Synthesis and Characterization of Block Copolymers Based on Natural Rubber and Polypropylene Oxide

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ABSTRACT: Segmented block copolymers from different grades of hydroxyl terminated liquid natural rubber (HTNR) ($\overline{M}_n$ 3000, 8800, 10,000, and 17,000) and polypropylene oxide (PPO) ($\overline{M}_n$ 1000, 2000, 3000, and 4000) have been synthesized and characterized by spectral analysis, thermal analysis, scanning electron microscopy (SEM), and mechanical testing. The glass transition temperature of NR block was found to be at about $-64°C$, which is independent of the PPO whose transition is around $15°C$. The thermogravimetric analysis (TGA) shows that the thermal degradation of the samples proceeded in two steps characteristic of the immiscible components. The inability of PPO segments to provide physical crosslinking and the subsequent formation of hard domains is reflected in the low tensile properties and tear properties. The amorphous nature of the PPO phase and its immiscibility with NR phase are evidenced by the SEM studies. The effect of molecular weight of PPO as well as HTNR on the properties of the block copolymers has also been discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 955–962, 2007

Key words: segmented block copolymer; liquid natural rubber; polypropylene oxide

INTRODUCTION

Segmented polyurethane elastomers are linear block copolymers of alternating polyurethane hard segments and different types of soft segments. In conventional block copolymers, soft segments are based on either polyether or polyester. These blocks are termed as soft segments because at the service temperature they exist in a rubbery state. The other block is a polyurethane oligomer, which is termed as hard segment. It is in the glassy or semicrystalline state at the service temperature. Dimensional stability is provided through microphase separation of the hard segments into domains, which then act as a reinforcing filler and multifunctional crosslinks.[1–4] Thermoplastic properties are displayed by these materials, as heating above their glass transition or melting will allow the materials to flow. A wide range of physical properties and morphologies has been reported based on the soft segments.[4–8]

Recently, polyurethane block copolymers with hydroxyl terminated liquid natural rubber (HTNR) as soft segments have been developed and investigated.[9–15] These materials are of interest in the study of structure–property relationships in segmented block copolymers. The potential for hydrogen bonding is and other interactive forces are absent in them when compared with the conventional polyether or polyester-based block copolymers. Hence they tend to be completely phase separated materials.[16–22] Paul and coworkers[9–12] studied the block copolymers based on PU and HTNR. The polyurethanes were prepared from toluene diisocyanate (TDI) and diols such as 1,2-ethylene diol, 1,2-propane diol, 1,3-butane diol, and bisphenol-A. These materials possess phase-separated morphology with amorphous characteristics. The present work involves the synthesis and characterization of this kind of block copolymers from HTNR and a polyether, viz., polypropylene glycol.

EXPERIMENTAL

Natural rubber (ISNR-5): viscosity average molecular weight = 820,000, intrinsic viscosity in benzene at $30°C = 4.45 \times 10^{-4}$ cm^3/g, Wallace plasticity, P_0 = 39.0. It was obtained from Rubber Research Institute of India, Kottayam. Hydrogen peroxide (30%) was supplied by Merck, India. Toluene (reagent grade) was obtained from Merck, India, and used as the solvent without any further purification. Methanol (reagent grade) was obtained from BDH, India, and used without further purification. Toluene diisocyanate (TDI) (80/20 mixture of 2,4- and 2,6-isomers) was obtained from Fluka, Switzerland, and was used

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TABLE I
**Composition and Molecular Weight of the Components
in NR/PPO Block Copolymers**

Sample designation	Molecular weight of HTNR	HTNR content (%)	Molecular weight of PPO	PPO content (%)
NR/PPO (3,000/1,000)	3,000	75	1,000	25
NR/PPO (3,000/2,000)	3,000	60	2,000	40
NR/PPO (3,000/3,000)	3,000	50	3,000	50
NR/PPO (3,000/4,000)	3,000	43	4,000	57
NR/PPO (8,800/1,000)	8,800	90	1,000	10
NR/PPO (8,800/2,000)	8,800	81	2,000	19
NR/PPO (8,800/3,000)	8,800	75	3,000	25
NR/PPO (8,800/4,000)	8,800	69	4,000	31
NR/PPO (10,000/1,000)	10,000	91	1,000	9
NR/PPO (10,000/2,000)	10,000	83	2,000	17
NR/PPO (10,000/3,000)	10,000	77	3,000	23
NR/PPO (10,000/4,000)	10,000	71	4,000	29
NR/PPO (17,000/1,000)	17,000	94	1,000	6
NR/PPO (17,000/2,000)	17,000	89	2,000	11
NR/PPO (17,000/3,000)	17,000	85	3,000	15
NR/PPO (17,000/4,000)	17,000	81	4,000	19

as received. Polypropylene oxide (PPO) was supplied by Aldrich. Dibutyl tin dilaurate (DBTDL) supplied by Fluka, Switzerland, was used as catalyst in the synthesis. Chloroform supplied by BDH, India, was used after distillation.

HTNR of number–average molecular weight 3000, 8800, 10,000, and 17,000 were prepared in the laboratory by the photochemical degradation of natural rubber as per reported procedure.[23] It was reprecipitated thrice from toluene using methanol and dried at 70–80°C in vacuum.

Synthesis of block copolymers

The segmented block copolymers with varying compositions were synthesized in solution by two shot process. The overall compositions of the reactants used for both the processes are given in Table I.

HTNR in chloroform (35% w/v) along with DBTDL (1% by weight of HTNR) were placed in a flat-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, a reflux condenser, and a dropping funnel. The solution was brought to reflux at a temperature between 70 and 80°C and stirred vigorously. The stoichiometric amount of TDI (2.01 mol/mol of HTNR) was dropped into it over a period of 30 min, followed by 2 h of the reaction to endcap HTNR. This was accompanied by the dropwise addition of the required amount of PPO as a solution in chloroform (35%) during 1.5 h, followed by 3 h of the reaction. The viscous liquid 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 h in a vacuum oven to remove residual solvent,

followed by 1 week aging at room temperature in a dry atmosphere.

Polymer designation

The samples were designated as follows. As an example, NR/PPO (3000/1000) means that the sample was synthesized by using HTNR of 3000 molecular weight and PPO of 1000 molecular weight. The exact composition is given in Table I.

Measurements

Infrared spectra of the samples were recorded on a Shimadzu FTIR-8400S Spectrometer (Japan). The ^{1}H-NMR spectrum was recorded on a Bruker AC 200 MHz NMR Spectrometer. Differential scanning calorimetry (DSC) was performed with a PerkinElmer Delta Series DSC 7 calorimeter (USA) at a heating rate of 10°C/min. All DSC scans were first scans. Glass transition temperature was noted as the temperature corresponding to one half the increases in heat capacity at the transition. Thermogravimetric analysis (TGA) was carried out using a PerkinElmer TGA 7 analyser (USA) at a scanning rate of 10°C/min. The peak temperature in the DTG curve is taken as the decomposition temperature. Stress–strain behavior was studied on a Zwick 1474 Universal Testing Machine (Germany), as per 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 ~ 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.

RESULTS AND DISCUSSION

Synthesis of the block copolymer was carried out by the chain extension of HTNR and PPO by two shot process. HTNR of molecular weight ($\overline{M}_n$) 3000, 8800, 10,000, and 17,000 were block copolymerized with PPO of four different molecular weights, viz., 1000, 2000, 3000, and 4000 to get samples with concomitant increase in PPO content. Thus, four series of block copolymers based on the four different HTNR samples of varying molecular weight were synthesized for this study. The characterization of the block copolymers and the effect of PPO molecular weight and HTNR molecular weight on the properties of the block copolymers are discussed in this section. Molecular weight and the percentage content of each component in the sample are listed in Table I. All the samples were characterized by various analytical techniques such as spectral (IR, NMR), thermal (TG and DSC), mechanical, and morphological studies.

Spectral analysis

The IR spectra of a representative block copolymer, viz., NR/PPO (3000/2000) is given in Figure 1. The sample shows all the characteristic features of the NR and PPO segments. ¹H-NMR spectra also support the formation of the block copolymer structure (Table II). The shielding characteristic of HTNR and PPO are observable in ¹H-NMR spectrum of NR/PPO (3000/2000) (Fig. 2). The signal at 1.6 ppm is due to the —CH₃ protons of the isoprene unit in NR segments. The singlet at 5.1 ppm is ascribed to the methyne proton of isoprene unit. The aromatic protons of TDI are observed around 7.35 ppm. The —CH₂— protons in the structural unit are seen at 2.0 ppm. On the basis of foregoing analysis, Scheme 1 has been proposed for the chemical reactions leading to the formation of the block copolymer.

Differential scanning calorimetric analysis

The DSC thermograms of samples containing PPO segments of molecular weight 2000 and 4000 are displayed in Figure 3. All the data are for the first heating of the samples. They display two distinct transition temperatures, one in the vicinity of the transition temperature of PPO and the other close to the T_g of NR. The glass transition at −64°C is caused by the NR component and the glass transition temperature of NR/PPO (3000/2000), NR/PPO (8800/2000), and NR/PPO (17,000/4000) are around 15°C, which is close to the T_g of PPO homopolymers. Closeness of the transition temperatures to that of the corresponding homopolymers suggests that phase separation is almost complete in the block polymers. Lack of interaction between the two segments leads
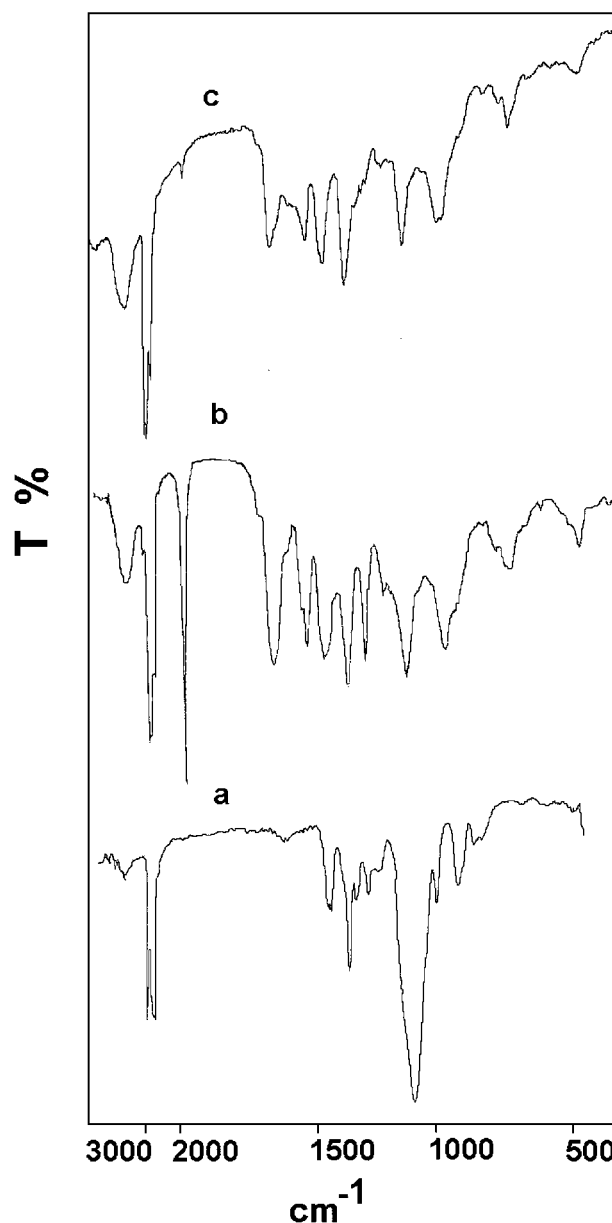

Figure 1 IR spectra of (a) PPO, (b) TDI endcapped HTNR, and (c) NR/PPO (3000/2000).

to such a situation. There is a large difference in the polarity between the two polymers. Solubility parameter values for HTNR and PPO are 16.5 and 18.7 (MPa$^{1/2}$) respectively.[23] Completely nonpolar NR segments and the PPO segments with polar character do not have the potential for intermolecular interaction, which explains the complete phase separation of the two components. Presence of a single glass transition for PPO indicates that the PPO segments possess narrow molecular weight distribution.

Thermogravimetric analysis

Thermogravimetric data of the representative samples are given in Table II and the TG curves of sam-

TABLE II
Thermal Data of NR/PPO Block Copolymers Based on HTNR-3,000 and HTNR-17,000 Molecular Weight

Sample	Onset of mass loss (°C)		Mass loss (%)		Peak temperature (°C)	
	Stage 1 (T_i)	Stage 2 (T_i)	Stage 1	Stage 2	Stage 1 (T_{max})	Stage 2 (T_{max})
NR/PPO (3,000/1,000)	250	380	27.7	71.27	295	436
NR/PPO (3,000/2,000)	250	380	44.3	55	298	436
NR/PPO (3,000/3,000)	251	382	56.4	42	299	438
NR/PPO (3,000/4,000)	253	382	63.1	35	301	440
NR/PPO (17,000/1,000)	249	360	10.7	88	300	424
NR/PPO (17,000/2,000)	251	362	14	83	300	426
NR/PPO (17,000/3,000)	250	349	18.4	80.6	301	421
NR/PPO (17,000/4,000)	249	361	24	75	298	428

ples based on NR-3000 molecular weight are shown in Figure 4. All the samples undergo decomposition in two stages during the thermal degradation. The two stages are separated by a plateau of temperature. This is indicative of the presence of two phases in the block copolymer, which degrade at two different ranges. Plateau between the two stages is very narrow showing that the decomposition of the two phases occurs at close ranges. For example, the final temperature in the Stage 1 degradation of NR/PPO (3000/1000) is found to be 380°C and the Stage 2 onset occurs at 405°C. The temperature gap is only 25°C. This is the trend seen in the case of other samples, also shown in Figure 4, viz., NR/PPO (3000/2000), (NR/PPO) (3000/3000), and NR/PPO (3000/4000). The temperature gaps for these samples are found to be 22, 20, and 17°C respectively.

In general, the extent of mass loss during the first stage of mass decomposition is close to the proportion of PPO in the sample. For example, in the case of NR/PPO (3000/1000), the percentage of mass loss in the first stage of decomposition is 27.73%, which corresponds to the percentage of PPO present in the block copolymer (25%). Therefore, decomposition in the first stage could be due to PPO. The onset of degradation (T_i), peak temperature (T_{max}), and the degradation temperature of the NR phase are found to be unaffected by the nature of the other phase. This is an indication that the two phases are isolated and remain without any sort of mutual interaction. The above-mentioned values are found to be more or less same irrespective of PPO molecular weight, indicating that PPO segments are present in an amorphous and flexible state.

Tensile properties

The tensile curves of a representative series of sample, viz., the one based on NR of molecular weight 3000 are shown in Figure 5. These curves exhibit the elastomeric nature of the samples. The curve shows a small elastic region initially. After 100% elongation, it runs almost parallel to the strain axis up to 200% elongation with a nominal rise in stress. Above this, the stress–strain curve shows a slight increase in the slope up to 300% elongation, which is followed by failure of the sample. This sample has a PPO content
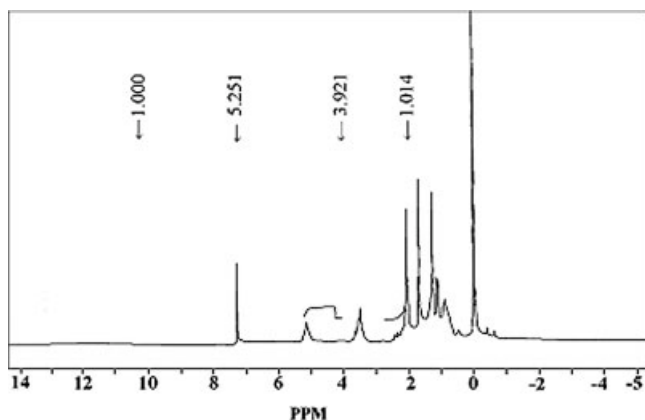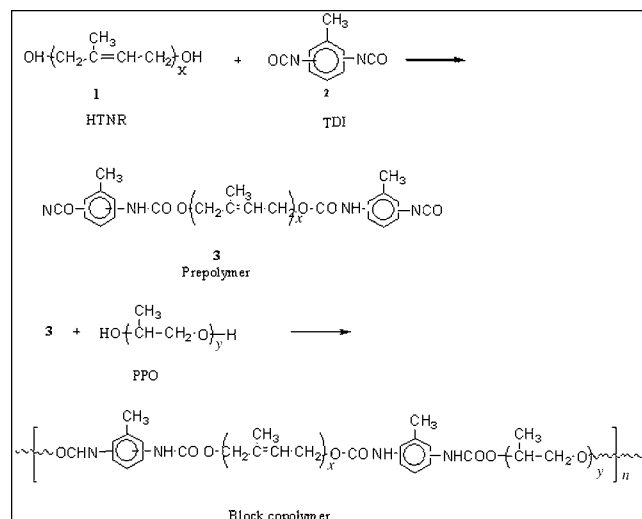
Figure 2 ^{1}H-NMR spectrum of NR/PPO (3000/2000).

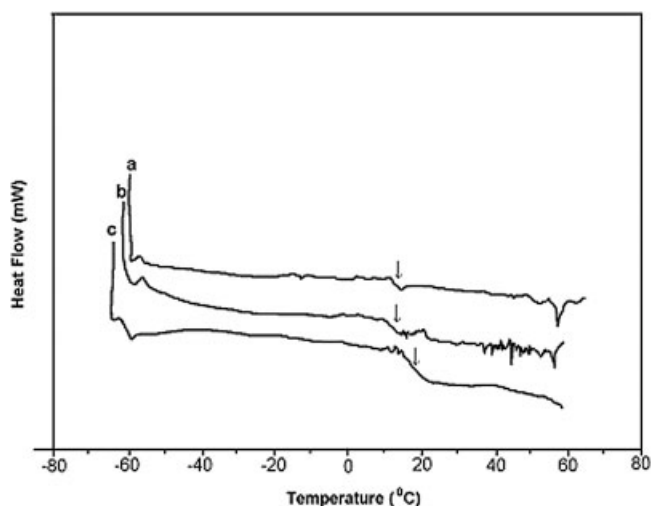**Scheme 1** Course of the reaction.

Figure 3 DSC curves of the NR/PPO block copolymers: (a) NR/PPO (3000/2000), (b) NR/PPO (8800/2000), and (c) NR/PPO (17,000/4000).
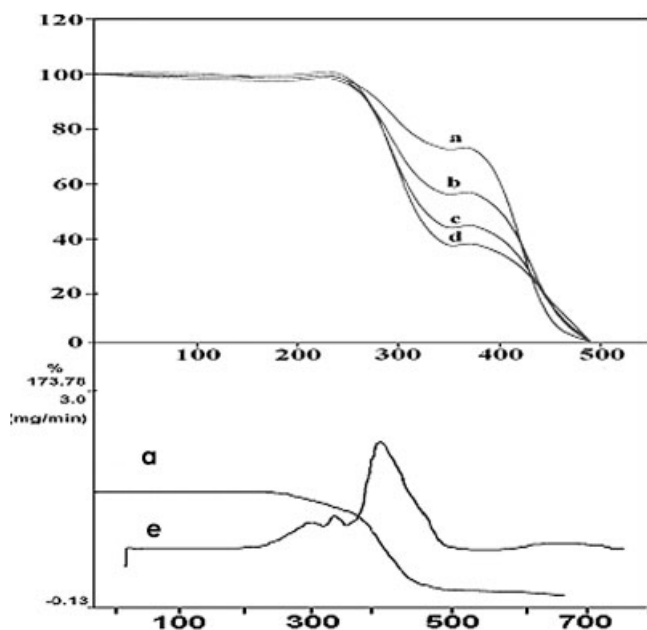

Figure 5 Tensile curves of NR/PPO block copolymers based on HTNR17000: (a) NR/PPO (17,000/1000), (b) NR/PPO (17,000/2000), (c) NR/PPO (17,000/3000), and (d) NR/PPO (17,000/4000).

of 25% and NR content of 75%. On increasing the molecular weight of PPO to 2000, 3000, and 4000 with a concomitant increase in PPO content to 40, 50, and 75%, the tensile curves of the corresponding samples shift towards the stress axis in the above order. The variation in tensile properties with respect to PPO molecular weight is shown in Figures 6–8. It is found that the tensile strength and modulus of elasticity increase with an increase in the molecular

weight of PPO. The tensile strength increases from 3.44 MPa for 25% PPO content sample to 5.26 MPa for the 75% PPO content in the case of NR-17,000 series on the other extreme (Fig. 6). This data also show that the series with higher NR molecular weight shows better tensile strength. Young's modulus also varies in the same way (Fig. 7). Wide variation in the values is found in the case of NR-3000 series of samples. The modulus for these samples increases from 0.8 to 2.4 MPa as the PPO molecular weight varies from 25 to 75%. As the NR molecular weight increases to 17,000, the modulus tends to vary in a lower range. As expected, elongation at

Figure 4 TGA curve of NR/PPO block copolymers based on HTNR3000: (a) NR/PPO (3000/1000), (b) NR/PPO (3000/2000), (c) NR/PPO (3000/3000), (d) NR/PPO (3000/4000), and (e) DTG curve of NR/PPO (3000/1000).
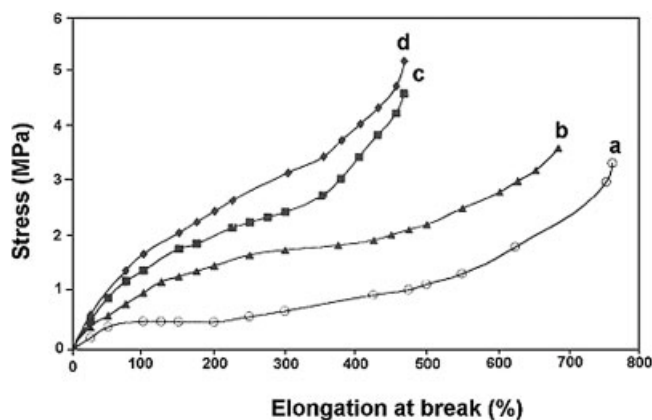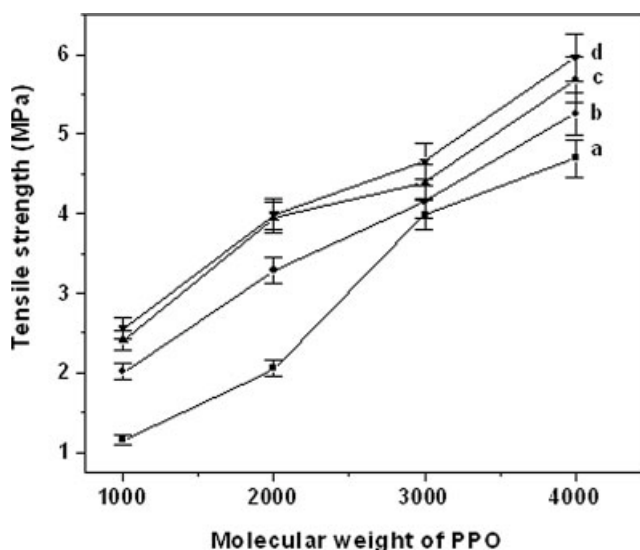

Figure 6 Variation of tensile strength of NR/PPO block copolymers with PPO molecular weight: (a) HTNR-3000, (b) HTNR-8800, (c) HTNR-10,000, and (d) HTNR-17,000.
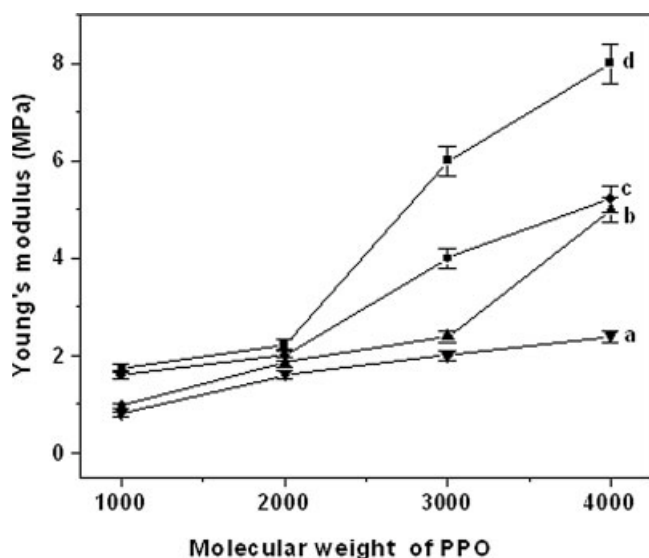
Figure 7 Variation of Young's modulus of NR/PPO block copolymers with PPO molecular weight: (a) HTNR-3000, (b) HTNR-8800, (c) HTNR-10,000, and (d) HTNR-17,000.

acteristics irrespective of the molecular weight of the component segments and the block copolymer composition. All the micrographs show the presence of two immiscible phases in the form of cloud-like presence of one phase that occurs in the matrix of the other. This indicates the absence of crystalline structures, suggesting that both components of the block copolymers are amorphous in nature. The polyether domains are magnified and shown in the micrographs. Amorphous nature of the PPO phase and its immiscibility with NR has already been accounted for in the former sections.

The effect of HTNR molecular weight is not very significant in the block copolymer systems studied. Thermal properties are not affected by the molecular weight of the NR segments, which indicates lack of intermolecular interactions. Microscopy also yielded similar results for all the block copolymers irrespective of the NR molecular weight. The mechanical properties show variations, which lie in a small range (Fig. 5). This is visible in samples based on PPO-1000, which showed a rise in tensile strength from 1.15 to 3.44 MPa as the HTNR molecular weight was varied from 3000 to 17,000. However, other series based on PPO-3000 and PPO-4000 does not exhibit any such rise in tensile strength. Modulus of elasticity is found to increase as the molecular weight was increased from 3000 to 8800 and then falls for samples containing HTNR-10,000 and HTNR-17,000. Elongation at break increases in all cases with the increase in the HTNR molecular weight, whereas the reverse effect was observed in the case of tear strength. Thus, the soft segment
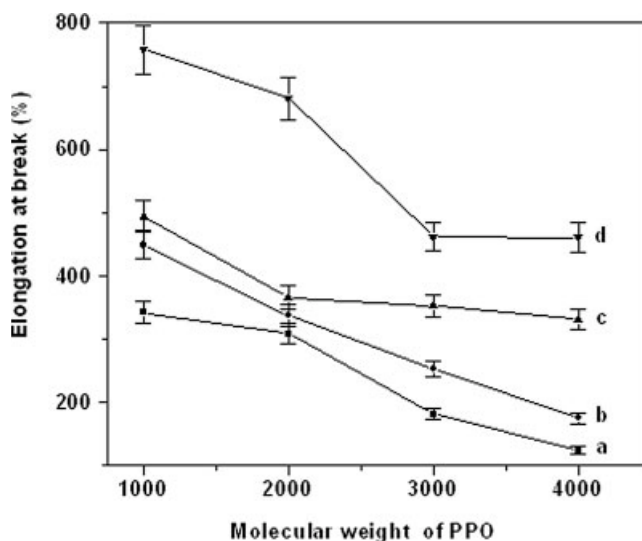
break decreases with increase in PPO molecular weight. Also, the values are higher for the series of samples with higher NR molecular weight (Fig. 8).

Generally, domain morphology is reported to be influencing the tensile strength of block copolymers. Polypropylene glycol is amorphous as the atactic methyl substituent prevents the crystallization of the PPO segments. This is supported by DSC and SEM results. DSC shows transition temperatures, which lie below room temperature for PPO segments. So, these segments are unable to provide physical crosslinks by forming hard domains. The chains entangle each other providing the only binding force (weak crosslinks) in the block copolymer system. Entanglement of chain would be the stress distribution point. There may be interloop between chains, which may slip and take up new positions without disengaging under stress. Because of their slippage, stress is more equitably distributed by the entanglements. Variation of the NR molecular weight from 3000 to 8800, 10,000 and 17,000 does not add much to the chain entanglements. In the absence of strong binding force, the application of stress causes slippage of the polymer chains and the materials exhibit only low tensile properties. The tensile behavior is typical of soft, flexible elastomers.

Morphology of the sample

The TEM micrographs of three samples, viz., NR/PPO (3000/1000), NR/PPO (3000/4000), and NR/PPO (8800/4000) are shown in Figure 9. It was found that the samples have identical morphological char-

Figure 8 Variation of elongation at break of NR/PPO block copolymers with PPO molecular weight: (a) HTNR-3000, (b) HTNR-8800, (c) HTNR-10,000, and (d) HTNR-17,000.
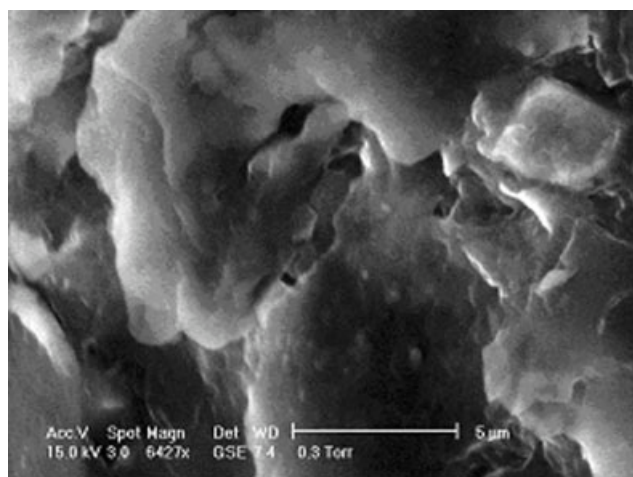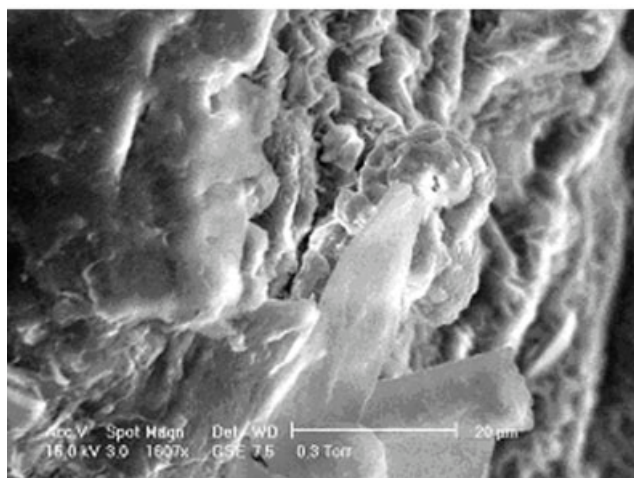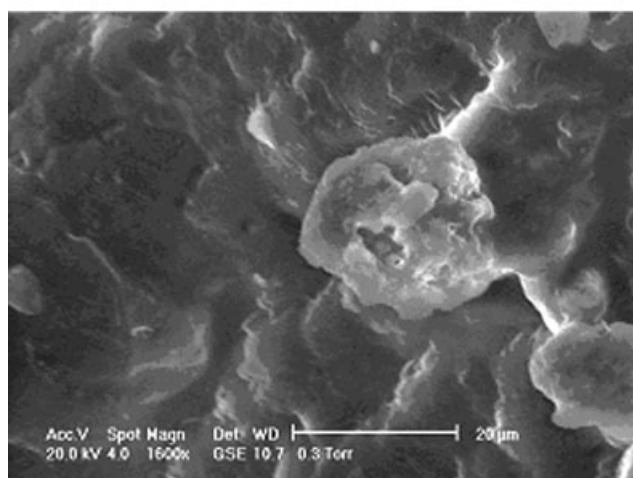
Figure 9 TEM micrographs of block copolymers: (a) NR/PPO (3000/1000), (b) NR/PPO (3000/4000), and (c) NR/PPO (88,000/4000).

length did not cause any appreciable effect on the block copolymer properties.

CONCLUSIONS

The formation of the block copolymers based on the natural rubber and polypropylene have been established by different analytical methods. These samples display two distinct transition temperatures, which indicate the phase separation in the systems. All the samples undergo decomposition in two stages during the thermal degradation corresponding to the two phases. From stress–strain data, it is found that the tensile strength and Young's modulus increases, whereas elongation at break decreases on increasing the molecular weight of PPO. The tensile properties show variation with respect to the molecular weight of PPO and HTNR. There is an overall increase in tear strength with the PPO molecular weight. The scanning electron micrographs of fracture surfaces show that they are characteristic of ductile materials. All the samples have identical morphological characteristics irrespective of the molecular weight of the component segments and the block copolymer composition. The micrographs of the samples also show the presence of two immiscible phases in the form of random cloud like distribution of one phase that occurs in the matrix of the other. Crystalline structures are totally absent suggesting that both the components of the block copolymers are amorphous in nature.

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