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Accelerated weathering performance of polylactide and its montmorillonite nanocomposite

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ABSTRACT

The goal of this study was to compare accelerated weathering performance of neat polylactide (PLA) and its 1 mass% organically modified montmorillonite (Mt) nanocomposite; compounded and shaped by twin-screw extrusion melt mixing and injection molding, respectively. Accelerated weathering test system applied consecutive steps of UV irradiation and humidity in accordance with ISO 4892-3 standards for 200 h. Chain scission reactions such as photolysis, photooxidation and hydrolysis resulted in significant decrease in the molecular weight of PLA; consequently reductions in the mechanical properties of modulus, strength, ductility and toughness of the specimens occurred. However, after comparing mechanical properties of PLA and Mt–PLA before and after 200 h accelerated weathering, use of PLA with only 1 mass% Mt was extremely beneficial not only for “indoor applications” but also for “outdoor applications”. This was due to the effective nanoscale reinforcing and barrier actions of intercalated/exfoliated Mt layers. For example, flexural strength was 6% beneficial before weathering, but after weathering the benefit was 88%.

1. Introduction

Poly(L-lactic acid) (PLA) is a biodegradable biopolymer having aliphatic polyester structure with thermoplastic character. It has found wide range application in food packaging and biomedical applications and increasing commercial interest due to its desired mechanical strength, thermal stability and biocompatibility. PLA is also the center of interest with being an alternative to petroleum-based polymers, because PLA is synthesized from agricultural renewable resources.

One of the drawbacks of PLA is its sensitivity to atmospheric conditions, i.e. UV irradiation, moisture and temperature. When viewed from this aspect, PLA with the enhanced outdoor performance is essential in many engineering applications such as automotive parts. Therefore, its weathering performance should be determined either naturally or artificially. In natural weathering, sun is the UV irradiation and temperature source while rain and atmospheric humidity are the source of moisture.

Testing of polymeric materials under “natural weathering” conditions strongly depends on the chosen site and chosen exposure time which are usually very long periods such as 1–5 years. On the other hand, “artificial weathering” conditions are reproducible by applying constant or cyclic exposure of certain levels of UV irradiation, temperature and moisture via an electronic control unit such as “accelerated weathering tester” systems. If a correlation can be established between natural and artificial weathering, use of accelerated weathering tester systems is very practical and quick compared to the time consuming natural weathering.

Until recently, biodegradation of PLA based materials have been clarified by many researchers, but less study has been performed on the weathering performance (hydrolytic degradation and/or photodegradation) of neat PLA (Zhang et al., 2011; Bocchini et al., 2010; Copinet et al., 2004; Tsuji et al., 2006; Deroine et al., 2014; Shinzawa et al., 2012; Dopico-García et al., 2013; Tsujia et al., 2004), and the PLA composites with inorganic fillers such as talc (Jo et al., 2013), calcium sulfate (Gardette et al., 2011; Pluta et al., 2008), silica (Liu et al., 2012), carbon nanotube (Gorrasi et al., 2013) and titanium dioxide (Buzarovska and Grozdanov, 2012; Mana et al., 2012).

Some of the studies (Tsuji et al., 2006; Gardette et al., 2011) indicated that photodegradation of PLA proceed via the Norrish II type photocleavage reaction leading to random chain scission (decrease of molecular weight), and the formation of $C=C$ double bonds and carboxylic acid groups at newly formed chains. Some of them (Zhang et al., 2011; Copinet et al., 2004; Gardette et al., 2011; Gorrasi et al., 2013; Buzarovska and Grozdanov, 2012; Mana et al., 2012) indicated that UV irradiation leading to random main chain scission in certain chemical bonds of the PLA structure occurs via “photolysis” and/or “photooxidation” mechanisms leading to formation of carboxylic acid and diketone groups. Later on, Bocchini et al. (2010) proposed that photooxidation could also lead to formation of anhydride groups.

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Another group of studies (Deroine et al., 2014; Shinzawa et al., 2012; Dopico-García et al., 2013; Tsujia et al., 2004; Jo et al., 2013; Pluta et al., 2008) revealed that hydrolytic degradation of PLA due to the moisture mainly proceed via "hydrolysis"; that is cleavage of the ester bonds in the PLA backbone leading to successive chain scission with reduced molecular weight.

In the literature, there are studies investigating the weathering performance of PLA composites reinforced with certain clay minerals such as bentonite (Solarski et al., 2008), semectite (Rapacz-Kmita et al., 2015), halloysite (Tham et al., 2015) and the most attractive one montmorillonite (Mt) (Araújo et al., 2013; Bocchini and Frache, 2013; Zaidi et al., 2010; Balakrishnan et al., 2011; Kontou et al., 2012; Derho et al., 2014; Pluta et al., 2006; Gumus et al., 2012).

Some of these Mt–PLA studies investigated effects of photodegradation either under artificial UV lamb irradiation (Bocchini et al., 2010; Araújo et al., 2013; Bocchini and Frache, 2013) or under natural outdoor sunlight (Zaidi et al., 2010); some of them revealed effects of hydrolytic degradation either in certain solutions (Balakrishnan et al., 2011; Kontou et al., 2012; Paul et al., 2005) or under ambient humidity for very long periods (Zaidi et al., 2010; Derho et al., 2014; Pluta et al., 2006; Gumus et al., 2012). In some of these Mt nanocomposites the matrix was not neat PLA, but blends of PLA; with linear low density polyethylene (LLDPE) (Balakrishnan et al., 2011), poly(ethylene oxide) (PEO) (Derho et al., 2014) and poly(ethylene glycol) (PEG) (Pluta et al., 2006; Gumus et al., 2012). Unfortunately, none of these studies conducted accelerated weathering tests exposing both UV irradiation and moisture consecutively.

There seems to be only one recent study (Chavez-Montes et al., 2015) investigating the artificial weathering (both UV and moisture) of Mt–PLA nanocomposites. The authors compared accelerated weathering performance of Mt nanocomposites having amorphous and semicrystalline PLA matrices. Their comparison was based on the decrease of the molecular weight of PLA. They reveal that weathering degradation was favored more in the amorphous matrix compared to semicrystalline PLA matrix. That work also includes a correlation between natural and artificial weathering, but no comparison in the changes of mechanical or thermal properties.

Therefore, as the first of its kind, the purpose of this study was to determine accelerated weathering (both UV and moisture) performance of neat PLA and its 1 mass% Mt nanocomposite by comparing their mechanical properties and thermal behavior at four different weathering periods.

2. Experimental

2.1. Materials used

Commercial L-lactic acid polylactide (PLA) supplied from NaturePlast (France) with an extrusion grade (PLE 001) was used as the matrix material. According to its technical data sheet, it has a melting temperature range of 145–155 °C, degradation temperature range of 240–250 °C, while the melt flow index range at 190 °C under 2.16 kg is 2–8 g/10 min, as well as a density of 1.25 g/cm^3.

The montmorillonite (Mt) used was Cloisite 30B obtained from Southern Clay Products (Gonzalez, TX). Cloisite 30B was organically modified with methyltallow bis-2-hydroxyethyl quaternary ammonium cation (MT2EtOH). The particle size range of the nanoclay was 2–13 μm.

2.2. Compounding and shaping of the Mt–PLA nanocomposite

Mt–PLA nanocomposite specimens were produced by two industrially compatible steps; i.e. "twin-screw extrusion melt-compounding" and "injection molding melt-shaping" with laboratory size equipment.

In the first step, PLA granules and Mt powders were pre-dried for 15 h in a vacuum oven at 60 °C, and then pre-mixed manually. This mixture was melt compounded via Rondol Microlab 300 laboratory size (D = 10 and L/D = 20) twin-screw extruder. Typical temperature profile from feeder to die were 115°–170°–180°–175°–150 °C while the typical screw speed was 70 rpm throughout the compounding stage; followed by four-blade cutting of the continuous strands into pellets of 2–3 mm.

In the second step, prior to shaping, pellets were allowed to re-dry for 15 h in a vacuum oven at 60 °C. Standard sized specimens required for testing and analyses were melt-shaped via laboratory scale DSM Xplore Micro injection molder. Typical barrel and mold temperatures used were 185 °C and 35 °C, respectively. The melting time in the barrel was approximately 7 min, with the subsequent three-step pressure–time profile determined as 14 bar for 3 s, 12 bar for 5 s, and 12 bar for 5 s.

When investigating the effects of various Mt contents and interfacial compatibilization on the behavior of PLA, our unpublished results revealed that use of 1 mass% Mt resulted in the best optimum mechanical properties. Therefore, in this study, accelerated weathering performance of neat PLA was compared with its nanocomposite having only 1 mass% Mt.

2.3. Characterization of the nanocomposite structure

Formation of Mt–PLA nanocomposite structure was first determined by X-ray diffraction (XRD) analysis on a Rigaku D-Max 2200 with CuKα radiation (40 kV, 40 mA) over a scanning range of 1°–8° at a rate of 0.5°/min. Then, in order to evaluate dispersion and level of intercalation/exfoliation of Mt silicate layers in PLA matrix, transmission electron microscopy (TEM) analysis was conducted with FEI Tecnai G2 Spirit Bio TWIN at an acceleration voltage of 80 kV. Samples were prepared under Leica EM UC6 ultra-microtome with diamond knife. Around 100 nm thick sections sliced were transferred onto copper grids of 400 mesh.

2.4. Accelerated weathering of PLA and its Mt nanocomposite

In order to investigate the weathering behavior of neat PLA and its 1 mass% Mt nanocomposite, an *accelerated weathering tester* (Q-LAB Model QUV/se) was used. The weathering conditions were in accordance with the Cycle-C of the SAE J2020, ASTM G154-05 and ISO 4892-3 standards. Fluorescent lamps (UVB-313) with 0.49 W/m^2 irradiance (at 310 nm) were used with cycles of 8 h UV irradiation at 70 °C, followed by 4 h dark condensation at 50 °C. These consecutive cycles were applied to the specimens attached to the test panels without any interruption. Effects of accelerated weathering were investigated for four periods: 50, 100, 150 and 200 h. Specimens for each period were designated as Mt–PLA-*x*h, where *x* denotes the accelerated weathering period.

Effects of each period of accelerated weathering on the behavior of the neat PLA and its 1 mass% Mt nanocomposite specimens were investigated by comparing the changes in the results of the following tests and analyses conducted.

2.5. Analysis of the variation in the Mt intercalation and PLA crystallinity

Due to its higher sensitivity in the scanning range of 1°–8°, the same XRD equipment (Rigaku D-Max 2200) and the same parameters mentioned above was also used to reveal the effects of each accelerated weathering period on the variation in the intercalated structure of Mt layers. For the variation in the crystallinity of the neat PLA specimen and the PLA matrix of 1 mass% Mt nanocomposite specimen, XRD were conducted via Bruker D8 Advance A25 (CuKα radiation, 0.154 nm wavelength, 40 kV, 40 mA) over a scanning range of 5°–25° at a rate of 1°/min.