



## Technical Report

# Mechanically improved and optically transparent polycarbonate/clay nanocomposites using phosphonium modified organoclay



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## ABSTRACT

The present study deals with the properties of polycarbonate (PC)/clay nanocomposites prepared through melt and solution blending at two different clay loadings (0.5 phr and 1 phr) with preserved optical transparency of PC. The organoclay was prepared by exchanging the Na<sup>+</sup> ions presented in the clay galleries of Na-MMT with butyltriphenylphosphonium (BuTPP<sup>+</sup>) ions, and denoted as BuTPP-MMT. The outstanding thermal stability of the BuTPP-MMT (~1.44 wt% loss at 280 °C, after 20 min), concomitant with the increase in gallery height from 1.24 nm to 1.83 nm, proved its potentiality as nanofiller for melt-blending with PC. The X-ray diffraction analysis (XRD) revealed the destruction of the ordered geometry of aluminosilicate layers in the nanocomposites. However, from direct visualization through transmission electron microscopy, a discernible amount of clay was found to be localised in PC matrix in the 1 phr clay loaded nanocomposites (TEM). The differential scanning calorimetric (DSC) study revealed a nominal increase in glass transition temperature ( $T_g$ ) of the PC in the nanocomposites. The thermal stability of the nanocomposites was increased with increase in clay loading. The nanocomposites possessed improved tensile strength and modulus than that of the virgin PC and the properties were related to the amount of clay loading and degree of clay dispersion. The dynamic mechanical analysis (DMA) revealed that the storage modulus increased in both the glassy and rubbery region with increase in clay loadings in the nanocomposites. Moreover, the optical transparency of the PC was retained in the PC/clay nanocomposites without development of any colour in the nanocomposites.

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## 1. Introduction

Polymer/clay nanocomposites have attracted many researchers of both industry and academia for its fabulous sets of properties originating from the reinforcement generated from the incorporation of nanoscopic clay layers into the polymer matrix. Such properties in these nanocomposites are associated with the high aspect ratio and surface area of the nanoscopic silicate layers even at very low clay loading [1]. The polymer/clay nanocomposites appear as a material possessing improved tensile properties [2], thermal stability [3], flame retardancy [4] and impermeability to gas [5] compared to the unfilled or conventional filler filled composites. The dispersion of the clay layers into the polymer matrix as well as the interaction between polymer and clay are considered to be the determining factor for such improvement in properties. In ideal case, the individual clay platelets are supposed to be fully delaminated into the polymer matrix, resulting largest improvements in properties, because of possibly highest area of interaction between polymer and clay for a particular loading of clay [6]. Intercalated nanocomposites are formed when the interaction between

polymer and clay is insufficient to delaminate the clay platelets. The penetration of some of the polymer chains into the clay galleries increases the layer spacing of the clay with moderate increment in property. In conventional composites or microcomposites, the interaction between the polymer and filler is very weak and the filler particles remain in agglomerated form, resulting very nominal improvement in properties. Generally, three methods are used to prepare polymer/clay nanocomposites: (a) *in situ* polymerization of the monomers in the presence of clay [7], (b) melt processing [8–15], and (c) solution casting [16].

In order to incorporate hydrophilic clay silicate layers into the hydrophobic polymer matrix, either the clay or the polymer need to be modified to enhance their compatibility. In practical purpose the first one is chosen, for its simplicity and better dispersion of clay layers into the polymer matrix. To make the clay compatible to the polymer matrix, bulky ions such as quaternary ammonium [8–13], quaternary phosphonium [17–22], and imidazolium [22,23], are generally incorporated into the clay galleries. The choice of the modifier is based on the processing temperature of the nanocomposites and desired property in the final nanocomposites.

Polycarbonate (PC) is a high performance amorphous engineering thermoplastic possessing outstanding thermal stability, heat distortion temperature (HDT) and optical transparency. The

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thermal and mechanical properties of polymers are reported to be increased on incorporating inorganic fillers into the polymer matrix. If it can be done without significant loss in optical transparency, PC based composites can be used in a wide application areas. 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 [24], which favours degradation of PC matrix through Fries rearrangement [25] converting PC into coloured quinoid form, and thus, results colour in the PC/clay nanocomposites. This sort of degradation of PC matrix is associated with the reduction in molecular weight, mechanical strength, glass transition temperature ( $T_g$ ), optical transparency and colour development in the final nanocomposites.

Various attempts have been reported to prepare PC/clay nanocomposites via incorporation of different modified clays through both the melt and solution blending process. Brittain et al. [8] applied ring opening polymerization technique to prepare PC/clay nanocomposites with intercalated-exfoliated morphology, using low molecular weight cyclic carbonate oligomers and ditallow dimethyl quaternary ammonium substituted montmorillonite. Han [9] reported that the higher degree of clay exfoliation and good compatibility between PC and clay in the twin-screw extruded PC/clay nanocomposites was caused by the H-bonding between the active functional group of modifier and the carbonyl group presented in PC. Paul et al. [10] investigated the effect of molecular weight of PC and the structure of the organoclay on the morphology and properties of PC/clay nanocomposites. The higher degree of dispersion of the clay platelets into the high molecular weight PC was achieved by the high shear force generated during the melt processing of high molecular weight PC. Their study also revealed that the reduction of molecular weight and appearance of colour in the melt blended PC/clay nanocomposites depends on residence time in the extruder, chemical structure of the modifier, and the iron content of the clay [11]. Okamoto et al. [12] investigated the effect of a compatibilizer during melt intercalation of the PC/clay nanocomposites. They reported that the mechanical property of the PC was increased on incorporating clay into the PC/clay nanocomposites. Their study also revealed that, the morphology of the clay in the nanocomposites and degradation of the PC during processing can be varied by changing the surfactants in the modified clay and the compatibilizer. Hsieh et al. [13] studied the effect of clay loading on the mechanical performance and rheological properties of melt-intercalated PC/clay nanocomposites. They concluded that, with increase in the clay loading the  $T_g$  and molecular weight of the PC in the nanocomposites were decreased during melt compounding due to the degradation of the PC matrix. Nevalainen [14] studied the morphology and mechanical properties of twin screw extruded PC/clay nanocomposites, using two different ammonium modified clays. The tensile strength and young modulus of the nanocomposites were increased, whereas, impact strength was decreased on incorporating the clay into the virgin PC, irrespective of the nature of modifier. On incorporating clay into the PC, a transition from ductile to brittle was also evident from their study. Zhang et al. [15] studied the efficiency of epoxy resin in compatibilization of the melt-intercalated PC/clay nanocomposites. Addition of small amount of epoxy resin favoured the dispersion of clay platelets into the PC matrix, whereas, the epoxy at higher loading acted as plasticizer causing undesirable degradation of the PC matrix. Swaminathan [22] have recently reported the preparation of exfoliated PC/clay nanocomposites using phosphonium and imidazolium modified organoclay via *in situ* melt polycondensation. In spite of the occurrence of thermally stable bisphenol functionality in the modifier, the final PC/clay nanocomposites appeared dark brown in colour.

The literature on PC/clay nanocomposites deals mainly with the morphological and mechanical properties of the nanocomposites in the presence of various modified clays. However, a very small stress has been given towards the optical transparency and colour issues of the PC/clay nanocomposites. Here, we report the preparation of optically transparent PC/clay nanocomposites through conventional melt and solution blending process and properties of the nanocomposites. The effect of blending technique on the morphology, mechanical and optical properties and colour issues are described in detail in the manuscript.

## 2. Experimental details

### 2.1. Materials used

Commercial grade bisphenol-A polycarbonate (PC) (Lexan 143, MFI  $\approx$  10.5 g/10 min at 300 °C and 1.2 kg load) used in this study was supplied by SABIC Innovative Plastics. The unmodified nanoclay (sodium montmorillonite, Na-MMT) was purchased from Southern Clay Products, Inc., USA. The cation exchange capacity (CEC) value of the supplied Na-MMT is 92 mequiv/100 gm of clay. The organic modifier, butyl triphenylphosphonium bromide (BuTPP-Br) was procured from Sigma-Aldrich. Methanol and dichloromethane were obtained from Merck Germany.

### 2.2. Modification of the clay

The modification of the unmodified clay, Na-MMT was done through the ion exchange reaction using BuTPP-Br in water medium. In a 500 ml beaker, 2.5 g Na-MMT was dispersed in 250 ml de-ionized water and ultrasonicated at room temperature for 1 h to break the layered structure of clay in the water medium. The resulting Na-MMT/water suspension was then transferred in a 2L three neck round bottom flask (R. B. flask) containing 500 ml water and stirred for 45 min, using an overhead stirrer. The temperature of the reactor was maintained at 80 °C throughout the ion exchange reaction. Based on the CEC value of the Na-MMT (given by the supplier), slightly higher amount ( $\sim$ 1 g) of the quaternary phosphonium salt (BuTPP-Br) was dissolved in 50 ml de-ionized water. The higher amount of BuTPP-Br facilitated the modification of the Na-MMT clay as much as possible. The BuTPP-Br solution was then added drop wise over a period of 10 min to the dispersed Na-MMT suspension in round bottom flask under stirring condition. The reaction was allowed to continue for another 2 h to complete the ion exchange reaction. The settling down of the clay agglomerates in the reaction flask indicated the completion of the reaction. The incorporation of the organic moiety inside the clay galleries was responsible for the generation hydrophobicity in the clay, which resulted in settling down of the clay. The resulting agglomerates were then filtered by using vacuum pump and washed in a vessel containing 250 ml of water under stirring at 80 °C for 20 min to remove the undesired impurity (NaBr and unexchanged butyltriphenylphosphonium bromide). The organoclay-water suspension was re-filtered. The washing process was continued until the filtrate was free from bromide ion, as examined by a dilute  $\text{AgNO}_3$  solution. The final washing was done by 250 ml methanol to eliminate the excess butyltriphenylphosphonium ion presented in the clay galleries. The moist clay was first air-dried and then under vacuum at 80 °C for 12 h. The oven-dried clay aggregates were then grinded to fine powder with the help of mortar and pestle. The schematic for the modification of the clay is shown in Fig. 1.

### 2.3. Preparation of the PC/clay nanocomposites

Two different blending techniques (melt and solution blending) were used for the preparation of PC/clay nanocomposites at two

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