

Preparation and Characterization of Nanocomposites Based on Thermoplastic Elastomers from Rubber–Plastic Blends

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ABSTRACT: In the present work, thermoplastic elastomer (TPE)–clay nanocomposites (TPN) based on different rubber–plastic blends from ethylene–octene copolymer [Engage]–Polypropylene and brominated poly(isobutylene-*co*-paramethyl styrene)–nylon 6 were prepared by melt blending. Hexadecyltrimethylammonium bromide and octadecyl amine-modified sodium montmorillonite were used as organoclays. The nanocomposites were prepared by adding the nanoclay separately into the rubber and plastic phases. The TPNs were characterized with the help of transmission electron microscopy (TEM) and X-ray diffraction. The X-ray diffraction peaks observed in the range of 3–10° for the modified clays disappeared in the thermoplastic elastomeric

nanocomposites. TEM photographs showed exfoliation and intercalation of the clays in the range of 20–30 nm in the particular phase where the clay was added. Excellent improvement in mechanical properties like tensile strength, elongation at break, and modulus was observed on incorporation of the nanoclays in the rubber phase of TPN. When the nanoclay was added to the plastic phase, the mechanical reinforcement is comparatively poorer due to partial destruction of the crystallinity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1645–1656, 2006

Key words: thermoplastic elastomers; nanocomposite; sodium montmorillonite; rubber; plastic

INTRODUCTION

Polymer–clay nanocomposites are an interesting field of research in recent years. The polymers that have been extensively studied are nylon,^{1–11} polypropylene,^{12–16} polyurethane,¹⁷ natural rubber (NR),¹⁸ epoxidized natural rubber (ENR),¹⁸ ethylene–vinyl acetate copolymer (EVA),¹⁹ styrene–butadiene rubber (SBR),^{20,21} butadiene rubber (BR),²² acrylonitrile–butadiene rubber (NBR),²² etc. Among the thermoplastic elastomers (TPE)/clay nanocomposites (TPN), EVA containing 28% vinyl acetate (EVA-28)²³ and SBS²⁴ with organomodified montmorillonite have been reported so far. The nanocomposites based on the TPE from rubber–plastic blends have not been reported yet. Scientifically, it is also interesting to investigate the location of the nanoclays in such blends and their influence on properties.

In the last few decades, elastomer–thermoplastic blends have become technologically interesting for use as TPE.²⁵ They need not be vulcanized during fabrication into the end-use parts. Thus, they offer a substantial economic advantage with respect to the fabrication of the finished parts.

Polymer blends, in general, are prepared commercially by melt mixing, solution blending, or latex mixing. Elastomer–plastic blends of the type discussed here, containing large amounts of elastomers, are generally prepared by melt-mixing techniques. Melt-mixing avoids the problems like contamination and solvent removal. In general, internal mixers, mixing extruders, and the twin-screw mixers are suitable for melt-mixing of elastomers with plastics. Sometimes the rubber–plastic blends are dynamically vulcanized (the rubber phase is cured during blending) to get better properties.²⁶ Dynamic vulcanization is the process of vulcanizing elastomer during its intimate melt-mixing with a nonvulcanizing thermoplastic polymer. The elastomer droplets are dispersed within the thermoplastic matrix to give a particulate-vulcanized elastomer phase as a stable domain morphology during melt processing. We have reported preparation and properties of a large number of thermoplastic elastomeric rubber–plastic blends.^{27–30}

In the present work, two different TPEs have been prepared from rubber–plastic blends. One of them has been made of completely saturated, nonpolar rubber and plastic viz. ethylene–octene copolymer (Engage®) and polypropylene (PP), and the other one is a blend of a saturated-polar rubber, brominated poly(isobutylene-*co*-paramethylstyrene) (BIMS) and polar plastic, polyamide 6 (nylon 6). Formation of TPE using these plastics and rubbers and their properties have not been reported in the scientific literature so far, al-

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though EPDM-PP³¹ blend has been extensively covered. As little work has been done on rubber-plastic (thermoplastic elastomeric) blend/clay nanocomposite, nanocomposites made of these TPE are worth investigating. It may be mentioned here that we have recently reported nanocomposites based on BIMS and Engage separately, which have shown excellent improvement in various properties.³²⁻³³

EXPERIMENTAL

Materials used

BIMS (grade-BIMS-7745; paramethyl content, 7.7 wt %; bromine content, 1.2 wt %; ML_{1+8} at 125°C, 45; M_n , 2×10^5 g/mol) was supplied by Exxon Mobil Chemical Company, Baytown, TX. The general purpose polyolefin elastomer, Engage[®] 8150 (comonomer octene content, 25 wt %, ML_{1+4} at 121°C: 35) was kindly provided by DuPont-Dow Elastomers, Wilmington, DE. Polypropylene (PPCP, 12 MFI) was supplied by Machino-Basell India Ltd., Gurgaon, India. Nylon 6, Ultramid B3 (Specific gravity, 1.14 at 23°C, Melting point 226°C) was obtained from BASF, Germany. Sodium montmorillonite was generously supplied by Southern Clay Products, Gonzales, TX. Its cation exchange capacity was reported to be 90 mequiv/100g. Octadecyl amine ($C_{18}H_{37}NH_2$), hexadecyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$), the clay modifiers were supplied by Sigma Chemical, St. Louis, MO. Toluene (analytical grade) was procured from Nice Chemicals Pvt. Ltd., Cochin, India. Ethyl alcohol was supplied by Bengal Chemicals and Pharmaceuticals, Kolkata, India. Phenolic resin, (novolac type, softening range 70–80°C), used as the curative for BIMS, was obtained from indigenous sources.

Preparation of modified clay

The clay was modified with different amines, namely octadecyl amine (primary amine) and hexadecyltrimethylammonium bromide (tertiary amine).

For the preparation of primary amine modified clay, 5 g of the clay was mixed with 400 cc water and stirred thoroughly at 80°C for half an hour. The octadecyl amine was melted at 50°C, then mixed with conc. HCl (5 cc) and stirred for few minutes with addition of 200 cc of water. This solution was then mixed with the clay dispersion slowly, with constant stirring to obtain the modified clay. This modified clay was then filtered and washed thoroughly until it was free of chloride ion. Then, it was dried in vacuum oven at room temperature (30°C).

For the preparation of tertiary amine modified clay, 5 g of the clay was mixed with 400 cc water and stirred thoroughly at 80°C for half an hour. The hexadecyltrimethylammonium bromide was dissolved in 200 cc

TABLE I
Different Designations Used for Clays

Name	Designation
Octadecylamine-modified sodium montmorillonite	OC
Hexadecyltrimethylammonium bromide-modified sodium montmorillonite	HD

water at 80°C. The solution was then mixed slowly, with the clay dispersion with constant stirring to obtain the modified clay. This modified clay was then filtered and washed thoroughly. It was dried in vacuum oven at room temperature (30°C).

Table I reports various clays used for the work and their designations.

Preparation of different rubber-plastic blends and nanocomposites made from them

Engage[®]-PP blends were prepared in a Brabender Plasticorder (PLE 330). PP was melted at 190°C. Afterwards, Engage[®] was added and mixed for 4 min at 60 rpm. The mix obtained from the Brabender Plasticorder was then allowed for a single pass through the two-roll mill (Schwabenthan, Berlin). The material was remixed for 2 min at 190°C. Finally, it was compression molded into a 1 mm thick sheet at 210°C for 3 min in a hydraulic press.

From the different blend ratios, the appropriate composition of EN and PP for TPE was chosen. In this particular composition, the nanoclay (OC) was mixed with the rubber initially in the solution phase (in toluene), and then the dry rubber-clay masterbatch was melt-blended with the PP following the earlier method. This nanocomposite has been designated as ENOC4/PP. In another case, PP-OC masterbatch was prepared by melt-intercalation method at 190°C. It was then melt-mixed with Engage[®] following the same method. This has been designated as EN/PPOC4. All the TPN were sheeted out in a compression mold following the same condition as that in the case of the blends.

BIMS-nylon 6 blends were prepared in a Sigma mixer (manufacturer: S.C. Dey and Co., Kolkata, India). Nylon 6 was first melted at 230°C for 1 min, then BIMS and resin (in the case of dynamic vulcanized samples only) were added to it and mixed initially for 2 min at 60 rpm. The material was then remixed for another 2 min at 60 rpm till no variation in torque was noticed. The samples were compression molded for 2 min at 250°C into 1 mm thick sheets.

Here also, from the different blend ratios, the appropriate composition for TPE was chosen. A masterbatch of rubber, phenolic resin, and nanoclay (HD) was prepared in solution process. It was air dried and

TABLE II
Different Rubber-Plastic Blends, Nanocomposites, and Their Designation

Composition	Designation
Engage	EN
Polypropylene	PP
Engage:polypropylene 50:50	EN/PP 50/50
Engage:polypropylene 60:40	EN/PP 60/40
Engage:polypropylene 70:30	EN/PP
Engage:polypropylene 70:30 (recycled)	EN/PP (re)
Engage:polypropylene 80:20	EN/PP 80/20
Engage + 4 phr OC:polypropylene 70:30	ENOC4/PP
Engage:polypropylene + 4 phr OC 70:30	EN/PPOC4
BIMS:nylon 6 100:0	BN 100:0
BIMS:nylon 6 80:20	BN 80:20
BIMS:nylon 6 70:30	BN
BIMS:nylon 6 60:40	BN 60:40
BIMS:nylon 6 0:100	BN 0:100
BIMS + 2.5 phenolic resin:nylon 6 70:30	BR2.5N
BIMS + 5 phenolic resin:nylon 6 70:30	BR5N
BIMS + 10 phenolic resin:nylon 6 70:30	BR10N
BIMS + 5 phenolic resin:nylon 6 70:30 (recycled)	BR5N (re)
BIMS:nylon 6 + 4 phr HD 70:30	BNHD4
BIMS + 5 phenolic resin:nylon 6 + 4 phr HD 70:30	BR5NHD4
BIMS:nylon 6 + 4 phr HD 70:30 (recycled)	BNHD4 (re)
BIMS + 5 phenolic resin:nylon 6 + 4 phr HD 70:30 (recycled)	BR5NHD4 (re)
BIMS + 4 phr HD:nylon 6 70:30	BHD4N
BIMS + 5 phenolic resin + 4 phr HD:nylon 6 70:30	BR5HD4N
BIMS + 4 phr HD:nylon 6 70:30 (recycled)	BHD4N (re)
BIMS + 5 phenolic resin + 4 phr HD:nylon 6 70:30 (recycled)	BR5HD4N (re)

then melt-mixed with nylon 6 following the above method. In another method, nylon 6 and HD masterbatch was made first and then mixed with BIMS, keeping all the processing conditions identical as that in the case of the blends. The samples were compression molded for 2 min at 250°C into 1 mm thick sheets.

The composition-detail of different composites and their designation are reported in Table II.

Characterization of the nanocomposites

X-ray diffraction studies (XRD)

The orientation of the silicate layers of modified and unmodified clay and dispersion within the TPE matrix were investigated by using a Rigaku CN 2005 X-Ray Diffractometer (Model:Miniflex) in the range of 3–10° (= 2 θ) for the clays and 3–32° in the case of TPN with a Cu target ($\lambda = 0.154$ nm). The corresponding d -spacing of the clay particles was calculated using the Bragg's law. The samples were scanned at 1000 counts/s, at a scanning speed of 2°/min. They were placed vertically in front of the X-ray source Cu K α and perpendicular to the goniometer where the goniometer was fixed, but the sample was rotating.

Transmission electron microscopy (TEM)

The samples for TEM analysis were prepared by ultra cryomicrotomy using Leica Ultracut UCT. Freshly

sharpened glass knives with cutting edge of 45° were used to get the cryosections of 90 nm thickness. Since these samples were elastomeric in nature, the sample temperature during ultra cryomicrotomy was kept at –130°C (well below T_g of the rubbery phase). The cryosections were collected and directly supported on a copper grid of 300-mesh size. The microscopic study was performed using a PHILIPS (Model no. CM 12) transmission electron microscope, operating at an accelerating voltage of 120 kV. The magnification of the nanocomposites is indicated by scale bars present in the photographs.

Physicomechanical properties

Tensile specimens were punched out from the molded sheets using ASTM Die C. The tests were carried out as per the ASTM D412–98 method in a Universal Testing Machine (Zwick 1445) at a cross-head speed of 500 mm/min at (25 \pm 2)°C. The average of three test results is reported here.

Tensile specimens were punched out from the molded sheets of rubber-plastic blends, using ASTM Die C, for measuring the tension set. The test was carried out following ASTM D412 method in a universal testing machine (Zwick 1435). The average of three measurements is reported.

The hardness of the rubber-plastic blends was measured in accordance with ASTM D2240 using a shore D type durometer.

TABLE III
Physicomechanical Properties of Engage-Polypropylene Blends

Sample name	Modulus at elongation (MPa)				Tensile strength (MPa)	Elongation at break (%)	Tension set at 100% elongation (%)	Hardness (shore D)
	50%	100%	200%	300%				
EN/PP 50/50	10.6	—	—	—	12.1	85	51	25
EN/PP 60/40	5.5	7.0	8.1	10.5	10.6	306	14	23
EN/PP	3.2	4.1	5.3	5.7	10.4	780	10	20
EN/PP (re)	3.0	3.9	4.8	5.0	9.8	765	10	16
EN/PP 80/20	2.9	3.6	4.6	4.7	9.8	866	6	19
ENOC4/PP	4.4	5.3	5.5	5.6	13.5	755	10	14
EN/PPOC4	4.2	5.1	5.8	6.1	12.8	750	10	13
ENQC4/PP (re)	3.8	4.7	5.1	5.3	12.8	740	10	13
EN/PPOC4 (re)	3.8	4.8	5.6	5.8	11.8	734	10	13

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical spectra of the blends were obtained by using a DMTA IV, (Rheometric Scientific, NJ) dynamic mechanical thermal analyzer. The sample specimens were analyzed in tensile mode at a constant frequency of 1 Hz, a strain of 0.01%, within the temperature range of -80°C to 80°C at a heating rate of $2^{\circ}\text{C}/\text{min}$. The data were analyzed by RSI Orchestrator application software on an ACER computer attached to the machine. Storage modulus (E') and loss tangent ($\tan \delta$) were measured as a function of temperature for all the samples under identical conditions. The temperature corresponding to the peak in $\tan \delta$ versus temperature plot was taken as the glass-rubber transition temperature (T_g).

RESULTS AND DISCUSSION

Physicomechanical properties of different blends

Optimization of rubber-plastic composition in EN-PP blends to obtain TPE characteristics

Engage[®]-PP blends have been made by using four different blend ratios (Engage:PP 50:50, 60:40, 70:30, and 80:20 by weight). The mechanical properties are reported in Table III and the tensile stress-strain curves are shown in Figure 1.

The elastomer portion is gradually increased in the blends. With increasing rubbery portion, the tensile strength decreases, but the elongation at break increases (Fig. 1). The tensile strength values of 50:50, 60:40, 70:30, and 80:20 blends are 12.1, 10.6, 10.4, and 9.8 MPa, respectively, and the corresponding elongation at break values are 85, 306, 780, and 866%. Although the changes in tensile strength are within 23% in the above four blends, the elongation at break shows a drastic change (183%) from 60:40 to 70:30 blends. For the TPE elongation at break plays a great role, the compound must have elongation at break

more than 100%. So, 60:40, 70:30, and 80:20 blends fulfill the requirements of the TPE. The tension set at 100% elongation and hardness values of the corresponding blend composition (EN:PP 50:50 to 80:20) register values of 51, 14, 10, and 6% and 25, 23, 20, and 19 shore D, respectively. For a TPE, the blend should have less than 50% tension set when kept at 100% elongation for 10 min at 25°C (ASTM D412). This criterion has also been fulfilled by 60:40, 70:30, and 80:20 blends. So, these three blends can be considered as TPE. But on recycling, the change in mechanical properties lies within 10% only for the 70:30 blend. Hence, 70:30 blend ratio has been chosen for its optimum TPE properties. Nanocomposite has been made with this blend for further investigation.

Optimization of rubber-plastic composition in BIMS-nylon 6 blends to obtain TPE characteristics

Three different blends were prepared with three different BIMS:nylon 6 ratios (60:40, 70:30, and 80:20).

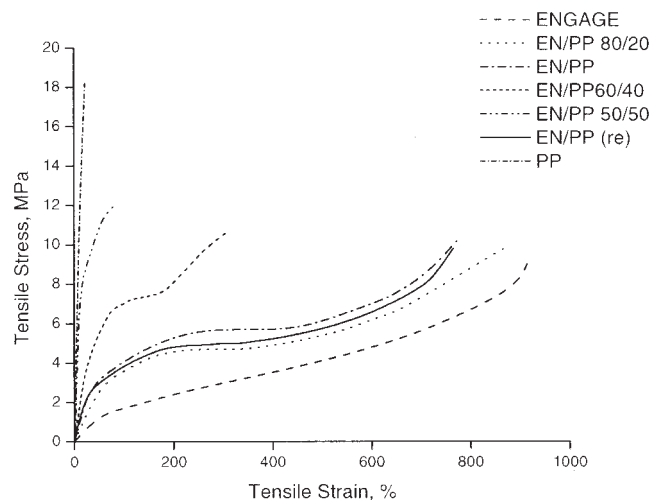


Figure 1 Stress-strain curve of different EN/PP blends.

TABLE IV
Physicomechanical Properties of BIMS-Nylon 6 Blends

Sample name	Modulus at elongation (MPa)			Tensile strength (MPa)	Max. stress (MPa)	Elongation at break (%)	Tension set at 100% elongation (%)	Hardness (shore D)
	50%	100%	200%					
BN 100:0	0.2	0.2	0.2	0.01	0.2	355	—	—
BN 80:20	0.5	0.6	0.6	0.22	0.6	427	51	7
BN	1.4	1.5	1.1	0.84	1.5	211	22	11
BN 60:40	3.3	—	—	2.87	3.3	67	51	19
BN 0:100	—	—	—	41.9	—	27	—	50
BR2.5N	2.7	3.5	—	3.7	—	138	—	21
BR5N	3.8	5.6	—	5.9	—	118	12	19
BR10N	6.5	—	—	6.6	—	55	12	27
BR5N (re)	3.5	5.1	—	5.4	—	120	12	18
BNHD4	1.8	2.7	3.3	3.3	—	200	12	11
BR5NHD4	5.0	5.9	—	6.0	—	111	12	12
BNHD4 (re)	1.3	2.0	2.6	2.6	—	200	12	11
BR5NHD4 (re)	4.3	5.7	—	6.1	—	118	12	12
BHD4N	2.9	4.0	—	4.3	—	127	12	14
BR5HD4N	4.2	5.8	—	6.0	—	110	12	21
BHD4N (re)	1.8	3.0	—	4.0	—	150	12	13
BR5HD4N (re)	3.6	5.0	—	−5.0	—	101	12	21

The mechanical properties are reported in Table IV and the stress–strain curves are shown in Figure 2(a).

BN 60:40 blend shows highest tensile strength of 2.87 MPa among the three blends followed by 0.84 MPa of BN and 0.22 MPa of BN 80:20. Though the tensile strength is highest in BN 60:40, the elongation at break is only 67%, which is less than 100%. The tension set is 51% in the case of BN 60:40. Hence, this blend is not considered as a TPE. So, the BN, which exhibits 22% tension set, has been chosen for further studies as it has optimum mechanical properties that satisfy the criteria for a TPE.

Because of the poor strength of BN, phenolic resin has been used as crosslinker for the rubber-phase to achieve an overall improvement in strength. Three different doses of the resin, 2.5, 5, and 10 phr, have been tried for the dynamic vulcanization technique. The blend shows gradual increase in tensile strength, with the increase in resin concentration, with a concomitant decrease in elongation at break values (Fig. 2(b)). From the figure, it is clear that BR5N exhibits typical TPE characteristics. It is further confirmed by considering the tension set and strength values of the blend before and after recycling (Table IV).

Therefore, for further investigation, BR5N has been chosen for its optimum properties.

Characterization of nanocomposites

The nanocomposites were made from EN/PP, BN, and BR5N by the addition of the modified clay either in the rubber or in the plastic phase. Their characteristic properties are given below.

XRD of nanocomposites

The X-ray diffractograms of the modified clays and their nanocomposites are shown in Figures 3(a)–3(c). The peak at 2θ equal to 7.4° is shifted to the lower value of 4.6° in the case of the modified clays compared with that of the unmodified one. It indicates that the clay stacks are pushed wider by the incorporation of the amines. However, in the case of nanocomposites ENOC4/PP and EN/PPOC4 there is no peak in the range of $3\text{--}10^\circ$ (Fig. 3(b)). It may indicate the exfoliation of the clay layers within the nanocomposites. In the case of EN/PP and ENOC4/PP there are two broad peaks in $13\text{--}22^\circ$ region (Fig. 3b). It may be due to the monoclinic α crystal phase present in PP.³⁴ In EN/PPOC4, where clay has been added to the PP phase, the peak height has been lowered and also the peaks are broadened. It may be due to the disordering of the crystal structure of PP because of the advent of the clay.

The four nanocomposites made of BIMS and nylon 6 do not show any peak in the region of $3\text{--}10^\circ$ (Fig. 3(c)). It may also indicate possible exfoliation of the nanoclay in the nanocomposites. In the X-ray diffraction pattern of pure nylon 6, there are three peaks at 2θ values of 23.6° , 25.4° and 27.8° .³⁵ These peaks are due to different crystal phases namely α_1 , γ , and α_2 in nylon 6, which differ as far as the stacking of the molecules is concerned. But, in the blend BN, there is a shift of the peaks toward lower Bragg's angle (15° , 21.6° , and 22.6°). This figure also suggests reduced crystallinity of the nylon 6 phase due to the presence of the rubber. With the addition of the clay in nylon 6

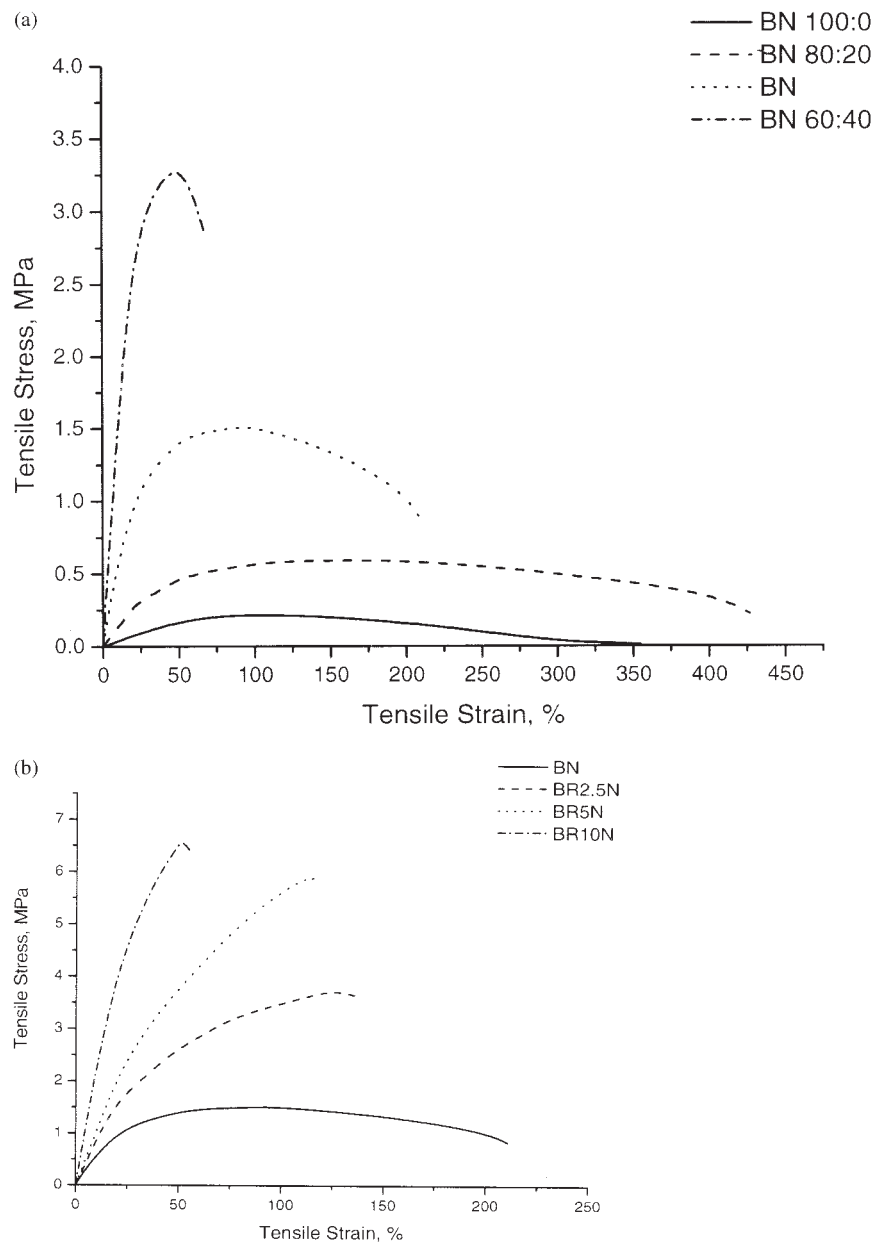


Figure 2 (a) Stress–strain curve of different BIMS/nylon 6 blends; (b) Stress–strain curve of different BIMS/nylon 6 blends, with different loadings of phenolic resin.

portion, there are only two peaks in the spectra (Fig. 3(c)) [absence of one peak from the doubly splitted peak of BN], indicating absence of one crystalline phase in nylon 6. The peaks further shift toward smaller Bragg's angle (14° and 21°) for BNHD4, BHD4N, BR5NHD4, and BR5HD4N. This may be due to the intercalation of polymer chains into the clay layers.

Transmission electron microscopy (TEM)

TEM photographs of the TPEs–EN/PP and BN are shown in Figures 4(a)–4(g). It is known that the ideal

morphology of the TPE from rubber–plastic blends comprises of finely divided rubber particles dispersed in minimum volume of plastic, as the plastic component forms the main matrix.³⁶ The TEM picture of the EN/PP blend reveals the two components of the blend (Fig. 4(a)) in layers. Such a morphology has been earlier observed for NR/PP blends.²⁸ The dark strips represent the rubber-phase.

In the BN, BIMS is dispersed (black domain) in the nylon 6 matrix (Fig. 4(b)), but the particle size is larger. When it is dynamically vulcanized, it shows smaller particle size of the dispersed rubber phase, which is in accord with the observations on some

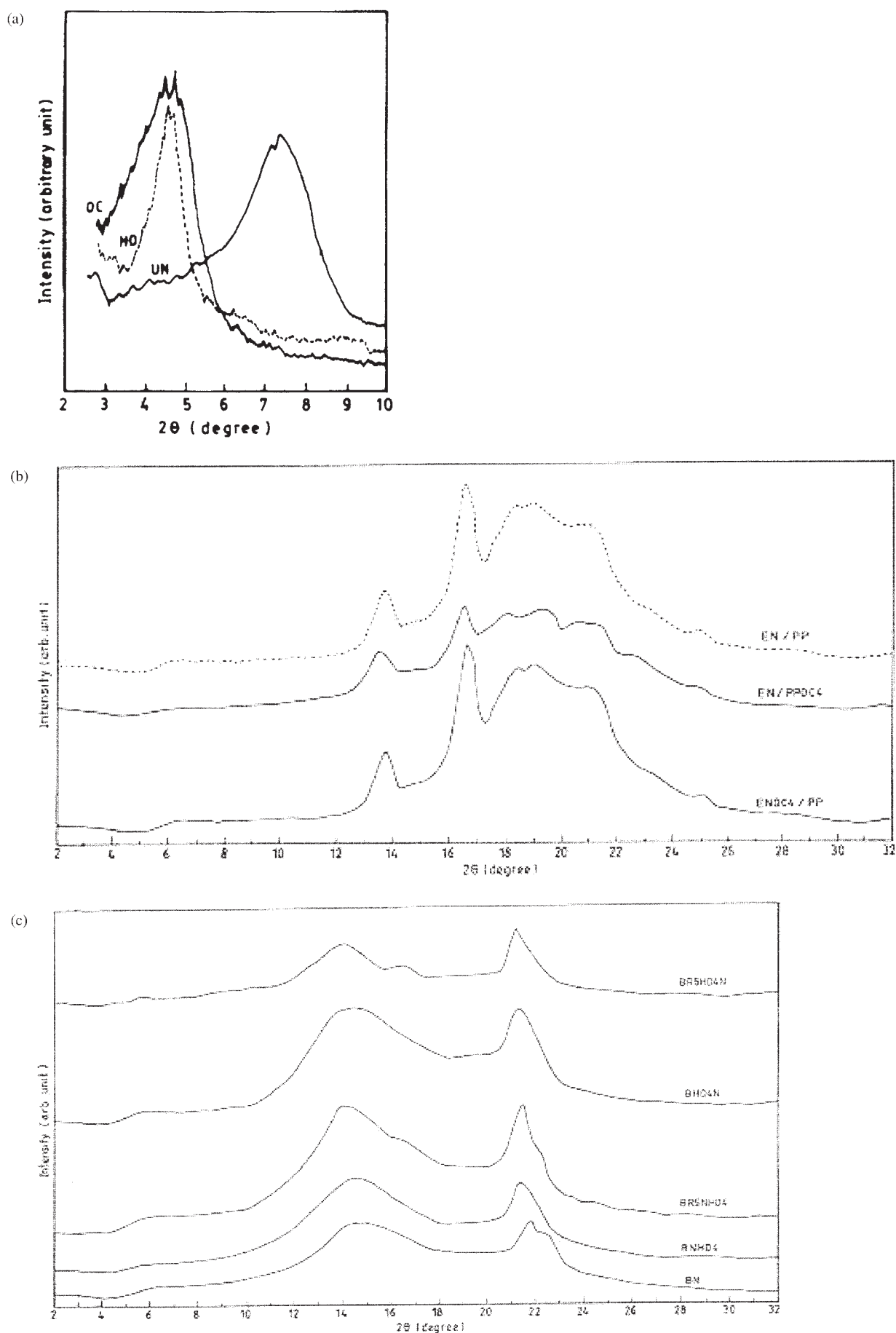


Figure 3 (a) XRD of OC, UN, and HD; (b) XRD of EN-PP blends; (c) XRD of BIMS-nylon 6 blends.

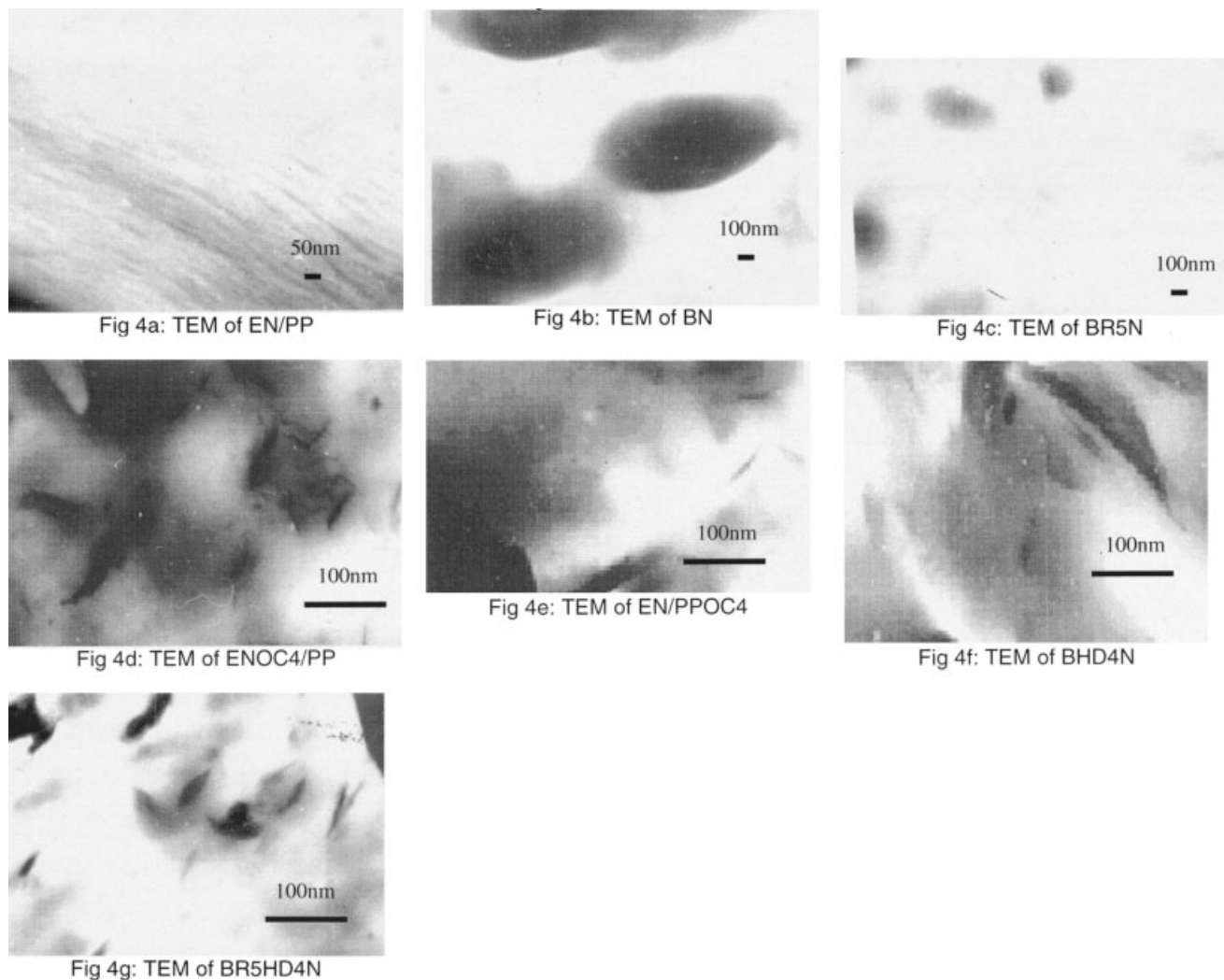


Figure 4 (a) TEM of EN/PP; (b) TEM of BN; (c) TEM of BR5N; (d) TEM of ENOC4/PP; (e) TEM of EN/PPOC4; (f) TEM of BHD4N; (g) TEM of BR5HD4N.

similar rubber–plastic dynamically vulcanized blends³⁶(Fig. 4(c)).

It can be clearly seen that in ENOC4/PP, the clay particles are principally distributed in the rubber-phase (black domain) (Fig. 4(d)). The average width of the particles is 26 nm. The clay particles can be seen predominantly in the plastic-matrix of EN/PPOC4 (average particle width 20 nm) (Fig. 4(e)). The photographs reveal a combination of both intercalation and partial exfoliation, though there is no peak in 3–10° range of the corresponding XRD. It may arise due to the orientation of the clay layers in different directions. The distance between the clay stacks is also larger as observed from the TEM micrographs. However, the inability of the XRD for studying the morphology of nanocomposites and the appearance and disappearance of clay peak in the XRD pattern with changing orientation of the samples with respect to the X-ray beam has been described in the literature.^{37–38}

Some representative samples of BHD4N and BR5HD4N have been shown in Figures 4(f) and 4(g), respectively. Here also we can see that the clay is present in the rubber phase.

Physicomechanical properties of different nanocomposites

Physicomechanical properties of Engage®–PP TPE–TPN

The mechanical properties of nanocomposites based on 70:30 blend are reported in Table III and the corresponding tensile stress–strain curves are shown in Figure 5.

The values of modulus at 100% elongation for EN/PP, ENOC4/PP and EN/PPOC4 are 4.1, 5.3, and 5.1 MPa, respectively. It means there is an increment of 29 and 24% for ENOC4/PP and EN/PPOC4, respec-

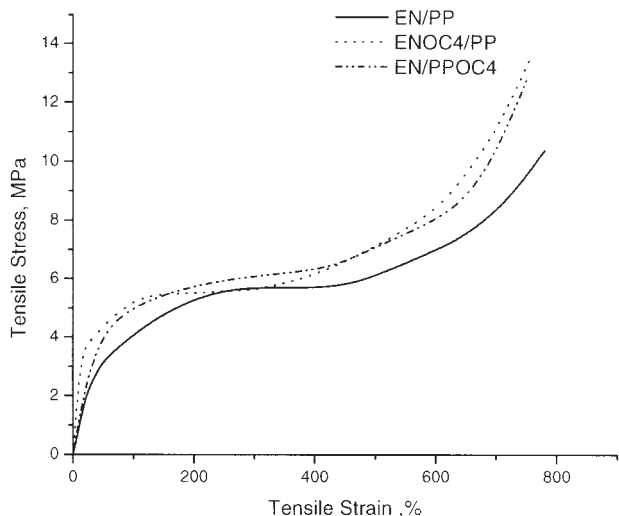


Figure 5 Stress–strain curve of different EN/PP blends and nanocomposites.

tively. This reflects the better polymer–filler interaction in the case of ENOC4/PP than EN/PPOC4.

The same observation is made with tensile strength, as ENOC4/PP shows higher improvement (30%) compared with EN/PPOC4 (23%). The elongation at break values for the blends are 755 and 750% respectively. The results indicate that ENOC4/PP forms a mechanically reinforced, tougher TPN than that of EN/PPOC4.

The lower strength of EN/PPOC4 may be due to the fact that the clay disturbs the crystallinity (83% in EN/PP decreases to 65% in EN/PPOC4) of the plastic phase (supported by XRD).

Physicomechanical properties of BIMS–nylon 6 TPE–TPN

The tensile properties are reported in Table IV and the representative tensile stress–strain curves are shown in Figure 6.

A radical change of 294% in tensile strength and 80% increment in modulus at 100% elongation can be seen in BNHD4 when the results are compared with BN; however, elongation at break decreases to 120% from 200% in BN and tension set is 12%. Therefore, it can be said that the amine-modified clay can interact with the polar substrate after exfoliation/intercalation to a higher extent (supported by XRD). After recycling, tensile strength decreases marginally by 12%. But in the case of BR5NHD4, there is no remarkable improvement in the tensile properties compared with that of BR5N. This may be due to the fact that the resin in BR5N may interfere with the clay exfoliation during dynamic vulcanization. After recycling, the physico-mechanical properties remain almost unchanged.

BHD4N shows a tensile strength value of 4.3 MPa and modulus value of 4.0 MPa (Table IV). It means that there is an increment of 412% in the tensile strength and 167% increment in modulus compared with that of BN. It even shows 30% higher tensile strength than BNHD4. Thus, the effect of clay is more pronounced when it is added to the BIMS part. The lower strength in BNHD4 may be due to the fact that the addition of clay in nylon 6 disturbs the crystallinity (72% in BN decreases to 58% BNHD4) of the plastic, similar to the case of PP, mentioned earlier. After recycling, only 7% decrement in tensile strength can be observed. But the elongation at break increases after recycling from 127% in BHD4N to 150% in BHD4N (re).

The toughness increases by 42 and 76% in the case of BHD4N and BNHD4, respectively.

When the sample is dynamically vulcanized, it shows the same thing as in the case of BR5NHD4. Again there is no remarkable change in tensile properties compared to that of BR5N and also after recycling, the properties remain almost unchanged. Hence, the nanoclay does not have much influence on the dynamic vulcanized BIMS/nylon blends, although the nanoclay improves the properties of the individual phase.

Dynamic mechanical properties of Engage®–PP blends

The storage modulus and $\tan \delta$ versus temperature curves of different blends are shown in Figures 7(a)–7(b). The glass transition temperatures and the $\tan \delta$ and storage moduli at 25°C and at 70°C (chosen arbitrarily) of different nanocomposites are listed in Table V. In the rubbery region, both the nanocomposites show higher storage modulus than that of virgin

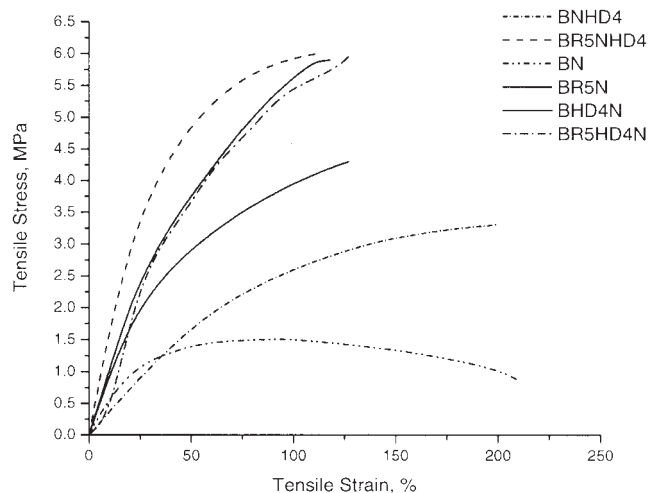


Figure 6 Stress–strain curve of different BIMS/nylon 6 based nanocomposites.

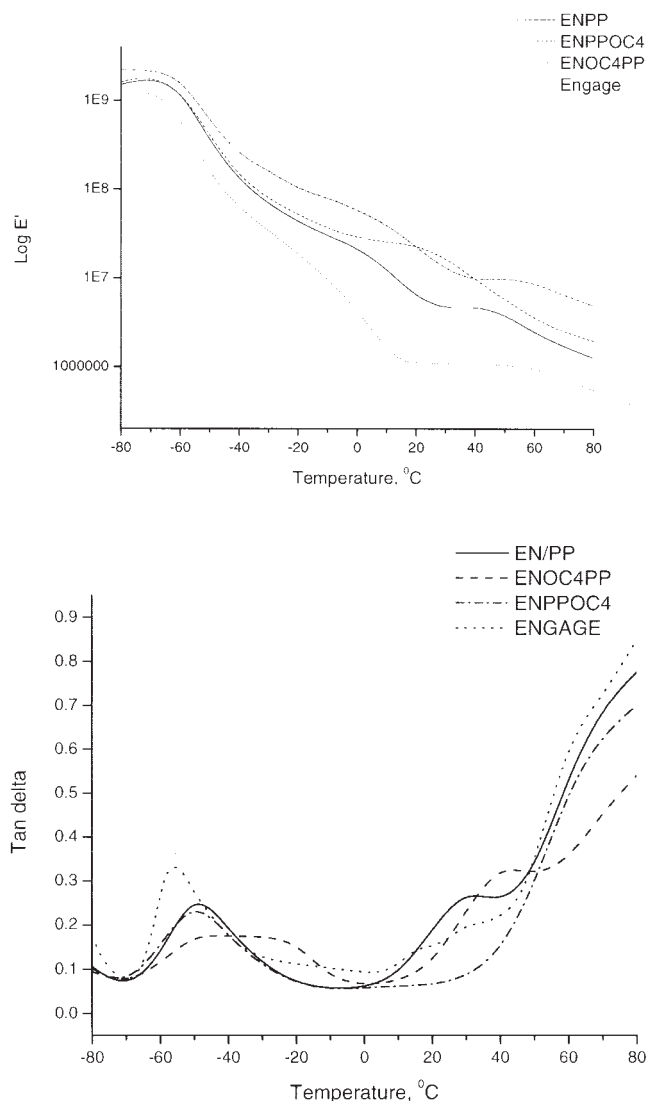


Figure 7 (a) Plot of storage modulus versus temperature (EN-PP BLENDS). (b) Plot of $\tan \delta$ versus temperature (EN-PP BLENDS).

blend. The reinforcing effect of clay is the principal reason behind this. ENOC4/PP shows higher storage modulus compared with EN/PPOC4, which is in line with the tensile properties. The modulus at 100% elongation is also higher in the case of ENOC4/PP than that of EN/PPOC4, discussed earlier.

In the EN/PP blend, the $\tan \delta$ peak for Engage[®] has been shifted from -55°C to -51°C . It actually implies technological compatibility between the two phases in the blend. In ENOC4/PP, the peak of Engage[®] is lower in height and also the peak is broadened. This is due to the better interaction between the filler, nanoclay, and the polymer. The nanoclay anchors at different positions in the Engage[®] matrix, thus restricting the movement of the rubber matrix and giving broad molecular weight distribution between the points of interaction, which is reflected in the broadening of \tan

δ peak. The second peak at 30°C in EN/PP due to the crystalline peak of PP phase is not seen in EN/PPOC4, where the clay has been added to the PP portion. As the clay is mostly exfoliated (supported by XRD), there is a better polymer-filler interaction, which may cause the lowering of the peak in the nanocomposite.

Dynamic mechanical properties of BIMS-nylon 6 blends

The storage modulus and $\tan \delta$ versus temperature curves of different blends are shown in Figures 8(a)–8(b). Similarly, the T_g , $\tan \delta$, and the storage moduli at 25°C and at 70°C of the nanocomposites are reported in Table VI. The storage modulus curve of BN lies in between those of BIMS and nylon 6 as anticipated, showing interaction between the components. The moduli of the TPN are higher compared with that of BN in the rubbery region. This is again due to effective polymer-filler interaction and is in line with that of the tensile modulus values, discussed earlier.

In the BN blend, the $\tan \delta$ peak for BIMS has been shifted from -43°C of virgin to -37°C . Although there is not much shifting in the broad peak of nylon 6 around 22°C , the peak height decreases. In BHD4N, the peak of BIMS has lowered and broadened. This is again due to the better polymer-filler interaction. In the case of BNHD4, the peak of BIMS almost remains at the same position at that of BN. The peak for nylon 6 in both the nanocomposite, BHD4N and BNHD4, has lowered. In the case of BNHD4, it is obvious as there is better polymer-filler interaction due to partial exfoliation of the nanoclay. But in the case of BHD4N, it may be due to transfer of clay in the nylon portion also.

CONCLUSIONS

From the present investigation, the following conclusions could be made:

1. The TPE from EN-PP and BIMS-nylon 6 blends have been successfully prepared. The optimum

TABLE V
Dynamic Mechanical Properties of the Engage[®]-Polypropylene Blends

Sample name	T_g ($^{\circ}\text{C}$)	$\tan \delta$ at T_g	$\log E'$ at 25°C (MPa)	$\log E'$ at 70°C (MPa)
EN	-55	0.33	6.05	5.87
EN/PP	-51	0.24	6.70	6.23
ENOC4/PP	—	0.18	7.23	6.81
EN/PPOC4	-51	0.22	7.31	6.40

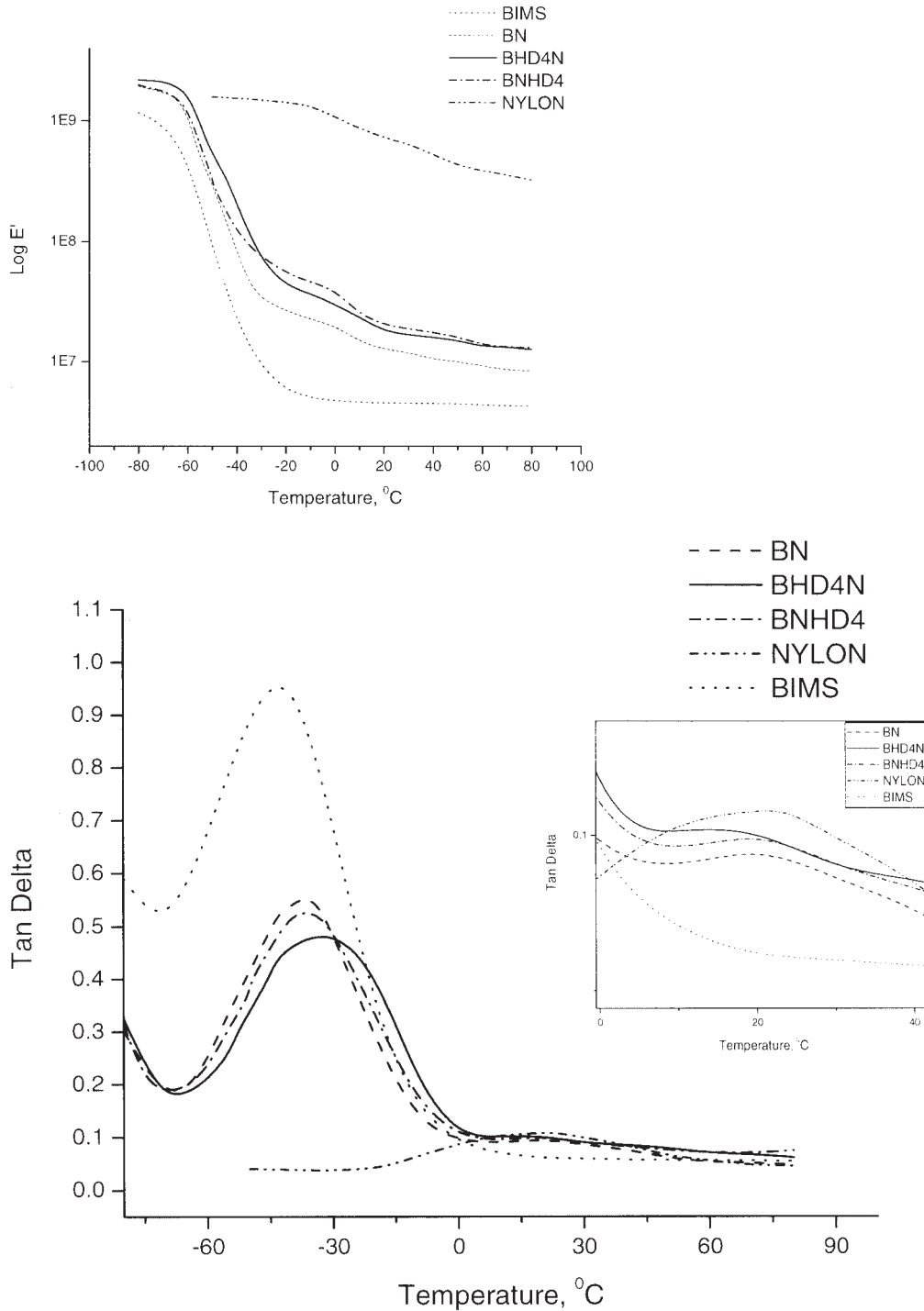


Figure 8 (a) Plot of storage modulus versus temperature (BIMS–nylon 6 BLENDS). (b) Plot of $\tan \delta$ versus temperature (BIMS–nylon 6 BLENDS).

blend composition is 70:30 rubber:plastic in both the cases.

2. The pristine clay, NaMMT, has been modified to organoclay by the cation exchange reaction with octadecyl amine, a primary amine and hexadecyltrimethylammonium bromide, a tertiary

amine, and then dispersed within the TPE to prepare the TPN.

3. The nanocomposites have been characterized by XRD and TEM. The X-ray diffractograms do not show any peak in the 2θ region of $3\text{--}10^\circ$ in the nanocomposites, which was present earlier in

TABLE VI
Dynamic Mechanical Properties of the
BIMS-Nylon 6 Blends

Sample name	T_g (°C)	$\tan \delta$ at T_g	$\log E^t$ at 25°C (MPa)	$\log E^t$ at 70°C (MPa)
BIMS	-43	0.95	6.66	6.60
BN	-37	0.55	7.09	6.94
BHD4N	-31	0.52	7.24	7.11
BNHD4	-36	0.48	7.26	7.11
NYLON	22	0.11	8.82	8.55

both the unmodified and the modified clays. It indicates possible exfoliation of the clay layers within the nanocomposites. The TEM study display a combination of intercalation and exfoliation of the clays, as the width of the discrete clay particles is in the range 20–30 nm.

4. The nanocomposites from EN/PP and BIMS/nylon 6 show significant improvement in mechanical properties only when the clay has been added to the rubber phase prior to the blending with the plastic. In the case of BN type TPE, the dynamically vulcanized samples do not exhibit any improvement with the organoclay.

5. The improvement in dynamic mechanical properties has been reflected through the increment in storage modulus values and also with the lowering of loss tangent peak heights of the mechanically reinforced samples.

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