Effect of Carbon Black on Properties of Rubber Nanocomposites

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ABSTRACT: Polymer based nanocomposites were prepared using brominated poly(isobutylene-*co*-paramethylstyrene) (BIMS) rubber and octadecyl amine modified montmorillonite nanoclay. The effect of nature and loading of carbon black on these nanocomposites and the control BIMS was investigated thoroughly using X-ray diffraction technique (XRD), Fourier transform infrared spectroscopy (FTIR), and mechanical properties. The addition of 4 parts of the modified nanoclay to 20 phr N550 carbon black filled samples increased the tensile strength by 53%. Out of the three different grades of carbon black (N330, N550, and N660), N550 showed the best effect of nanoclay. Optimum results were obtained with the 20 phr filler loading. For comparison, china clay and silica at the same loading were used. Fifty-six and 46% improvements in tensile strength were achieved with 4 parts of nanoclay added to the silica and the china clay filled samples, respectively. N330 carbon black (20 parts) filled styrene butadiene rubber (SBR) based nanocomposite registered 20% higher tensile strength with 4 parts of the modified nanoclay. In all the above carbon black filled nanocomposites, the modulus was improved in the range of 30 to 125%. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 443–451, 2005

Key words: BIMS; SBR; nanocomposites; nanoclay; carbon black

INTRODUCTION

Nanocomposites are an interesting field of research in recent years. There are several types of nanocomposites based on both plastics and rubbers reported in the literature. The first polymer nanocomposite was developed by Toyota Central Research Lab in Japan teamed up with Ube Industries Ltd., a Japanese resin supplier, and consisted of nylon 6 interspersed with layers of montmorillonite, a layered silicate clay.[1] Afterwards, polymers like nylon,[1–11] polypropylene,[12–16] polyethylene,[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. have been used to prepare nanocomposites.

However, in actual applications there are several ingredients added to impart various properties to a composite. For example, in the rubber industry, rubbers are mixed with sometimes 10 to 15 different ingredients to improve processing and properties like tear strength, abrasion resistance, aging behavior, etc. Though a few reports are available on rubber based nanocomposites, there is no report on the influence of these ingredients on the nanocomposite properties.

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Carbon black is one such ingredient, which is used extensively to improve tensile properties, tear and abrasion resistance, hardness, etc. of a rubber vulcanizate. Earlier workers have reported the properties of carbon black filled rubber vulcanizates.[23–25] It has been amply demonstrated that the structure, particle size, and functional groups on the surface influence the above-mentioned properties.

In our earlier work, the effect of nanoclays on mechanical and dynamic mechanical properties and morphology of pristine rubber has been reported.[22,26] In the present work, we report the influence of the nature of filler (carbon black of different particle sizes, silica, and clay) and degree of filler loading on the properties of nanocomposites based on brominated poly(isobutylene-*co*-paramethylstyrene) (BIMS). Styrene butadiene rubber (SBR) has also been used to investigate similar effects.

EXPERIMENTAL

Materials used

BIMS (grade-BIMS-7745; paramethyl content, 7.7 wt %; bromine content, 1.2 wt %; ML_{1+8} @125°C, 45; M_n 2×10^5 g/mol) was supplied by Exxon Mobil Chemical Company, Baytown, TX. Styrene-butadiene rubber (SBR) (Synaprene-1502) having Mooney Viscosity, $M_v = 52$, and styrene content of 23.5%, was supplied by Synthetics and Chemicals Ltd., Bareilley, India. Sodium montmorillonite was generously supplied by Southern Clay Products, Gonzales, USA. Its cation

TABLE I
Unfilled Nanocomposites and Their Designation

Composition	Designation
BIMS + 10 phr phenolic resin	BIMS
BIMS + 10 phr phenolic resin + 4 phr OC	BIMSOC4
SBR + 1 phr DCP	SBR
SBR + 1 phr DCP + 4 phr OC	SBROC4

exchange capacity was 90 meq/100g. Octadecyl amine, $C_{18}H_{37}NH_2$, was supplied by Sigma Chemical Co., 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 (softening point 70–80°C), which was used as the curing agent, was obtained from indigenous sources. Dicumyl peroxide produced by Aldrich Chemical Co. Inc., Milwaukee, WI, was used as the crosslinking agent for SBR. Different grades of carbon black [N330 (mean size = 24–28 nm, surface area = 75–95 m^2/g), N550 (mean size = 30–50 nm, surface area = 40–70 m^2/g), and N660 (mean size = 50 nm, surface area = 45 m^2/g)] were supplied by Phillips Carbon Black, Durgapur, India. Silica and china clay were procured from Bayer India Ltd. Mumbai, India, and Bata India Ltd., Batanagar, India, respectively.

Preparation of modified clay

The clay was modified with octadecyl amine (a primary amine). 5 g of the clay was mixed with 400 c.c. 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 a few minutes with the 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 a vacuum oven at room temperature (30°C). The abbreviation used for the modified clay is OC.

Preparation of rubber–clay nanocomposite

The rubber was first dissolved in toluene, and 10 phr of phenolic resin for BIMS and 1phr DCP for SBR was added to it. The clay was dispersed in ethyl alcohol. Then, the rubber solution was added to the clay dispersion at the required proportion and thoroughly stirred to make a homogeneous mixture, which was then kept in a vacuum oven at 30°C to drive off the solvents. Table I reports the various compositions prepared for this investigation.

Preparation of carbon black filled nanocomposite

The rubber (BIMS) was first dissolved in toluene, and then phenolic resin (also dispersed in toluene) was added to it. Carbon black (/silica/china clay) was dispersed in the rubber solution and stirred to make a homogeneous solution. The nanoclay was dispersed in ethyl alcohol. It was added to the rubber solution and thoroughly stirred to make a homogeneous mixture, which was then kept in air to drive off the solvents. The samples were compression molded at 150°C for 22 min (optimum cure time determined from a Rheometer) into 1 mm thick sheets in a hydraulic press.

The SBR was dissolved in toluene and the clay was dispersed in ethyl alcohol. The nanoclay dispersion was added to the rubber solution and stirred well. After drying off the solvent at room temperature, the carbon black and curative (DCP) was mixed in a two-roll mill (Schwanbenthan, Germany). Then the composite was cured at 160°C for 15 min (optimum cure time) in a compression mold to prepare a 1 mm thick sheet. Table II reports various filled compositions prepared for this investigation and their designation.

X-ray diffraction studies (XRD)

For characterization of the clays and the rubber composites, X-ray diffraction studies were done using a Rigaku CN2005 X-Ray Diffractometer "Miniflex" model in the range of 3° to 10° (= 2θ) and Cu- target (λ = 0.154 nm). Then, d-spacing of the clay particles was calculated using Bragg's law. The samples were scanned at 1000 cps at a scanning speed of 2°/min and placed vertically in front of the X-ray source and perpendicular to the goniometer, where the goniometer was fixed but the sample was rotating.

Mechanical properties

Tensile specimens were punched out from the molded sheets using ASTM Die - C. The tests were carried out as per the ASTM D 412–98 method in a Universal Testing Machine (Zwick 1445) at a cross-head speed of 500 mm/min at 25°C. The average of three tests is reported here.

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 a tensile mode at a constant frequency of 1 Hz, a strain of 0.01% over a temperature range from −80 to 80°C at a heating rate of 2°C/min. The data were analyzed by RSI Orchestrator application software on an ACER computer attached to the machine. Storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were measured as a function of temperature for all the samples under identical conditions. The temperature corresponding

TABLE II
Filled Nanocomposites and Their Designation

Composition	Designation
BIMS + 10 phr phenolic resin + 10 phr N550	BIMSFEF10
BIMS + 10 phr phenolic resin + 10 phr N550 + 4 phr OC	BIMSFEF10 OC4
BIMS + 10 phr phenolic resin + 20 phr N550	BIMSFEF20
BIMS + 10 phr phenolic resin + 20 phr N550 + 4 phr OC	BIMSFEF20 OC4
BIMS + 10 phr phenolic resin + 30 phr N550	BIMSFEF30
BIMS + 10 phr phenolic resin + 30 phr N550 + 4 phr OC	BIMSFEF30 OC4
BIMS + 10 phr phenolic resin + 20 phr N660	BIMSGPF20
BIMS + 10 phr phenolic resin + 20 phr N660 + 4 phr OC	BIMSGPF20 OC4
BIMS + 10 phr phenolic resin + 20 phr N330	BIMSHAF20
BIMS + 10 phr phenolic resin + 20 phr N330 + 4 phr OC	BIMSHAF20 OC4
BIMS + 10 phr phenolic resin + 20 phr china clay	BIMSCC20
BIMS + 10 phr phenolic resin + 20 phr china clay + 4 phr OC	BIMSCC20 OC4
BIMS + 10 phr phenolic resin + 20 phr silica	BIMSSi20
BIMS + 10 phr phenolic resin + 20 phr silica + 4 phr OC	BIMSSi20 OC4
SBR + 1 phr DCP + 20 phr N330	SBRHAF20
SBR + 1 phr DCP + 20 phr N330 + 4 phr OC	SBRHAF20 OC4

to the peak in tan δ versus temperature plot was taken as the glass-rubber transition temperature (T_g).

RESULTS AND DISCUSSION

Effect of nanoclay on mechanical properties

To understand the effect of nanoclay on the mechanical properties of unfilled rubber, BIMS and SBR have been chosen. The tensile properties are reported in Table III.

The tensile strength value of BIMS and BIMSOC4 are 1.40 and 2.80 MPa, respectively. The strength increases by 100% in BIMSOC4. The values of elongation at break of BIMS and BIMSOC4 are 84 and 154%, showing 83% increase in elongation at break with the incorporation of 4 phr OC to the gum rubber. The modulus (at 50% elongation) registers an increase from 1.01 MPa to 1.60 MPa (58%) under the same condition.

Stress-strain properties of the SBR gum and the modified nanoclay filled samples have also been determined. Addition of 4 parts of the modified clay to the control SBR improves tensile strength from 1.20 MPa to 2.50 MPa (108% increase) and elongation at break from 94 to 180% (91% increase). The modulus at 50% increases from 0.66 to 0.78 MPa with the addition of OC.

The results can be explained by XRD (Fig. 1).

The traces in Figure 1 show complete exfoliation of the modified nanoclays in both the rubber matrices in the sense that the peaks observed for the pristine modified clays disappear when these are mixed with the rubber. The long chain amine modifiers facilitate the polymer chains to intercalate. After modification, the organophilic OC interacts well with the nonpolar part of the rubber. BIMS contains polyisobutylene, which is nonpolar. Also, the dispersion is improved as a result of exfoliation. Similarly, SBR being a nonpolar rubber, it has a very good interaction with the organophilic clay. It is known that the tensile properties are a function of rubber-filler interaction. This causes the improvements in the above-mentioned mechanical properties.

Effect of carbon black on nanocomposite

The effect of carbon black on nanocomposite properties was investigated using N550, which was mixed with the gum BIMS and OC filled BIMS at 20 phr loading. The stress-strain curves are shown in Figure 2, which indi-

TABLE III
Mechanical Properties of Different Unfilled Nanocomposites

Sample name	Modulus (MPa) at elongation		Tensile strength (MPa)	Elongation at break (%)
	50%	100%		
BIMS	1.01	—	1.40	84
BIMSOC4	1.60	2.33	2.80	154
SBR	0.66	—	1.20	94
SBROC4	0.78	1.29	2.50	180

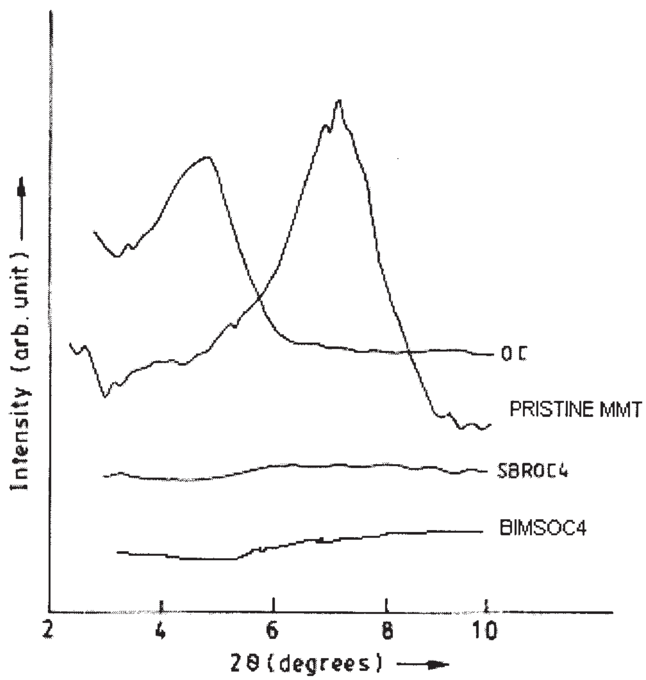

Figure 1 XRD of nanoclays and nanocomposites.

TABLE IV
Mechanical Properties of Filled Nanocomposites

Sample name	Modulus (MPa) at elongation 50%	Modulus (MPa) at elongation 100%	Tensile strength (MPa)	Elongation at break (%)
BIMSFEF10	1.30	2.00	2.20	132
BIMSFEF10 OC4	1.60	2.60	3.70	146
BIMSFEF20	1.70	2.90	3.40	129
BIMSFEF20OC4	1.90	3.90	5.30	150
BIMSFEF30	1.80	—	3.20	92
BIMSFEF30 OC4	2.00	3.80	3.90	111
BIMSFEF24	1.70	3.10	3.40	108
BIMSHAF20	1.70	3.00	3.40	116
BIMSHAF20 OC4	1.80	3.30	4.00	129
BIMSGPF20	1.00	2.30	2.80	131
BIMSGPF20 OC4	1.50	2.40	3.70	152
BIMSSi20	1.80	—	2.10	79
BIMSSi20 OC4	2.10	—	3.20	86
BIMSCC20	1.20	—	1.50	70
BIMSCC20 OC4	1.50	—	2.20	76
SBRHAF20	0.90	1.50	5.90	300
SBRHAF20 OC4	1.50	2.40	8.60	338

cates higher stress at a particular strain for the OC filled FEF nanocomposites (BIMSFEF20OC4 versus BIMSFEF20). The moduli at 50 and 100%, tensile strength, and elongation at break have been calculated from the curves. The results are reported in Table IV.

The N550 filled BIMS (BIMSFEF20) shows tensile strength of 3.40 MPa, elongation at break of 129%, and modulus at 50% elongation of 1.70 MPa. BIMSFEF20OC4 registers 5.30 MPa, 150%, and 1.90 MPa, respectively, for the same properties. These results depict that the carbon black filled nanocomposite has better tensile strength and modulus when these are compared either with the conventional carbon black filled vulcanizate or the OC filled nanocomposites. Hence, we can infer that even in the presence of carbon black, the influence of nanoclay is dominant and the tensile properties are improved further. BIMSFEF20OC4 displays 55 and 89% improvement in tensile strength and +16% and −2% change in elongation at break over the conventional carbon black filled and nanoclay filled samples, respectively. To check the additional loading of 4 parts in BIMSFEF20, a mix with 24 phr of N550 has been prepared and its properties have been compared. The tensile strength of the new mix is 3.40 MPa, which is the same as that of the BIMSFEF20, and elongation at break has a value of 108%, which is slightly lower than that of the BIMSFEF20. From this experiment, it is concluded that 4 phr of nanoclay can reinforce the matrix manifold, which cannot be achieved by further addition of 4 phr carbon black.

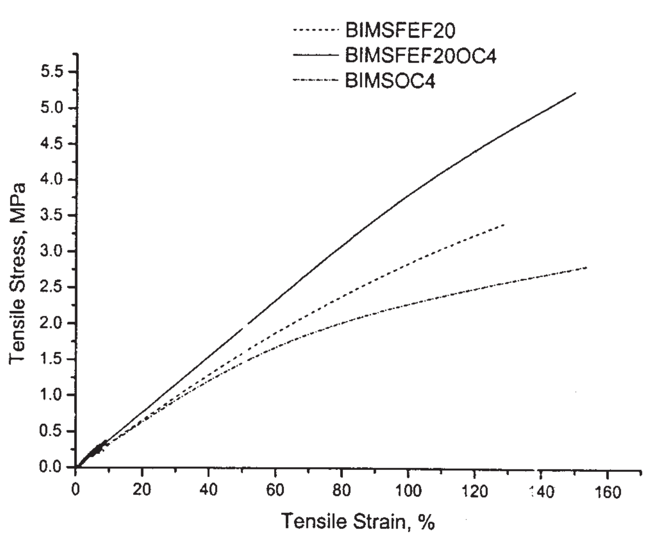

Figure 2 Stress-strain curve of BIMS, BIMSFEF20, and BIMSFEF20OC4.

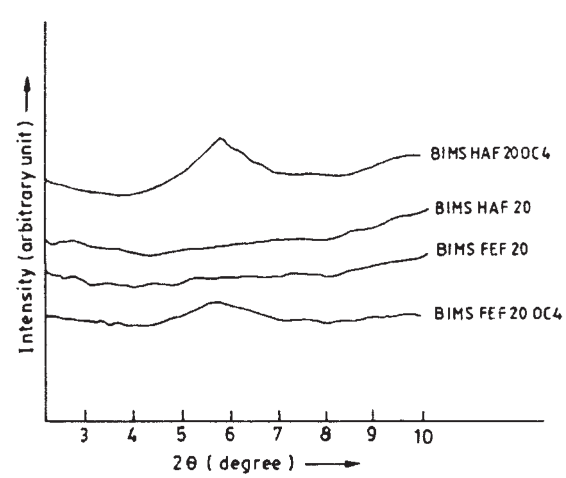

Figure 3 XRD of different carbon black filled composites.

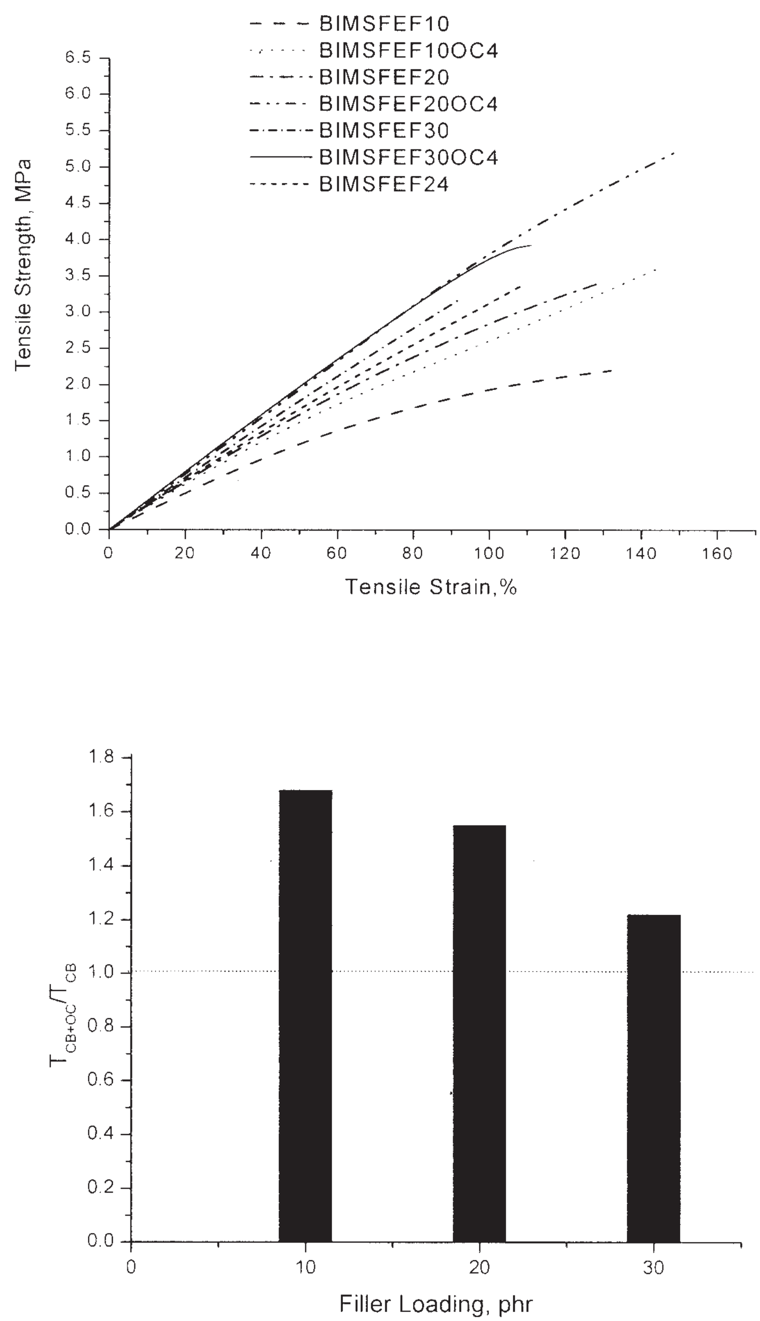

Figure 4 (a) Stress-strain curve of filled composites at different filler loadings; (b) Comparison between tensile strength of nanocomposites and that of conventional composites at different filler loadings of FEF (where T_{CB+OC} = tensile strength of N550 filled nanocomposites, T_{CB} = tensile strength of N550 filled composites).

Here again the results can be explained with the help of XRD (Fig. 3). The X-ray diffractograms of BIMSFEF20OC4 show a small hump, which is absent in BIMSFEF20, indicating presence of the nanoclay in the matrix of the former. In the presence of carbon black, the clay particles probably are partially exfoliated. The small hump is an indication of intercalation, which arises due to the restricted segmental mobility of the carbon black filled sample and its inhibition to enter into the gallery gap in the nanoclay. Also, some of the nanoclays may be trapped in the occluded structure of carbon black, thus reducing the chances of exfoliation. Thus, both the carbon black and the exfoliated clays contribute towards the higher tensile strength.

Effect of carbon black loading on nanocomposite

To understand the effect of carbon black loading on the mechanical properties of the nanocomposite, loading of N550 is varied from 10 phr to 30 phr. The stress-strain curves are shown in Figure 4a, which elucidate positive influence of the nanoclay. The results are given in Table IV. A bar graph indicating improvement in tensile strength in carbon black filled nanocomposite with respect to the conventional carbon black filled composites at different filler loadings is also shown in Figure 4b. The ratio of the tensile strength of the nanocomposite to that of the conventional composite is always higher than one. The effect of the nanoclay is, however, reduced at higher filler loading.

With increasing filler loading, the tensile strength increases up to 20 phr loading, beyond which the value decreases. On the other hand, the elongation at break decreases and the modulus increases with increasing filler loading, as expected. The incorporation of OC enhances the tensile strength by 68%, 56%, and 22%, and elongation at break by 10%, 16%, and 20% for the 10, 20, and 30 phr black loaded nanocomposites, respectively. Thus, it can be said that, although with the addition of OC there is some improvement over carbon black filled samples at every loading, the best improvement in tensile strength can be seen with 10 phr of carbon black loading. With increasing carbon black loading, the absolute strength initially increases to a certain extent because of reinforcement and then decreases due to dilution effect.

Effect of nature of fillers on nanocomposite properties

Three different grades of blacks (N330, N550, and N660) have been used. Besides these, china clay and silica fillers have been compared. The stress-strain graphs of different blacks, silica, and china clay filled composites are shown in Figures 5a and b. The values of the mechanical properties are reported in Table IV.

Tensile strength, elongation at break, and modulus at 50% elongation of N330 and N660 filled BIMS samples are 3.40 MPa, 116%, and 1.70 MPa, and 2.80 MPa, 131%, and 1.00 MPa, respectively. On addition of OC to the N550 filled sample, tensile strength of 5.30 MPa, elongation at break of 150%, and the 50% modulus value of 1.90 MPa are observed; N330 and N660 register the corresponding values of 4.00 MPa, 129%, and 1.80 MPa, and 3.70 MPa, 152%, and 1.50 MPa, respectively. Hence, there is 55%, 18%, and 32% increment in tensile strength in the case of N550, N330, and N660, respectively. N550 gives the highest value of tensile strength, followed by N330 and N660 in the black filled and the OC black filled BIMS. Higher strength was expected with N 330 carbon black. The anomalous result may be due to that fact that there may be a problem of dispersion in the case of N330 in solution mixing as the particle size is smaller than N550. From the XRD diffractogram (Fig. 3), it is observed that there is a small peak at 5.8° (2θ) in the case of N330, indicating the existence of some regular and ordered structure in the sample. However, in the case of N550,

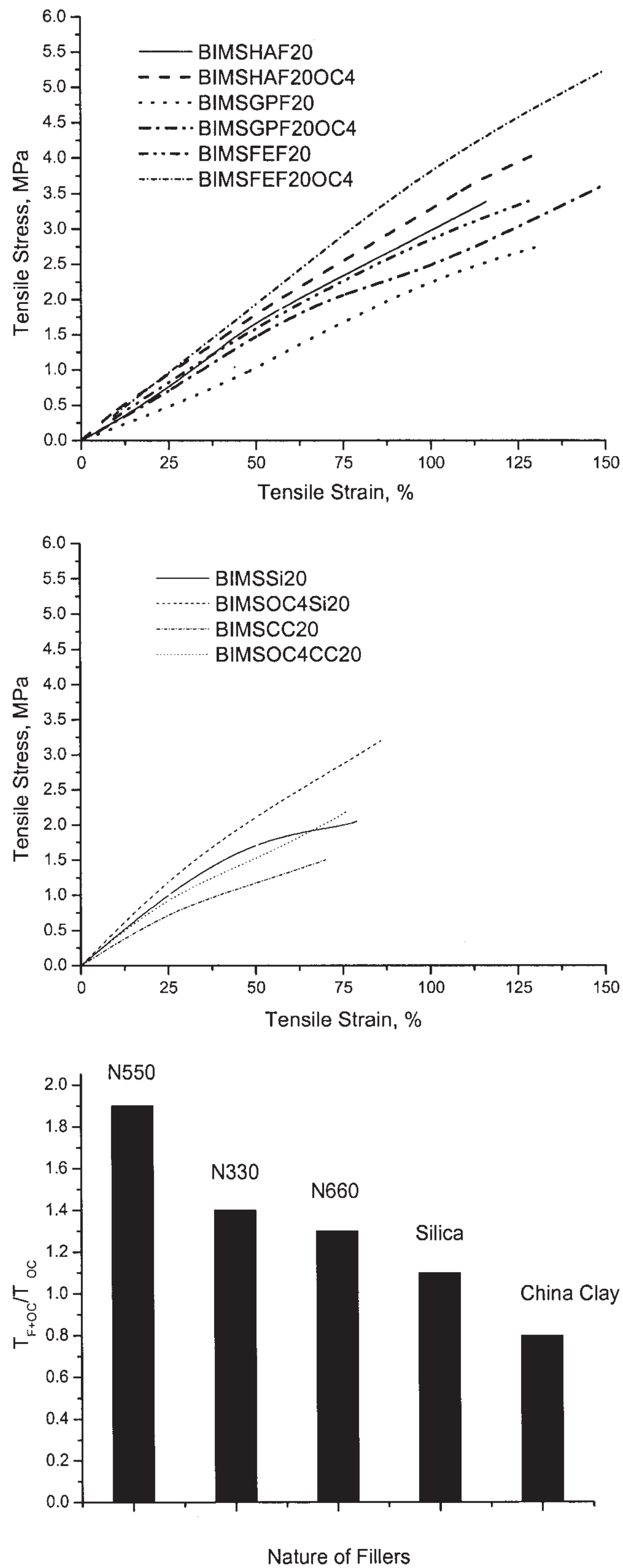

Figure 5 (a) Stress-strain curves of carbon black filled conventional composites and nanocomposites; (b) Stress-strain curves of silica and china clay filled conventional and nanocomposites; (c) Comparison between tensile strength of different nanocomposites containing different fillers (where T_{F+OC} = tensile strength of 20 phr filler + 4 phr OC filled composite, T_{OC} = tensile strength of 4 phr OC filled composite).

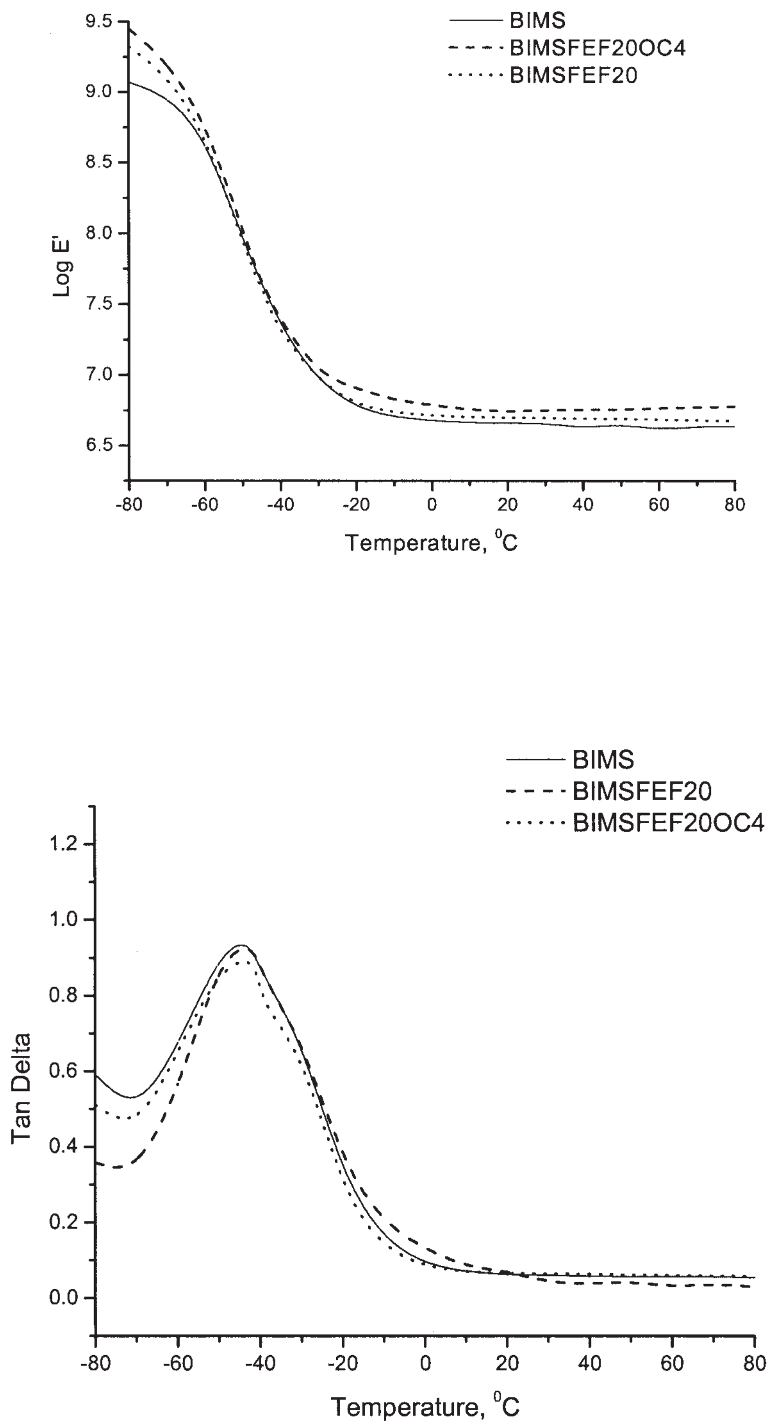

Figure 6 (a) Plot of log (storage modulus) versus temperature; (b) Plot of tan δ versus temperature.

there is a smaller hump only, indicating the clay is mostly exfoliated. The reason for appearance of the hump/peak has been explained earlier. Due to higher occlusion phenomenon for the small size of N330, more clays are entrapped and thus are unable to exfoliate/intercalate. This may be the reason behind the fact that N550 filled samples have better mechanical properties than those of N330—both with and without having OC.

With 20 phr of silica, the tensile strength is 2.10 MPa and elongation at break is 79%. With the addition of 4 phr OC, the corresponding values are 3.20 MPa and 86%. This means that there is an increment of 52% in tensile strength and 8% in elongation at break. With 20 phr of china clay, the tensile strength is 1.50 MPa and elongation at break is 70%. With the addition of 4 phr of OC, an increased value of 2.20 MPa and 76% have been observed. This implies that there are 47 and 9% increments in tensile strength and in elongation at break, respectively. A comparison of tensile strength of various filled samples is shown in Figure 5c.

Dynamic mechanical thermal analysis

The values of storage modulus and tan δ against temperatures are shown in Figures 6a and b. The glass transition temperatures and the storage modulii at 25°C and at 70°C of different composites are listed in Table V.

The T_g has been slightly shifted towards higher temperature in the case of BIMSFEF20 and BIMSFEF20OC4. There is a lowering in the tan δ peak height at T_g in the case of both BIMSFEF20 and BIMSFEFOC4, indicating reinforcement. These two phenomena jointly reflect that there is a better polymer-filler interaction in both the cases.

The storage modulus value is also higher in the rubbery region in the case of BIMSFEF20 as well as in BIMSFEF20OC4 over the control. In the case of carbon black filled nanocomposite, it shows higher value than that of conventional filled composite. Hence, from the dynamic mechanical properties, it can be concluded that the effect of nanoclay is still predominant in the presence of conventional filler.

Effect in another rubber

To establish the influence of carbon black, SBR has been taken. The SBROC4 is loaded with 20phr of black (N330), as this loading gave the optimum properties with BIMS. The N330 has been chosen as this is known to give the best properties with SBR matrix. Due to a mixing problem with the black in solution, the filler mixing has been done in an open two-roll mill. The mechanical properties are reported in Table IV and the stress-strain curve in Figure 7. The tensile strength for N330-filled SBROC4 is 7.80 MPa, elongation at break is 338%, and modulus at 50% elongation is 1.30 MPa, while the same for N330-filled SBR are 5.80 MPa, 300%, and 0.90 MPa, respectively. The percent increase is 34% for tensile strength, 13% for elongation at break, and 44% for modulus at 50% elongation. Thus, comparing these results it is concluded that the effect of carbon black on nanocomposites is visible in the case of both the rubbers investigated here.

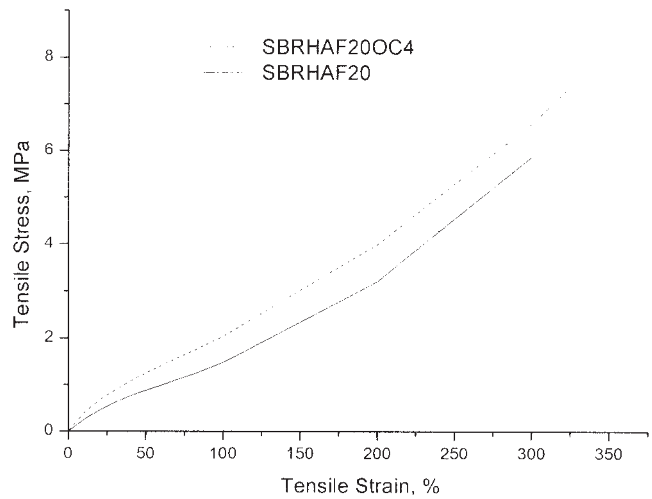

Figure 7 Stress-strain curve of SBR composites.

CONCLUSIONS

Nanocomposites, along with conventional filled composites based on BIMS and SBR, have been prepared. Their mechanical properties have been extensively studied. XRD and dynamic mechanical properties of some representative samples have been measured.

1. 4 phr of octadecyl amine modified nanoclay improves the tensile strength and modulus of BIMS and SBR vulcanizates significantly.
2. Optimum mechanical properties can be obtained at 20 phr loading of the fillers.
3. The best effect of the modified clay on mechanical properties has been observed with N550.
4. Dynamic mechanical properties of 20 phr N550 loaded nanocomposite show clear reinforcement.
5. The results can be explained by exfoliation, intercalation, dispersion, and occlusion.

TABLE V
Dynamic Mechanical Properties

Sample name	T_g, °C	Tan δ at T_g	Log E′ at 25°C (in MPa)	Log E′ at 70°C (in MPa)
BIMS	−43.0	0.95	6.66	6.60
BIMSFEF20OC4	−41.0	0.88	6.74	6.77
BIMSFEF20	−42.0	0.91	6.70	6.67

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