



## RHEOLOGICAL PROPERTIES OF IMPACT MODIFIED PBT/PTT BLENDS BASED NANOCOMPOSITES

**Ranjana Sharma<sup>1</sup>, Purnima Jain<sup>2</sup> and Prabhat K Upadhyay<sup>1</sup>**

<sup>1</sup>Birla Institute of Technology-Offshore Campus, Ras Al Khaimah, UAE

<sup>2</sup>Netaji Subhas Institute of Technology, University of Delhi, New Delhi, India

prnm\_j@yahoo.co.in

### Abstract:

This paper explains the rheological behaviour of impact modified PBT/PTT blends based nanocomposites. Impact modified PBT/PTT blends based nanocomposites have been prepared by melt blending. ULDPE-g-GMA was used as an impact modifier for PBT and PTT polymeric matrix. It has been observed from results that the storage modulus, loss modulus and complex viscosity of the nanocomposites increased with the incorporation of organoclay (OMMT). Addition of organoclay to polymer matrix increased the storage modulus by several orders of magnitude and alters the shear thinning behaviour at low frequencies. Compositions having 5 wt % of organoclay shows high value of the storage modulus, loss modulus and complex viscosity. Moreover, storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of impact modified 25/75 PBT/PTT (NA3) and 50/50 PBT/PTT (NB3) blends based nanocomposites with 5 wt % organoclay loading increased more significantly at lower frequency range relative to other compositions. PBT/PTT blends based nanocomposites followed a strong shear thinning flow behaviour and decreased with increasing shear rates or frequency. This change in behaviour showed a solid like behaviour and it is related to the morphological changes. The Complex viscosity of neat PBT, neat PTT and impact modified PBT and PTT decreased with increasing frequency because of the shear thinning behaviour. The morphology of PBT/PTT blends and its nanocomposites has been confirmed by FEG-SEM microscopy.

**Keywords:** PBT, PTT, Blends, Nanocomposites, Rheology, Morphology

### Introduction

Rheological techniques expose valuable information on the process behaviour of polymer melts. Rheometry has been renowned as a powerful tool in polymer science and engineering to investigate the internal microstructures of nanocomposites, such as the dispersion of clay and the confinement effect of silicate layers on the motion of polymer chains [1-5]. Mostly oscillatory testings with rotational rheometers and parallel-plate geometries have been used for these investigations. The complete rheological response of a polymer melt consists of its viscous and elastic components. Moreover, structural information like molar mass distribution, degree of crosslinking as well as crystallization effects has been related to the rheological behaviour of polymeric systems [6,7]. The structure and rheology of a polymer is interconnected to each other. Applications of rheology are important in many areas of industries involving metal, plastic, and many other materials. The results from rheological investigations provide the mathematical description of the viscoelastic behaviour of matter. Wu et al. [3] have studied the rheological behaviour of the intercalated PBT/MMT (montmorillonite) nanocomposites and noticed the formation of liquid crystalline-like phase structure in nanocomposites. It might be the major driving force for the formation of percolated nanoclay network. The correlation of

the morphology and rheological response of PTT/m-LLDPE (metallocene linear low density polyethylene) blends has been investigated by Jafari et al. [8]. Moreover, rheology may provide some useful guidance to overcome the possible difficulties resulting from the large changes in melt viscoelastic properties observed in the nanocomposites [9].

This paper explains the rheological and morphological behaviour of impact modified PBT/PTT blends based nanocomposites in terms of loss modulus, storage modulus and complex viscosity. Amplitude oscillatory shear experiments have been employed to measure the storage ( $G'$ ) and loss modulus ( $G''$ ), which is related to the elastic and viscous character of the material and the complex viscosity ( $\eta^*$ ) the function of angular frequency. Dynamic measurements have been carried out using advanced Anton Paar MCR 300 rheometer.

### Experimental

**2.1 Materials:** PBT (T06 200) obtained from DSM Engineering Plastics (Pune, India). It has melting temperature ( $T_m$ ) is 223 °C and having density 1.3 g/ml. PTT (Futura CPTT) obtained from Futura Polymers. Ltd., Chennai, India. It has a melting temperature ( $T_m$ ) of 227 °C and having density 1.3 g/ml. Organoclay supplied by Southern Clay Product Inc. under the trade name Cloisite30B, modified with methyl, tallow, bis-2-hydroxy ethyl

ammonium. Ultra low density polyethylene grafted glycidyl methacrylate (ULDPE-g-GMA) (trade name GE-344) which contained 2 % grafted GMA was used as Impact modifier and supplied by Pluss Polymers, India.

**2.2 Sample Preparation:** PBT/PTT blends and impact modified PBT/PTT blends based nanocomposites were prepared via melt intercalation by using co-rotating Twin Screw Extruder (TSE). Prior to melt mixing both the PBT and PTT pellets and OMMT were dried under vacuum oven at 80 °C for 10 hr. Impact modifier (IM) ULDPE-g-GMA was used as received and the screw speed was set at 70 rpm. The dried samples were then melt blended in the respective extruders maintaining a temperature profile of 210°C to 260 °C. The extruded strands were quenched immediately in a water bath kept at room temperature. The details of compositions prepared using twin screw extruder are given in Table 1 and Table 2.

**2.3 Rheological measurements:** The rheological measurements have been carried out using a MCR300 oscillatory rheometer (Anton Paar) with parallel plate geometry using 25 mm diameter (gap between plates ca. 1 mm). Instrument was equipped with RHEOPLUS/32 Service V3.61 21000071-33086 software package. Dynamic frequency ( $\omega$ ) sweep tests are conducted in the  $\omega$  range of 0.01-100 rad/sec. The temperature of testing was 260°C. The strains used were within the linear viscoelastic range. The complex viscosity ( $\eta^*$ [Pas]), storage modulus ( $G'$  [Pa]), and loss modulus ( $G''$  [Pa]) have been measured as a function of frequency ( $\omega$ ).

## Results and Discussion

The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) data resulting from the dynamic frequency scan measurements for impact modified PBT/PTT/OMMT nanocomposites with various clay loadings have been compared in figure 1 (a, b) and figure 2 (a, b), respectively. The magnitude of  $G'$  linearly increased with the inclusion of clay in the covered frequency range, as shown in figure 1 (a, b). The same trend has also been observed in figure 2 (a, b) for the  $G''$  curves. The increase in  $G'$  and  $G''$  modulus is well known in the lower frequency range and decreased with increasing frequency. This is due to the shear thinning function [10]. The prominent difference in  $G'$  and  $G''$  is clearly visible in low frequencies because there is enough time to polymers to unravel the entanglements so that a large amount of relaxation occurs, which results in lower loss

and storage moduli. When a polymer sample is deformed at a large frequency, the polymeric matrices entanglements did not have the time to relax and, therefore, the modulus increased [10, 11]. It is believed that the degree of dependence of low frequency  $G'$  on the frequency,  $\omega$ , reflects sensitively the effect of clay on the viscoelastic properties of the nanocomposites [3]. The compositions NA3, and NB3 show high value of  $G'$  and  $G''$  at high frequency range. Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of impact modified 25/75 PBT/PTT (NA3) and 50/50 PTT/PBT (NB3) blends based nanocomposites with 5 wt % organoclay loading increased more significantly at lower frequency range. Moreover, the  $G'$  and  $G''$  increased with increasing the organoclay loading content in the whole frequency region. This is because of the strengthening effect of organoclay with large aspect ratio and refinement of co-continuous morphology [12]. This may also be due to the interfacial interaction between the intercalated and exfoliated silicate layers and the polymer matrix [13]. Increase in organoclay loadings in nanocomposites may experience a transition from liquid-like behaviour to solid-like or elastic behaviour of nanocomposites [13, 14]. The changes of  $G'$  and  $G''$  in the viscoelastic range sensitively reflect the effect of clay dispersion [15]. The rheological properties of polymer composites at high frequency region reflect the dynamics of polymer entanglement [16]. At high angular frequencies the materials short term behaviour is measured whereas at low angular frequencies the long term behaviour is measured [17]. At high frequency region, the silicate platelets (organoclay) or stacks of platelets get aligned in the direction of the flow, therefore, less increase in  $G''$  has been observed [13, 15]. It has been observed that the increase of the storage modulus of all the 5 wt% organoclay reinforced PBT/PTT blends based nanocomposites is greater than the increase of the loss modulus at low frequency range. Therefore, all these compositions (NA3 and NB3) behaved as a solid in the low frequency range as  $G' > G''$ , because the structure of the polymer composites was sensitively reflected on the storage modulus ( $G'$ ) than on the loss modulus ( $G''$ ) [16].

To further investigate the individual role of organoclay on the rheological properties of impact modified blends based nanocomposites, the melt viscosities have been investigated. The effect of the clay loading on the complex viscosity ( $\eta^*$ ) is quite prominent at low frequency and decreased with increasing frequency

because of the shear thinning behaviour [10]. As the filler concentration increases, the complex viscosity increases mainly at low frequencies [14]. Figure 3 (a, b) shows the complex viscosity ( $\eta^*$ ) of the impact modified PBT/PTT blends based nanocomposites at 260 °C. The PBT/PTT blends based nanocomposites having 5 wt % of organoclay shows high value of complex viscosity ( $\eta^*$ ) in low frequency range. The observed enhancement of viscosity due to the incorporation of clay indicates the existence of a significant polymer-filler (organoclay) interaction. It may also likely due to the partly exfoliated and intercalated silicate layers which restrict the melt flow of the polymeric matrix [13, 17]. The viscosity of all the PBT/PTT blends based nanocomposites follows a strong shear thinning flow behaviour and decreases with increasing shear rates or frequency. This change in behaviour indicated a solid like behaviour and it is related to the morphological changes i.e. refinement of the co-continuous structure by addition of clay to this system [12]. Shear-thinning characteristic has been observed due to the alignment of the silicate layers in the direction of the shear or attributed to the percolated network by the increase in the content of clay particles [14, 18]. At high frequencies, complex viscosities coincided with each other. Small effect of cloisite 30B (organoclay) addition has been observed at high frequencies. At high frequencies relaxation mechanism is mainly dominated, whereas at low frequencies, the relaxation is due to the particle-particle interactions inside the percolation network of the silicate layers [12, 18].

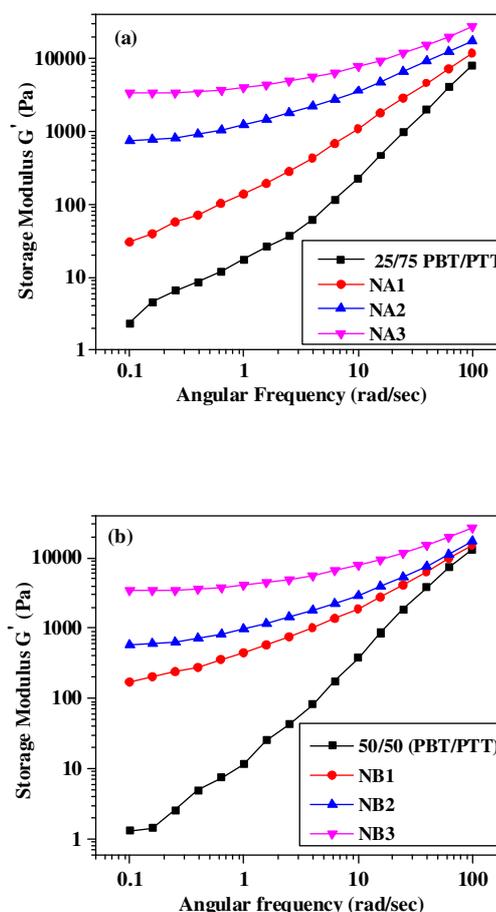
Figure 4 (a, b) shows the SEM micrographs of the fractured surface of impact modified PBT/PTT blends based nanocomposites with 3 wt% organoclay. It appears that the OMMT layers are dispersed uniformly within PBT/PTT blends.

**Table 1.** Sample identification and composition of PBT/ PTT blends

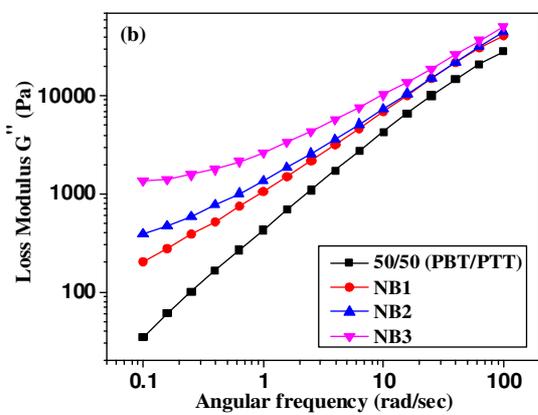
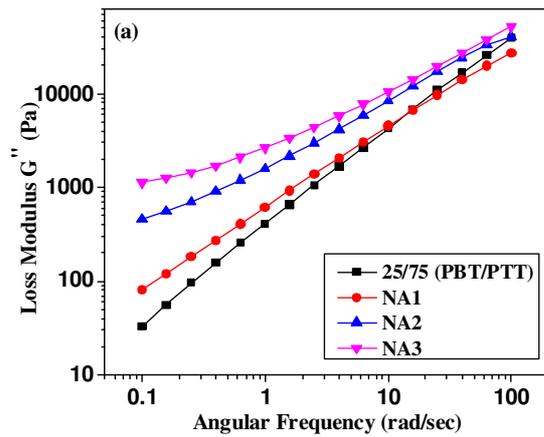
Sample Code	Composition (wt%)	
	PBT	PTT
BL A	25	75
BL B	50	50

**Table 2.** Sample identification and composition of impact modified blends based nanocomposites

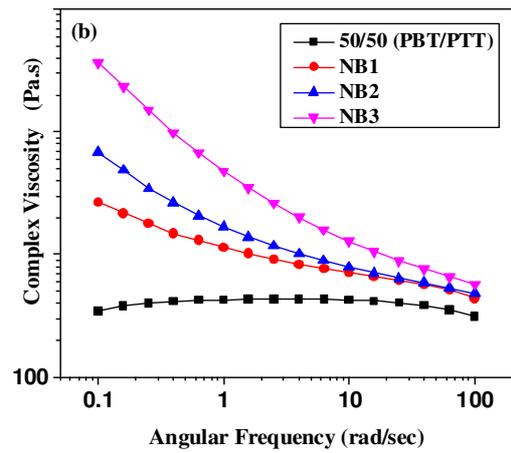
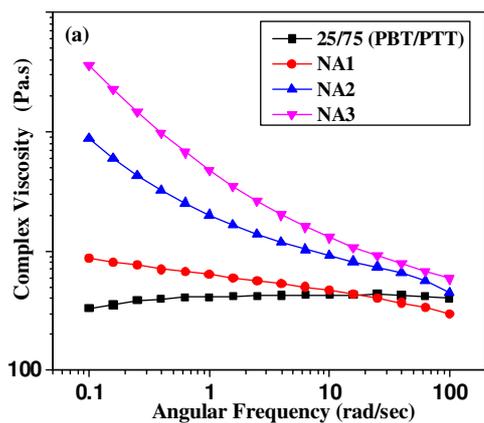
Sample code	Composition (wt%)			
	PBT	PTT	ULDPE -g-GMA (IM)	OMMT
NA1	23	73	2	2
NA2	22.5	72.5	2	3
NA3	21.5	71.5	2	5
NB1	48	48	2	2
NB2	47.5	47.5	2	3
NB3	46.5	46.5	2	5



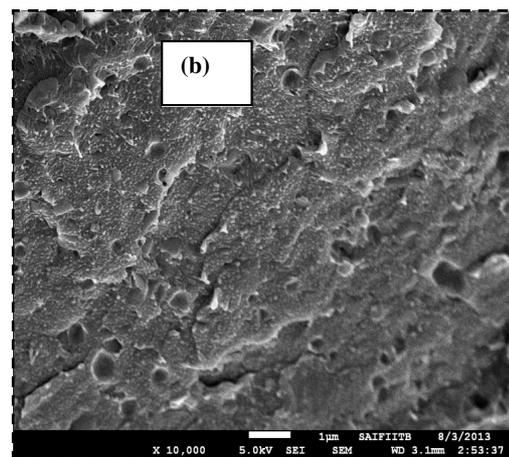
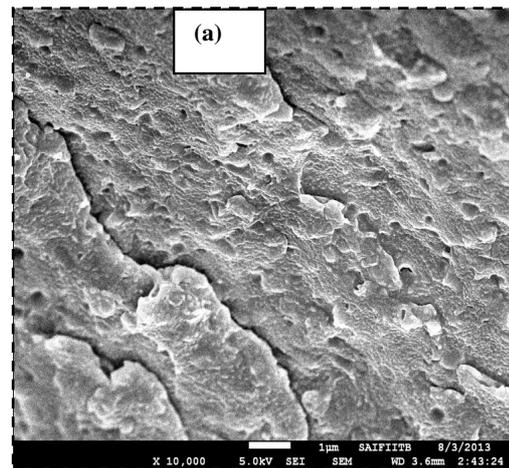
**Figure 1.** Storage modulus of impact modified (a) 25/75 PBT/PTT and (b) 50/50 PBT/PTT nanocomposites having 2, 3 and 5 wt % organoclay.



**Figure 2.** Loss modulus of impact modified (a) 25/75 PBT/PTT nanocomposites and (b) 50/50 PBT/PTT nanocomposites nanocomposites having 2, 3 and 5 wt % organoclay



**Figure 3.** Complex viscosity of impact modified (a) 25/75 PBT/PTT nanocomposites, (b) 50/50 PBT/PTT nanocomposites having 2, 3 and 5 wt % organoclay



**Figure 4.** SEM micrographs of impact modified PBT/PTT blends based nanocomposites with 3 wt% organoclay (a) 25/75PBT/PTT and (b) 50/50 PBT/PTT blends.

## Conclusion

From the results of rheological tests, we observed that in the high frequency ( $\omega$ ) region, there was no significant difference in  $G'$  and  $G''$  in nanocomposite samples. Furthermore, the  $G'$  and  $G''$  increased on increasing the organoclay content in the whole frequency region. This may be due to the strong interfacial interaction between silicate layers and the polymer matrix, and the strengthening effect of organoclay with large aspect ratio. From the graphs, it has been observed that all the nanocomposites having 5 wt % organoclay (NA3 and NB3) reported high value of complex viscosity ( $\eta^*$ ) at low frequency range. The observed enhancement of viscosity due to the addition of clay depicted the existence of a significant polymer-filler (organoclay) interaction. PBT/PTT blends based nanocomposites followed a strong shear thinning flow behaviour and decreased with increasing shear rates or frequency. This change in behaviour showed a solid like behaviour and it is related to the morphological changes. The morphology of PBT/PTT blends based nanocomposites have been confirmed by FEG-SEM microscopy. FEG-SEM micrographs revealed that the clay layers are uniformly dispersed in PBT/PTT blends.

## Acknowledgments

The authors are grateful to ICT, Matunga, Mumbai for their generous support for the compounding facility. The authors would like to thank DSM Engineering Plastics, Futura Polyesters Ltd and Pluss Polymers, India for kind donation of the PBT, PTT and the Impact modifier (ULDPE-g-GMA). The authors gratefully acknowledge the company Anton Paar for performing rheological characterization and SAIF, IIT, Bombay for FEG-SEM.

## References

1. D. Wu, C. Zhou, W. Yu, X. Fan, J. Polym. Sci.: Part B: Polym Phys. 43, 2807-2818 (2005).
2. J. Yang, D. Shi, Y. Gao, Y. Song, J. Ying, J. Appl. Polym. Sci. 88, 206-213 (2003).
3. D. Wu, C. Zhou, Z. Hong, D. Mao, Z. Bian, Eur. Polym. J. 41, 2199-2207 (2005)
4. Monticciolo, P. Cassagnau, A. Michel, Polym. Eng. Sci. 38, 1882-1889 (1998).
5. J. S. Choi, S. T. Lim, H. J. Choi, J. Mater. Sci. 41, 1843-1846 (2006).
6. J.M. Dealy and R.G. Larson, Structure and Rheology of Molten Polymers, Carl Hanser Verlag, Munich, 2006.
7. T.G. Mezger, The Rheology Handbook, 2nd Edition, Vincentz Network, Hannover, 2006.
8. S.H. Jafari, A. Yavari, A. Asadinezhad, H.A. Khonakdar, F. Bohme, Polym. 46, 5082-5093 (2005).
9. D. Wu, C. Zhou, X. Fan, D. Mao, Z. Bian, Polym. Degrad. Stab. 87, 511-519 (2005).
10. K.Wang, Y. Chen, Y. Zhang, Polym 49, 3301-3309 (2008).
11. J.S Hong, J.L. Kim, K. H. Ahn, S.J Lee, J. Appl. Polym. Sci. 97, 1702-1709 (2005).
12. L. Ashabi, S.H. Jafari, B. Baghaei, H.A. Khonakdar, P. Pötschke, F. Böhme, Polym. 49, 2119-2126 (2008).
13. W.S. Chow, A. Abu Bakar, Z.A. Mohd Ishak, J. Karger-Kocsis, U.S. Ishiaku, Eur. Polym. J. 41, 687-696 (2005).
14. Bhatia, R. K. Gupta, S.N. Bhattacharya, H. J. Choi, J. Appl. Polym Sci. 114, 2837-2847 (2009).
15. J. Li, C. Zhou, G. Wang, D. Zhao, J. Appl. Polym. Sci. 89, 3609-3617 (2003).
16. C.A. Mitchell, J.L. Bahr, S. Arepalli, J.M. Tour, R. Krishnamoorti, Macromol. 35, 8825-8830 (2002).
17. Y.T. Sung, M.S. Han, K.H. Song, J.W. Jung, H.S. Lee, C.K. Kum, J. Joo, W.N. Kim, Polym. 47, 4434-4439 (2006).
18. D- H. Kim, P-D. Fasulo, W.R. Rodgers, D.R. Paul, Polym. 48, 5308-5323 (2007).
19. J.S. Narkhede, V.V. Shertukde, J. Appl. Polym. Sci. 119, 1067-1074 (2006).