RJC

http://www.rasayanjournal.com

THERMAL AND MORPHOLOGICAL BEHAVIOURS OF POLYBUTYLENE TEREPHTHALATE/POLYETHYLENE TEREPHTHALATE BLEND NANOCOMPOSITES

P.R. Rajakumar[1] and R. Nanthini[2]

[1]Dept of Chemistry, Government Arts College Chidambaram, Tamilnadu, India
[2]Dept of Chemistry, Pachayappa's College Chennai, Tamilnadu, India
*E-mail: prrajkummar@gmail.com

ABSTRACT

Polybutylene Terephthalate (PBT) / Polyethylene Terephthalate (PET) nanocomposite blend was fabricated using melt blending technique in a twin extruder. The blend composition was optimized at PBT-PET weight ratio of 80-20. The effect of incorporation of Organically Modified Montmorillonite (OMMT) and naturally occurring sodium Montmorillonite (MMT) on the mechanical, thermal and morphological properties of the nanocomposites blend has been investigated. It was observed that the Izod impact strength, tensile strength and flexural strength demonstrated a significant increase with the increase in clay loading from 1-7 weight % due to homogeneous dispersion of clay within the blend matrix. Thermo gravimetric analysis revealed an increase in thermal stability of the blend with the incorporation of nanoclay. There is also decrease in the melting temperature and crystallisation temperature as observed from DSC thermograms. DMA add the evidence for TGA, DSC and mechanical results. PBT - PET blend with clay exhibited featureless XRD indicative of exfoliated structure. TEM micrographs also confirm the same that the clay has exfoliated into individual layers.
Key words: - PBT, PET, TGA, DSC, DMA, XRD, TEM, Nanoclay, Untreated clay- MMT and organically modified clay-OMMT.

INTRODUCTION

Blending of two or more polymers has emerged as an established route to design tailor made polymeric materials with desired attributes for various high performance applications[1-4]. It provides a means of producing new materials, which combine the useful properties of all the constituents. However, most of the polymer pairs are inherently immiscible that results in incompatibility with subsequent phase separation in the blend matrix. Different approaches such as use of compatibilising agents, copolymers, grafting agents, reactive extrusion etc., have been the commonly used techniques to modify the interfacial region between the blends and increase the compatibility[5, 6].

More recently, PLS nanocomposites have attracted great interest both in industry and in academic, because they often exhibit remarkable improvements in properties when compared with virgin polymers or conventional micro and macro composites. These improvements can include high moduli[7], increased strength and heat resistance[8], decreased gas permeability[9] and flammabilit[10] and increased biodegradability of biodegradable polymers . Layered silicates, with its inherent high aspect ratio ranging from 100 to 2000 offers more surface contact per unit filler within the polymer matrix resulting in enhanced performance characteristics with a minimum loading of 3-5 %[11].

However, PBT is strongly notch sensitive, give low notched Izod impact strength[12] and break in a brittle fashion when standard notched specimens are tested. Hence, PBT is fairly resistant to crack initiation but have only modest resistance to crack propagation. The strong notch sensitivity of PBT can be eliminated by the incorporation of impact modifiers[13] such as, nanoclays or in general nanomaterials which increase the surface area which in turn increases the mechanical properties. Thus, polymer nanocomposites, at loading levels of 2-3 % of nanomaterials exhibit enhanced mechanical properties,

improved thermal properties when compared with neat polymers or their blends[14]. The cost difference between the neat matrix and its polymer nanocomposites is about 10-15 %.

EXPERIEMENTAL

Materials

The polymer matrix used in this research is a commercial PBT (DUPONT ^{TM} CRASTIN® S610SF NC010). PET was supplied by GE plastics under the trade name of Lexan® F2000. The filler was sodium montmorillonite (MMT) unmodified clay having CEC 92.6 meq/100 g of clay and modified clay (cloisite ® 20A) (MMT modified by 2M2HT dimethyl dehydrogenated Tallow, quaternary ammonium - OMMT) having CEC of 95 meq/100g of clay were obtained from M/s Southern Clay Products Inc, USA. (HT is made of approximately 65% $C_{18}H_{37}$, 30% $C_{16}H_{33}$ and 5% $C_{14}H_{29}$). PBT was blended with PET in different ratios like 90-10, 80-20 and 70-30. From the experimental results, 80% weight of PBT gives better results with 20% weight of PET and it was considered as an optimized ratio. Fillers MMT and OMMT were incorporated in the ratio of 1%, 3%, 5% and 7% by weight with 80% PBT toughened by 20% PET. TGA were performed in a Perkin Elmer, USA PYRIS ITGAC under N_2 atmosphere. The temperature range was 50°C to 900°C at a heating rate of 20°C/min and corresponding weight loss was recorded.. The DSC scans were carried out by using a Perkin Elmer (Diamond DSC) calorimeter in a nitrogen atmosphere **.** Dynamic Mechanical Analysis (DMA) was performed using Netzsch DMA 242 . XRD was recorded using Philips X' pert MPD . TEM analysis of the specimens was carried out using JEOL JEM 2100 HRTEM.

Preparation of Blends

Initially PBT and PET were blended without filler, to get 90-10, 80-20 and 70-30 weight ratio to establish optimized blend ratio. Based on the tensile and impact strength, the optimized percentage of PET is 20% by weight. Then PBT/PET 80:20 blend mixture was mixed with two different nanoclays – one untreated clay called sodium montmorillonite (MMT) and the other is treated clay or organically modified clay called (cloisite ® 20A) (OMMT) with different ratios such as 1%, 3%, 5% and 7%. PBT was dried at 100°C in an air circulated oven for 8 hours prior to blending. The blend was prepared via melt compounding method using twin screw extruder (Bersfort FRG Germany) at temperature range of 220°C with a screw speed of 150 rpm. After the extrusion, the extrudate was cooled in water bath and palletized. Finally these granules were injection molded as per ASTM using SP130 injection molding machine (Windsor, India) having clamping force 100T fitted with dehumidifier at a temperature range of 250 - 285°C.

RESULTS AND DISCUSSION

Thermal studies on PBT-PET blends and their nanocomposites

Thermal analysis is a technique in which a physical property of a substance measured as a function of temperature, while the substance is subjected to controlled temperature programmer[15]. Knowledge of thermal behaviour is not only essential for proper processing and fabrication, but also to complete the characterisation of materials especially for thermal stability and for selection of appropriate end users. Thus, thermo analytical techniques are used for characterisation of polymers towards melting properties, Tg which is the working temperature of a polymer, and stress and strain over a range of temperatures . Thermal analysis thus plays a vital role in the studies of polymers .

Thermo gravimetric analysis

TGA involves heating a sample to some temperature and then monitoring its weight as a function of time. Change in weight, result from bond forming or breaking at elevated temperatures[15,16]. TGA is commonly used to monitor polymer degradation reactions. In the present investigation, TGA has been carried out for the pure PBT, PBT-PET 80-20 blends and to their nanocomposites to assess the rate of decomposition and thermal stability of the samples etc.

Effect of loading clay with PBT-PET 80-20 blend

Characteristic degradation temperatures and associated TGA data obtained from these thermograms are summarised in Table 1. The thermal degradation behaviour of PBT and PBT-PET 80-20 weight ratio

blend are depicted in Fig 1. The TGA thermograms of PBT–PET 80-20 nanocomposites with MMT clay in 3 % and 5 % weight ratios and OMMT clay also in 3 % and 5 % weight ratios are given in Fig 2.

During the thermal degradation, the TGA curves displayed a single step degradation process in all the cases and the sample weight in percentage decreases continuously to a residual level after mass loss has commenced. From the data provided for PBT-PET blend and its nanocomposites, the onset of degradation temperature of PBT-PET 80-20 weight ratio blend has decreased from the value of pure PBT. Thus, the addition of PET to PBT in the weight ratio of 20 % has decreased the thermal stability of virgin PBT.

On the addition of MMT clay to PBT-PET 80-20 weight ratio, it is observed that 3 % addition of MMT clay increases the thermal stability marginally while 5 % addition of MMT clay increases the thermal stability considerably. Addition of OMMT clay also imparts thermal stability to PBT-PET 80-20 blend. After the initial onset of degradation temperature, there is only marginal change in temperatures for the weight loss of 90 % to 50 % and end degradation value, on adding both types of clay. The residue percentage is low in all the results presented for PBT-PET nanocomposites. Residue percentage increases marginally on OMMT clay addition.

The study of mechanical properties of PBT-PET blend nanocomposites shows that the addition of clay decreases the impact strength considerably from the value of PBT-PET 80-20 blend. The addition of 5 % OMMT clay improves the impact strength value equal to the PBT-PET 80-20 blend value. Thus, the TGA curves imply that clay addition exhibits dispersion of clay material with the polymer matrix bringing up the required changes in mechanical properties and thermal properties.

The impact strength of the nanocomposite was enhanced on the addition of MMT clay while it was much improved on adding OMMT clay. Thus, the nano silicate layers have better adhesion with the polymer matrix which is reflected in the both mechanical properties and TGA thermal studies. It is also clear that OMMT clay exhibits better dispersion with the polymer matrix than MMT clay.

The decrease in permeability due to the formation of char is usually observed in intercalated as well as exfoliated platelets of clay in the polymer-organo clay nanocomposites[17]. The improvement in thermal stability is much more significant in the exfoliated nanocomposites than intercalated ones.

The increase in the degradation temperature for OMMT clay in the present work is mainly resulted from the efficiently dispersed nano scale silicate layers in the presence of organic moiety than MMT clay and in particular 5 % OMMT clay brings about better stability. Similar results have been observed by other researchers[18]. The improvement in thermal stability is a direct reflection of excellent thermal barrier effect of layered clay within the matrix[19]. The enhancement of thermal stability of the nanocomposite is attributed to the clay layer structure, which limits the mobility of the small molecules produced during thermal decomposition . The morphology of the clay with the polymer blend matrix decides whether the clay is intercalated or exfoliated.

Differential scanning calorimetry

Thermal analysis plays a vital role in the characterisation of polymer . DSC is one of the most important tools used to investigate the thermal properties of the polymers. Melting temperature Tm, crystalline temperature Tc, enthalpy of melting ΔHm and percentage of crystallinity Xc has been detected from DSC thermograms.

Effect of loading clay with PBT-PET blend

Table 2 gives the data of DSC thermograms and is depicted in Fig. 3 and Fig 4. It is evident that the DSC thermograms of the virgin matrices, blend matrices as well as the blend nanocomposite systems depicted single melting endotherms at a relatively constant melting temperature of about 220°C. Tm values of the nanocomposites and the PBT-PET 80-20 blend decrease from the pure PBT. All the Tm values show very little variation. 5 % MMT clay,
3 % OMMT clay nanocomposites and PBT-PET 80-20 blend have same Tc values and marginally higher than neat PBT. On adding 3 % MMT clay, Tc increases by 4°C but on adding 5 % OMMT clay, Tc decreases by 2°C. Addition of 3 % OMMT clay and 5 % OMMT clay increases the percentage of crystallinity from pure PBT. 5 % MMT clay shows the minimum of Xc while 3 % MMT clay shows the

maximum of Xc among nanocomposites. Therefore, there is no organised trend observed in Tc values and percentage of crystallinity values on the addition of clay to PBT-PET 80-20 blend.

DSC analysis of PET-PBT 30-70 and 70-30 blends has reported only one melting point corresponding to the major component. Melting temperatures are slightly reduced. Results on miscible PET and PBT in amorphous phase below melting temperature show suppression of crystallisation of minor components[20].

It has been reported that immediately after preparation, the PBT-PET blends are amorphous regardless of the composition . The existence of a single Tg between those of the pure components in polymer blends is an evidence for their miscibility[21]. The reported theoretical predications of compatibility of PET and PBT blends, based on calculations of the heat of mixing, interaction parameter and free energy lead to the conclusion that PBT-PET system behaves as a compatible polymer pair[22]. Blends containing up to 60% PET start to crystallize at a some what lower Tc than pure PBT[23]. The addition of PET to PBT matrix does not suppress and is even favourable for the crystallisation process [23]. Hence, it is clear that PBT-PET blends have compatibility and blends show decreased Tc values which are in agreement with the results obtained in the present work. The compatibility increases with OMMT clay due to larger surface area, high aspect ratio and the presence of organic moiety.

Dynamic mechanical analysis, DMA

DMA has emerged out as one of the most powerful tools available for the study of the behaviour of plastic materials. DMA gives the fundamental aspects of morphological structure of polymer. The low storage modulus indicates that the material is easily deformed by an applied load .The reduction in the storage modulus through the glass transition, can serve as a relative indicator of degree of crystallinity.

Loss modulus is the contribution of the viscous component in the polymer, that portion of the material will flow under conditions of stress. The rapid rise in the loss modulus indicates an increase in the structural mobility of the polymer, a relaxation process that permits motion along larger portions of the individual polymer chains which would be possible below the transition temperature. During the glass transition, which is the largest and most important relaxations, those regions within the polymer structure that are not either cyrstallised or cross linked, become capable of moving freely. Under an applied load, this new mobility will take the form of organised movement or flow.

The peak of the loss modulus is conventionally identified as the Tg, even though the DMA plot clearly shows that the transition is a process that spans a temperature range. The loss modulus provides the best agreement with determinations made by other thermal analysis methods and ASTM has recently codified this into D-4065. The lack of shift in the Tg indicates that this is an immiscible blend.

Effect of loading clay with PBT-PET 80-20 blend on DMA

Table 3 provides the DMA data and Fig 5 and 6 gives the DMA curves for the pure PBT, PBT-PET 80-20 blend and its nanocomposites. A gradual decline in E' with increase in temperature was observed in all the cases.

It has been reported that addition of PET to PBT, due to the amorphous miscibility PET/PBT blends is characterised by good mechanical properties[22]. It was found that quenched PET/ PBT 50:50 blend exhibits relative elongation at break equal to 400 % while pure PET is brittle[24]. The presence of copolymer improves the compatibility of the system .

Storage modulus value decreases on the addition of 20 % weight ratio of PET to pure PBT. Addition of clay improves the storage modulus value from pure PBT as well as PBT-PET 80-20 blend. 5 % MMT clay has increased the value of storage modulus while addition of 5 % OMMT clay displays a nominal rise in the value of E'. This is supported by the literature that PBT-PET blend system needs compatibiliser and the nanoclays serve as compatibilising agents. The high surface area and high aspect ratio alters storage modulus values. Thus, it is clear that nanoclays improve the mechanical properties of the pure PBT matrix. Clay makes the matrix stiffer and effective dispersion of the clay improves the properties on study.

The loss modulus curves for the PBT-PET nanocomposites are given in Fig 6.20 and all of them found to exhibit only one relaxation peak, the primary relaxation peak associated with glass transition.

Table-1: TGA data of PBT, PBT-PET 80-20 blend and their nanocomposites

Polymer type	Onset of degradation temperature ^{O}C	T-90% ^{O}C	T-80% ^{O}C	T-70% ^{O}C	T-60% ^{O}C	T-50% ^{O}C	End of degradation temperature ^{O}C	Residue percentage
100 % PBT	393	395	401	407	412	416	432	0
80 % PBT 20 % PET	360	380	390	400	405	410	446	1.2
80 % PBT 20 % PET 3 % MMT clay	365	390	398	403	410	413	439	1.3
80 % PBT 20 % PET 5 % MMT clay	391	392	400	406	411	415	433	2.9
80 % PBT 20 % PET 3 % OMMT clay	382	389	397	404	409	414	430	3.8
80 % PBT 20 % PET 5 % OMMT clay	387	389	400	405	410	415	434	2.9

Table-2: DSC data of PBT, PBT-PET 80-20 blend and their nanocomposites

Polymer type	Melting temperature Tm °C	Heat of fusion H_f J/g	Crystallisation temperature Tc °C	Percentage of crystallinity Xc
100 % PBT	224.25	21.63	188.04	15.23
80 % PBT 20 % PET	222.97	26.03	188.67	18.33
80 % PBT 20 % PET 3 % MMT clay	222.51	28.98	192.52	20.41
80 % PBT 20 % PET 5 % MMT clay	221.27	10.20	188.65	7.18
80 % PBT 20 % PET 3 % OMMT clay	221.57	23.85	188.64	16.80
80 % PBT 20 % PET 5 % OMMT clay	222.30	26.52	186.39	18.68

Table-3: DMA data of PBT, PBT-PET 80-20 blend and their nanocomposites

Polymer type	Storage modulus E' MPa	Loss modulus Tg temperature ^{o}C	Tan delta peak temperature ^{o}C
Pure PBT	2125	68.04	82.16
PBT-PET 80-20	1960	60.43	71.58
PBT-PET 80-20 + 5 % MMT	2500	68.04	83.68
PBT-PET 80-20 + 5 % OMMT	2200	69.80	91.50

The loss modulus curve peak temperature designated as Tg, decreases on the addition of PET in 20 % weight ratio but, the addition of 5 % MMT clay as well as
5 % OMMT clay exhibit increased values. Thus, the increased value of Tg resulting on the addition of clay implies that there is a significant increase in thermal stability of the nanocomposite samples. The results confirm that small amount of nano particles can effectively restrain the movements of polymeric chain segments which in turn affect the toughness of the matrix especially in the regions near Tg[25].

Morphology studies of PBT-PET blend and their nanocomposites

XRD and TEM have been regarded as complementary in characterising the micro structure of the PLS nanocomposites. In the present work the morphology studies of PBT-PET blends and their nanocomposites have been carried out.

PBT-PET 80-20 blends

From the DMA analysis, carried out for the sample PBT-PET 80-20 blend, it is observed that only one Tg peak is seen. The existence of a single Tg between those of the pure components in polymer blends is evidence for their miscibility[26]. DSC analysis of PET-PBT 30-70 and 70-30 blends carried out by Marcin et al.,[26] indicated only one melting point corresponding to the major component present. Results of miscible PET and PBT, below melting temperature, shows the suppression of crystallisation of minor components and possible chemical interaction in the blend[27]. In the present work also, DSC thermogram of PBT-PET 80-20 blend exhibits only one melting point corresponding to the major component PBT has occurred. The improvement in mechanical properties particularly the impact strength also proves the better miscibility of PBT-PET 80-20 blends.

Effect of loading clay with PBT-PET 80-20 blend

The wide angle X-ray diffraction patterns of MMT clay, Fig 7 shows a diffraction peak at $2\theta = 8.025°$ corresponding to a d-spacing of 1.2 nm. The XRD pattern of organically modified clay OMMT given in Fig 8, exhibits a reflection peak at $2\theta = 4°$ with a d-spacing of 2.42 nm. X-ray diffraction patterns of PBT-PET 80-20 blend nanocomposites prepared using MMT and OMMT clays at 3 % and 5 % weight ratio loading, Fig 9 and Fig 10 did not show any peak at 2θ less than 10°, indicating the absence of intercalated clay structure in the film[28]. The absence of basal plane peaks indicates the delamination and dispersion of the clay nano layers within the PBT-PET matrix[29]. This suggests that the clay has exfoliated and dispersed in the PBT-PET matrix.

It should be noted that a few completely exfoliated PLS nanocomposites exhibit no peak, but instead display a gradual increase in the diffraction intensity towards low diffraction angles[30], this is not always the case, however. In fact, it was extensively reported that some PLS nanocomposites show featureless XRD patterns when they exhibit exfoliated or delaminated structures[31]. Vain et al.,[32] and Galgali et al.,[33] also observed featureless XRD patterns even for partially exfoliated nano structures.

The TEM micrographs of PBT-PET 80-20 loaded with 5 % MMT clay and 5 % OMMT clay are depicted in Fig 11 and Fig 12 respectively. Both the micrographs show that the dispersion of the clay particles was poor and many large aggregates in microns were observed. However, there are some finely exfoliated clay layers and some unexfoliated individual clay particles. This confirms that the polar interactions between the matrix polymer and MMT clay would conglomerate to form large aggregates [34]. The nanocomposites prepared using OMMT clay depicts well dispersed exfoliated morphology of the clay layers but amount of aggregates are lesser in number. Modification of the clay facilitates exfoliation and the efficient dispersion of the clay[34] may be the reason for the little enhanced mechanical properties when compared to MMT clay. PET seems to form wider and more disordered morphology including immiscible, intercalated and/or delaminated, as reported by Costache et al.,[35] for MMT nanocomposites. Thus, to conclude, PBT-PET 80-20 blends showed better miscibility and improved mechanical properties. Addition of MMT clay with poor morphology structure exhibited poor mechanical properties than PBT-PET 80-20 blends. Addition of OMMT clay improved the situation slightly, still with disordered morphology structure and aggregation and the mechanical properties improved slightly better than with MMT clay.

The PBT-PET blend undergoes transesterification reaction between PET and PBT during melt processing. As per the work carried out by Feng Wang et al., PET/PBT transesterification reactions were inhibited by nano fillers including SiO_2[36]. It is clear that clay has exfoliated and dispersed in PBT-polymer blend matrix. TEM micrographs also confirm the same that the clay has exfoliated into individual layers. Thus, it is observed that modification of the clay facilitates exfoliation and efficient dispersion of the clay. Aggregates were observed with PBT-PET nanocomposites which may be the reason for the moderately improved mechanical properties.
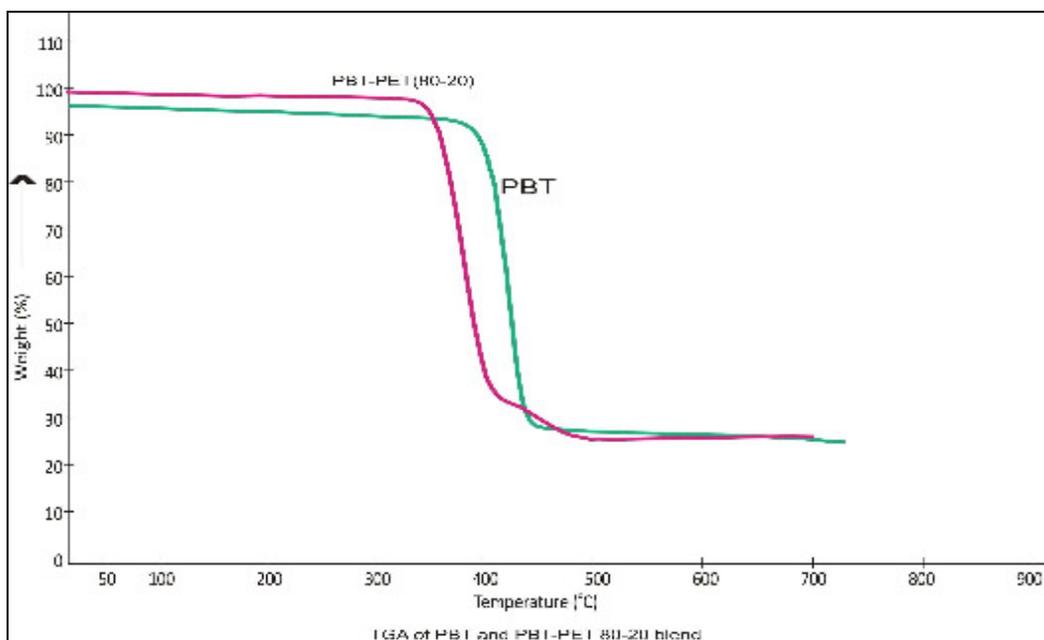
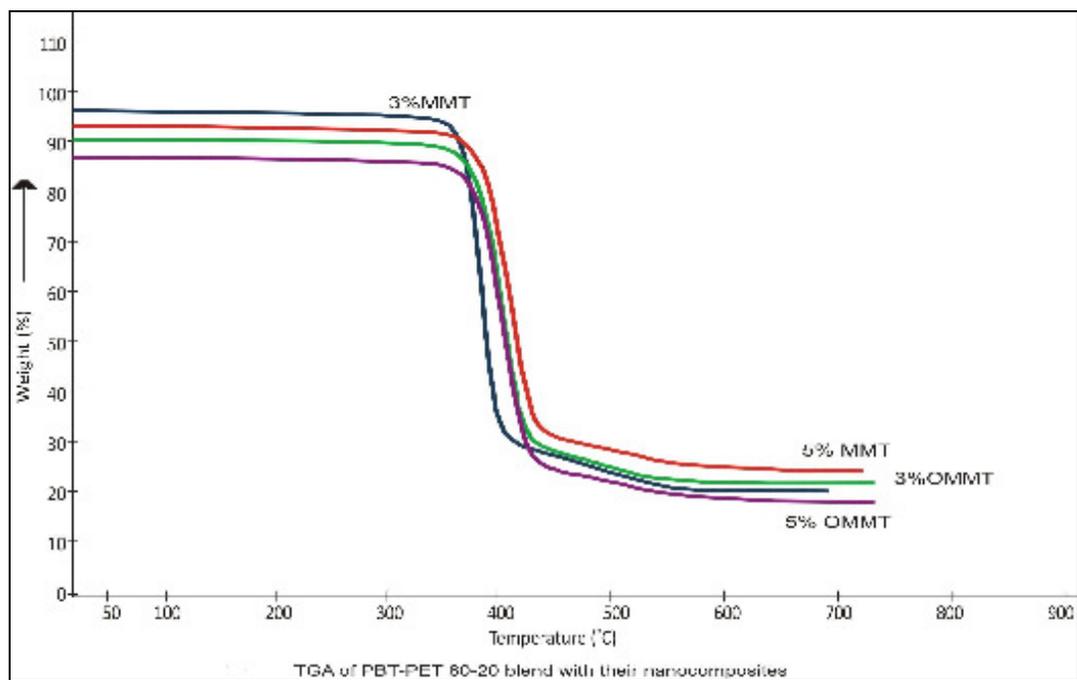Fig.-1: TGA of PBT and PBT-PET 80-20 blend

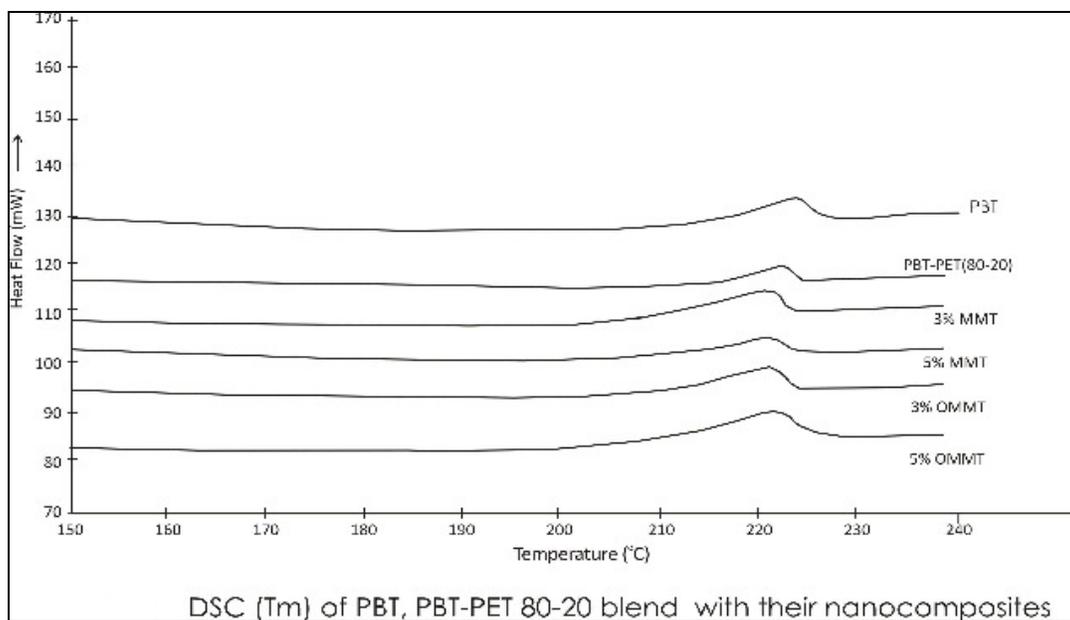Fig.-2: TGA of PBT-PET 80-20 blend nanocomposites

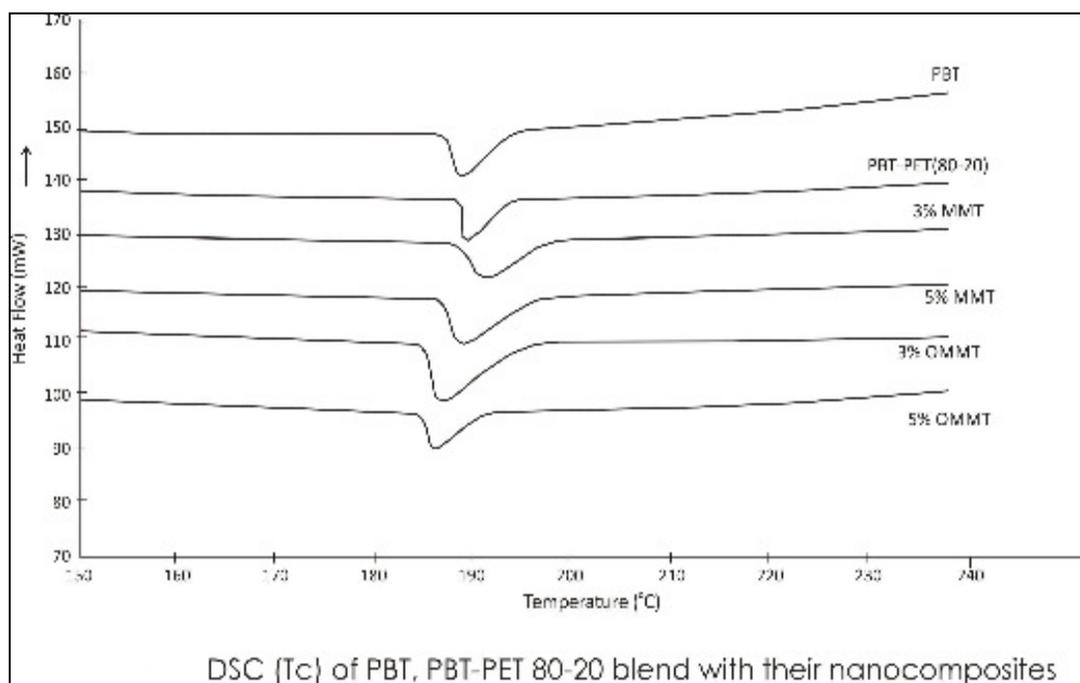Fig.-3: DSC (Tm) of PBT-PET 80-20 blend with their Nanocomposites

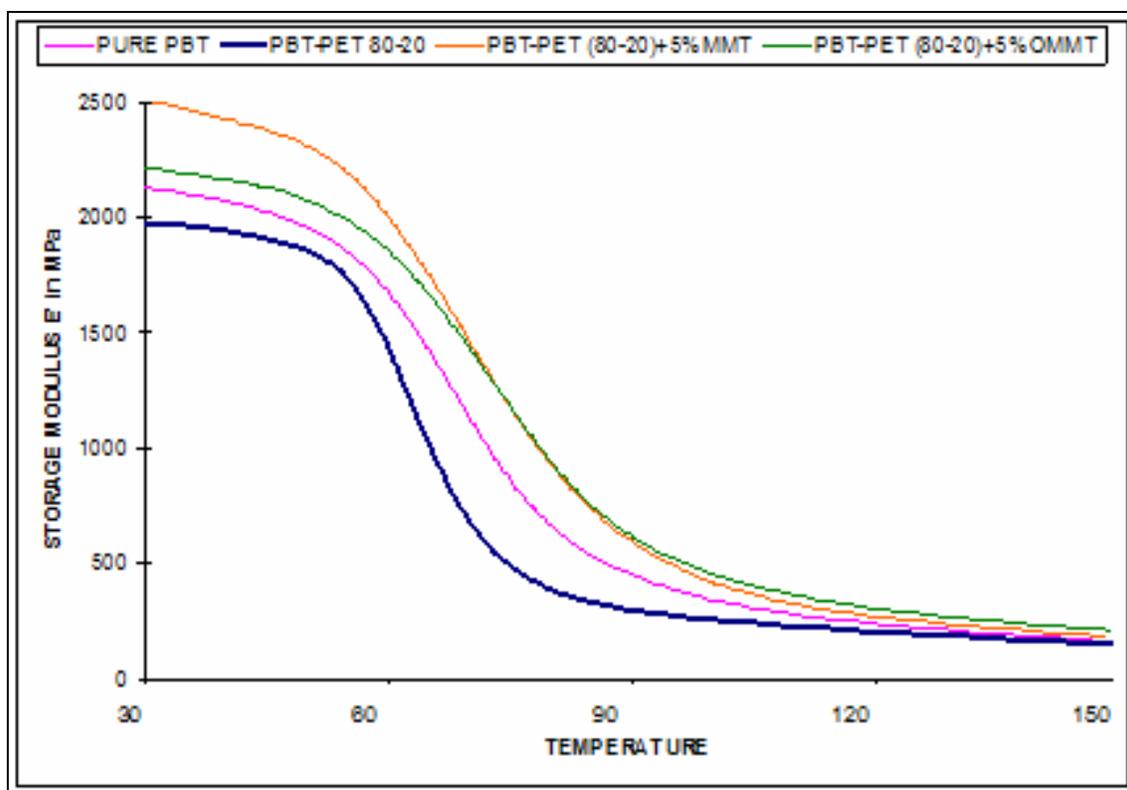Fig.-4: DSC (Tc) of PBT-PET 80-20 blend with their Nanocomposites

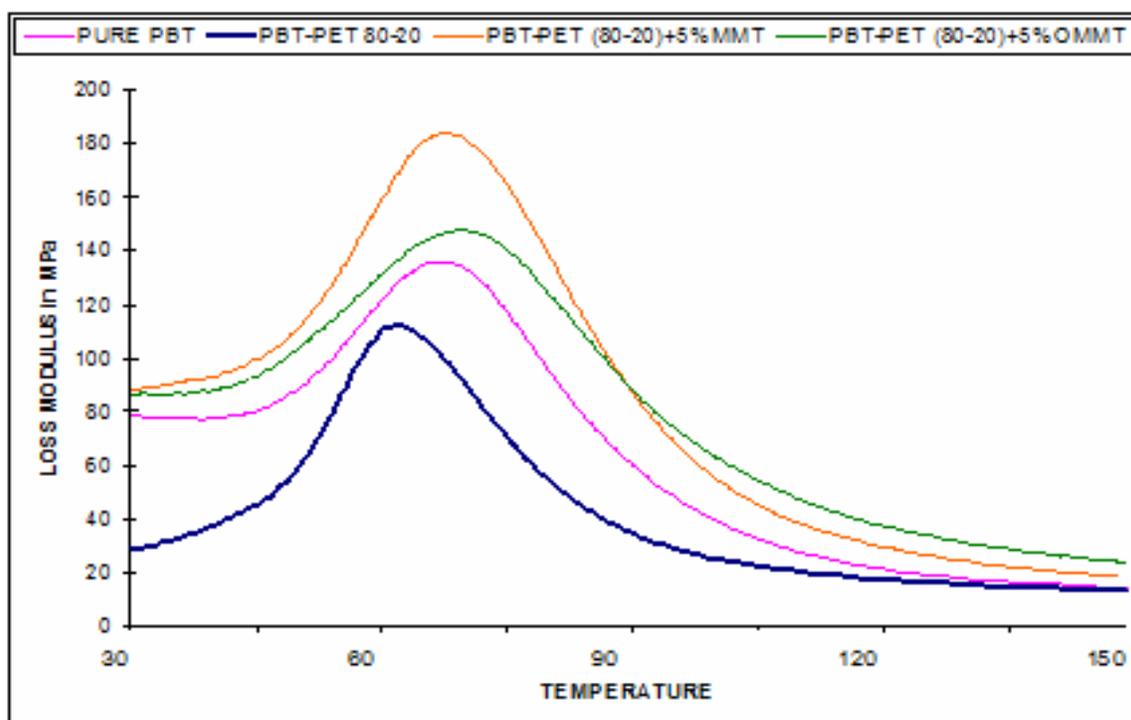Fig.-5: DMA of PBT, PBT - PET 80-20 and their clay nanocomposites

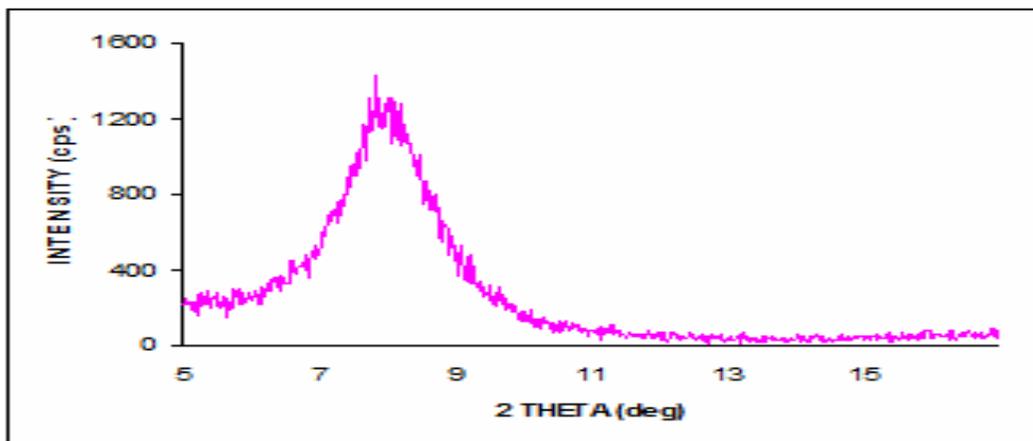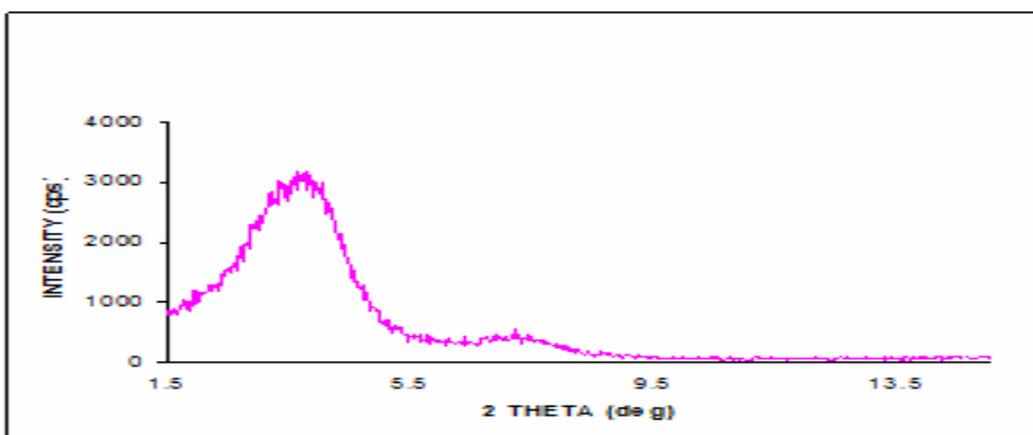Fig.-6: DMA of PBT, PBT - PET 80-20 and their clay nanocomposites
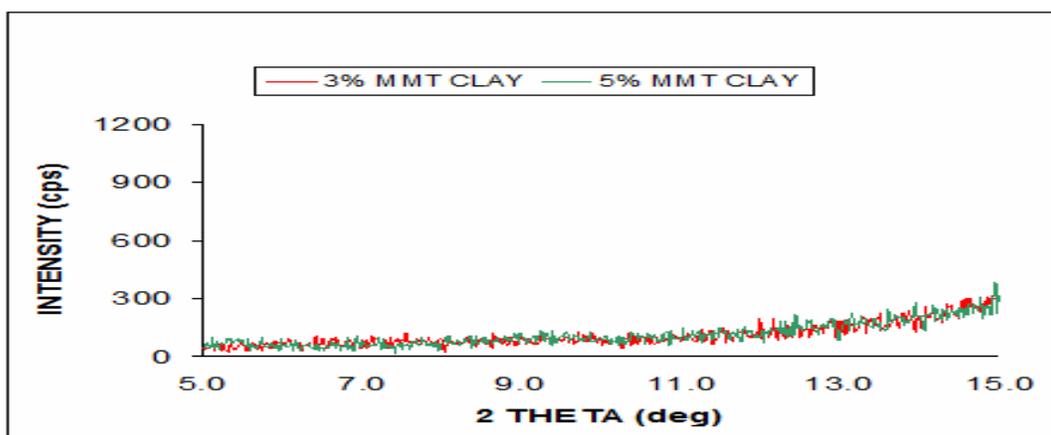
Fig.-7:XRD of MMT clay

Fig.-8: XRD of OMMT clay

Fig.-9: XRD of PBT-PET 80-20 blend with MMT clay
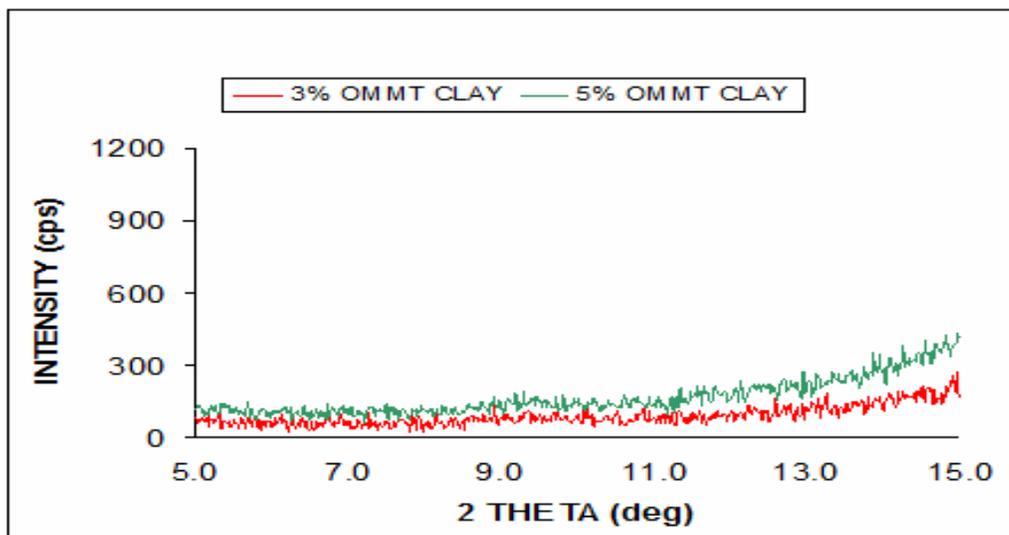
Fig.-10: XRD of PBT-PET 80-20 blend with OMMT clay

Fig .-11: TEM micrograph of PBT-PET 80-20 with 5 % MMT clay
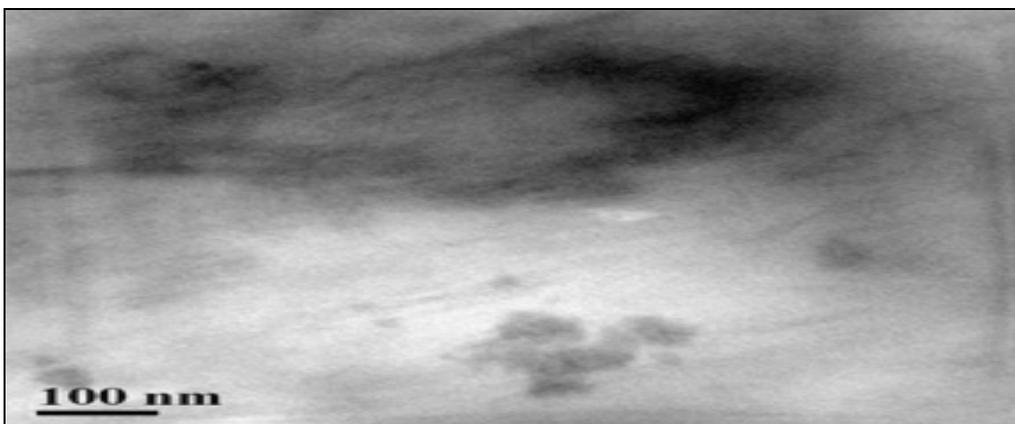
Fig.-12: TEM micrograph of PBT-PET 80-20 with 5 % OMMT clay

CONCLUSION

PBT/PET blend nanocomposites were prepared by employing melt compounding technique.Incorporation of PET to the PBT matrix increases the impact strength of the virgin matrix and tensile and flexural properties. However, incorporation of OMMT and MMT nanoclays along with PBT/PET decreases impact strength .Blending of PBT with PET and nanoclay accelerates the crystallisation process. In case of PBT/PET blend nanocomposites, the storage modulus increased with the incorporation of the nanoclays. A slight improvement in the thermal stability of the PBT-PET 80-20 wanoticed after the incorporation of the nanoclay. XRD and TEM clearly show that clay has exfoliated and dispersed in PBT-PET blend matrix.

REFERENCE

1. S. P. Mishra, and L. Deopure, *Polymer Bull.,***26** ,5(1985)
2. Y. Yu, and K. Choi., *Polym. Engg. Sci.,***37**, 91(1977)
3. D. Nabisaheb, and J. P. Jog., *Polym. Sci. Part B, Polym. Phys*, **37** , 2439(1979)
4. N. Avramova, *Polymer,***36**, 801(1995)
5. J. M. Wfer, US Patent,21 ,485 (1984)
6. C. F. Pratt, S. V. Phadke and E. Oliver, US Patent,111 ,965 (1990)
7. A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigaito, Synthesis and properties of nylon-6/clay hybrids, (Ed. D.W. Schaefer , J.E. Mark), **45**,171(1990)
8. E. P. Giannelis, *Appl. Organomet Chem*,**12**, 675 (1998)
9. R.Xu, E.Manias, A.J.Snyder and J. Runt,*Macromolecules*, **34**,337(2001)
10. J. W. Gilman, T. Kashiwagi, and J. D. Lichtenhan, *J. SAMPE* , **33**,40(1997)
11. J. W. Lim, A. Hassan, A. R. Rahmat and M. U. Wahit., *Polym. Int.,***55**,204(2006)
12. E A Flexman., Polym. Engg. Sci.,**19**,564(1979)
13. R. J. Gaymans., D. R. Paul and C. B. Bucknall, *Polymer Blends,***25**,2(2000)
14. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushuma, T. Kurauchi and   O. Kamigaito., *J. Mater Res.,***8**,1185(1993)
15. Wunderlich, Thermal Analysis, Academic Press, New York, (1990).
16. M. E. Brown and P. K. Gallagher , Handbook of Thermal Analysis, Elsevier, Amsterdam, **2**,112(2003)
17. A. V. Borruso, *Technon Petro. Chemical Seminar*, **5**,144(1994)
18. J. Lee , T. Takekoshi and E. P. Giannelis , *Mater. Res. Soc., Symp. Proc.*, **4**,57(1997)
19. C. F. Ou, M. T. Ho, J .R. Lin , *J. Appl. Polymer Sci.*, **91**,140(2004)
20. Anton Marcincin, Eva Kormendy, Marcela Hricova, Andrej Runstack and Arun Pal Aneja, *J. of Appl. Polymer Science*, **10**, 4222(2006)
21. D. R. Paul and S. Newman , Polymer Blends, Academic Press, New York, (1978).
22. S. P. Mishra and B. L. Deopura, *Polym. Commun.*, **26**,5(1985)
23. N. Avramova , *Polymer*, **36** (4),801(1995)
24. J. Avramov , S. Fakirov and I. Avramova , *Agnew Macromol. Chem.*, **99**,129(1992)
25. Huizhang, Zhong Zhang, Jing-Lei Yang and Klaus Friedrich, *Polymer*, **47**,679(2006)
26. Anton Marcincin, Eva Kormendy, Marcela Hricova, Andrej Runstack, Arun Pal Aneja, *J. of Applied Polymer Science*, **102**,4222(2006)
27. Suprakas Sinha Ray and Masami Okamoto, *Prog Polymer Sci.*, **28**,1539(2003)
28. A. B. Morgan, and J. W. Gilman, *J. Appl. Polym. Sci.,***87**, 1329 (2003)
29. T. Liu, K. P. Lim, W. C. Tjiu,K. P. Pramoda, and Z. K. Chen, *Polymer,***44**,3529(2003)
30. A. Usuki, Y. Kawasumi, M. Kojima, Y. Fukushima, T. Kurauchi, and D. J. Kamigaito, *Mater. Res.,***8**,1179(1993)
31. X. Fu, and S. Qutubuddin, *Polymer,***42**,807(2003)
32. R. A. Vain, K. D. Jandt, E. J. Kramer, E. P. Giannelis, *Chem. Mater.,***8**,2628(1996)
33. G. Galgali, C. Ramesh, and A. Lele, *Macromolecules,***34**,852(2001)

34. D. R. Paul, and S. Newman,. Polymer Blends, (Academic Press, New York). (1978).
35. Smitha Mohanty, S. Samal , Y. K. Tripathy , S. K. Nayak , S. K. Verma , *Int. J of Plastics Tech*, **9**,436(2005)
36. H. W. Starkweather, *Macromolecules*, **21**, 1798(1998)

[RJC-828/2011]