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DEGRADATION OF NANOCLAY-FILLED POLYLACTIDE COMPOSITES

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Abstract: Nanoclay-filled polylactide (PLA 3051D) composite materials were tested in this study and their capacity for degradation was investigated. Activated and lyophilized smectite clay was used. The filler, its morphology, and grain size distribution were characterized by the use of transmission electron microscopy, scanning electron microscopy, and the dynamic light scattering technique. Samples of pure polylactide and polylactide filled with 3% wt., 5% wt., and 10% wt. of nanoclay in subsequent series were obtained by injection molding. The optimum amount of the filler in the nanocomposites was evaluated based on an assessment of mechanical properties as well as capacity to degrade. The 3% wt. mass fraction of nanofiller in the polylactide matrix was found to be the most effective in enhancement of both tensile strength (R_M) and Young's Modulus (E). It was also reported that polylactide nanocomposites filled with 3% wt. of smectite clay were characterized by the highest decrease in molecular mass of the matrix polymer after degradation tests (6 weeks incubation in water at 80°C). The observed decrease in degradation time and the overall changes distinguished in the nanocomposite structure suggest the potential for application of the material in the packaging industry.

Keywords: *nanocomposite materials, food packaging, polymer, smectite clay*

Introduction

Polymers, polymer blends, and polymer composites (i.e. polymers filled with fibers or particles) are very often used as conventional food packaging materials. However, some drawbacks related to their use, such as quality of packaging (mechanical proper-

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ties, suitability, and durability in operating conditions), potential influence on food, and total costs of production, guarantee an ever-growing need for new kinds of materials with improved properties (Appendini and Hotchkiss, 2002; Auras et al., 2004; Drumright et al., 2000; Platt, 2006). Polymer-based nanocomposites are among the most promising materials, which nowadays are subjected to a great deal of research all over the world. A relatively small amount of nanofiller (up to 10%) with a high level of refinement (at least one dimension below 100 nm) results in the creation of a filler-matrix interface with surface development several times higher than traditional composite materials. This enables either second-order bonding or electrostatic interactions, and influences physicochemical/mechanical (higher stiffness and strength), thermal (better stability), and chemical (resistance to solvents) properties of materials and their capacity for controlled degradation. All these features argue for the extension of their range of application in the packaging industry (Alexandre and Dubois, 2000; Pfaendner, 2010; Sinha Ray and Bousmina, 2005; Sorrentino et al., 2007).

The use of nanocomposite materials for food packaging applications enables the design and manufacture of materials with improved properties compared to conventional materials (Avella et al., 2005; Murariu et al., 2010). Enhancements include improved stability over time (*in vitro* condition), better barrier properties, and lower spoilage (Matusik et al. 2011). Among others, one may name improved mechanical properties and durability. The first may be achieved by the introduction of nanofiller into a polymer matrix and by very good overall homogenization of the material. The second feature, durability, is the result of the limited release of water into the bulk of the polymer matrix, considered a step in promoting the hydrolysis process (Solarski et al., 2008; Tsuji and Ikarashi, 2004). This promotion is decelerated due to the presence of nanoparticles such as clays, silica, carbon nanotubes and others in the polymer matrix. The most promising nanofillers acting as water storage materials in this case are clays: montmorillonite (MMT), bentonite, kaolinite (Fukushima et al., 2010; Sinha Ray et al., 2003; Tsuji et al., 1998).

This paper presents the results of the study on properties of nanocomposite materials based on degradable polylactide modified by different amount of nanofillers (smectite clay).

Experimental

As a degradable matrix for preparation of nanocomposite samples, poly-L-lactide (PLA 3051D), manufactured by Nature Works, was used. The manufacturer has provided typical parameters of PLA pertinent to the molding process, as shown in Table 1. The PLA was modified with a nanometric smectite clay filler (SM), Veegum F, manufactured by R.T. Vanderbilt Company, Inc.

Table 1. Producer data sheet for PLA

Properties of PLA 3051D	
Melt temperature	200°C
Feed temperature	165°C
Glass transition temperature	55–65°C
Screw speed	100–175 rpm
Density	1.24 g/dm^3
Relative viscosity	3–3.5
Molecular mass	25 kDa

Nanocomposite samples were prepared in two stages. The initial stage of the experiment consisted of modifying smectite clay by chemical treatment, followed by exfoliation. The effects of this procedure were analyzed by the DLS method. Smectite was treated with ionic activation in 2 M NaCl solution, centrifuged, and rinsed up to the extinction of chlorine ion reaction. The obtained nanofiller product was lyophilized in the subsequent step, and the morphology of the particles was characterized using the transmission electron microscope TEM (JEOL JEM-1011). Both types of powders, i.e. pure and modified smectite, were dispersed in isopropanol and covered with a carbon layer prior to observation. Samples prepared for SEM observations (Nova NanoSEM 200, FEI) were also covered with a carbon layer. The smectite particle size distribution was evaluated by the dynamic light scattering method (Zetasizer Nano ZS, Malvern Instruments) in a water suspension at 25°C. Prior to measurement, the powder was mixed with water and homogenized with an ultrasonic horn.

In the next stage of the experiment, smectite clay powder was homogenized with PLA pellets. The nanoadditive, in amounts of 3, 5 or 10% wt., was added to a charge of polymer pellets and milled in a roller mill for 48 h. As a result, the smectite particles covered the polymer pellets, which then were used as a charge for the injection molding process. The nanocomposite samples (paddle-shaped 75×5×2 mm, following Polish Standard PN-EN ISO 527) were manufactured by the use of injection molding. The injection was carried out at 165°C under a pressure of 60 kg/cm^2 in a vertical injection molding machine (Multiplas).

The mechanical properties and the degradation ability of the nanocomposite were investigated. A standardized tensile test was used for determining mechanical properties such as tensile strength and Young's modulus according to ISO 527 standards by using the Instron 3367 testing machine. The extensometers were used for precise measurements of strain.

The degradation capacity of the nanocomposite materials filled with smectite clay in water environment was observed during the incubation (6 weeks/80°C/H_2O with an initial water pH of 6.35). Pure polylactide was used as a reference material in the study. All the samples were monitored for changes of pH in the immersion solution and viscosity of the polymer. The viscosity coefficient (η) of the materials was measured by the Hoppler method and calculated by equation (1) (Lunt, 1998; Tsuji, 2002).

$$\eta = k \quad \rho - \rho' \quad \cdot t \tag{1}$$

where: η – viscosity coefficient,
k – constant describing conditions of the experiment,
ρ – density of the ball material,
ρ' – density of the liquid phase,
t – flow time of the ball.

The nanocomposite materials were dissolved in DCM (dichloromethane, POCh Gliwice) without separating the nanofiller from the polymer solution. The initial concentration of the polymer solution was 0.1 g/cm^3.

The molecular mass of the polymer was evaluated according to the Mark-Houwnik equation (2) for a given polymer-solvent system (PLA/DCM; $K = 2.21 \cdot 10^{-4}$ cm^3/g, a = 0.77) (Lunt, 1998; Tsuji, 2002):

$$\eta = K \cdot M_n^a \tag{2}$$

where: K – coefficient characteristic for the PLA/DCM system,
M_n – molecular mass of the polymeric material,
a – constant describing conditions of the experiment.

Results and discussion

The base smectite powder was characterized by a strong tendency both to agglomerate and aggregate, which was clearly visible in SEM images (Fig. 1). The grain size distribution analysis showed monomodal distribution, in which aggregates of 600-750 nm in size dominate rather than separate single particles (Fig. 2).

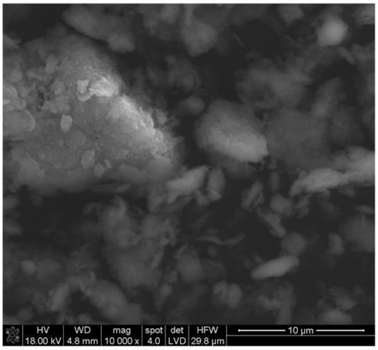

Fig. 1. SEM microphotograph of smectite clay powder before activation

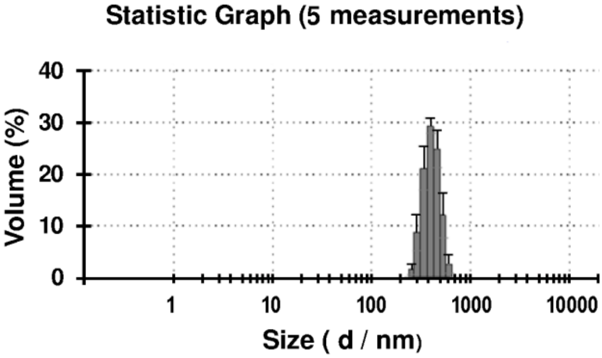

Fig. 2. Particle size distribution of smectite clay powder before activation

The thermal treatment process, followed by the lyophilization of the nanofiller, led to its activation and to the decomposition of the aggregates. A noticeable change in grain size distribution was reported after the activation process, with the resulting size of the filler particles estimated at about 80–100 nm (Fig. 4).

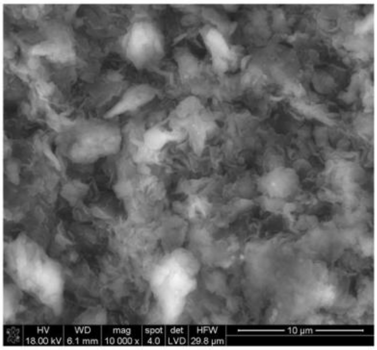

Fig. 3. SEM microphotograph of smectite

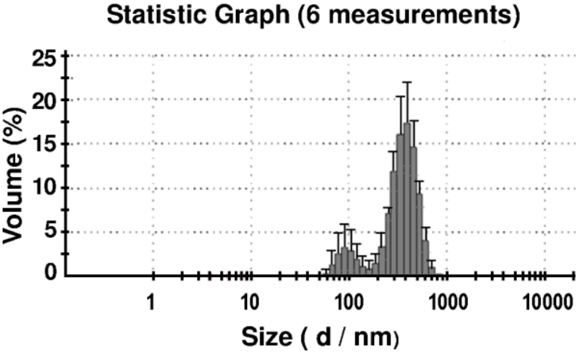

Fig. 4. Particle size distribution of smectite clay powder after activation

The bimodal distribution of the filler confirmed that aggregates were still present but their frequency was lowered by 30% compared to the base unmodified smectite clay powder. This was due to the lyophilization process which leads to “freezing” the chaotic structure of montmorillonite tiles. As a result, the grain morphology also changed (Fig. 3), leading to the appearance of the so-called texturization effect (the tendency of montmorillonite tiles to align parallel to one another) (Fukushima et al., 2009).

Thus, modification of the smectite powder influenced both powder morphology and powder grain size distribution. These changes were confirmed by TEM analysis, and the grain size distribution was reported to have become nanometric in its major dimensions, which had not been observed for the unmodified smectite powder before activation (Fig. 5).

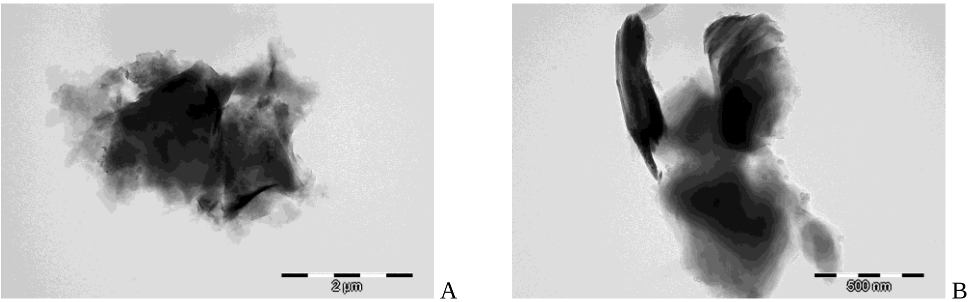

Fig. 5. TEM image of smectite clay powder before (A) and after (B) activation

Different mass fractions of smectite were used to evaluate its influence on the mechanical properties of the composites. This procedure was also designed to optimize the amount of smectite along with the mechanical performance. The results of mechanical tests indicated that 3% wt. of smectite in the polylactide matrix can be considered the optimum value. Addition of 5% wt. in the matrix resulted in mechanical performance similar to that of the unfilled polylactide, while 10% wt. led to a reduction of the mechanical strength reported during the tests. This behavior can be explained by the presence of agglomerates in the matrix which act as inclusions and can be treated as stress concentrators rather than reinforcements (Fig. 6). Considering changes in the overall stiffness, it can be stated that the presence of smectite filler in the matrix increases the value of Young's modulus of composites by about 10% compared to unfilled polylactide (PLA) (Fig. 7). This can be explained by the likely occurrence of electrostatic and/or second-order interactions between the filler and matrix. However, this must be clarified by further research.

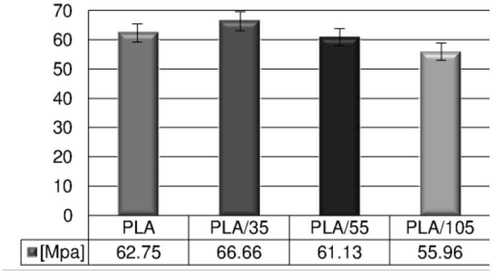

Fig. 6. Tensile strength results of nanocomposites and reference polylactide samples

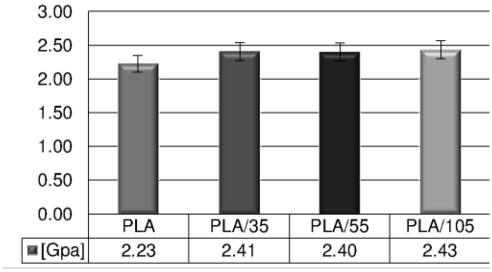

Fig. 7. Young's modulus results of nanocomposites and reference polylactide samples

Due to its potential application as degradable packaging material, the impact of filler content on degradation time of the composites was also evaluated. After 6 weeks of incubation in water at 80°C, structural degradation of all composites filled with smectite (excluding pure polylactide) was observed (Fig. 8). According to the literature, PLA degradation is a two-step process. In the initial step the polymer molecular weight decreases (bulk degradation) and in the second step degradation is observed both in bulk and on the surface of the PLA. During this step the molecular weight remained constant, but a weight loss in the material could be measured. For this reason a change in the coefficient of viscosity was also reported for all nanocomposite materials. It was shown that viscosity was strongly dependent on the amount of nanofiller. The most noticeable decrease in viscosity was observed for materials with 5% wt. and 3% wt. of nanofiller. This may indicate accelerated degradation in materials filled with 5% wt. and 3% wt. smectite, both in comparison to the pure polymer material and the composite filled with 10% wt. smectite (Table 2). This phenomenon was due to the modified (i.e. activated and lyophilized) nanofiller's strong absorption of water, so that hydrolytic degradation of the material (hydrolysis of polylactide) occurred not only at the surface but also within the bulk polymer matrix (Nakamura et al, 1989; Padua and Wang, 2012). This resulted in a decrease of the molecular weight of the polymer, which led in turn to a reduction in the durability and consistency of the material. The rate of hydrolysis strongly depends on environmental conditions: ions, pH and temperature. It was expected that the nanofiller present in the polymer matrix would serve as a reservoir of water. Additionally, degradation would be faster because of chlorine ions which might be present in the smectite after its chemical modification (NaCl). The nanofiller present in the polylactide matrix also changed the crystallinity of the nanocomposite materials, mostly by disordering the polymer chain. This effect hydrolyzed amorphous regions significantly faster than crystalline regions. An exceedingly low concentration of the polymer solution made it difficult to note results of viscosity correctly, so all samples were measured in the same way.

Table 2. Viscosity and molecular weight of the nanocomposite materials and the reference polymer after incubation in *in vitro* conditions

Materials	Initial polymer concentration [g/100 dm^3]	Viscosity coefficient, η [Pa·s]	Molecular weight, Mn [kDa]
PLA	0.01	0.78	20.0
PLA/3SM	0.01	0.45	12.0
PLA/5SM	0.01	0.55	7.7
PLA/10SM	0.01	0.74	4.4

During the durability experiment, the immersion medium (water) of the nanocomposite samples significantly changed pH, from a starting value of 6.35 to 6.05 by the end of the test. Probably hydroxyl ions migrated inside the smectite structure, or chlorine ions were released from the smectite and influenced the pH of the medium. The degradation of the polymer matrix was much more significant above its glass transition temperature, i.e. 65°C (an incubation in *in vitro* conditions was performed at 80°C). The duration time of the experiment (6 weeks/80°C) was enough to destroy the nanocomposite materials, a phenomenon not observed in the case of the pure polymer samples (Fig. 8). During the test all nanocomposite materials were completely degraded. Hence the weight loss could not be measured.

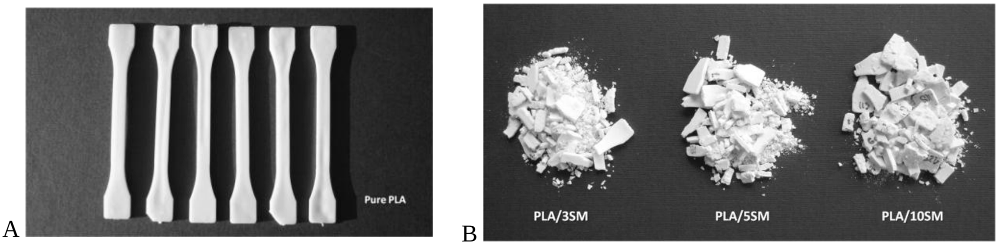

Fig. 8. Macroscopic changes after 6 weeks incubation: (A) limited degradation of pure polylactide samples, (B) excessive degradation of smectite-filled polylactide

Conclusions

Chemical modification, i.e. the activation and the lyophilization of a nanofiller (smectite), favorably affected its structural form by increasing its surface development and the number of active chemical groups, which led to improved dispersion within the polymer matrix (PLA). The presence of the activated nanofiller improved the strength of the nanocomposite materials and their Young's modulus (overall stiffness). The best material properties were achieved for the nanocomposite material filled with 3% wt. of smectite. The greater the amount of the nanofiller, the faster their hydrolysis was, but the presence of the nanofiller accelerated the overall degradation of the material. The nanofiller's presence accelerated the overall degradation of the material. As a result, a dramatic decrease was observed in the mass of material, followed by macroscopic disintegration. Good strength, in combination with a shorter disintegration time, make the nanocomposites potential candidates for an application in the packaging industry.

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