



Research paper

Preparation and properties of montmorillonite/poly(ethylene glycol) grafted polypropylene/polypropylene nanocomposites[☆]Shipeng Zhu^{a,b}, Jinyao Chen^a, Huilin Li^{a,*}, Ya Cao^a, Yunhua Yang^b, Zhihai Feng^b^a State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, PR China^b Science and Technology on Advanced Functional Composites Laboratory, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, PR China

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ABSTRACT

Poly(ethylene glycol) grafted polypropylene (PP-g-PEG), as a new montmorillonite (Mt) modifier, was used to prepare Mt/polypropylene (PP) nanocomposites by melt blending. The results of X-ray diffraction (XRD) and transmission electron micrographs (TEMs) indicated that the PEG segments of PP-g-PEG diffused in Mt, enlarging its interlayer spaces and the silicates dispersed homogeneously in the PP matrix. The Mt/PP-g-PEG/PP nanocomposites exhibited an unusual combination of rheological behaviors and mechanical properties. The melt viscosity of Mt/PP-g-PEG/PP nanocomposites was significantly reduced and the mechanical properties were improved. The plasticization effect of PEG segments caused the Mt/PP-g-PEG/PP nanocomposites significantly more shear thinning than that of the pure PP. Compared with those of the pure PP, the Izod-notched impact strength and elongation at break of Mt/PP-g-PEG/PP nanocomposites increased by 148% and 43%, respectively. In addition, the tensile strength was also improved. For the above results, a possible structure of Mt/PP-g-PEG/PP nanocomposites was suggested. During the melt blending, the PEG segments in PP-g-PEG diffused in the interlayer spaces of Mt, then interacted with the surfaces of silicates and formed double layer conformation. The PEG segments could fix at the surfaces of Mt while the PP segments were compatible with the PP matrixes. The Mt particles would break up under shear and dispersed well in the PP.

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1. Introduction

Clay polymer nanocomposites (CPNs) have attracted great interests from researchers since they exhibit enhanced properties over the recent twenty years. There are many methods to prepare the CPN. But direct polymer melt intercalation is the most versatile and environmental approach (Hejazi et al., 2011; Moucka et al., 2010; Okada and Usuki, 2006; Pavlidou and Papaspyrides, 2008; Ray and Okamoto, 2003).

Polypropylene (PP) is one of the most widely used thermoplastics because of its attractive combination of good process ability and mechanical properties. However, its inadequate brittleness limits its versatile application to some extent. An effective and economical method to improve the mechanical properties of PP is compounding with inorganic particles (Alkbari and Bagheri, 2009; Chen et al., 2011; Chinellato et al., 2010; Gianelli et al., 2005; Kondo et al., 2010; Maiti et al., 2002; Martin et al., 2010; Tang et al., 2004). Because the backbone of PP has no any polar groups, it is very difficult to directly prepare intercalated or exfoliated montmorillonite (Mt)/PP nanocomposites. Lots of efforts were conducted to improve the compatibility between Mt and PP by using functional oligomers as compatibilizer (Chen and Chang, 2001;

Cui and Paul, 2007; Garcia-Lopez et al., 2003; Kawasumi et al., 1997; Lopez-Quintanilla et al., 2006; Moncada et al., 2006; Szazdi et al., 2005; Wang et al., 2005, 2006). The compatibilizer most widely used was maleic anhydride modified PP (PP-g-MA). The driving force of the intercalation originated from the hydrogen bonding between the COOH group generated from the hydrolysis of maleic group and the oxygen groups of silicates (Hasegawa et al., 1998, 2000; Kawasumi et al., 1997). The effects of PP-g-MA on composite morphology and the correlation between the achieved morphology and the material properties are widely investigated (Chiu et al., 2004; Hasegawa et al., 2000; Joshi and Viswanathan, 2006; Kanny et al., 2008; Kodgire et al., 2001; Mittal, 2007). The results showed that Mt was not only well dispersed, but also exfoliated. The modulus, tensile strength and thermal properties of Mt/PP nanocomposites were enhanced while the melt viscosity and toughness were not obviously improved.

Recently, intercalation of poly(ethylene oxide) (PEO) and the low molar mass poly(ethylene glycol) (PEG) into the interlayer space of Mt led to the formation of hybrid structures with a wide range of interesting properties and important applications (Aranda and Ruiz-Hitzky, 1999; Guégan, 2010; Huang et al., 2010; Lin et al., 2007; Loyens et al., 2005; Miwa et al., 2008; Ratna et al., 2007; Vaia et al., 1995; Zampori et al., 2010). It is well known that PEG is easily intercalated into the interlayer spaces of Mt. And the interaction between PEG and silicates is rather strong (Aranda and Ruiz-Hitzky, 1999). In previous work, the Mt/PEG hybrids as fillers were melted with PP. The addition of the Mt/

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PEG hybrids in PP matrix led to a significant reduction of melt viscosity and enhancement in toughness while the tensile strength was a little decreased (Zhu et al., 2009). Liao et al. (2001) considered polyethylene (PE)-PEG diblock copolymer/ Na^+ -montmorillonite (Na^+ -Mt) nanocomposites as fillers for reinforcement of PE. These authors found that by only adding a small amount of Na^+ -Mt/PE-PEG hybrids, tensile strength of PE was enhanced significantly. However, PE-PEG diblock copolymer is not suitably applied in industry at present due to high cost.

In the present work, Mt/PP nanocomposites were prepared using poly(ethylene glycol) grafted polypropylene (PP-g-PEG) as a new Mt modifier. The PEG segments of PP-g-PEG could fix at the surfaces of Mt while the PP segments were compatible with PP matrixes. The melt rheological behaviors and mechanical properties of Mt/PP-g-PEG/PP nanocomposites were also investigated.

2. Experiment

2.1. Materials

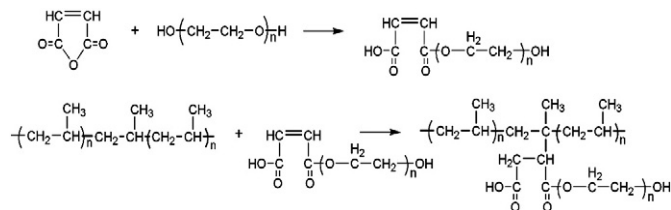
A commercially isotactic PP ($M_w = 380000$ g/mol) was supplied from Lanzhou Chemical Industry Factory (Lanzhou, China). PEG ($M_w = 1500$ g/mol) was provided by Liaoyang Aoke Chemical Co. (Liaoning, China). Maleic anhydride (MA) and dicumyl peroxide (DCP) were provided by Kelong Chemical Co. (Chengdu, China). Paratoluenesulfonic acid (PTSA) used as a catalyst was also provided by Kelong Chemical Co. PP-g-MA ($M_w = 160000$ g/mol, 1 wt.% of MA) was purchased from Chenguang Chemical Industry Research Institute (Chengdu, China). Ca^{2+} -montmorillonite (Ca^{2+} -Mt) with a cation-exchange capacity (CEC) of 90 meq/100 g and organophilic montmorillonite (OMt) were supplied from Zhejiang Fenghong Clay Chemicals Co. (Zhejiang, China). OMt was sodium montmorillonite modified with octadecyl trimethylammonium chloride. All the chemicals were used as received.

2.2. Synthesis routes of PP-g-PEG

PP-g-PEG was synthesized by two following routes: (a) PP-g-MA directly reacted with PEG (Scheme 1). (b) MA reacted with PEG, and then the reaction products were melted blending with PP and an initiator by using twin-screw extruder (Scheme 2).

2.3. Preparation of Mt/PP-g-PEG/PP nanocomposites

Mt/PP-g-PEG/PP nanocomposites were prepared via melt blending according to two methods: (a) In a 500 ml three-necked flask under a nitrogen atmosphere, 50 g PP-g-MA (0.005 mol MA) was first dissolved in 300 ml xylene at 135 °C. When dissolution was complete, 7.5 g PEG (0.005 mol) and 0.2 g catalyst were added under vigorous stirring. After reaction for 4 h, the resulting products (PP-g-PEG graft copolymer) were dried in vacuum at 60 °C for more than 72 h, pulverized, and then blended with Mt. The PP-g-PEG/ Ca^{2+} -Mt and PP-g-PEG/OMt with mass ratio 1:1 were designated as PMMt and PMOMt, respectively. The abbreviations of modified Mt were listed in Table 1. The PP resins were firstly mixed with 1–5 phr (per hundred parts of PP by mass) PMMt or PMOMt hybrids, and then extruded by a general three-section twin-screw extruder. (b) Firstly, 150 g PEG (0.1 mol) was melted in 250 ml three-necked flask under a nitrogen atmosphere at 80 °C. 9.8 g MA (0.1 mol) and 0.6 g catalyst were added under vigorous



Scheme 2. Reaction between PP and MPEG.

stirring. After reaction for 4 h, the resulting products (MPEG) were dried in vacuum at room temperature more than 72 h, pulverized, and then blended with Mt with mass ratio 1:1. The MPEG/ Ca^{2+} -Mt and MPEG/OMt were designated as MPMt and MPOMt, respectively (Table 1). 1–5 phr of MPMt or MPOMt hybrids and initiator (DCP) were blended with PP by using the twin-screw extruder. The screw speed of twin-screw extruder ($D = 20$ mm, $L/D = 40$) was set at 200 rpm and the temperatures were 175 °C, 190 °C, and 190 °C for each section of the barrel and 185 °C for the die. An injection-molding machine (K-TEC400, Clarke international Co., Ltd.) was used to prepare the standard specimens for the mechanical tests.

2.4. Characterization of the CPN

Fourier transform infrared (FTIR) spectroscopy was performed in the transmission mode with a Nicolet-560 spectrometer (Bruker). The spectra were collected at 4 cm^{-1} resolution between 400 and 4000 cm^{-1} with collection times of approximately 1 min. In order to remove the unreacted MA, PEG and MPEG in Mt/PP-g-PEG/PP nanocomposites, all samples were molded into film and extracted by boiling acetone for 72 h before testing.

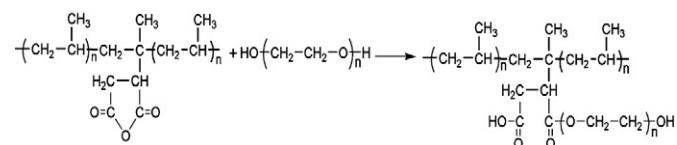
X-ray diffraction (XRD) patterns were recorded with a DX-1000 CSC diffractometer (China). The X-ray beam was nickel-filtered Cu K α ($\lambda = 0.1542$ nm) radiation operated at 40 kV and 25 mA. Ca^{2+} -Mt and OMt were studied as powders. Samples of Mt/PP nanocomposites were cut from the injection molded specimens. The scanning range was varied from $2\theta = 1.5^\circ$ to 10° with a rate of $1.8^\circ/\text{min}$.

Transmission electron microscopy (TEM) was carried out with an H-7100 (Tokyo, Japan) instrument with an accelerating voltage of 100 kV. The ultrathin sections of the samples with a thickness of 50 nm were obtained from injection molded at 20 °C by a Reichert Ultracut cryoultramicrotome without staining.

Thermal behaviors were performed on a DSC1 (Mettler Toledo Co., Switzerland) differential scanning calorimeter under constant nitrogen flow. Sample mass was maintained at low level (5–6 mg) for all measurements. All samples were first heated to 200 °C, held at 200 °C for 5 min, and then cooled with a rate $10^\circ\text{C}/\text{min}$ to 50 °C, and held at 50 °C for 5 min. They were then scanned from 50 to 200 °C at a rate of $10^\circ\text{C}/\text{min}$.

Tensile tests were carried out according to GB/T 1040-92 standard on CMT 4104 machine (Sans Material Testing Technical Co., Shenzhen, China). Elongation at break was measured at a cross-head speed of 50 mm/min. Izod-notched impact strength was measured with ZQK-20 (Dahua Material Testing Technical Co., China) according to the GB/T1043-93 standard.

The rheological measurements were carried out on a Gottfert Rheograph 2002 (Gottfert Co., Germany). The capillary diameter and



Scheme 1. Reaction between PP-g-MA and PEG.

Table 1

Abbreviation of the modified Mt prepared at different routes.

Modifier	Montmorillonite	Mass ratio	Abbreviation
PP-g-PEG route (a)	Ca^{2+} -Mt	1:1	PMMt
	OMt	1:1	PMOMt
MPEG route (b)	Ca^{2+} -Mt	1:1	MPMt
	OMt	1:1	MPOMt

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