

## Microstructure and Properties of PBT/EVA-g-MAH/Organoclay Ternary Nanocomposites

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### Abstract

Three different polymer/layered silicate nanocomposites based on poly(butylene terephthalate)(PBT) were prepared via melt intercalation; PBT/organoclay nanocomposite, maleic anhydride grafted poly(ethylene-co-vinyl acetate) (EVA-g-MAH)/organoclay nanocomposite, and PBT/EVA-g-MAH/organoclay ternary nanocomposite. It was found that the PBT/EVA-g-MAH/organoclay ternary nanocomposite showed much enhanced impact strength in comparison to PBT without severely sacrificing the tensile strength of PBT.

Key words: nanocomposite, organoclay, poly(butylene terephthalate), epoxy, maleic anhydride grafted poly(ethylene-co-vinyl acetate)

### Introduction

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic with many useful properties including high degree and rate of crystallization, good chemical resistance, thermal stability, and excellent flow properties. However, pure PBT has low impact strength and heat distortion temperature. Many attempts have been made to improve the impact properties of PBT by blending PBT with a rubber-like polymer such as poly(ethylene-co-vinyl acetate) (EVA) [1,2]. Unfortunately, the existence of a rubber-like polymer often decreased other properties of the PBT such as the tensile strength, modulus and heat distortion temperature.

On the other hand, polymer/layered silicate (PLS) nanocomposites have attracted much attention recently

as examples of a newly developed polymer reinforcement technique [3-5]. To overcome the drawbacks of the elastomer toughened PBT, therefore, we tried to introduce the PLS technique to the PBT/EVA blend system.

In this paper, we will review our previous works on the microstructure and properties of three different polymer/layered silicate nanocomposites based on PBT, which were prepared via melt intercalation; PBT/organoclay nanocomposite [6], maleic anhydride grafted EVA (EVA-g-MAH) / organoclay nanocomposite [7], and PBT/EVA-MAH/organoclay ternary nanocomposite [8].

### Experimental

### Raw materials

Materials used in this work are all commercially available grades; Poly(butylene terephthalate) (PBT), poly(Bisphenol A-co-epichlorohydrin), a glycidyl end-capped epoxy resin, EVA with vinyl acetate content of 18 mol %, maleic anhydride (MAH), and dicumyl peroxide(DCP). The organoclay was supplied by Southern Clay Products Inc., under the trade name of Cloisite 30B.

### Preparation of nanocomposites

PBT/organoclay nanocomposite, EVA-g-MAH/organoclay nanocomposite, and PBT/ EVA-g-MAH/organoclay ternary nanocomposite were prepared by melt intercalation in an internal mixer (Haake Rheocord Mixer). For comparison, EVA/organoclay nanocomposite was also prepared. Details of preparation are described elsewhere[7,8]. The contents of organoclays in those nanocomposites was fixed at 3 wt.% unless otherwise specified.

### Characterization

XRD studies of the samples were carried out using a Rigaku D/max 2200H X-ray diffractometer (40kV, 50mA) at a scanning rate of 0.5°/min. Tensile properties were measured using a Hounsfield universal testing machine (model H25KM ) with the crosshead speed of 0.1 m/min using dog-bone shaped samples. Izod pendulum impact strength was measured according to the ASTM D256 (method A).

### Results and Discussion

#### 1. PBT/organoclay nanocomposite

Fig.1 shows the XRD results of the PBT/organoclay nanocomposite as well as the Cloisite 30B as an organoclay in this work. The original peak of the

organoclay (at 4.73 °) has shifted to 2.44 °, meaning that the PBT has intercalated in the gallery of the silicate layers.

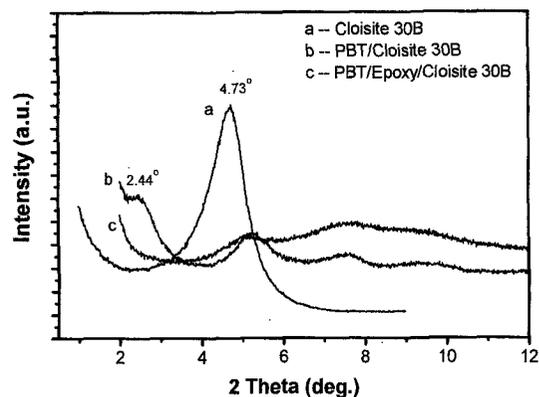


Fig.1. XRD patterns of (a)Cloisite 30B (b)PBT/organoclay nanocomposite, and (c) PBT/Epoxy/Cloisite30B nanocomposites.

Due to the existence of hydroxyl groups, the methyltallow bis-2-hydroxyethyl ammonium cation in the organoclay interlayer has strong polar interaction with the carboxyl groups present in PBT, favoring the intercalation of PBT chains and the formation of PBT/organoclay nanocomposite. However, the introduction of these polar hydroxyl groups also enhances the interaction of the ammonium cation with the silicate surface. As a result, replacement of the surface contacts by PBT chains will be less favorable, impeding the extensive intercalation and further exfoliation of organoclay in a PBT matrix.

Due to the existence of polar epoxy group, epoxy resins can easily intercalate into the galleries of organoclay. Epoxy resin is also miscible with PBT at temperatures above 210°C with high agitation. Based on these considerations, 2 wt% of epoxy resin was added during melt blending of PBT with organoclays in order to investigate its influence on the dispersion state of the PBT/organoclay nanocomposite. Fig.1 shows the influence of the epoxy resin on the XRD

Table I. Tensile and Impact Properties of PBT, PBT/EVA-g-MAH blend, and PBT/EVA-g-MAH/organoclay ternary nanocomposite.

Sample	Tensile Strength(MPa)	Elongation at break (%)	Tensile Modulus (MPa)	Impact strength (J/m)
PBT	56.4	42.8	370	24.7
PBT/EVA-g-MAH	38.6	72.3	268	90.6
PBT/EVA-g-MAH/organoclay	42.4	45.6	325	65.4

pattern of the PBT/organoclay nanocomposite. It is seen that the diffraction peak characteristic of the intercalated silicate structure at  $2.44^\circ$ , in the absence of epoxy resin, has disappeared, indicating a high degree of intercalation with layer spacings higher than 4-5 nm, and/or exfoliation of the organoclay silicate layers.

## 2. EVA-g-MAH/organoclay nanocomposite

To compare the microstructure of the EVA-g-MAH/organoclay nanocomposite, EVA/organoclay nanocomposite was also prepared. In Fig.2, the XRD pattern of the EVA/organoclay nanocomposite shows a weak peak at  $1.69^\circ$  with a shoulder at  $4.42^\circ$ , meaning a high degree of intercalation with layer spacings higher than 4-5 nm, and/or exfoliation of the silicate layers in the EVA matrix, whereas the EVA-g-MAH/organoclay nanocomposite showed only a weak peak at  $5.74^\circ$ , meaning no intercalation.

It is difficult to understand why the dispersibility of Cloisite 30B becomes worse after grafting MAH to EVA. Grafting EVA with MAH renders EVA higher polarity, which should be favorable to match the polarities of EVA with the slightly hydrophilic organoclay, so does the intercalation. But the result is quite the opposite. Maybe the existence of MAH groups along the EVA chain interrupts the original

optimum combination of EVA with Cloisite 30B, or too strong polymer-organic silicate layer interactions may increase the frictional coefficient associated with polymer transport within the interlayer and result in slower melt intercalation kinetics [7].

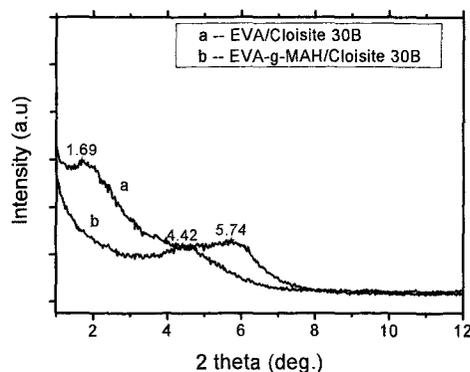


Fig.2. XRD diagrams of the EVA/organoclay and the EVA-g-MAH/organoclay nanocomposites.

## 3. PBT / EVA / organoclay nanocomposite

Fig. 3 shows the XRD patterns of the PBT/ EVA-g-MAH/ organoclay ternary nanocomposite as well as that of the PBT/organoclay nano-composite. The ternary nanocomposite exhibits microstructure of moved from  $4.72^\circ$  (of the organoclay) to around  $2.54^\circ$  as for the PBT/organoclay nanocomposite does. Table 1 gives the tensile and impact properties of the PBT/EVA-g-MAH/organoclay ternary nanocomposite

as well as those of PBT and PBT/EVA-g-MAH blend. It can be found that the impact strength of the ternary nanocomposite is in between that of the PBT and PBT/EVA-g-MAH blend. Unfortunately, however, the impact strength of the ternary nanocomposite is lower than that of the PBT/EVA-g-MAH blend. Usually, PLS nanocomposites show increased Young's modulus but simultaneously a loss in the impact strength. It should be noted, however, the uniform dispersion of the intercalated organoclay in the continuous PBT phase leads to higher tensile strength and modulus of the ternary nanocomposite compared to the PBT/EVA-g-MAH blend.

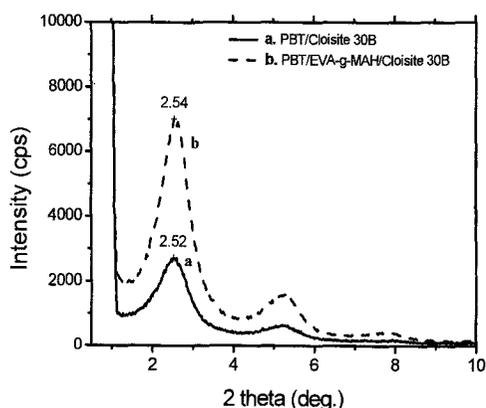


Fig. 3. XRD patterns of the PBT/organoclay nanocomposite in the presence of 2wt% of Epoxy and its blend with EVA-g-MAH.

### Conclusions

PBT/organoclay nanocomposites can be prepared through the polymer melt intercalation process. Epoxy resin enhanced the intercalation and further exfoliation of organoclay in the PBT matrix, due to the strong hydrogen bonding interactions and even possible

chemical reactions between the epoxy and the organoclay, and the compatibility between epoxy and PBT.

The PBT/EVA-g-MAH/organoclay ternary nanocomposite showed much enhanced impact strength in comparison to PBT without severely sacrificing the tensile properties of PBT. The strong polar interaction between PBT and organoclay in the presence of the compatibilizer, epoxy resin, keeps the organoclay from migrating to the dispersed EVA-g-MAH phase.

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