Materials Science-Poland, Vol. 23, No. 1, 2005

Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers

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Segmented block copolymers were synthesized from hydroxyl terminated liquid natural rubber (HTNR) and polyurethane oligomers (PU), formed from 1,4-butanediol (1,4-BDO) and toluene diisocyanate (TDI). The samples were synthesized in solution in two series by the one-step and two-step methods. They were characterized by spectral analysis, thermal analysis, etching studies, microscopy and mechanical testing. IR and NMR spectral data, along with etching studies, support the notion that a chemical reaction leads to block copolymerization. Differential scanning calorimetric (DSC) analysis showed a soft segment glass transition temperature between –62 °C and –63 °C and a hard segment glass transition temperature between 87 °C and 100 °C for different samples. This observation and two-stage thermal decomposition of the samples in thermogravimetric analysis (TGA) clearly indicate that the block copolymers are completely phase-segregated systems. The amorphous heterophase morphology of the samples is indicated by SEM, which shows well-defined beads of hard phase dispersed in a matrix. SEM results, along with the etching studies, revealed that the samples are systems consisting of block copolymers and some quantity of uncoupled polyurethane homopolymers in the form of beads. The homopolymer beads suggest that the efficiency of the chain extension in the present method of synthesis is slightly lower than expected. Tensile properties improved with the hard segment content in the samples. Low hard segment content leads to a flexible elastomer, while at the high one rigid plastics are formed. Intermediate compositions yielded rigid elastomers. Two-step samples showed slightly better properties compared to the one-step samples. This may be due to the systematic way by which the reaction progresses in two-step synthesis. The overall properties are found to be lower than that of the conventional polyurethane elastomers. This is attributed to the absence of phase mixing and the inability of the soft segments to crystallise under strain due to their short segments.

Key words: *segmented block copolymer; liquid natural rubber; polyurethane*

1. Introduction

The chemical modification of natural rubber has been studied for many years and a great number of derivatives have been prepared from this naturally occurring poly-

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mer. As a result of these studies, many of the physical and mechanical properties of NR, such as glass transition temperature, compatibility, gas permeability, vulcanising properties, adhesive strength, oil resistance, tensile strength etc. can be modified to a great extent.

Modification involves the liquefaction of NR by photochemical degradation and subsequent block copolymerization with thermoplastic segments such as polyurethanes [1–4] or polyethylene glycols [5]. These block copolymers were found to be completely phase-separated systems with properties ranging from soft elastomers to rubber-toughened plastics as the hard segment content increases. This variation of mechanical properties could be caused by a change in sample morphology as is discernible in studies of block copolymers of natural rubber with polyethylene glycol hard segments of higher molecular weight (4000 and 6000), being crystalline solids [5]. At low hard segment content, the NR soft segment is a continuous phase, in which the hard segment domains act as physical crosslinks and reinforcing fillers. At higher hard segment content, the block copolymers appear to be bicontinuous in nature.

Of all the diols used for chain extension in the synthesis of polyurethane-based block copolymer, 1,4-butanediol yielded the best results in terms of material properties. The present work is an attempt to synthesise and characterise a series of block copolymers of NR and polyurethane using 1,4-butanediol as a chain extender. A small part of this work has already been presented as a symposia paper [1]. This contribution is an attempt to report findings after carrying out more work on the subject involving different routs of synthesis and elaborate studies on product characterisation.

2. Experimental

2.1. Materials

Natural rubber (ISNR-5) with viscosity average molecular weight – 820,000, intrinsic viscosity in benzene at 30 °C = 44.5 cm^3/g, Wallace plasticity, P_0 = 39.0 was obtained from Rubber Research Institute of India, Kottayam. Hydrogen peroxide (30%) was supplied by Merck, India. Toluene (reagent grade, Merck, India), ethanol (reagent grade, BDH, India), toluene diisocyanate (TDI) (80/20 mixture of 2,4- and 2,6-isomers, Fluka, Switzerland), were used without further purification. 1,4-Butanediol (1,4-BDO, Fluka, Switzerland) was dehydrated with anhydrous calcium oxide and then distilled under reduced pressure. Tetrahydrofuran (THF, BDH, India) was dried using sodium wire and distilled before use. Dibutyltin dilaurate (DBTDL, Merck, Germany), was used as the catalyst without further purification. N,N’-dimethyl formamide (DMF, Merck, India), was dried by phosphorous pentoxide and distilled before use.

Hydroxyl-terminated liquid natural rubber (HTNR) of number average molecular weight 3000 was prepared in the laboratory by the photochemical degradation of natural rubber as per a reported procedure [6]. It was reprecipitated three times from toluene using methanol and dried at 70–80 °C in vacuum.

2.2. Synthesis

Segmented block copolymers with varying compositions were synthesized in solution by the one-step and two-step processes. The overall compositions of the reactants used are given in Table 1.

Table 1. The overall compositions of the one-step and two-step block copolymers

Sample	Molar composition HTNR/TDI/1,4-BDO	Per cent of hard segment
NR/1,4-BDO(70/30)-1&2	1.0/5.97/4.86	33.0
NR/1,4-BDO(60/40)-1&2	1.0/8.74/7.57	42.3
NR/1,4-BDO(50/50)-1&2	1.0/12.60/11.35	51.2
NR/1,4-BDO(40/60)-1&2	1.0/18.39/17.03	61.2
NR/1,4-BDO(30/70)-1&2	1.0/27.04/26.49	70.3

The two-step process. The stoichiometric amount of HTNR dissolved in THF (30% w/v) was placed in a flat-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel. The catalyst, DBTDL (0.03 wt. % of HTNR) was added and the solution was brought to reflux at a temperature between 70 and 80 °C. The final stoichiometric amount of TDI dissolved in THF was dropped into it over a period of 30 min followed by 90 min of reaction time to ensure the complete end-capping of HTNR. The required amount of 1,4-BDO (30% w/v) was then added and stirring was continued for 3 hours. The product was poured into a tray treated with silicon release agent and kept overnight for casting into a sheet. The sheet was then subjected to heat treatment at 70 °C for 24 hours to remove residual solvent followed by one week of aging at room temperature in a dry atmosphere.

The one-step process. The required stoichiometric amounts of HTNR and 1,4-BDO in THF (30% w/v) were placed in a flat-bottomed flask. DBTDL catalyst (0.03 wt. % of HTNR) was added and the solution was brought to reflux at a temperature between 70 and 80 °C. The final stoichiometric amount of TDI was dropped into it over a period of 45 min. Stirring and refluxing were continued for 4 hours. The viscous liquid was then cast, cured, and aged, as described in the case of two-step samples.

2.3. Extraction study

Etching studies on the block copolymer were done by keeping a known weight of the NR/1,4-BDO(50/50)-2 as a film in N,N′-dimethyl formamide for two days. The insoluble part (gel fraction) was separated by filtration. This etching process was repeated three times on the same gel fraction. It was finally dried to a constant weight.

2.4. Polymer designation

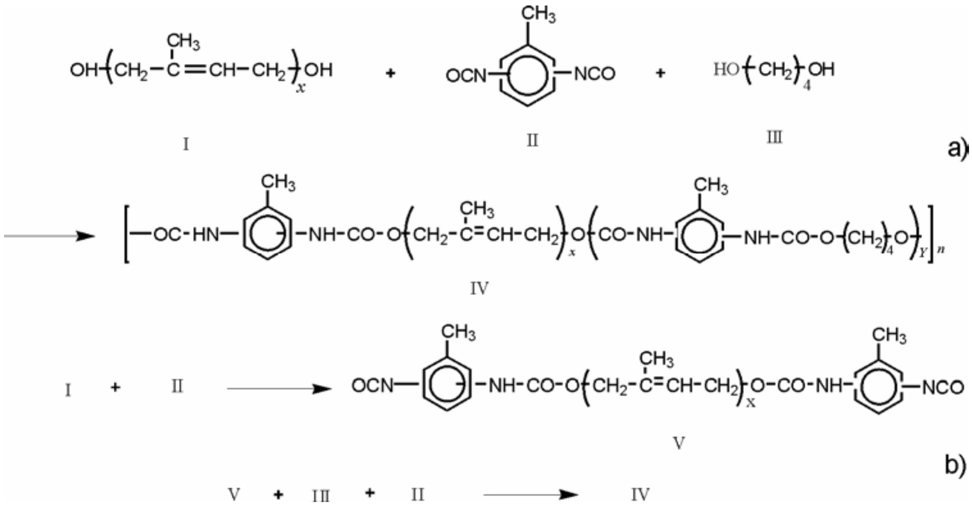
The samples were designated as follows. As an example, NR/1,4-BDO (70/30)-1 means that the sample contained around 70 wt. % of HTNR and 30 wt. % of polyurethane hard segment, based on 1,4-BDO and toluene diisocyanate. The exact compositions are given in Table 1. The number 1 given at the end indicates that the sample was made by the one-step process. The number 2 is given for samples made with the two-step process.

2.5. Measurements

Infrared spectra of the samples were recorded on a Shimadzu FTIR-8400S spectrometer (Japan). The ^{1}H NMR spectra were recorded on a Bruker AC 200 MHz NMR spectrometer and ^{13}C NMR spectra on a Bruker AC 50 MHz NMR spectrometer (USA). Differential scanning calorimetry (DSC) was performed with a Mettler Inc (TA 300) microcalorimeter (USA) and with a Perkin Elmer Delta Series DSC 7 calorimeter (USA) at a heating rate of 10 K/min. All DSC scans were first scans. Glass transition temperature was noted as the temperature corresponding to one half of the increases in heat capacity at the transition. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA 7 analyser (USA) at a scanning rate of 10 K/min. The peak temperature in the DTG curve is taken as the decomposition temperature. Stress-strain behaviour was studied on a Zwick 1474 Universal Testing Machine (Germany) as per the ASTM D 412-80 test method at a constant cross head speed of 500 mm/min. The fracture surfaces of the samples from tensile tests were sputter coated with approximately 300 Å of gold and examined on a JEOL JSM-35C scanning electron microscope (Japan) at 15 kV using magnifications of 400 to 1000× to study the morphology of the materials.

3. Results and discussion

The test samples were prepared in two series basing on different routes of synthesis – one-step and two-step processes. All syntheses were done in solution and the samples were made in sheet form by casting the reaction mixture and subsequent heat treatment and ageing as described in the previous section. The sheets do not dissolve but swell to a great extent in suitable solvents which is characteristic of a crosslinked product. This indicates that the chemical reactions continue through the casting stage, resulting in the crosslinking of the product. The probable reactions leading to the formation of the one-step and two-step products are presented in Scheme I. Reactions leading to the end-capping of HTNR, formation of polyurethane, and chain extension occur simultaneously in the case of the one-step products, whereas for two-step products end-capping occurs in the first stage, followed by chain extension with polyurethane in the second stage.



Scheme 1. Course of the reactions in one-step (a) and two-step processes (b)

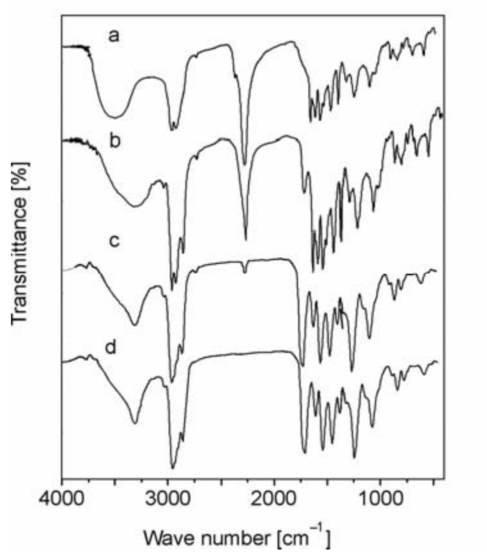


Fig. 1. IR spectra at different intervals of synthesis of NR/1,4-BDO(50/50) by one-step process: a) at the beginning, b) after one hour, c) after three hours, d) final product

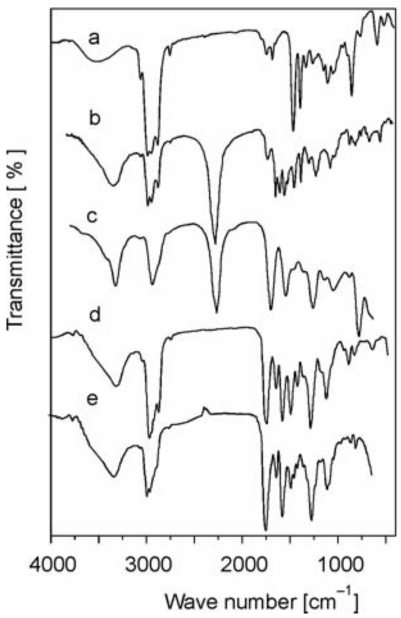


Fig. 2. IR spectra of: a) HTNR, b) NCO endcapped NR, c) PU hard segment based on TDI and 1,4-BDO, d) block copolymer by two-step process, e) etched block copolymer (gel fraction)

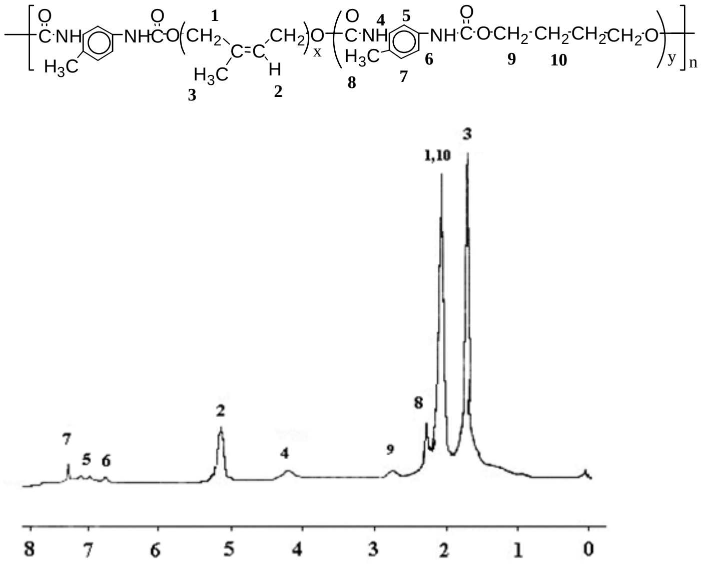


Fig. 3. ^{1}H-NMR spectrum of NR/1,4-BDO(50/50)-2

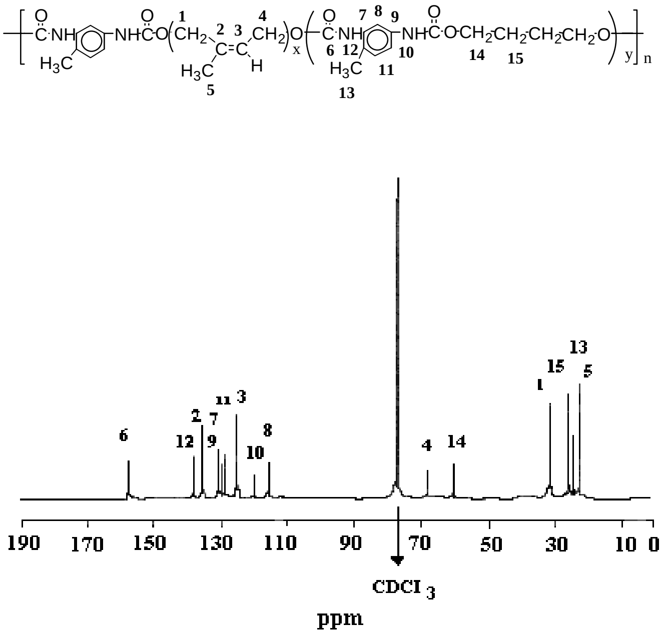


Fig. 4. ^{13}C-NMR spectrum of NR/1,4-BDO(50/50)-2

Evidence for this effect is seen in the IR spectra given in Figs. 1 and 2. Various stages in the formation of a typical one-step product are shown in Fig. 1a–d. Very high intensities of the –OH and –NCO peaks, positioned at 3470–3600 cm^{-1} and 2258 cm^{-1}

respectively, shows the presence of excess reactants at the beginning, which decreases after one hour of reaction time with the emergence of a new peak at 3314 cm^{-1} due to the =NH group (Fig. 1b). The isocyanate peak and broad hydroxyl peak almost disappear after three hours of reaction time, as seen in Fig. 1c, indicating high conversion. The cast product shows (Fig. 1d) the combined features of NR and polyurethane segments. The shoulder peak appearing at 3420 cm^{-1} in Fig. 2b, d is attributed to the non -hydrogen bonded =NH groups in polyurethane.

The series of reactions leading to the formation of the two-step product is also supported by the IR spectra in Figs. 2a–d. Fig. 2a shows the IR spectrum of liquid NR with a broad hydroxyl band at 3490–3580 cm^{-1}. End-capped liquid NR shows the presence of the =NH and isocyanate peaks as in Fig. 2b. When the chain is extended with 1,4-butanediol, this gives the final product with IR features as shown in Fig. 2d. Both the isocyanate peak and hydroxyl peak are absent in this spectrum, indicating their involvement in the reaction. The spectrum of the final product bears all the features of NR and polyurethane components as in the case of the one-step block copolymer. Figure 2c, which is a spectrum of the polyurethane reaction mixture prepared separately by reacting slightly excess TDI and 1,4-BDO, is given for comparison purposes. The proton NMR (Fig. 3) and ^{13}C NMR (Fig. 4) spectra of a typical two-step product, NR/1,4-BDO(50/50)-2, support the copolymer structure. Peak assignments are shown in the respective figures. The peaks characteristic of hard segments are found to be relatively weak in these spectra. As noted above, block copolymers were found to be insoluble in common solvents and in such cases the NMR solvent, $CDCl_3$, could solvate the NR segments and cause high mobility, whereas the solvation of PU segments becomes difficult owing to the inability of the solvent to break the high intersegmental interaction existing in them. This causes low mobility of the hard segments and renders the respective NMR peaks weak.

A notable feature of the spectral analysis is that no major shift in the absorption frequency of NR and PU segments is observed in the spectra. This indicates that intersegmental interaction between NR and PU segments is absent in the block copolymers and that they are present as separate phases. This is supported by the large difference in the solubility parameter of the polyurethane segments (25 $(J\cdot cm^{-2})^{1/2}$) and NR segments (16,6 $(J\cdot cm^{-2})^{1/2}$). The closeness of the respective solubility parameters is shown to be a criterion for the miscibility of two components. These observations are viewed in the light of the nonpolar and polar character of NR and polyurethane segments, respectively, which do not mutually interact.

Phase separation in the block copolymer is further evidenced by DSC studies. Curves a and c in Fig. 5, being the thermograms of two typical two-step block copolymers, NR/1,4-BDO(60/40)-2 and NR/1,4-BDO(40/60)-2, respectively, show two different transitions corresponding to the NR andpolyurethane segments. This is characteristic of a phase separated product. Moreover, the T_g values of NR in both cases are the same (–63 °C), irrespective of the composition of the block copolymers. This indicates that the rubber and polyurethane phases exist without mutual interaction, which otherwise would have lead to shifted T_g values. Thermograms of another two-step sample and of all the one-step samples are taken at higher temperature only, since the subambient regions of the thermograms used for reading the value of T_g for NR is expected to be similar for all samples (due to the structural identity and identical grade of the liquid NR used for synthesis). The polyurethane phase shows only a glass transition, since crystallinity is absent due to the dissymmetry of TDI, which bears isocyanate groups at the 2- and 4- positions, affecting the uniformity of the polyurethane chain. Higher values of T_g for the polyurethane segments are explained on the basis of their rigidity, which is caused by hydrogen bonding and other interactive forces existing between the urethane groups.

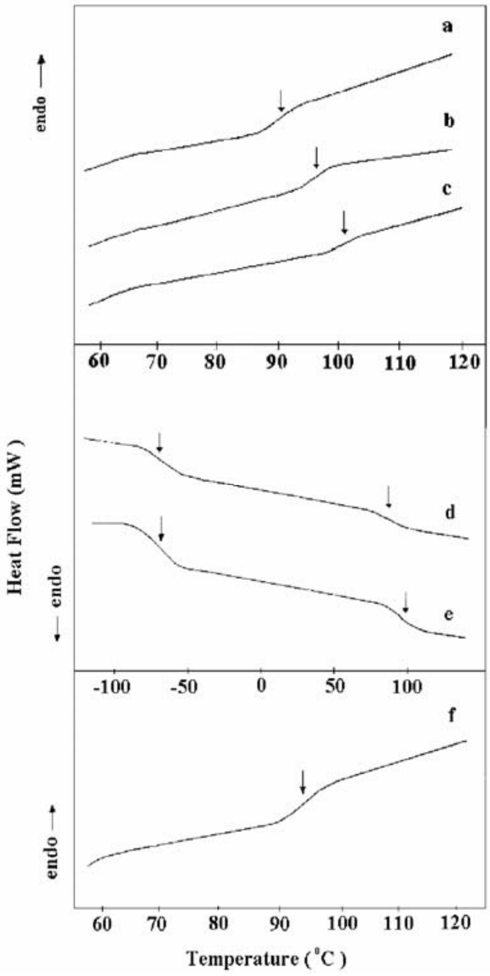


Fig. 5. DSC thermograms of the block copolymers:
a) NR/1,4-BDO(60/40)-1 (Perkin-Elmer),
b) NR/1,4-BDO(50/50)-1 (Perkin-Elmer),
c) NR/1,4-BDO(40/60)-1 (Perkin-Elmer),
d) NR/1,4-BDO(60/40)-2 (Mettler),
e) NR/1,4-DO(40/60)-2 (Mettler),
f) NR/1,4-BDO(50/50)-2 (Perkin-Elmer)

The aromatic ring structures present in the diisocyanate moiety of the hard segment structural units also contribute to segment rigidity. Single hard segment T_g values are observed in all samples, showing a narrow distribution of hard segment lengths in them. This is expected, since synthesis was carried out in solution, where polymerization proceeds in a nearly systematic way. Unlike soft segment T_g, the hard segment T_g varies with composition as given in Table 2. It increases with hard segment content. This is due to the fact that samples with the higher hard segment content possess longer PU blocks, resulting from the respective OH/NCO ratio. The longer the blocks, the higher the extent of intermolecular forces existing between them, which causes a rise in T_g.

Table 2. DSC results of the block copolymers

Sample	T_g [°C]	
	Soft segment	Hard segment
NR/1,4-BDO(60/40)-1	–	88.0
NR/1,4-BDO(50/50)-1	–	94.0
NR/1,4-BDO(40/60)-1	–	99.0
NR/1,4-BDO(60/40)-2	–63.0	87.0
NR/1,4-BDO(50/50)-2	–	94.0
NR/1,4-BDO(40/60)-2	–62.0	96.0

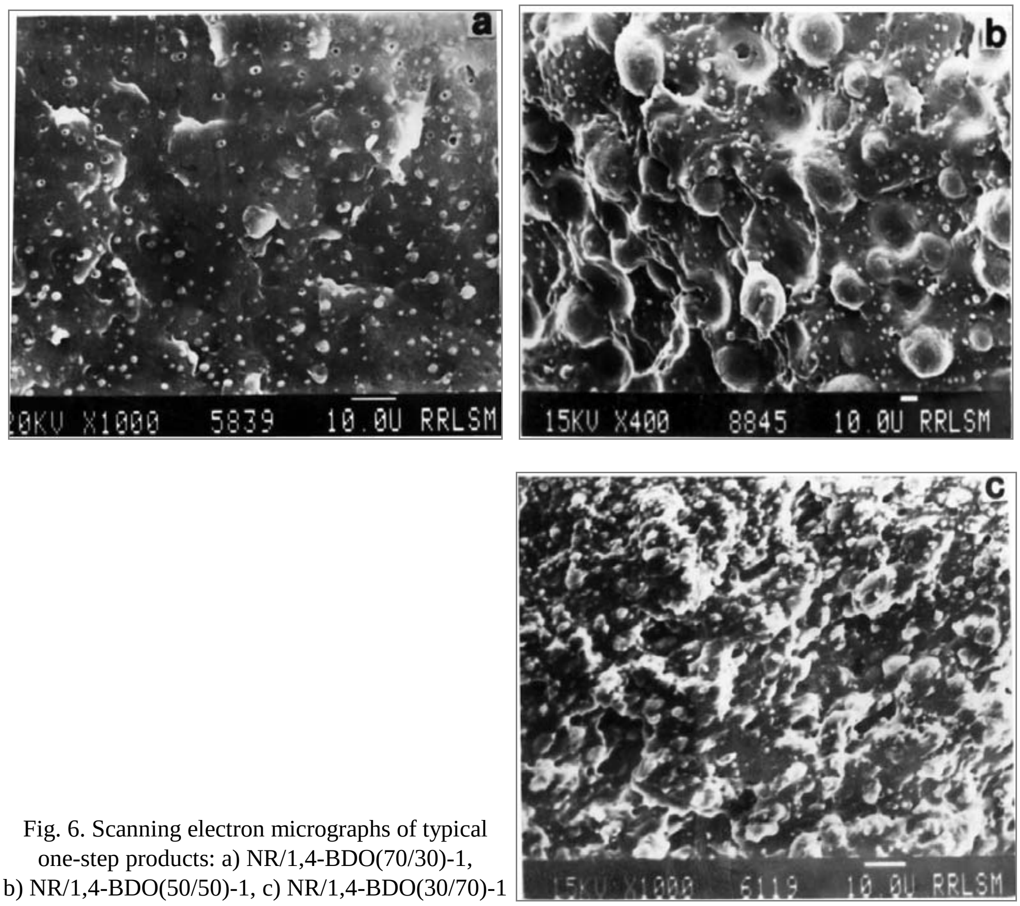


Fig. 6. Scanning electron micrographs of typical one-step products: a) NR/1,4-BDO(70/30)-1, b) NR/1,4-BDO(50/50)-1, c) NR/1,4-BDO(30/70)-1

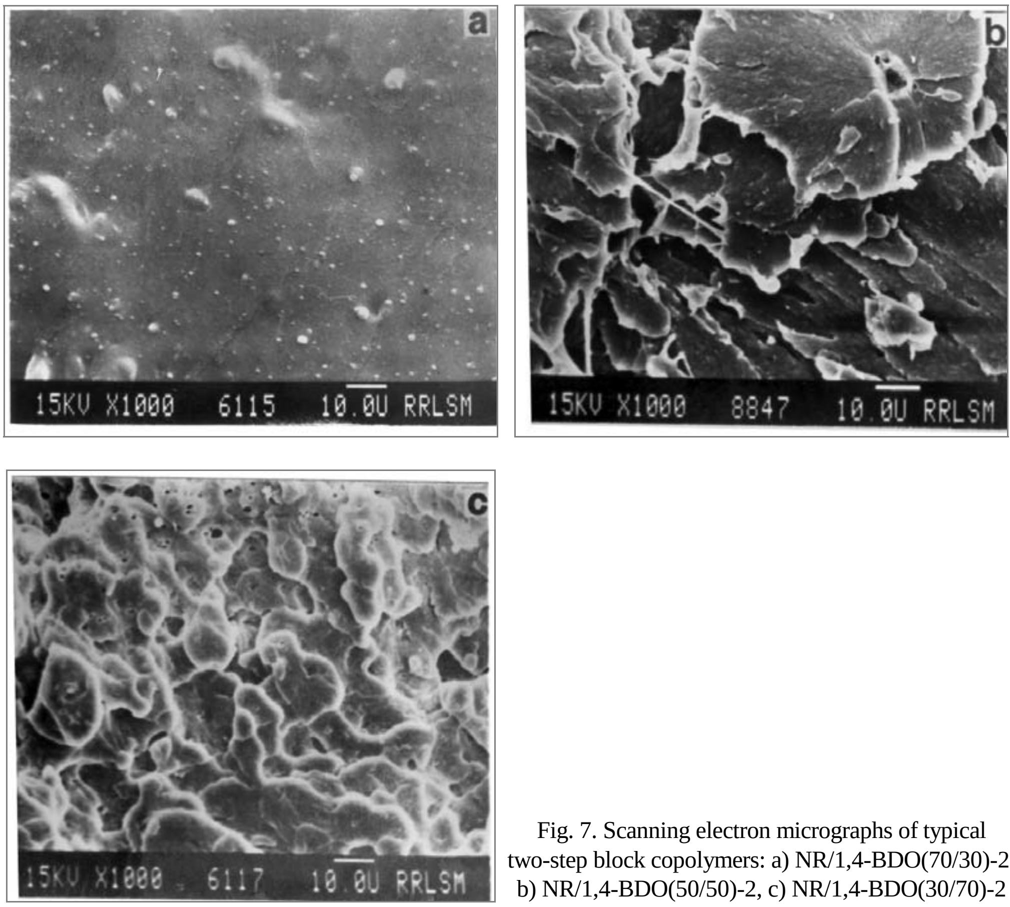


Fig. 7. Scanning electron micrographs of typical two-step block copolymers: a) NR/1,4-BDO(70/30)-2, b) NR/1,4-BDO(50/50)-2, c) NR/1,4-BDO(30/70)-2

Heterophase morphology is further shown by SEM analysis. These micrographs (Figs. 6, 7) exhibit the presence of incompatible phases forced to coexist. Hard segments agglomerate into discrete amorphous phases, which are seen as well-defined boundary surfaces in the SEM micrographs. Their sizes range from 3.75 to 20.66 μm. These are, however, much larger sizes compared to hard domains usually observed in block copolymer morphology, which tend to vary from discrete spherical dispersions of nano size at low hard segment content to regular lamellar distributions at higher hard segment content. Due to extremely small size, hard domains in block copolymers would be visible only in high resolution TEM studies. It was thus inferred that the beads observed in the present case are larger agglomerations of polyurethane homopolymers, which remain unbonded with the rubber chains during synthesis.

Such a possibility was further explored by conducting quantitative etching studies on the NR/1,4-BDO(50/50)-2 sample, so as to separate the unbonded polyurethane fraction. The solvent used for this purpose was N,N′-dimethyl formamide, which is a very good polyurethane solvent. It was found that 25.62% of the total sample weight was extracted. The etched sample (gel fraction) was subjected to IR analysis. A comparison of its IR spectrum with that of the unetched original sample shows similar features of NR and PU segments, indicating that both samples have the same structural characteristics. These findings suggest that block copolymerization taks place as envisaged in Scheme 1, but with slightly lower efficiency, so that a part of the PU remains a homopolymer.

Table 3. Variation of bead size and bead density
with the polyurethane content in the block copolymers (measured from SEM)

Sample	Weight % of hard segment	Mean domain size [μm]	Domain density on surface ($\times 10^8$ m^{-2})
NR/1,4-BDO(70/30)-1	33.0	3.75	1.98
NR/1,4-BDO(50/50)-1	51.2	20.66	6.78
NR/1,4-BDO(30/70)-1	70.3	not measurable	not measurable
NR/1,4-BDO(70/30)-2	33.0	4.25	2.01
NR/1,4--BDO(50/50)-2	51.2	not reliable	not reliable
NR/1,4-BDO(30/70)-2	70.3	not measurable	not measurable

The size and population of the random beads observed in the SEM micrograph was tabulated in Table 3. The population is given in terms of bead density, which is the number of beads per square meter on the sample surface. The overall bead size and bead density are found to vary with hard segment content in the sample. For example, in NR/1,4-BDO(70/30)-1, the minor component, i.e., polyurethane, is present as discrete particles of a small size at lower densities in the continuous matrix of NR segments. When hard segment content is increased to 51.217%, as in NR/1,4-BDO(50/50)-1, the hard domain size and domain density increase to a great extent. With further increase of hard segment content to 70.328%, the hard domains tend to coalesce and form a continuous phase. Domain size and density are hence not measurable in this case. The corresponding two-step samples, except NR/1,4-BDO(50/50)-2, give similar results. In the case of NR/1,4-BDO(50/50)-2, the micrograph shows a deformed surface containing torn fragments, which is characteristic of a flexible material. Domains are not visible. This can probably happen if major quantities of the PU component were incorporated into the block copolymer structure. The present samples hence can be considered to be systems consisting of three separate phases, viz., the NR soft phase, the polyurethane hard phase (present in the block copolymer), and the homopolymer polyurethane phase (as beads). However, DSC studies showed only one glass transition corresponding to the polyurethane phase. This may be due to comparable chain lengths of the polyurethane block copolymer phase and the homopolymer phase, which would hence be represented by a single transition in the DSC thermogram.

A two-phase morphology is further supported by thermogravimetric analysis. All samples decomposed in two stages (Figs. 8, 9), indicating the coexistence of two components. The onset of weight loss, the temperature of complete decomposition, the DTG peak temperatures, and the percentage of weight loss in each stage are summarized in Table 4.

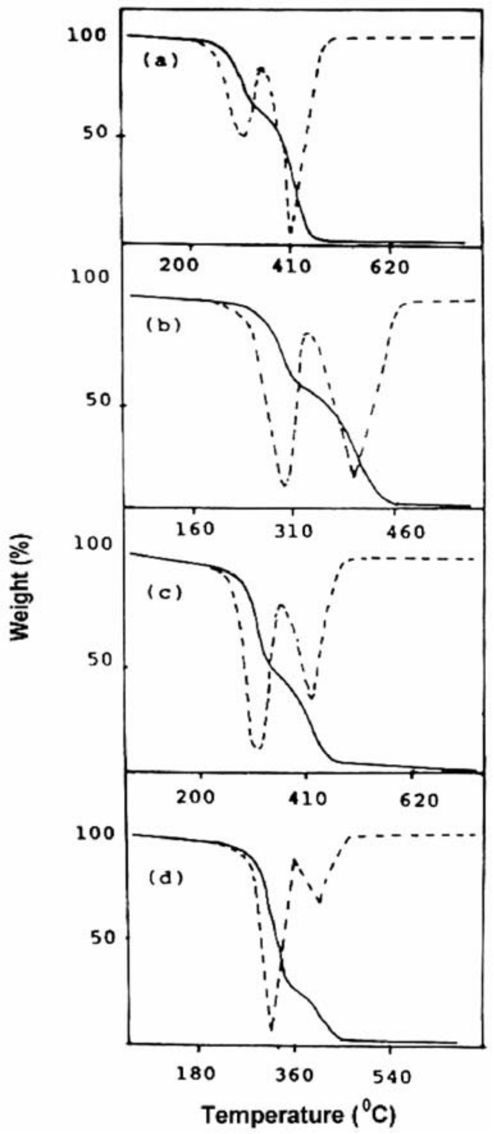


Fig. 8. Thermograms of the one-step block copolymers from TGA analysis:
a) NR/1,4-BDO(70/30)-1, b) NR/1,4-BDO(60/40)-1,
c) NR/1,4-BDO(50/50)-1, d) NR/1,4-BDO(30/70)-1

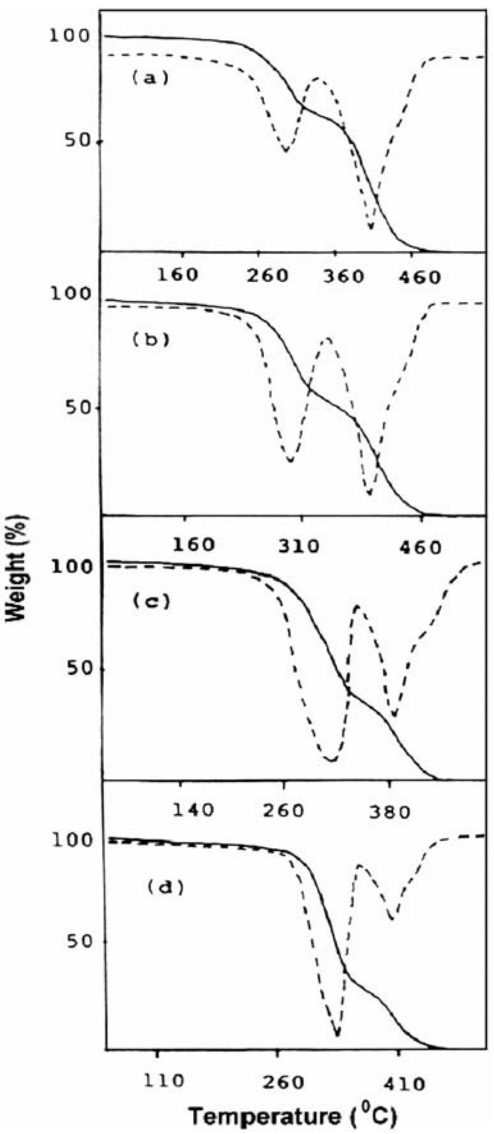


Fig. 9. Thermograms of the two-step block copolymers from TGA analysis:
a) NR/1,4-BDO(70/30)-2, b) NR/1,4-BDO(60/40)-2,
c) NR/1,4-BDO(40/60)-2, d) NR/1,4-BDO(30/70)-2

The onset of weight loss in the first stage occurs between 240 °C and 290 °C. The percentage of weight loss in this stage increases with increasing hard segment content, which indicates that the first stage of decomposition is due to hard segments. Obviously, the second stage of decomposition is due to the soft segments, since the percentage of weight loss here increases with increasing soft segment content. The first stage of decomposition is completed in the temperature range 295–340 °C. The second stage of decomposition is rather rapid – it begins around 300 °C and is completed in the range 440–490 °C. A plateau of temperature separating the two stages of decomposition indicates that the two components decompose at different temperatures. Two stage decomposition is a clear indication of the heterophase nature of block copolymers.

Table 4. Phenomenological data of thermal decomposition of the one-step and two-step block copolymers

Sample	Onset of weight loss [°C]		Per cent of weight loss		Peak temperature [°C]	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR/1,4-BDO(70/30)-1	244.00	341	36.00	63.00	307.00	410.00
NR/1,4-BDO(60/40)-1	254.00	333	43.00	55.00	316.00	422.00
NR/1,4-BDO(50/50)-1	270.00	352	56.00	42.00	312.00	419.00
NR/1,4-BDO(30/70)-1	280.00	356	72.00	26.00	314.00	408.00
NR/1,4-BDO(70/30)-2	244.00	342	35.00	64.00	296.00	405.00
NR/1,4-BDO(60/40)--2	253.00	355	45.00	54.00	297.00	393.00
NR/1,4-BDO(40/60)-2	252.00	354	61.00	38.00	313.00	387.00
NR/1,4-BDO(30/70)-2	273.00	359	70.00	29.00	322.00	403.00

3.1. Activation energy of decomposition

The activation energy of block copolymer decomposition was derived from the TG curves by applying an analytical method proposed by Coats and Redfern [7]. The integral equation used has the form

$$\ln \frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

where $g(\alpha)$ is the kinetic model function, α – the decomposed fraction at any temperature T, ϕ – the heating rate, A – a numerical constant, and E stands for activation energy. The slope of the plot of left hand side against $1/T$ is a straight line, from which the energy of activation E was calculated.

All TG data were analyzed using the nine mechanistic equations proposed by Satava [8] and their kinetic parameters were calculated. It was found that the Mampel equation ($-\ln(1-\alpha) = kt$) best represents the experimental data and gives a proper mechanism of the reaction in all samples, which corresponds to a random nucleation mechanism for thermal decomposition with one nucleus in each domain.

In the one-step samples, the activation energy for the first stage of thermal decomposition increases from 101 $\mathrm{KJ \cdot mol^{-1}}$ to 136 $\mathrm{KJ \cdot mol^{-1}}$ as the hard segment content is increased from 30% to 70% (Table 5). An increase in activation energy indicates an increase in the thermal stability of the hard segments. Thermal stability, however, is a property determined by chemical structure and hard segment content only influences a segment length. Structural factors that vary with hard segment content seem to play a decisive role in this respect.

Table 5. Tensile properties of the block copolymers

Sample	Young's modulus [N/mm^2]	Tensile strength [N/mm^2]	Elongation at break [%]
NR/1,4-BDO(70/30)-1	3.93	4.06	194
NR/1,4-BDO(60/40)-1	7	7.88	161
NR/1,4-BDO(50/50)-1	20.78	12.01	98
NR/1,4-BDO(40/60)-1	64.43	16.28	65
NR/1,4-BDO(30/70)-1	97.76	29.86	30
NR/1,4-BDO(70/30)-2	11.58	4.91	225
NR/1,4-BDO(60/40)-2	12.97	8.02	177
NR/1,4-BDO(50/50)-2	21.06	14.53	82
NR/1,4-BDO(40/60)-2	69.12	22.20	68
NR/1,4-BDO(30/70)-2	104.92	31.56	39

The allophanate linkage that can form crosslinks in polyurethane segments in the presence of free diisocyanate may be a factor worth considering in this case. Since the quantity of diisocyanate being introduced into the reacting system increases with hard segment content, allophanate formation is enhanced, which in turn leads to a higher level of crosslinking in polyurethane segments (Fig. 11). Such an increase in crosslinking obviously increases the thermal stability of the segments. A similar increase in activation energy with PU content is observed in the two-step samples for the degradation of polyurethane segments. Comparing the one-step and two-step products it is observed that the PU components in both series of products have comparable values of activation energy. This indicates that the polyurethane segments in both the types of products possess similar structural characteristics.

Regarding soft segment degradation, the activation energy for one-step samples is found to decrease with hard segment content. The value is 126 KJ mol^{-1} for 30 % PU content, which decreases to 90 KJ mol^{-1} for 70 % PU content. On the other hand, the two-step products exhibit an activation energy of soft segment degradation that varies only in a narrow range, irrespective of hard segment content. For example, the value is 180 KJ mol^{-1} for 30 % PU content and 190 KJ mol^{-1} for 70 % content. It was also found that the activation energy of soft segment degradation differs greatly between one-step and two-step products at all hard segment contents. The two-step samples exhibit much higher values compared to the one-step samples. The direct effect of PU content on the stability of NR is not expected since these are phase separated systems. It seems, however, that NR structure stands modified so as to alter the activation energy for its degradation, depending on the method of synthesis and also with the variation in PU content.

The above observations may be explained based on the occasional multifunctionality of liquid NR. In addition to terminal hydroxyl groups, liquid NR molecules may possess hydroxyl functionality in the molecular chain. This arises by the opening of a few number of epoxy groups, which were inducted into the chain during the depolymerisation process. The multifunctionality of liquid NR leads to the crosslinking of segments during chain extension in the presence of diisocyanate and diols (Fig 10). Crosslinking obviously causes NR segments in the block copolymer to be stable.

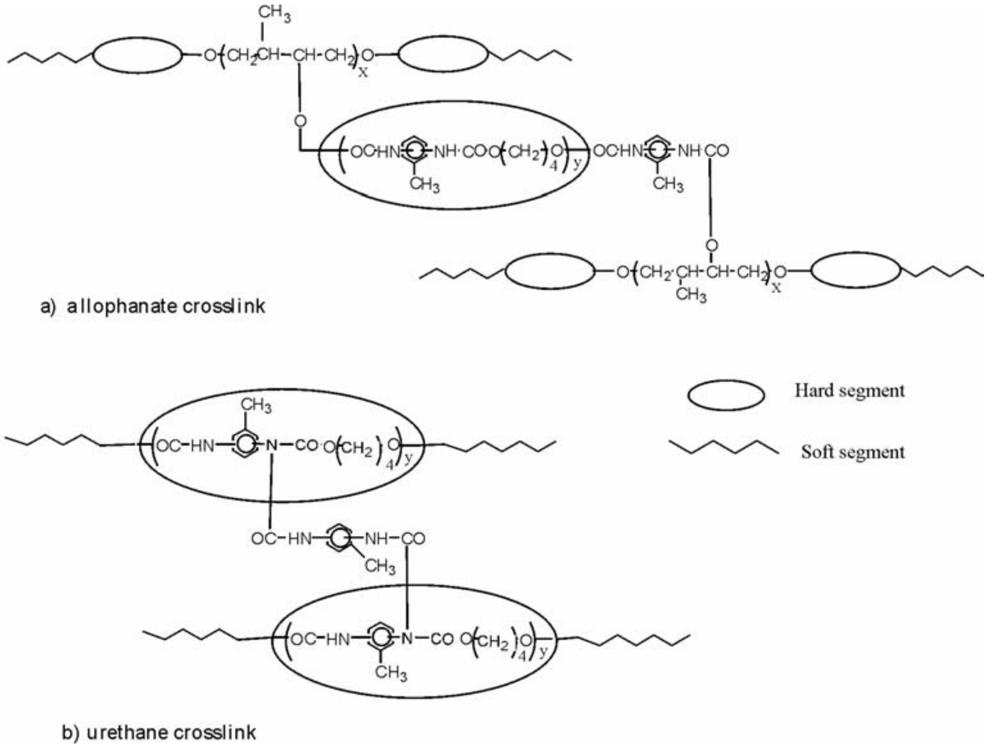


Fig. 10. Schematic representation of crosslinks formed in one-step and two-step block copolymers: a) allophanate crosslink in hard segment; b) urethane crosslink in soft segment

In one-step synthesis, diisocyanate is added to a mixture of NR and extender diol. Diisocyanate reacts preferentially with the extender diol in the initial stages of forming the polyurethane segments, since the extender diol is present in large excess compared to NR in the reaction mixture. As the relative concentration of diol decreases, diisocyanate tends to react with the hydroxyl group of NR chains, forming isocyanate endcapped NR molecules. These undergo chain extension with the hydroxyl bearing polyurethane segments. Multifunctionality in NR thus causes chain extension from all centers of hydroxyl occupation, which finally leads to crosslinking. The one-step product with 30 % PU content thus gives a value of 126 KJ·mol^{-1} for the activation energy NR segment degradation. As the PU content increases, however, the activation energy tends to decrease and finally settles at 90 KJ mol^{-1} for 70% PU content. This decrease in the activation energy with increasing PU content for two-step samples can be explained basing on the fact that at higher PU content the reaction mixture contains a large excess of extender diol, so that the preferable reaction is between diisocyanate and the extender diol rather than the less reactive secondary hydroxyl groups in the NR chains. This results in a lower level of crosslinking in the NR soft segments as the hard segment content increases. In such cases, the activation energy for NR degradation decreases.

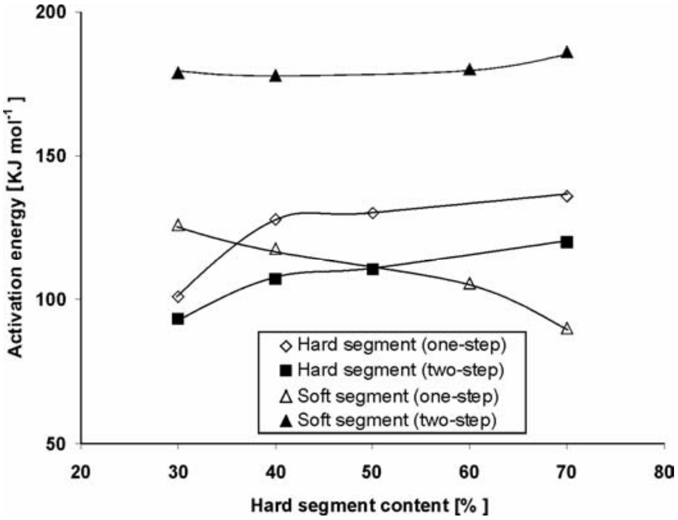


Fig. 11. Change of activation energy for the degradation
with hard segments content in one- step and two-step block copolymers

Two-step synthesis, however, involves the introduction of excess isocyanate into NR solution during the initial stages, so that all the hydroxyl multifunctional centres in the NR chain react with –NCO groups. This is the case for all two-step syntheses, which means that two-step products should be crosslinked to a similar extent irrespective of PU content and hence the activation energy values remain almost steady as seen in Fig. 11. A higher level of crosslinking in two-step products explains the higher values of activation energy as compared to one-step products.

3.2. Stress-strain behaviour

The shapes of stress-strain curves are indicative of the nature of the materials (Fig. 12). Samples with low hard segment content resemble flexible rubber, while samples with higher hard segment content, which exhibit yielding and necking, resemble flexible plastics. A sample with hard segment content of approximately 70 wt. % undergoes a failure at yield point, characteristic of a rigid plastic. An increase in the hard segment content thus tends to improve the tensile properties of both the one-step and two-step samples. This is due to pseudo crosslinking and reinforcing filler effects offered by hard segments [9]. Changes in the nature of the continuous phase of the material, from predominantly soft to hard with increasing hard segment content, also contribute to the improvement in tensile properties [10]. It has been reported that tensile strength increases suddenly above 60 % hard segment content [11], due to a marked change in domain morphology that results from an inversion of the hard and soft phases in polyurethane elastomers. Materials with intermediate hard segment content exhibit the tensile properties of rigid elastomers. This observation is in accordance with the findings of Chang et al. [12].

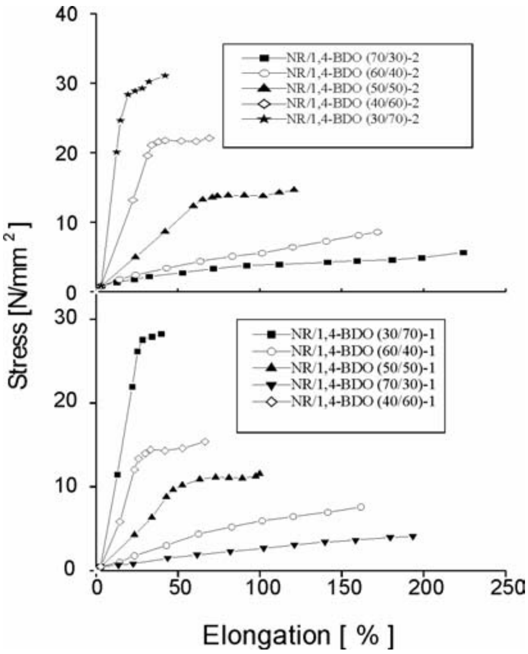


Fig. 12. Stress–strain curves of: a) one-step block copolymers
b) two-step block copolymers

Two-step materials are found to possess slightly a higher tensile strength, ultimate elongation, and Young's modulus than the one-step products (Table VI). This could be explained basing on the higher level of crosslinking in the NR segments as described in the previous section. This could also be due to more systematic chain extension reactions as compared to one-step synthesis, which would reduce the number of loose NR chain ends in the product and enhance its tensile properties. An increase in both the tensile strength and elongation at break of the two-step samples compared to the respective one-step samples also support this view. Moreover, a systematic chain extension reaction leads to smaller interconnected PU domains, hence two-step products possess a large total surface area of these domains, which are more effective at stopping catastrophic crack growth through the NR matrix. This view is supported by the findings of Smith [13].

The ultimate properties of these materials, however, are lower compared to those of conventional polyurethane elastomers. This is attributed to the absence of phase mixing, and to the inability of the soft segments to crystallize under strain [14]. The absence of strain-induced crystallinity may be due to the short length of the NR segments in the block copolymer.

The mode of failure as observed in SEM micrographs also supports the stress –strain behaviour of the samples. For example, Fig. 7b shows the presence of ridges of torn fragments on the fracture surface, which is in a highly deformed state. This indicates that the corresponding sample, viz., NR/1,4-BDO(50/50)-2, undergoes fracture by stretching and tearing, which is a characteristic feature of elastomers. In the case of NR/1,4-BDO(30/70)-2, SEM indicates a broken surface with a continuous network of hard phase, which could be formed by the brittle fracture of the sample. Such behaviour is characteristic of a rigid material and such variations in the mechanical nature of samples with increasing PU content have been supported by tensile properties as well. The matrices of the samples as seen in the SEM micrographs contribute basically to the mechanical behaviour. Therefore, an increase in PU content from 30 % to 70 % changes the ductile matrix into a rigid one due to phase inversion.

4. Conclusion

Liquid NR formed by the photochemical depolymerisation of NR is found to be useful for the synthesis of newer macromolecular structures such as block copolymers. In the present case, the block copolymers lack solubility, which indicates that they are crosslinked materials. The highly phase separated systems, however, are useful for structure–property relations in block copolymers. Further investigation may lead to the formation of a soluble product, which will extend the utility of the products into other areas such as surfactant etc.

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Received 16 July 2004
Revised 23 September 2004