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AB CROSSLINKED POLYURETHANES THROUGH IONIC CROSSLINKING: INFLUENCE OF CROSSLINKING NETWORKS ON PHYSICO CHEMICAL PROPERTIES

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ABSTRACT

Isocyanate-terminated prepolymers were synthesized using poly(tetramethylene oxide)glycol of molecular weight 1000 ($PTMG_{1000}$) with tolylene-2,4-diisocyanate (TDI). The prepolymers were chain extended with *N*-methyldiethanolamine (N-MDEA) to form polyurethanes containing tertiary nitrogen. These polyurethanes were crosslinked with bromine terminated polyurethane, poly(urethane-imide), and poly(urethane-siloxane) through the formation of cationomers at tertiary nitrogen sites across the backbone polyurethanes.

The crosslinked cationomeric polyurethanes were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), mechanical analyses, (static and dynamic), and static contact angles measurements. FTIR spectral studies confirms the formation of bromine terminated poly(urethane-imide) and poly(urethane-siloxane), as well as quaternization of the tertiary nitrogen which leads to crosslinking. A comparison of thermal stabilities of crosslinked polymers with respect to the chemical nature of bromine terminated prepolymers (BTP) indicates improved thermal stability for poly(urethane-imide) based ABCP. Stress-strain analysis shows high elongation values for poly(urethane-siloxane) and poly(urethane-imide) based ABCPs. Dynamic mechanical analysis reveals better damping for poly(urethane-siloxane) based AB crosslinked polymers.

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Key Words: Chain extended; Poly(urethane-imide); Poly(urethane-siloxane); Damping; AB crosslinked polymers.

INTRODUCTION

Polyurethanes are a versatile class of materials, their end applications dictate the structure and morphology during synthesis. From the prepolymer stage through chain extension and in the required cases of final crosslinking, there are innumerous ways to influence final characteristics of the polyurethanes [1].

Crosslinked networks are obtained through ionic crosslinking and the different approaches produce cationic [2-4], anionic [5-7] and Zwitter ionic [8-10] polyurethanes. These networks find a variety of applications as coatings, adhesives, shoe soles, and vibration damping materials.

Ionomers are a specific class of ion containing polymers which typically possess less than 10 mol% of ionic groups attached to a polymer backbone. Those polymers with higher ionic groups are classified as polyelectrolytes [11, 12]. The combination of low ionic groups and low polarity backbone results in a class of polymeric materials which are of scientific, technological, and commercial interest [13-15].

The concept of polyurethane ionomers arose from the extension of the ionic polymer field to polyurethanes. Introduction of ionic functionality display dramatic changes in physico-chemical properties due to strong interactions of ionic moieties [16] compared to the parent polymers which do not have ionic groups. Blocked ionomers [17] in which one of the blocks is ionic, have been reported to show a greater driving force for phase separation than nonionic system. The introduction of ionic groups in the polyurethane significally increases the phase separation, yielding products of superior properties. Polyurethane cationomers are prepared by the synthesis of polyurethanes containing potential sites for functionalization. They are prepared using isocyanate terminated prepolymers and an ionic diol at the chain extension stage or by post modification of a preformed polyurethane.

AB crosslinked polymers (ABCP) [18-25] refer to structures in which polymer A is bonded to polymer B at both ends or at various points along the main chain [19]. Although bonded primarily to polymer B, polymer A is not crosslinked to itself. These systems having improved physical properties are best studied for controlling vibration and noise [26-29].

Chain extenders containing polymers exhibit interesting properties in that the tertiary nitrogen can be quaternized to prepare ionic polymers [30, 31].

In this paper, we report the synthesis and characterization of cationomeric AB crosslinked polymers prepared by crosslinking chain extended polyurethane containing tertiary nitrogen atom with bromine terminated polyurethane, poly(urethane-imide), and poly(urethane-siloxane), respectively. Studies have been done to obtain information about the thermal and mechanical properties of crosslinked networks.

EXPERIMENTAL

Analytical grade N,N′-dimethylformamide (DMF) (SD Fine Chem., India) was vacuum distilled and middle portions were used after storing over a type 4 Å molecular sieves. Dibutyltindilaurate (DBTDL),1,4-diazabicyclo(2.2.2)octane, 98% (DABCO), a mixture of 80% 2,4-and 20% 2,6-tolylene diisocyanate (TDI), pyromelltic dianhydride (PMDA) (Aldrich, USA) and N-methyldiethanolamine (NMDEA) (Sisco, India), were used as received. Poly(tetramethylene oxide)glycol of molecular weight 1000 ($PTMG_{1000}$) (Aldrich, USA) was used after drying at 105° under vacuum for 4 hours. 2-Bromoethanol (Aldrich, USA), distilled and stored over type 4 Å molecular sieves, was used. Bis(hydroxypropyl)tetramethyldisiloxane was prepared from 1,1,3,3-tetramethyldisiloxane as reported earlier [32]. All other chemicals were analytical grade and used as received.

Synthesis of Chain-Extended Polyurethane A

Poly(tetramethylene oxide)glycol ($PTMG_{1000}$) (0.02M) was added dropwise to TDI (0.04 M) with stirring in a 250 ml three necked round bottom flask, kept in an oil bath at 40°C in nitrogen atmosphere for 1 hour. The temperature was then raised to 70°C and the reaction was allowed to proceed till the isocyanate content reached half the initial value (as determined by dibutylamine titration). The chain extender, NMDEA (0.02 M) in 20 ml DMF was added dropwise. 0.01 g of DBTDL catalyst was added and the reaction was allowed to proceed for 4 hours

Synthesis of Bromine Terminated Prepolymer

Polyurethane Based Prepolymer B(I)

Isocyanate-terminated prepolymer was prepared by the above procedure in the mole ratio (polyol/TDI = 0.01/0.02) and end-capped by the dropwise addition of 2-bromoethanol (0.02 M). Then, 0.01 g of DBTDL catalyst was added, at 70°C and the reaction was allowed to go to completion as confirmed by FTIR by the disappearance of isocyanate peak.

Poly(Urethane-Imide) Based Prepolymer B(II)

The isocyanate-terminated prepolymer was prepared by the above procedure, and 0.01 mol of PMDA in 10 ml N-methyl pyrrolidone (NMP) and a catalytic amount of DABCO were added. The mixture was stirred at 125°C until carbon dioxide evolution ceased. The temperature was reduced to 70°C, and the isocyanate-terminated poly(urethane-imide) was end-capped by a dropwise addition of 2-bromoethanol (0.02M). 0.01g of DBTDL catalyst was then added and the reaction was allowed finish as confirmed by FTIR.

Polyurethane Siloxane Based Prepolymer B(III)

The isocyanate-terminated prepolymer was prepared by the above procedure, and 0.01 mol of bis(hydroxypropyl)-tetramethyldisiloxane was added at 70°C and stirred for 4 hours. This isocyanate-terminated poly(urethane-siloxane) prepolymer was end-capped by the dropwise addition of 2-bromoethanol (0.02M). Then 0.01g of the DBTDL catalyst was added and the reaction was allowed to go to completion as confirmed by FTIR.

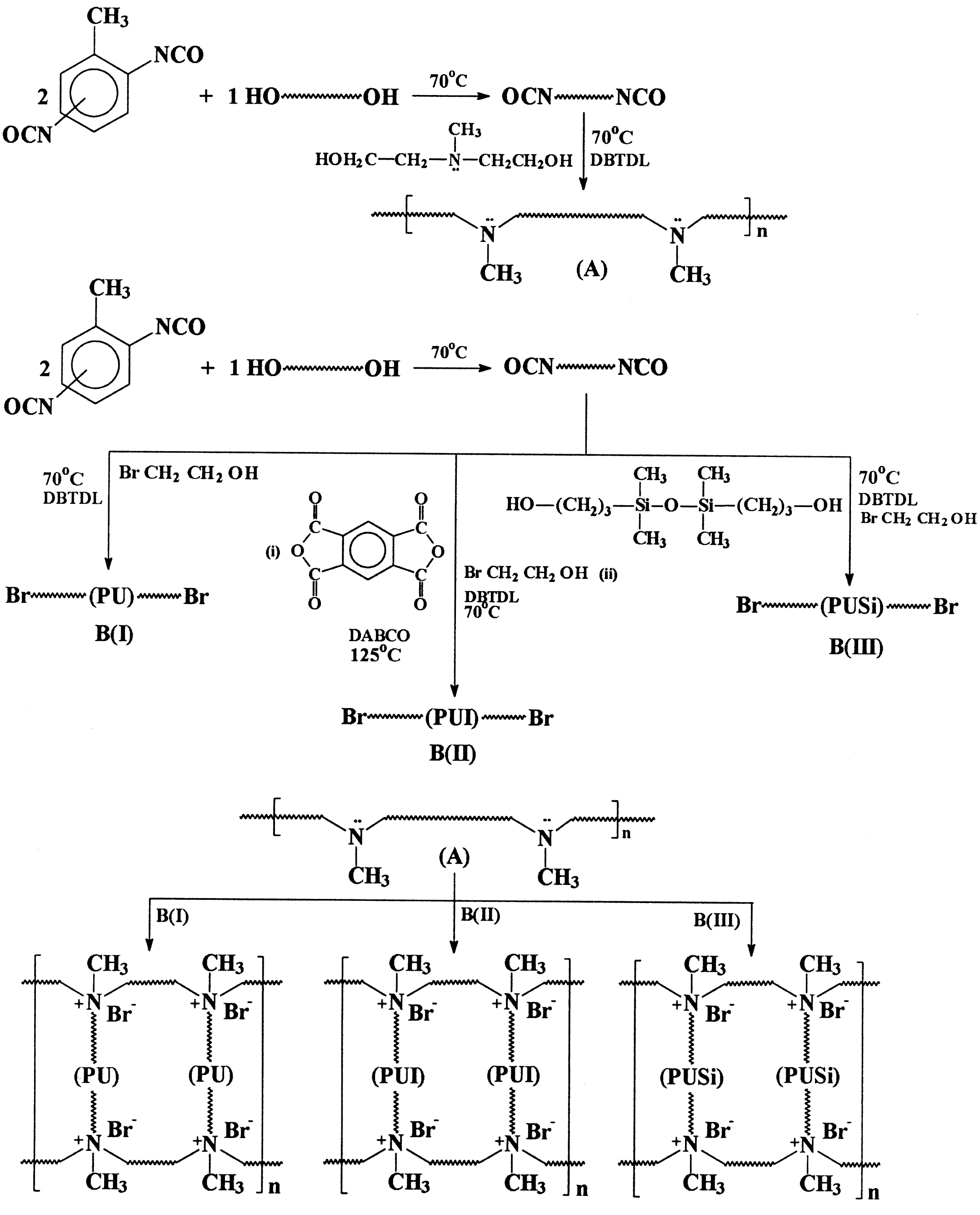
Synthesis of ABCPs

The chain extended polyurethane (A) was mixed with each bromine-terminated prepolymer, namely polyurethane B(I), poly(urethane-imide) B(II), and poly(urethane-siloxane) B(III) in the weight ratio of 1:1, stirred for 10 minutes, and cast over a silicon trough. The solvent was evaporated at 60°C to give cationomeric AB crosslinked polymers, which were vacuum-dried at 60°C to remove the solvent completely. The steps involved in preparation of cationomeric ABCPs are presented in Scheme 1.

Measurements

Contact angle measurements for ABCP's cast as thin films over a silicon trough were characterized for surface property. Liquids used for the contact angle measurements included H-bonding and non H-bonding compounds covering a wide range of surface tension at 20°C. The static contact angles for these liquids were estimated on the polyurethane samples using a goniometer telescope (home built). Each contact angle recorded is that which was duplicated within the first 10-20 seconds after slowly leading the sessile drop over a fresh surface region. All measurements were made with the liquids equilibrated at 20% and 60% relative humidity.

The Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Avatar 360. The molecular weights of the polymer were determined by using a Waters Associates gel permeation chromatography (GPC) equipped with a Waters 410 RI detector, the solvent being DMF stabilized with 0.01% of LiBr. The molecular weight was calibrated using polystyrene standards. Thermal analysis was carried out using a DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/min. in a nitrogen atmosphere. Strips ($20 \times 10 \times 2.0$ mm^3) of each material were examined in a DMA 2980, Dynamic mechanical analyzer, TA instruments, USA, in the tensile mode (tension film) over a temperature range of -100°C to +100°C at a heating rate of 5°C/min., strain amplitude of 20 µm and a frequency of 1 Hz. The samples (5 specimens each) of stress-strain analysis were cut at a geometry of 40 mm × 10 mm and kept for conditioning at a temperature 20 ± 2°C and relative humidity of 65 ± 2% for 24 hours before testing. The tensile testing


2
OCN
CH3
NCO
+ 1 HO~~OH
70°C
OCN~~NCO
HOH2C—CH2—N—CH2CH2OH
CH3
70°C
DBTDL
N
CH3
(A)
n
Br CH2 CH2 OH
DBTDL
(i)
DABCO
125°C
Br CH2 CH2 OH (ii)
DBTDL
HO—(CH2)3—Si—O—Si—(CH2)3—OH
Br~~(PU)~~Br
B(I)
Br~~(PUI)~~Br
B(II)
Br~~(PUSi)~~Br
B(III)
+N
Br-
(PU)
(PUI)
(PUSi)

Scheme 1.

was done using an Instron Universal Testing machine model 4501 at an elongation rate of 100 mm/min. The specimens conformed to a ASTM standard.

RESULTS AND DISCUSSION

As shown in Scheme 1, chain extended polyurethane A and bromine-terminated prepolymers B are synthesized and GPC results are given in Table 1.

Contact Angle Measurements

Surface mediated incompatibility of material is traced to hydrophilic/hydrophobic balance [33]. When both hydrophobic and hydrophilic chains are grafted onto polyurethane, it should be possible to a certain extent to create a hydrophobic rich or hydrophilic rich surface. The surface properties are closely related to the surface tension γ_s. Estimation of γ_s of the polymer films has been made by a contact angle method [34, 35] by measuring the contact angle (q) of various organic liquids on the polymer films. The plot cos q vs. surface tension of the liquids g_L was linear. The value critical surface tension g_c at cos q = 1 was obtained by extrapolating the straight line.

In this work, the contact angles of polyurethane, polyurethane copolymers based on poly(urethane-imide) and poly(urethane-siloxane) have been measured. The critical surface tension values γ_C of crosslinked films have been evaluated by a Zisman plot (Figure 1) and related to the functional groups on the surface of these polymers. Three cationomeric crosslinked polymers have been investigated. All the liquids used in contact angle measurements were of high purity and behaved reliably and all films examined by the contact angle method were investigated in duplicate using independently prepared samples. The measured contact angles were reproducible within 1° (Table 2). Standard deviation was ± 0.01° for all measurements. Glycol behaved abnormally on all the films investigated here, and this could be due to the fact that glycol is hygroscopic and uptake of some water in this liquid during measurement could increase its surface tension leading to this anomaly. There seems to be a clear separation between H-bonding and non

Table 1. GPC Results for Chain Extended Polyurethane (A) and Bromine Terminated Prepolymers (B)

Polymer Code	$Mn \times 10^{-3}$	$Mw \times 10^{-3}$	Mw/Mn
A	31.5	44.1	1.4
BI	1.58	2.38	1.5
BII	3.15	5.0	1.6
BIII	3.18	5.1	1.6

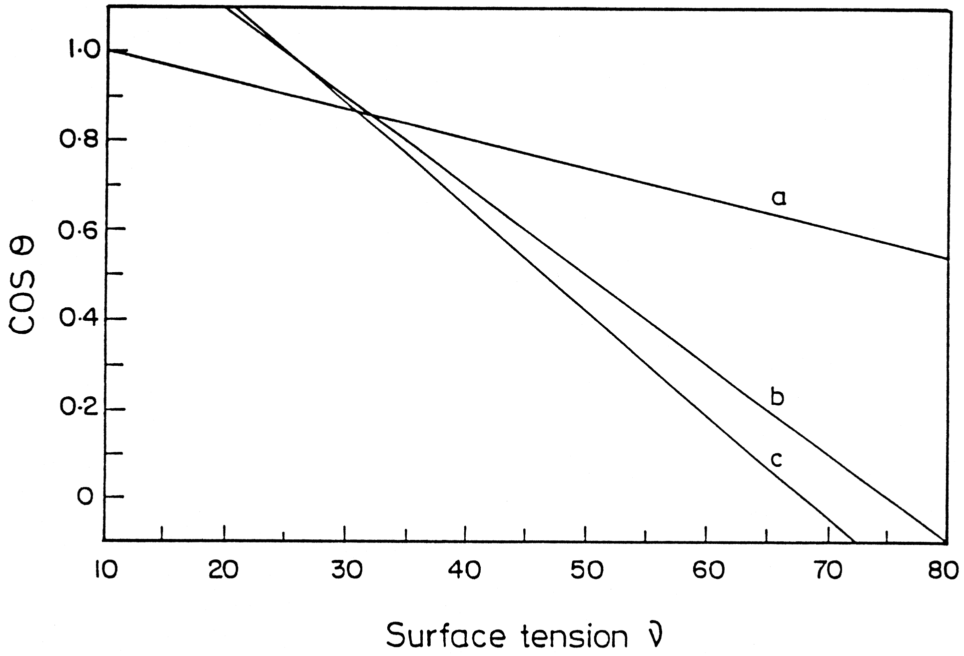


Figure 1. Contact angle measurements of ABCP's based on (a) PU; (b) PU-I; (c) PU-Si.

H-bonding liquids as seen from the plot of cos θ vs γ_C values for the films which showed a decrease in critical surface tension values.

Solvent Extraction

All the ABCPs were subjected to solvent extraction for 72 hours in a soxhlet apparatus using THF as the solvent. A very low weight loss percentage (2-4%) in

Table 2. Contact Angle Measurements for Cationomeric AB Crosslinked Polymers

Liquids	Surface Tension MN/m	AB Crosslinked Polymers PU based	PU-I based	PU-Si based
Ethyl acetate	26.5	0.93	1	1
Hexadecane	27.8	0.99	1	1
Xylene	29.0	0.75	1	1
Glycol	47.7	0.82	0.40	0.25
Glycerol	63.4	0.57	0.13	0.10
Water	72.8	0.63	0.20	0
ν_C (CST) mN/m	—	10.64	24.64	24.64

all three cases may be due to effective quaternization of tertiary nitrogen atom leading to crosslinking.

Fourier Transform Infrared Spectroscopic Analysis

The FTIR spectra, of crosslinked cationomeric polymers (Figure 2), show characteristic peaks due to urethane **>NH** around 3300 cm^{-1} and **>C=O** stretching of urethane linkage around 1750 cm^{-1}. The symmetric and asymmetric stretching of **$-CH_2-$** of $PTMG_{1000}$ is observed between 3000 and 2750 cm^{-1}. The polyurethane cationomers exhibit a strong absorption around 1640 cm^{-1} as reported in several references [36-38], which is specifically due to **$>N^+$—C**. The peak around 1540 cm^{-1} is due to **C–N** stretching and **>NH** deformation. The **>C–O–C<** and **–Si–O–Si–** stretching of polyurethane and poly(urethane-siloxane) are observed as broad peaks at 1100 cm^{-1} showing that the ether group is involved in H-bonding. In the case of poly(urethane-imide) based ABCP, in addition to urethane peaks, characteristics imide absorption [39, 40] at 1774, 1724, 1360, and 723 cm^{-1} were observed which confirm the formation of poly(urethane-imide). Poly(urethane-siloxane) based ABCP showed broad absorption at 1223 cm^{-1} corresponding to **$Si-CH_2$** and **$Si-CH_3$**

Thermal Studies

Thermal stability of the crosslinked polymers were evaluated by Thermogravimetric Analysis (TGA). The TGA curves of ABCPs based on polyurethane, poly(urethane-siloxane), and poly(urethane-imide) are given in Figure 3. The polymers showed no significant weight loss up to 300°C, which is higher than that for conventional polyurethanes. Thus, crosslinking has led to improved thermal stability. Comparing the three systems, poly(urethane-imide) based ABCP having imide linkage with main chain exhibit higher thermal stability than the other systems.

Dynamic Mechanical Analysis

The loss tangent curves of cationomeric polyurethane and polyurethane copolymer based ABCPs are presented in Figure 4 and the data are given in Table 3. The glass transition temperature (T_g) was measured from the peak of tan δ curve. Even though all three systems exhibited nearly the same glass transition temperature, the tan δ values were different. The highest value of tan δ exhibited by poly(urethane-silioxane) based ABCP is a direct manifestation of the flexibility of **–Si–O–Si–** incorporated in the chain extension stage, while a comparatively low value for poly(urethane-imide) based ABCP reflects the rigidity of imide linkage. Polyurethane based ABCP showed an intermediate value of tan δ. Single tran-

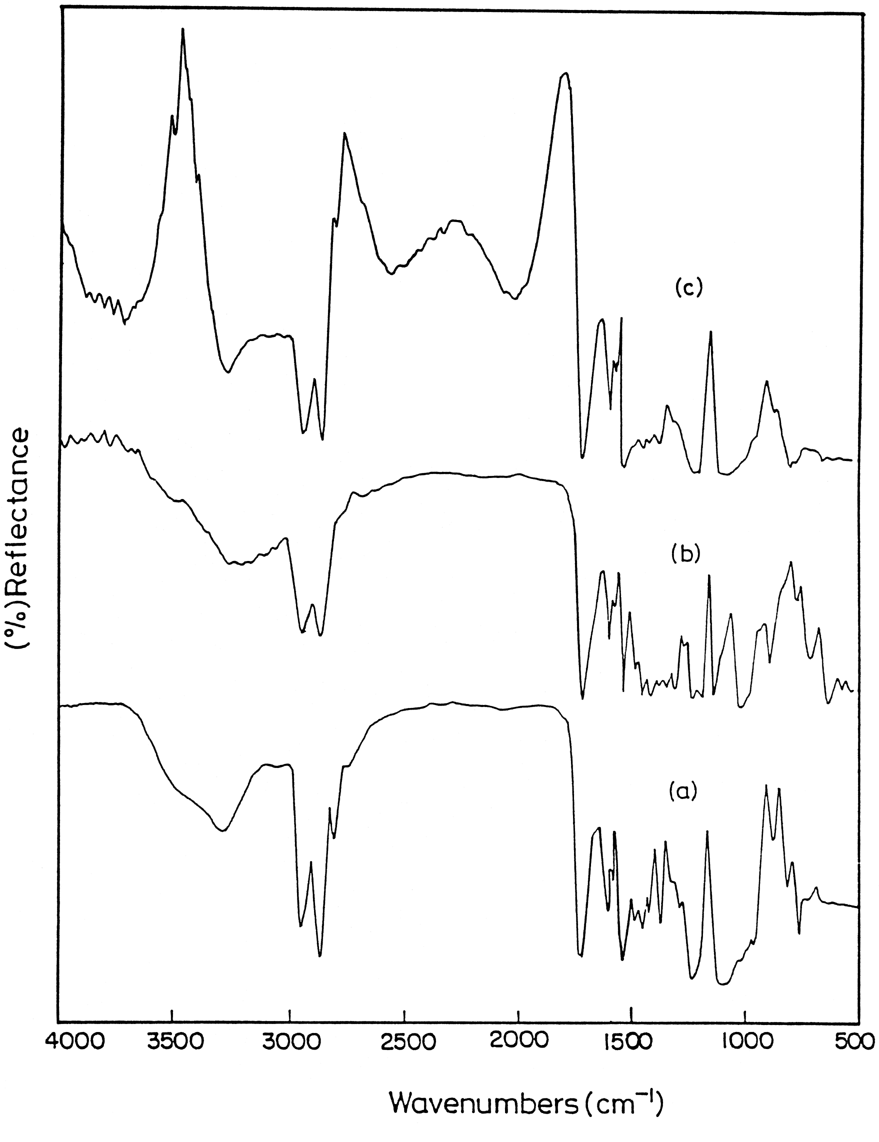


Figure 2. FT-IR spectra of ABCP's Based on (a) PU; (b) PU-I; (c) PU-Si.

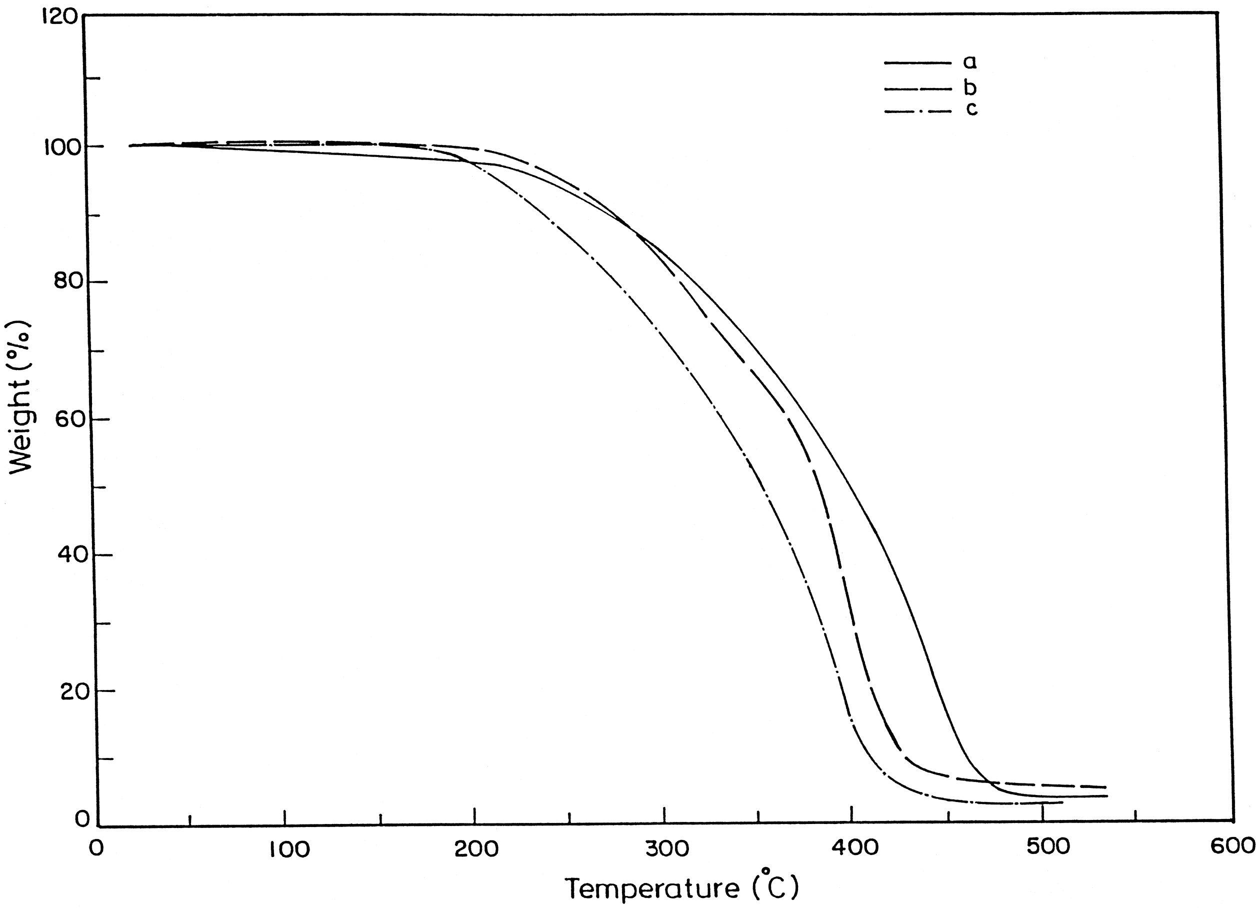


Figure 3. TGA thermograms of ABCP's based on (a) PU; (b) PU-I; (c) PU-Si.

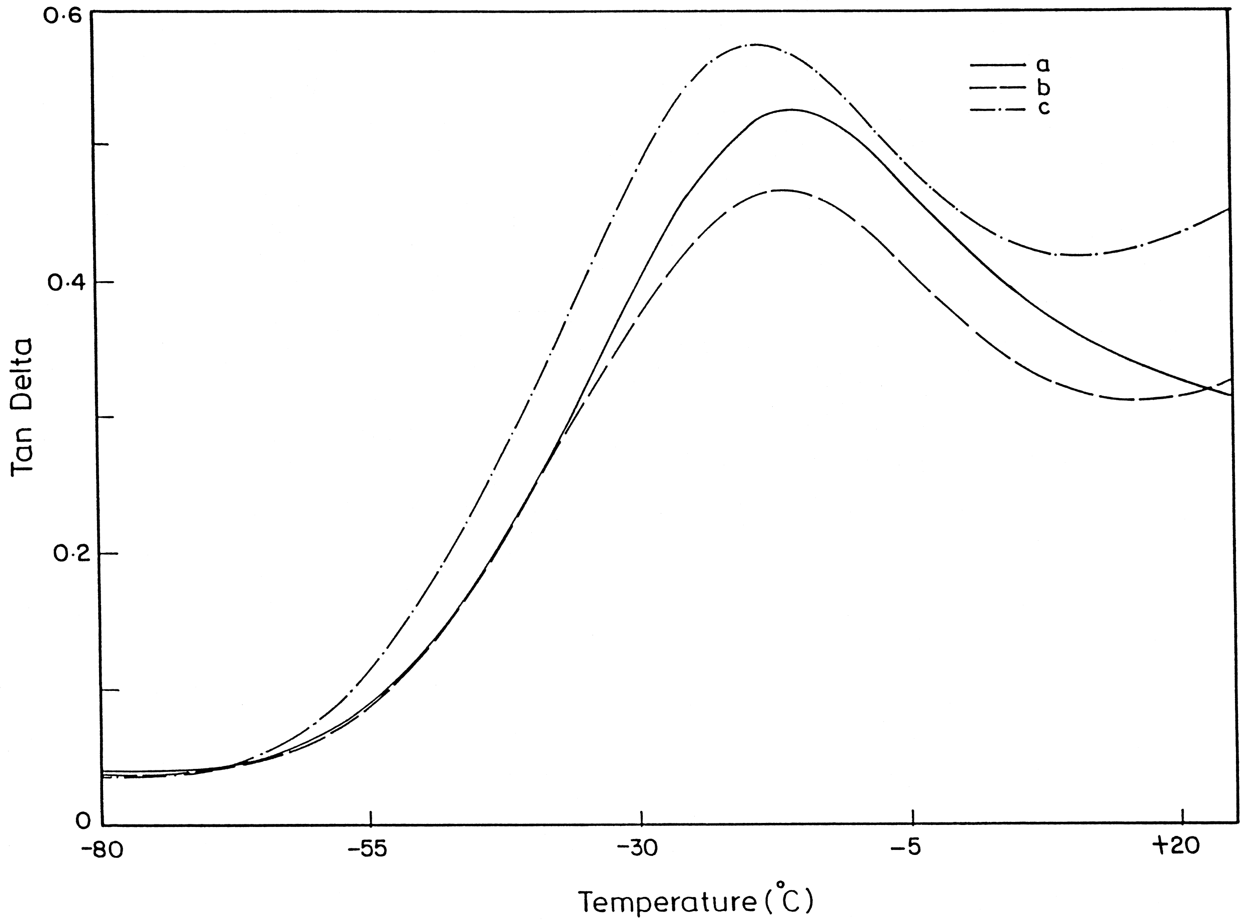


Figure 4. Plot of Tan δ vs. temperature of ABC”P’s based on (a) PU; (b) PU-I, (c) PU-Si.

Table 3. Mechanical Properties of ABCPs

Polymer code	Max. Tensile Strength Mpa	Elongation (%)	Tan δ	T_g (°C)
PU	2.3	913	0.53	−15
PU-I	7.2	2213	0.47	−19
PU-Si	1.3	2771	0.58	−21

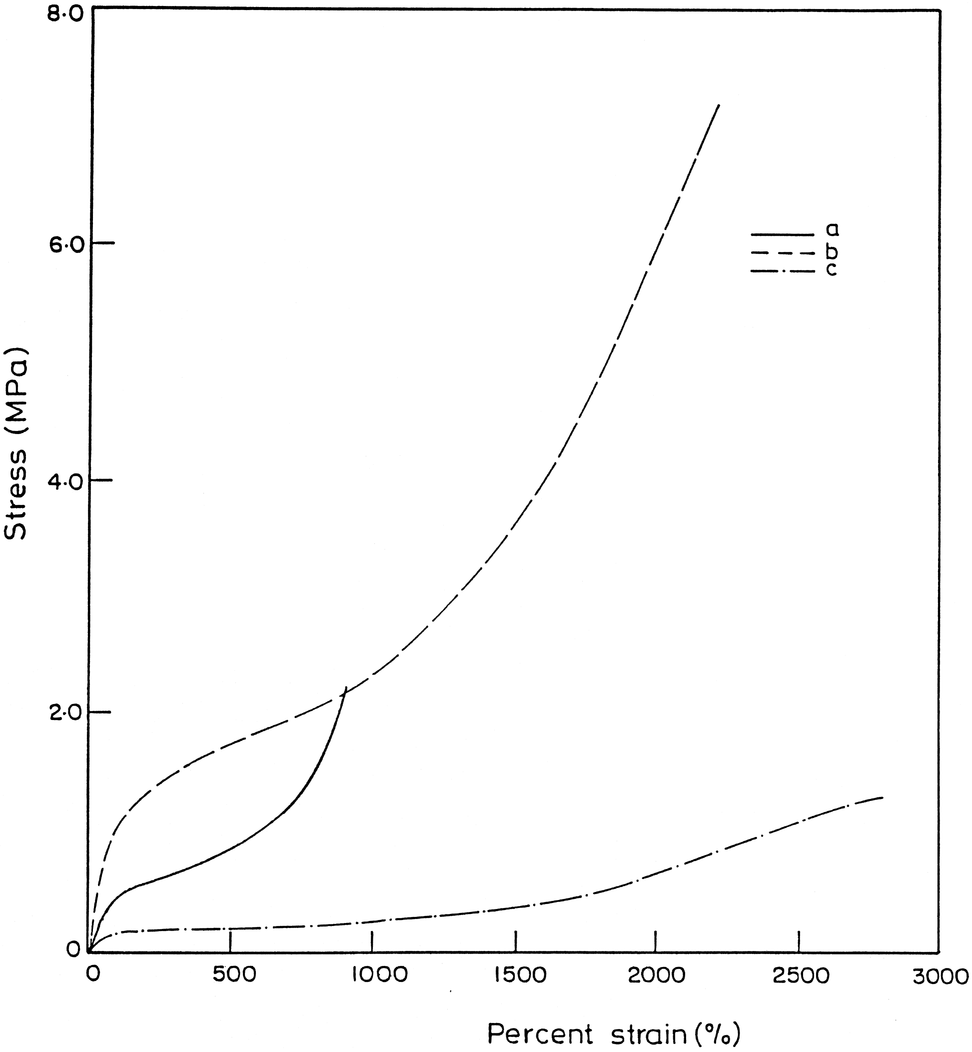


Figure 5. Stress-Strain measurements of ABCP's based on (a) PU; (b) PU-I; (c) PU-Si.

sition in all the three damping curves indicates the compatibility of two polymer chains namely chain extended polyurethane (A) and bromine terminated polymer chains (B). The broad damping peaks reflect good damping behavior of the crosslinked networks.

Tensile Testing

Stress-strain curves of the three systems are given in Figure 5, and results are tabulated in Table 3. Polyurethane imide ABCP exhibited a high value of tensile strength which indicates the contribution of a rigid imide group to the additional strength. Though the molecular weight of poly(urethane-siloxane) was comparable to that of poly(urethane-imide), the ABCP based on it showed much less tensile strength and a higher elongation at break, which is due to the flexible nature of **-Si-O-Si-** linkage. Polyurethane based ABCP shows an intermediate value of tensile strength but lower elongation. This may be due to the shorter polymer chains B (Table 1) (bromine terminated polymer), while the polymer chains 'B' are much longer due to chain extension in the case of polyurethane siloxane and polyurethane imide based ABCPs. One can observe from the curves that all the systems behave as thermoplastic elastomers with yield point.

CONCLUSION

Poly(urethane-imide) based ABCP exhibited improved thermal stability and higher tensile strength. Dynamic mechanical analysis revealed good damping property of poly(urethane-siloxane) based ABCPs. The crosslinked polymers clearly modulated the surface polarity as well as other related interactions.

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