorate the mechanical properties over the composite part life cycle. Therefore, it is necessary to create detailed studies of each potentially biodegradable material in reference to the stability of its properties when affected by time and different environmental factors, such as: cyclic temperature changes, humidity and UV light exposure [12, 13].

There have been many studies which investigated the influence of different artificial aging processes on properties and structure of biodegradable polymeric composites with organic fillers, however in each case the results were strongly dependent on the weathering procedure [14–17]. In most studies accelerated aging under UV light exposure and variable temperature conditions an increase in the crystallinity of the PLA matrix was observed [14, 17]. It should be noticed that amorphous domains of PLA are much more susceptible to both hydrolytic and enzymatic degradation [18]. Hydrolytic degradation occurring during immersion in water is strongly dependent on the temperature; samples conditioned in water environment below glass transition temperature usually degrade much more slowly [19, 20]. Therefore, one of the biggest problems resulting from complex effects occurring during accelerated weathering tests is the simultaneous occurrence of various, intensified artificial factors, which change the macromolecular structure of the tested PLA samples in a way not observable in a normal product lifecycle, leading to improved resistance to UV light or water induced degradation. On the other hand, accelerated weathering tests allow to determine precisely the influence of natural filler degradation on the deterioration of biodegradable composite properties [16]. Most studies focus on the degradation of PLA composites filled with natural fibers (*e.g.*, kenaf or sisal), which are characterized by higher water absorption of the composites due to the shape of the filler, which in effect causes hydrolytic degradation in the whole material volume. The main goal of the present study is therefore to determine the influence of accelerated weathering on mechanical and thermomechanical properties of the poly(lactic acid) composites filled with ground chestnut shell used as particle-shaped waste filler.

EXPERIMENTAL PART

Materials

Injection molding grade poly(lactic acid) Ingeo™ 3001D (Nature Works, USA) with *MFI* of 22 g/10 min (2.16 kg, 210 °C) and density of 1.24 g/cm^3 was used as the polymeric matrix. Ground chestnut shell (CN, *Aesculus hippocastanum*) with mean particle size of 10.7 μm was used as a particle-shaped filler for preparing biocomposites. Detailed description of physicochemical properties of the filler was presented in our previous work [21, 22].

Sample preparation

Natural composites containing waste organic filler with CN content 2.5 wt % up to 30 wt % were prepared by mixing in molten state using Zamak EH-16.2D twin screw co-rotating extruder with barrel temperature profile: 190–188–185–181–180–178–177–175–168 °C and screw rotational speed of 100 rpm, which results in approx. 3.6 kg/h extrusion throughput. Standardized samples were manufactured by injection molding with an Engel HS 80/20 HLS injection molding machine operated at 190 °C and following processing parameters: mold temperature 25 °C, injection speed 70 mm/s, forming pressure 5 MPa and cooling time 45 s. Prior to each melt processing materials were dried in a vacuum at 50 °C for 24 h.

Accelerated weathering process

After 7-day conditioning at room temperature, samples were subjected to accelerated weathering process using QLAB QUV according to ISO 4892-3 standard. 500-hour aging process was conducted under 0.76 W/m^2 UV light irradiance at 340 nm wavelength, cyclic temperature ranging from 60 °C during 8 h dry UV light exposure period to 50 °C at 4 h condensation dark period. The samples subjected to accelerated aging were assigned with a prefix "a", *e.g.*, a30CN is a composite containing 30 wt % of the CN filler after accelerated weathering.

Methods of testing

The differential scanning calorimetry (DSC) measurements were performed with a Netzsch DSC 204F1 Phoenix apparatus for 5 ± 0.1 mg samples placed in aluminum crucibles in nitrogen atmosphere. A temperature program operating in cycles was applied, heating from 20 °C to 230 °C and cooling back to the initial temperature, with a heating/cooling rate of 10 °C/min. The crystallinity level was calculated using following formula (1):

$$X_c = (\Delta H_{M} - \Delta H_{CC})/[(1 - \phi) \cdot \Delta H_{MPLA}] \cdot 100\ \% \qquad (1)$$

Table 1. Crystallinity (X_c) of PLA and PLA composites before and after aging process

Material	X_c, 1st heating, %		X_c, 2nd heating, %	
	Before aging	After aging	Before aging	After aging
PLA	28.3	44.8	30.6	41.6
2.5CN	36.6	40.5	24.4	27.8
5CN	37.2	51	28.9	24.9
10CN	37.4	44.4	26.7	25.9
20CN	30.6	38.1	24.7	24.2
30CN	33.7	45	24.3	25

where: ΔH_M – melting enthalpy, ΔH_{CC} – cold crystallization enthalpy, ΔH_{MPLA} – melting enthalpy corresponding to a 100 % crystalline PLA (106 J/g) [23], ϕ – filler amount.

In order to determine tensile strength T_s, tensile modulus E and elongation at break ε_b values, a static tensile test was conducted using a Zwick Z020NT universal testing machine with a crosshead speed of 1 mm/min during Young's modulus determination and 50 mm/min for the remaining parameters, according to ISO 527-2 standard. 15 samples of each kind were tested.

Impact strength measurements of 15 × 10 × 4 mm unnotched samples were performed according to the DIN 53435 standard with using 0.98 J hammer and Dys-e 8421 apparatus. 20 samples of each series were tested.

The dynamic mechanical properties of the composites, with 10 × 4 × 50 mm dimensions, were studied using DMTA method in a torsion mode using Anton Par MCR301 rheometer, operating at the frequency of $f = 1$ Hz, strain $\gamma = 0.01$ % in the temperature range between 25 °C and 110 °C, and at the heating rate of 2 °C/min.

RESULTS AND DISCUSSION

Table 1 shows the crystallinity values calculated for 1st and 2nd heating according to Eq. (1) of pure PLA and composite samples submitted to accelerated weathering process. It can be seen that the exposition to UV light and cyclic heating of the polymeric and composite samples resulted in improved crystallinity of the materials. X_c values recorded for the 1st heating were in all cases higher after aging. This effect results from the recrystallization of the biodegradable polyester during heating temperature variations induced by changing weathering conditions and temperature generated by UV lamps. It should be mentioned that materials subjected to the aging process did not show any cold crystallization effect during 1st heating, while all samples during 2nd heating exhibit about 2 °C decrease of cold crystallization temperature in comparison to untreated samples. A comparison of X_c values from 1st and 2nd heatings shows that erasing thermal history decreases the improvement in crystallinity observed during the 1st heating. The only difference was observed for pure PLA sample between a sample unsubjected and subjected to the aging process. Thus, it can be stated that only in this case noticeable structural changes based on chemi-crystallization resulting from PLA chain scission occurred [14]. For composite materials the effect of improved crystallinity decayed after erasing of thermal history by re-melting the polymer structure. This effect may be attributed to improved crystallinity of the untreated composites, induced by the incorporation of CN filler, which reveals nucleating ability on PLA [21]. This finding corroborates the conclusions from the literature that the higher crystallinity, the better resistance for hydrolytic degradation of the PLA [24–26]. Permanent increase of crystallinity of pure PLA is connected with more significant occurrence of the first step of hydrolytic degradation, when random hydrolytic scission of ester bonds takes place with the diffusion of water into amorphous domains, which amount is much higher in case of unfilled sample. In the second stage, hydrolytic attack takes place from the surface towards the center of the crystalline phase with the degradation of the significant amounts of the amorphous domains [27]. Lower crystallinity of composite materials during 2nd heating may be a result of different cooling conditions and different sample size between solidification of the material at DSC measurement and solidification of thick-walled sample at injection molding realized with short cycle time and later after-process free cooling in the air.

In Fig. 1 SEM images present the surface of PLA and PLA composite containing 30 wt % of the filler before and after the aging process. It was found that accelerated weathering did not significantly change the structure of the pure PLA sample. The presence of microscopic cracks on the sample surface could be caused by cyclic dilatation of the sample during the aging process [14]. Moreover, at the rapidly cooled surface of injection molded samples contain higher amounts of amorphous PLA domains which are much susceptible for hydrolytic degradation. In case of the 30CN sample, a visible aging effect was observed. Usually composite samples filled with natural particular fillers are characterized with a thin polymeric layer created on the surface of the injection molded sample, which suppresses water absorption of hydrophilic filler dispersed in hydrophobic polymer. As a result of cyclic exposure to elevated temperature and UV light, the surface of the PLA samples was covered with microscopic cracks, which in effect allowed water penetration into the polymeric sample and resulted in improved water

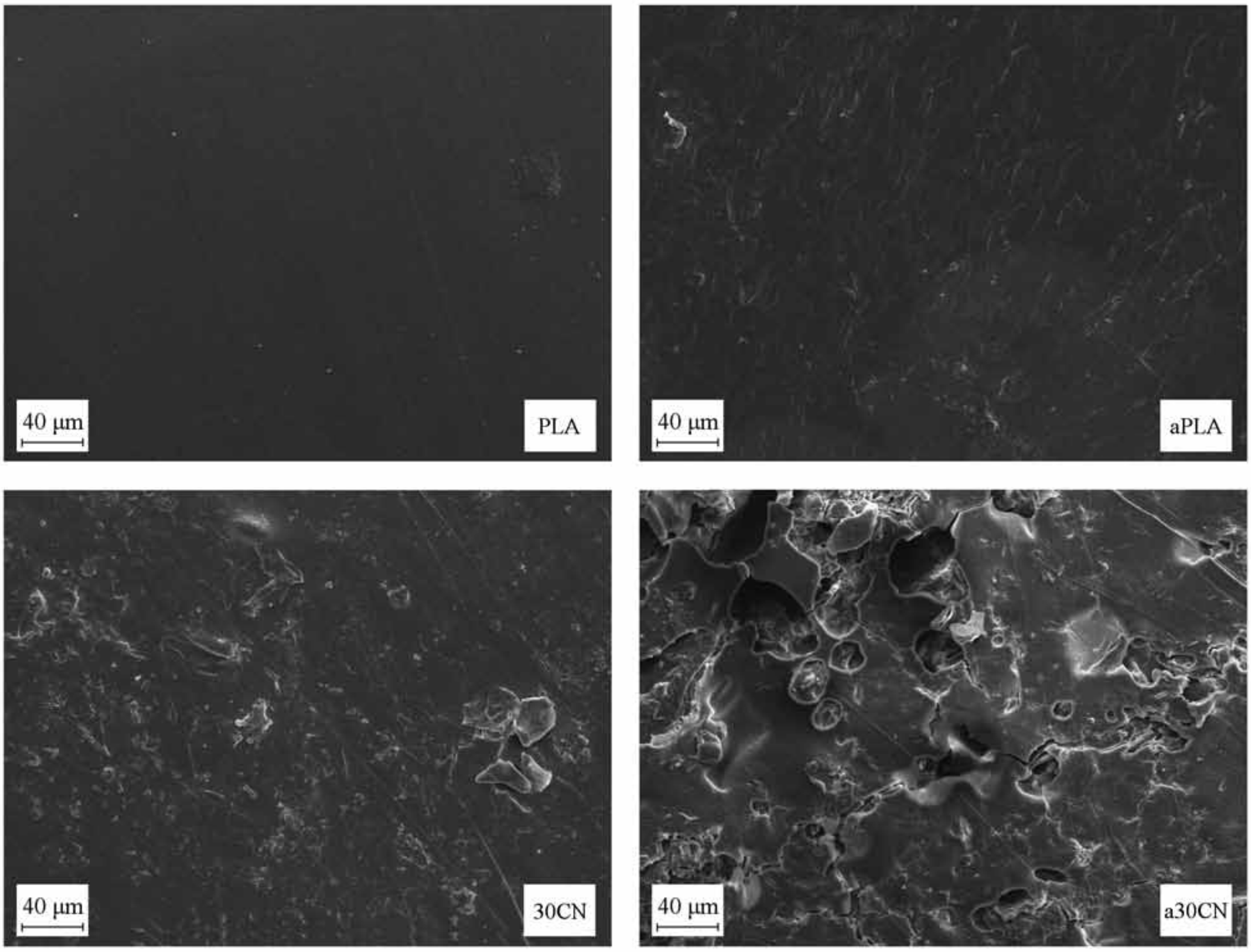

Fig. 1. SEM images of the surface of PLA and 30PLA composite injection molded samples before and after aging process, mag. 1000×

absorption by the lignocellulosic filler. In case of 20CN and 30CN samples the filler particles came into mutual contact [22], which induced a significant increase in water absorption and improved degradation of composites structure.

Figure 2 shows mechanical properties of PLA and composites obtained by tensile test and impact strength experiments. As can be seen, accelerated weathering caused a decrease in all mechanical parameters evaluated by tensile test. Elasticity modulus for both pure PLA as well composite materials decreased after aging process, the biggest difference between the untreated and aged sample was observed for composite containing 30 wt % of the filler. Despite the fact that the effect of accelerated weathering on elasticity modulus is similar for pure PLA and composites, the mechanism occurring during the aging process was different. Increase of PLA crystallinity usually causes an increase in elasticity modulus [26], whereas in considered case inverse effect was observed, which is connected with first step of hydrolytic degradation of PLA [27]. In case of composite samples the decrease of Young's modulus is additionally an effect of deterioration of reinforcing the ability of natural particles and may be connected with the degradation of the CN caused by UV light, temperature variations, as well as water absorption [21]. For the reference PLA sample the change in mechanical properties resulted from different phenomena. Composite samples before being subjected to the aging process showed higher crystallinity than unmodified PLA, therefore the CN-filled polymeric matrix was not expected to show such an intensive photo- and hydrolytic degradation as the more amorphous PLA. Usually degradation occurs predominantly in the amorphous PLA regions by chain scission [14, 27]. This phenomenon may be confirmed by the already mentioned improved crystallinity of pure PLA sample after 2nd heating during DSC test, which suggests partial degradation of unmodified polymer during accelerated weathering, not observed in case of composite materials. For tensile strength the difference between untreated and aged samples was observed only for composites with filler content above 5 wt %. In case of untreated composite samples a significant decrease in tensile strength was noted for 20CN and 30CN samples. After accelerated weathering a visibly limited ability to transfer stress was observed in composites containing 10 wt % of CN and more, however, for samples a20CN and a30CN tensile strength was 50 % lower than for untreated reference samples. This phenomenon is mainly connected with the swelling of the natural filler which may deteriorate interface and cause creation cracks around the CN particles [19]. As expected, the elongation at break decreased with an increased

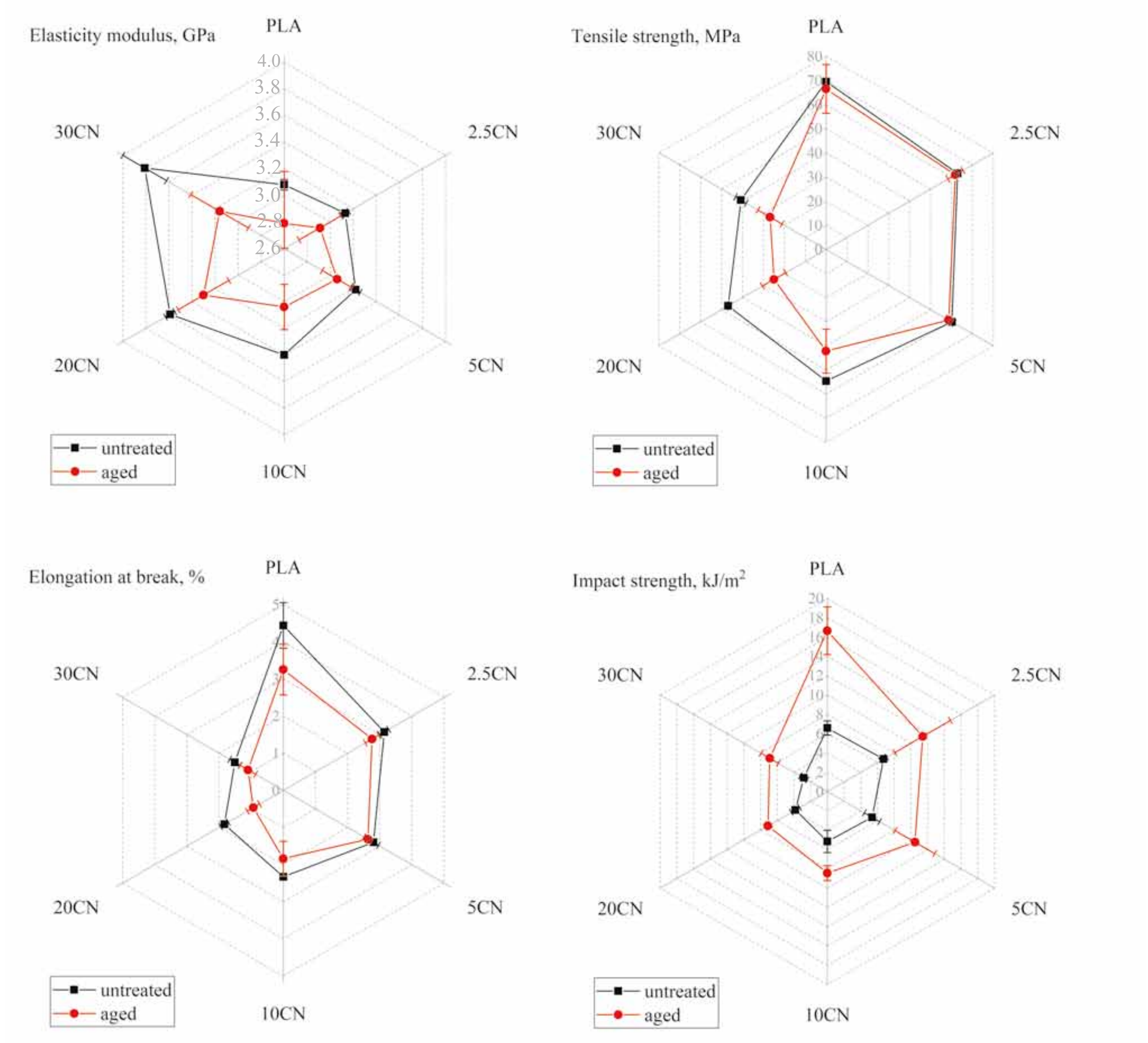

Fig. 2. Mechanical properties of PLA and PLA composites before and after the aging process

amount of the filler in composites, which is reasonable due to a higher amount of particle-shaped filler dispersed in polymeric matrix which act as notches. After the aging process, elongation at break values was additionally limited, probably due to the creation of microcracks at the surface of the aged samples, which caused earlier propagation of the cracking during the mechanical load [14]. In Fig. 3 strain-stress curves of selected PLA and composite samples before and after aging process are presented. It can be seen that in case of materials subjected to accelerated weathering no yield point was observed, all specimens reveal brittle fracture during tensile test.

The results of impact strength tests of both PLA and composite samples after artificial weathering corresponded with the results of tensile test. All the materials showed improved resistance to dynamic load after being subjected to UV light and cyclic temperature variations in humid atmosphere. For untreated and aged samples a similar tendency was observed: the higher the amount of the filler, the lower the impact strength. However, in each case the treated material showed at least doubled impact

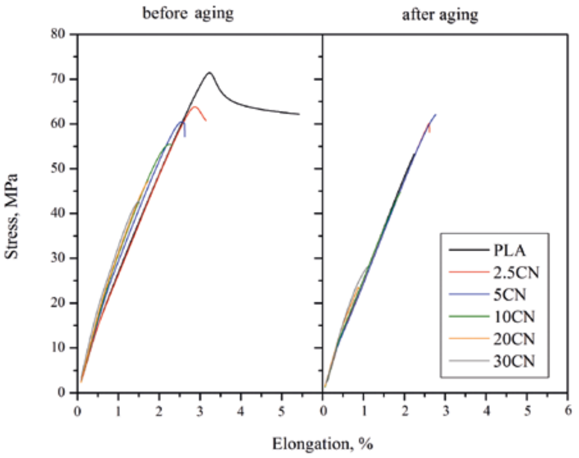

Fig. 3. Stress-strain curves of selected PLA and composite samples before and after aging process

strength, which may be related to the improvement of PLA matrix crystallinity of the all aged samples [26]. The dependence between simultaneous increasing impact strength with crystallinity of PLA is well described in literature [28–30] and is connected with modification of amorphous structures in the interlamellar region [28].

The influence of accelerated weathering on thermomechanical properties of PLA and its composites was determined using DMTA. The variations of storage modulus (*G′*) and damping factor (tan δ) as a function of temperature for all the considered materials are presented in Fig. 4. It can be clearly seen that all the samples subjected to accelerated weathering reveal no significant decrease in *G′* in the temperature range of 55–65 °C and later an increase connected with the presence of cold crystallization (90–100 °C), typical for amorphous PLA. Higher *G′* values in the temperature range after T_g were observed for composites containing more CN, which is connected with the higher crystallinity of the composites as well as presence of rigid lignocellulosic structures of the filler. Improved thermomechanical stability in the whole temperature range of aged PLA and composites resulted from about 40 % content of PLA crystalline phase observed during DSC evaluation. Decreased *G′* values of aged materials in the range before glass transition correlate with elasticity modulus presented in Fig. 2, and a decrease in the sample stiffness caused by cold crystallization occurring as a result of cyclic heating, as well as partial degradation of PLA matrix during accelerated aging. Despite different behavior of untreated and aged samples, in both cases incorporation of the filler resulted in significant improvement of *G′*. Glass transition temperature (T_g) of PLA and PLA-CN composites was determined as a temperature corresponding to peak of tan δ curve. It can be seen that the aging process improved T_g through an improvement of aged samples crystallinity [17]. In our previous work [21] we described a decrease in this parameter observed as a function of increased amount of the CN resulting from insufficient interfacial adhesion between hydrophobic matrix and a hydrophilic filler, which in this case was observed also for samples subjected to aging. Glass transition temperature for unmodified samples decreased from 70 °C to 67.2 °C for PLA and 30CN samples, respectively. After aging, T_g values were higher however the lowering tendency was the same as before applying the artificial weathering process: for aPLA T_g it was 75 °C and 73.6 °C for a30CN. Improved crystallinity of the samples encouraged the decrease in the tan δ, which may be interpreted as a lower ability to dissipate mechanical energy and vibrations.

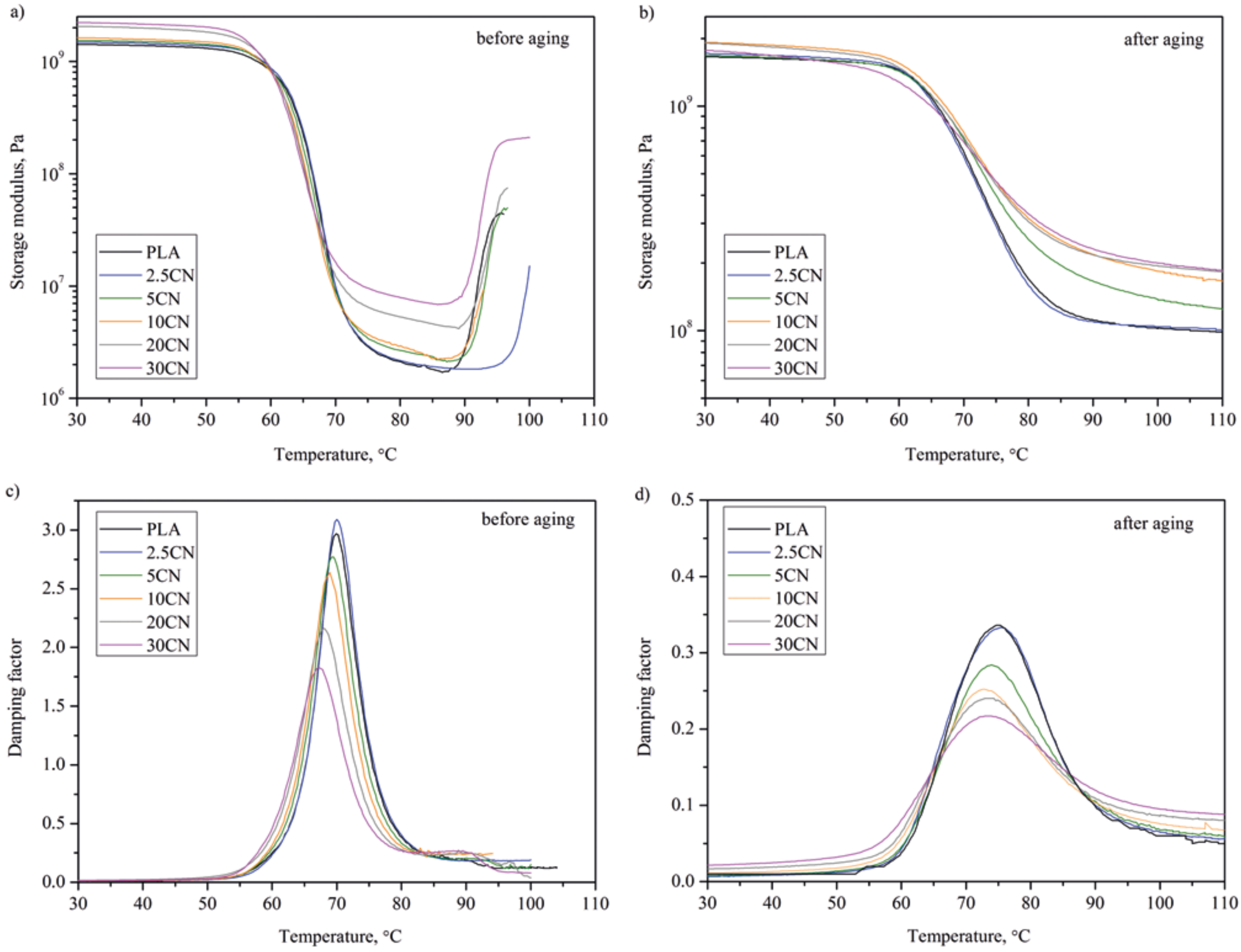

Fig. 4. a, b) Storage modulus (*G′*), c, d) damping factor (tan δ) of PLA and PLA composites before (a, c) and after (b, d) aging process

CONCLUSIONS

Accelerated weathering of PLA and PLA-based composites filled with lignocellulosic waste filler conducted under high humidity, various temperatures and UV light exposure caused structural changes, including improved crystallinity of polymeric matrix and degradation of chestnut particles. Due to a significant increase in the crystallinity of the samples, their resistance to hydrolytic degradation during artificial aging was increased. The dominant effects observed in composites properties changes were based on deterioration of the mechanical properties evaluated under static tensile conditions, resulting from decreased interfacial adhesion between polymer and filler as well as degradation of the chestnut structure. Initial lower crystallinity of pure PLA was the reason for the much stronger degradation effect than for composite materials. Moreover, in case of pure PLA, DSC experiments confirmed permanent changes in macromolecular structure. Improved crystallinity of PLA matrix as an effect of UV light exposure, cyclic short-term exceeding of cold crystallization temperature as well as hydrolytic degradation of biodegradable polyester amorphous domains caused higher resistance of both pure PLA as well as PLA composites to impact load and improved thermomechanical stability. Therefore, it should be stressed that the ground chestnut shell can be successfully applied as a particle-shaped waste filler for polylactide composites.

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