

Segmented Block Copolymers Based on Liquid Natural Rubber

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SYNOPSIS

Segmented block copolymers were prepared from hydroxyl-terminated liquid natural rubber (HTNR) and poly(ethylene oxide) (PEO). Toluene 2,4 diisocyanate (TDI) was used as the coupling agent for combining both types of segments. Keeping the molecular weight of HTNR constant, a series of materials were prepared using PEO with varying molecular weights. Their thermal and mechanical properties were evaluated. With increasing the PEO content, the properties vary from soft to rigid elastomers and rubber-toughened plastics. This variation in properties is caused by the changes in the sample morphology, which depends on the relative fractions of the hard and soft segments. Water absorption capability of these block copolymers was determined. Hydrogels with water content approximately up to 80% were obtained.

INTRODUCTION

Thermoplastic natural rubber has emerged as a remarkable material in the extensive studies carried out on natural rubber for property modifications.¹⁻⁹ It is produced mainly by blending natural rubber with thermoplastics.¹⁻⁷ Grafting of thermoplastic oligomers onto natural rubber has also been investigated.^{8,9} Although block copolymerization is a more ideal method for synthesizing a structural pattern suitable for thermoplastic rubbers, it was not successful with natural rubber because of the unavailability of its telechelic oligomers. Recently, we have developed a method^{10,11} for the production of hydroxyl-terminated liquid natural rubber that has been utilized in the synthesis of segmented block copolymers with the general formula $(A-B)_n$.

Block copolymers have been well characterized by the incompatibility of the segments present and the subsequent phase segregation of the hard and soft segments into separate microdomains.^{12,13} However, the conventional polyurethane elastomers,

which are based on polyesters and polyethers and possessing high strength and toughness, are not completely phase-separated systems.¹⁴⁻¹⁶ A certain degree of phase mixing is present in these materials that is attributed to the interaction of the hard and soft segments, both containing polar groups, through secondary bond forces.^{12,13,17-21} Moreover, block polymers containing nonpolar hydrocarbon soft segments were found to possess inferior properties despite the increased degree of phase separation. Materials based on polybutadiene,¹⁷⁻¹⁹ polyisobutylene,²⁰ and polymyrcene²¹ soft segments are reported examples. Hence, it was argued that the useful properties of block copolymers are not entirely due to the high degree of phase separation.²² Factors such as the soft segment functionality, molecular weights of the segments, glass transition temperature of soft segment, compositional heterogeneity, degree of phase mixing, morphology, etc. also accounted for the characteristic properties of the block polymers.

Block copolymers consisting of nonpolar soft segments, which possess high degree of phase separation, can be considered as ideal systems on the basis of which structure-property relation can be well followed. Here we report the synthesis and studies of such materials in which the nonpolar soft

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segment is derived from natural rubber and the hard segment is polyethylene oxide.

EXPERIMENTAL

Materials

HTNR of molecular weight (\bar{M}_n) 3000 was prepared in our lab having a functionality of 1.94 by a method reported previously.¹¹ Toluene diisocyanate (80/20 mixture of 2,4 and 2,6 isomers) obtained from Fluka, Switzerland, was used after distilling. Poly(ethylene oxide) obtained from Fluka was used as received. Tetrahydrofuran (BDH) was dried and distilled before use. Dibutyl tin dilaurate (DBTDL) (Fluka) was used as catalyst without further purification.

Synthesis of Block Copolymers

The materials were synthesized by the bulk and solution polymerization techniques. The overall composition of the reactants are given in Table I.

Two-Stage Bulk Copolymerization

HTNR along with DBTDL (0.03% by weight of HTNR) was taken in a resin kettle provided with a dropping funnel, mechanical stirrer, and an inlet and outlet for nitrogen. TDI was added dropwise with constant stirring. The reaction continued for 1 h at 80°C. This was followed by the addition of molten PEO with vigorous stirring for 3 s and the contents were cast into a preheated tray coated with silicone release agent and cured at 100°C for 8 h followed by aging at room temperature for one week in a moisture-free atmosphere.

Two-Stage Solution Polymerization

HTNR was dissolved in 100 mL tetrahydrofuran (THF) taken in a flat-bottomed flask equipped with

a magnetic stirrer, nitrogen inlet, and a reflux condenser. DBTDL catalyst (0.03% by weight of HTNR) was added and the solution was brought to reflux. The final desired stoichiometric amount of TDI was added in drops followed by 1 h reaction to endcap HTNR. This was followed by the addition of the required amount of PEO as a solution in 50 mL THF dropwise during 2–3 h followed by 1.5 of reaction. The excess THF was distilled off and viscous polymer was cast into trays treated with silicone release agent and kept for curing at 70°C for 24 h, followed by one week aging at room temperature in a dry atmosphere.

Measurements

Infrared (IR) spectrum of the samples was recorded on a Perkin-Elmer model 377 I.R spectrometer. Differential scanning calorimetry (DSC) was performed with a DuPont 9000 thermal analyzer system. A heating rate of 20°C min⁻¹ and a sensitivity of 5 m cal/s was used. Thermal stability of these materials were studied using DuPont 1090 thermogravimetric analyzer (TGA) at a heating rate of 20°C min⁻¹. Stress-strain data were obtained on a Zwick 1445 universal testing machine as per ASTM D412-80 test method at 20°C using dumbbell-shaped test pieces. Optical micrographs of the samples were taken on a "Leitz" Orthoplan microscope.

Polymer Designation

The samples are designated as follows. As an example NR : PEO-4000(B) indicates the sample where NR represents the hydroxyl-terminated liquid natural rubber soft segment, PEO represents the polyethylene oxide hard segment, 4000, the \bar{M}_n of the hard segment and (B) shows that the sample was bulk polymerized. The letter *s* in the place of *B* indicates the sample prepared by solution polymerization.

Table I Overall Composition of the Block Copolymers

Sample	Molar Composition HTNR/TDI/PEO	PEO Content (%)
NR : PEO-1000	1/2.01/1	22.8
NR : PEO-2000	1/2.01/1	37.2
NR : PEO-3000	1/2.01/1	46.9
NR : PEO-4000	1/2.01/1	54.2
NR : PEO-6000	1/2.01/1	63.8

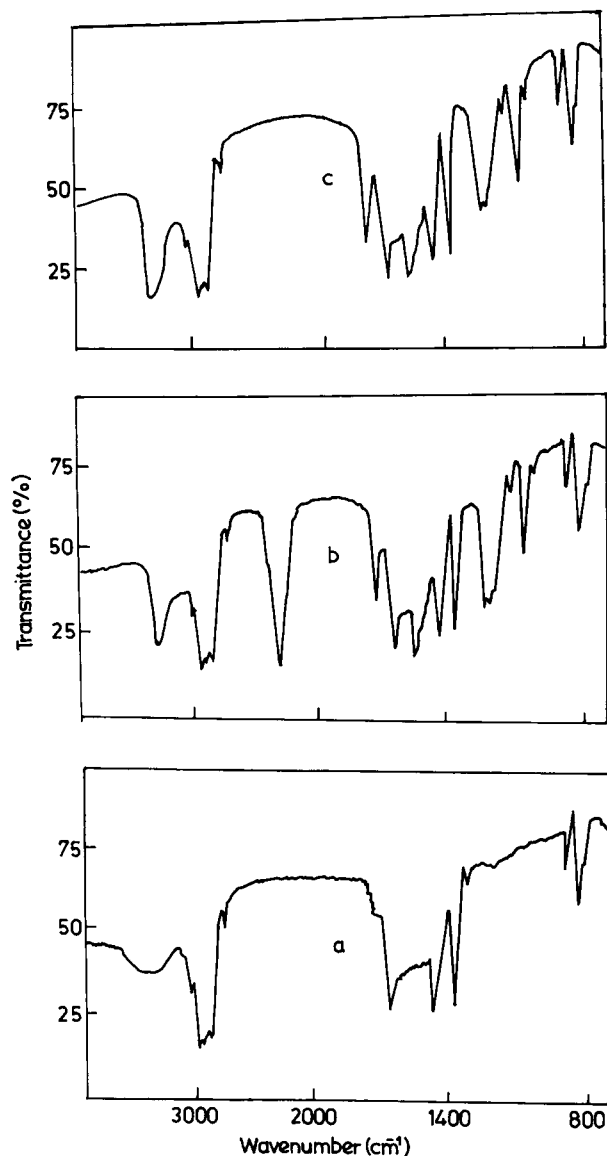
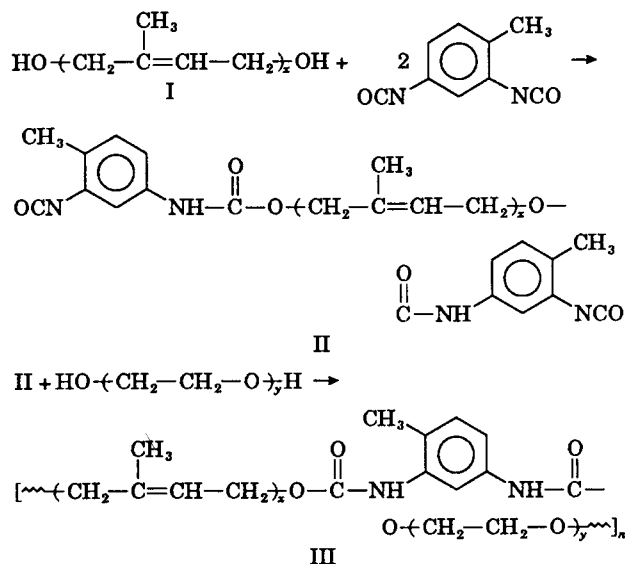


Figure 1 Infrared spectra of (a) HTNR, (b) NCO end capped NR, (c) block copolymer.

RESULTS AND DISCUSSION

The infrared spectra of the soft segment (HTNR), its encapped form, and the final sample prepared by the solution polymerization are given in Figure 1. Disappearance of the hydroxyl band from Figure 1(a) with the emergence of NH and CO bands at $3440\text{--}3150\text{ cm}^{-1}$ and 1690 cm^{-1} , respectively, in Figure 1(b) indicates the endcapping reaction. This is further evidenced by the presence of the strong absorption band of the NCO group at 2260 cm^{-1} in Figure 1(b). The final product formed by chain ex-

tension does not contain the -NCO band, which indicates that the chain extension reaction goes to completion. Thus, the two-stage reaction proceeded in a regular manner yielding the block copolymers. The course of the reactions and the structure of the final product can be represented as follows:



The coupling agent toluene diisocyanate reacts well with both the components yielding the final product.

Thermal Analysis

The DSC curves of the solution-polymerized samples are given in Figure 2. The transition temperatures observed are tabulated in Table II along with that of the bulk-polymerized samples. It shows that there are only two transitions associated with each of the samples examined. The glass transitions (T_g) and the melting transition (T_m) correspond to the natural rubber and poly(ethylene oxide) segments, respectively. The T_g values of all the materials are found to be very close to each other irrespective of the method of preparation and the hard segment length. They differ only by a maximum of 5°C with the T_g of the hydroxyl-terminated liquid natural rubber, viz. -68°C . Pascault and Camberlin²³ have shown that an increase in T_g of 4°C of the soft segment above the corresponding T_g of the homopolymers suggests complete phase separation. This observation can be very well applied to the present materials so that they can be considered as systems in which the phase segregation is complete or very nearly so.

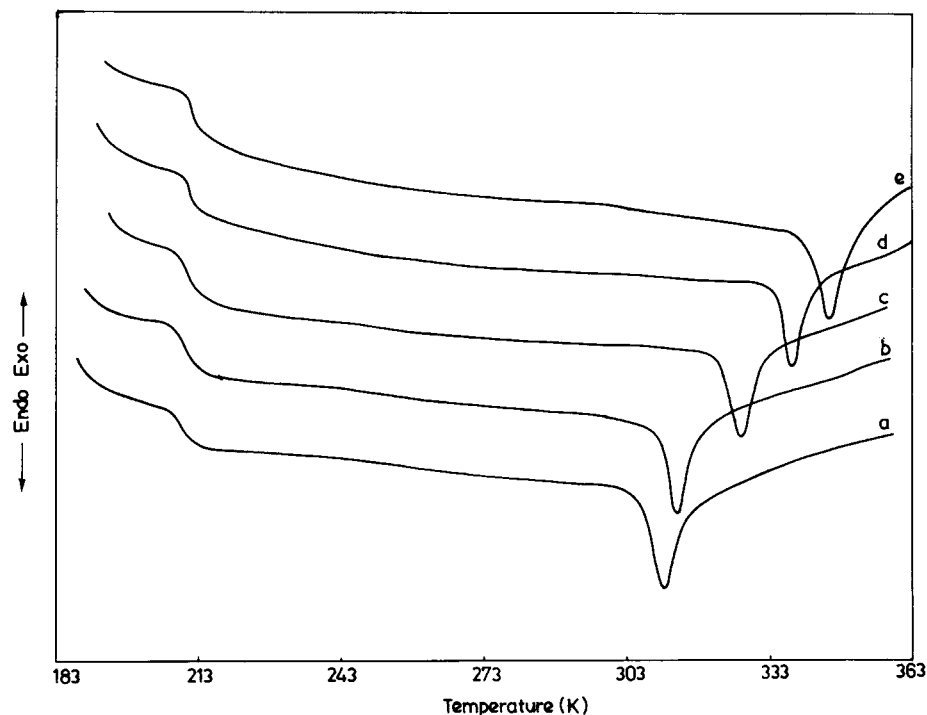


Figure 2 DSC curves of the solution-polymerized samples: (a) NR : PEO-1000, (b) NR : PEO-2000, (c) NR : PEO-3000, (d) NR : PEO-4000, (e) NR : PEO-6000.

The crystallinity of the hard segments is evidenced by the nature of the melting transition. The melting temperature increase with the molecular weight of the poly(ethylene oxide), and the values correspond well with the melting temperatures of the homopolymers once again, indicating that almost complete phase separation occurs in the polymers. Only a single hard segment transition was observed in all cases irrespective of the method of their preparation. There are reported cases where the bulk polymerization leads to more than one hard segment

transition.¹² This was attributed to the polydispersity of the hard segment length when they were formed *in situ* during the chain extension reactions. Our observation of a single hard segment transition for all the samples is consistent with the fact that preformed hard segments with very narrow molecular weight distributions were employed in their preparation.

Thermal stability of the materials was studied using thermogravimetric analysis (TGA), and the typical thermograms of a solution and bulk sample

Table II DSC Results of Block Copolymers

Sample	Bulk Polymerized		Solution Polymerized	
	T_g of the Soft Segment (°C)	T_m of Hard Segment (°C)	T_g of the Soft Segment (°C)	T_m of the Hard Segment (°C)
NR : PEO-0	-68	—	-68	—
NR : PEO-1000	-66	39	-65	40
NR : PEO-2000	-64	42	-65	43
NR : PEO-3000	-64	56	-65	58
NR : PEO-4000	-64	59	-65	63
NR : PEO-6000	-63	62	-64	69

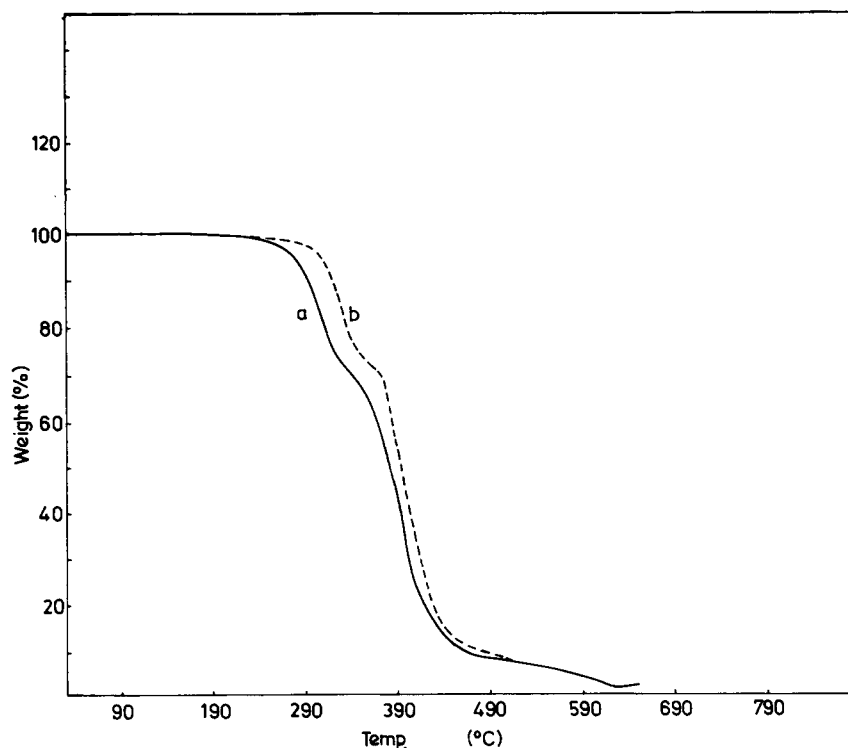


Figure 3 Typical TGA curves of (a) NR : PEO-3000(B) and (b) NR : PEO-3000(S).

are shown in Figure 3. The results are tabulated in Table III. Most of the copolymers decompose in two stages, corresponding to the two phases present. The onset of weight loss (T_0) occurs between 280 and 300°C for bulk-polymerized samples and 300 and 320°C for solution-polymerized samples, respectively. The first-stage weight loss is complete at 360°C for bulk samples and 380°C for the solution-polymerized samples. The second-stage decomposition is rapid with a maximum rate in the vicinity of 430°C for both the samples. A plateau separating

the two stages of decomposition also suggests that the two domains decompose at different temperatures. The higher thermal stability of the solution-polymerized samples is obviously due to the higher degree of structural regularity of the polymer chains.

Optical Microscopy

The optical micrographs of a microtomed section of NR : PEO-2000(s) and NR : PEO-6000(s) are given in Figures 4 and 5, respectively. They were taken in

Table III TGA Results of Blockcopolymers

Sample	Bulk Polymerized			Solution Polymerized		
	Decomposition Temperature (°C)			Decomposition Temperature (°C)		
	T_0	T_{10}^a	T_{50}^b	T_0	T_{10}^a	T_{50}^b
NR : PEO-1000	280	348	410	304	383	408
NR : PEO-2000	283	354	410	308	387	414
NR : PEO-3000	287	357	420	310	394	418
NR : PEO-4000	290	360	423	315	397	424
NR : PEO-6000	296	365	430	319	410	436

^a Temperature corresponding to 10% wt. loss.

^b Temperature corresponding to 50% wt. loss.

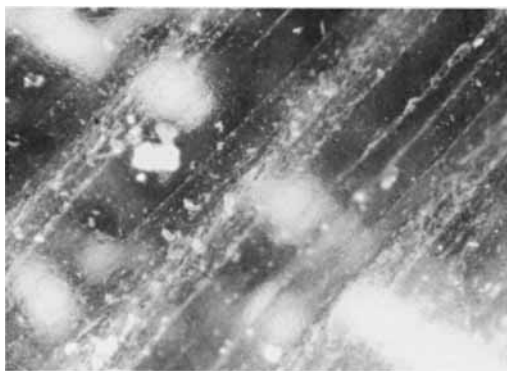


Figure 4 Optical micrograph of a microtomed thin section of NR : PEO-2000(S) ($\times 25$).

plane polarized light. The hard phase is visible as white regions and the rubber phase as black regions. Both the samples are phase-separated systems, but large difference in their morphology is observed in the micrographs. NR : PEO-2000(s) is phase separated into parallel regions of hard and soft phases. The rubber phase is the continuous phase and the polyethylene oxide appears as a dispersed phase. This is consistent with the low hard segment content of the sample. Crystallite formation is hardly noted in the micrograph. The low molecular weight of the hard segment whose melting temperature remains close to the ambient temperature may not aid the crystallite formation. The NR : PEO-6000(s) is characterized by the spherulites of hard segments as seen in the micrograph in Figure 5. An increase in the molecular weight of polyethylene oxide to 6000 facilitates the crystallite formation, and the well-defined crystallites indicate the highly crystalline nature of the polyethylene oxide. The increase in molecular weight caused an increase in hard segment content of the sample to 63%. As a result a phase inversion occurs in the sample such that the hard and the soft phases become the continuous phase and the dispersed phase, respectively, which is evidenced by the micrograph in Figure 5. Bicontinuous phase and other intermediate compositions could be observed in between these two extreme samples.

Stress-Strain Behavior

The stress-strain properties of the block polymers are summarized in Table IV. Figure 6 represents the tensile curves of the solution-polymerized samples. The tensile strength of all the materials studied is much lower than the conventional block copolymers, which was not expected from materials with high

degree of phase separation. The variation in properties observed is attributed to various factors that are discussed later.

One of the contributing factors of the high mechanical properties of polyurethane elastomers was found to be the existence of a certain extent of phase mixing in the materials consisting of polar soft and hard segments. The present materials are deprived of this phenomenon since the hard and soft segments do not possess polar groups for mutual interaction. Similar materials were reported in the literature that possess comparatively low mechanical properties.^{22,24} The nature of hard domains, which act as physical crosslinks between soft segments, plays an important role in the mechanical properties of block polymers. Unlike in the case of polyurethane hard domains where strong intermolecular attractive forces bring about firm segmental cohesion, the polyethylene oxide hard segment cohesion is only due to crystallization. The low strength and the nature of the tensile curves shows that crystallization of the soft segments does not occur under strain in the present materials.

The tensile strength of the materials increases with the poly(ethyleneoxide) content. NR : PEO-1000(s) in which the hard segment content is 22% gives a tensile strength equal to 2.46 MPa. The value increases to 5.64 MPa for NR : PEO-6000(s) having a hard segment content equal to 63%. Similar increase in tensile strength was observed for the bulk samples also. In both the cases the elongation at break decreases with the hard segment content.

On the basis of the stress-strain curves shown in Figure 6 the solution-polymerized materials can be classified into three general types. Materials with hard segment content below 40% give the tensile curve similar to soft elastomers. The strain pro-



Figure 5 Optical micrograph of microtomed thin section of NR : PEO-6000(S) ($\times 25$).

Table IV Mechanical Properties of Blockcopolymers

Sample	Bulk Polymerized		Solution Polymerized	
	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
NR : PEO-1000	1.92	310.6	2.46	421.0
NR : PEO-2000	2.18	307.9	3.24	396.0
NR : PEO-3000	2.85	235.6	3.97	267.4
NR : PEO-4000	3.06	174.9	4.72	230.3
NR : PEO-6000	2.94	132.0	5.64	214.2

gressively increases with the applied stress until the material breaks. This behavior along with the low initial modulus is consistent with the sample morphology and the low hard segment contents in NR : PEO-1000 (s) and (B) and NR : PEO-2000 (s) and (B). In these samples the soft segments are the continuous phase, with the hard domains not fully developed into crystallites (Fig. 4). The lack of well-defined crystalline phase of polyethyleneoxide causes reduction in tensile strength and modulus.

Second, samples with hard segment content above 40% behave like rigid elastomers. They possess higher modulus and tensile strength. There is a de-

crease in the initial strain and the tendency of showing yield point develops. These results suggest that the sample morphology changes with increased molecular weight of the polyethylene oxide segments in such a way that crystalline hard domains are developed in the rubber matrix.

The third type of samples has high hard segment content of 60% and above. NR : PEO-6000 (s) and (B) show high initial modulus and tensile strength. The tensile curve exhibits distinct yield behavior and the elongation at break drops to about 200%. The samples behave as rubber-toughened plastic materials showing necking and strain whitening.

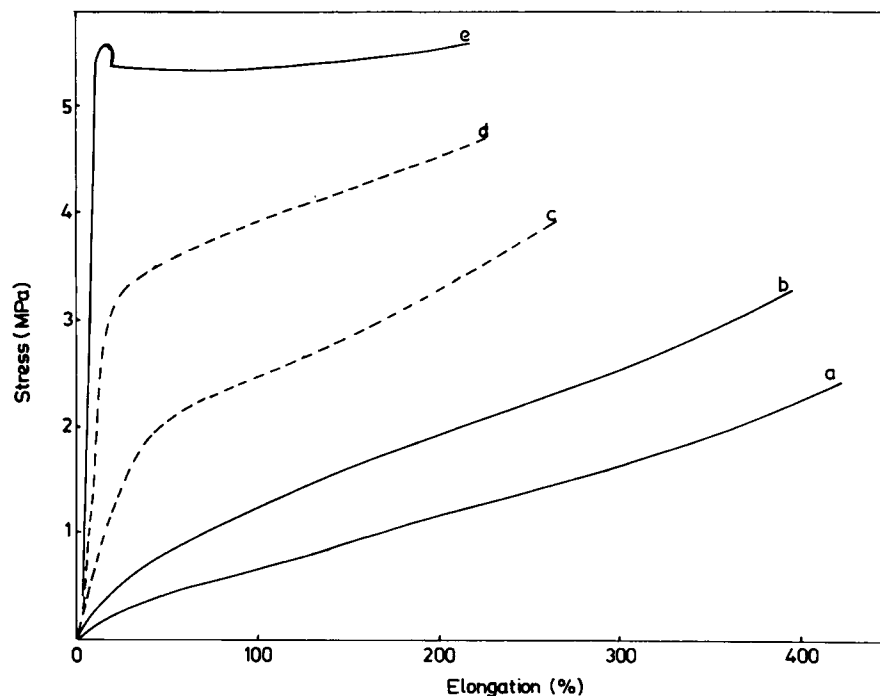


Figure 6 Tensile curves of solution-polymerized samples: (a) NR : PEO-1000, (b) NR : PEO-2000, (c) NR : PEO-3000, (d) NR : PEO-4000, (e) NR : PEO-6000.

Table V Percentage of Swelling of Block Copolymers in Water and Toluene

Sample	PEO Content	Water Absorption		Water Absorption by PEO in Block Copolymers	Toluene Absorption		Toluene Absorption by NR in Block Copolymers
		Weight Increase	Water Content		Weight Increase	Toluene Content	
NR : PEO-1000(S)	22.8	7.5	6.9	33	201.3	66.8	298
NR : PEO-2000(S)	37.2	22.3	18.2	60	141.4	58.5	256
NR : PEO-3000(S)	46.9	51.6	34.0	110	90.6	47.5	194
NR : PEO-4000(S)	54.2	165.8	62.3	306	72.3	41.9	179
NR : PEO-6000(S)	63.8	360.5	78.2	565	41.7	29.4	132

According to the tensile curves initial deformation occurs to the hard domains followed by the soft segment elongation. This result combined with the observations of the optical micrograph in Figure 5 corroborate the phase inversion that occurs at high hard segment content.

Although the bulk- and solution-polymerized samples show the same trend in stress-strain behavior, a comparison of the test results given in Table IV shows marked differences in properties between the two series of materials. The solution-polymerized samples possess much improved properties than the bulk samples. Also the variation in properties with composition of bulk samples occurs over a narrower range. As the hard segment content increases beyond 50%, the material becomes brittle and does not show any further improvement in tensile properties. The deterioration in properties of the bulk samples is mainly attributed to the compositional heterogeneity. The incompatibility of the two reacting components leads to nonuniform mixing during the bulk polymerization stage. Consequently, macrophase separation occurs leading to uneven reaction and thus the final product may be a multicomponent mixture containing homopolymers of soft and hard segments and copolymers with a wide distribution of molecular weights.

The block copolymers are capable of forming hydrogels due to the highly hydrophilic nature of polyethyleneoxide. Swelling behavior is also observed in nonpolar solvents such as toluene due to the interaction of the rubber segments with the solvent. In both the solvents sol fraction was not observed in the case of the solution-polymerized samples indicating complete reaction of the components. The swelling data are presented in Table V. Samples with higher soft segment content swell highly in toluene whereas those with higher hard segment content swell highly in water. The water uptake increases

with an increase in the hard segment content. More than 500% water absorption was recorded for sample with 63% hard segment content.

CONCLUSION

The bulk and solution polymerization processes for the preparation of block copolymers from HTNR and PEO led to highly phase-segregated materials. The solution-polymerized samples exhibited higher breaking stresses than the bulk-polymerized samples at the same nominal hard segment molecular weight. With increasing hard segment molecular weight, the properties of the materials vary from soft to rigid elastomers and rubber-toughened plastics. This variation in properties is caused by the changes in sample morphology, which depends on relative fractions of PEO and HTNR segments.

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