Interpenetrating Polymer Networks based on Nitrile Rubber and Metal Methacrylates

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ABSTRACT: Interpenetrating polymer networks (IPNs) based on nitrile rubber (NBR) as first component and zinc dimethacrylate (ZnDMA), aluminum trimethacrylate (AlTMA), or zirconium tetramethacrylates (ZrTeMA) as second component were synthesized. Sequential IPNs (SeqIPN) were formed by two routes such as compression molding (CM) and swelling/curing (SC). The IPNs were found to have superior properties compared to metal oxide/hydroxide-filled NBR. Tensile strength has increased to a large extent while maintaining appreciable elongation. Total crosslink density (covalent and ionic) was found to increase in the order NBR/metal oxide or hydroxide < SeqIPN(CM route) < SeqIPN (SC route).

IPNs are found to retain high storage modulus even in the rubbery region. It is observed that change of technique for IPN formation has drastically changed the modulus of the present system. Decrease in tan δ value and inward shifting of peaks were observed because of IPN formation. Morphology of SeqIPN by SC process was found to be more uniform compared to others. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2542–2548, 2006

Key words: elastomer; interpenetrating polymer network; metal methacrylate; storage modulus

INTRODUCTION

Reinforcing of an elastomer is a necessity for its practical utilization. Carbon black and silica are the two mostly used reinforcing fillers, which enhance the mechanical properties of elastomers. There is a constant search for new methods to reinforce rubber so that special properties are imparted to rubber products. A relatively new material, metal methacrylates, when added to styrene butadiene rubber, enhanced the mechanical properties to a large extent.[1]

Metal salts of unsaturated carboxylic acids were used in conjunction with peroxide for curing of the elastomer. They increase both crosslinking efficiency and crosslink density.[2,3] Metal salts of methacrylic acids used for curing of natural rubber and nitrile rubber (NBR) exhibited high modulus at low strain.[4] When zinc dimethacrylate (ZnDMA) was loaded to hydrogenated NBR and cured with peroxide, the product was found to possess high tensile strength.[5] Chemical analysis of the cured product showed that polymerization of zinc methacrylates took place during the curing process. Obviously, such vulcanizates contain both covalent and ionic crosslinks.[6] Fine particles of diameter 20–30 nm have been observed in the matrix.[7] It was also reported that, instead of adding methacrylates to rubber, they can be produced inside the matrix to impart superior properties.[8] Oxides or hydroxides were incorporated as fillers and methacrylic/acrylic acid was added to form metal methacrylates/acrylates. Few articles have appeared in the literature and have shown the specific effect of various metal oxides to methacrylic/acrylic acid ratios on the final properties.[9–12]

The metal methacrylates/acrylate-incorporated vulcanized rubbers can be considered as interpenetrating polymer networks (IPNs). It was reported that metal methacrylates/acrylates undergo homopolymerization and graft copolymerization.[4] As the functionality of metal methacrylates/acrylate is >2, they undergoes crosslinking as well. This may be the reason for achieving extraordinarily high tensile strengths. These types of materials should be discussed under the heading of IPNs.

In the present study, an attempt has been made to synthesize IPNs by incorporating various metal methacrylates in NBR matrix. Sequential IPNs (SeqIPNs) were made via both compression molding (CM) and swelling/curing (SC) routes. The products were characterized using various techniques.

EXPERIMENTAL

Materials

NBR (Acrylonitrile content: 35 mol %; from Kosyan, Korea), zinc oxide (ZnO), zirconium oxide (ZrO₂), aluminum hydroxide (Al(OH)₃; all from SD Fine Chem.,

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TABLE I
Composition of NBR/ZnDMA-, AlTMA-, and ZrTeMA-based IPNs

Sample	Concentration (phr)						
	NBR	ZnO	ZrO_2	$Al(OH)_3$	ZnDMA	AlTMA	ZrTeMA
NBR-ZnO	100	20	-	-	-	-	-
NBR-ZnDMA SeqIPN	100	-	-	-	87	-	-
NBR-Al(OH)$_3$	100	-	-	20	-	-	-
NBR-AlTMA SeqIPN	100	-	-	-	-	84	-
NBR-ZrO$_2$	100	-	20	-	-	-	-
NBR-ZrTeMA SeqIPN	100	-	-	-	-	-	95

India), and dicumyl peroxide (DCP; Merck) were used as received. Methacrylic acid (MA; Merck) was purified by distilling under vacuum through a copper turnings-filled column. Azo-bisisobutyronitrile (AIBN; Merck) was purified by recrystallization from chloroform/ethanol (80/20, v/v) mixture. Osmium tetroxide (OsO_4; Acros) was used as received.

Methods

Synthesis of metal methacrylate

Metal oxide/hydroxide was stirred with excess amount of MA in acetone at ambient temperature for 4 h. The product was filtered, washed with acetone, and dried in vacuum at ambient temperature.

Synthesis of sequential IPN via CM route (method a)

NBR and ZnO were first mixed in a Brabender mixer (Plast-Corder) at ambient temperature, maintaining a rotor speed of 50 rpm. After initial mixing of the components, the rotor speed was raised to 80 rpm, and MA was added and mixed. DCP was added and thoroughly mixed. The compound was cured by using the CM technique at 150°C under 12 MPa load for 30 min. ZrO_2 and $Al(OH)_3$ based IPNs were made in a similar way. The compositions of IPNs are given in Table I.

Synthesis of sequential IPN via SC route (method b)

NBR and ZnO were mixed thoroughly in a two-roll mill. Further, DCP was added and dispersed in the mix. The compound was cured in a CM machine at 150°C under 12 MPa for 30 min.

The cured sheet was swelled in MA solution containing 0.5 wt % of AIBN, till weight gain was slightly higher than the stoichiometric amount. ZnO reacted with MA to form ZnDMA. ZnDMA-incorporated NBR sheet, thus obtained, was kept under vacuum until excess MA was removed from the rubber matrix. ZnDMA was cured by placing the NBR/ZnDMA sheet in an air oven at 150°C for 8–10 h. Similar procedure was adopted for making aluminum trimethacrylate (AlTMA) and zirconium tetramethacry-

late (ZrTeMA) based IPNs, using $Al(OH)_3$ and ZrO_2, respectively. Composition of IPNs is shown in Table I.

Characterization

FTIR spectra

FTIR spectra were taken by using a Perkin–Elmer (1650) spectrophotometer. MA was characterized by a liquid sampling technique, and solid samples (metal methacrylates) were characterized by dispersing in KBr. NBR/metal methacrylate/DCP were smeared on an NaCl window using acetone and dried before recording spectrum. Film of cured NBR/Metal methacrylate was directly used for taking spectra.

Differential scanning calorimetry

NBR/metal methacrylate mix was sealed after placing in an aluminum capsule and differential scanning calorimetry (DSC) measurements were done on a Differential Scanning Calorimeter (T.A. Instrument; Model 910) in the temperature range of 25–200°C, under nitrogen atmosphere.

Tensile/dynamic mechanical properties

Tensile properties, dynamic/loss modulus, and loss tangent measurements were done similarly, as described earlier.[13] Tensile strength and elongation-at-break of IPNs were measured by using a Universal testing machine (Hounsfield; S series) at room temperature at a crosshead speed of 20 mm/min, with dumbbell-shaped specimens, according to ASTM D 638. Hardness was measured by using a hardness meter (Durometer; Blue Steel Engg. Pvt. Ltd., India). Dynamic mechanical analysis was performed by using Dynamic Mechanical Thermal Analyzer (Rheometric Scientific). The samples were cut to pieces (16 mm × 10 mm × 3 mm) and DMTA scans were done at 1 Hz frequency at a heating rate of 5°C/min in the temperature range of −60 to 250°C.
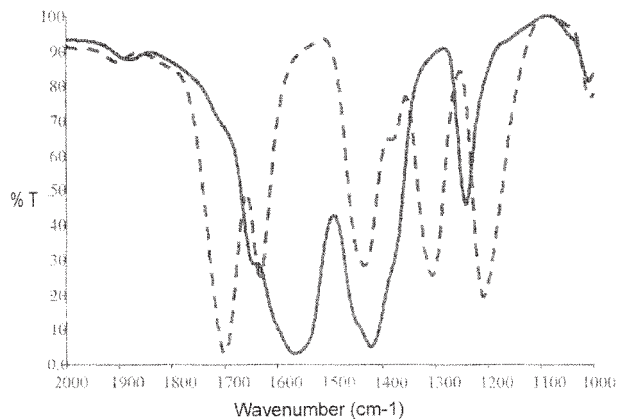
Figure 1 FTIR spectra of MA (- - - -) and ZnDMA (——).

Crosslink density

Crosslink density was determined by equilibrium swelling. The samples were swollen in toluene at room temperature for 72 h. The samples were removed from solvent and the adhering solvent on surfaces was removed using tissue paper. Samples were immediately weighed and then dried under vacuum at 70°C to constant weight. The volume fraction of NBR in the swollen matrix, Vr, was calculated by using the following equation [10]

$$V_r = m_0\phi(1 - \alpha)\rho_n^{-1}/[m_0\phi(1 - \alpha)\rho_n^{-1} + (m_s \\ - m_d)\rho_s^{-1}]$$

where, m_0, m_s, and m_d are, respectively, the weight of the sample before swelling, before drying, and after drying, ϕ is the weight fraction of rubber in the vulcanizate, α is the weight loss of gum vulcanizate during swelling, and ρ_n and ρ_s are the rubber and solvent densities.

Thermogravimetric analysis (TGA)

The samples were analyzed using Hi Res TGA (Model 2950, TA Instruments) under constant flow of nitrogen at a heating rate of 20°C/min in the temperature range of ambient to 800°C

Scanning electron microscopy

IPN samples were fractured after cooling in liquid nitrogen. Fractured samples were exposed to OsO_4 vapor while maintaining over 1% aqueous solution for 24 h at room temperature. The exposed samples were used for scanning electron microscopy study. Micrographs were taken by using scanning electron microscope (Philips, XL-30).

RESULTS AND DISCUSSION

In the present study, an attempt was made to form elastomeric IPNs using metal methacrylates leading to SeqIPNs by following CM and SC routes, respectively. Dimethacrylate (ZnDMA), trimethacrylate (AlTMA), and tetramethacrylate (ZrTeMA) were used for making IPNs. It is expected that crosslink density of tetramethacrylate will be maximum and the enhancement of tensile strength will also be very high. These types of IPN contain both covalent and ionic crosslinks.[6,11] Ionic crosslink density was found to be directly proportional to tensile strength. It was expected that SeqIPNs made by two routes would have differences in properties due to their different modes of synthesis. Metal oxide/hydroxide loading to NBR is kept fixed at 20 phr.

FTIR spectra

Figure 1 shows the FTIR spectra of MA and ZnDMA, respectively. The peak around 1700 cm^{-1} in MA can be attributed to —COOH group. When MA was reacted with ZnO, the peak at 1700 cm^{-1} disappears and a new peak around 1588 cm^{-1} appears. The peak can be attributed to the ionized carboxyl group. This indicates the formation of metal carboxylate. Other metal methacrylates have shown similar FTIR spectra.

Figure 2 shows the FTIR spectra of NBR/ZnDMA/DCP mix before and after curing. In the spectrum of sample before curing (A), the shoulder peak around 1650 cm^{-1} indicates the presence of C—C double bond. The double bond pertains to both NBR and metal methacrylate. After curing the sample, the peak is not traceable in the spectra (B). This indicates the opening of double bond leading to polymerization, crosslinking, and grafting.

Mechanical properties

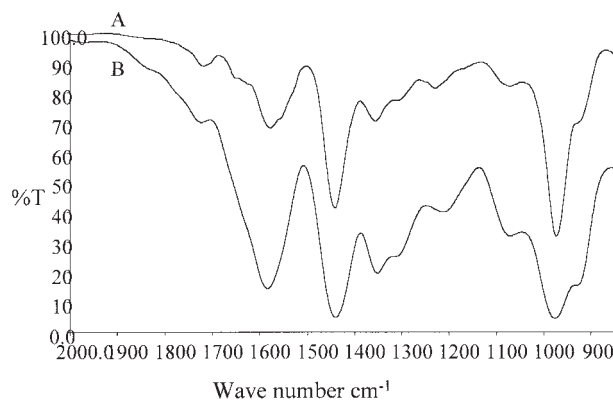Table II shows the tensile properties of the SeqIPNs *via* CM and SC routes. As expected, the tensile strength

Figure 2 FTIR spectra of NBR/ZnDMA/DCP mix before curing (A) and after curing (B).

TABLE II
Mechanical Properties of NBR/ZnDMA-, AlTMA-, and ZrTeMA-based IPNs

Sample	Tensile strength (MPa)	% Elongation	Hardness (shore)	Crosslink density (mol/cm^3)
NBR-ZnO	1.45	520	45A	0.006
NBR-ZnDMA SeqlPN (CM)	11	300	88A	0.083
NBR-ZnDMA SeqlPN (SC)	17	60	45D	0.300
NBR-Al(OH)$_3$	8.2	860	45A	0.009
NBR-AlTMA SeqlPN (CM)	13	200	75A	0.041
NBR-AlTMA SeqlPN (SC)	15.5	15	65D	0.325
NBR-ZrO$_2$	2.3	592	40A	0.003
NBR-ZrTeMA SeqlPN (CM)	8.5	200	45A	0.003
NBR-ZrTeMA SeqlPN (SC)	19	123	90A	0.330

increases due to IPN formation. The increase of tensile strength for ZnDMA via CM route is maximum (about seven times), whereas that for AlTMA is minimum (two times). This increase is the indication of reinforcement by interpenetration of crosslinked polymer of metal methacrylate. Further increase of tensile strength was observed when IPNs are made via SC route. The higher value of tensile strength for IPNs made via SC route compared to CM route may be attributed to greater continuity of crosslinked metal methacrylate. By the CM route, metal methacrylates are first formed, which undergo crosslinking during vulcanization. By the SC route, the oxide/hydroxide particles are distributed thoroughly during mixing and the vulcanized matrix is swelled in MA. This ensures greater continuity and probably maximum

conversion of oxide/hydroxide to methacrylate. The increase of tensile strength is maximum for ZrTeMA. This may be due to higher crosslink density as well as higher metal methacrylate weight ratio in the matrix compared to others.

Elongation (%) shows a decline on IPN formation. There is a sharp drop of elongation for all the IPNs. Maximum decrease is observed for ZrTeMA containing IPN. This is understandable, as the crosslink density is expected to be highest in this system. Hardness was found to increase in the order of NBR/metal oxide or hydroxide < SeqIPN (CM route) < SeqIPN (SC route). Maximum increase is observed for AlTMA-based IPN. The increase from NBR-Al(OH)$_3$ to NBR-AlTMA SeqIPN via the SC route is from shore 45A to shore 65D.
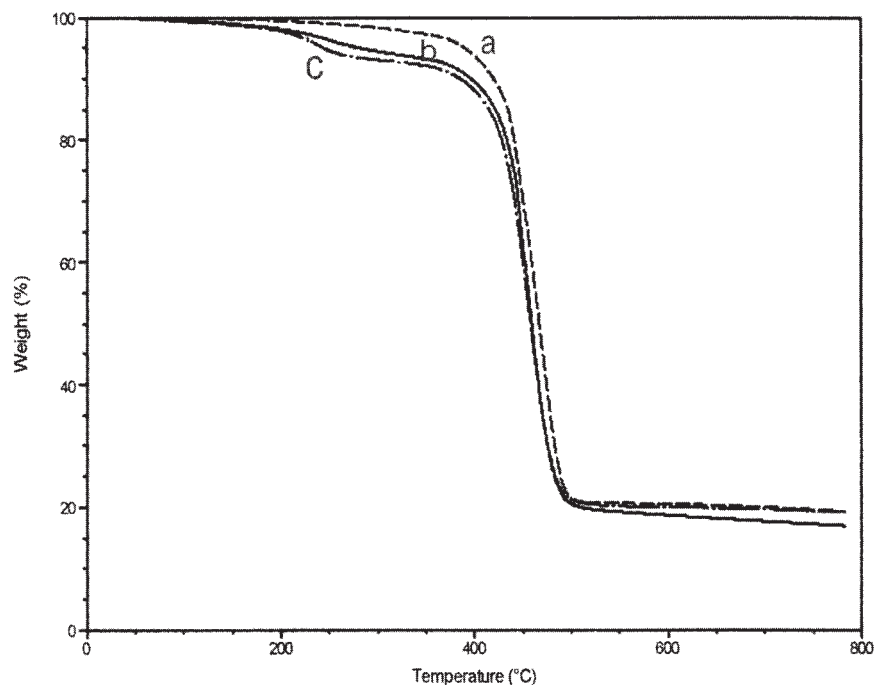

Figure 3 TGA thermogram of NBR/ZrTeMA-based IPNs: (a) NBR/ZrO2; (b) NBR/ZrTeMA SeqIPN (CM route); and (c) NBR/ZrTeMA SeqIPN (SC route).
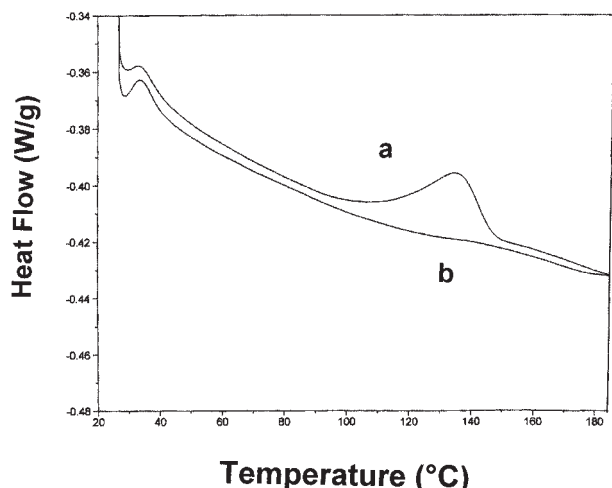
Figure 4 DSC thermogram for thermal curing of NBR: (a) first run and (b) second run.

Figure 5 DSC thermogram for thermal curing of NBR/ZnDMA: (a) first run and (b) second run.

Crosslink density

It has been mentioned that metal salts of unsaturated carboxylic acids, when polymerized, make both covalent and ionic crosslinks. NBR cures only by forming covalent crosslinks. The total crosslink density is found to be minimal for metal oxide-filled cured NBR. The value increases by 10 times, when metal methacrylates formed are cured along with NBR vulcanization to make IPN via the CM route. Maximum value is found for IPN via the SC route. ZrTeMA-based SeqIPN exhibits maximum crosslink density around 0.33. ZrTeMA contains four methacrylates per Zr atom. However, the values for three metal methacrylates are very close.

TGA studies

Figure 3 shows the TGA thermogram of ZrDMA-based IPNs. It can be seen that NBR/ZrO$_2$ shows only one decomposition around 450°C, which can be assigned to NBR. IPNs prepared by both the routes show an additional weight loss around 250°C. This weight loss may be attributed to the decomposition of metal methacrylate unit. Similar behavior is observed for all the other IPNs in this study.

DSC study

Figure 4 shows the DSC thermogram for NBR. The exotherm observed around 90–140°C in the first run indicates thermal curing via double bond. The second run is also shown in the figure. No exotherm is observed in the plot, indicating completion of curing reaction. Figure 5 shows the DSC thermogram for NMR/ZnDMA blend. In the first run, one exotherm is observed around 90–125°C and the other around 150–
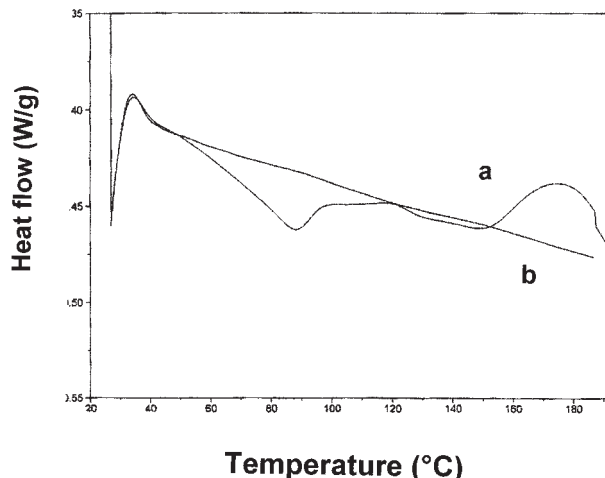
190°C. The first one corresponds to NBR, as seen earlier. The second one can be assigned to polymerization of ZnDMA, leading to polymerization. Here, also in the second run, no exotherm is observed. Aforementioned observations indicate the radical polymerization of metal methacrylate, leading to IPN formation.

DMTA studies

Figure 6 shows the plot of storage modulus (E′) versus temperature for NBR-AlTMA system. E′ values in the glassy region are found to be in the range of 1500–2500 MPa. Even in the rubbery region, the E′ values of IPNs are very high. At 35°C, E′ value for SeqIPN via the SC route is around 350 MPa, which is 14 times higher than that via the CM route. As mentioned
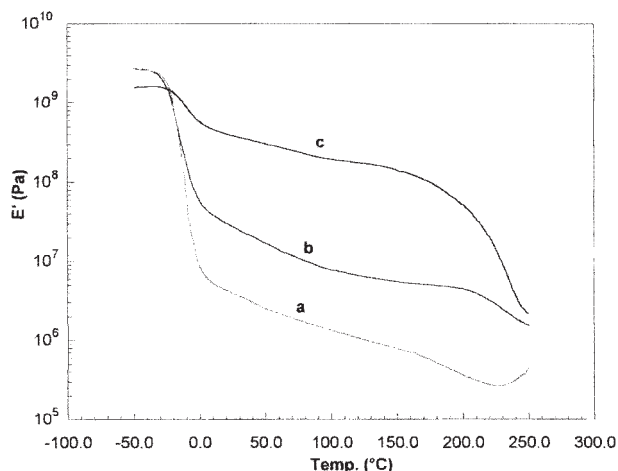

Figure 6 Storage modulus of NBR/AlTMA-based IPNs: (a) NBR/Al(OH)3; (b) NBR/AlTMA SeqIPN (CM route); and (c) NBR/AlTMA SeqIPN (SC route).
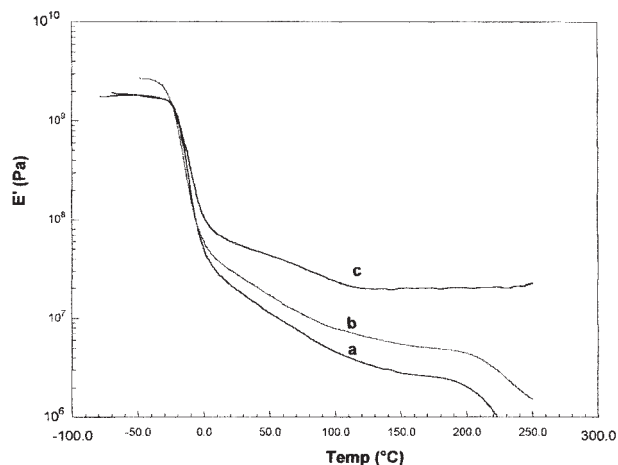
Figure 7 Storage modulus of NBR/metal methacrylate SeqIPNs (CM route): (a) NBR/ZrTeMA; (b) NBR/AlTMA; and (c) NBR/ZnDMA.

Figure 8 The tan δ value of ZrTeMA-based IPNs: (a) NBR/ZrO2; (b) NBR/ZrTeMA SeqIPN (CM route); and (c) NBR/ZrTeMA SeqIPN (SC route).

earlier, this is due to greater continuity in the matrix.

Figure 7 shows the plot of E' versus temperature for the three IPNs via the CM route. All the IPNs exhibit much greater E' values compared to those of pure metal oxide-filled NBR. E' values for IPNs via SC route are much higher than CM, in all the cases. Table III incorporates E' values at 35°C for all IPNs. Maximum E' value is recorded for ZnDMA by the CM route. For ZrTeMA system, the E' value via the SC route is about 20 times higher than that for the CM route.

Figure 8 shows the plot of tan δ versus temperature for NBR-ZrTeMA. The peak at −12°C is due to NBR. On IPN formation, the peak at −12°C shifts to −8°C and the peak height (tan δ_{max}) reduces from 1.15 to 0.62. Inward shifting and peak height reduction indicate the formation of IPN. IPN formed via SC route shows further shift to around −6°C, without much change in tan δ_{max} value. Because of IPN formation, the segmental mobility of NBR is impeded, and consequently, the tan δ value decreases.

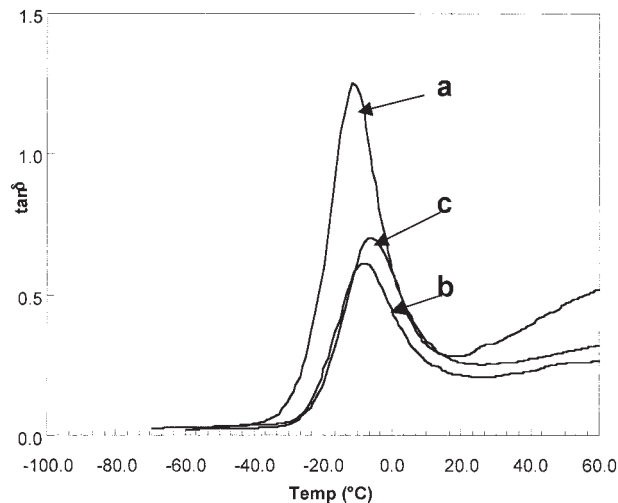## Scanning electron microscopy

Figure 9 shows the optical micrographs of fractured surfaces of NBR-ZrTeMA-based IPNs. It can be observed that the morphology of NBR-ZrO$_2$ (a) is single phase in nature, with ZrO$_2$ particles distributed in NBR matrix. The morphology of NBR-ZrTeMA IPN is biphasic in nature as can be seen in (b) and (c), respectively. The presence of microphase-separated morphology in the system indicates the formation of IPN. One important feature of the morphology of IPN via SC route is more homogeneity of the phases. This may lead to enhanced properties, as we have observed in other studies detailed earlier.

CONCLUSIONS

IPNs based on NBR and ZnDMA/AlTMA/ZrTeMA were synthesized. SeqIPNs via CM and SC routes were formed. The IPNs were found to have superior properties compared to metal oxide/hydroxide filled

TABLE III
E' and tan δ of NBR/ZnDMA-, AlTMA-, and ZrTeMA-based IPNs

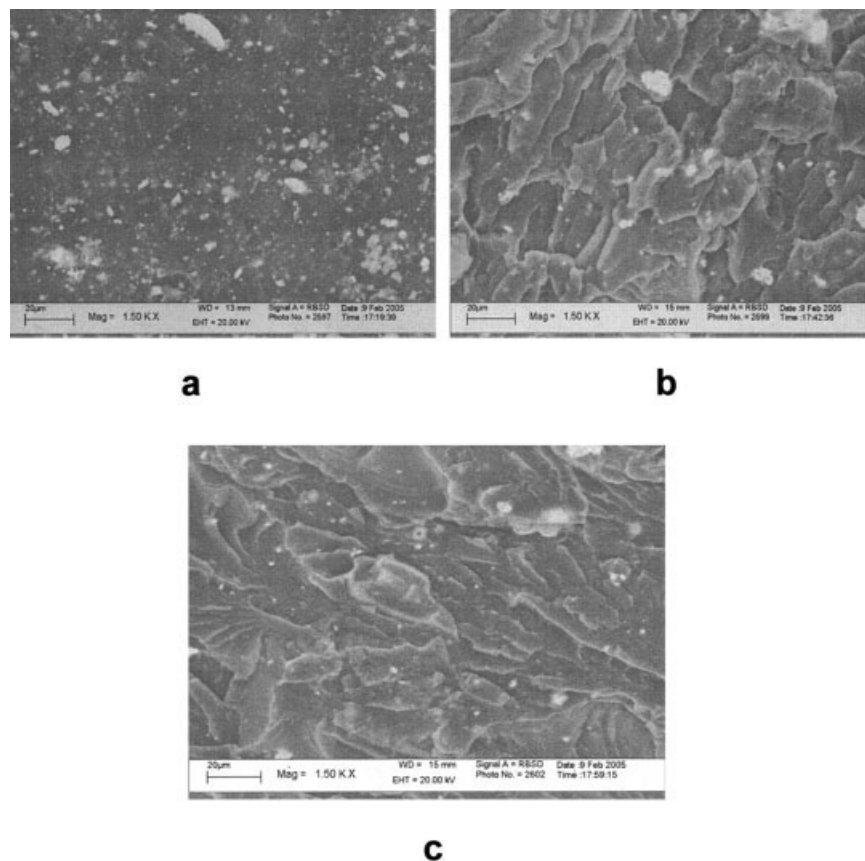| Sample	E' at 35°C (MPa)	Temp. for tan δ_{max} (°C)	tan δ_{max}
NBR-ZnO	3.07	−13.6, 159	1.08, 2.13
NBR-ZnDMA SeqIPN (CM)	50.40	−7.5, 107	0.44, 0.18
NBR-ZnDMA SeqIPN (SC)	127.20	−9.4, 114.7	0.29, 0.16
NBR-Al(OH)$_3$	3.38	−11.7, 222	1.54, 0.70
NBR-AlTMA SeqIPN (CM)	23.96	−10.6	0.62
NBR-AlTMA SeqIPN (SC)	349.26	−7.1	0.16
NBR-ZrO$_2$	1.77	−9.1, 159	1.09, 3.08
NBR-ZrTeMA SeqIPN (CM)	11.86	−8.8	0.62
NBR-ZrTeMA SeqIPN (SC)	203.53	−5.7	0.70

Figure 9   Scanning electron micrograph of NBR/ZrDMA IPNs: (a) NBR/ZrO2; (b) NBR/ZrTeMA SeqIPN (CM route); and (c) NBR/ZrTeMA SeqIPN (SC route).

NBR. Tensile strength has increased to a larger extent while maintaining appreciable elongation. However, there is a drastic reduction of elongation in the case of the SC route. Because of the presence of metal methacrylate in IPN there is tremendous enhancement of hardness. Total crosslink density (covalent and ionic) was found to increase in the order NBR/metal oxide or hydroxide < SeqIPN (CM route) < SeqIPN (SC route). IPNs are found to retain high storage modulus even in the rubbery phase. One point to note is that the modulus/hardness of IPNs differs immensely when the process for IPN formation was changed. Decrease in tan δ value and inward shifting of peaks were observed because of IPN formation. Morphology of SeqIPN *via* SC route was found to be more uniform compared to others.

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