Morphology and Properties of Nanocomposites based on Polymer Blend and Organoclay

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INTRODUCTION

Forming a polymer blend is a convenient method for obtaining materials with improves property performance. However, most chemically different polymers are immiscible and their blending leads to a material with weak interfacial adhesion and thus poor mechanical performance. Numerous researchers have reported the use of a compatibilizer to modify the interfacial tension in polymer blend and their effect on the thermodynamic phase behaviour which governs the final morphology of the polymer blend with highly improved properties.[1-4] Such a compatibilizer may be a homopolymer, a block, graft or star copolymer. However, there are few reports on clay containing nanocomposites based on polymer blends, whether miscible or immiscible. Such composite materials offer unique opportunity to prepare new and novel high performance polymeric materials by the combination of advantages of both polymer blend and nanocomposite technologies. In our present study our objectives is to understand the exact mechanism on the change of phase morphology and properties of organoclay modified polypropylene/poly[(butylene succinate)](PP/PBS) blends.

EXPERIMENTAL

Materials and Methods

Materials
The syndiotactic polypropylene (from now PP) used in this study is a commercial product from Sigma- Aldrich with molecular weight M_w = 174k g/mol and a melting point of 165°C. Poly(1,4-butylene succinate) (PBS) used in this study is a commercial product from Sigma- Aldrich with melting point of 120°C. According to the supplier, PBS is extended with 1,6-diisocyanatohexane. The organoclay, Cloisite® 20A (commercially abbreviated as C20A), was purchased from Southern Clay Products. According to the supplier, the original clay was Na+ - MMT and intercalated with 38 wt% of N, N-dimethyldihydrogenated tallow ammonium chloride (2M2ODA) salt. Tallow is a mixture of octadecyl, hexydecyl, and tetradecyl with octadecyl being the major component (>60%).[2]

Preparation of Nanocomposites

Prior to met-blending all samples were dried at 70°C under reduced pressure for overnight. The PP/PBS blend and blend nanocomposites were prepared by using a twin rotor ThermoHaake batch mixer (Polylab system) at a temperature of 170°C (set temperature) and a rotor speed of 60 rpm for 8 min. The ratio of PP and PBS was kept at 70:30 and two weight percentages of C20A, 0.5 and 5, were used. The pure blend and nanocomposite strands were then compression molded into different shapes using a Carver Laboratory press at 170°C for 8 min and then cool down to room temperature.

Characterization

The freeze-fractured surface morphologies of pure blend and nanocomposite were investigated by scanning electron microscopy (SEM) (LEO 1525 FE-SEM), operated at an acceleration voltage of 6 kV. The degree of dispersion of silicate layers in the PP/PBS blend matrix were investigated by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). The temperature dependences of the dynamic mechanical properties of pure PP, C20A modified and unmodified PP/PBS

blends were conducted by using an Anton-Paar Physica MCR501 Rheometer, operated in the tension-torsion mode.

Results and Discussions
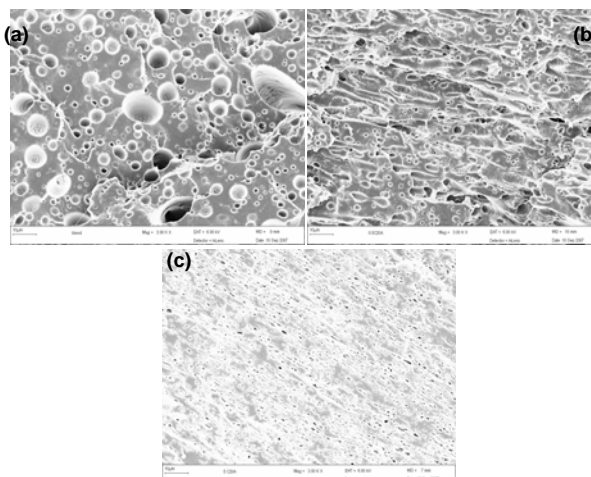
Fig. 1a,b,c. are SEM images of blend and nanocomposites containing 0.5wt% and 5wt% organoclay respectively.

The surface morphology is expected to mimic that of the bulk phase morphology. The latter is affected by the degree of interfacial interactions between the components, rheological behaviour and also nucleation, as well as other factors[5]. **Fig. 1** shows FE-SEM images of the chemically etched freeze-fractured surface morphology of unmodified and C20A-modified blends. The freeze-fractured surface of the PP/PBS blend is showing the PBS phase dispersed in the PP matrix. The PBS particles appear spherical in the unmodified blend. The presence of cavities indicates that the interfacial interactions between PBS and PP are poor. Addition of as little as 0.5 wt% of C20A to the PP/PBS blend caused a reduction in the size of the dispersed PBS phase and the morphology of most dispersed particles changes from spherical to ellipsoidal (**Fig. 1(b)**). This observation suggests that the intercalated silicates suppress the coalescence and the agglomeration of the dispersed PBS particles. Two things happen as the addition of C20A is increased to 5 wt% in **Fig 1c**. The first thing is the change of particle from ellipsoidal to spherical, and secondly the domain size of the dispersed PBS phase is reduced significantly when the clay weight percentage is increased and very fine particles of PBS were observed. In terms of current understanding of organoclay-compatibilized, immiscible polymer blend systems, two possible explanations might be proposed for the observed size reduction of the PBS phase domains upon addition of organoclay. The first one is related to the interfacial activity of the intercalated silicate at the interphase and the second one to the change in the rheological behaviour of the blend components because of the final morphology of a binary polymer blend is basically controlled by viscosity ratio of two components.

The XRD patterns of pure C20A powder, blend, C20A modified blend and polymer nanocomposites were shown in **Fig. 2.** The mean interlayer spacing of the (001) plane ($d_{(001)}$) for pure C20A powder obtained by XRD measurement is 2.45 nm (2θ = 3.6°).
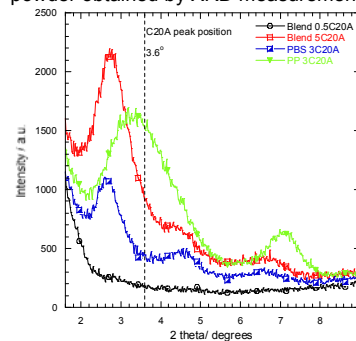

Fig. 2. XRD patterns

In all the cases the characteristic mean peaks of C20A modified and polymer nanocomposites shifts towards small diffraction angle with an exception of a blend/0.5C20A which shows a featureless diffraction. The peak shifts toward the lower angle side indicated the intercalation of polymer chains in the clay gallaries, while the featureless diffraction could be a reason of many factors other than the disorder, such as intercalate composition, and silicate concentration. TEM was used to confirm the degree of interaction of clay surface with polymer matrices by directly and qualitatively visualize the dispersion of intercalated silicate layers in the polymer matrices.
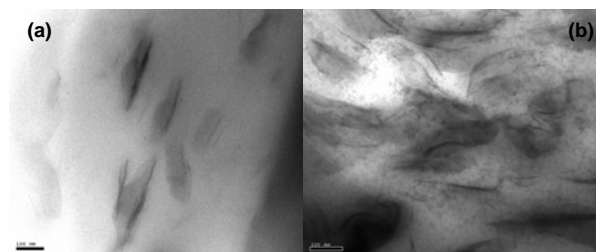

Fig. 3. TEM bright-field images of (a) Blend/0.5C20A and (b) Blend /5 C20A

Figure 3 shows bright-field TEM images of organoclay modified blend with C20A weight concentration of 0.5 and 5 wt%. In **Fig. 3.a**, TEM image of PP/PBS/0.5C20A nanocomposites, shows the presence of stacked and intercalated silicate layers. This indicates that most of the silicates layers are preferentially intercalated by PBS polymer chains, however, the absence of XRD pattern in the case of the PP/PBS/0.5C20A (**Fig. 2**) can be ascribed to the effect of dilution. In the case of the PP/PBS/5C20A nanocomposite highly disorder common intercalated silicate layers are dispersed in both polymer matrix.
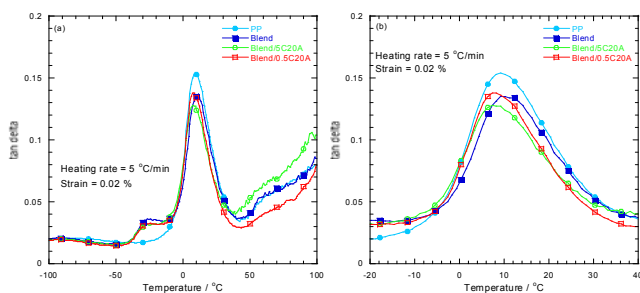
Fig 4. tan δ vs. temperature curves of various unmodified

Figure 4 shows the tan δ curves of the PP, PP/PBS blend with 0.5 and 5 amounts of C20A loading. **Fig. 4b** curves are magnified to assist in visualizing points in **Fig.4a**. Pure PP/PBS blend shows three distinct peaks at the temperatures of -29.3, 10.8, and 60°C. The first two peaks are corresponding to the glass transition temperature (T_g) of the individual components, PP and PBS, and the third one is related to the relaxation of PP polymer chains. Addition of as small as 0.5 wt % C20A contributes to the T_g shift of PP components while the tan δ curve remains the same. Increasing weight percentage of C20A to 5, shows a grammatically decrease of the PP-rich phase T_g, and with the peak width becoming broader. Also the position of the characteristic T_g peak of PP further moved to the higher temperature region. These results support that the increase in weight concentration of C20A, is an indication that the blend morphology is controlled by the viscosity ratio of the blend components.
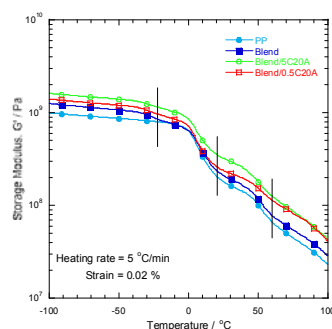
Figure 5. The temperature dependence of storage modulus of PP, unmodified and C20A modified blends.

Sample	Modulus / GPa				
	-100°C	0°C	25°C	50°C	75°C
PP	1.0	0.62	0.18	0.1	0.04
Blend	1.26	0.62	0.21	0.12	0.05
Blend/0.5C20A	1.40	0.69	0.24	0.15	0.08
Blend/5C20A	1.63	0.79	0.32	0.18	0.09

Table 1. Data from DMA tests of various samples.

The temperature dependence of the storage modulus curves of the blends with 0.5 and 5 wt% C20A loading are presented in **Figure 5** and the results are summarized in **Table 1**. The increased in intercalation and dispersion of silicate layers in polymer matrix is also associated with a large enhancement of the modulus, in both above and below T_g of individual polymer components.

Conclusion
In the present study, the effect of layered silicates on the morphology and properties of immiscible PP/PBS blends has been investigated. A small amount of organoclay added into immiscible blend reduces the size of the disperse phase domain significantly. While the addition of 5 wt % of organoclay into blend, changes the highly phase-separated morphology of unmodified blend to homogeneous dispersion of a very fine particles of dispersed phase. The basal change in the silicate layers as the homopolymer intercalates is confirmed by XRD and, while XRD images confirms intercalation. DMA reavels the TG's of the polymer blend components and the changes in them as organoclay is added.

References:
1. Suprakas Sinha Ray, Steve Pouliot, Mosto Bousmina, Leszek A. Ultracki. *Polymer*. **2004**. 45, 8403-8413.

2. Suprakas Sinha Ray, Jayita Bandyopadhyay, Motso Bousmina. *Macromolecular Materials and Engineering*. **2007**, 292, 729-747.

3. Mayu Si, Tohru Araki, Harald Ade, A. L. D. Kilcoyne, Robert Fisher, Jonathan C. Sokolov, and Miriam H. Rafailovich. *Macromolecules* **2006**, 39, 4793-4801.

4. I. González, J.I. Eguiazábal, J. Nazábal. *European Polymer Journal*. **2006**. 42, 2905-2913.

5. M. Mehrabzadeh, MR. Kamal, Canadian J Chem Eng. **2002**;80,1083.