Mechanical Properties and Rheological Behavior of Poly(butylene terephthalate)/Clay Nanocomposites with Different Organoclays

Jitendra S. Narkhede, Vikrant V. Shertukde

Department of Polymer Engineering and Technology, University Institute of Chemical Technology, Matunga (East), Mumbai 400019, India

ABSTRACT: Poly(butylene terephthalate)–clay nanocomposites with three different organically modified clays were prepared via melt blending in a twin-screw extruder. Decyl triphenylphosphonium bromide, hexadecyl triphenylphosphonium bromide, and cetyl pyridinium chloride were used to modify the naturally occurring montmorillonite clay. The organically modified clays were characterized with X-ray diffraction for the d_{001}-spacing and with thermogravimetric analysis to determine the thermal stability. The prepared nanocomposites were injection-molded and examined for the dispersion quality of the clay, the mechanical properties, and the rheological behavior. The tensile strength of the nanocomposites increased with a 1% addition of clay; however, more clay decreased the tensile strength. Nanocomposites with finely dispersed clay platelets and nanocomposites with poorly dispersed clay platelets showed very different rheological behaviors. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1067–1074, 2011

Key words: nanocomposites; organoclay; rheology

INTRODUCTION

The dispersion of clay in polymers to form nanocomposites has been claimed to offer improved polymer properties, including mechanical strength and thermal stability.[1–3] The mechanical properties have been found to be anisotropic in comparison with those of fiber-reinforced polymers because the reinforcement from the inorganic layer occurs in two dimensions rather than in one dimension as in the case of fibers.[3–5] The properties of nanocomposites strongly depend on the intercalation and exfoliation of the silicate layers in the polymer matrix.

The most commonly used clay is montmorillonite (MMT) because of its natural abundance and low cost. Mined bentonite ore is a common source of MMT. MMT is a clay mineral consisting of stacked silicate sheets approximately 1 nm thick. This results in a high aspect ratio and a platelike morphology.[6] Naturally occurring MMT is incompatible with most polymers because of its hydrophilic nature. Ion exchange is widely practiced to modify the MMT surface to increase its compatibility with most polymers. Organoammonium, organophosphonium, organosulfonium, and imidazolium salts can be used to modify MMT. Organophosphonium and imidazolium salts are advantageous in that they are generally more thermally stable than organoammonium salts and organosulfonium salts.[7]

Several methods have been used to obtain polymer nanocomposites with the incorporation of organoclays, that is, solution intercalation, melt intercalation, and *in situ* interlayer intercalation. Among these, melt intercalation is a convenient method for making polymer–clay nanocomposites as it can produce both intercalated and exfoliated composites with a wide range of commercially available thermoplastic polymers.[8–11]

Poly(butylene terephthalate) (PBT) is used worldwide as an engineering plastic and has many useful properties, including good thermal stability, excellent flow properties, and good chemical resistance. However, PBT has poor mechanical properties and a low heat distortion temperature. Many attempts have been made to improve these properties of PBT via blending with various fillers. Among these blends, polymer nanocomposites with organically modified clays are the materials most commonly used for this purpose.[12–14] Xiao et al.[15] reported PBT–clay nanocomposites prepared via melt intercalation with the use of alkyl ammonium modified MMT. However, in the case of these nanocomposites, the high temperature that is required for melt intercalation and processing leads to decomposition of the alkyl ammonium cations in organically modified montmorillonite (OMMT). It alters the interface

Correspondence to: V. V. Shertukde (vikrantsher@rediffmail.com).

between the filler and polymer matrix and leads to degradation of the polymer, which decreases the desired levels of the properties. To obtain nanocomposites without thermal degradation of the organoclay during processing at temperatures of 250°C and higher, an organoclay that is thermally stable at temperatures higher than the processing temperatures must be used.

In this study, MMT clay was modified with three different intercalating agents: decyl triphenylphosphonium bromide (DP), hexadecyl triphenylphosphonium bromide (HDP), and cetyl pyridinium chloride (CPC). The thermal stability of these three intercalating agents was evaluated with respect to withstanding higher processing temperatures and maintaining the dispersion morphology. PBT–clay nanocomposites were obtained by the melt blending of PBT with modified clay at clay loadings varying from 1 to 5%. The obtained nanocomposites were analyzed with respect to their mechanical and rheological behavior.

EXPERIMENTAL

Materials

Na^+ MMT clay was provided by Crystal Nanoclay, Ltd. (Pune, India). The cation-exchange capacity (CEC) was 95 mequiv/100 g. Triphenyl phosphine, hexadecyl bromide, decyl bromide, and CPC were purchased from S.D. Fine Chemicals, Ltd. (Mumbai, India). PBT (Arnite T08 200) was purchased from DSM Engineering Plastics, Ltd. (India).

Methods

Synthesis of DP

In a round-bottom flask were placed 10.48 g of triphenyl phosphine and 8.84 g of n-decyl bromide (1 : 1 mol/mol). The mixture was maintained at 80–90°C for 10 h. The final viscous product was washed with diethyl ether three times and dried overnight at 50°C in a vacuum oven.
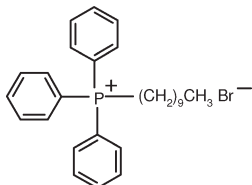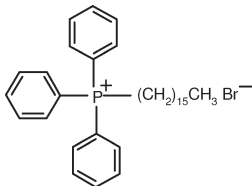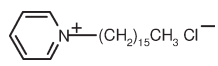
^{1}H-NMR (D20): 7.26–7.77 (m, 15H), 3.25 (br, 2H), 1.46 (br, 2H), 1.01–1.42 (m, 14H), 0.64 (t, 3H).

Synthesis of HDP

In a round-bottom flask were placed 10.48 g of triphenyl phosphine and 11.64 g of n-hexadecyl bromide (1 : 1 mol/mol). The mixture was maintained at 80–90°C for 10 h. The final viscous product was washed with diethyl ether three times and dried overnight at 50°C in a vacuum oven.

^{1}H-NMR (D20): 7.53–7.86 (m, 15H), 3.26 (2H), 1.44 (br, 2H), 1.05–1.38 (m, 26H), 0.73 (t, 3H).

TABLE I
Structures of the Intercalating Agents

Intercalating agent	Structure
DP	
HDP	
CPC	

Treatment of the MMT clay

MMT was treated with different intercalating agents (DP, HDP, and CPC) via an exchange reaction to replace the sodium cations present in MMT with quaternary alkyl phosphonium/ammonium cations of the intercalating agents. Table I shows the structures of the salts used for the modification of MMT. The equation for calculating the amount of the intercalating agent used for the cation-exchange reaction is as follows:

$$(CEC/100) \times \text{Weight of clay(g)} \times 1.2$$
$$= (X/Mw) \times 1 \times 1000$$

where X is the amount of the intercalating agent, M_w is the molecular weight of the intercalating agent, and 1.2 (>1) indicates the excess amount of the intercalating agent.

In 2 L of distilled water, 20 g of MMT clay was dispersed at 80°C for 2 h. A solution containing a calculated amount of the intercalating agent in distilled water was stirred for 1 h. The protonated solution was then added slowly to the MMT dispersion. This mixture was then stirred for 4 h. The organoclay was separated by filtration from the dispersion. The treated clay was purified by repeated washing and filtering to remove any excess intercalating ions. Clay treated with DP, HDP, and CPC is henceforth called MMTDP, MMTHDP, and MMTCPC, respectively.

Preparation of the PBT–clay nanocomposites with melt intercalation

The melt compounding of PBT and organoclay (1, 3 and 5%) was performed with a laboratory-scale twin-screw, corotating extruder (model MP19PC,

TABLE II
Compositions of the PBT–Clay Nanocomposites

Compound code	Type of organoclay	Feed composition	
		PBT	Organoclay
PBT	—	100	0
PBTDP1	MMTDP	99	1
PBTDP3	MMTDP	97	3
PBTDP5	MMTDP	95	5
PBTHDP1	MMTHDP	99	1
PBTHDP3	MMTHDP	97	3
PBTHDP5	MMTHDP	95	5
PBTCPC1	MMTCPC	99	1
PBTCPC3	MMTCPC	97	3
PBTCPC5	MMTCPC	95	5

APV Baker, Peterborough, United Kingdom) with a length-to-diameter ratio of 25 : 1 and a diameter of 16 mm. Extrusion was carried out with a temperature profile of 210–230–240–250°C from the hopper to the die with a screw speed of 60 rpm. The extruded strands were pelletized and then injection-molded in a microprocessor injection-molding machine (Boolani Engineering, Ltd., Mumbai, India). Table II lists the compositions of the prepared composites.

Characterization and testing

X-ray diffraction (XRD)

Wide-angle XRD analyses of the organoclay and polymer–clay nanocomposites were carried out on a Rigaku Miniflex+ instrument (Geldermalsen, The Netherlands (30 kV, 15 mA) with Cu Kα radiation, an NaI detector, a variable slit, a 0.05-step size, and a 2°/min scan rate.

Thermogravimetric analysis (TGA)

TGA measurements were obtained on an SDT Q600 from TA Instruments (New Castle, Delawre). The samples were measured against an alumina standard in a 90 mL/min N_2 flow with a temperature ramp of 20°C/min up to 600°C.

Transmission electron microscopy (TEM)

The morphology of the nanocomposites was observed with a JEOL JEM 1010 electron microscope (Tokyo, Japan) with an 80-kV accelerating voltage. Ultrathin specimens, approximately 80 nm thick, were cut at room temperature from the middle of the injection-molded bar with an Ultracut microtome equipped with a diamond knife. The sections were transferred from the knife edge to a 300-mesh copper grid.

Mechanical properties

The tensile strength and elongation at break of the samples were evaluated according to ASTM D 638 at the crosshead speed of 50 mm/min. The flexural
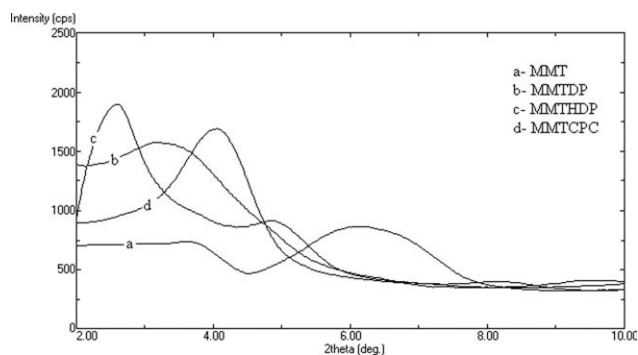

Figure 1 XRD patterns of the untreated and treated clays.

modulus was measured according to ASTM D 790. A jaw speed of 2.8 mm/min was maintained for three-point bending, and the specimen span was 100 mm. The tests were performed with an LR 50K universal testing machine (Lloyd Instruments, Fareham, Hants, United Kingdom). All the reported values are averages of at least five samples. The impact strength was determined according to ASTM D 256 with an Avery Denison model 6709 pendulum-type impact-strength tester with a striking velocity of 3.46 m^2/s and a 2.7-J striker at room temperature. The notch was cut into the rectangular bar specimen with a motorized notch-cutting machine (model 1 Polytest, Ray Ran, United Kingdom).

Rheological properties

The melt rheology of the virgin polymers as well as their nanocomposites was studied with a rotational rheometer (RT 10, Haake, Karlsruhe, Germany) with cone and plate geometry (plate diameter = 35 mm). Dynamic frequency (ω) sweep tests were executed in the ω range of 0.01–100 rad/s. The temperature of testing was 250°C.

RESULTS AND DISCUSSION

Characterization of the OMMT

Figure 1(a–d) presents the XRD peaks of Na^+ MMT and OMMT. The d_{001} reflection for Na^+ MMT was found at $2\theta = 6.16°$, which corresponds to the interlayer spacing of 1.443 nm. The XRD curves for OMMT show a shift of the peak at lower 2θ values, which indicates an increase in the interlayer spacing.

TABLE III
XRD Data of the Clay

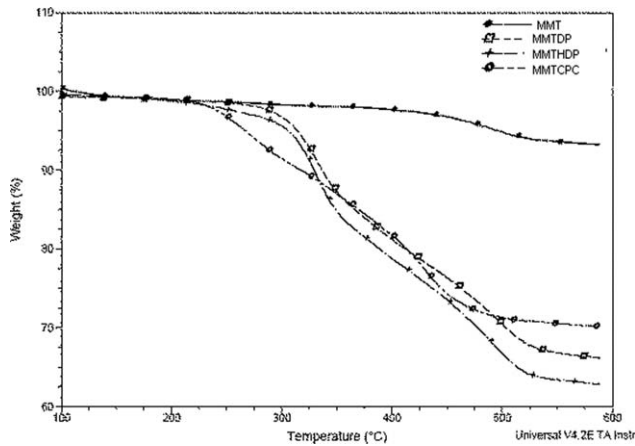| Curve	Intercalating agent	2θ	d_{001} value (nm)
a	Na^+ MMT	6.16	1.443
b	DP	3.14	2.811
c	HDP	2.42	3.647
d	CPC	4.04	2.196

Figure 2 TGA curves of the untreated and treated clays.

Table III lists the 2θ values and the corresponding basal spacing for Na$^+$ MMT and OMMT. Clay treated with HDP yielded the highest basal spacing in comparison with DP- and CPC-treated clays.

The thermal stability of the clay was studied with TGA. Figure 2 shows the TGA curves for Na$^+$ MMT and OMMT. TGA indicated that there was almost no weight loss for Na$^+$ MMT between 110 and 500°C, at which OMMT showed a large weight loss due to the decomposition of organic compounds present in the clay galleries of OMMT. Also, clays treated with the phosphonium intercalating agents (DP and HDP) were thermally more stable than the clay treated with CPC. The phosphonium-treated clays were stable up to 280°C, whereas the
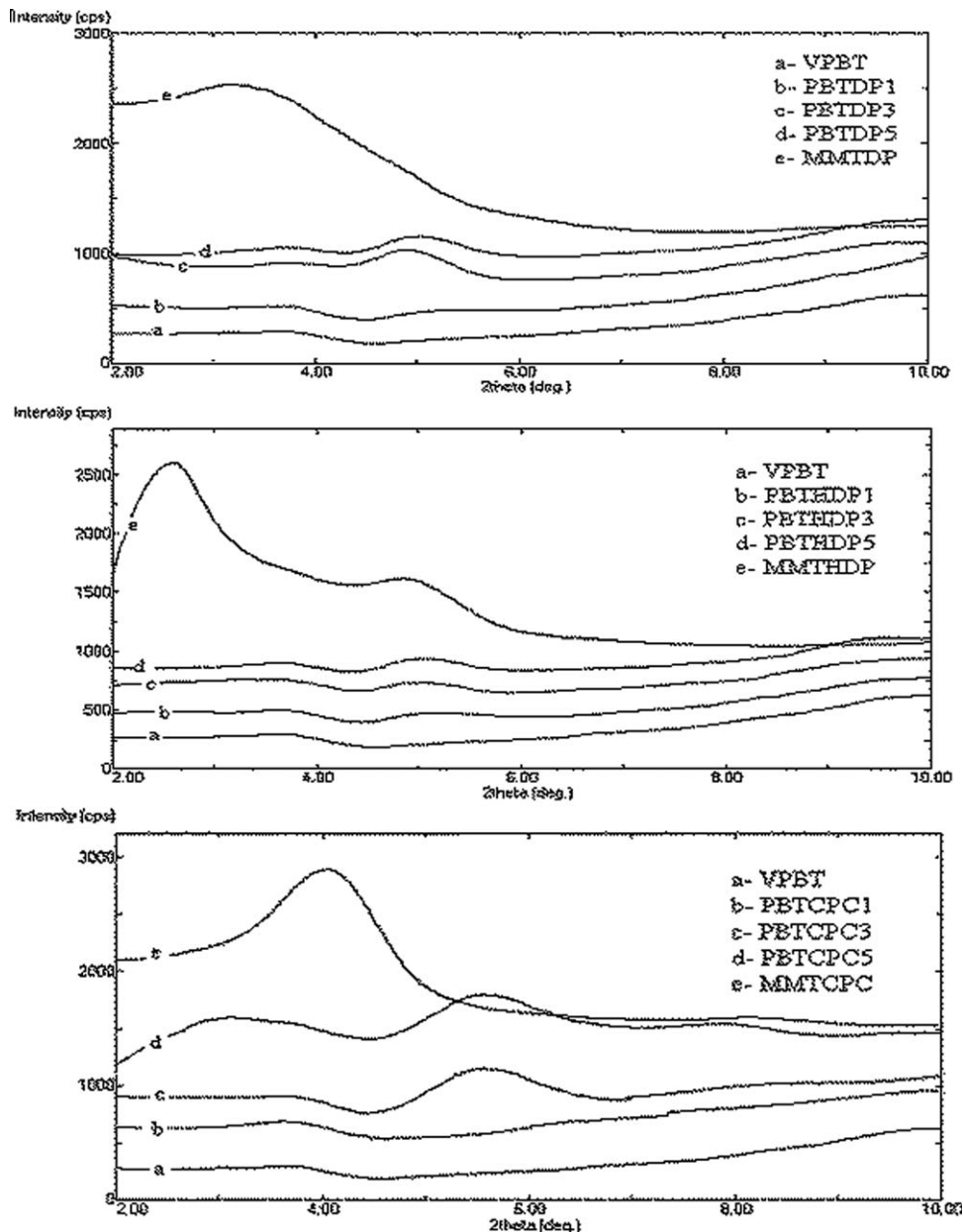

Figure 3 XRD curves of the PBT–clay nanocomposites (VPBT- virgin PBT).
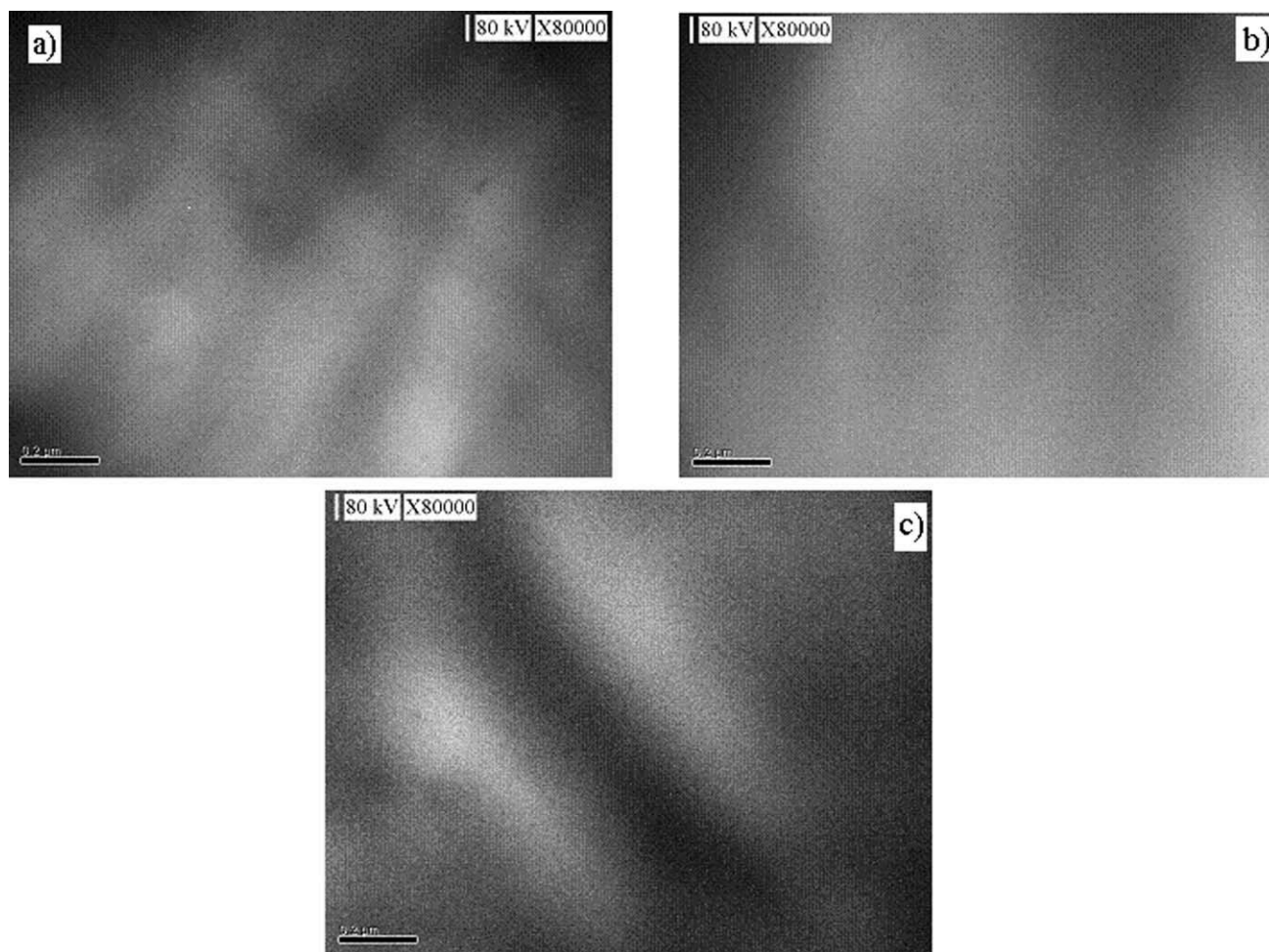
Figure 4 TEM images of the PBT–clay nanocomposites: (a) PBTDP1, (b) PBTHDP1, and (c) PBTCPC1.

decomposition of the CPC-treated clay started at 220°C. The weight percentage losses of MMTDP, MMTHDP, and MMTCPC at 550°C were 34.43, 38.37, and 28.9%, respectively.

XRD characterization of the PBT–clay nanocomposites

Figure 3 shows the XRD patterns in the 2θ range of 2–10° for clay-filled PBT nanocomposites. For nanocomposites containing 1% organoclay treated with DP, HDP, and CPC, no diffraction peak was observed in the 2θ range of 2–10°, and this indicated the dispersion of the exfoliated clay layers in the PBT matrix. Nanocomposites containing 3 or 5% concentrations of the MMTDP and MMTHDP organoclays showed broad diffraction in the 2θ range of 4.5–5.5°, which was due to the stacking of clay platelets. For nanocomposites containing 3 or 5% MMTCPC organoclay, the diffraction peak was observed at 2θ = 5.64°. The shift of the diffraction peak to higher 2θ values for the nanocomposites with 3 or 5% organoclay corresponded to a lower d-spacing, which was

due to partial degradation of the organic modifier with a reduction of the interlayer distance.

TEM

TEM images of nanocomposites containing 1% organoclay were taken to confirm the exfoliation of the clay in the PBT matrix. Figure 4 presents TEM images of the PBTDP1, PBTHDP1, and PBTCPC1 compositions are defined in TABLE II; they show that exfoliated nanocomposites were produced. The dark lines represent the intersections of silicate layers, whereas the white background corresponds to the PBT matrix. TEM images of nanocomposites containing 3 or 5% organoclay were not taken as the XRD results for these compositions showed that intercalated systems were produced.

Mechanical properties

Figures 5–7 depict the tensile strength, flexural modulus, and impact strength of neat PBT and PBT–clay nanocomposites. In comparison with neat PBT, the results showed that 1% incorporation of the
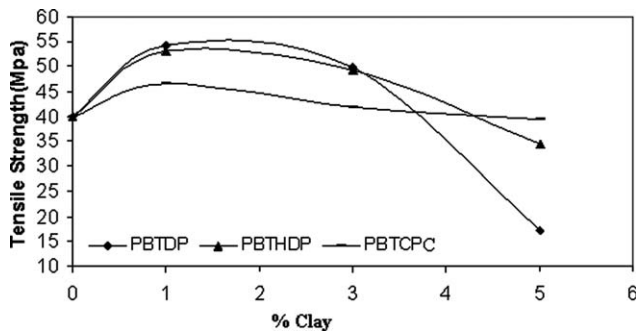
Figure 5 Tensile strength of the PBT–clay nanocomposites.

organoclay, dispersed via melt blending in the PBT matrix, improved the tensile strength. This result is consistent with the general observation that the introduction of an organoclay into a polymer matrix increases its tensile strength.[16–18] The increase in the tensile strength was due to the absorption of macromolecular layers on the clay platelet surface. With an excess clay loading (3 or 5%), the tensile strength decreased as a result of more coherent agglomeration of clay platelets at these concentrations. Also, the increase in the tensile strength for nanocomposites containing phosphonium-treated clay (PBTDP and PBTHDP) was more in comparison with the nanocomposites containing CPC-treated clay (PBTCPC). The lower tensile strength for PBT–clay nanocomposites containing CPC-treated clay was due to the partial degradation of the intercalating agent at the processing temperature of PBT, which resulted in stacking of the clay platelets.

The flexural properties of the PBT–clay nanocomposites were found to increase with the concentration of the organoclay increasing up to 3%, and with a 5% clay loading, no significant increase was observed for PBTDP or PBTHDP. However, the flexural properties of PBTCPC increased up to a 3% clay loading and decreased with a higher clay loading (5%). The increased modulus with the 1 and 3% organoclay loadings was attributable to the high stiffness of the clay platelets with a high aspect ratio. The modulus of the composites at a higher organoclay loading might not have been increased because the clay agglomerates inhibited plastic deformation
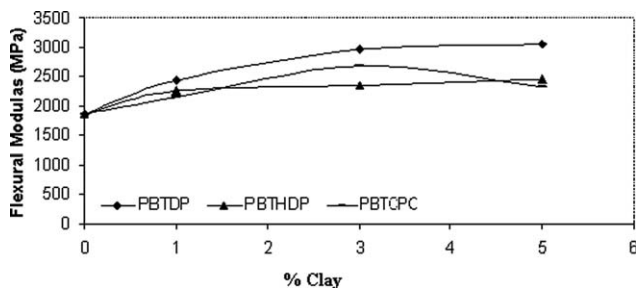
of the matrix by a constraining effect, as reported by Rong et al.[19]

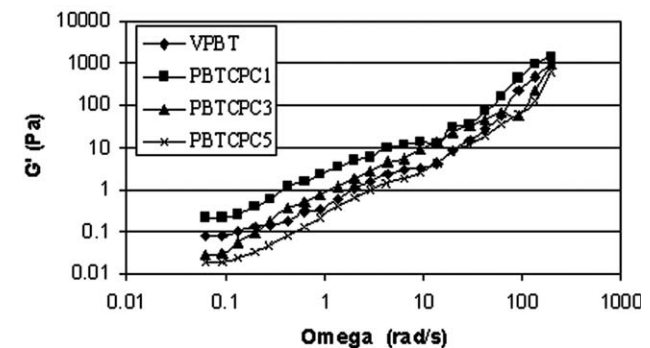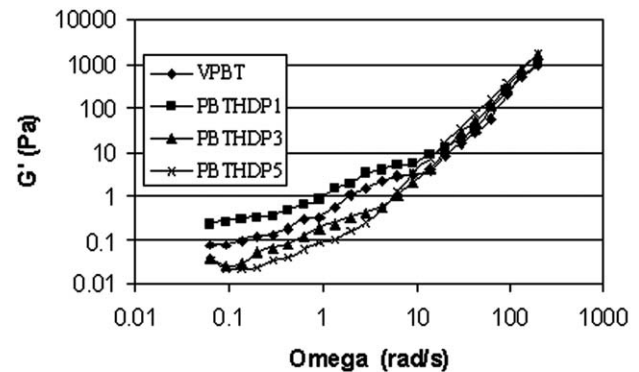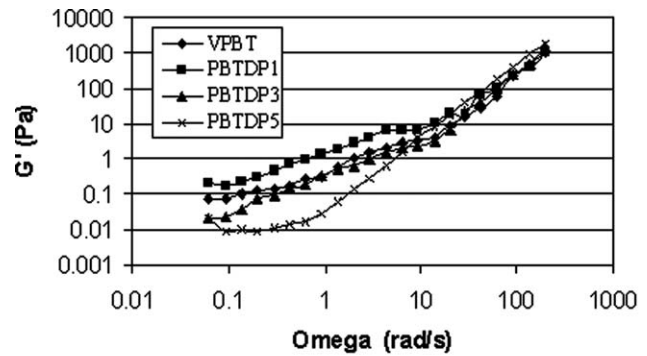Figure 7 illustrates the effect of the organoclay on the impact strength of the PBT–clay nanocomposites.

Figure 7 Impact strength of the PBT–clay nanocomposites.

Figure 6 Flexural modulus of the PBT–clay nanocomposites.

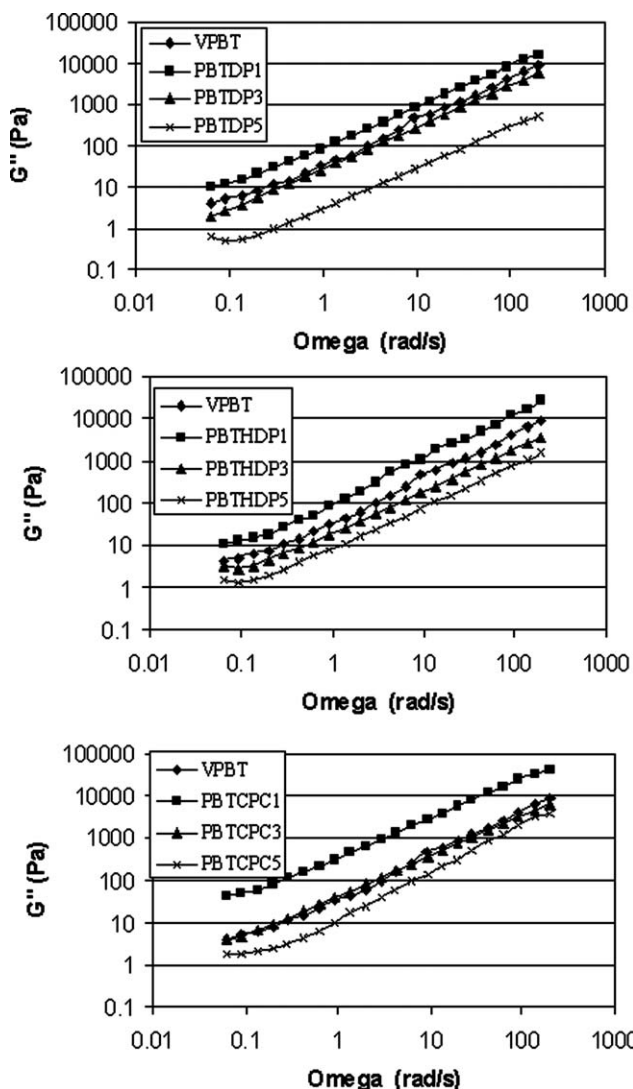**Figure 8** G' of the PBT–clay nanocomposites (VPBT-virgin PBT).

Figure 9 G'' of the PBT–clay nanocomposites (VPBT- virgin PBT).

The impact strength decreased as the percentage of the organoclay increased; this occurred because the clay platelets acted as stress concentrators and sites for crack propagation.

Rheological behavior

The rheological property of particulate suspensions depends on the structure, particle size, and shape; therefore, rheology can be used to examine the structural evolution and dispersion quality of polymer–clay nanocomposites in the melt state. Two dynamic viscoelastic properties, the storage modulus (G') and loss modulus (G''), can be obtained as a function of the applied value of ω.

Figures 8 and 9 show G' and G'' of virgin PBT and PBT–clay nanocomposites (with MMTDP, MMTHDP, and MMTCPC), respectively, at 250°C. In the high ω region corresponding to movement within a small

timescale, not much difference in G' was seen for the different samples of the nanocomposites, and this implied that the movement of polymer chain segments was not affected by the addition of clay. However, G' in the low region was significantly dependent on the addition of clay. Therefore, the rheological behavior in the low ω region can be considered to reflect the dispersion quality of the clay in the polymer. Figure 7 shows that G' in the low ω region for a 1% blend of the clay with PBT was greater than G' for virgin PBT. This indicates that the free movement of PBT chains was restricted by clay platelets, and this resulted in incomplete relaxation of the chains with the applied small-amplitude strain over a long time range. With the further addition of clay (3 and 5%), the G' value in the low ω region decreased, and this may have been due to the agglomeration of clay platelets at a higher concentration. The ω dependence of G'' showed a similar trend.

The complex viscosity (η^*) of PBT and PBT–clay nanocomposites versus ω is shown in Figure 10. PBT with 1% clay displayed higher η^* values than the
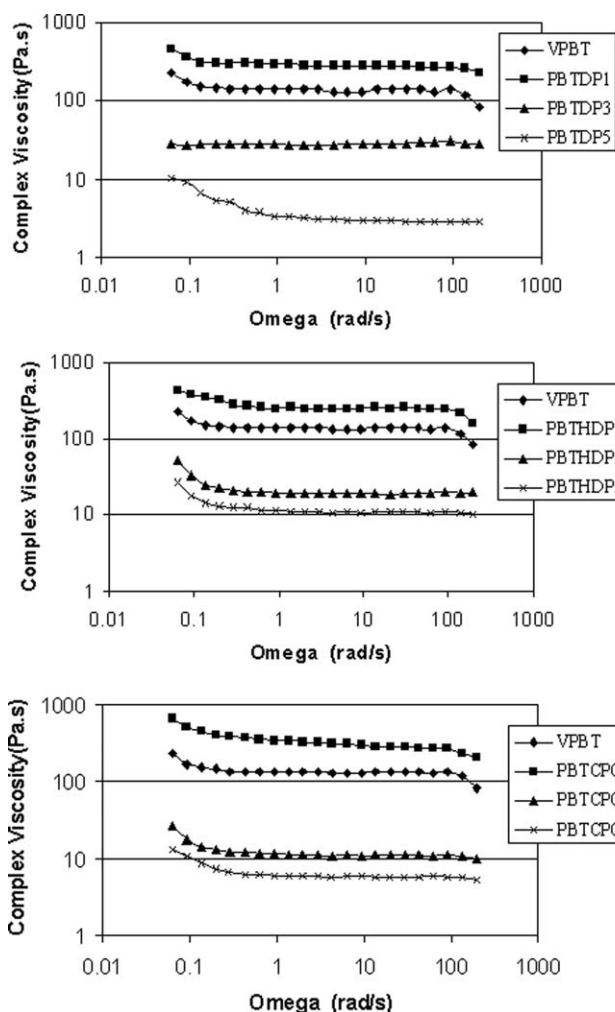

Figure 10 η^* curves of the PBT–clay nanocomposites (VPBT- virgin PBT).

virgin PBT, whereas with a 3 or 5% addition of clay, η^* was less than that of the virgin PBT. The increase in the viscosity with a 1% addition of clay, which represented the dispersion quality of the clay in the matrix polymer or the interaction between the polymer and clay, could become a criterion for a rheological percolation threshold indication of the onset of the formation of a physical network. The nanocomposites based on three different clays (MMTDP, MMTHDP, and MMTCPC) exhibited similar rheological behavior.

CONCLUSIONS

PBT–clay nanocomposites were prepared by melt intercalation in a twin-screw extruder and then injection-molded for the evaluation of the mechanical properties and rheological behavior. Naturally occurring MMT clay was modified by three intercalating agents: DP, HDP, and CPC. Organic modification of the MMT clay increased its d_{001}-spacing and resulted in increased compatibility with the polymer. Clay modified with phosphonium intercalating agents showed more thermal stability than clay modified with pyridinium salts (CPC), as confirmed by TGA and reflected in the mechanical properties of the nanocomposites. The mechanical properties of PBT–clay nanocomposites with 1% organoclay showed improved mechanical properties; the addition of more clay reduced the properties. The increase in the mechanical properties of the PBT–clay nanocomposites based on the CPC-modified clay (PBTCPC) was less than that of the nanocomposites based on the phosphonium-treated clays (PBTDP and PBTHDP). The addition of clay to the polymers resulted in decreased impact strength. From the results of dynamic rheological tests, we observed that in the high ω region, there was not much difference in G' for the nanocomposite samples, whereas G' in the low ω region was significantly dependent on the addition of clay. The dispersion quality of clay at a 1% concentration in PBT resulted in increased viscosity of the melt.

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