Segmented Block Copolymers of Natural Rubber and Bisphenol A–Toluene Diisocyanate Oligomers

C. J. PAUL,¹ M. R. GOPINATHAN NAIR,¹ PETER KOSHY,² BHASKAR B. IDAGE³

¹ School of Chemical Sciences, Mahatma Gandhi University Priyadarshini Hills, Kottayam 686 560, Kerala, India

² Instrumentation and Electron Microscopy Division Regional Research Laboratory, Thiruvanathapuram 695 019, India

³ National Chemical Laboratory, Pune 411 008, India

Received 21 July 1998; accepted 8 March 1999

ABSTRACT: Segmented block copolymers were synthesized from hydroxyl-terminated liquid natural rubber and polyurethane oligomers based on Bisphenol A and toluene diisocyanate by one-shot and two-shot processes in solution. Structural features were characterized by infrared and nuclear magnetic resonance spectroscopic analysis. The spectra of the one-shot materials were identical with those of the two-shot materials, indicating their chemical identity. The soft segment T_g was well defined and almost invariant around -64° C, but the hard segment T_{g} varied from 75 to 105°C as the hard segment content increased from 30 to 60 wt %. Two relaxation temperatures were observed for each sample in dynamic mechanical analysis (DMA). These observations and the two-stage thermal decomposition by random nucleation mechanism, as investigated in thermogravimetric analysis unambiguously confirmed complete phase segregation in these materials. The scanning electron microscopy and optical micrographs showed well-defined domains dispersed in a matrix, indicating the two-phase morphology. Systematic changes in hardness and tensile properties with hard segment content were also observed. The samples behaved like soft elastomers at lower hard segment content, toughened plastics at high hard segment content, and rigid elastomers at intermediate compositions. Variations in hardness and tear strength were consistent with this behavior. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 706-721, 1999

Key words: liquid natural rubber; polyurethanes; segmented block copolymers; thermoplastic elastomer; phase separation

INTRODUCTION

Microphase separation and domain structure in polyurethane elastomers depend mostly on the nature of hard segments. Diphenyl methane-4,4'diisocyanate (MDI)-based polyurethane elastomers in contrast to toluene diisocyanate (TDI)-based materials possess a more perfect domain organization^{1,2} due to long-range order and show a higher extent of segregation between soft and hard segments. Thermodynamically phase separation is more complete with aromatic hard segments because of increased thermodynamic incompatibility between hard segments and aliphatic soft segments. However, from a kinetic point of view, phase separation becomes more complete with aliphatic hard segments because of increased mobility. Studies conducted by Li et al.³ support the kinetic point of view. The aromatic diisocyanates lead to polyurethanes, which turn yellow on exposure to ultraviolet (UV) light.⁴ Hexamethylene diisocyanate (HDI) is an obvious choice to light stability. Improved resistance to discoloration, thermal, and hydrolytic attack are achieved by 4,4'-dicyclohexylmethane di-

Correspondence to: M. R. Gopinathan Nair. Journal of Applied Polymer Science, Vol. 74, 706–721 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/030706-16

Sample	Molar Composition HTNR–TDI–BPA	Hard Segment (%)
NR-BPA (70/30)	1.0/4.27/3.19	32.89
NR-BPA (60/40)	1.0/6.09/4.97	42.26
NR-BPA (50/50)	1.0/8.62/7.45	51.63
NR-BPA (40/60)	1.0/12.42/11.18	61.09
NR-BPA (30/70)	1.0/18.76/17.39	70.67

Table IThe Overall Compositions of the BlockCopolymers of NR-BPA

isocyanate, xylene diisocyanate, and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate. The effect of diisocyanate structure on the physical properties and morphology of polyurethane elastomers was studied by Gibson et al.⁵ and Zhao.⁶ The effect of different chain extenders^{7–10} and diisocyanates^{11–15} on the thermoplastic polyurethane morphology and properties was reported by Wang and Kenney.⁴ Synthesis and characterization of block copolymers containing natural rubber soft segments have been reported recently.^{16–18} These works also deal with the structure-property relation existing in the materials. The present work envisages the study of the effect of aromatic chain extenders on the morphology and properties of a series of polyurethane elastomers based on natural rubber soft segments.

EXPERIMENTAL

Materials

Natural rubber (ISNR-5) has been supplied by Rubber Research Institute of India, Kottayam. Toluene diisocyanate (TDI; 80 : 20 mixture of 2, 4and 2, 6-isomers) was obtained from Fluka, Switzerland, and was used as received. Bisphenol A (BPA) (Merck) was fused and dried in vacuum before use. Tetrahydrofuran (THF) was dried by sodium wire and distilled before use. Dibutyl tin dilaurate (DBTDL) (Fluka) was used as received.

Preparation of Hydroxyl-Terminated Liquid Natural Rubber

Hydroxyl-terminated liquid natural rubber (HTNR) was made in the laboratory by a procedure reported earlier.¹⁹ The sample has got a number-average molecular weight equal to 3000 and an average functionality of 1.94.

Synthesis of the Block Copolymers

One-Shot Process

The stoichiometric amounts (Table I) of HTNR and bisphenol A were dissolved in THF and taken



Figure 1 IR Spectra of (a) HTNR; (b) —NCO endcapped NR; (c) BPA-based polyurethane hard segment; (d) block copolymer by the two-shot process.



Scheme 1 Course of the reaction (one-shot process).

in a flat-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel. DBTDL catalyst (about 0.03% by weight of HTNR) was added, and the solution was kept under reflux. The required quantity of TDI was added through the dropping funnel over a period of 45 min with constant stirring. A 2% excess TDI was used in order to compensate any loss during transfer. The reaction was continued for a further period of 4 h. The excess THF was distilled off, and the viscous polymer solution was cast in trays treated with a silicon releasing agent and kept for curing at 70°C for 24 h, followed by 2 weeks of aging at room temperature in a dry atmosphere.

Two-Shot Process

The stoichiometric amount (Table I) of HTNR was dissolved in THF and taken in a flat-bottomed



Scheme 2 Course of the reaction (two-shot process).

flask to get a 20% solution. The flask was equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel. About 0.03% of DBTDL catalyst (by weight of HTNR) was added to the solution and refluxed at 80°C. TDI dissolved in THF was added dropwise with constant stirring, and the reaction was continued for 90 min to ensure endcapping of HTNR. The required quantity of bisphenol A in THF (20% w/v) was then added over a period of 45 min. The reaction was continued for 3 h. The excess THF was distilled off, and the viscous polymer solution was then cast, cured, and aged, as described above.

Polymer Designation

V + III

IV

The samples have been designated as follows. As an example, NR–BPA (70/30) means that the sample contains 70% by weight of HTNR and 30% by weight of polyurethane based on bisphenol A and toluene diisocyanate. The compositions of the block copolymers are summarized in Table I.



Figure 2 ¹H-NMR spectrum of NR–BPA (50/50).



Figure 3 ¹³C-NMR spectrum of NR–BPA (50/50).





Figure 4 DSC Thermograms of typical one-shot products: (a) NR–BPA (70/30) (Mettler analyzer); (b) NR– BPA (60/40) (Mettler analyzer); (c) NR–BPA (50/50) (Perkin–Elmer analyzer); (d) NR–BPA (40/60) (Perkin– Elmer analyzer).

Figure 5 DSC thermograms of typical two-shot products: (a) NR–BPA (70/30) (Perkin–Elmer analyzer); (b) NR–BPA (60/40) (Perkin–Elmer analyzer); (c) NR–BPA (50/50) (Perkin–Elmer analyzer); (d) NR–BPA (40/60) (Perkin–Elmer analyzer).

	T_g of the Soft Segment (°C)	$T_{_S}$ of the segment $T_{_S}$	ne Hard ent (°C)
Sample	One Shot	One Shot	Two Shot
NR-BPA (70/30)	-65.60	75.70	74.60
NR–BPA (60/40)	-65.30	93.20	91.80
NR-BPA (50/50)	—	98.40	97.70
NR-BPA (40/60)		105.10	103.40

Table II	Glass	Transition	Temperatu	res of
NR-BPA	Block	Copolymer	s Observed	in the
DSC The	rmoor	ams		

Measurements

Infrared (IR) spectra of the samples were recorded on a Shimadzu IR-470 Spectrometer. The ¹H nuclear magnetic resonance (¹H-NMR) spectrum was recorded on a Bruker AC 200 MHz NMR Spectrometer and ¹³C nuclear magnetic resonance (¹³C-NMR) on a Bruker AC 50 MHz NMR Spectrometer. Differential scanning calorimetry (DSC) was performed with a Mettler Inc (TA 300) microcalorimeter and with a Perkin-Elmer Delta Series DSC 7 calorimeter at a heating rate of 10°/min. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA 7 analyzer at a scanning rate of 10°/min. The dynamic mechanical measurements (DMA) was carried out on a processor controlled Rheovibron, model RHEO-426B DDV IIC (Japan) at a fixed frequency of 35 Hz. Samples were heated at a nominal rate of 1.5°C per minute under dry nitrogen atmosphere. Stress-strain behavior was studied on a Zwick 1474 Universal Testing Machine (UTM) as per the ASTM D 412-80 test method at a constant crosshead speed of 500 mm/min. Tear strength of the samples was tested on a Zwick 1474 UTM as per ASTM D624-81 test method using nicked 90°

angle specimen. The shore-A hardness of the samples were measured at 25°C by using 60 13805 type A durometer as per ASTM D 2240-75 test method. The morphology of the materials was studied by using JEOL JSM-35 C scanning electron microscope (SEM) and Leitz Orthoplan microscope.

RESULTS AND DISCUSSION

IR Spectroscopy

The IR spectra of the block copolymers prepared by the two-shot and one-shot processes exhibit all the features of NR and polyurethane segments. The results are presented in Figure 1. Figure 1(a) shows the IR spectrum of HTNR, Figure 1(b) shows that of -NCO endcapped NR, and Figure 1(c) shows polyure than e oligomer prepared from TDI and bisphenol A, and Figure 1(d) shows the block copolymer synthesized by the two-shot process. It clearly indicates the endcapping of HTNR with TDI and subsequent chain extension with BPA in the two-shot process. It is found that the band at 2260 cm^{-1} is absent in Figure 1(d), which indicates that the reaction is complete and the products contain no residual diisocyanate. These results agree well with the course of the reaction given in Schemes 1 and 2. It is also observed that the IR spectra of the one-shot and two-shot products are identical indicating that all the products are chemically identical, irrespective of their method of synthesis.

NMR Spectroscopy

The ¹H-NMR and ¹³C-NMR spectra of the block copolymers support the IR spectra in characterizing the features of the soft and hard segments. The NMR spectra of the one-shot and two-shot samples are also found to be identical. Figure 2 represents the ¹H-NMR spectrum of NR–BPA

Fable III	T_g Values	of the Various	Polyurethanes
-----------	--------------	----------------	---------------

~	T_g of the Hard Segment (°C)					
NR–PU	NR–EG	NR–PG	NR–1,3-BDO	NR–1,4-BDO	NR–BPA	
70/30	82.10	74.05	_	_	75.70	
60/40	90.67	78.30	73.53	88.70	93.20	
50/50	94.50	82.20	76.43	94.15	98.40	
40/60	98.80	88.90	83.33	99.55	105.10	



Figure 6 Thermograms of the one-shot products from TGA analysis: (a) NR-BPA (70/30); (b) NR-BPA (60/ 40); (c) NR-BPA (50/50); (d) NR-BPA (40/60).

(50/50), and Figure 3 is the ¹³C-NMR spectrum of the same sample, which include all the features of the hard and soft segments. Some minor peaks are also observed in the spectra, which are attrib-

uted to probable side products. The peaks characteristic of the hard segments are found to be relatively weak due to the low solubility and, hence, the low mobility of the hard segments in the solvent.



WEIGHT (%)

TEMPERATURE (^OC)

Figure 7 Thermograms of the two-shot products from TGA analysis: (a) NR-BPA (70/30); (b) NR-BPA (60/ 40); (c) NR-BPA (50/50); (d) NR-BPA (40/60).

	Onset of Mass Loss (°C)		Mass Loss (%)		Peak Temperature from DTG Curve (°C)	
Sample	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR-BPA (70/30)	192.00	334.00	31.56	68.03	267.53	386.05
NR-BPA (60/40)	205.00	335.21	41.17	58.00	267.00	395.80
NR–BPA (50/50)	202.80	333.12	50.50	49.40	263.85	396.01
NR-BPA (40/60)	205.90	342.00	61.20	38.51	276.85	388.65

Table IVPhenomenological Data of Thermal Decomposition of NR-BPA Block Copolymersof One-Shot Process

Differential Scanning Calorimetry

The differential scanning calorimetric analysis of selected products has been carried out, and the thermograms are presented in Figures 4 and 5, respectively, for the one-shot and two-shot samples. The glass transition temperatures observed on these thermograms are tabulated in Table II.

The soft segments exhibit a well-defined glass transition temperature around -64° C [Fig. 4(b)]. This temperature is very close to that of HTNR (-68°C), and its variation with the variation in the hard segment content is very small. Camberlin and Pascault²⁰ attribute this behavior to a complete or almost complete phase separation in the samples. This also confirms the two-phase nature of the products.

The hard segments in all the samples show a single T_g , which varies with the variation in hard segment content. Among the one-shot products, the copolymer with 30% hard segment has a T_g value of 75°C, which increases to 105°C when the hard segment increases to 60%. A similar increase in hard segment T_g is observed among the two-shot products also. This gradual increase in hard segment T_g value with increase in hard segment content is attributed to the higher molecu-

lar weight of the hard segments. Observation of a single hard segment T_g for the samples is an indication of a narrow molecular weight distribution for the hard segments.

On comparing the T_g values of these samples with those of the polyurethane elastomers based on aliphatic chain extenders,²⁰ such as ethylene glycol (EG), propylene glycol (PG),¹⁸ 1,3-butane diol (1,3-BDO), and 1,4-butane diol (1,4-BDO), it is observed that the methyl and phenyl groups in BPA have got some remarkable influence in their thermal properties. Table III presents a comparative account of the T_g values of various polyurethanes.

NR–BPA samples exhibit higher values for hard segment T_g , and the values increase in the range of 75 to 105°C for the one-shot products and 74 to 103°C for the two-shot products as the hard segment content varies from 30 to 60 wt %. The corresponding T_g values of NR–PG samples are 74 and 88°C for the one-shot products and 71 and 88°C for the two-shot samples. Polyurethanes based on other aliphatic chain extenders also exhibit a similar lower range of T_g values (Table III). The higher T_g value of NR–BPA samples may be due to the chain stiffening caused by the

Table VPhenomenological Data of Thermal Decomposition of NR-BPA Block Copolymersof Two-Shot Process

	Onset of Mass Loss (°C)		Mass Loss (%)		Peak Temperature from DTG Curve (°C)	
Sample	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR-BPA (70/30)	205.90	332.50	32.17	67.80	279.88	387.56
NR-BPA (60/40)	206.50	334.80	38.13	61.82	244.13	388.21
NR-BPA (50/50)	206.20	335.90	52.00	48.00	258.65	385.61
NR-BPA (40/60)	209.80	340.10	61.43	37.30	284.65	408.60

Composition NR–PU			Onset of Mass Loss	(°C)	
	NR–EG	NR–PG	NR–1,3-BDO	NR–1,4-BDO	NR–BPA
70/30	229.47	274.75	203.00	244.71	205.90
60/40	236.35	259.36	208.00	253.38	206.50
50/50	248.03	261.35	198.00	_	206.20
40/60	253.43	267.90	201.00	252.42	209.80

Table VIThe Onset of Mass Loss in the First Stage of Decomposition of the Various BlockCopolymers of Two-Shot Process

aromatic ring system and the methyl substituents present in the hard segments.

Thermogravimetric Analysis

The thermogravimetric analysis of the block copolymers showed a two-stage thermal decomposition of the samples corresponding to the two phases present. The thermograms are given in Figures 6 and 7, respectively, for the one-shot and two-shot samples. Tables IV and V summarize the respective phenomenological data of thermal decomposition.

The extent of mass loss in each stage was proportional to the percentage of composition of the block copolymers. As an example, decomposition of NR–BPA (40/60) (one-shot) took place with 61% mass loss in the first stage and 38% mass loss in the second stage. These values correspond to the weight percentage of the hard and soft segments, respectively, present in the copolymer. All other samples of both one-shot and two-shot processes also decomposed in the same pattern. Hence, the first stage of decomposition is due to the hard segment phase, while the second stage is due to the soft segment phase.

The onset of mass loss in one-shot samples took place between 192 and 205°C and completed be-

tween 332 and 341°C. The second stage of decomposition started in the temperature between 333 and 342°C and completed in the temperature range 528–575°C. In two-shot samples, the onset of mass loss and the temperature of decomposition fall in the same range as those in the one-shot products. Table VI gives a comparison of the onset of mass loss between the various block copolymers of two-shot process.

Kinetic Parameters from the Thermal Decomposition Data

The integral method using the least square technique reported by Madhusudanan et al.²¹ is applied to calculate the kinetic parameters for the decomposition of the block copolymers from the thermogravimetric (TG) curves. The integral equation²² is

$$\ln g(\alpha)/T^2 = \ln[AR/\Phi E(1 - 2RT/E] - E/RT]$$

where $g(\alpha)$ is the kinetic model function [α = the fraction decomposed]. *A* is the Arrhenius parameter, which is calculated from the intercept by the following relation: intercept, ln *AR*/ ΦE ; R, the universal gas constant; *E*, the energy of activa-

 Table VII
 Kinetic Parameters for the Thermal Decomposition of NR-BPA Block Copolymers of the

 One-Shot Process
 Process

	Activation Energy E (KJ/mol)		Arrhenius Parameter A (s ⁻¹)		Entropy of Activation ΔS	
Sample	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR–BPA (70/30) NR–BPA (60/40) NR–BPA (50/50) NR–BPA (40/60)	$65.4 \\ 67.2 \\ 70.0 \\ 76.0$	64.0 69.0 66.0 67.3	$\begin{array}{c} 4.778 \\ 3.228 \\ 5.029 \\ 8.168 \end{array}$	$2.57 imes 10^{-2} \ 1.03 imes 10^{-1} \ 1.04 imes 10^{-1} \ 6.46 imes 10^{-1}$	-236.84 -240.11 -236.34 -232.53	-281.94 -251.37 -270.41 -255.16

Activation Energy <i>E</i> (KJ/mol)		Energy <i>E</i> (mol)	Arrhenius Parameter A (s ⁻¹)		Entropy of Activation ΔS	
Sample	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR-BPA (70/30)	65.9	65.4	1.19	$1.26 imes10^{-2}$	-229.45	-211.26
NR-BPA (60/40)	66.8	70.8	3.54	$1.59 imes10^{-1}$	-238.97	-221.74
NR-BPA (50/50)	69.7	67.4	5.52	$1.76 imes10^{-1}$	-235.52	-269.26
NR-BPA (40/60)	73.8	74.1	5.08	$1.93 imes10^{-1}$	-236.60	-265.45

 Table VIII
 Kinetic Parameters for the Thermal Decomposition of NR-BPA Block Copolymers of the Two-Shot Process

tion; and T, the absolute temperature. The entropy of activation ΔS is calculated using the following relation: $A = kT_s/he^{\Delta S/R}$; where k is the Boltzmann constant; T_s , the peak temperature in the DTG curve; and h, the Planck's constant.

Several mechanistic equations have been derived by different authors based on the integral method to determine the decomposition kinetics. Satava²³ has chosen nine equations based on nine different mechanisms [i.e., nine different forms of $g(\alpha)$]. The equation which best represents the experimental data gives the proper mechanism.

In the present work, all the TG data were analyzed using the nine mechanistic equations. It is found that the highest correlation coefficient and, hence, the best fit curve, was obtained from Mampel equation,²⁴ irrespective of the composition and the method of synthesis of the block copolymers. Hence, it is concluded that the thermal decomposition of these segmented block copolymers follows a random nucleation mechanism with one nucleus on each particle, which is the rate-controlling process. The kinetic parameters calculated from the TG curves of one-shot and two-shot products are summarized in Tables VII and VIII, respectively.

A remarkable observation made in this study is that the activation energy of thermal decomposition of these block copolymers has much lower values than those reported for the aliphatic chain extender-based block copolymers. Table IX presents a comparative account of the activation energy values of thermal decomposition of various block copolymers synthesized by the two-shot process.²⁰ The low values of activation energy for these samples indicate that the block copolymers based on aromatic chain extenders are thermally less stable than block copolymers based on aliphatic chain extenders. The low thermal stability of the former is caused by the aromatic ring system, which tends to weaken the urethane linkage by the -I effect from either end.

Dynamic Mechanical Analysis

The relaxation behavior of selected products has been examined and presented in Figures 8 and 9. Figure 8 represents the temperature dependence of the storage modulus (E') and loss modulus (E'')of typical two-shot samples. The corresponding tan δ versus temperature curves are given in Figure 9. The samples exhibit two principal relaxations corresponding to the two phases present in the materials. The major relaxation around -37° C characterized by a decrease in the storage modulus of about two orders of magnitude is at-

Table IXActivation Energy Values for the First Stage of Thermal Decomposition of the VariousBlock Copolymers of the Two-Shot Process

			Activation Energy E (F	(J/mol)	
Composition NR–PU	NR–EG	NR–PG	NR–1,3-BDO	NR–1,4-BDO	NR–BPA
70/30	78.8	101.4	68.9	103.7	65.9
60/40	91.6	105.7	86.5	106.2	66.8
50/50	94.1	109.8	87.8		69.7
40/60	98.0	106.2	89.6	108.6	73.8



Figure 8 Temperature dependence of the storage modulus (E') and loss modulus (E'') of typical two-shot products.

tributed to the glass transition temperature of the NR soft segments. This value is found to be unaffected by the hard segment content, indicating that the soft segment is completely phase-segre-



Figure 9 Temperature dependence of tan δ of typical two-shot products.

Table XRelaxation Temperatures of the Softand Hard Segments of NR-BPA BlockCopolymers of the Two-Shot Process from DMA

Sample	T_g of the Soft Segment (°C)	T_g of the Hard Segment (°C)
NR-BPA (60/40)	-36.1	134.7
NR-BPA (60/40)	-37.8	151.7
NR-BPA (60/40)	-37.5	155.5

gated from the hard segments. The loss modulus curves also exhibit a second relaxation indicated by a second peak or shoulder at a higher temperature, the position of which advances as the hard segment content increases. Obviously, this is attributed to the glass transition of the polyurethane hard segments.

The relaxation values observed from the DMA curves are summarized in Table X. The relaxation behavior of these block copolymers closely parallels their DSC thermal transition behavior. However, the relaxation temperatures observed in DMA are fairly higher than the T_g values obtained from DSC. The difference in soft segment T_g is found to be about 25°. A corresponding increase in the hard segment T_g is also observed. This difference is presumably due to the difference in heating rate and the different types of analyzers used in the two methods.

Consistent with the observations on other phase segregated systems,²⁵ the level plateau storage modulus above the soft segment T_g increases with increasing hard segment content. This may be attributed to an increase in volume fraction of the hard segment. The reinforcing nature of the hard domains is responsible for the increase in modulus.

An interesting observation is that the magnitude of the soft segment damping peak (Fig. 9) decreases with increase in hard segment content. This clearly reflects a change in sample morphology from a continuous soft-segment-rich matrix to a continuous hard-segment-rich matrix.

Stress-Strain Behavior

The stress-strain curves of the block copolymers prepared by the one-shot and two-shot processes are given in Figure 10, and the results are summarized in Table XI. Systematic changes in tensile properties are observed as the percentage of hard segments increases. For example, the



Figure 10 Stress-strain curves of (a) one-shot and (b) two-shot products.

strength of one-shot sample with 30% hard segment is 7.21 N/mm². It increases to 28.60 N/mm² as the hard segment content increases to 60%. The two-shot samples have the corresponding values 8.34 and 30.65 N/mm², respectively. The initial modulus increases with increase in the hard segment content (Table XI), which indicates that the hard segments impose greater rigidity on the samples and the less mobile hard segment domains have much difficulty in sliding past one another. Ferguson and Ahmad²⁶ explain that the change in initial modulus is associated with phase change that occurs with variation in hard segment content. As expected, the elongation at break decreases with increasing hard segment content. It is the continuous phase that determines the elongation behavior.

Smith²⁷ correlates the better mechanical properties of samples with high hard segment content to the strengthening effect contributed by the hard domains. They act as virtual crosslinks and mechanically reinforce the elastomer, providing rigidity and high-level cohesiveness. They also dissipate strain energy by undergoing plastic deformation and cavitations and prevent failure by deflecting and bifurcating propagating cracks. However, these samples possess only lower tensile properties compared to those of conventional polyurethanes. The relatively low mechanical properties of these block copolymers may be attributed to (1) the absence of phase mixing between the two types of segments and (2) the inability of the short rubber chains to crystallize under strain.²⁸ The two phases are debonded at

	Tensile (N/r	Strength nm ²)	Elastic Modu	ulus (N/mm ²)	Elongation	at Break (%)
Sample	One-Shot	Two-Shot	One-Shot	Two-Shot	One-Shot	Two-Shot
NR-BPA (70/30)	7.21	8.34	0.40	0.53	242	264
NR-BPA (60/40)	8.98	10.35	0.63	0.67	137	219
NR-BPA (50/50)	15.22	18.71	2.75	3.21	82	106
NR-BPA (40/60)	28.60	30.65	6.65	8.15	43	59

Table XI Tensile Properties of NR-BPA-Based Block Copolymers

relatively low stress creating craters in the rubber matrix.

Bengston et al.²⁹ explain the variation of mechanical properties with an increase in hard segment content as due to changes in sample morphology. In materials with relatively low hard segment content, the NR soft segment is the continuous phase with hard segment domains acting as physical crosslinks and reinforcing filler. Thus, the material behaves as soft elastomers [e.g., NR-BPA (70/30)] and exhibits relatively low mechanical properties. In materials with high hard segment content, the hard segment is expected to be the continuous phase with domains of the elastomer toughening the material. This material behaves like toughened plastics and exhibits high mechanical properties. It also exhibits necking and yielding during the deformation process. Intermediate materials (with 40 and 50% hard segments) appear to be bicontinuous in nature. They possess moderate mechanical properties.

The two-shot materials, in general, have slightly higher tensile strength and ultimate elongations than the one-shot materials. It is attributed to a more interconnected hard segment domains in two-shot samples due to a more ordering of the hard segments, which is more effective at stopping the convulsive crack growth through soft segment matrix.

A comparison of the tensile properties of these block copolymers with those of the aliphatic chain-extender-based systems²⁰ shows that the former has better tensile properties than the latter. This may be attributed to the strengthening effect offered by the aromatic ring system present in the hard segments. Table XII presents a comparative data of the tensile strengths of the various block copolymers²⁰ synthesized in our laboratory.

Scanning Electron Microscopy

The scanning electron micrographs of tensile fracture surface of the block copolymers synthesized by the one-shot and two-shot processes are given in Figures 11 and 12, respectively. In both figures, (a), (b), and (c) are micrographs of samples containing 30, 50, and 60% urethane, respectively.

All the micrographs exhibit the coexistence of two immiscible phases in the products. A continuous matrix is observed in which some beadlike structures are found dispersed in a random manner. The size and density of these beads are found to vary from sample to samples. The large size

Table XII	Comparison of	f the Tensile	Strengths of	Various Bloc	ok Copolymer	S				
Composition					Tensile Stren	gth (N/mm ²)				
NR-PU	NR-	-EG	NR-	-PG	NR-1,5	3-BDO	NR-1,4	-BDO	NR	BPA
	One-Shot	Two-Shot	One-Shot	Two-Shot	One-Shot	Two-Shot	One-Shot	Two-Shot	One-Shot	Two-Shot
70/30	2.30	3.25	2.45	5.64	4.80	5.38	4.06	4.91	7.21	8.34
60/40	3.46	6.12	4.03	8.07	8.40	8.45	7.88	8.02	8.98	10.35
50/50	9.52	13.53	9.90	14.14	12.20	15.18	12.01	14.53	15.22	18.71
40/60	14.00	23.79	14.25	24.67	19.50	25.50	16.28	22.20	28.60	30.65
30/70	27.00	28.35	29.20	33.04	30.93	34.80	29.86	31.56		







(c)

Figure 11 Scanning electron micrographs of typical one-shot products: (a) NR–BPA (70/30); (b) NR–BPA (50/50); (c) NR–BPA (40/60).

and the nature of the beads suggest that they are independent of the block copolymer structure. It is presumed that they are formed by the agglomeration of the polyurethane homopolymers, which remain unbonded to the rubber chains during the block copolymerization reactions. The matrix could be the block copolymer formed from the NR soft segments and the polyurethane hard seg-



(a)



(b)



Figure 12 Scanning electron micrographs of typical two-shot products: (a) NR–BPA (70/30); (b) NR–BPA (50/50); (c) NR–BPA (40/60).

		Mean Doma	in Size (µm)	Domain De	nsity (m ⁻²)
Sample	Hard Segment (%)	One-Shot	Two-Shot	One-Shot	Two-Shot
NR–BPA (70/30) NR–BPA (50/50) NR–BPA (40/60)	38.53 47.77 57.39	5.26 55.29 27.20	$5.04 \\ 55.24 \\ 26.57$	$9.72 imes 10^8 \ 1.44 imes 10^8 \ 2.98 imes 10^8$	$9.99 imes 10^8 \ 1.46 imes 10^8 \ 3.10 imes 10^8$

 Table XIII
 Variation of Bead Size and Bead Density with the Urethane Content (Measured from SEM)

ments. A domain morphology could naturally be expected of this matrix. However, the microphase separation of the soft and hard segments in the matrix could not be observed due to the low resolution in the SEM analysis.

A domain morphology of the block copolymers is expected on the basis of the following facts. The hard segments are highly polar with high potential for hydrogen bonding. These highly polar segments would be almost incompatible with the nonpolar rubber segments so that the former could form well-defined hard domains showing sharp boundaries with the matrix. Moreover, the solubility parameters of the polyurethane and NR differ largely and, hence, segments of similar chemical composition segregate and form discrete domains. These characteristics of the two types of segments are further evidenced by the presence of well-defined beads in the SEM micrographs. Hence, phase mixing is practically absent in these segmented block copolymers.

Table XIII displays the variation of the bead size and bead density with the urethane content. The mean size in sample with 30% urethane content is found to be 5.26 and 5.04 μ m, respectively for the one-shot and two-shot samples. The corresponding values in 50% samples are 55.29 and 55.24 μ m, respectively; and in 60% samples, the respective values are 27.20 and 26.57 μ m. Not much difference in the size and distribution of the beads is observed between the one-shot and two-shot samples of this system. This indicates that the chain extension reaction takes place more or less uniformly in both the methods of synthesis.

Optical Microscopy

The optical micrographs of NR–BPA (50/50) of one-shot and two-shot materials are shown in Figure 13(a) and (b), respectively. Both the micrographs clearly exhibit the incompatibility of the soft and hard phases and the segregation of phases, leading to domain structure. The hard domains are visible as white regions and the rubber phase as dark regions. Both the samples exhibit a network morphology at the macro level (low resolution in optical microscopy) with welldefined hard domains distributed uniformly in the matrix.





Figure 13 Optical micrographs of NR–BPA (50/50) (a) one-shot and (b) two-shot method.

	Tear Strength (N/mm)			
Sample	One-Shot	Two-Shot		
NR-BPA (70/30)	24.7	25.5		
NR-BPA (60/40)	27.0	29.4		
NR-BPA (50/50)	28.2	30.6		
NR-BPA (40/60)	31.6	33.7		

Table XIVTear Strengths of the BlockCopolymers of BPA-Based PU and NR

Tear Strength

The tear strength of the samples prepared by both processes have been presented in Table XIV. A gradual increase in the values is observed with increase of hard segment content. This could be attributed to the increased degree of phase separation, the increase in the molecular weight, and the ordering of domains within the hard segments. However, the materials have lower tear strength in comparison with the conventional phase-segregated elastomeric materials.

Hardness

The shore A hardness of the block copolymers has been measured by a hand-held Shore A durometer according to ASTM 2240-75 standards. Specimens were rectangular, 25 mm in length, and 3 mm wide. Six plies of samples were used to achieve a thickness of 6.4 mm. The results are summarized in Table XV. A linear increase in hardness with increase in the hard segment content is observed.

CONCLUSION

The segmented block copolymers synthesized from HTNR and polyurethane oligomers based on BPA and TDI were essentially amorphous phasesegregated systems exhibiting a two-phase morphology. The phase segregation was almost complete, and the driving force behind it was the extreme incompatibility of the nonpolar soft segment and the strongly polar hard segment units. Absence of any secondary bonding between the two types of segments further increased the incompatibility of the phases. The two-phase morphology was supported by the presence of two relaxation temperatures in DMA, of which one was subambient and the other was above ambient. It was also reflected in their thermal analysis. The DSC analysis gave two well-defined transition temperatures. The soft segment glass transition temperature was observed around -64° C, which was almost invariant with the increase in the hard segment content. The hard segment transition temperature varied from 75 to 105°C as the hard segment content increased from 30 to 60% by weight. TGA exhibited a two-stage thermal decomposition of the materials by random nucleation mechanism suggested by Mampel.

A systematic variation of the mechanical properties such as the Young's modulus and tensile strength with variation in hard segment content was investigated. Variation in hard segment content gave rise to three possible different microstructures: (1) the discrete hard segment domains were distributed in the continuous rubber segments so that the sample behaved like quasielastomer as in samples with low hard segment contents; (2) domains of rubber phase were distributed in the continuous hard phase, and, thus, the sample behaved like toughened plastics as in samples with high hard segmentcontent; (3) a bicontinuous structure of the intermediate compositions, which behaved like rigid elastomers, resulted. This behavior was better reflected by the two-shot products. Variations in tear strength and hardness also supported this behavior. The SEM and optical microscopic studies confirmed these morphological variations. SEM studies showed also some beadlike dispersions in the continuous matrix of the block copolymer, which were independent of the block copolymer structure. These were presumed to be the agglomeration of polyurethane homopolymers formed during the course of the chain extension process. Comparison of the properties of these materials with those of the aliphatic chain extended systems showed that the aromatic rings present in the hard segments of these materials offer a stiffening effect.

Table XVShore A Hardness of the BlockCopolymers of BPA-Based PU and NR

	Shore A Hardness	
Sample	One-Shot	Two-Shot
NR-BPA (70/30)	75	80
NR-BPA (60/40)	84	82
NR-BPA (50/50)	90	85
NR-BPA (40/60)	92	92

REFERENCES

- Koberstein, J. T.; Stein, R. S. J Polym Sci, Polym Phys Ed 1983, 21, 1439.
- Seefried, C. G.; Koleske, J. V.; Critchfield, F. E. J Appl Polym Sci 1975, 19, 2493.
- Li, Y.; King, W.; Stiffer, J. O.; Chu, B. Macromolecules 1994, 27, 15.
- Chun, C.; Wang, S.; Kenney, D. J. J Elasto Plastics 1995, 27, 182.
- Gibson, P. E.; Vallance, M. A.; Cooper, S. L. in Developments in Block Copolymers; Goodman, I., Ed.; Elsevier: London, UK, 1982.
- 6. Zhao, Q. University of Detroit, unpublished results.
- Blackwell, J.; Nagarajan, M. R.; Hoitink, T. B. Polymer 1982, 23, 950.
- Hong, J.; Lillya, C. P.; Chein, J. C. W. Polymer 1992, 33, 4347.
- Mevlida, V.; Enes, T.; Asia, S.; Vahid, S. Polimeri (Zagreb), 1990, 11, 15.
- Pandya, M. V.; Deshpande, D. D.; Hundiwale, D. G. J Appl Polym Sci 1988, 35, 1803.
- 11. Shu, L. Chem Abstr 1990, 112, 120372a.
- Oan, A. T.; Yeol, L. S.; Won, L. S.; Mo, J. H. Pollimo 1990, 14, 497.
- 13. Oan, A. T.; Pyo, H. I.; Ho, K. J.; Mo, J. H. Pollimo 1990, 14, 608.
- Pandya, M. V.; Deshpande, D. D.; Hundiwale, D. G. J Appl Polym Sci 1986, 32, 4959.

- 15. Schneider, N. S.; Sung, C. S. P.; Matton, R. W.; Illinger, J. L. Macromolecules 1975, 8, 62.
- Ravindran, T.; Nayar, M. R. G.; Francis, D. J. J Appl Polym Sci 1991, 42, 325.
- 17. Paul, C. J.; Nair, M. R. G. Ind J Nat Rubber Res 1992, 5, 199.
- Paul, C. J.; Nair, M. R. G.; Neelakantan, N. R.; Koshy, P. Polym Eng Sci 1998, 38, 450.
- Ravindran, T.; Nayar, M. R. G.; Francis, D. J. J Appl Polym Sci 1988, 5, 1227.
- Paul, C. J. School of Chemical Sciences, M. G. University, Kottayam, Ph.D. Thesis, 1997.
- Madhusudanan, P. M.; Yusuf, K. K. M.; Nair, C. G. R. J Therm Anal 1975, 8, 311.
- El-Sonabati, A. Z.; Diab, M. A. Acta Polym 1988, 39, 124.
- 23. Satava, V. Thermochim Acta 1971, 2, 423.
- 24. Mampel, K. L. Z Phys 1940, 187, 43.
- Brunette, C. M.; Hsu, S. L.; Rossman, M.; MacKnight, W. J.; Schneider, N. S. Polym Eng Sci 1981, 21, 668.
- Ferguson, J.; Ahmad, N. Eur Polym J 1977, 13, 865.
- 27. Smith, T. L. Polym Eng Sci 1977, 17, 129.
- Speckhard, T. A.; Hwang, K. K. S.; Yang, C. Z.; Laupan, W. R.; Cooper, S. L. J Macromol Sci, Phys 1984, 23, 175.
- Bengston, B.; Feger, C.; MacKnight, W. J.; Schneider, N. S. Polymer 1985, 26, 895.