Analysis of the Decomposition using the Short Degradation Technique of Polylactic Acid/Halloysite Nanotube Biocomposites

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Abstract. The article presents results on the decomposition of polylactic acid (PLA)/halloysite nanotube (HNT) biocomposites. Experiments were carried out in laboratory conditions simulating composting in the industrial pile using the so-called short degradation method. In this paper, the effects of the composting process (duration from 30 to 90 days) on the behavior of PLA/HNT composites were studied. In addition, the selected physicochemical properties of PLA/HNTs biocomposites such as the average molecular weight were investigated. The results obtained confirmed the viability of composting PLA with halloysite which contributes to the reduction of plastic waste and the use of this material in technological applications.

1 Introduction

Polymer Matrix Composites (PMC) can be an extremely beneficial solution in many aspects of engineering technology [1-4]. However, they can also significantly threaten the natural environment. Lau et al. identified the main problems related to the exploitation of polymer composites [5-6]. It was found, that some fiber-reinforced polymer composites, e.g. carbon fibers are too strength and therefore difficult to grinding and decomposition. The cost of production of polymeric materials is sometimes too high. Also, recycling of composite materials is very difficult due to the toxins released during the decomposition process and the long-time of their decomposition [6-10]. Composite materials are difficult to recycle due to the heterogeneous hybrid structure [10]. In addition, the decomposition process can take place in a completely natural way, such as under the influence of temperature, humidity, sunlight and sea water. Therefore, contamination with waste from composites is very harmful to the natural environment and worries many researchers [6, 8-11], who try to solve the problem of utilization of polymer composites.
For example, Li et al. described the dangers of the huge amount of litter in the seas and oceans. They have analysed [8] the potential absorption of hydrophobic pollutants resulting from the degradation of PMC. Yangxiang Y. et al. [10] focused on design, manufacturing,

and end-of-life management, new separation and recycling technologies for the composite materials recycling.

Rhim et al. noted [9] that there is an urgent need to develop biodegradable polymer composite products for disposable and multi-use items. They proved [9] that there are great advantages of bioplastics over plastics, such as lower carbon dioxide emission in production and composting, more eco-friendly and no harmful side effects, etc.

Due to the increasingly restrictive environmental standards, it is therefore important to use polymers the so-called "Environmentally friendly". Renewable polymers are currently considered a promising alternative to traditional (petrochemical) polymers, as they comply with current environmental regulations in terms of environmental pollution, greenhouse gas emission and fossil depletion [12-24]. It is known, that each year the production and combustion of plastics contribute to the emission of around 400 million tonnes of CO_2 worldwide, some of which could be avoided by improving the recycling technique or the use of biomaterials [16]. An example of such a material is polylactide (PLA), which is a so-called polymer biodegradable, biocompatible and shows good thermomechanical properties [20-24].

Poly (lactic acid) (PLA) is a polymer derived from renewable sources, mainly maize, and has been identified as a promising material requiring reduction solid waste disposal and suitable material for household items and packaging applications [18]. PLA can also be used in the biomedical field for implants, internal sutures, and scaffolding tissues due to its widespread availability, low manufacturing cost, and limited molecular weight [19]. As it has functional and processing properties similar to poly(ethylene terephthalate) - PET or polyethylene (PE) [20-24], it can also be used in automotive and electronics [12-15, 20-21]. To improve properties poly (lactic acid) is being subjected to modification by blending with other polymers, or incorporating various fillers, plasticizers or compatiblizers. A better understanding of the significance of these properties with available improvement strategies is the key to the successful use of PLA and its composites/blends to maximize their match to the needs of applications worldwide [18, 24].

One of the solutions may be the production of polylactidebiocomposites modified with the nanofiller in the form of a halloysite. Halloysite nanotube (HNT) is an individual type of nanofiller, i.e. structurally very similar to nanoclay and at the same time geometrically analogous to the carbon nanotube. HNTs are morphologically similar to polyhedral carbon nanotubes, which are technologically very expensive. However, unlike the neutral surfaces of carbon nanotubes, the surfaces and edges of the HNT contain hydroxyl groups, which makes it possible to further modify them with various organic compounds [25]. Halloysite with the molecular formula $[Al_2Si_2O_5\ (OH)_4\ nH_2O]$ is similar to kaolinite or montmorillonite, where n represents hydration or dehydration. [25-29]. The length of HNT ranges from 100 to 2000 nm, with the inner diameter from 10 to 30 nm and the outer diameter from 30 to 50 nm [27-29]. HNT nanotubes are widely used in the industry for the production of ceramics, cement, and fertilizer products, as an animal feed additive. In the past, they were also used to produce the highest quality porcelain [25, 27]. Currently, there is a steady increase in interest in halloysite applications is observed, and this trend is expected to continue in the future [25-29]. The advantage of creating composites with a biopolymer-polylactide matrix and its natural origin, which is ceramics, is their recycling, which in the case of other composites, as already mentioned, is problematic [30-32].

The choice of a suitable technique for recycling polymer waste depends on many factors, including the type and the polymer structure, its source of origin, purity, etc. The process of mechanical recycling of plastics involves structural changes that cause changes in the mechanical and usage properties (reduction of elongation and strength at break, increase in stiffness or loss of gloss and colour) of polymeric materials.

The effect of structural changes in polymer macromolecules is chain breakage, leading to a reduction in the average molecular weight [33]. In the case of organic polymers, i.e. PLA, environmental factors, such as water, radiation, microorganisms, environmental pollutants, etc., have a very large impact on the process of their degradation, which promote the process of organic recycling, including composting [34-42].

Composting is a controlled process of waste degradation under aerobic conditions, the product of which is compost [42-43]. Composting can potentially transfer biodegradable waste, including biodegradable polymers, to useful soil improvers [44]. The decomposition of polyester materials in the composting process combines the action of ester bond hydrolysis and the action of enzymes [43, 45-53], but the composting process requires the presence of compounds such as carbon, nitrogen, oxygen, water [43-44]. The soil burial tests show that the degradation of PLA in the soil is slow and takes a long time to start. For example, no degradation was observed of PLA sheets after 6 weeks in soil [48]. Urayama et al. [51] reported that the molecular weight of PLA films with different optical purity of lactate units decreased by 20 and 75%, respectively, after 20 months of staying in the soil. On the other hand, PLA may be degraded in the composting environment, where it is hydrolyzed into smaller molecules (oligomers, dimers and monomers), which are then broken down into CO_2 and H_2O [44,50].

The processing of biodegradable plastics by composting is now considered in many parts of the world as an appropriate form of material recovery. In the UK, this is an allowed recovery option under the producer responsibility legislation (packaging waste) [44,50]. The development of new polymeric materials with favorable processing properties and degradable under industrial composting conditions may contribute to the improvement of the condition of the natural environment by reducing the deposition of traditional plastics waste in landfills [51]. In the papers [37, 43-44, 48, 50-51], the authors indicate the legitimacy of polylactide degradation as a result of the composting process.

To evaluate the composite structure, including the degree of dispersion of the filler particles, their compatibility, and consequently the susceptibility of halloysite to rapid decomposition, rheological tests of the obtained PLA/HNT composites were carried out. Determining the viscosity of polymer composites is important from a processing and recycling point of view. In this study, changes in the average molecular weight of the produced polylactide-halloysite nanocomposite (with a different mass fraction of gelatin-modified halloysite filler) made after the composting process in the pile were determined. The aim of this experiment was to evaluate the influence of nanofiller content on the polylactide decomposition process in the organic recycling process.

2 Experimental

2.1 Materials

A commercially grade of amorphous polylactideIngeo 3260 HP by Nature Works (Minnetonka, MN, USA) with a melt flow index of 65 g/10 min $_{(190\,°C,\,2.16\,kg)}$ and the density of 1.24 g/cm^3, liner shrinkage of 0.3%, tensile strength at yield of 63 MPa and elongation at break of 3%) was used as the matrix of the biocomposites. Halloysite nanotubes (HNTs) with a density of 2.53 g/cm^3 and a specific surface area of 64 m^2/g was purchased from Sigma Aldrich (Milwaukee, WI, USA) and used as the nanofiller for the fabrication of PLA/HNT nanocomposites. The halloysite nanotubes content of the PLA matrix was 1, 2.5, and 5 wt.%, respectively.

2.2 Nanocomposites processing

The PLA/HNT production process of the composite firstly consisted of the procedure of modification of the strengthening phase with gelatin. The modification of the HNTs was performed based on the operation of the ultrasonic field with a frequency of 250 kHz in demineralized water, in the mass ratio of gelatin to halloysite 1:2. The process was carried out at 80°C for 3 hours. After the reaction was completed, the water was evaporated and the dry product was made into a fine, loose powder. Finally, the powder was ground double stages: first using a knife mill and then grinding using a ball mill. Halloysite, modified with gelatin was introduced into the polylactide by dosing the nanopowder in the injection process in a pre-dispersed form in the polymer carrier (masterbatch), which facilitated the production of a composite with good filler dispersion in the polymer matrix. The composites were produced by means of melt mixing PLA with HNT; with a HNT content of 1, 2.5, and 5 wt.%. Prior to composites manufacturing, the granulate was dried in a dynamic vacuum at 70°C for 12 h. The melt-mixing of the blends was carried out in a LSM30 (LeistritzLaborextruder, Nuremberg Germany) modular intermeshing counter-rotating twin screw extruder, operating at 200°C with a screw rotational speed of 50 rpm. The extruded rod was cooled in a water bath and subsequently pelletized. Test samples were produced by injection molding using a Boy 15 machine (Dr Boy GmbH & Co, Neustadt-Fernthal, Germany) with an L/D ratio of 22.9. The processing parameters were as follows: injection temperature of 200°C; hold pressure of 50 MPa; mold temperature of 60°C.

2.3 Composting (degradation) process

In order to evaluate the degree of degradation (the study of material decomposition over time) of the produced PLA/HNT composites, a composting process was carried out. The study of the decomposition of biocomposites over time was carried out in laboratory conditions simulating composting in an industrial pile, the so-called by the abbreviated degradation method. The composting process was carried out in a substrate consisting of 30% leaves, 20% wood chips and 30% grass, 10% soil and 10% compost. The composting process was carried out at an average temperature of 52°C, relative humidity of 55% and pH of 6.7.

3 Characterization

To determine the intrinsic viscosity by using the viscometric method, samples weights of 0.25 ±0.5 g was prepared, and next placed in clean and dry 50 ml flasks. Then, the samples were flooded with about 25 ml of solvent-chloroform. In the next stage, the samples were thermostated in an ultrasonic bath until the material was completely dissolved. The temperature of the water bath was of 35±5°C. In practice, the intrinsic viscosity is often measured to estimate the average molecular weight of a polymer [54-57].
The relative viscosities of the PLA/HNT before and after degradation with H_2O_2 were determined at 35 ± 0.5°C using an Ubbelohde'a capillary viscometer (Instrument Co., Ltd., China). The intrinsic viscosity $[\eta]$ values can be deduced according to the following experience equations (eq. 1,2)[54-57]:

$$\eta_r = \frac{t_s}{t_0},\ \eta_{sp} = \eta_r - 1 \qquad (1,2)$$

where t_s and t_0 is the efflux times of the PLA/HNT solution and the solvent [*s*], respectively, η_r is the relative viscosity, η_{sp} is the incremental viscosity.
The intrinsic viscosity $[\eta]$ values can be deduced according to the following equation (eq. 3) Salomona – Ciuta [54]:

$$[\eta] = \frac{\sqrt{2}}{c\sqrt{\eta_{sp} - ln\eta_r}} \tag{3}$$

where η_r is the relative viscosity, η_{sp} is the incremental viscosity, and c is the concentration of HNT (g/dl), c=2 m, and m is the sample mass in g.
The intrinsic viscosity of a polymer in a given solvent increases with the polymer's molar mass. This relation is the base for the viscometric method to assess the molar mass of a polymer from the equation of Mark–Houwink(eq. 4) [57]:

$$[\eta] = K(\bar{M}_v)^a \tag{4}$$

where is ($\bar{M}_v$) the mean molecular weight, K and a are the viscometric constants, which vary in function of the nature of the solvent, temperature and chemical structure of the polymer [54-57]. The exponent a takes values between 0.5 and 0.8 for flexible chain polymers. Thus, log-log plots of $[\eta]$ against molecular weight have the intercept log(K) and slope a. The *K* and a value for PLA were found to be 1.25×10^{-4} and 0.65, respectively [56].

4 Results and Discussion

Table 1 shows the data results of the viscosity average molecular weight (eq. 4) of the composites composted during 30, 60, 90 days. The results of the average molecular weight of the PLA and its PLA/HNT composites before and after biodegradation was illustrated in Figure 1.

Table 1. The results of the average molecular weight ($\bar{M}_v$)of the PLA and its PLA/HNT composites before and after biodegradation.

Sample	Before biodegradation	Composting condition at temperature 58±5°C		
		30 days	60 days	90 days
PLA (reference)	3715	2869	2524	2008
PLA/1%HNT	3846	2943	2530	2001
PLA/2.5%HNT	3927	2996	2547	1947
PLA/5%HNT	4054	3045	2558	1896

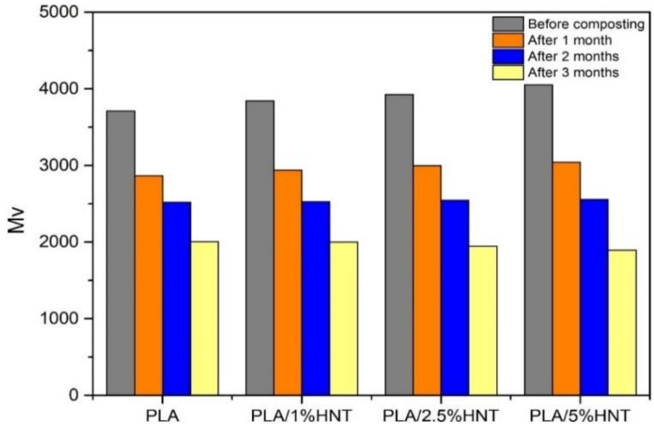

Fig. 1. Comparison of the average molecular weight ($\overline{M}_v$) of poly(lactic acid)-PLA and its composites before and after composting process.

Figure 1 shows the increase in viscosity average molecular weight for the PLA/HNT composites with increasing content of HNT nanotubes. It was observed, that the addition of 1wt.% HNT to the PLA matrix increases the viscosity-average molecular weight by 3.5%, and adding 5wt.% HNT by approx. 9% compared to pure PLA. This may be due to the increase in the thermal stability of the mass containing nanotubes filler. Generally, analysing the results of the viscosity average molecular weight presented in the Table 1, it can be observed that as a result of composting all PLA/HNT composites are degraded. However, none of these composites materials completely decomposed. The obtained results make it possible to describe the degradation process in conditions similar to composting in an industrial pile. In case of all composites, at the first stage of composting, the process responsible for the systematic reduction of the average molecular weights of the tested samples is the hydrolysis process of polylactide, and the formed small-molecule oligomers penetrate into the environment, wherein the second stage they are bio-assimilated by the microorganisms present there, which is confirmed by the papers [44-46]. In the initial stage of degradation of composites, water penetrated into PLA, leading to hydrolytic cleavage of PLA ester bonds, leading to a rapid decrease in average molecular weight. This decrease in molecular weight allowed for the creation of crystalline structures among the short chains of PLA, and therefore the crystallinity of PLA increased at once in the first step, which is showed in the turbidity of the sample. It was observed that the addition of the halloysite promotes the breakdown of the polymer matrix (Fig. 1). As a result of composting for 1 month, a decrease in viscosity-average molecular weight was observed by approx. 23% for pure PLA and about 25% for a composite containing 5 wt.% HNT. The result found the highest decrease in average molecular weight for a sample containing 5 wt.% HNT, composted within 3 months was conducted.

5 Conclusions

The aim of the study was to evaluate the average molecular weight of polylactide-halloysite composites (with a different mass fraction of gelatin-modified halloysite filler) made after the composting process in conditions simulating an industrial pile. The results of the viscosity average molecular weight clearly show that as a result of composting all materials undergo the process of biodegradation. Viscosity average molecular weight results indicate that all materials are degraded by composting. However, none of the materials have completely degraded. Further research is needed on specific microbial strains that are capable of biodegradation of PLA/HNT composites and their influence on the rate of biodegradation. Single-use products such as packaging would greatly benefit from the biodegradable properties of PLA-matrix composites, as this would allow them to be disposed of with other organic waste in composting plants.

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