

# Morphology of Pyrolyzed Polystyrene–Isoprene–Styrene and Polystyrene–Butadiene–Styrene Block Copolymers

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**ABSTRACT:** The surface morphology of thermooxidative-degraded polystyrene–isoprene–styrene (SIS) and polystyrene–butadiene–styrene (SBS) thermoplastic block copolymers were 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 crossing linking during the thermooxidative degradation are discussed. Morphological study of these thermally degraded polymer samples show

very good correlation with the thermodegradation results. The rate of thermodegradation is fast in case of SBS compared with SIS block copolymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3178–3182, 2006

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

## INTRODUCTION

Thermoplastic elastomers (TPEs) are polymers having high strain capability in low temperature region such as elastomers and high order of structural integrity at elevated temperatures such as plastics. They can be softened at elevated temperatures and regain original physical properties on cooling.<sup>1</sup> 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 macrochains form the amorphous phase.

Amorphous domains result in soft segments having glass transition temperature ( $T_g$ ) well below the room temperature and crystalline domains contribute to the hard segment 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 the application point of view depend on the mole fraction of crystalline hard segment in the continuous amorphous polymer phase.

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

faces of polymer films and fibers,<sup>2–4</sup> structure of block copolymers,<sup>5–7</sup> polymer blends,<sup>8–10</sup> and morphology of fracture surfaces.<sup>11,12</sup>

Morphological behavior of SIS and SBS polymers have been studied in the past.<sup>13,14</sup> Photo and thermal degradation of these block copolymers are well documented in the literature.<sup>15,16</sup> 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 heat aging of SIS and SBS block copolymers by scanning SEM. In these block copolymers, polyisoprene and polybutadiene forms the soft segments, whereas polystyrene forms the hard segment.

## EXPERIMENTAL

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

The isomeric structures of the 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 6–8 mol %.

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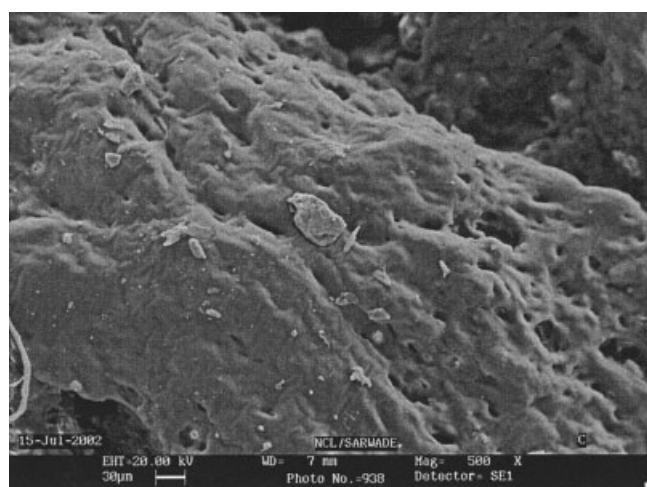
TABLE I  
Soft Segment Content of SIS and SBS

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

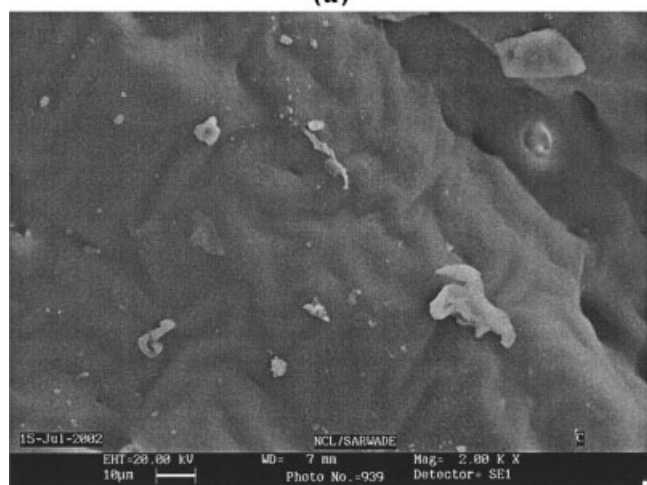
<sup>a</sup> Calculated from NMR.

### Pyrolysis of sample

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

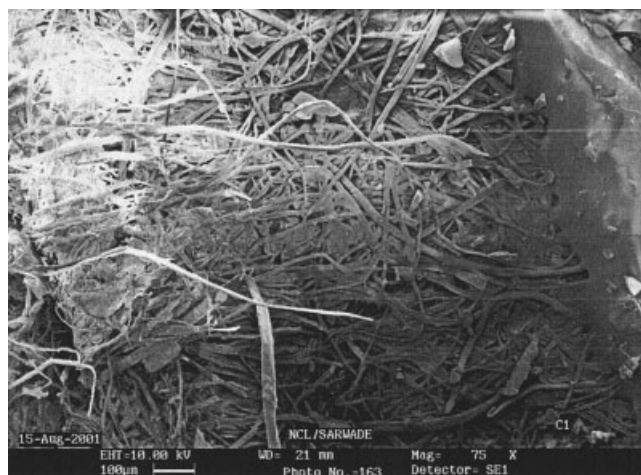


(a)

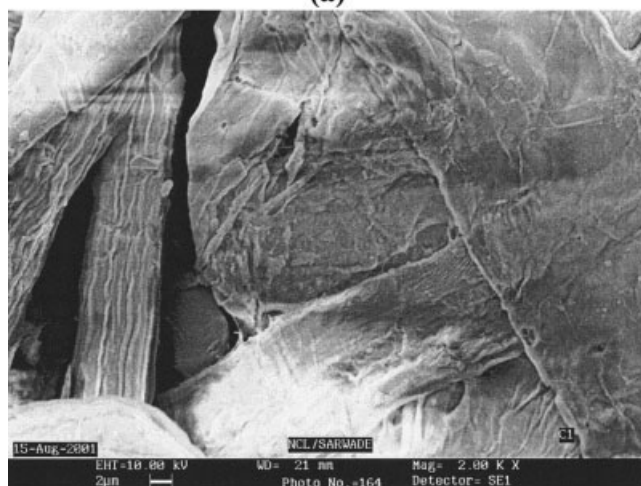


(b)

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 pyrolyzed SIS sample at 300°C: (a) 15 min (magnification  $\times 500$ ) and (b) 15 min (magnification  $\times 2000$ ).

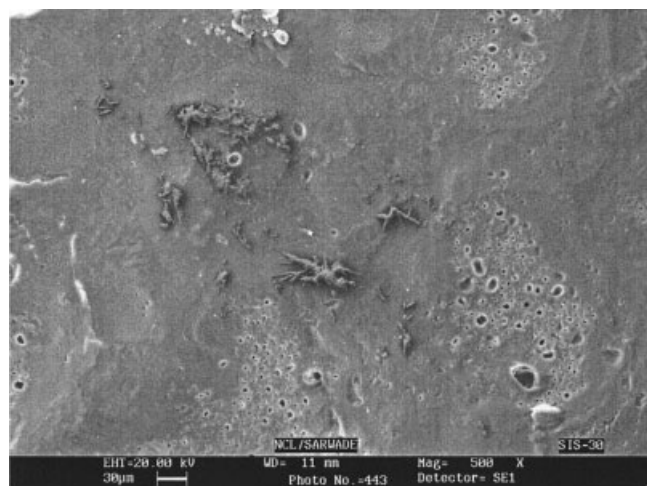
### Characterization

Polyisoprene and polybutadiene content of SIS and SBS block copolymers were determined by NMR spectroscopy (Bruker AC 200 FT NMR). Surface morphology of pyrolyzed samples was studied using Leica Cambridge (Steroscan 440) SEM (Cambridge, UK). The samples were coated with gold in an automatic sputter coater (Polaron Equipment, SEM Coating Unit E 5000, UK) to make 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 polybutadiene blocks are susceptible to thermal degradation on exposure to heat and ultraviolet (UV)





(a)



(b)

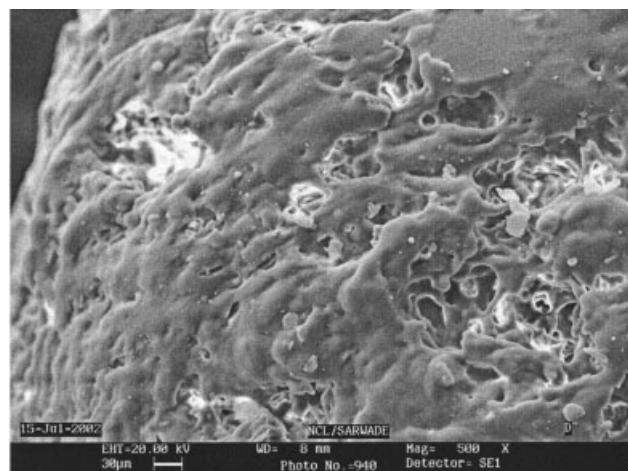
**Figure 3** SEM microphotographs of pyrolyzed SIS sample at 300°C: (a) 30 min (magnification  $\times 500$ ) and (b) 30 min (magnification  $\times 2000$ ).

light, resulting in discoloration and surface embrittlement. The main degradation products are monomers, dimers, and trimers resulting from extensive chain fragmentation and depolymerization.

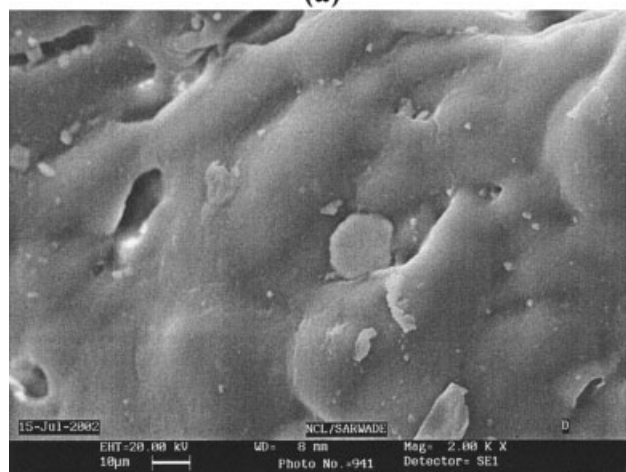
The morphological changes observed on thermal treatment of SIS and SBS are presented in different micrographs. The Figures 1(a,b) show the micrographs of the SIS sample before thermal treatment. The surface of the SIS granules before thermal treatment does not appear to be clear. It has wrinkled appearance, with some foreign particles. The micrographs of the samples pyrolyzed for 15 min are presented in Figures 2(a,b). It does not reveal cracks formation as 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 inner crystalline layer, which is stable under these conditions, has become visible. Hence, the fibrous net-

work can be accounted for polystyrene segment present in the SIS block copolymer.<sup>17</sup> It may be mentioned that the etching of the polymer surface by solvents or acids is 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 pseudo-ordered under developed structure.<sup>18</sup> The fibers were 20–30  $\mu\text{m}$  in size. At higher magnification, the fibers appear to have wrinkled surface [Fig. 2(b)].

Figures 3(a,b) show the micrographs of SIS samples exposed to 300°C for 30 min. The formation of holes and voids take place along with formation of star like particles. The holes and voids may be resulting due to the formation of gaseous products during thermooxidative degradation, whereas star like particles of approximately 20–25  $\mu\text{m}$  size may be degraded pseudo-ordered structure.<sup>19–21</sup> These observations suggest that the fiber network that was thermally stable upto 15 min at 300°C is degraded on exposure for 30 min.



(a)

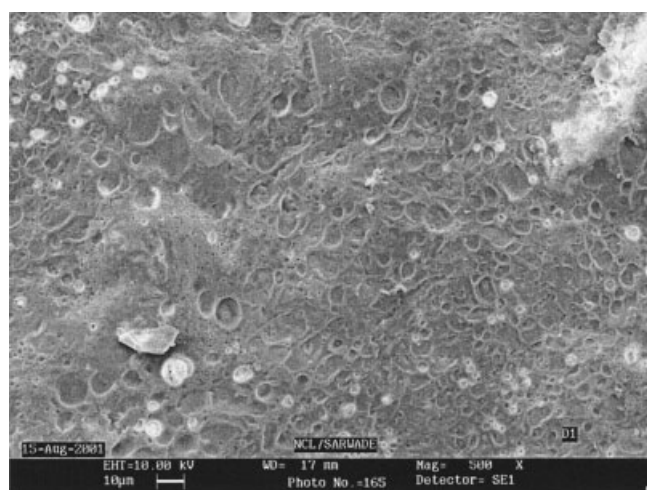


(b)

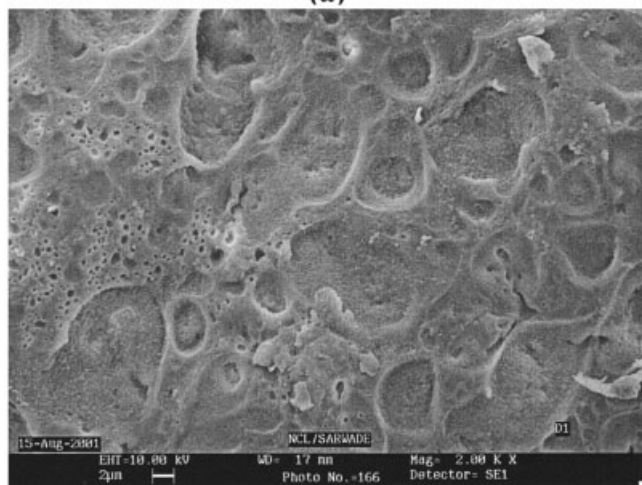
**Figure 4** SEM microphotographs of SBS sample before exposure to 300°C: (a) magnification  $\times 500$  and (b) magnification  $\times 2000$ .

Figures 4(a,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,b).

Figures 5(a,b) shows 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 alongwith holes. It is an outcome of evolution of gaseous products formed during the thermoxidative degradation. This phenomenon is very well explained in case of poly(vinyl chloride) and poly(methyl methacrylate)/poly(methacrylate)<sup>22</sup> and ethylene propylene copolymers.<sup>21</sup> The diameter of the cavities are in the range of 1.5–7  $\mu\text{m}$ . The cavities may be the actual domain size of the polybutadiene (PB) segment in the SBS matrix, as it is highly sensitive to 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

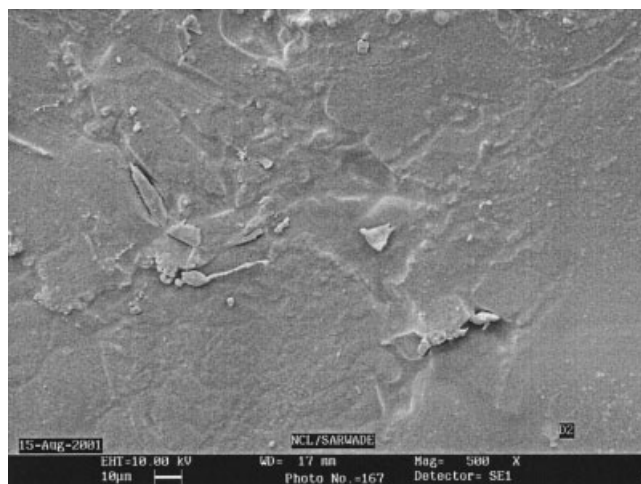


(a)

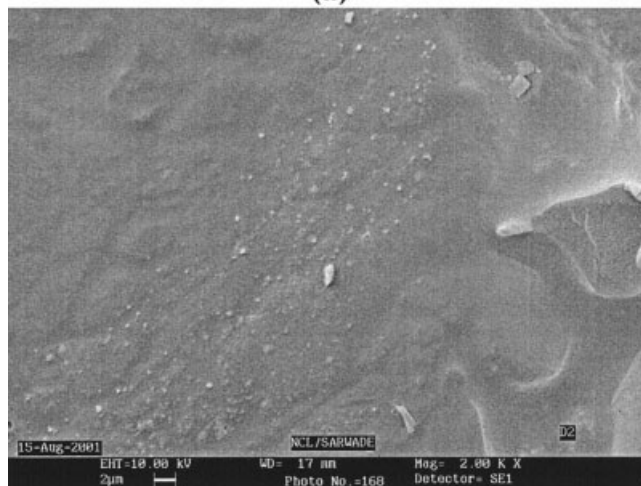


(b)

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



(a)



(b)

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

distribution of the elastomeric phase indicates a good compatibility between the hard and soft segment.<sup>23</sup> Oscar et al.<sup>24</sup> have studied the thermal degradation of PB and showed that the PB extensively undergoes chain fragmentation and depolymerization.

Figures 6(a,b) represent 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  $\mu\text{m}$  in size) platelet-like structures [Fig. 6(a)] suggest 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 longer time ( $>30 \text{ min}$ ) degrade very fast and it was difficult to see the further morphological changes.



SIS shows different morphology compared to SBS block copolymer after heating in furnace for 15 min (Figs. 2 and 5). The reason may be the presence of different isomeric forms of polyisoprene and polybutadiene 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 to SIS block copolymer. SIS shows better thermal stability compared with SBS due to change in structure and crosslinking.

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