

# Sequential Interpenetrating Polymer Network Based on Styrene Butadiene Rubber and Polyalkyl Methacrylates

M. Patri, C. V. Reddy, C. Narasimhan, A. B. Samui

Naval Materials Research Laboratory, Ambernath (East), Thane, Maharashtra 421506, India

Received 6 December 2005; accepted 7 February 2006

DOI 10.1002/app.24338

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of sequential interpenetrating polymer network (IPNs) based on styrene butadiene rubber (SBR) and polyalkyl (methyl, ethyl, and butyl) methacrylates have been prepared by using tetraethylene glycol dimethacrylate as crosslinker. The IPNs were characterized by infrared spectrophotometer, dynamic mechanical analyzer, thermogravimetric analyzer, and swelling study. IPNs have exhibited higher tensile properties compared with pure SBR. IPNs based on PMMA have shown higher tensile strength compared with others. Dynamic mechanical analysis has shown that the IPNs have superior

dynamic properties than SBR. Because of IPN formation,  $\tan \delta$  peak shifted inward between SBR and acrylates. Although the magnitude of  $\tan \delta$  decreased, the peaks were broadened because of micro heterogeneous phase separation. At higher concentration of methacrylate, splitting in  $\tan \delta$  peak was noticed because of phase separation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1120–1126, 2007

**Key words:** interpenetrating polymer networks; styrene butadiene rubber; polyalkyl methacrylates; damping

## INTRODUCTION

Polymeric materials are known for damping mechanical waves like low-frequency vibration and sound waves appreciably in the sonic and ultrasonic range.<sup>1</sup> The absorption of such waves in a polymer is a manifestation of mechanical relaxation of the segments of the long chains. The extent of absorption/damping is dependent on thermodynamic state of the polymer and on the frequency of the wave. A polymer has very well defined temperature and frequency range, where it shows pronounced absorption because it is related to the relaxation frequency of the chain segments. However, the range of temperature or frequency for high absorption is very narrow for common single polymers. Broadening the range by combination of polymers through various techniques has been attempted by many researchers. Some of these techniques are copolymer formation, chemical modification by grafting, physical blending, and of late, by making interpenetrating polymer network. Because copolymer formation and chemical modification have problems of synthesis and cost effectiveness, physical blending is preferred mostly because of its simplicity of the processing and cost effectiveness. However, if the parent polymers were not compatible, the ultimate properties of the blend would be very inferior for any practical applications.

Interpenetrating polymer networks (IPNs) are a new class of blends where two or more polymers are individually crosslinked in the presence of the other.<sup>2,3</sup> The method of synthesis of IPNs results in a blend of two (or more) crosslinked polymers having chains completely intermingled with each other. Unlike chemical blends, there are no induced covalent bonds between the two polymers. This results in tremendous improvement in the mechanical properties and also enhancement in the viscoelastic loss for wider frequency and temperature range. Because of these enhancements in properties, considerable amount of work on IPN formation has been reported over the years.<sup>3–18</sup> The selection of material has been purely based on end-use requirement and Sperling's group contribution theory.<sup>1</sup> Most of the elastomeric IPNs reported so far are mainly based on nitrile rubber or nitrile rubber/PVC blend because of their high damping ability.<sup>3–7,14,15</sup> Styrene butadiene rubber (SBR), another commercially available elastomer, is frequently used for many applications because of its excellent overall properties.

The present work deals with studying the synthesis and characterization of sequential IPN based on SBR-polyalkyl methacrylates.

## EXPERIMENTAL

### Materials

Styrene butadiene rubber (SBR, Kosyn 1502) was used as-received. Di cumyl peroxide (DCP, Rubo chem Industries, India), a rubber curative, was used

Correspondence to: A. B. Samui (absamui@rediffmail.com).

as crosslinker for SBR without further purification. Butylmethacrylate (BuMA), ethyl methacrylate (EMA), and methyl methacrylate (MMA) monomers (Merck) were freed from inhibitors and used. Azo-bis(isobutyronitrile) (AIBN, Fluka) was recrystallised from chloroform/methanol mixture (80/20 v/v) and used as initiator. Tetra ethylene glycol dimethacrylate (TEGDM, Fluka), a crosslinking agent, was used without further purification. Sodium hydroxide (NaOH) calcium chloride fused ( $\text{CaCl}_2$ ) (SD-Fine Chem, India) was used as-received.

#### Preparation of SBR sheet

About 100 g SBR, five parts DCP mixture was compounded and masticated in a two-roll miller. A small sample was tested in Elastograph machine at 150°C for 60 min to find the optimum cure characteristics. SBR compound was vulcanized in hot press compression molding for 30 min at 150°C using a  $250 \times 250 \times 2 \text{ mm}^3$  at a pressure of 150 kg/cm<sup>2</sup>. The cured SBR sheet was allowed to cool, and cleaned with soap solution to remove any dust or mold releasing agent adhering to it. Then sheets were dried and samples were cut for tensile, DMA, TGA, DSC, FT-IR, etc. For swelling in methacrylate monomers  $10 \times 10 \text{ cm}^2$  sheets were used.

#### Swelling of SBR sheets

Known quantity of TEGDM and AIBN were dissolved in the monomer by constant stirring. SBR sheet was swollen by inserting in monomer containing TEGDM and AIBN in glass mold. Mold was covered by aluminum foil to minimize the loss of monomer due to evaporation. The swelling was continued for different time period and subsequently the swollen sheets were removed and the surface was wiped with tissue paper to remove adhered monomer.

#### IPN synthesis

The swollen SBR sheet was wrapped with aluminum foil to minimize the evaporation of monomer during polymerization. The wrapped sheet was kept in between two stainless steel plates inside an oven at 80°C for 16 h for polymerization. Afterwards, the rubber sheet was vacuum dried to constant weight to remove unreacted monomer under reduced pressure at 60°C. The composition of IPNs was determined gravimetrically.

#### Characterization methods

##### Fourier transform infrared spectroscopy

The spectra of IPNs were recorded by using PERKIN ELMER 1650 FTIR spectrophotometer.

#### Tensile measurement

The tensile strength and elongation at break of IPNs were measured by an UTM-Hounsfield Model 50K-S with capacity of 50 KN at room temperature at a cross-head speed of 500 mm/min using dumbbell-shaped specimen according to ASTM D638.

#### Dynamic mechanical analysis

The dynamic mechanical spectra of the IPNs were obtained by using a rheometric scientific (PL MK 3) dynamic mechanical thermal analyzer (DMTA). The samples were heated from -100°C to 250°C at a heating rate of 3°C/min. The samples were tested in the fixed frequency (1 Hz) mode. The amplitude of oscillation (0.2  $\mu$ ) was kept constant for all the measurements. From the spectra, storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) were obtained.

#### Thermo gravimetric analysis

Thermo gravimetric analysis was carried out on a TA instruments 2950 model, under nitrogen atmosphere. Heating rate of 20°C/min, a sample size of 10 mg and nitrogen flow of 60 cm<sup>3</sup>/min were maintained for all the measurements. Heating was carried out from ambient temperature to 800°C. Primary thermogram was obtained directly with the aid of a suitable computer package and plotter. From the thermogram various decomposition temperatures were obtained.

#### Solvent resistance

Solvent resistance of SBR and IPNs was found by dipping a known weight of the sample in different solvents for 7 days. After 7 days, the samples were removed and extent of swelling in percentage was noted.

$$\text{Swelling \%} = \frac{(W - W_0)}{W_0} \times 100$$

where  $W$  is weight of sample after swelling and  $W_0$  is weight of sample before swelling.

## RESULTS AND DISCUSSION

For all the IPN synthesis SBR has been chosen as starting polymer. SBR is a general purpose synthetic polymer widely being used by tire industries because of its easy availability and low cost. As such the damping capability of SBR is quite pronounced in a selected zone of temperature/frequency. The selection of second polymer was purely based on Sperling's group contribution theory for damping.<sup>1</sup> It has

TABLE I  
Assignments for IR Spectra of IPNs

Peak wave number (cm <sup>-1</sup> )				Assignments
SBR	SBR-PBuMA IPN	SBR-PEMA IPN	SBR-PMMA IPN	
2913	2917	2916	2917	C—H stretching in —CH <sub>2</sub>
2858	2848	2846	2848	C—H stretching in —CH
	1739	1724	1739	C=O stretching in esters
1617	1638	1643	1645	C=C stretching
1589	1600	1597	1599	C=C in aromatic
1432	1442	1442	1442	C—H deformation
	1019	1017	1018	C—O stretching

been seen that ester groups contribute very high towards damping. The scope of selecting an acrylate is very broad as a large variety of acrylate monomers are available having wide range of  $T_g$ . TEGDM was selected as crosslinker mainly due to two reasons. Presence of ether linkage in the backbone would contribute towards toughness whereas ester groups would contribute to damping.

Initial attempts in preparation of IPN using less amount of initiator, as per the procedure reported in literature, were not very successful and the resultant IPNs used to have structural irregularity with poor reproducibility. After several experimentations, it was found that use of higher dose of initiator (1%) has provided solution to the problem and the IPNs were found to have homogeneous distribution of second component in the rubber matrix. This observation is because of the fact that at higher dose of initiator, the polymerization rate increases and the degree of polymerization decreases according to free radical addition polymerization. All the IPNs were characterized for their structure and property and the results are as follows.

TABLE II  
Results of the Tensile Measurements

Composition	% TEGDM	Tensile strength (kg/cm <sup>2</sup> )	% Elongation at break
SBR	—	9.9	39
SBR/PMMA			
81/19	2	21	47
68/32	2	40	69
67/33	2	60	89
59/41	2	110	100
SBR/PEMA			
90/10	2	15	50
80/20	2	20	57
72/28	2	23	53
64/36	2	53	114
SBR/PBuMA			
87/13	2	12	45
73/27	2	12	54
72/28	2	13	36
58/42	2	19	73

## FTIR/ATR

The structure of the IPNs was studied by FTIR spectrophotometer. The spectra were recorded using ATR facility as measurement by transmission mode was not possible due to opaqueness of the sample. The assignments<sup>19</sup> for various peaks are given in Table I. From the results it can be seen that SBR shows peaks due to styrene and butadiene. On IPN formation, in addition to all the peaks of SBR, there are additional peaks due to the presence of acrylates. Thus, the peak around 1720 and 1020 cm<sup>-1</sup> are due to the C=O and C—O stretching of ester and ether groups, respectively. However, as expected, there is no appreciable change in peak positions for different acrylates.

## Tensile properties

The tensile properties of styrene butadiene rubber (SBR) and IPNs were studied and results are presented in Table II. From the results it can be seen that SBR shows very low tensile strength and elon-

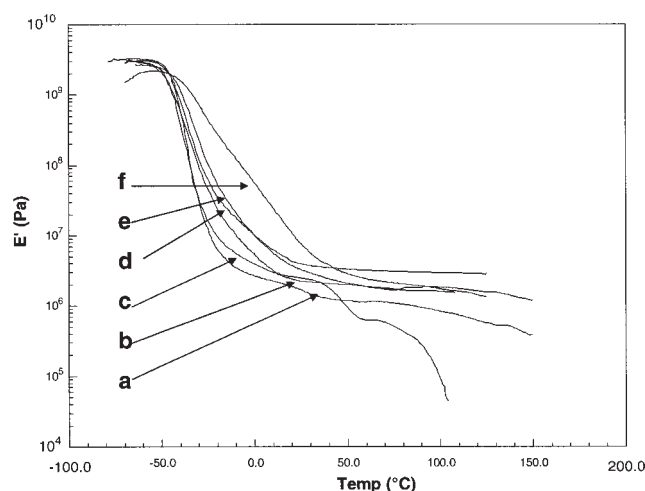
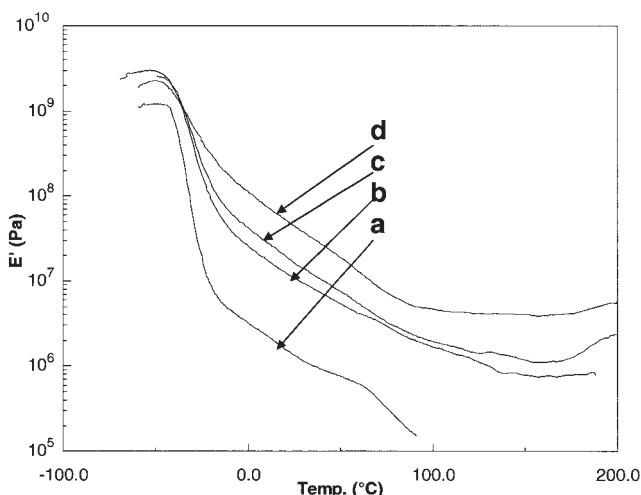
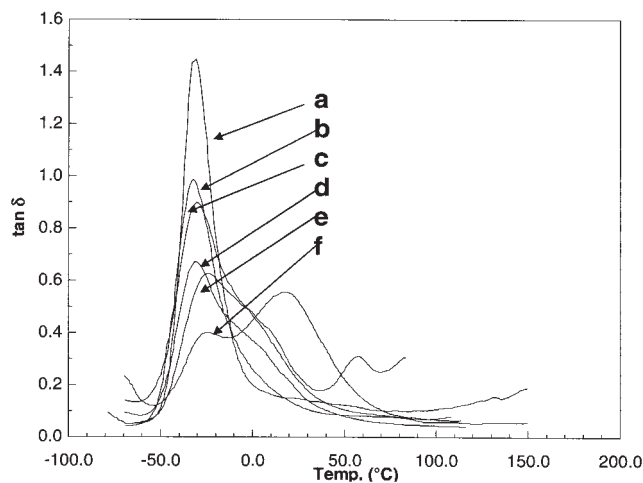


Figure 1 Storage modulus plot of SBR/PBuMA IPNs: SBR (a); SBR/PBuMA (87/13) (b); SBR/PBuMA (80/20) (c); SBR/PBuMA (73/27) (d); SBR/PBuMA (72/28) (e); SBR/PBuMA (57/42) (f).



**Figure 2** Storage modulus plot of SBR/PEMA IPNs: SBR/PEMA (90/10) (a); SBR/PEMA (80/20) (b); SBR/PEMA (72/28) (c); SBR/PEMA (64/36) (d).



**Figure 4** Damping plot of SBR/PBuMA IPNs: SBR (a); SBR/PBuMA (87/13) (b); SBR/PBuMA (80/20) (c); SBR/PBuMA (73/27) (d); SBR/PBuMA (72/28) (e); SBR/PBuMA (57/42) (f).

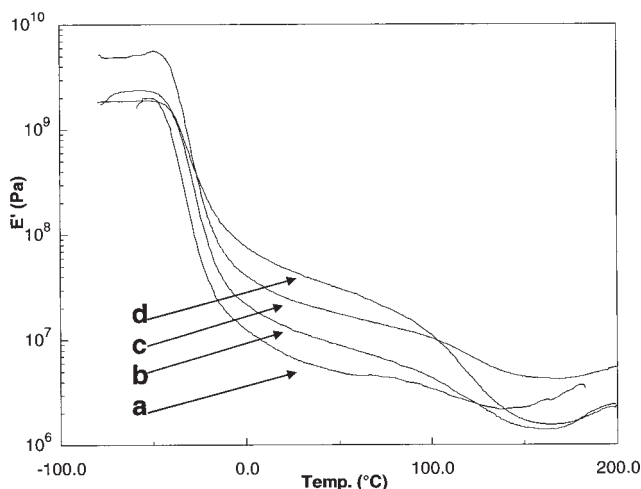
gation at break. It is quite obvious because of the fact that SBR is a random copolymer having no regular structure. However, on IPN formation the strength increases due to intimate mixing of the second crosslinked phase. This increasing trend continues as the content acrylate increases irrespective of nature of acrylate. This is possibly due to reduced domain size and increased crosslink density. The value of elongation at break for IPNs has increased considerably as compared to SBR. Increase in tensile strength and elongation indicates that the toughness of IPNs is quite high compared to SBR. The tensile strength for SBR/PMMA IPN is found to be highest. SBR/PBuMA IPN is found to be lowest among the three IPNs. This can be explained on the basis of

size of pendent acrylate group. Thus size of  $-CH_3$  group being the smallest among the three acrylates used for IPN synthesis, obviously the resultant network will have more compact structure resulting higher tensile properties. Conversely, butyl group being a bulkier group, the resultant network will have more free volume resulting in lower tensile properties.

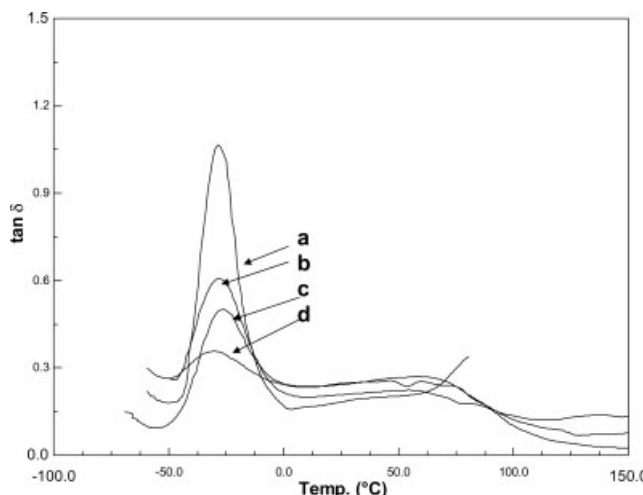
**Dynamic mechanical properties**

The dynamic mechanical properties of IPNs have been investigated by DMTA and the spectra have been presented in Figures 1–6. From the spectra  $E'$  at 25°C,  $\tan \delta_{max}$  and its temperature, and half-peak

F1–F6

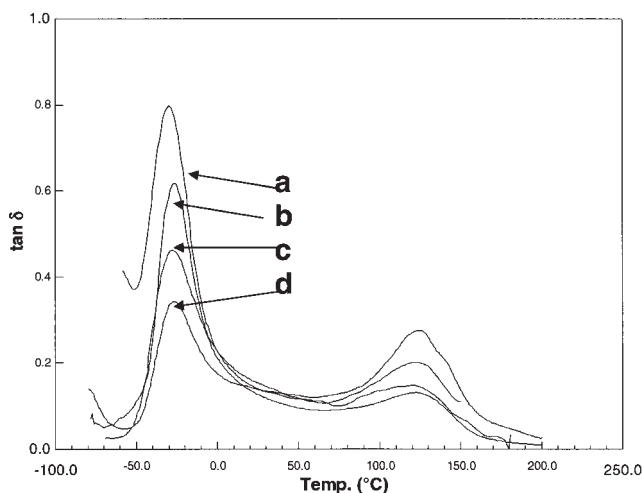


**Figure 3** Storage modulus plot of SBR/PMMA IPNs: SBR/PMMA (81/19) (a); SBR/PMMA (69/31) (b); SBR/PMMA (67/33) (c); SBR/PMMA (59/41) (d).



**Figure 5** Damping plot of SBR/PEMA IPNs: SBR/PEMA (90/10) (a); SBR/PEMA (80/20) (b); SBR/PEMA (72/28) (c); SBR/PEMA (64/36) (d).





**Figure 6** Damping plot of SBR/PMMA IPNs: SBR/PMMA (81/19) (a); SBR/PMMA (69/31) (b); SBR/PMMA (67/33) (c); SBR/PMMA (59/41) (d).

width of the  $\tan \delta$  peak are obtained and presented in Table III.

From figure, it can be seen that SBR has a very low storage modulus–temperature plateau compared to IPN. SBR being random copolymer, the low modulus plateau is expected. However, this plateau in case of IPN increases continuously on increasing the acrylate content irrespective of the nature of acrylate. This is evident from Table III that for all the acrylates, the  $E'$  at 25°C increases continuously with increase in acrylate content. The modulus value of PMMA based IPNs are higher than corresponding IPNs based on PEMA and PBuMA. This finding strengthens the contention observed in tensile properties that methyl group being smaller in size present in pendent ester group of MMA. Because of

this reason, PMMA has higher  $T_g$  compared to other acrylates. Similarly, PBuMA based IPNs showed lower  $E'$  value at 25°C as expected, and reason for this has already been explained in tensile properties.

SBR shows a sharp  $\tan \delta$  peak compared to IPNs. Thus,  $\tan \delta_{\max}$  peaks for SBR appeared at  $-31.5^\circ\text{C}$  having maximum value of damping (1.56). This indicates that SBR can be effectively used as damper in the vicinity of  $-30^\circ\text{C}$ . But the range of relaxation is very narrow, which is evident from the 1/2 peak width (Table III). The relaxation peak for all the IPNs shifts inwardly to a temperature between the two transitions of SBR and acrylate polymer and the peaks are broad. The magnitude of  $\tan \delta_{\max}$  has come down on introduction of second component, i.e., acrylate polymer. Although according to Sperling's<sup>1</sup> group contribution theory, acrylates contribute to large extent towards damping, the decrease in magnitude of damping is probably due to increase in cross-link density in the overall IPN. However, the  $\tan \delta$  peak of all the IPNs is broad, which is evident from the 1/2 peak width value (Table III). This indicates that IPNs can be used over a broad range of temperature. It can also be seen from Table III that the magnitude of  $\tan \delta_{\max}$  decreased with decrease in bulkiness of the acrylate group. Thus, IPNs based on PBuMA had highest  $\tan \delta$  value, whereas IPNs based on PMMA had lowest  $\tan \delta$  value.

Moreover, it is also seen that at higher concentration of second phase i.e., acrylate polymer, there is splitting in  $\tan \delta$  peak indicating two relaxation transition point. It appears that at higher concentration i.e., beyond 40% phase separation occurs. In case of SBR/PMMA two  $\tan \delta$  peaks were noticed due to SBR phase and PMMA phase. The magnitude of PMMA  $\tan \delta$  peak increased with increase in concen-

**TABLE III**  
Dynamic Properties of IPNs

Composition	$E'$ at 25°C (MPa)	Temperature for $\tan \delta_{\max}$ (°C)	$\tan \delta_{\max}$	1/2 Peak width of $\tan \delta$ curve (°C)
SBR	1.65	-31.5	1.56	20
SBR/PBuMA				
87/13	2.23	-30	1.12	23
80/20	2.44	-30	0.94	26
73/27	3.9	-31.4	0.72	39
72/28	3.23	-27.6	0.69	52
58/42	7.26	-26, 18.4	0.39, 0.55	73
SBR/PEMA				
90/10	1.31	-28.6	1.06	22
80/20	10.4	-26.9	0.61, 0.22	21, 42
72/28	15.9	-26.6, 61	0.50, 0.25	30, 50
64/36	44.6	-29.6, 64.7	0.36, 0.26	22, 48
SBR/PMMA				
81/19	6.56	-29.6, 120	0.80, 0.14	21, 44
69/31	12.0	-26.7, 126	0.62, 0.2	24, 65
67/33	23.7	-26.8, 126.5	0.47, 0.21	37, 46
59/41	44.6	-28.4, 127.4	0.36, 0.27	32, 55

TABLE IV  
TGA Results of IPNs

Composition	IDT (°C)	MDT (°C)	FDT (°C)
SBR	375	467	496
SBR/PBuMA	378	458	496
SBR/PEMA	380	444	497
SBR/PMMA	380	462	502

tration of PMMA. It appears that because of large difference in glass transition temperature as well as stiffness of the polymer, complete phase mixing was not possible. Others have also observed phase separation for other IPNs and have minimized the effect by using higher dose of crosslinker (TEGDM).

### Thermo gravimetric analysis

The thermo gravimetric analysis of the sequential IPNs was carried out in nitrogen atmosphere. It can be seen from the figures (not shown) that IPNs as well as SBR showed sigmoid type of decomposition indicating that there is not much difference in the degradation pattern of SBR and IPNs. The initial decomposition temperature (IDT), maximum decomposition temperature (MDT), and final decomposition temperature (FDT) were found from the thermogram and presented in Table IV. From the result presented in Table IV, it can also be seen that there is no significant difference between the various decomposition temperatures indicating that the overall degradation pattern of IPNs and SBR is same. Annakutty and Deb<sup>5</sup> have observed similar phenomena for P(VCA)/PBuMA semi-IPNs.

### Solvent resistance

The solvent-resistance characteristics of SBR and IPNs have been studied in different solvents and the results have been presented in Table V. On comparing the swelling values of SBR with those of IPNs, it can be seen that the introduction of acrylate content into the SBR matrix results in a sharp decrease in the swelling values in case of non-polar solvents such as xylene, hydraulic oil, and CCl<sub>4</sub>. On comparing the values of IPNs, it can be seen that as the size of side group i.e., ester group, decreases due to decrease in size of alkyl group, the polarity increases resulting in decrease in swelling in non-polar solvent. In case of MIBK, it appears that the solubility parameter of SBR/PBuMA is closer to resulting in highest swelling. Others such as SBR, SBR/PEMA, and SBR/PMMA have either lower or higher solubility parameter value compared to MIBK. Ethyl acetate being a polar solvent, SBR shows least swelling. In this case also, it is seen that SBR/PEMA shows maximum

swelling indicating closeness in solubility parameter of ethyl acetate and SBR/PEMA. In case of SBR/PBuMA and SBR/PMMA similar reason can be cited as explained for MIBK.

### CONCLUSION

A series of IPNs based on SBR and polyalkyl methacrylates has been prepared by sequential method. While, SBR (first phase) was cured by using DCP as crosslinking agent, TEGDM was used as crosslinker for polyalkyl methacrylates (second phase). For all the IPN synthesis, AIBN was used as initiator. IPNs having different compositions could be prepared by varying the swelling time of SBR in acrylate monomer.

The structure of IPNs was characterized by FTIR/ATR spectrophotometer. On comparing the spectra of SBR with IPNs, it was found that in addition to all the peaks due to SBR IPNs, have additional peaks around 1730 and 1020 cm<sup>-1</sup> due to presence of acrylate polymer.

In general, it was observed that IPNs had higher the tensile properties compared to pure SBR. The tensile strength of the IPN increased on increasing the acrylate content in the SBR matrix due to increase in concentration of hard acrylate segment and better mixing between the two components. The tensile strength of IPNs was also found to depend on degree of stiffness of acrylate segment. Thus, IPNs based on PBuMA showed lower strength, while IPNs based on PMMA had higher strength. Elongation at break also followed similar trend.

Dynamic mechanical analysis of IPNs shows that the IPNs have superior dynamic properties than SBR. Due to IPN formation, tan  $\delta$  peak shifted inward between SBR and acrylates. Although the magnitude of tan  $\delta$  decreased, the peaks were broad because of micro heterogeneous phase separation. At higher concentration of acrylate, splitting in tan  $\delta$  peak was noticed due to phase separation. In case of SBR/PMMA IPNs, two tan  $\delta$  peaks were observed irrespective of their composition. This was ascribed to large difference in  $T_g$  between SBR and PMMA.

TABLE V  
Results of Swelling Value of IPNs in Different Medium

Composition	Swelling %				
	MIBK	CCl <sub>4</sub>	Hydraulic oil	Xylene	Ethyl acetate
SBR	205	400	14	199	59
SBR/PBuMA	216	372	12.5	218	92
SBR/PEMA	192	349	9.8	189	104
SBR/PMMA	170	278	8.7	158	81

Thermogravimetric analysis of SBR and IPNs revealed that both SBR and IPNs were fairly stable upto 300°C and there was no significant difference in their degradation pattern.

The solvent-resistance study was carried out in variety of solvents having different polarity. IPNs offered better resistance to nonpolar solvents. Because of polar nature of acrylate, the swelling in polar solvents was slightly higher compared to SBR.

## References

1. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
2. Patri, M.; Samui, A. B.; Chakraborty, B. C.; Deb, P. C. *J Appl Polym Sci* 1997, 65, 549.
3. Sharma, Y. R. *Elementary Organic Spectroscopy, Principles and Chem Applications*; S. Chand and Company: New Delhi, 2002.
4. Mathew, A.; Deb, P. C. *J Appl Polym Sci* 1992, 45, 2145.
5. Sperling, L. H. In *Encyclopedia of Polymer Science and Technology*; Kroschwitz, J. I., Ed.; Wiley: New York, 1988; Vol. 8, p 279.
6. Samui, A. B.; Suryavanshi, U. G.; Patri, M.; Chakraborty, B. C.; Deb, P. C. *J Appl Polym Sci* 1998, 68, 255.
7. Pernice, R.; Frisch, K. C.; Navare, R. *J Cell Plast* 1982, 3/4, 121.
8. Patri, M.; Samui, A. B.; Deb, P. C. *J Appl Polym Sci* 1993, 48, 1709.
9. Siegfried, D. L.; Thomas, D. A.; Sperling, L. H. *J Appl Polym Sci* 1981, 26, 177.
10. Sperling, L. H. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., Eds.; Peragmon: Tarrytown, New York, 1989; Vol. 6, p 423.
11. Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. *J Appl Polym Sci* 1987, 34, 409.
12. Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. *J Polym Sci Part B: Polym Phys* 1988, 26, 1627.
13. Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. *J Polym Mater* 1989, 6, 61.
14. Mathew, A.; Chakraborty, B. C.; Deb, P. C. *J Appl Polym Sci* 1994, 53, 1107.
15. Manoj, N. R.; Ratna, D.; Dalvi, V.; Chandrasekhar, L.; Patri, M.; Chakraborty, B. C.; Deb, P. C. *Polym Adv Technol* 2002, 13, 1.
16. Fernandez, A. M.; Wignall, G. D.; Sperling, L. H. In *Proceedings of the ACS Division of Polymeric Materials, Science and Engineering*; ACS Symposium Series 51; The American Chemical Society: Washington, DC, 1984; p 478.
17. Singh, S.; Frisch, H. L. *Macromolecules* 1990, 23, 375.
18. Abu-Isa, I. A. *J Appl Polym Sci* 1991, 43, 1133.
19. Choi, Y.-J.; Kang, M.-S.; Moon, S.-H. *J Appl Polym Sci* 2003, 88, 1488.