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The preparation and properties of biodegradable polyesteramide composites reinforced with nano-$CaCO_3$ and nano-SiO_2

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Abstract

Composites were fabricated utilizing melt mixing aliphatic polyesteramide (PEA) with ordinary $CaCO_3$, nano-$CaCO_3$, and nano-SiO_2. The effect of filler on the matrix was studied by mechanical properties and hydrolysis rate measuring. The ordinary filler as well as the nano-filler had a negative effect on the stability of the polymer melt, and an improved mechanical property was obtained around a critical concentration of the filler where a percolation phenomenon appeared. When the composites underwent hydrolysis, the inert filler played a role as a mechanical obstacle in the matrix and retarded the hydrolysis; on the other hand, the interfacial area between the filler particle and the matrix resin increased with the filler, which would accelerate the hydrolysis. As a result of these two inverse effects, a minimum and a maximum value appeared in the plot of the degradation rate-filler content graph. For the ordinary filler filled polymer, the filler retarded the hydrolysis; in great contrast, the hydrolysis rate of nano-composites showed a maximum value around the critical concentration of the filler, and was much higher than the neat resin.

Keywords: Polyesteramide; Nano-composites; Preparation; Properties; Degradation

1. Introduction

Polymer nano-composites have received considerable attention since the discovery that polymer properties may be greatly improved by the presence of nano-sized particles. Some good news comes from the invention of nano-composites, which have much improved modulus [1–4], strength [1–4], thermal resistance [1–4], permeability [1–3,5,6], flammability resistance [3,4,7,8] and some of them even have improved biodegradability [9,10]. The mechanism behind the reinforcement of nano-composites is a physical cross-linking, which provides them with much high modulus as well as impact strength. In contrast, the conventional mineral-filler cannot provide the composite with high strength, high modulus and at

Table 1
Temperature (°C) at which certain weight loss of PEA and its composite occurs

Substance	T_{start} [a]	T_5 [b]	T_{10} [b]	T_{15} [b]	T_{30} [b]	T_{50} [b]	T_{onset} [c]
PEA [d]	270	350	373	385	407	442	372
CC 40% [e]	254	337	357	371	403	482	353
NCC 16% [e]	257	309	325	336	387	427	323
SiO_2 2% [e]	254	342	363	374	397	422	366
SiO_2 12% [e]	272	344	365	377	399	425	366

[a] Start of weight loss.
[b] Temperature where the weight loss is 5, 10, 15% and so on.
[c] Start of weight loss according to the TGA curves.
[d] PEA with antioxidant but no fillers.
[e] PEA composites with 40% CC (400 mesh), 16% NCC, 2% and 12% SiO_2, respectively.

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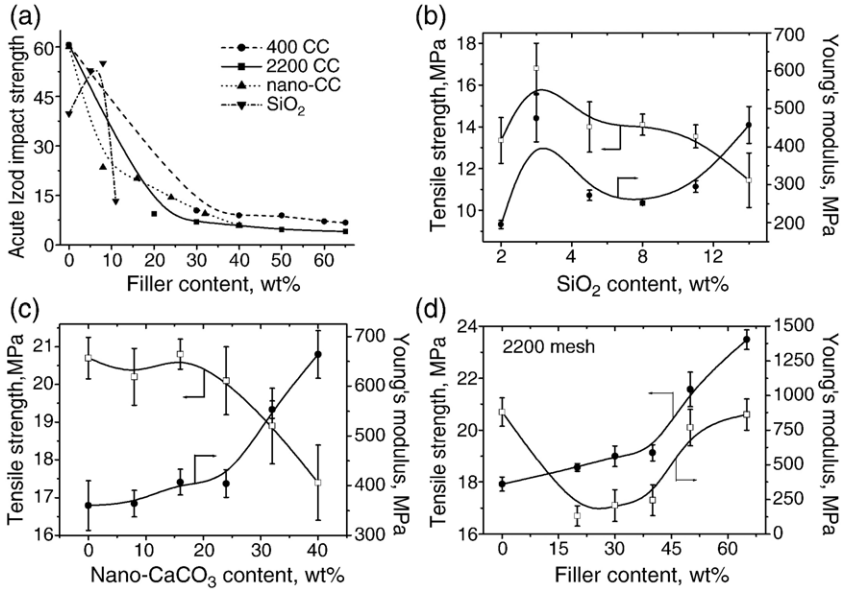

Fig. 1. Mechanical properties of filled PEA. (a) Acute notched Izod impact strength. Tensile and Young's modulus of PEA filled with SiO_2 (b), NCC (c) and 2200 mesh CC (d).

the same time with high impact strength. Their size of 1–50 nm is similar to the typical size of chain length; the nano-filler plays a role of a trapped entanglement [11], a kind of physical cross-linking. For the polymers having a glass transition temperature (T_g) lower than the room temperature (T_r), the reinforcement of the nano-filler on the matrix is extraordinarily good [12]. This is real good news for the biodegradable polymers which have a T_g lower than T_r. However, till now, there are limited papers related to the biodegradable polymer based nano-composites [9,10,13,14].

Among all of the properties of the composite, the first one, which is paid much attention, is how the nano-filler affects the biodegradability of the matrix. But the information about this question was full of contradictions. Lee et al. reported that clay had a retarded effect on the biodegradability of clay/aliphatic polyester [15]. S.Sinha Ray et al. reported the accelerated effect of montmorillonite on the biodegradability of PLA [9,10,16,17]. Fukuda et al. [18] reported the hydrolysis of the PLLA composite films containing $CaCO_3$ (CC) with the size of 90–200 nm in the presence of proteinase K, and the results revealed that the enzymatic hydrolysis rates of the PLLA composite films containing 5 and 10 wt.% of the CC particles were much higher than that of the pure PLLA film. Additional amounts of CC particles exceeding 10 wt.% led to a drop in the enzymatic hydrolysis rate. We here tried to explain why the confusing data was obtained.

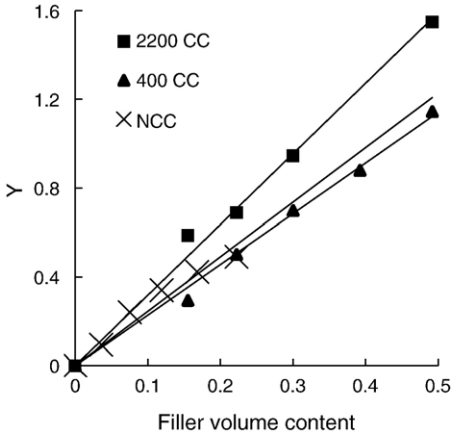

Fig. 2. Turcsanyi model for different sizes of CC (CC) filled PEA composites. ■: 2200 mesh CC, $y=2.6768\Phi$, $R^2=0.942$; ▲: 400 mesh CC, $y=2.2801\Phi$, $R^2=0.9949$; ×: NCC *X*-axis: $y=2.4575\Phi$, $R^2=0.9543$). *X*-axis: volume content Φ of filler. *Y*-axis: $\mathrm{Ln}(\sigma_c/\sigma_m)-\mathrm{Ln}((1-\Phi)/(1+2.318\Phi))$.

Aliphatic polyesteramides, which are biodegradable and have good processing and end-use properties, are interesting materials for environmental and biomedical applications [19–21]. Till now, the polyesteramide nano-composites based montmorillonites were reported by M.K. Rook et al. [22]. In this paper, we adopted the melt mixing technique to prepare nano-composites. We here report two kinds of nano-filler SiO_2 and nano-$CaCO_3$ (NCC) on the properties of a filled biodegradable aliphatic polyesteramide (PEA) by the melt mixing technique utilizing the twin-screw extruder.

2. Experimental

2.1. Materials

PEA with the density of 1.16 g/cm^3 was synthesized in our laboratory. The SiO_2 from Wacker-Chemie GmbH (Hydrophilic Wacker HDK® T40, with the density of 2.20 g/cm^3, BET surface area of 360–440 m^2/g), was treated with a silicon coupling agent 3-(trimethoxy-sily)propylmethacrylate KH-570. The nano-$CaCO_3$ (NCC, with the size of 100–120 nm) was a gift from Dongfang Insulting Co. Ltd, China. 400 mesh