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Partial delamination of the organo-montmorillonite with surfactant containing hydroxyl groups in maleated poly(propylene carbonate)

Zhihao Zhang [a,b,*], Qiang Shi [a,c], Juan Peng [a,c], Jianbin Song [a,c], Qingyong Chen [a,c], Junliang Yang [a,c], Yumei Gong [a,c], Ronghua Ji [a,c], Xiaofeng He [a], Joong-Hee Lee [b]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 People Street, Changchun 130022, PR China*
[b] *Polymer BIN Fusion Research Team, School of Advanced Materials Engineering, Chonbuk National University, Duckjin-dong 1Ga 664-14, Jeonju, Jeonbuk 561-756, Republic of Korea*
[c] *Graduate School of the Chinese Academy of Sciences, PR China*

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Abstract

Maleated poly(propylene carbonate) (PPC-MA)/organo-montmorillonite (OMMT) nanocomposites were first prepared via melt end-capping poly(propylene carbonate) (PPC) with maleic anhydride (MA) and melt-mixing the PPC-MA with commercial OMMT without and with hydroxyl groups in surfactants: Cloisite 20A (C20A) and Cloisite 30B (C30B), respectively. Intercalated and partially delaminated morphologies were corroborated via X-ray diffraction (XRD) and transmission electron microscopy (TEM). Dynamic mechanical analysis (DMA) revealed that PPC-MA was evidently reinforced by the partially delaminated C30B platelets. From XRD patterns of statically annealed PPC-MA/C20A and PPC-MA/C30B mixtures and Fourier transform infrared (FTIR) results of equivalent nanocomposites, partial delamination of C30B in PPC-MA was confirmed to be relevant to diffusion of PPC-MA molecular chains in C30B galleries, grafting of PPC-MA to C30B platelet surfaces and further separation of C30B platelets.

Keywords: Partial delamination; Organo-montmorillonite; Maleated poly(propylene carbonate)

1. Introduction

Poly(propylene carbonate) (PPC) is a copolymer of carbon dioxide with propylene oxide [1–3]. Fixation of carbon dioxide can mitigate the dreadful atmospheric pollution and utilize the abundant and low-cost natural resources. Owing to biodegradability and thermoplasticity, PPC has been processed into biomedical and packing materials. Nevertheless, the flexible carbonate groups in backbone chains have created many blemishes, including non-crystallizability, weaker processing stability and poorer mechanical properties.

The incorporation of a little organo-montmorillonite (OMMT) to polymers will result in the outstanding improvement of general properties [4–8]. Melt-mixing polymer with eco-friendly and low-cost OMMT has been an excellent technique [4–10] due to the pollution-free process and industrial feasibility. However, polymer nanocomposites with some other nanoparticles such as graphite nanosheet cannot be prepared by the similar method [11]. So the fabrication of PPC/OMMT nanocomposites via melt-compounding is a potential route to extend usages for biodegradable polymers and engineering plastics.

Unfortunately, PPC easily degrades when subjected to statically thermal treatment even at 180 °C [12]. In the dynamic shear field, heat derived from melt-processing makes material temperature 20–30 °C higher than barrel temperature and the degradation becomes more severe. Therefore, melt-mixing PPC with OMMT to prepare the nanocomposites will

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* Corresponding author. State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 People Street, Changchun 130022, PR China. Tel.: +86 431 5262963; fax: +86 431 5262126.
E-mail address: zhangzh@ciac.jl.cn (Z. Zhang).

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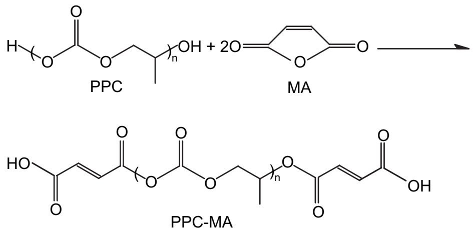

Scheme 1. Melt end-capping PPC with MA.

encounter more difficulties and challenges than fabrications of nanocomposites based on the other thermoplastic polymers [13–17].

Polymer/OMMT nanocomposites can be sorted into intercalated and exfoliated or delaminated structures. Owing to the homogeneous dispersion of individual silicate platelets in the polymer matrix, full exfoliated state is one of the ultimate aims in preparing polymer/OMMT nanocomposites [18]. However, only a few polymers, such as nylon 6 [19,20] and maleated polyethylene [18], have been melt-mixed with OMMT to achieve exfoliated structures, because it is very hard to separate the tightly stacked silicate platelets with van der Waals gap. Thus, melt-mixing PPC with OMMT to fabricate the exfoliated or delaminated, even partially delaminated nanocomposites with optimal properties is of academic significance and industrial merit.

In this contribution, intercalated and partially delaminated nanocomposites of maleated PPC (PPC-MA)/OMMT were prepared by melt end-capping PPC with maleic anhydride (MA) (Scheme 1) and melt-mixing the PPC-MA with OMMT. Commercial OMMT without and with hydroxyl groups in surfactants: Cloisite 20A (C20A) and Cloisite 30B (C30B), respectively, were selected. Morphologies were corroborated via X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mechanical properties were investigated by dynamic mechanical analysis (DMA). Partial delamination mechanism of C30B in PPC-MA was clarified via XRD patterns of statically annealed PPC-MA/C20A and PPC-MA/C30B mixtures and Fourier transform infrared (FTIR) results of equivalent nanocomposites. To our best knowledge, there has not yet been paper on PPC-MA/OMMT nanocomposite.

2. Experimental

2.1. Materials

Totally biodegradable poly(propylene carbonate) (PPC) with a number average molecular weight of 7.2×10^4 and a polydispersity of 6.49, synthesized via the copolymerization of carbon dioxide and propylene oxide with a ternary rare earth metal catalyst [21,22], was supplied by Melic Sea High-Tech Group Company, Internal Mongolia. The carbonate unit content, estimated from ^{1}H NMR spectrum using the method described elsewhere [23,24], was 95.76%. Analytical grade maleic anhydride (MA) was obtained from Beijing Yili Fine Chemical Co., Ltd. Commercial organo-montmorillonites (OMMT) Cloisite 20A (C20A) and Cloisite 30B (C30B), montmorillonites exchanged by quaternary ammonium salts, with characteristics given in Table 1, were purchased from Southern Clay Products, Inc.

Table 1
Characteristics of OMMTs

OMMT	Cationic exchange capacity (mequiv/100 g)	Quaternary ammonium salt
C20A	95	$(CH_3)_2(HT)_2N^+Cl^-$
C30B	90	$CH_3T(CH_2CH_2OH)_2N^+Cl^-$

T = tallow; HT = hydrogenated tallow (C18, ~65%; C16, ~30%; C14, ~5%).

2.2. Preparation of nanocomposite

PPC was triturated, passed through a 20 mesh sieve and dried under vacuum at 55 °C for 2 days. Powdered MA and OMMT were dried under vacuum at room temperature and 80 °C, respectively, for 24 h. Nanocomposites were fabricated by mixing 93.1 parts of PPC and 1.9 parts of MA, melt-blending in a Haake Rheomix 600P internal mixer at a barrel temperature of 160 °C and a rotation speed of 60 rpm for 5 min and adding 5 parts of OMMT for another 5 min. PPC-MA was prepared at the same temperature, speed and time. For elucidating the crucial role in which PPC-MA played, PPC/OMMT nanocomposites were fabricated by mixing 95 parts of PPC and 5 parts of OMMT and melt-compounding at the same temperature and speed for 5 min.

2.3. Characterization

Number average molecular weight and molecular weight polydispersity were measured on a Waters 410 GPC system at 35 °C using tetrahydrofuran as the eluent and monodisperse polystyrene as the standard.

Grafting degree of PPC-MA (G) was defined as weight percent of grafted MA in PPC and determined from the titration of the purified PPC-MA, similar to that of the purified polypropylene-graft-maleic anhydride [25]. PPC-MA was dissolved in chloroform at a concentration of 5 w/v% and precipitated by ethanol. The dissolution/precipitation procedure was repeated twice again to completely remove ungrafted MA. The purified PPC-MA was dried under vacuum at 55 °C for 2 days. 1.0 g of the well-dried PPC-MA was dissolved in 100 ml chloroform. The solution was titrated with 0.01 N potassium hydroxide solution in methanol using phenolphthalein as the indicator. A blank test for PPC was carried out by the same method. G was calculated from Eq. (1):

$$G(\mathrm{wt\%}) = \frac{\frac{V_1 - V_0}{1000} \cdot N \cdot M_{\mathrm{MA}}}{2W} \times 100\% = \frac{(V_1 - V_0) N M_{\mathrm{MA}}}{2W1000} \times 100\% \tag{1}$$

where, V_1 (ml) is base volume used for PPC-MA, V_0 (ml) the base volume used for neat PPC, N (mol/l) the base