

Morphology of Pyrolysed Polystyrene–Isoprene–Styrene and Polystyrene–Butadiene–Styrene Block Copolymers

B. D. Sarwade,¹ R. R. Sanghavi,² D. B. Sarwade,² S. N. Asthana²

¹Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India

²High Energy Materials Research Laboratory, Pune 411 021, India

Received 26 August 2003; accepted 27 April 2005

DOI 10.1002/app.22870

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The surface morphology of thermooxidative degraded polystyrene–isoprene–styrene (SIS) and polystyrene–butadiene–styrene (SBS) thermoplastic block copolymers was studied by scanning electron microscopy. Surface changes caused by heating the samples in a pyrolyzer for 15 and 30 min were presented in different micrographs. The morphological changes occurring due to the formation of polar groups and their crosslinking during the thermooxidative degradation are discussed. Morphological study of these thermally degraded polymer samples shows very

good correlation with the thermodegradation results. The rate of thermodegradation is fast in case of SBS when compared with SIS block copolymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2549–2553, 2006

Key words: morphology; polystyrene–isoprene–styrene; polystyrene–butadiene–styrene; block copolymers; thermoplastic elastomers; pyrolyzation; chain scission; thermooxidative degradation

INTRODUCTION

Thermoplastic elastomers (TPE) are polymers having high strain capability in low temperature region, like elastomers, and high order of structural integrity at elevated temperatures, like plastics. They can be softened at elevated temperatures and regain original physical properties on cooling.¹ Physical and mechanical properties of TPEs are dependent on the extent of physical and chemical crosslinks, forming a three-dimensional network. The ordered structures render them crystalline, and entangled macro chains form the amorphous phase.

Amorphous domains result in soft segments having glass transition temperature (T_g) well below the room temperature, and crystalline domains result in hard segments having melting temperature (T_m) much higher than the room temperature. Thereby, TPEs, which are basically the block copolymers, have a unique blend of strength and flexibility. The T_m and T_g of the copolymers, the key parameters, from processing and application point of view, depend on the mole fraction of the crystalline hard segment in the continuous amorphous polymer phase.

Scanning electron microscope (SEM) is a very powerful tool for studying the morphology of polymer surfaces. It has been successfully used to study the

surfaces of polymer films and fibers,^{2–4} structure of block copolymers,^{5–7} polymer blends,^{8–10} and morphology of fracture surfaces.^{11,12}

Morphological behavior of polystyrene–isoprene–styrene (SIS) and polystyrene–butadiene–styrene (SBS) polymers has been studied in the past.^{13,14} Photo and thermal degradation of these block copolymers are well documented in the literature.^{15,16} However, very little attention has been given toward the understanding of their surface changes upon pyrolyzation in a muffle furnace. The present investigation is undertaken to understand the surface morphological changes after hear-aging of SIS and SBS block copolymers by SEM. In these block copolymers, polyisoprene and polybutadiene (PB) form the soft segment, whereas polystyrene forms the hard segment.

EXPERIMENTAL

Commercial samples of SIS and SBS were obtained from Shell Co., USA. The polymers are composed of hard polystyrene and soft rubber (polyisoprene and PB) segments. The characteristics of these polymers are given in Table I.

The isomeric structures of SIS and SBS were calculated from proton NMR. Butadiene polymerizes in 1,4 and 1,2 form, in which 1, 4 form gives rise to cis and trans isomers. The isomers 1,4 and 1,2 were in the ratio of 9:1. Isoprene polymerizes in 1,3,3,4 and 1,2 fashion. From proton NMR, it was found that the 1,4 isomer is in the range of 6–8 mol %.

Correspondence to: B. D. Sarwade (sarwade@poly.ncl.res.in).

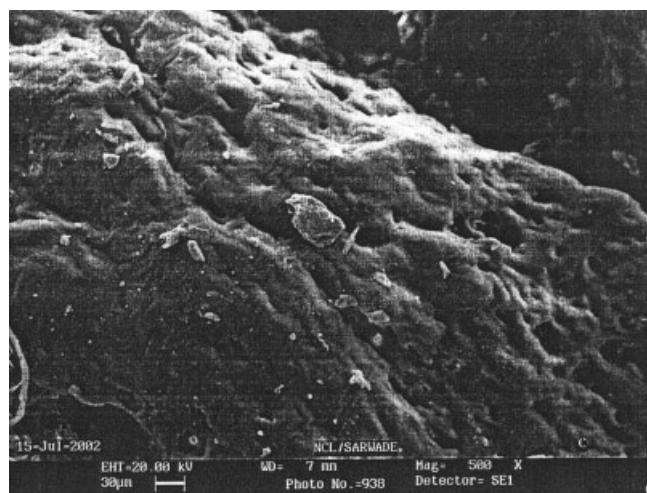
TABLE I
Soft Segment Content of SIS and SBS

Polymer	Soft segment ^a (mol %)	Hard segment ^a (mol %)	T_g (°C)	Melt flow index (g/mol)
SIS	86	14	-34	9
SBS	77	23	-14	6

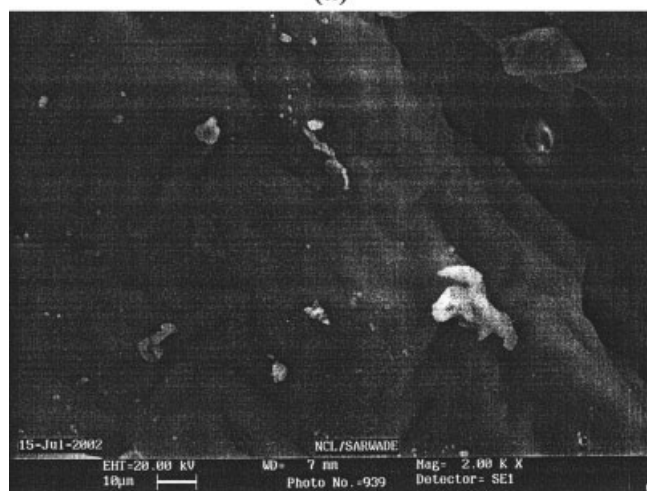
^a Calculated from NMR.

Pyrolysis of sample

A muffle furnace, supplied by Therelek, having a controlled heating system up to a temperature range of 1000°C was used for the pyrolysis. The samples in pellet form were placed in a crucible and heated in a furnace, with a heating rate of 10°C/min to attain a temperature of 300°C. The samples were exposed for 15 and 30 min at this temperature.

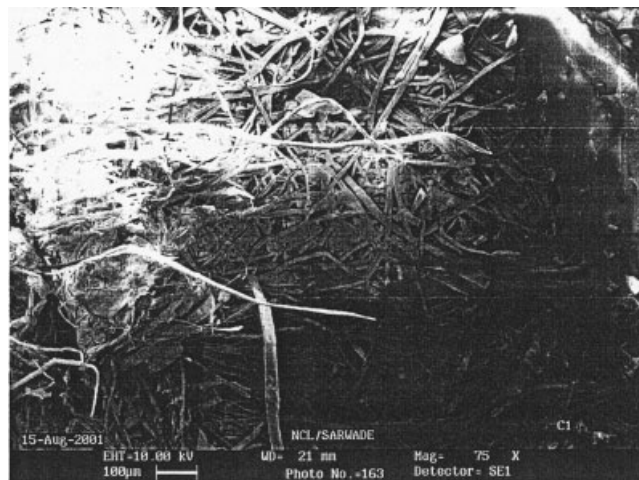


(a)



(b)

Figure 1 SEM microphotographs of SIS sample before exposure to 300°C: (a) magnification $\times 500$ and (b) magnification $\times 2000$.



(a)



(b)

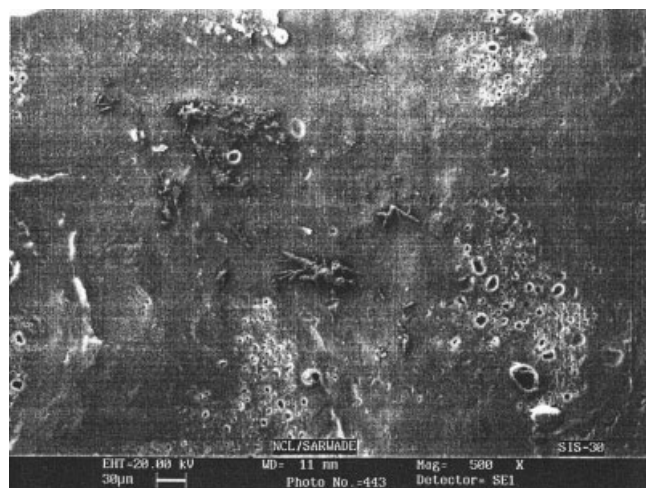
Figure 2 SEM microphotographs of pyrolysed SIS sample at 300°C: (a) 15 min (magnification $\times 500$) and (b) 15 min (magnification $\times 2000$).

Characterization

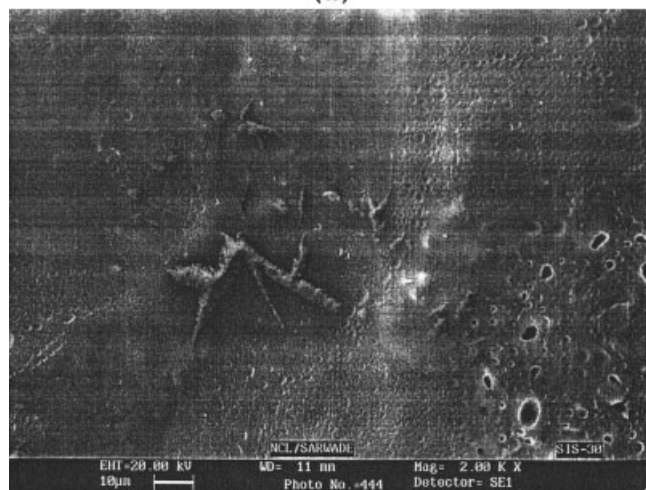
Polyisoprene and PB content of SIS and SBS block copolymers were determined by NMR spectroscopy (Bruker AC 200 FT-NMR). Surface morphology of pyrolysed samples was studied using Leica Cambridge (Steroscan 440) SEM (Cambridge, UK). The samples were coated with gold in an automatic sputter coater (Polaron Equipment Ltd, SEM Coating Unit E 5000, UK) to make the surface conductive. The samples were scanned at 10 as well as 20 kV, and the micrographs were recorded at different magnifications.

RESULTS AND DISCUSSION

In SIS and SBS copolymers, the polyisoprene and PB blocks are susceptible to thermal degradation on exposure to heat and ultraviolet light, resulting in dis-



(a)



(b)

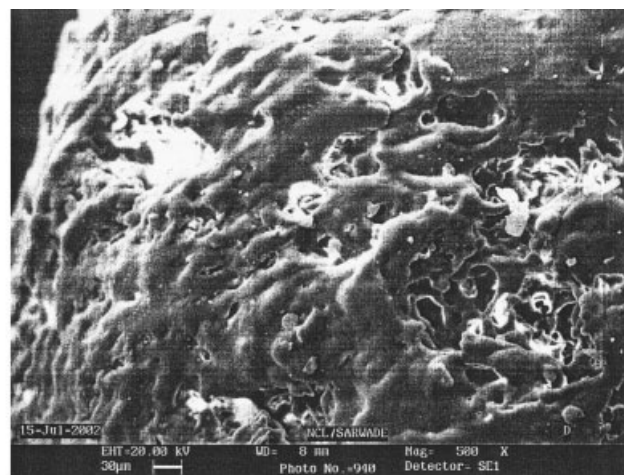
Figure 3 SEM microphotographs of pyrolysed SIS sample at 300°C: (a) 30 min (magnification $\times 500$) and (b) 30 min (magnification $\times 2000$).

coloration and surface embrittlement. The main degradation products are monomers, dimers, and trimers, resulting from extensive chain fragmentation on depolymerization.

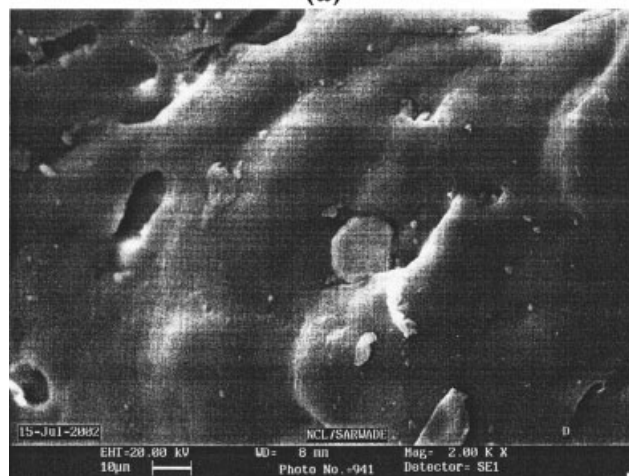
The morphological changes observed on thermal treatment of SIS and SBS are presented in different micrographs. The Figures 1(a) and 1(b) show the micrographs of the SIS sample before thermal treatment. The surface of the SIS granules before thermal treatment does not appear to be clear. It has wrinkled appearance, with some foreign particles. The micrographs of the samples pyrolysed for 15 min are presented in Figures 2 (a) and 2(b). It does not reveal crack formation, as it usually happens in case of photo and thermal degradation of polymers. However, the fiber network formation is observed. This indicates that the amorphous polyisoprene gets degraded/etched, and the inner crystalline layer, which is stable

under these conditions, has become visible. Hence, the fibrous network can be accounted for polystyrene segment present in the SIS block copolymer.¹⁷ It may be mentioned that the etching of the polymer surface by solvents or acids is a widely used technique to observe details of the internal structure, as it removes the amorphous portion from the surface. In the present experiments, the polystyrene does not appear in its typical crystalline form, but is seen as a pseudo-ordered under-developed structure.¹⁸ The fibers were 20–30 μm in size. At higher magnification, the fibers appear to have wrinkled surface (Fig. 2(b)).

Figures 3(a) and 3(b) show the micrographs of SIS samples exposed to 300°C for 30 min. The formation of holes and voids appears to take place along with the formation of star-like particles. The holes and voids may be due to the formation of gaseous photodegradation products, whereas the star-like particles of ~ 20 –25 μm size may be of degraded pseudo-ordered



(a)



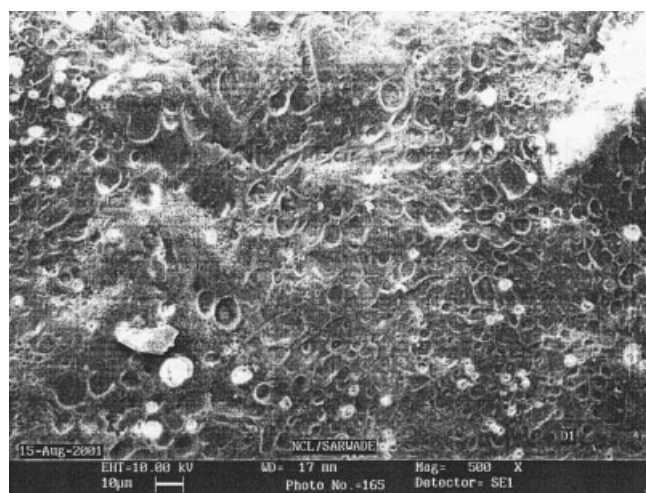
(b)

Figure 4 SEM microphotographs of SBS sample before exposure to 300°C: (a) magnification $\times 500$ and (b) magnification $\times 2000$.

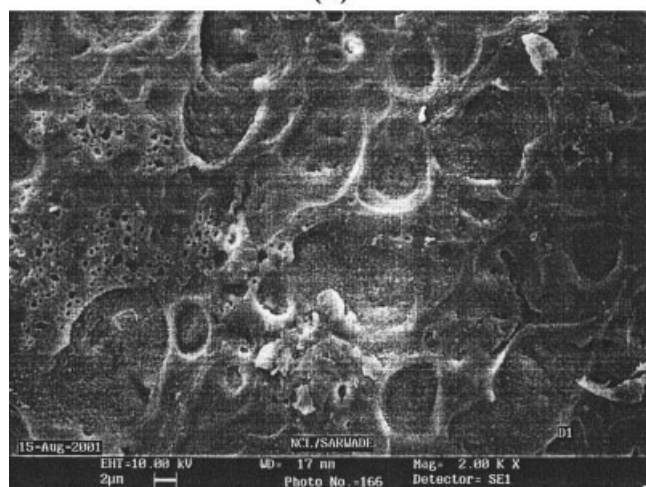
structure.^{19–21} These observations suggest that the fiber network, which was thermally stable up to 15 min at 300°C, is degraded on exposure for 30 min.

Figures 4(a) and 4(b) depict the micrographs of the SBS copolymer before thermal treatment. Both the micrographs showed the features similar to those in case of SIS Figures 1(a) and 1(b).

Figures 5(a) and 5(b) show the micrographs of the sample irradiated for 15 min in the furnace. Figure 5(a) shows more or less uniform distribution of the cavities on the surface along with holes. It is an outcome of evolution of gaseous products formed during the thermo-oxidative degradation. This phenomenon is very well explained in case of poly(vinyl chloride) and poly(methyl methacrylate)/poly(methacrylate)²² and ethylene-propylene copolymers.²¹ The diameter of the cavities was in the range of 1.5–7 μm in diameter. The cavities may be the actual domain size of the PB

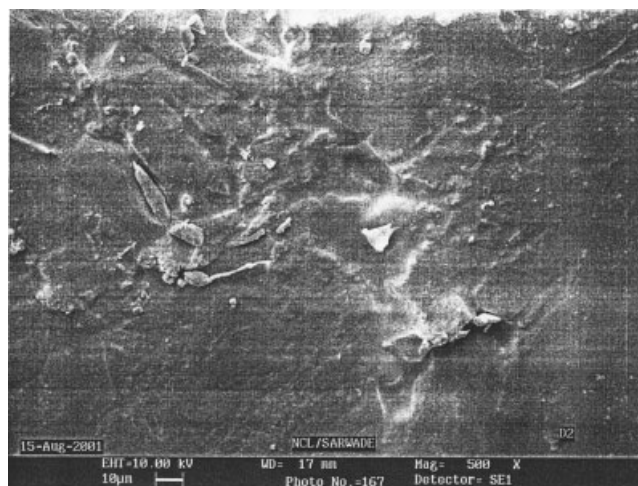


(a)

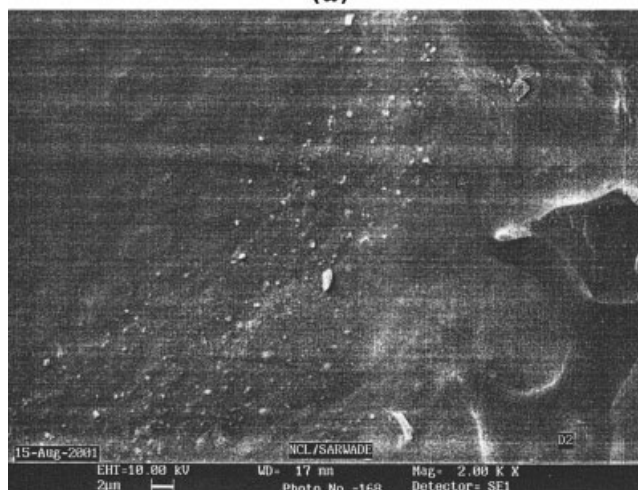


(b)

Figure 5 SEM microphotographs of pyrolysed SIS sample at 300°C: (a) 15 min (magnification $\times 500$) and (b) 15 min (magnification $\times 2000$).



(a)



(b)

Figure 6 SEM microphotographs of pyrolysed SBS sample at 300°C: (a) 30 min (magnification $\times 500$) and (b) 30 min (magnification $\times 2000$).

segment in the SBS matrix, as it is highly sensitive to photo and thermal energy, and thereby degrades first. The formation of holes and voids are clearly seen in Figure 5(b). The holes are $<1 \mu\text{m}$ in size. A regularity in the distribution of the elastomeric phase indicates a good compatibility between the hard and the soft segment.²³ Oscar et al.²⁴ have studied the thermal degradation of PB and showed that PB extensively undergoes chain fragmentation and depolymerization.

Figures 6(a) and 6(b) represents the micrographs of the SBS sample thermally treated at 300°C for 30 min. The formation of small ($<1 \mu\text{m}$) and medium size (7–10 μm in size) platelet-like structures (Fig. 6(a)) suggests the degradation of polystyrene hard segment, leading to the formation of particles. The particles may be low molecular weight thermodegradation products. At higher magnification, the back surface is

wrinkled along with fine particles (Fig. 6(b)). This indicates that the degradation of the second layer of the block copolymer is also initiated.

The samples heated for a longer time (>30 min) degrades very fast, and it was difficult to see further morphological changes.

SIS shows different morphology when compared with SBS block copolymer, after heating in a furnace for 15 min (Figs. 2 and 5). The reason may be the presence of different isomeric forms of polyisoprene and PB in the polymer matrix. Hence, formation, combination, and crosslinking of free radicals during thermooxidative degradation are different.

CONCLUSIONS

Surface morphologies of thermooxidatively degraded SIS and SBS thermoplastic block copolymers show changes upon thermal degradation. This study shows that the thermal degradation process is fast in case of SBS compared with SIS block copolymer. SIS shows better thermal stability compared with SBS because of change in structure and crosslinking.

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