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Research paper

Facile preparation of highly exfoliated and optically transparent polycarbonate (PC)/clay mineral nanocomposites using phosphonium modified organoclay mineral

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ABSTRACT

Here, we focus on the morphology, mechanical and optical properties of the polycarbonate (PC) in the PC/clay mineral nanocomposites prepared through both the melt and solution blending technique at two different loadings (0.5 phr and 1 phr) of propyl triphenyl phosphonium modified montmorillonite (PTPP-Mt). The modified organo-Mt was prepared by ion exchange reaction and verified through FTIR spectroscopy, EDS study and XRD analysis. The outstanding thermal stability of the PTPP-Mt at the processing temperature of PC (280 °C) made it a suitable candidate for the preparation of optically transparent PC/Mt nanocomposites. The XRD analysis over the PC/PTPP-Mt nanocomposites revealed the destruction of ordered geometry of the clay mineral, whereas, the presence of some localised zones of Mt was evident from transmission electron microscopic (TEM) analysis. Thermal analysis indicated an increase in glass transition temperature (T_g) and thermal stability of PC in the nanocomposites. The strength and modulus of the nanocomposites were increased with increase in Mt loadings. An increase in storage modulus in the nanocomposites was evident from the thermomechanical studies. Finally, the optical transparency of PC was retained without generation of any colour in the PC/PTPP-Mt nanocomposites.

1. Introduction

Polycarbonate (PC) is a well-known optically transparent, amorphous, engineering thermoplastic possessing excellent thermal stability, impact property and heat distortion temperature (HDT). But, it suffers from very poor chemical resistance (LeGrand and Bendler, 2000). Layered silicates of nanometre thickness are reported to increase chemical resistivity with concomitant increase in mechanical and thermal properties (Friessell and Bikales, 1967). If it can be done without affecting much the optical properties many practical and commercial applications can be resolved.

Montmorillonite (Mt), a smectite layered-silicate, consists of stacks of 1 nm thick aluminosilicate layers regularly spaced. Each layer contains a central sheet of octahedral-Al sandwiched between two tetrahedral silicate sheets. Isomorphic substitutions of trivalent aluminum by bivalent magnesium in the octahedral sheet result negative charges, which are being compensated by the alkaline earth- or hydrated alkali metal cations present in between two aluminosilicate layers (Bailey, 1980, 1984). The van der Waals and electrostatic forces holding the layers together are relatively weak in the Mt. The ease of swelling of high aspect ratio layers in water makes them suitable substrates for surface ion exchange with alkyl ammonium, phosphonium, imidazolium etc ions. These modifiers modify the surface of the clay mineral layers to make them compatible with organic polymer matrices to achieve good interaction between them (Lagaly and Beneke, 1991; Theng, 1974).

Polymer/layered silicate nanocomposites have attracted various research groups, because of its unique sets of properties depending on the range of interaction between the polymer and the nano-dispersed clay silicate layers (Sinha Ray and Okamoto, 2003). Naturally occurring clay mineral is hydrophilic in nature, whereas, major polymers are organophilic in nature. Thus, for better dispersion and interaction of the hydrophilic clay mineral with the organophilic polymers, clay mineral is required to be modified with quaternary ammonium (Carrion et al., 2008; Chow and Neoh, 2010; Guduri and Luyt, 2008; Hsieh et al., 2004; Huang et al., 2000; Lee and Han, 2003; Mitsunaga et al., 2003; Nevalainen et al., 2009; Wu et al., 2007; Yoon et al., 2003a, 2003b), phosphonium (Avalos et al., 2009; Cai et al., 2010; Calderon et al., 2008; Gilman et al., 2002; Patro et al., 2009; Rama and Swaminathan, 2010; Saitoh et al., 2011; Wang et al., 2012; Xiang et al., 2010; Xie et al., 2002) imidazolium (Cui et al., 2009; Gilman et al., 2002; Rama and Swaminathan, 2010) ions etc. These bulky ions not only help to increase the compatibility between polymer and clay mineral, but also favour the intercalation of polymer chains into the interlayer spaces of the clay.

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Depending on the method of composites preparation and state of dispersion of clay minerals in the matrix polymer, three different microstructures may appear in the polymer/clay mineral nanocomposites. When the polymer fails to intercalate between the silicate sheets, a phase separated composite is obtained. In intercalated structure, a single (or more) polymer chain intercalates between the silicate layers, resulting in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the ordered structure of the clay minerals gets destroyed and the individual silicate layers get completely and uniformly dispersed in the continuous polymer matrix, an exfoliated or delaminated structure is obtained. Polymer/clay mineral nanocomposites can be prepared by three conventional methods, such as, (a) *in-situ* polymerization of monomers in presence of clay mineral (Jash and Wilkie, 2005; Sain and Khatua, 2011; Su and Wilkie, 2003; Xie et al., 2003) (b) solution blending (Gao et al., 2001; Yeh et al., 2004) and (c) melt blending (Carrion et al., 2008; Chow and Neoh, 2010; Guduri and Luyt, 2008; Hsieh et al., 2004; Huang et al., 2000; Lee and Han, 2003; Mitsunaga et al., 2003; Nevalainen et al., 2009; Wu et al., 2007; Yoon et al., 2003a, 2003b). Among these three manufacturing methods, melt blending is most demanding because of its industrial acceptance.

A number of research articles have been reported in the literature concerning the properties of PC/clay mineral nanocomposites using different modified clay minerals. Huang et al., 2000 prepared successfully intercalated-exfoliated PC/clay mineral nanocomposites via ring opening polymerization using lower molecular weight cyclic carbonate oligomers and ditallow dimethyl quaternary ammonium substituted montmorillonite. Lee and Han, 2003 studied the effect of H-bonding on the morphology and properties of PC/Mt nanocomposites. Their study revealed that, the H-bonding between the carbonyl group of PC and the active functional group presents in the modifier was responsible for the exfoliation of the clay mineral in the twin-screw extruded PC/clay mineral nanocomposites. Yoon et al., 2003a, 2003b made a detailed study over various molecular weight PC and different ammonium modified clay minerals to investigate the effect of molecular weight of PC and organoclay mineral structure on the morphology and properties of PC/clay mineral nanocomposites. They reported that, the high shear force generated during the melt processing of high molecular weight PC resulted in high degree of dispersion of clay mineral layers into the PC matrix. A consequent paper revealed that, the reduction of molecular weight and occurrence of colour in the melt blended PC/clay mineral nanocomposites was dependent on residence time in the extruder, chemical structure of the modifier, and the iron content of the clay mineral (Yoon et al., 2003a, 2003b). Guduri and Luyt, 2008 studied the effect of PP-g-MA on the morphology and mechanical properties of melt intercalated PC/clay mineral nanocomposites. The morphological study revealed that, the extent of exfoliation of the clay minerals was increased with increasing amount of PP-g-MA in the nanocomposites. Hsieh et al., 2004 concentrated on the mechanical and rheological properties of melt-intercalated PC/clay mineral nanocomposites. They reported that, during melt blending, the degradation of PC matrix was related to the loading of clay mineral in the nanocomposites, which in turn decreased the T_g and molecular weight of the PC in the nanocomposites. Mitsunaga et al., 2003 studied the effect of a compatibilizer in the melt intercalated PC/clay mineral nanocomposites. Their study revealed that, the morphology of the clay mineral in the nanocomposites and the degradation of the matrix phase were dependent on the surfactants present in the modified clay mineral and the compatibilizer used. Wu et al., 2007 studied the effect of epoxy resin on the rheological properties of melt-intercalated PC/clay mineral nanocomposites. They reported that, the addition of epoxy at lower amount favoured the dispersion of clay mineral layers, whereas, the higher loading of epoxy played the role of a plasticizer that resulted in severe degradation of the PC matrix. Rama and Swaminathan, 2010 studied the morphology and optical properties of the PC/Mt nanocomposites prepared through *in-situ* melt polycondensation using phosphonium and imidazolium modified organoclay mineral. A highly exfoliated morphology was developed with generation of dark brown colour in the nanocomposites.

The literature discusses mainly the morphology and mechanical properties of the PC/clay mineral nanocomposites in presence of different modified clay minerals without giving much attention on the optical properties and colour issues. Moreover, most of the works deal with the ammonium modified organoclay minerals. Conventional ammonium modified organoclay minerals can hardly sustain at the processing temperature of PC (≈280 °C) and thus degrades during the preparation of PC/clay mineral nanocomposites. This sort of degradation of the modified clay minerals generates reactive radicals, which transform PC chains into coloured quinoid form and thus the optical transparency of PC gets destroyed (Feng et al., 2012; Xie et al., 2001). This work deals with the preparation and properties of PC/Mt nanocomposites through conventional melt and solution blending process, using phosphonium modified clay mineral. The effect of the thermally stable organoclay mineral on the morphology, mechanical and optical properties has been described in the manuscript in detail.

2. Experimental

2.1. Materials used

The bisphenol-A polycarbonate (PC), used as the base matrix, was of commercial grade (Lexan 143, MFI ≈ 10.5 g/10 min at 300 °C and 1.2 kg load), supplied by SABIC Innovative Plastics. The unmodified naturally occurring clay mineral (sodium montmorillonite, Na-Mt) was procured from Southern Clay Products, Inc., USA. The cation exchange capacity (CEC) of the supplied Na-Mt is 92 mequiv/100 g of clay mineral. The organic modifier, propyl triphenylphosphonium bromide (PTPP-Br) was purchased from Sigma-Aldrich. Methanol and dichloromethane were supplied by Merck, Germany.

2.2. Modification of the Mt

The modification of the pristine clay mineral (Na-Mt) was done through the ion exchange reaction following the method described in our previous paper (Suin and Khatua, 2012) using PTPP-Br in water medium. In a beaker 2.5 g of Na-Mt was dispersed in 250 ml de-ionized water by ultrasonication (OSCAR Model PR-250; ultrasonic power 250 W, frequency 25 kHz, probe tip diameter 6 mm) at room temperature for 1 h to destroy the ordered structure of the clay mineral in the water medium. The clay mineral/water suspension was then transferred in a 2 L three neck round bottom flask (R. B. flask) containing 500 ml water and stirred for 45 min, using an overhead stirrer. The reactor temperature was maintained at 80 °C throughout the reaction. Based on the CEC value (92 meqiv/100 g) of the Na-Mt, calculated amount (~1 g) of the quaternary phosphonium salt (PTPP-Br) was dissolved in 50 ml de-ionized water. The PTPP-Br solution was then added drop wise over a period of 10 min to the dispersion of Na-Mt in the reaction flask under stirring condition. The addition of the PTPP-Br solution was followed by the settling down of the clay mineral agglomerates. The introduction of the organic moiety into the interlayer space of the clay minerals was responsible for the generation of hydrophobicity in the clay mineral, which in turn helped the settling down of the clay minerals. The reaction was continued for another 2 h for the completion of the ion exchange reaction. The resulting clay mineral agglomerates were filtered by vacuum filtration and then washed by hot water to remove the undesired impurity (NaBr and unexchanged propyltriphenylphosphonium bromide). The washing was continued till the filtrate was free from bromide ions, as examined by a dilute $AgNO_3$ solution. The final washing was carried out by using 250 ml methanol to eliminate the excess propyltriphenylphosphonium ions present in the interlayer spaces of the clay mineral. The moist clay mineral, obtained after final filtration, was first air-dried and then under