Material Behaviour

Using multiple melt blending to improve the dispersion of montmorillonite in polyamide 6 nanocomposites

Jia-Horng Lin [a, b, c, d, e], Yi-Jun Pan [f], Chien-Teng Hsieh [g], Chen-Hung Huang [h], Zheng-Ian Lin [b], Yueh-Sheng Chen [i], Kuan-Hua Su [b], Ching-Wen Lou [e, j, *]

[a] School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China
[b] Laboratory of Fiber Application and Manufacturing, Department of Fiber and Composite Materials, Feng Chia University, Taichung City 40724, Taiwan
[c] School of Chinese Medicine, China Medical University, Taichung City 40402, Taiwan
[d] Department of Fashion Design, Asia University, Taichung City 41354, Taiwan
[e] Department of Chemistry and Chemical Engineering, Minjiang University, Fuzhou 350108, China
[f] Department of Materials and Textiles, Oriental Institute of Technology, New Taipei City 22061, Taiwan
[g] Department of Fashion Design and Merchandising, Shih Chien University Kaohsiung Campus, Kaohsiung City 84550, Taiwan
[h] Department of Aerospace and Systems Engineering, Feng Chia University, Taichung City 40724, Taiwan
[i] Department of Biomedical Imaging and Radiological Science, China Medical University, Taichung City 40402, Taiwan
[j] Graduate Institute of Biotechnology and Biomedical Engineering, Central Taiwan University of Science and Technology, Taichung 40601, Taiwan

ARTICLE INFO

ABSTRACT

Polyamide 6 (PA6) was multiple melt-blended with organically modified montmorillonite (MMT) Cloisite 20A and Cloisite 30B and unmodified MMT Na$^+$ in order to make three types of PA6/MMT nanocomposites. According to the morphology observation, the dispersion of silicate layers in the 20A nanocomposites was improved until it scattered, whereas the dispersion of silicate layers in the 30B nanocomposites is satisfactory. Moreover, the dispersion of silicate layers in Na$^+$ nanocomposites slightly improved with the increase in melt-blending cycles. After PA6 was melt-blended with MMT, its molecular weight (MW) decreased with the processing cycles, which resulted in easy degradation. The mechanical property tests show that multiple melt blending has a positive influence on the mechanical properties of three PA6/MMT nanocomposites. However, their elongation at break and impact strength both decrease as a result of the aggravating degradation of PA6. Increasing the melt-blending cycles causes the crystallization temperature to increase and the melting temperature to decrease.

1. Introduction

Recycling has become increasingly popular, and recyclable materials include newly invented resources like polymer/clay nanocomposites [1–3]. In general research, inorganically-layered materials can be divided into natural clays and artificial clays. Natural clay can be purified using special refining methods and is low-cost. At present, most polymer nano-composite research makes use of montmorillonite (MMT). MMT has outstanding mechanical properties and chemical resistance, which along with the rather high superficial area and aspect ratio of its layered structure, increase its contact area with polymer and the interface, resulting in many superior characteristics. Topics relating to these characteristics have already been widely explored and reported [4–11].

The reinforcement of polymer nanocomposites does not require the large amount of silicate clay needed for the reinforcement of conventional nanocomposites [12–15]. Polymer nanocomposites usually need less than 5 wt% of silicate clay, which gives them a smaller specific gravity than conventional nanocomposites; this fact is critical to their applications, particularly in the construction of vehicles which are light and consume less fuel [16–19]. Polymer nanocomposites effectively reinforce the stiffness and thermal resistance of a material, improve hygroscopicity, and reduce the coefficient of thermal expansion. Thus, they have unlimited marketing potential in the future development of high-end precision materials. In addition, unlike conventional nanocomposites, polymer nanocomposites need lower quantities of reinforcing materials

* Corresponding author. Graduate Institute of Biotechnology and Biomedical Engineering, Central Taiwan University of Science and Technology, Taichung 40601, Taiwan.

E-mail address: cwlou@ctust.edu.tw (C.-W. Lou).

and have a greater effectiveness in terms of scalability, impact resistance, surface gloss, and flatness.

In 1976, Fujiwara and Sakomoto from Unichika Corporation were the first to produce a nano-composite with a blend of organic clay and polyamide. After a decade, a research team from Toyota successfully prepared PA6/clay nanocomposites using improved situ polymerization which was similar to the Unichika process [20]. The PA6/clay nano-composite was the first to gain a large market share. It is primarily used for auto parts and components, auto interior materials, gas barrier packaging films, and containers. Polyamide 6 (PA6)/clay nanocomposite can be further applied in other industries, such as electronics, building construction, and biomedical engineering.

Therefore, many polymer scientists have become increasingly interested in related research topics such as how to recycle PA6 nanocomposites effectively and suppress their degeneration during processing and use [21,22]. M.C. Mistretta et al. examined the degradation behavior of LDPE/PA6/Cloisite 15A composites during the manufacturing process. The test results suggested that the degradation level of composite depended on the processing conditions, including processing times and nanoclay [22]. Moreover, in our previous study, PA6 was processed via multiple melt blending, which results in a lower molecular weight but a persistent chemical structure. Meanwhile, the tensile stress, flexural strength and modulus of PA6 were strengthened with more melt-blending cycles [21]. As there are few studies conducting multiple melt-blending on PVA/MMT nanocomposites in order to determine the reinforcement of the dispersion of MMT on PA6 matrices, this study proposes producing polymer nanocomposites. Multiple melt blending blends PA6 and three different kinds of montmorillonite (MMT), allowing us to examine its influence in terms of MMT dispersion, molecular weight of PA 6, and the mechanical properties of PA6/MMT nanocomposites.

2. Experimental

2.1. Materials

PA6 (SUNYLON 6N) was supplied by Formosa Chemicals and Fiber Corporation (Taiwan). Three different kinds of MMT composed of silicate layers., whose average particle size was 8 μm, were purchased from Southern Clay Products Inc. (USA). Table 1 summarizes the specified properties of unmodified MMT Cloisite Na^+ and organically modified MMT Cloisite 20A and Cloisite 30B.

2.2. Preparation of the PA6/MMT nanocomposites

PA6 was melt-blended with unmodified MMT Cloisite Na^+, organically modified MMT Cloisite 20A, and organically modified Cloisite 30B. The resulting samples were denoted as Na^+ nanocomposites, 20A nanocomposites, and 30B nanocomposites, respectively. After dehumidifying and drying, parts of these masterbatches were made into standard samples with an injection molding machine (SM-50, Chen Hsong Machinery Taiwan Co., Ltd., Taiwan, R.O.C.). The remaining masterbatches were repeatedly melt-blended five times using a twin screw extruder (KTX-30, Kobe Steel, Ltd., Japan) and an injection machine at temperatures of 240 °C, 250 °C, 255 °C, and 260 °C in the area between the feed zone and the nozzle and a mold temperature of 80 °C. Moreover, pure PA6 particles were melt-blended by the twin screw extruder at 140 rpm to form pure PA6.

In order to measure MMT content in PA6/MMT nanocomposites, dried masterbatches at 20–40 g are placed in a furnace (Thermolyne F4800, Barnstead International, Inc., US) at 900 °C for 45 min, thereby vaporizing the organic constituent in PA6 and quaternary alkylammonium salt (modifiers). The MMT ash is then weighed and analyzed with the equation as follows [23]. MMT content in PA6/MMT nanocomposites is yielded after the moisture loss of the MMT is calculated, and this information is summarized in Table 2.

$$\%MMT = MMT_{ash}/0.935 \tag{1}$$

where %organic content is the content of organic modifiers used in MMT, which is provided by the manufacturer, % MMT_{ash} is the ash weight percent after PA6/MMT nanocomposites are vaporized in a furnace, %MMT is the MMT weight percent after the moisture loss in MMT is calculated using the equation, and % $organoclay_{NC}$ is the weight percent of the added organically modified MMT.

2.3. Characterization

X-ray diffraction (XRD; Rigaku III) and transmission electron microscopy (TEM; JEOL JEM-1230) were applied to examine the samples for the dispersion of silicate layers in the PA6 matrices. The XRD pattern is further analyzed using Bragg equation as follows.

$$Bragg's\ Equation : 2d \cdot \sin \theta = \lambda \tag{2}$$

where d is the crystal plane spacing, θ is the diffraction angle of the crystal plane, and λ is the Cu $K\alpha$ X-ray wavelength at 1.54 Å.

Table 1
Physical properties of MMT [23].

Type of MMT	Organic modifiers[a]	Chemical structure of the modifiers	Concentration of the modifiers (meq/100 g clay)	d_{001}[b] (Å)
Cloisite 20A	Dimethyl, dihydrogenated tallow, quaternary ammonium chloride (2M2HT)	$CH_3 - N^+ - HT$ with CH_3 and HT	95	24.2
Cloisite 30B	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (MT2EtOH)	$CH_3 - N^+ - T$ with CH_2CH_2OH and CH_2CH_2OH	90	18.5
Cloisite Na^+	–	–	–	11.7

[a] Tallow (T) and hydrogenated tallow (HT) refer to unsaturated and saturated (protonated) alkyl long chains, which contain approximately 65% C_{18}, 30% C_{16}, and 5% C_{14}.
[b] d_{001} is the distance between silicate layers in MMT.