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Effects of nanofillers and sample dimensions on the mechanical properties of injection-molded polylactide nanocomposites

RAPID COMMUNICATION

Summary — Montmorillonite nanofillers (Cloisite 30B and Nanofil 2), added in the amounts of 3 and 5 weight parts to 100 weight parts of polylactide matrix, negligibly change mechanical properties of the resulting nanocomposites under the preparation conditions applied. Poly(ϵ -caprolactone), added in the amount of 20 weight parts, considerably reduces tensile strength of the nanocomposites and its use is justified only when the impact strength of the products has to be increased. The sample thickness (the values of 2 and 4 mm were used, according to operative standards) significantly determines the tensile strength, tensile stress at break, and tensile strain at maximal stress of the material.

Keywords: nanocomposites, polylactide, mechanical properties, sample thickness.

WPLYW NANONAPEŁNIACZY I WYMIARÓW PRÓBEK NA WYTRZYMAŁOŚĆ MECHANICZNĄ WTRYSKIWANYCH NANOKOMPOZYTÓW POLILAKTYDOWYCH

Streszczenie — Nanonapełniacze montmorillonitowe (Cloisite 30B lub Nanofil 2), dodawane w ilościach 3 i 5 cz. mas. do 100 cz. mas. osnowy polilaktydowej, w niewielkim stopniu zmieniają wytrzymałość mechaniczną wytworzonych nanokompozytów (rys. 1—3). Natomiast poli(ϵ -kaprolakton), dodawany w ilości 20 cz. mas., znacznie zmniejsza wytrzymałość na rozciąganie tych nanokompozytów. Z tego powodu jego stosowanie może być uzasadnione wówczas, gdy należy zwiększyć udurowienie materiału. Badając próbki o grubościach 2 i 4 mm (wymiaru te są zgodne z obowiązującymi normami) stwierdzono, że grubość próbek istotnie wpływa na wyniki badań wytrzymałości na rozciąganie, naprężenia przy zerwaniu i wydłużenia względnego przy maksymalnym naprężeniu.

Słowa kluczowe: nanokompozyty, polilaktyd, właściwości mechaniczne, grubość próbek.

Mechanical properties determined under static tension are among basic quantities characterizing the polymeric materials. They have to be examined according to the Polish Standards: PN-EN ISO 527-1:1998, PN-EN ISO 527-2:1998, and PN-EN ISO 527-3:1998. These standards include nine tensile rates and several types of samples of various shapes and dimensions. As a consequence, different ways to perform measurements are available, which, however, creates some difficulties when the results obtained in various laboratories are compared directly.

The choice of the tensile rate significantly affects the results obtained under static tension, because it may influence the way how the samples are deformed and broken [1, 2]. The higher the tensile rate, the larger the amount of heat dissipated in the material. At the same time, the deformation process transforms from the isothermal to adiabatic one, which affects the measured

values [3]. For example, the tensile stress at yield of polypropylene as determined at the tensile rate of 1000 mm/min, is by about 43 % higher than that at 1 mm/min [4].

Mass fractions of individual composite components and kind of the applied compatibilizers considerably influence the properties determined under static tension [5, 6]. Also, the procedure of sample preparation has a clear effect on structural characteristics of the products, including crystallinity, crystallite size, orientation of polymer macromolecules, and the number of structural defects. Therefore, temperature, pressure, and rate of injection (or extrusion) and rate (or time) of cooling of the samples significantly affects the results obtained under static tension [7, 8].

The papers on investigation of the effect of thickness of polymeric nanocomposite samples on their mechanical properties are relatively scarce. As reported, the tensile strength of the nanocomposite containing montmorillonite and polyamide-6 (PA 6) decreases as the sample thickness increases from 0.75 to 2 mm [9]. We have earlier found that the thickness of the samples of polyolefines, polystyrene, and poly(ethylene terephthalate) notably influences their mechanical properties [10].

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In the present work, we discuss tensile strength (σ_M), tensile stress at break (σ_B), and tensile strain (ϵ_M) at tensile stress of the nanocomposites composed, alternatively, of two montmorillonite nanofillers, poly(ϵ -caprolactone) as a compatibilizer, and the polylactide matrix. The effects of composition and standard thickness of the sample on the mechanical properties were examined.

The choice of subject and a range of our investigations results from the growing significance of polylactide nanocomposites, containing montmorillonite fillers [11–13].

EXPERIMENTAL

Materials

The studied samples were prepared from the following materials:

— polylactide (PLA) type 2002D (NatureWorks®, USA), characterized by melt flow rate $MFR = 5\text{--}7$ g/10 min (2.16 kg, 210 °C) and density $d = 1.24$ g/cm³, was served as a polymer matrix of the studied nanocomposites;

— Cloisite 30B (C) or Nanofil 2 (N) (both obtained from Southern Clay Products, USA), which were modified by ion exchange and used as montmorillonite nanofillers;

— poly(ϵ -caprolactone) (PCL) type CAPA 6800 (Solvay Caprolactones, UK), with $MFR = 3$ g/10 min (2.16 kg, 160 °C) and $d = 1.15$ g/cm³, was applied as a compatibilizer.

The nanofillers and compatibilizer are referred to additives.

Sample preparation and measurements

The granulated materials containing virgin PLA or PLA with C or N with or without addition of PCL in amount specified in Table 1 were extruded. These materials were used to prepare the samples by injection molding. The samples, denoted with the same symbols as those of the original materials, were dumbbell-shaped, 2 or 4 mm thick, and prepared in accordance to appropriate standards (PN-EN ISO 527-1:1998 and

PN-EN ISO 527-2:1998), using a laboratory injection molding press Plus 35/75 UNILOG B2 (Battenfeld GmbH, Germany) with a 22 mm screw, 38 cm³ injection volume, and 200 MPa nominal injection pressure.

Determination of the material strength under static tension was performed using TIRATEST 27025 (TIRA GmbH, Germany) tensile testing machine. The testing speed for each sample was 50 mm/min. Ten samples of each nanocomposite were made and an arithmetic mean of ten individual measurements was assumed as a final result of the determination of a given quantity. When comparing the mean values of the quantities, established for the samples of the two thicknesses, the test of significance for the respective two means was performed, assuming the significance level $\alpha = 0.05$ and applying the Snedecor's F-test and Student's t-test.

RESULTS AND DISCUSSION

The results of investigation of σ_M and their standard deviations are shown in Fig. 1. The 2- and 4-mm thick samples are denoted as A and B, respectively. The results indicate that addition 3 or 5 weight parts of C, likewise as 3 weight parts of N does not affect tensile strength of the nanocomposites. The results of the Student's t-test are especially decisive; they do not enable one to reject the null hypothesis about equality of the σ_M values for

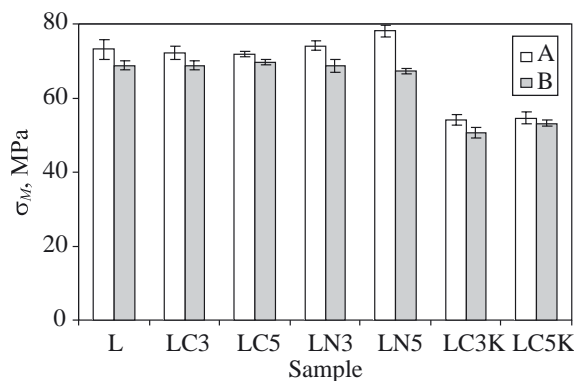


Fig. 1. Tensile strength (σ_M) of polylactide nanocomposites samples of thicknesses of 2 mm (A) and 4 mm (B); for samples symbols, see Table 1

Table 1. Compositions of nanocomposites samples prepared

Symbols of a sample	Content of a component, weight parts			
	PLA	C	N	PCL
L	100	—	—	—
LC3	100	3	—	—
LC5	100	5	—	—
LN3	100	—	3	—
LN5	100	—	5	—
LC3K	100	3	—	20
LC5K	100	5	—	20

the following sample pairs: L and LC3, L and LC5, and L and LN3. The negligible effect of the nanofillers may result from their inappropriate dispersion in PLA or too small content. On the other hand, the addition of 5 weight parts of N essentially influences the σ_M values of LN5, which are higher by 6.8 % (sample A) or lower by 2 % (sample B) as compared to σ_M values of L. The explanation of different effects of N nanofiller in the samples varying in thickness requires further investigation.

The σ_M values of LC3K and LC5K are considerably lower (by ca. 26 % for both A and B samples) in relation

to σ_M values of L. Presumably, the macromolecules of PCL compatibilizer penetrate the space between PLA macromolecules due to mutual attraction forces among functional groups of these polymers. The penetration leads probably to an increase in the distance and decrease in the van der Waals forces between the PLA macromolecules, which causes reduction in strength of the nanocomposites.

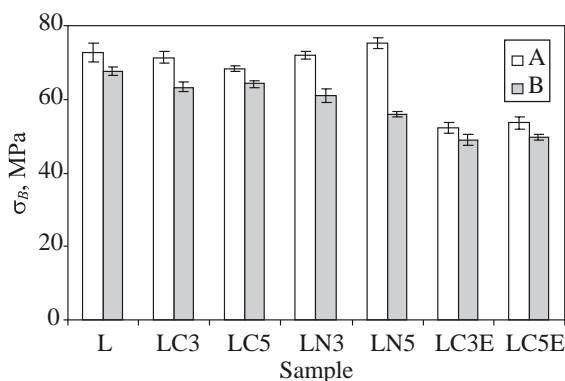


Fig. 2. Tensile stress at break (σ_B) of poly lactide nanocomposites samples of thicknesses of 2 mm (A) and 4 mm (B); for samples symbols, see Table 1

In Figure 2 the results of measurements of σ_B are presented. The σ_B values of samples A essentially do not change under addition 3 weight parts of C or N. However, addition 5 weight parts of C reduces σ_B by 5.7 % and that of N enhances σ_B by 3.6 %. The drop in σ_B caused by the addition of PCL is significant and similar for LC3K and LC5K *i.e.* 26.8 and 21.8 %, respectively. On the other hand, the σ_B values of all B samples decrease due to the additives while the influence of PCL is the highest (22.7 %), as in A samples.

Figure 3 illustrates the results of ϵ_M investigations. The ϵ_M values of all the studied samples decrease due to the additives. These reductions are rather small — up to 1.4 % of the initial length of the samples. Tensile strain at

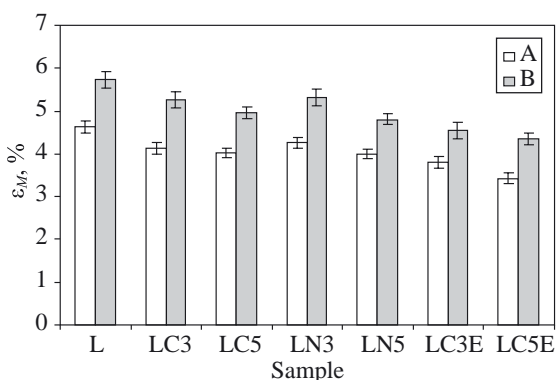


Fig. 3. Tensile strain at maximal stress (ϵ_M) of poly lactide nanocomposites samples of thicknesses of 2 mm (A) and 4 mm (B); for samples symbols, see Table 1

break is only slightly larger than ϵ_M for all the samples; thus, that quantity is not analysed in this paper.

The results of the statistical test show that the differences between individual values determined for A and B samples are significant (Figs. 1—3). Independently on the kind and content of the additives, the σ_M and σ_B values of A samples are larger than those of B samples by 2—16 and 7—34 %, respectively, while the ϵ_M values of A samples are smaller than those of B samples by 16—21%.

CONCLUSIONS

Tensile strength of most of the studied nanocomposites changes insignificantly due to montmorillonite nanofillers (Cloisite 30B or Nanofil 2) added to the PLA matrix in the amounts of 3 or 5 weight parts. Therefore, these compounds are very important materials for the improvement of the barrier properties of the nanocomposites. On the other hand, PCL considerably reduces tensile strength of the PLA nanocomposites. Its use is justified only when impact strength of these materials has to be increased.

Tensile stress at break of all the studied samples is lower than tensile strength, the differences being larger for thicker samples. However, they are insignificant to functional quality of the materials.

Tensile strain at tensile stress and tensile strain at break insignificantly differ each from other, being 3.5—7.5 % of the initial length of the samples.

The sample thickness considerably influences the mechanical properties of the materials under investigation. Tensile strength and tensile stress at break are higher for thinner samples while tensile strain at maximal stress values are higher for the thicker ones.

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