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MICROSTRUCTURE AND FEATURES OF THERMAL BEHAVIOR OF POLYMER COMPOSITES BASED ON POLYLACTIC ACID AND CARBON NANOTUBES

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This study investigates the thermal behavior of biodegradable polylactide (PLA) modified with multi-walled carbon nanotubes (MWCNTs), conducted to determine the influence of the nanofiller and the prehistory on the structural and phase transformations in the polymer matrix. Experimental samples with different MWCNT contents were analyzed using differential scanning calorimetry to determine the glass transition temperatures, melting and crystallization features, as well as light microscopy methods to study the morphology. The obtained data made it possible to trace the dynamics of thermal transitions in nanocomposites considering the thermal prehistory and to identify trends in the formation of the crystalline structure depending on the MWCNT concentration. The results of the study indicate a complex interaction between the nanofiller and the polymer matrix, which is of significant importance for the development of new functional materials based on PLA with improved heat-resistant and mechanical properties.

Keywords: polylactide, carbon nanotubes, nanocomposites, differential scanning calorimetry, crystallization, thermal properties

INTRODUCTION

The development of nanotechnology has opened up broad prospects for the creation of highly effective materials with specified properties at the micro and nano level. In recent decades, special attention has been paid to polymer nanocomposites. Owing to the high surface area and unique physical properties of nanofillers, it is possible to substantially improve the properties of the base polymer, including the mechanical strength, thermal stability, thermal conductivity and electrical conductivity [1].

Among different types of nanofillers, carbon nanotubes (CNTs) are of particular interest, which possess outstanding mechanical (Young's modu-

lus of the order of terapascals), electrical and thermal conductivity properties. Their inclusion in polymer matrices allows the creation of new-generation nanocomposites that find applications in electronics, biomedicine, packaging, transport and energy [2]. However, achieving a uniform distribution of CNTs in the polymer, as well as ensuring strong interfacial adhesion, remain significant technological and scientific challenges [3].

Polylactic acid is an aliphatic polyester derived from renewable resources, predominantly lactic acid, produced by the fermentation of starches [4]. The overall chemical structure of PLA allows a degree of crystallinity, which is cru-

cial for its thermal properties. The degree of crystallinity in PLA plays an essential role in determining its glass transition temperature (T_g) and melting temperature (T_m). For example, a higher crystallinity correlates with a higher T_m , influencing the applicability of PLA in its thermal processing and end-use applications. Additionally, the T_g of PLA is typically around 40–65°C, and its T_m can reach approximately 160–185°C, depending on its molecular weight and thermal history [5]. Nevertheless, pure PLA has several limitations, such as low impact strength and poor thermal conductivity, which limits its widespread application in technically complex areas.

The creation of nanocomposites based on PLA with the addition of CNTs is one of the most promising ways to modify its physicochemical properties. In this case, the microstructural features of the material are critically important: the nature of the distribution of nanotubes in the matrix, their orientation, the degree of aggregation, as well as the interaction at the phase boundary [6]. These parameters directly influence the formation of heat transfer, mechanical properties and stability of the material during operation.

As has been shown in a number of studies, PLA has a slow crystallization rate [7, 8]. This feature makes PLA very resistant to heating-cooling processes. In this case, the values of temperature transitions must lie within the cooling fluid of the polymer matrix.

Crystallinity is another property closely tied to the processing conditions of polymer nanocomposites [9]. The incorporation of CNTs has been shown to refine the crystallinity of the surrounding polymer matrix, which subsequently affects the thermal properties. As illustrated by Lin et al., the thermal conductivity of nanocomposites can be shaped by the interfacial interactions between the polymer and fillers, with the crystalline structure of the polymer matrix significantly influencing the thermal transitions [10]. While these findings emphasize the relation between the crystalline structure and thermal properties, it remains crucial to explore how variations in processing can affect these interactions.

The thermal history of a polymer material plays a crucial role in the formation of its microstructure and, consequently, its performance properties. This aspect is particularly crucial in the case of polymer nanocomposites, where the thermal regime directly affects the distribution of the nanofiller, the crystallinity of the polymer matrix, and interphase interactions [11]. Moreover, the dispersion of nanofillers like CNTs is influenced by the thermal history during processing, which affects the resulting packing density and interlayer interactions within the polymer matrix, thereby significantly altering the thermal conductivity. For example, Nevalainen et al. highlight that the entangled hierarchical structures of CNTs in a polypropylene matrix can lead to poor dispersion, impacting both the thermal conductivity and mechanical properties overall [12]. Such findings reiterate that the mechanical and thermal attributes of nanocomposites are deeply sensitive to the processing parameters, including the temperature and mixing conditions, thereby affecting their crystallinity and thermal transitions. At the same time, excessively high temperatures or prolonged thermal exposure can cause aggregation of the nanofiller and the destruction of interfacial adhesion, resulting in a reduction in the functional properties of the material.

The influence of prehistory on the thermal properties, temperature transitions, and crystallinity in polymer nanocomposites filled with carbon nanotubes is a critical area of research, underscoring the complex relationships between the fabrication history, filler dispersion, and the resultant material properties. The aim of this work is a comprehensive study of the microstructure and features of the thermophysical properties of polylactide nanocomposites filled with carbon nanotubes.

EXPERIMENTAL PART

Materials

High purity polylactic acid (PLA), manufactured by Musashino Chemical Laboratory, LTD, was chosen as the polymer matrix. At $T = 20^\circ\text{C}$, PLA is a solid with a density of $\rho = 1250 \text{ kg/m}^3$.

Before use, the polymer was dehydrated by heating for four hours at 80°C.

Multi-walled CNTs (MWCNTs) manufactured by Spetsmash, LTD (Ukraine), were made of ethylene by chemical vapor deposition. The content of mineral impurities was no more than 0.1%. The specific surface area was 190 m²/g, the outer diameter was 20 nm, and the length was (5÷10) µm [13].

Preparation of nanocomposite polymer materials

To prepare the materials for the study, the polymer was dissolved in a mixture of solvents: dimethyl sulfoxide and dimethylacetamide (1:1), which gave a 10% polymer solution. The nanocomposites were prepared by ultrasonic mixing in the polymer solution utilizing an ultrasonic disperser UZD A-650 (Ukraine). Dispersion was performed continuously for 5 min at the frequency of 22 kHz; the ultrasound power was 300 W. The CNT content was varied within 0.1 ÷ 1.5 wt% (hereinafter %). Following ultrasonic treatment, the resulting mixture was poured onto a glass surface and dried until the solvents were completely removed at a temperature of 80-100°C.

Research methods

Transmitted light micrographs of the polymer-MWCNT systems were obtained by means of a Si-geta light microscope equipped with a DMC-800 digital video eyepiece and an image processing system. The samples under study were mounted in a glass cell with a thickness of 80 µm.

The study of the temperature dependence of the heat flow was conducted in a dry air atmosphere of nitrogen in the temperature range from –100°C to 150°C at the heating rate of 10°C/min by differential scanning calorimetry on a DSC-60 Plus device (Shimadzu, Japan). The absolute error in determining the temperature of the phase and relaxation transitions was 0.1°C.

RESULTS AND DISCUSSION

The thermal behavior of the polymer nanocomposites plays a crucial role in determining their processing conditions, stability, and functional properties. Differential scanning calorimetry (DSC) is one of the most informative methods for studying thermal transitions in nanocomposite systems.

In nanocomposites based on polylactic acid filled with carbon nanotubes, the presence of nanofillers can significantly affect these temperature transitions. CNTs, due to their high aspect ratio, surface energy, and potential nucleation ability, can change the kinetics of PLA crystallization, promote or inhibit crystal growth, and change the mobility of polymer chains.

To study the effect of the filler on the thermophysical properties of PLA-based nanocomposites, the system was investigated by DSC with two heating-cooling cycles. The first heating cycle was used to determine the real state of the samples and monitor the physical aging of the material. The second heating scan was carried out to study the properties of the materials after erasing the thermal history by melt crystallization.

Analysis of the DSC thermograms for the unfilled PLA and the nanocomposites based on it with different carbon nanotube contents demonstrated significant differences between the first and second heating cycles, which is directly related to the thermal history of the samples.

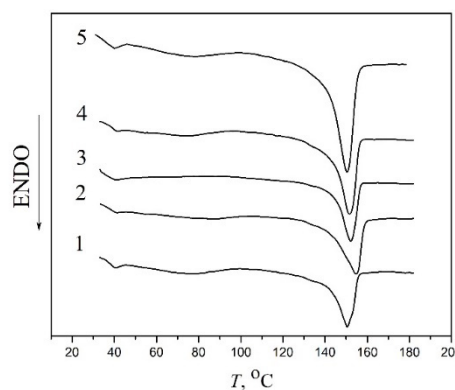


Fig. 1. DSC curves (first heating) for systems based on PLA (1) filled with 0.25% (2), 0.5% (3), 1% (4) and 1.5% (5) MWCNTs

Fig. 1 shows the DSC curves obtained as a result of the first scan of the PLA-MWCNT systems. The graphs of the first heating record temperature transitions reflect the structure of the material formed during the manufacturing and storage of the samples. PLA and its nanocomposites are characterized by the presence of a glass transition phase (characterized by temperature T_g), associated with the transition of amorphous regions from the glassy state to the viscous-fluid state. This transition is observed for all the studied systems in the temperature range from 30°C to 50°C. Another temperature transition that is clearly visible in the graphs is melting (characterized by temperature T_m), caused by the destruction of crystalline regions formed during the manufacturing of the materials.

Therefore, in this state, the material retains residual crystallinity, the level of which is determined by the cooling conditions after processing. During the preparation process, the nanocomposite material samples were dried for a long period of time, hence the PLA crystallites had time to form. The degree of crystallinity of the nanocomposites based on PLA and MWCNTs was calculated based on the relationship of heat flow and temperature using the equation:

$$\chi_{cr} = \frac{\Delta H_m}{\Delta H_{m,c}} \cdot 100\% \quad (1)$$

where ΔH_m is the measured melting enthalpy, $\Delta H_{m,c}$ is the melting enthalpy of 100% crystalline polymer (for PLA $\Delta H_m^0 = 93$ J/g [14]).

Table 1. Thermal parameters for PLA-MWCNT nanocomposites

MWCNT content	1 st scan				2 nd scan					
	T_g , °C	T_m , °C	ΔH_m , J/g	χ_{cr} , %	T_g , °C	T_{cc} , °C	ΔH_{cc} , J/g	T_m , °C	ΔH_m , J/g	χ_{cr} , %
0	35.9	150.5	26.6	24.6	58.0	110.9	22.5	149.7	17.8	5.0
0.25	37.3	153.3	23.7	25.5	56.9	109.7	21.8	148.7	19.5	2.5
0.5	37.1	152.0	27.1	29.1	56.4	108.1	21.9	148.1	21.4	0.5
1.0	37.3	151.5	24.4	26.2	57.2	108.3	20.8	148.7	18.9	1.9
1.5	37.8	150.4	21.7	23.4	56.9	109.0	22.5	148.5	21.8	0.7

Fig. 2 shows the dependence of the melting temperatures and degree of crystallinity on the content of nanotubes.

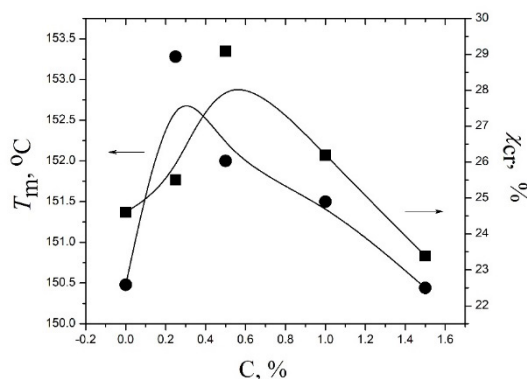


Fig. 2. Dependences of melting point and degree of crystallinity on the content of carbon nanotubes for polylactide-based nanocomposites.

The melting point and degree of crystallinity of polylactide demonstrate a characteristic nonlinear dependence with increasing carbon nanotube content. With an increase in the MWCNT concentration from 0% to 0.5%, growth of these parameters is observed, after which, with a further increment in the nanofiller content, their decrease occurs to values close to the initial ones.

The rise in the melting point and degree of crystallinity at low MWCNT concentrations may be due to the action of nanotubes as nucleating agents [15]. MWCNTs contribute to the ordering of PLA macromolecular chains, which facilitates their packing into crystalline domains and raises the energy barrier for melting. Nonetheless, with

a MWCNT content exceeding 0.5%, the agglomeration of nanotubes occurs, which reduces their effective interaction with the polymer matrix. This leads to the formation of defects in the crystal structure, a drop in the degree of crystallinity and a corresponding decrease in the melting temperature.

The obtained results are consistent with the known phenomena characteristics of polymer nanocomposites containing MWCNTs [16, 17], and confirm the importance of optimal selection of the nanofiller concentration to achieve improved physical and mechanical properties of the polymer material.

After the first heating, the PLA-MWCNT samples were cooled to room temperature. It occurred that the cooling rate under the DSC analysis conditions is insufficient for the effective crystallization of PLA. This is a consequence of its slow kinetics of crystal formation, especially in the absence of high concentrations of nucleating agents. As a result, after cooling the material is mainly in an amorphous state. This is evidenced by the second heating curves shown in Fig. 3 for the PLA-MWCNT systems.

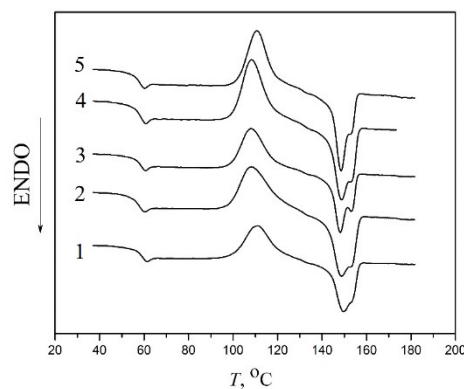


Fig. 3. DSC curves (second heating) for systems based on PLA (1) filled with 0.25% (2), 0.5% (3), 1% (4) and 1.5% (5) MWCNTs.

From Fig. 3 it is seen that during the second heating, an additional endothermic transition is observed in the thermograms, which is absent in the first cycle – cold-crystallization. This process accounts for the recrystallization of amorphous areas upon heating, when macromolecules gain suf-

ficient mobility to organize into crystalline structures. This phenomenon is characteristic of PLA because of its weak tendency to crystallize upon cooling, but active crystal formation upon reheating [18]. In addition, a feature of the second heating is the appearance of bimodal melting peaks. They indicate the presence of crystals of varying degrees of perfection. The first peak is associated with the melting of less stable, defective crystals formed during the cold-crystallization process. The second peak results from the melting of more stable crystals that could have reorganized or formed during the heating process after cold-crystallization [19].

Table 1 shows the values of the enthalpies of melting and cold crystallization. The enthalpy of melting (ΔH_m) indicates how much energy is required to destroy all the crystalline structures upon heating. The enthalpy of cold crystallization (ΔH_{cc}), on the contrary, reflects the energy released during the formation of new crystals from the amorphous phase upon heating.

For these systems, the degree of crystallinity of the material can be calculated by determining the difference between the enthalpy of melting and cold crystallization, since during the second heating it was recorded that part of the material first crystallizes and then melts.

Taking into account these effects, the degree of crystallinity of the system is determined by the following formula [20]:

$$\chi_{cr} = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100\% \quad (2)$$

The calculated values of the degree of crystallinity are given in Table 1. It is worth noting that the difference between the enthalpy values ($\Delta H_m - \Delta H_{cc}$) is minimal, and the degree of crystallinity obtained from the results of the second heating is very close to zero. This effect can be explained by the fact that at the beginning of the second heating the sample was almost completely amorphous. This phenomenon can be attributed to a certain reorganization of the MWCNTs in the

system, which after cooling, have a different effect on the polymer matrix.

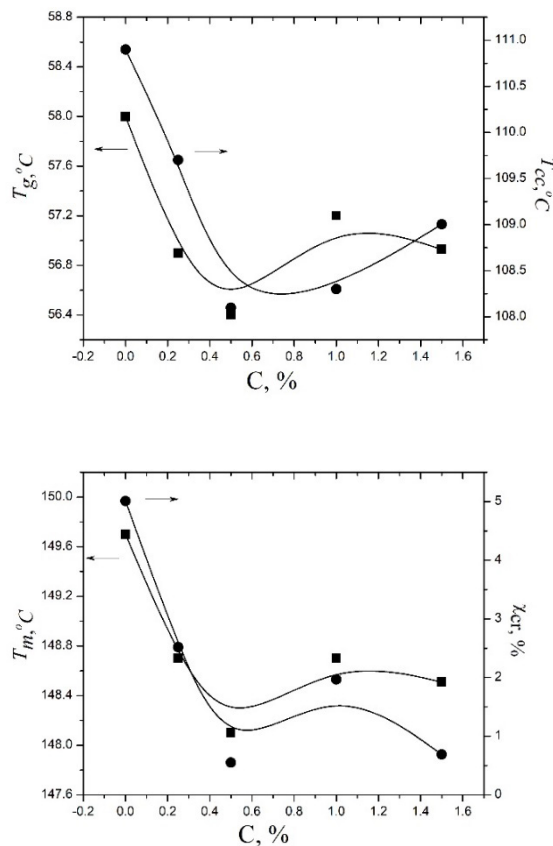


Fig. 4. Dependences of glass transition, cold crystallization and melting temperatures, as well as degree of crystallinity on carbon nanotube content for polylactide-based nanocomposites (based on second heating results)

To understand this effect in detail, we analyzed the dependences of the glass transition, cold crystallization and melting temperatures, as well as the degree of crystallinity on the MWCNT content (Fig. 4), obtained as a result of the second heating. The DSC data demonstrate a significant difference in the behavior of key thermal parameters between the first and second heating. During the first heating, these parameters initially rise with the MWCNT content, reach a maximum at 0.5%, and decrease with a further increment in concentration (Fig. 2). However, during the second heating, the opposite trend is observed. The parameters initially dwindle, reaching a minimum at 0.5% MWCNTs. A similar effect was observed for other polymer nanocomposites, where poorly

dispersed MWCNTs led to a drop in the transition temperatures as a consequence of increased polymer chain mobility [21]. After that, the corresponding parameters grow slightly or remain almost unchanged.

This phenomenon suggests that during cooling after the first heating, the MWCNTs undergo structural rearrangement. As discussed above, during the first heating, MWCNTs act as nucleating agents at low concentrations. After the first heating, during cooling, the MWCNTs may redistribute or partially aggregate, changing their role in the crystallization process. If they initially acted as nucleating agents, their rearrangement may disrupt the formation of an ordered crystalline structure during the next heating. This structural change may explain the reverse trend observed during the second heating, where the MWCNTs now act as defects that hinder crystallization rather than promote it. In addition, the presence of MWCNTs during the second heating may interfere with the recrystallization of polymer chains, disrupting their ability to form well-ordered crystalline regions. This may be due to the increased interactions between MWCNTs and polymer chains after thermal cycling, which reduces chain mobility and, as a result, suppresses crystallinity.

The assumption of the structural rearrangement of MWCNTs in the PLA matrix after reheating is confirmed by light microscopy data. Fig. 5 presents micrographs of the PLA-MWCNT systems before and after reheating. Fig. 5 shows that at a low nanotube content (0.1%), the MWCNTs are distributed more evenly in the case before heating. With such a distribution, they can act as nucleating agents for the formation of the PLA crystalline phase. After heating, a small aggregation of MWCNTs is observed, which may prevent the formation of crystals from the PLA macromolecules. Similar behavior before and after reheating is observed for systems with a higher MWCNT content (0.5 and 1%). After reheating, larger aggregates are visually observed, which may affect the repeated recrystallization of PLA chains after glass transition.

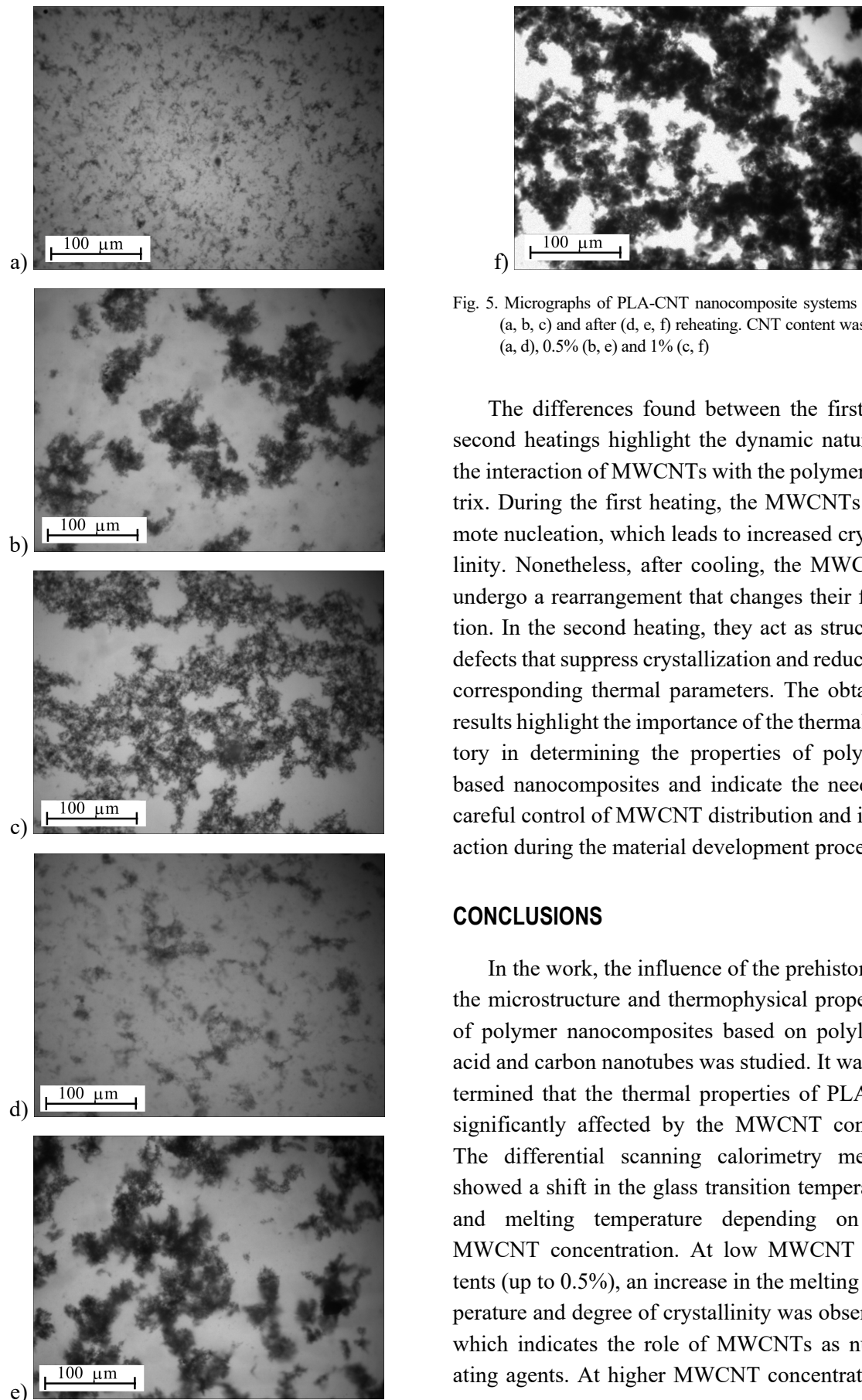


Fig. 5. Micrographs of PLA-CNT nanocomposite systems before (a, b, c) and after (d, e, f) reheating. CNT content was 0.1% (a, d), 0.5% (b, e) and 1% (c, f)

The differences found between the first and second heatings highlight the dynamic nature of the interaction of MWCNTs with the polymer matrix. During the first heating, the MWCNTs promote nucleation, which leads to increased crystallinity. Nonetheless, after cooling, the MWCNTs undergo a rearrangement that changes their function. In the second heating, they act as structural defects that suppress crystallization and reduce the corresponding thermal parameters. The obtained results highlight the importance of the thermal history in determining the properties of polymer-based nanocomposites and indicate the need for careful control of MWCNT distribution and interaction during the material development process.

CONCLUSIONS

In the work, the influence of the prehistory on the microstructure and thermophysical properties of polymer nanocomposites based on polylactic acid and carbon nanotubes was studied. It was determined that the thermal properties of PLA are significantly affected by the MWCNT content. The differential scanning calorimetry method showed a shift in the glass transition temperature and melting temperature depending on the MWCNT concentration. At low MWCNT contents (up to 0.5%), an increase in the melting temperature and degree of crystallinity was observed, which indicates the role of MWCNTs as nucleating agents. At higher MWCNT concentrations,

their aggregation occurred, which negatively affects these parameters. It was shown that after cooling, the samples remain amorphous, which results from the slow kinetics of PLA crystallization. Cold crystallization was observed in the thermograms of the second heating, indicating active recrystallization of amorphous areas upon reheating. The presence of bimodal melting peaks was also found in the thermograms of the second heating, indicating the formation of crystals with varying degrees of perfection: less stable crystals formed during cold-crystallization and more stable crystals formed as a result of further reorganization of the structure.

It was found that during the first heating, the MWCNTs effectively act as nucleation agents, but after reheating they no longer perform this function. On the contrary, MWCNTs can become defects that prevent the formation of an ordered crystalline structure. Light microscopy confirmed the presence of MWCNT aggregation at higher concentrations, which negatively affects crystallization and is consistent with the DSC results. It was confirmed that effective control over the uniform distribution of MWCNTs in the matrix is a key factor for achieving optimal thermoplastic and mechanical properties of PLA nanocomposites.

Thus, the results of the study demonstrate that the thermal behavior of PLA nanocomposites largely depends on the content and dispersion of carbon nanotubes, as well as on the prehistory, which should be taken into account when developing new materials with improved thermomechanical properties.

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