Effect of Epoxidation on Morphology and Properties of Styrenic Block Copolymers

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Introduction

Block copolymers represent a class of self-assembled heterogeneous materials. The microphase separated morphology can be adjusted by changing the composition (Fig. 1), varying processing conditions, via modification of molecular architecture and by blending.

The microphase separated morphology can be used to produce different functional nanostructures by using selective chemical modification of one or more of the copolymer blocks. The selective epoxidation and sulfonation of the diene block in styrenic block copolymers belongs to such ways. The aim of this work has been to investigate the influence of epoxidation of diene block of styrene/diene block copolymer on their morphology and mechanical properties.

Figure 1: Common microphase separated structures observed in block copolymers (e.g., SB diblock copolymer, dark component as polybutadiene).

Materials

The Polymer used in this work was polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer with 74 wt.% PS, molecular weight (M_w) =127 300 g/mol. The sample was supplied by the BASF, Ludwigshafen, Germany.

The AR grade chemicals required for synthetic procedures were purchased from Merck India and were used without further

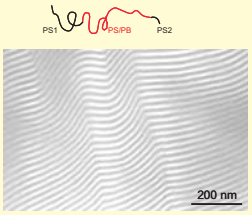


Figure 2: Typical morphology of the SBS block copolymer

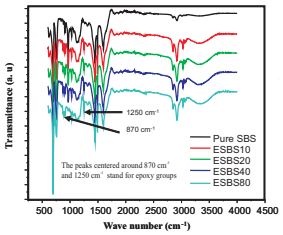
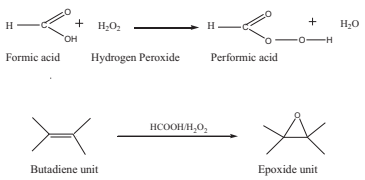


Figure 3: FTIR spectra of SBS copolymer epoxidized to different targetted epoxy values



Scheme 1: Epoxidation reaction in the butadiene phase of SBS

Synthesis and Characterization

The SBS block copolymer was epoxidized to different degrees following the standard procedures discussed in literature using *in situ* generated performic acid . Calculated amount of formic acid, hydrogen peroxide and two drops of PEG-400 were added to the polymer solution which was heated slowly to 60°C and stirred with magnetic stirrer for four hours. The resulting polymer was coagulated by adding methanol. The residue was filtered and dried until constant weight. The epoxidation reaction is described in Scheme 1

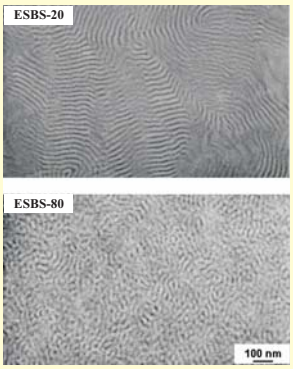


Figure 4: TEM images of epoxidized SBS copolymer, OsO_4 staining renders butadiene phase appear dark

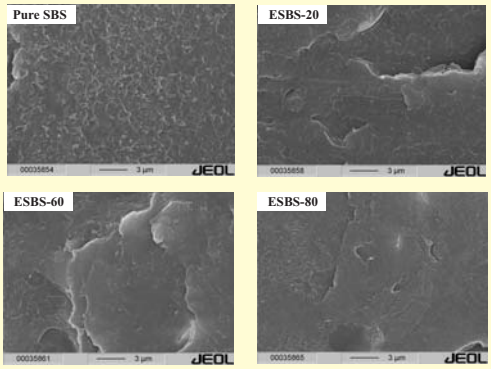


Figure 5: SEM images SBS copolymer and epoxidized SBSs to different targetted extents

Morphological Characterization by SEM and TEM

The cryo-fracture surfaces of the samples were investigated by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used for characterization of microphase separated morphology of the block copolymers , Figs. 4 and 5.

❑ The microphase separation behaviour is strongly influenced by epoxidation. Morphological disordering evolves with increase in epoxidation.

❑ Macrophase-separation could not be proved by TEM analysis inspite of ist indication of on the SEM micrographs.

❑ Local appearance of cracks on fracture surface correlates with worsening in mechanical properties at higher epoxidation.

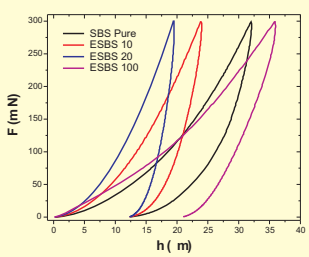


Figure 6: Force - indentation depth (P-h) curves of some of the samples epoxidated to different degrees

Mechanical Behaviour

The depth-measuring microhardness tests show the increase in stiffness and the ease to plastic deformation (see the P-h diagrams in Fig. 6 and Table 1).
Beyond 20% epoxidation, the sample behaved

Table 1: Characteristic average mechanical parameters of the samples

Samples	*HM (MPa)*	*E_{IT} (MPa)*	*W_r/W_{pl}*
SBS	12.2	288	0.8
ESBS-10	20.1	496	0.6
ESBS-20	30.2	897	0.4

Conclusions

❑ The SBS block copolymers were succesfully epoxidated which can be used for further functionalization of the block copolymers.

❑ The microphase separation behaviour and mechanical properties are strongly influenced especially at higher epoxidation degrees.

Acknowledgements

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