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Phosphonium modified organoclay as potential nanofiller for the development of exfoliated and optically transparent polycarbonate/clay nanocomposites: Preparation and characterizations

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ABSTRACT

Here, we report the preparation and properties of optically transparent polycarbonate (PC)/clay nanocomposites through the conventional methods of nanocomposites preparation (melt blending and solution blending) leading mainly to the exfoliation of thermally stable phosphonium modified organoclay. The organic modification of the sodium montmorillonite (Na-MMT) was done by the inclusion of ethyl triphenylphosphonium (ETPP) ion inside the layer spacing of Na-MMT clay through ion exchange reaction. The resulting quaternary phosphonium modified organoclay showed outstanding stability against thermal degradation in isothermal TGA analysis at the processing temperature of PC (280 °C). Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) studies revealed that, the MMT layers were well exfoliated at lower loading (0.5 phr) of ETPP-MMT, whereas, presence of a mixed clay morphology of exfoliation with minor intercalation was obtained at higher loading (1 phr) of the clay in both the melt and solution blended PC/ETPP-MMT nanocomposites. The tensile strength and Young modulus were increased, whereas, elongation at break was decreased with increase in clay loading in both the melt and solution blended ETPP-MMT nanocomposites. The thermo-mechanical properties of the nanocomposites were superior to that of the neat PC in both the glassy and rubbery regions. The optical transparency of PC was retained without development of any colour in the PC/ETPP-MMT nanocomposites.

1. Introduction

The attainment of desired property via introduction of nanoscopic clay layers into the polymer matrix has been extensively studied over the past decade or so because of their abundance and relatively low cost [1–3]. The resulting class of compounds are designated as polymer/clay nanocomposites, in which the thickness of individual clay platelet is in the nanometer scale. These nanocomposites possess enhanced properties, such as tensile properties [4–7], impermeability to gases [8–11], thermal stability [12–15], flame retardancy [16–19] compared to the unfilled or conventionally filled nanocomposites. The dispersion of clay silicate layers into the polymer matrix is the key factor for such increment in properties. Complete delamination of individual clay platelets into the polymer matrix usually gives rise to the largest improvements in properties, because of possibly highest area of interaction between polymer and clay for a particular loading of clay [20]. In intercalated nanocomposites, there is some interaction between polymer and clay, but it is inadequate to delaminate the clay platelets. The migration of polymer chains into the clay galleries gives rise to moderate enhancement in property. The conventional composites or microcomposites form when the interaction between the polymer and clay is very weak and the clay remains

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in aggregated or tactoid form. This kind of composites gives rise to marginal improvement in properties.

Since the clay is hydrophilic in nature, it is organically modified to make the clay more compatible with the polymer (which is organophilic). Quaternary ammonium [21–30], quaternary phosphonium [32–42], imidazolium [40–42], pyridinium [39] etc. ions (bulky ions) are generally incorporated into the clay galleries to make it compatible with the polymer matrix and desired set of properties. Three different techniques are generally employed to prepare polymer/clay nanocomposites: (a) *in situ* polymerization of the monomers in the presence of clay [43–44], (b) melt processing [22–31] and (c) solution casting [45–46].

Polycarbonate (PC) is a high impact amorphous engineering thermoplastic with excellent thermal stability, heat distortion temperature (HDT) and optical transparency. Different modified clays are generally incorporated into the PC matrix to tailor the properties of PC. However, the quaternary ammonium ions, generally used for clay modification fail to sustain at the very high processing temperature (≈280 °C) for PC and thus degrades [47,48]. The radical fragments formed during degradation of quaternary ammonium ions promotes degradation of PC during melt processing. This sort of degradation of PC reduces the molecular weight, mechanical strength, glass transition temperature (T_g), optical clarity of PC and develops colours in the final nanocomposites [24,49].

Various attempts have been made to prepare PC/clay nanocomposites via incorporation of different modified clays for desired sets of properties. Brittain and co-workers [21] prepared PC/clay nanocomposites with intercalated-exfoliated morphology via ring opening polymerization using low molecular weight cyclic carbonate oligomers and ditallow dimethyl quaternary ammonium substituted montmorillonite. Han and co-workers [22] reported that the H-bonding between the active functional group of the modifier and the carbonyl group present in PC is effective for higher degree of clay exfoliation in the twin-screw extruded PC-clay nanocomposites. Paul and co-workers [23] investigated the effect of molecular weight of PC and organoclay structure on the morphology and properties of PC/clay nanocomposites by using PC with various molecular weight and different ammonium modified clays. The high shear force generated during the melt processing of high molecular weight PC caused high degree of dispersion of clay platelets into the PC matrix. In a consequent paper, they showed that the reduction of molecular weight and occurrence of colour in the melt blended PC/clay nanocomposites depend on residence time in the extruder, chemical structure of the modifier, and the iron content of the clay [24]. Hsieh et al. [25] studied the mechanical performance and rheological properties of melt-intercalated PC/clay nanocomposites. Their study revealed that, the degradation of PC matrix in presence of the clay decreased the T_g and molecular weight of the PC in the nanocomposites during melt compounding. Okamoto et al. [26] studied the effect of a compatibilizer in the melt intercalated PC/clay nanocomposites. They concluded that, the morphology of the clay in the nanocomposites and degradation of the PC during processing can be altered by varying the surfactants in the modified clay and the compatibilizer. Zhang et al. [27] studied the effect of epoxy resin (as compatibilizer) on the rheological properties of melt-intercalated PC/clay nanocomposites. The addition of small amount of epoxy resin favoured the dispersion of clay platelets into the PC matrix, whereas, the higher loading of epoxy played the role of a plasticizer and degraded the PC matrix adversely. Nevalainen [29] used two different ammonium modified clays to study the morphology and mechanical properties of twin screw extruded PC/clay nanocomposites. Both the nanocomposites possessed an increased tensile strength and Young modulus of the nanocomposites but, decreased impact strength compared to neat PC, irrespective of the nature of the modifier. Chow et al. [30] studied the effect of maleic anhydride grafted styrene ethylene butadiene styrene (SEBS-g-MA) on the morphological, mechanical and thermal properties of melt intercalated PC/Na-MMT nanocomposites. Their study revealed that, the nanocomposites possessed greater impact strength, showing the toughening effect of SEBS-g-MA on the PC/Na-MMT nanocomposites. Swaminathan et al. [40] prepared exfoliated PC/clay nanocomposites using phosphonium and imidazolium modified organoclay via *in situ* melt polycondensation. In spite of the presence of thermally stable bisphenol functionality in the modifier the resulting nanocomposites appeared dark brown in colour.

The extensive studies over PC/clay nanocomposites suggest that, irrespective of the method of nanocomposites preparation, development of highly exfoliated PC/clay nanocomposite with retention of optical clarity is still a great deal. The high processing temperature of PC (280 °C) causes degradation of quaternary ammonium modifier (generally used as modifier) through Hoffmann elimination reaction, generating reactive radical [50], which favours degradation of PC matrix through Fries rearrangement [51], resulting colour in the final PC/clay nanocomposites. This led to further scope of research in this regard on PC/clay nanocomposites. Here, we describe the preparation of colour free transparent PC/clay nanocomposites through both melt and solution blending process. The effect of blending techniques on the morphology, mechanical and optical properties of the nanocomposites has been described in detail in the article.

2. Experimental

2.1. Materials used

Bisphenol-A polycarbonate (PC) used as base polymer 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 nanoclay (sodium montmorillonite, Na-MMT) used in this study was procured from Southern Clay Products, Inc., USA. The cation exchange capacity (CEC) value of the Na-MMT is 92 mequiv/100 g of clay. The organic modifier, ethyltriphenylphosphonium bromide (an aromatic quaternary phosphonium salt, ETPP-Br) was obtained from Sigma–Aldrich. Methanol and dichloromethane were purchased from Merck, Germany.