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ORIGINAL PAPER

Mechanical properties and fractography of block copolymers based on NR and MDI-based polyurethanes

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Abstract Five series of block copolymers were synthesized from hydroxyl-terminated liquid natural rubber (HTNR) and polyurethane (PU) oligomers, from various diols and diphenyl methane-4,4′-diisocyanate (MDI). They were characterized by mechanical testing and fracture studies (SEM analysis). The block copolymer characteristics were assessed on the basis of the composition and the type of extender diols. Mechanical properties were found to be strongly dependent on the copolymer composition in all the series. Tensile properties were found to improve with the hard segment content. At low hard segment content samples resemble flexible elastomers whereas at high hard segment content they behave as rigid plastics. Where bisphenol A (BPA) is used as the extender diol sample rigidity was higher compared to the samples with aliphatic diols which is attributed to the presence of aromatic ring system in the former samples. Fracture mechanism was found to vary from ductile fracture to rigid and brittle fracture as the hard segment content increased. Fractography also shows the presence of some beads disposed on the sample surface which could be the uncombined polyurethane homopolymer fractions.

Keywords Natural rubber · Polyurethanes · Block copolymers · Fractography · Mechanical properties · SEM · Phase segregation

Introduction

Block copolymers and their heterophase morphology offer scope for studying the structure–property relation present in this class of block copolymers. The studies on

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microphase segregation of the hard and the soft segments [1–3] have ascribed a wide range of properties for the block copolymers on this basis [4, 5]. Besides, other factors such as soft segment functionality, molecular weight of the segments, glass transition temperature of the soft segment, compositional heterogeneity, degree of phase mixing, morphology, etc. also accounted for the characteristic properties of the block copolymers. However, it has been argued that a certain level of phase mixing is also necessary for the polymers to exhibit improved properties [6]. The conventional polyurethane elastomers with polyester/polyether soft segments and polyurethane hard segments show higher properties since both the blocks involve in intermolecular interactions which obviously lead to interphase mixing [7, 8]. On the other hand block copolymers derived from non-polar polydiene soft segment and polar hard segment give completely phase separated systems [7, 9]. However, their properties seem to be slightly inferior to the polyurethane elastomers. This must be due to the absence of phase interaction. Block copolymers based on polyisobutylene [10], polybutadiene [11], polydimethyl siloxane [12] and polymyrcene [13] are well known examples for this category of materials. Studies on these block copolymers revealed that microphase separation in block copolymers is influenced by factors such as differential solubility parameter, segment length, crystallinity of either segment, compositional heterogeneity of the segments, intermolecular interactions, etc. Superior hydrolytic stability, higher oxidative stability, improved low temperature flexibility and variations in gas permeability are certain advantages of this type of materials. Recent example to this category of block copolymers is those based on liquid natural rubber and polyurethane oligomers [14–18]. The latter constituent is the hard phase and it has been derived from a dissymmetric diisocyanate, viz., 2,4-toluene diisocyanate on reaction with a chain extender diol such as propylene glycol, 1,3-butane diol or bisphenol A. However, it is interesting to follow the effect of symmetric diisocyanate such as MDI (4,4′-diphenyl methane diisocyanate) on the properties of this group of block copolymers. Regarding this study, the synthesis of five series of block copolymers [20] from NR and MDI-based polyurethanes and their thermal properties were reported in a previous article. As a sequel to that study mechanical properties and the fracture mechanism of these five series of block copolymers are presented in this article.

Experimental

Materials

Natural crumb rubber (ISNR-5) with weight average molecular weight of 820,000, intrinsic viscosity in benzene at 30 °C = 4.45 dL/g and Wallace plasticity, $\rho^\circ = 39.0$ was supplied by Rubber Research Institute of India, Kottayam. Hydrogen peroxide (30% aqueous solution was used as such. Toluene (reagent grade, E. Merk, India) and methanol (E. Merck, India) were used without further purification. Diphenylmethane-4,4′-diisocyanate (MDI, Synthesis grade, Merck, Germany) was used as such without further purification. Ethylene glycol (EG, E. Merck, India), propylene glycol (PG, E. Merck, India), 1,3-butanediol (1,3-BDO, Merck, Germany) and 1,4-butanediol (1,4-BDO, Merck, Germany) were dried with anhydrous calcium oxide and then distilled under reduced pressure. Bisphenol-A (BPA, Merck, Germany) was dried under vacuum before use. Dibutyl tin dilaurate (DBTL), Fluka, Switzerland was used without further purification Tetrahydrofuran (THF, reagent grate, BDH, India) was dried by sodium wire and distilled before use. Chloroform (Synthesis grade, E. Merck, India) was used after distillation.

Hydroxyl-terminated liquid natural rubber (HTNR) of number average molecular weight 4,000 with OH value 1.94 was prepared in our laboratory by the photochemical degradation of natural rubber as per prereported procedure [19]. It was precipitated thrice from toluene using methanol and dried at 70–80 °C under vacuum.

Synthesis of block copolymer was carried out as per prereported procedure [20]. The synthesis has been carried out in five series based on the type of chain extender used, viz., EG, PG, 1,3-BDO, 1,4-BDO and BPA. Required stochiometric amounts of HTNR and the chain extender diol used in the synthesis are given in Table 1. The overall composition for the synthesis of various block copolymers was calculated in molar ratios of the respective reactants. For example, the overall composition for the synthesis of NR/EG (70/30) is 1.0/7.17/6.17 which is the ratio of the number of moles of HTNR, MDI and EG. The above ratio was calculated as follows on the

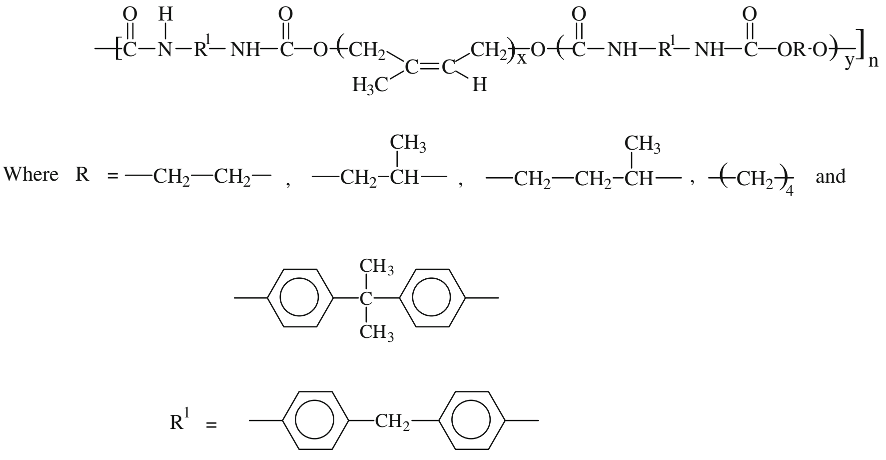
Table 1 Overall composition of NR/PU block copolymers

Sample	Molar composition HTNR/MDI/Diol	% of NR soft segment	% of PU hard segment
NR/EG (70/30)	1.0/7.17/6.17	67.3	32.6
NR/EG (60/40)	1.0/10.60/9.60	58.02	41.94
NR/EG (50/50)	1.0/15.41/14.41	48.06	51.94
NR/EG (40/60)	1.0/22.61/21.61	39.14	60.86
NR/EG (30/70)	1.0/34.63/33.62	29.51	70.49
NR/PG (70/30)	1.0/6.91/5.91	67.3	32.6
NR/PG (60/40)	1.0/10.19/9.19	58.02	41.94
NR/PG (50/50)	1.0/14.74/13.79	48.06	51.94
NR/PG (40/60)	1.0/21.69/20.68	39.14	60.86
NR/PG (30/70)	1.0/33.18/32.18	29.51	70.49
NR/BDO[a] (70/30)	1.0/6.66/5.66	67.3	32.6
NR/BDO (60/40)	1.0/9.81/8.81	58.02	41.94
NR/BDO (50/50)	1.0/14.22/13.22	48.06	51.94
NR/BDO (40/60)	1.0/20.83/19.83	39.14	60.86
NR/BDO (30/70)	1.0/31.85/30.85	29.51	70.49
NR/BPA (70/30)	1.0/5.03/4.03	67.3	32.6
NR/BPA (60/40)	1.0/7.27/6.27	58.02	41.94
NR/BPA (50/50)	1.0/10.40/9.4	48.06	51.94
NR/BPA (40/60)	1.0/15.11/14.11	39.14	60.86
NR/BPA (30/70)	1.0/22.95/21.95	39.14	60.86

[a] BDO: 1,3-BDO and 1,4-BDO

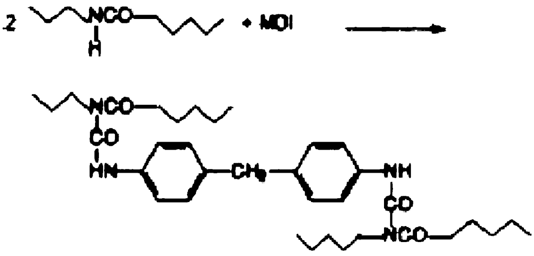
assumption that the reaction between EG and MDI is fast and instantaneous under the given reaction conditions. The number average molecular weight of HTNR was determined by gel permeation chromatography to be 4,500. Molecular mass of polyurethane required for NR/EG (70/30) is 3 × 4,500/7 = 1928.5. This mass of PU is constituted by 1928.5 × 62/(62 + 250.21) = 382.96 g or 6.17 mol of EG and 1928.5 × 250.21/(62 + 250.21)5 = 1545.53 g or 6.17 mol of MDI, where 62 and 250.21 are the molecular weight of EG and MDI, respectively. Thus, it becomes an equimolar reaction which could yield PU chains of unspecified higher molecular weight. Hence the growth of the chain is to be restricted to the required range by using one mole less MDI, i.e., 5.17. This would yield hydroxyl terminated PU chains of the required molecular weight. An additional 2 mol of MDI were required to end cap HTNR with isocyanate groups. Thus, the total number of moles of MDI required = 5.17 + 2 = 7.17 mol = 1794.00 g. Now the weight percentage of hard segment (PU) = [(1794.00 + 382.54)/(1794.00 + 382.54 + 4500)] × 100 = 32.6%. An excess of 5% of MDI (equal to 0.36 mol) was added to compensate any loss during transfer and side reactions. Similar calculation was adopted for other compositions as well.

The weight percentage of the PU content is kept constant for all series involving the different extender diols by varying the molar composition of the reactants as in Table 1. Thus, the calculated values of the polyurethane content of different samples in each series of the block copolymers work out to be 32.60, 41.94, 51.37, 60.86 and 70.49% for NR/PU (70/30), NR/PU (60/40), NR/PU (50/50), NR/PU (40/60) and NR/PU (30/70), respectively. PU stands for the polyurethanes formed from the respective extender diol and the diisocyanate. Scheme 1 shows the structure of the block copolymers. Although this scheme indicates the structure of the repeated unit in the polymer chain, the polymer seems to possess a low degree of crosslinking as observed by its insolubility but a high extent of swelling in solvents like tetrahydrofuran. The crosslinking is explained on the basis of allophanate formation as shown in Scheme 2.



Scheme 1 Structure of NR/PU block copolymers

Scheme 2 Formation of allophanate linkage in block copolymers



Polymer designation

The samples of block copolymers prepared have been designated as follows. As an example NR/EG (70/30) means that the sample contains 70% by weight of natural rubber (NR) and 30% by weight of polyurethane based on ethylene glycol and diphenyl methane diisocyanate.

Measurements

Scanning electron microscopy analysis (SEM) was done on the fracture surfaces of samples from tensile tests. The surface was sputter coated with gold and SEM analysis was done using a Hitachi model S-415 A, Scanning electron microscope. Tensile testing of the sample was done at 25 + 2 °C according to ASTM D 412-80 test method using dumb-bell shaped test pieces at a cross head speed of 50 mm/min on a Zwick 1474 Universal Testing Machine. The test pieces were punched out from the moulded sheets using a die. The thickness of the dumb-bell specimen was measured using a screw gauge having accuracy of 0.01 mm. For the measurements, a minimum of five specimens per sample were tested and average of these values were reported.

Results and discussion

The block copolymers prepared in different series were subjected to tensile testing and tensile fracture studies. The tensile curves are shown in Figs. 1, 2, 3, 4 and 5. Tensile properties are summarized in Table 2.

The shapes of tensile curves of NR/EG samples shown in Fig. 1 indicate the nature of the block copolymers. The sample with the highest hard segment content, viz., 70% gives tensile curves running very close to the stress axis. At the end of the elastic deformation the curve enters a yield region where it abruptly stops, which is a feature characteristic of a brittle material. Relatively high tensile strength (10.82 N/mm^2), small elongation at break (20%) and high Young's modulus (90 N/mm^2) lend credence to the above conclusion. As the hard segment content comes down to 60% the curve drifts away from the stress axis. The yield point is distinct and the sample deforms slightly after yielding. Tensile strength is reduced to 9.81 N/mm^2, a higher elongation at break of 33.3% and a lower

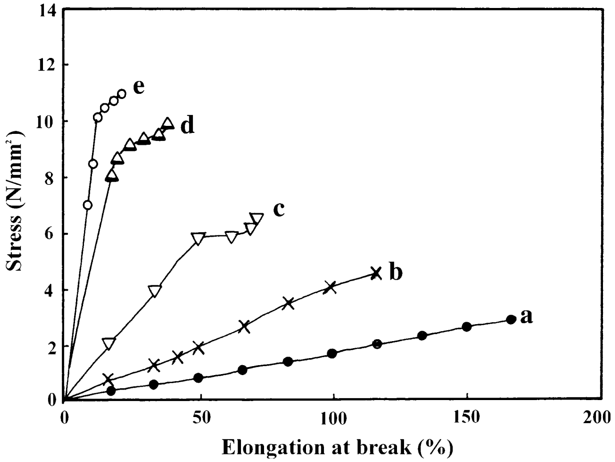


Fig. 1 Stress–strain curves of NR/EG block copolymers of (*a*) 70/30, (*b*) 60/40, (*c*) 50/50, (*d*) 40/60 and (*e*) 30/70 compositions

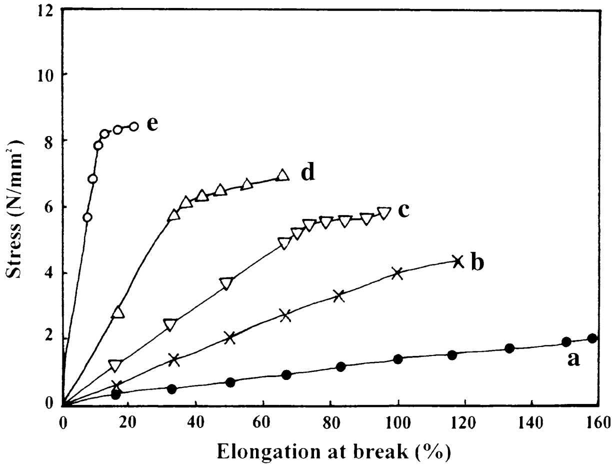


Fig. 2 Stress–strain curves of NR/PG block copolymers of (*a*) 70/30, (*b*) 60/40, (*c*) 50/50, (*d*) 40/60 and (*e*) 30/70 compositions

modulus of elasticity of 46.6 N/mm^2 are observed. The yield strength is found to be 9.3 N/mm^2, with a yield strain of 28.3%. All these features suggest that the sample behaves as a material with lower brittleness compared to the previous sample, i.e., NR/EG (30/70), due to the presence of 10% higher soft segment in the sample. Further reduction in the hard segment to 50% in NR/EG (50/50) gives a tensile curve which runs midway between the stress and the strain axis. Although the curve retains the shape of the previous curve, the lower tensile strength of 6.43 N/mm^2 and other data shown in Table 2 indicate that the sample behaves like a rigid material with improved toughness. Tensile curve of the next

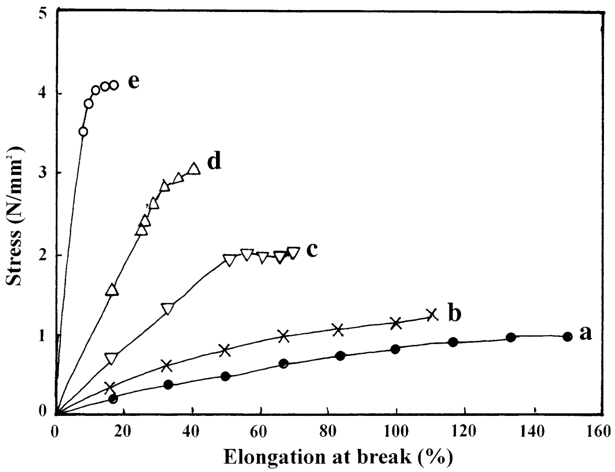


Fig. 3 Stress–strain curves of NR/1,3-BDO block copolymers of (*a*) 70/30, (*b*) 60/40, (*c*) 50/50, (*d*) 40/60 and (*e*) 30/70 compositions

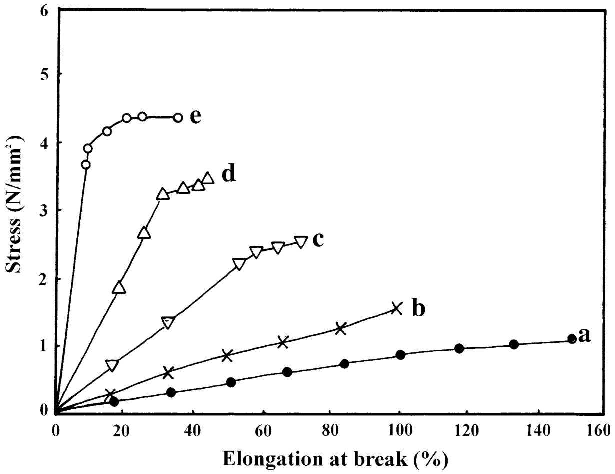


Fig. 4 Stress–strain curves of NR/1,4-BDO block copolymers of (*a*) 70/30, (*b*) 60/40, (*c*) 50/50, (*d*) 40/60 and (*e*) 30/70 compositions

sample with 40% hard segment (NR/EG 60/40) runs closer to the strain axis and the tensile data (Table 2) suggest that it behaves as a flexible elastomer, with low tensile strength (4.5 N/mm^2). The sample with 30% hard segment (NR/EG 70/30) shows a tensile curve very close to the strain axis. Its low tensile strength of 2.81 N/mm^2 and the elongation at break correspond to a very soft and flexible elastomer.

Figures 2, 3, 4 and 5 show the tensile curves of the samples in the series NR/PG, NR/1,3-BDO, NR/1,4-BDO and NR/BPA block copolymers. In each of these series, the samples of the composition 30/70, 40/60, 50/50,60/40 and 70/30 depict tensile curves which moves from stress axis to the strain axis, indicating the transition from

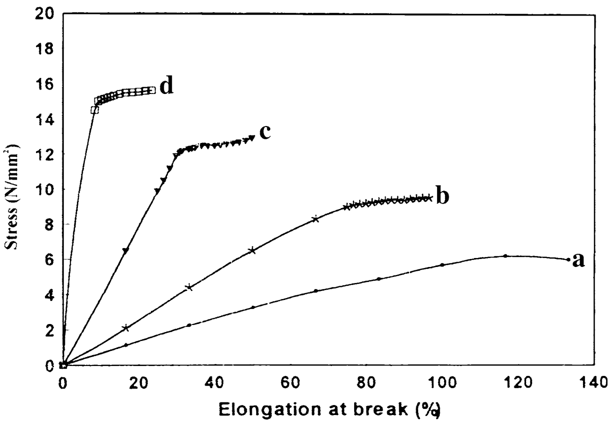


Fig. 5 Stress–strain curves of NR/BP A block copolymers of (*a*) 70/30, (*b*) 60/40, (*c*) 50/50 and (*d*) 40/60 compositions

Table 2 Tensile properties of NR/PU block copolymers

Sample designation	Tensile strength N/mm^2	Young's modulus N/mm^2	Elongation at break (%)
NR/EG (70/30)	2.8 ± 0.1	1.8 ± 0.1	166.6 ± 2
NR/EG (60/40)	4.5 ± 0.2	3.9 ± 0.2	116.6 ± 2
NR/EG (50/50)	6.4 ± 0.2	11.4 ± 0.2	71.6 ± 1
NR/EG (40/60)	9.8 ± 0.2	46.6 ± 1	33.3 ± 1
NR/EG (30/70)	10.8 ± 0.3	90.0 ± 2	20.0 ± 1
NR/PG (70/30)	2.0 ± 0.1	1.5 ± 0.1	158.3 ± 2
NR/PG (60/40)	4.4 ± 0.2	3.9 ± 0.2	118.3 ± 2
NR/PG (50/50)	5.8 ± 0.2	7.3 ± 0.2	96.6 ± 3
NR/PG (40/60)	6.9 ± 0.2	16.6 ± 0.4	66.6 ± 2
NR/PG (30/70)	8.3 ± 0.2	68.6 ± 1	22.7 ± 1
NR/1,3-BDO (70/30)	1.0 ± 0.1	0.6 ± 0.1	151.6 ± 3
NR/1,3-BDO (60/40)	1.2 ± 0.1	1.4 ± 0.1	110.0 ± 3
NR/1,3-BDO (50/50)	2.0 ± 0.1	3.9 ± 0.2	71.7 ± 2
NR/1,3-BDO (40/60)	3.0 ± 0.2	13.8 ± 0.4	43.3 ± 2
NR/1,3-BDO (30/70)	4.1 ± 0.2	42.0 ± 1	16.6 ± 1
NR/1,4-BDO (70/30)	1.1 ± 0.1	0.8 ± 0.1	150.0 ± 3
NR/1,4-BDO (60/40)	1.6 ± 0.1	1.6 ± 0.1	103.3 ± 3
NR/1,4-BDO (50/50)	2.6 ± 0.1	4.8 ± 0.2	71.6 ± 2
NR/1,4-BDO (40/60)	3.4 ± 0.2	13.1 ± 0.3	45.0 ± 2
NR/1,4-BDO (30/70)	4.4 ± 0.2	45.0 ± 2	26.7 ± 1
NR/BPA (70/30)	6.0 ± 0.2	6.3 ± 0.2	133.3 ± 3
NR/BPA (60/40)	9.5 ± 0.2	13.1 ± 0.3	96.6 ± 2
NR/BPA (50/50)	12.9 ± 0.2	40.0 ± 1	50.0 ± 2
NR/BPA (40/60)	15.6 ± 0.2	90.0 ± 2	23.3 ± 1

brittle curves to soft and flexible elastomers after passing through the intermediate states such as rubber toughened plastics, rigid elastomers, etc. The data in Table 2 also support the above conclusion. The pronounced increase in ultimate mechanical properties such as tensile strength and modulus of elasticity with hard segment content is due to change in the composition of the material from predominantly soft, at low hard segment content to hard, at high hard segment content. Besides, the hard phase serves as physical crosslinks and mechanically reinforces the NR segment providing strength, rigidity and high level cohesiveness. Whenever the hard segment content is very low, the crosslink density and the hard segment filler effect become so inadequate that the samples remain as very soft and flexible elastomers. As the hard segment content increases, the above factors would contribute more, so that the material becomes increasingly rigid. The sample behaviour changes from soft elastomers to rigid elastomers and to flexible plastics.

From Table 2 it is clear that NR/BPA series has got the highest range of tensile strength from 6.0 N/mm^2 for NR/BPA (70/30) to 15.6 N/mm^2 for NR/BPA (40/60). Below this at low range are the tensile strength of NR/EG and NR/PG, viz., 2.8 N/mm^2 for NR/EG (70/30) to 10.8 N/mm^2 for NR/EG (30/70) and 2.0 N/mm^2 for NR/PG (70/30) to 8.3 N/mm^2 for NR/PG (30/70). The tensile strength of NR 1,3-BDO and NR/1,4-BDO are in very close ranges and are below those of NR/EG and NR/PG series.

The highest tensile strength of NR/BPA series is attributed to the high rigidity due to the presence of aromatic ring systems in the hard segments which tend to reduce the chain flexibility and also due to the two methyl side groups in BPA unit which cause steric effect leading to a further reduction in flexibility of the hard segments. The lower tensile strength of all samples formed from the aliphatic chain extenders are accounted for on the basis of higher flexibility of the respective aliphatic carbon chain. However, the shorter carbon chains in EG and PG compared to 1,3-BDO and 1,4-BDO leads to lower spacing between polyurethane groups which offer the intersegmental interaction through hydrogen bonding. Thus, NR/EG and NR/PG series of block copolymers show higher tensile strength than NR/1,3-BDO and NR/1,4-BDO series. This is supported by FTIR analysis of these block copolymers. Figure 6 gives FTIR spectra of 50/50 composition of NR/1,4-BDO, NR/1,3-BDO, NR/PG and NR/EG samples. It is found that NH and C=O stretching frequencies of PU show variation which can be readily explained on the basis of extent of intersegmental interactions existing between the PU segments. The relative intensities of the bonded N–H band decreases accompanied by band broadening. Band broadening accompanied by lowering in absorption frequency of NH and C=O bands of PU in these samples suggests that hydrogen bonding occurs between the PU segments. The observed N–H stretching frequencies are 3327, 3312, 3301 and 2985 cm^{-1}, respectively. Similarly the C=O and C–O–C stretching occurs at 1722, 1715, 1710, 1706 and 1072, 1064, 1059, 1056 cm^{-1}, respectively. This indicates that the chain alignment effect is in the order NR/EG>NR/PG>NR/I,3-BDO>NR/1,4-BDO. For the same reason, the modulus of elasticity of NR/BPA series is the highest compared to NR/EG and NR/PG series, which in turn is higher than NR/1,3-BDO and NR/1,4-BDO.

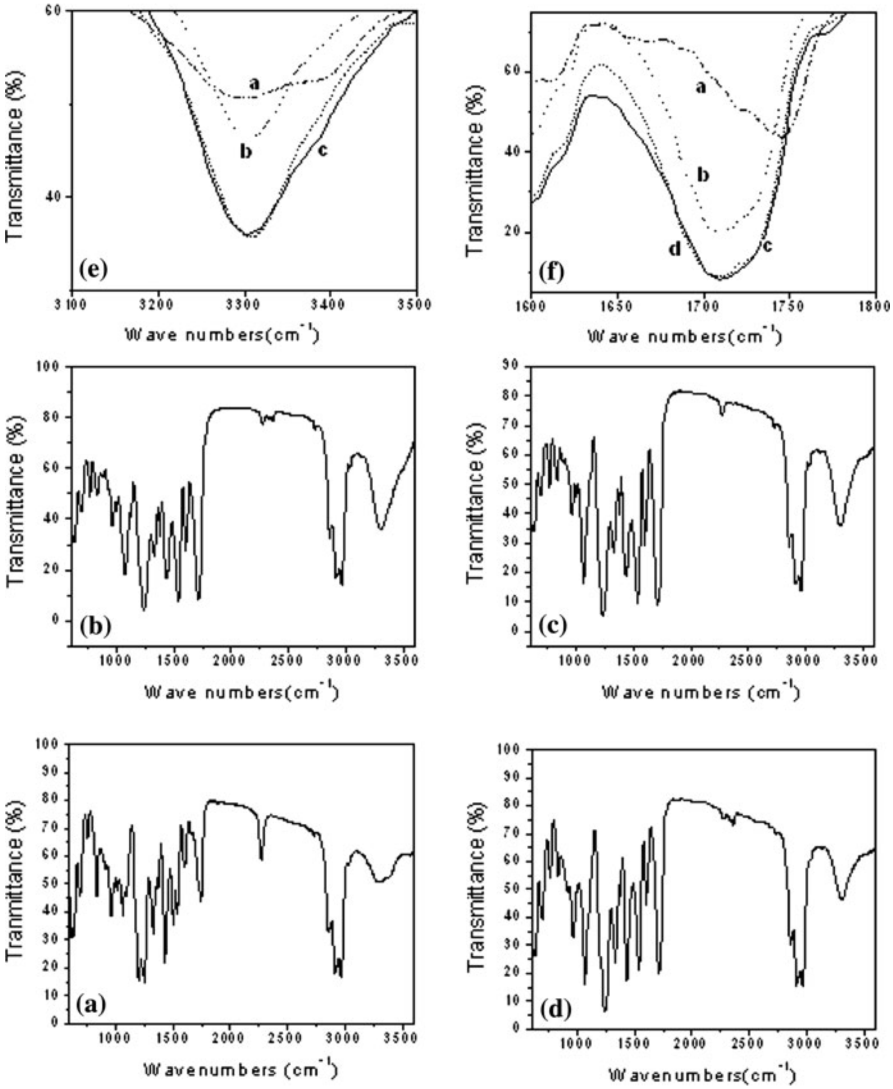


Fig. 6 FTIR spectra of the NR/PU block copolymers **a** NR/1,4-BDO, **b** NR/1,3-BDO, **c** NR/PG and **d** NR/EG (*Top*) **e** magnified N–H and **f** C=O peaks of the block copolymers

The elongation behaviour of the different series of samples as given in Table 2 is also in agreement with the general trend. In all series the elongation at break sharply decreases with an increase in the hard segment content. At all composition, the NR/BPA samples show lower values compared to the other series containing the aliphatic chain extenders. Among the latter samples, at intermediate compositions, viz., 50 & 60% of hard segment, NR/PG and NR/1,3-BDO samples show higher elongation at break compared to NR/EG & NR/1,4-BDO samples. This could be attributed to the nature of hard phase deformation that takes place beyond the yield point as follows. This hard phase deformation and further drawing of segments cause strain-induced alignment in the case of NR/EG and NR/1,4-BDO hard segments because of the linearity of the aliphatic chains involving EG and 1,4-BDO units. This alignment restricts further elongation. On the other hand, such a factor is absent in the case of PG and 1,3-BDO-based polyurethane segments due to protruding methyl side groups which would hinder the close alignment of the segments. Hence, they elongate to a greater extent showing higher values of elongation at break. As the hard segment reaches 70%, the samples show very low elongation at break of 22.7% without much variation. This reflects the highly rigid nature of the samples at these compositions at which the matrix predominantly is made up of the PU segments. The pronounced increase in the ultimate mechanical properties such as tensile strength and modulus of elasticity with hard segment content is due to the change in the composition of the material from predominantly soft at low hard segment content to hard at high hard segment content. In other words the tensile properties are influenced to a great extent by composition of the samples. This could be explained with the help of a schematic diagram as shown in Fig. 7. The Fig. 7a for the soft elastomers represents a matrix of the soft segments which are present in the amorphous state in a randomly distributed manner. Over this matrix a few hard domains are kept dispersed. The soft segments end in the hard domain where they are connected to the hard segments. Because of the high Tg and high intermolecular forces the hard segments agglomerate into hard domains which are incompatible with the rubber phase and hence remain as a dispersion in the soft matrix. As the percentage content of the hard segment is very small in the case of the soft elastomers the block copolymer structure involves lengthy soft segments and short hard segments. These short hard segments unite to form the hard domain and hence the volume fraction is very small compared to the soft matrix as represented in Fig. 7a.

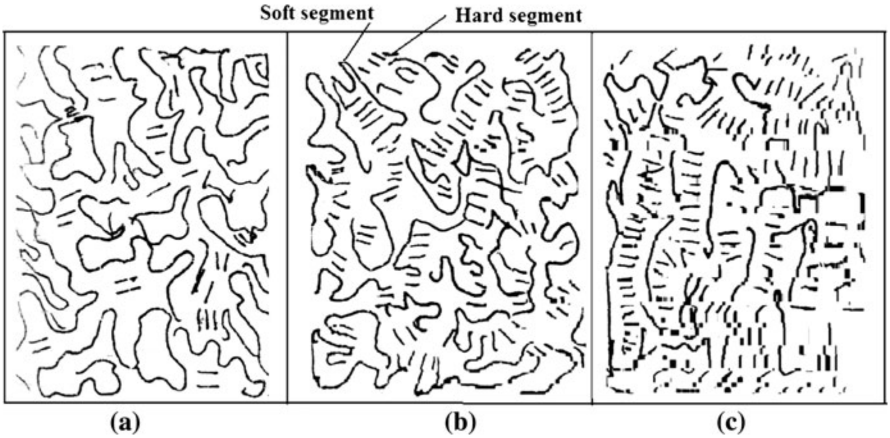


Fig. 7 Schematic diagram for the distribution of NR and PU in NR/PU block copolymers

Tensile fracture mechanism

The tensile fracture surface of selected sample of different series of block copolymers was analyzed by scanning electron microscopy. The result points to the fracture mechanism which has a bearing on the tensile properties of the different samples of a series.

The SEM micrographs of the fracture surface of samples with 70/30, 50/50 and 30/70 compositions of all the four series, viz., NR/EG, NR/PG, NR/1,4-BDO and NR/BPA are shown in Figs. 8, 9, 10 and 11. A random dispersion of beads is seen in the micrographs which could be uncombined homopolymers of the polyurethane fraction. The bead content increases in all the figures, as the proportion of the polyurethane component becomes higher. The sharp boundary between the beads and the matrix indicates incompatibility of the two phases present in the sample. The immiscibility of the polyurethane and rubber phases are supported by the large difference between the respective solubility parameter values, viz., PU formed from

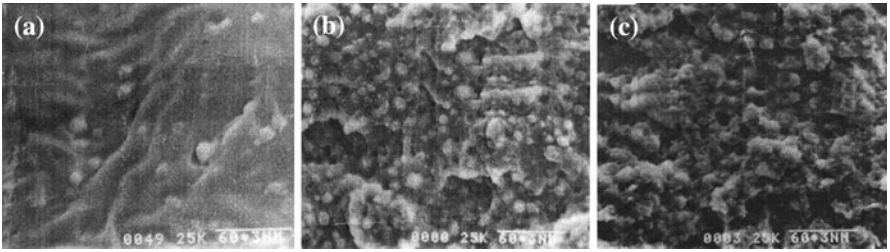


Fig. 8 Tensile fractographs of **a** NR/EG 70/30, **b** NR/EG 50/50, **c** NR/EG 30/70

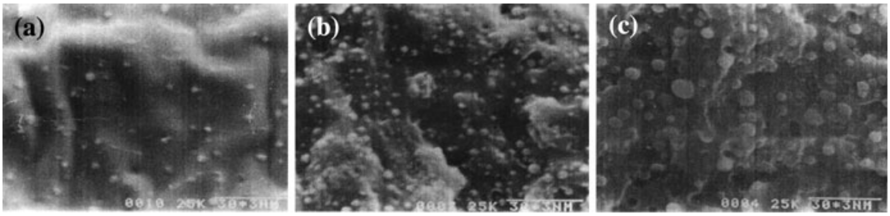


Fig. 9 Tensile fractographs of **a** NR/PG 70/30, **b** NR/PG 50/50, **c** NR/PG 30/70

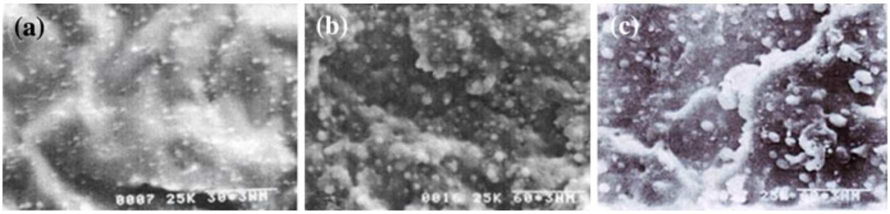


Fig. 10 Tensile fractographs of **a** NR/1,4-BDO 70/30, **b** NR/1,4-BDO 50/50, **c** NR/1,4-BDO 30/70

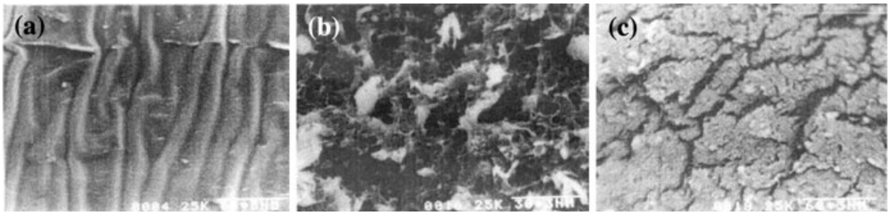


Fig. 11 Tensile fractographs of **a** NR/BPA 70/30, **b** NR/BPA 50/50, **c** NR/BPA 30/70

MDI and 1,4-BDO has the solubility parameter equal to 20.5×10^{-3} $(\mathrm{J/m^3})^{1/2}$ while NR has got a different value equal to 16.2×10^{-3} $(\mathrm{J/m^3})^{1/2}$. The voids seen on the micrograph might be formed by the pulling out of the beads during tensile fracture.

All the fractographs in Figs. 8a, 9a, 10a and 11a appear wavy and corrugated over the fracture surface, which is characteristic of a soft and flexible material undergoing ductile fracture. The fracture occurs with slow propagation of crack fronts. The stress–strain curve is also supporting these observations. The shape of tensile curve in Figs. 1, 2, 3, 4, 5 and low tensile properties of samples with 70/30 composition support this behaviour which is characteristic of a material containing high proportion of NR and low hard segment content.

Figures 8b, 9b, 10b and 11b are fractographs of the respective 50/50 composition which show tearing and ridges to a lesser extent. This conforms to the fact that higher level of polyurethane content leads to enhanced rigidity of the samples and thus fracture characteristics become that of a flexible plastic for this composition. This view is in agreement with the tensile curves of the respective samples. As the hard segment increases further to 70% the fracture surface of samples appears almost undeformed indicative of highly rigid materials (Figs. 8c, 9c, 10c, 11c). Failure of the samples occurs obviously through a rigid fracture mechanism. The PU content at this level causes high rigidity of the samples as confirmed by the value of the respective tensile curve. Thus, the change in the fracture mechanism as going from NR/PU (70/30) to (30/70) composition is well in agreement with the transition by the nature of the samples from soft and flexible elastomers to rigid plastics through intermediate flexible plastics. However, a noteworthy change is observed in the micrographs of NR/BPA samples. At low hard segment content, they show lesser waviness and at higher hard segment content shows more cracks indicative of brittle characteristics. The enhanced rigidity of these samples is the consequence of aromatic ring structures present in the respective polyurethane segments.

Conclusion

The tensile properties of all the five series of samples reveals a common trend, viz., transition from elastomers to that of a rigid plastic and through a flexible plastic as the polyurethane content increases from 30% to 70%. The fracture mechanism depends on the hard segment content but not on the type of the extender diols except in the case of BPA-based samples. As the hard segment content increases the fracture mechanism changes from ductile fracture to brittle fracture. BPA-based samples show enhanced rigidity at all compositions compared to other diols which is attributed to the aromatic ring structure. Samples with 30% hard segment in all cases exhibit ductile fracture and fractographs are characterized by a highly sheared and torn surface with ridges. Samples with intermediate hard segment content (around 50%) show fracture surface with lesser extent of tearing and ridges. This is characteristic of a rigid elastomer or flexible plastics. When the hard segment content is high, the micrograph exhibits rigid fracture surface. Tearing and shearing is not observed. The corresponding tensile curves indicate failure of the material at the yield points. This is consistent with the brittle fracture of a rigid plastic. NR/BPA samples possess the highest tensile properties among all the samples due to reduced flexibility of the PU chain. Block copolymers with aliphatic chain extender diol have relatively lower tensile properties caused by the higher flexibility of the polyurethane chains. However, among these, EG and PG-based samples were found to be better in terms of tensile properties compared to 1,3-BDO and 1,4-BDO-based samples. This is because the former diols possess shorter carbon chains which lead to lower spacing between urethane groups that causes stronger inter segmental interaction.

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