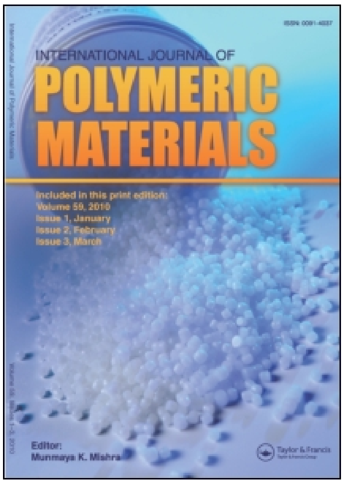

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STYRENE BUTADIENE RUBBER/EPOXIDIZED NATURAL RUBBER BLENDS: COMPATIBILIZER EFFECTS

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The effects of a compatibilizer, styrene-(epoxidized butadiene) – styrene triblock copolymer (ESBS) on dynamic properties, curing characteristics and swelling behavior of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR 50) blends were studied. Results indicate that the presence of ESBS improved the processability, increase the scorch time, t_2 and reduce the cure time, t_{90} of the SBR/ENR 50 blends. The improved interfacial interaction between SBR and ENR 50 in the presence of ESBS also resulted in SBR/ENR 50 blends having better oil resistance than similar blends without a compatibilizer.

Keywords: styrene butadiene rubber, epoxidized natural rubber, blend, compatibilizer, dynamic properties, swelling behavior

INTRODUCTION

Blends of different polymers are of considerable importance as blending provides a means of improving physical and mechanical properties. Epoxidized natural rubber (ENR) is obtained from natural rubber by replacing some of the double bonds with epoxide groups. ENR with 50 mol% epoxidation (ENR 50) has been shown to be polar with properties similar to those of acrylonitrile butadiene rubber and butyl rubber [1]. In our previous work [2] the dynamic properties, curing characteristics and swelling behavior of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR 50) blends were studied. The incorporation of ENR 50 in the blends improved processability, stiffness, resilience and reduced the

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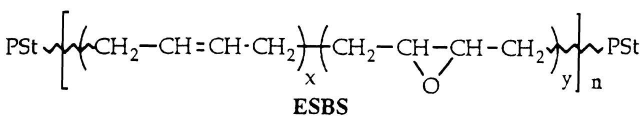
damping property. The incorporation of ENR 50 also decreases the scorch time, t_2, curing time, t_{90}, and the swelling degree of the SBR/ENR 50 blends.

It was reported that the addition of compatibilizers into blends improved the physical properties [3–6]. The compatibilizer helps to induce interaction between the polymers interphase and thereby increases the homogeneity of the blends. In this study, the dynamic properties, curing characteristics and swelling behavior of SBR/ENR 50 blends at three blend composition ratio, *viz*. 75/25, 50/50 and 25/75, with and without a compatibilizer, styrene-(epoxidized butadiene) – styrene triblock copolymer (ESBS) were investigated.

EXPERIMENTAL

Materials and Formulations

ENR 50 was supplied by the Rubber Research Institute of Malaysia (RRIM) while SBR 1502 and other ingredients such as sulfur, zinc oxide, stearic acid, *N*-Cyclohexyl-1-benzothiazyl sulfenamide (CBS), Poly-1,2-dihydro-2,2,4-trimethyl quinoline (Flectol H) and process oil (Dutrex 729) were obtained from Bayer (M) Ltd while carbon black, N330, was purchased from Malayan Carbon (M) Ltd. A compatibilizer, ESBS was obtained from Daicel Co. Ltd., Japan. The microstructure of ESBS is given below (Scheme 1):



SCHEME 1

All materials were used as supplied and semi efficient vulcanization (semi-EV) system was employed. The full recipes of the blends are shown in Table 1.

Mixing Procedure

Mixing was carried out in an internal mixer, Haake Rheomix, Model CTW 100. SBR and ENR 50 were first premixed, prior to the addition of other ingredients. Mixing was carried out at temperature of 60°C and at a rotor speed of 60 rpm. The total mixing cycle was ~7 min. Finally the carbon black filled blend was sheeted out on a two-roll mill.

TABLE 1 Formulations of carbon black filled SBR/ENR 50 rubber blends

Ingredients	*phr*
SBR 1502	75–25
ENR 50	25–75
Carbon black (N330)	40
Process oil	5
Zinc Oxide	5
Flectol H	1
CBS	1.1
Sulfur	1.6
Stearic acid	2.0

Measurement of Curing Characteristics and Dynamic Properties

The MDR 2000 moving die rheometer (MDR), a rotorless curemeter, has gained much acceptance by the rubber industry since its introduction in 1988. In many cases, this equipment is replacing the oscillating disk rheometer (ODR) as described in ASTM Standard Test Method D 2084. The dynamic properties of the blends before, during and after cure were studied at 150°C. A unique signal processing system and Fourier transform software separates the complex torque into elastic torque (S') and viscous torque (S''). The $\tan\delta$ is derived by dividing S'' by S'. In addition to the dynamic properties, the MDR gives digital outputs of curing characteristics such as scorch times, cure times, cure rates and torque values.

Measurement of Swelling Behavior

Determination of swelling percentage of blends was carried out according to ASTM D 471. Cured test pieces of blends of dimension 30 mm × 5 mm × 2 mm were weighed using an electrical balance and considered as original weight (W_i). The test pieces were immersed in ASTM#3 oil (which is similar to IRM 903) at room temperature and 100°C for 72 h and 26 h respectively. The test pieces were then removed from the oil, wiped with tissue paper to remove excess oil from the surface and weighed (W_t). The swelling percentage of the blends was then calculated as follows:

$$\text{Swelling percentage} = \frac{W_t - W_i}{W_i} \times 100$$

RESULTS AND DISCUSSION

Figure 1 shows the effect of ENR 50 composition on ML (elastic torque at minimum value) for three different ratios of SBR/ENR 50 blends with and

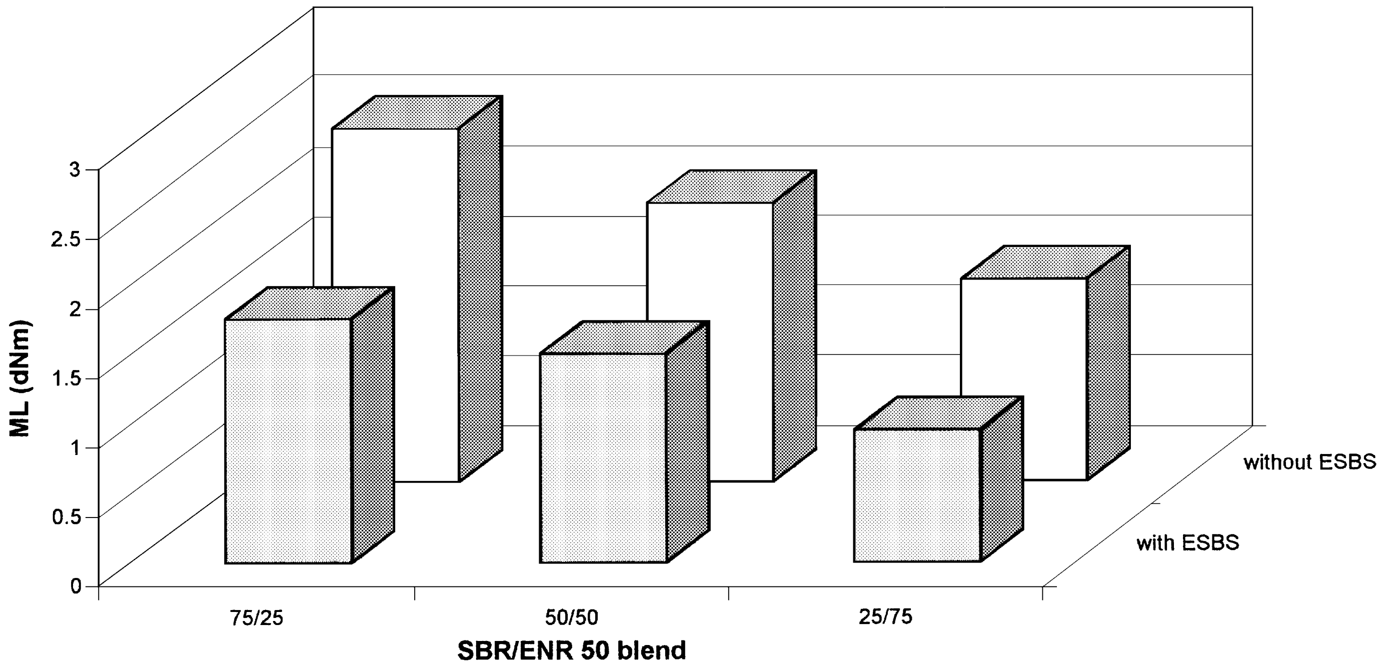


FIGURE 1 Comparative effect of a compatibilizer, ESBS on elastic torque at minimum value, ML of SBR/ENR 50 blends.

without a compatibilizer, ESBS. It can be seen that the ML decreases with increasing of ENR 50 in the blend. As reported before [2], these results show that the incorporation of the ENR has improved the processability of the SBR/ENR 50 blend. According to Sezna et al. [7] ML is commonly considered as representative of the uncured blend's elastic modulus. The lower the ML value the better the processability of the blend. It can be seen in Figure 1 that at a similar blend ratio, the incorporation of ESBS improved the processability of the blend by reducing the value of ML. Go and Ha [8] also reported that the addition of a homogenizer AAHR (mixture of aliphatic and aromatic hydrocarbon resins) improved the processability of the EPDM/BR blends by reducing the melt viscosity of the blends. In our case the improved processability of the SBR/ENR 50 blends might be due to the ESBS functioning as a compatibilizer for the blends.

According to Paul et al. [9–11] compatibilizers have been commonly used to enhance the compatibility of incompatible polymer blends, where the compatibilizers, often referred to as "interfacial agents" are able to improve interfacial adhesion between otherwise gross-phase-separated polymer pairs by reducing the interfacial energy between the phases. In our case, from the molecular structural aspect, the epoxidized butadiene block of ESBS should be compatible with ENR 50 while styrene block of ESBS should be compatible with SBR. It can be seen in Figure 2 that the $\tan\delta$ @ MH ($\tan\delta$ at maximum value) decreases with increasing ENR 50 content in the blends. The incorporation of ENR 50 reduces the blend hysteresis and improves its resilience [2]. At similar blends ratio, the incorporation of ESBS further reduces the $\tan\delta$ @ MH of the blend. This again indicates that ESBS can function as a compatibilizer for the SBR/ ENR 50 blends.

The effect of the SBR/ENR blends ratio on S'' @ MH (viscous torque at maximum value) is shown in Figure 3. It can be seen that S'' @ MH decreases as the ENR increases in the blend. As viscous torque (S'') relates to the damping characteristics or loss modulus, this result shows that ENR 50 has a beneficial effect by reducing the damping characteristics of the blends. With the incorporation of ESBS, the S'' @ MH is reduced further.

Figure 4 shows the effect of blend ratio on the scorch time, t_2 for SBR/ ENR 50 blends with and without ESBS. It can be seen that t_2 decreases with increasing ENR 50 content in the blends. Owing to the activation of an adjacent double bond by the epoxide group, the scorch time for ENR50 is shorter than that of SBR. However at a similar blend ratio, SBR/ENR 50 blends with ESBS exhibit longer scorch time than SBR/ENR 50 blends without ESBS. This indicates that the incorporation of ESBS increases the processing safety of the blends.

The relationship between cure time, t_{90} and blend ratio of SBR/ENR 50 blends with and without ESBS is shown in Figure 5. As for scorch time, t_2,

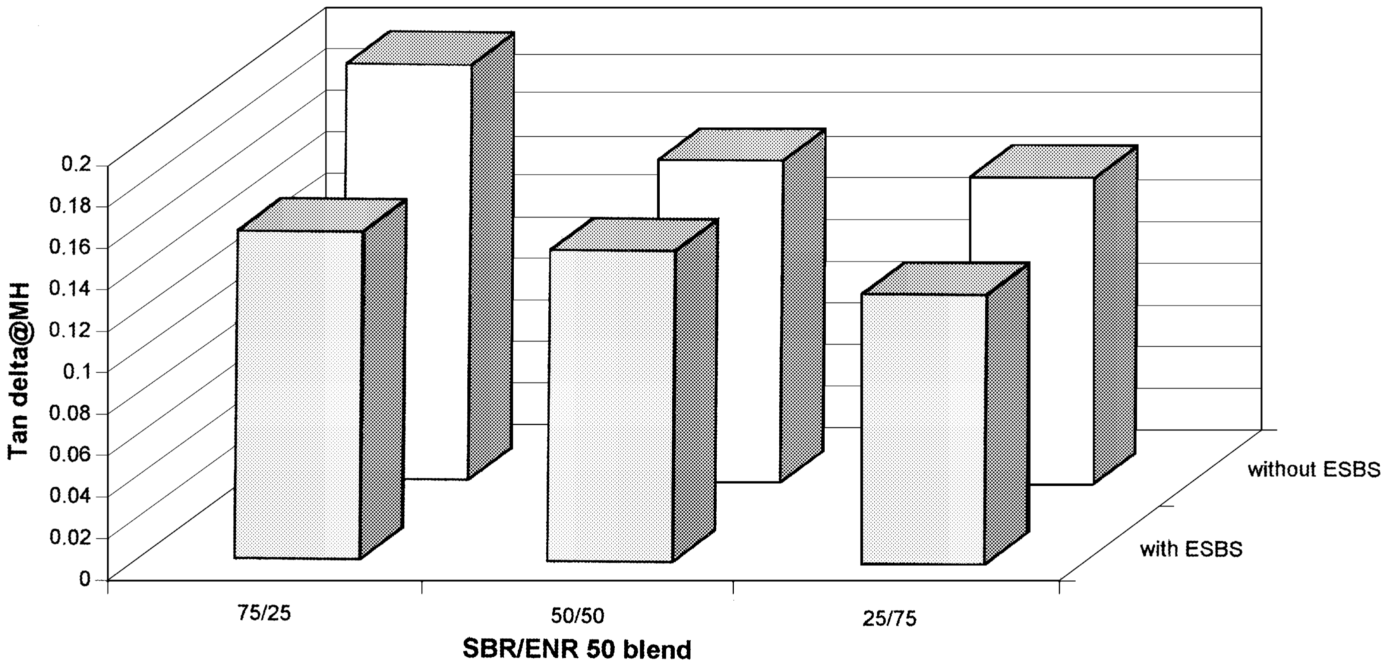


FIGURE 2 Comparative effect of a compatibilizer, ESBS on tan δ @ MH of SBR/ENR 50 blends.

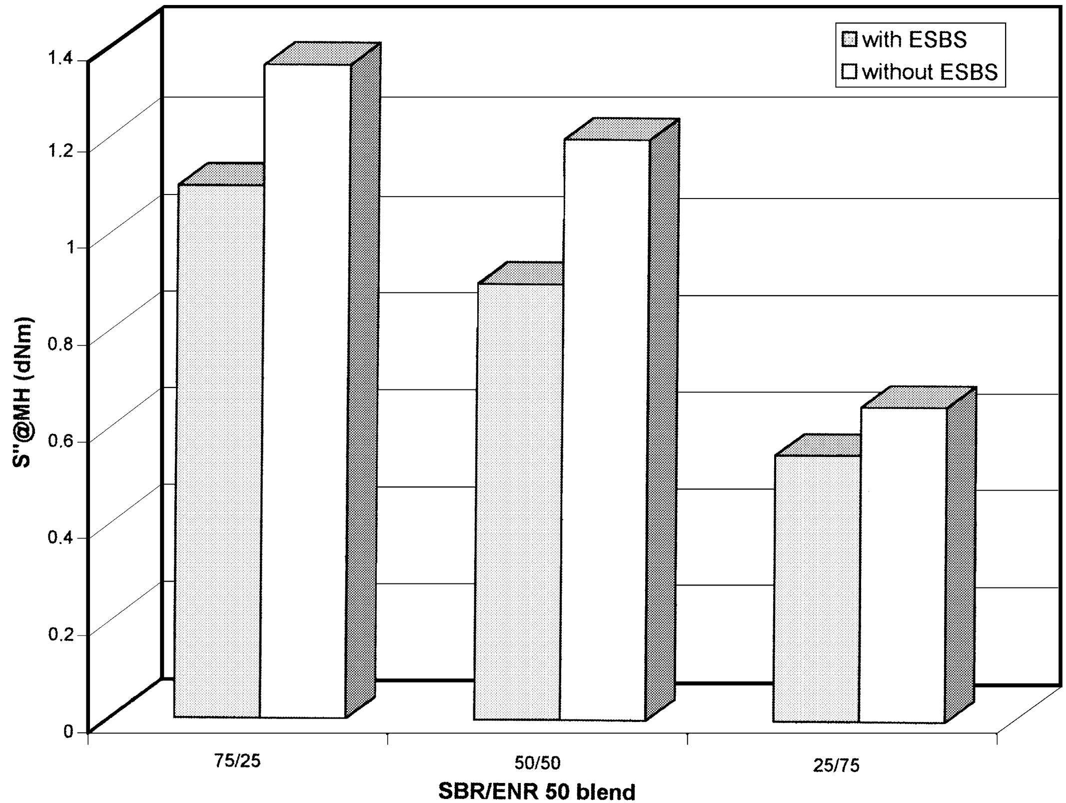


FIGURE 3 Relationship between S'' @ MH and SBR/ENR 50 blend ratio with and without ESBS as a compatibilizer.

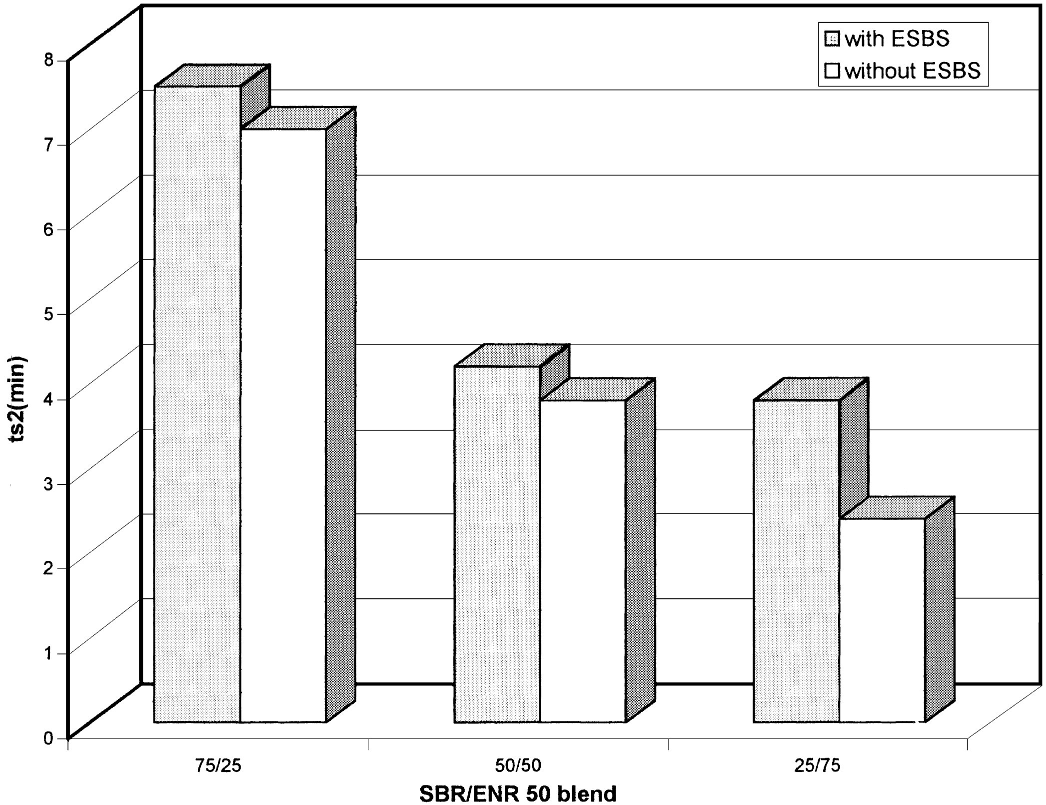


FIGURE 4 Relationship between scorch time, t_2, and SBR/ENR 50 blend ratio with and without ESBS as a compatibilizer.

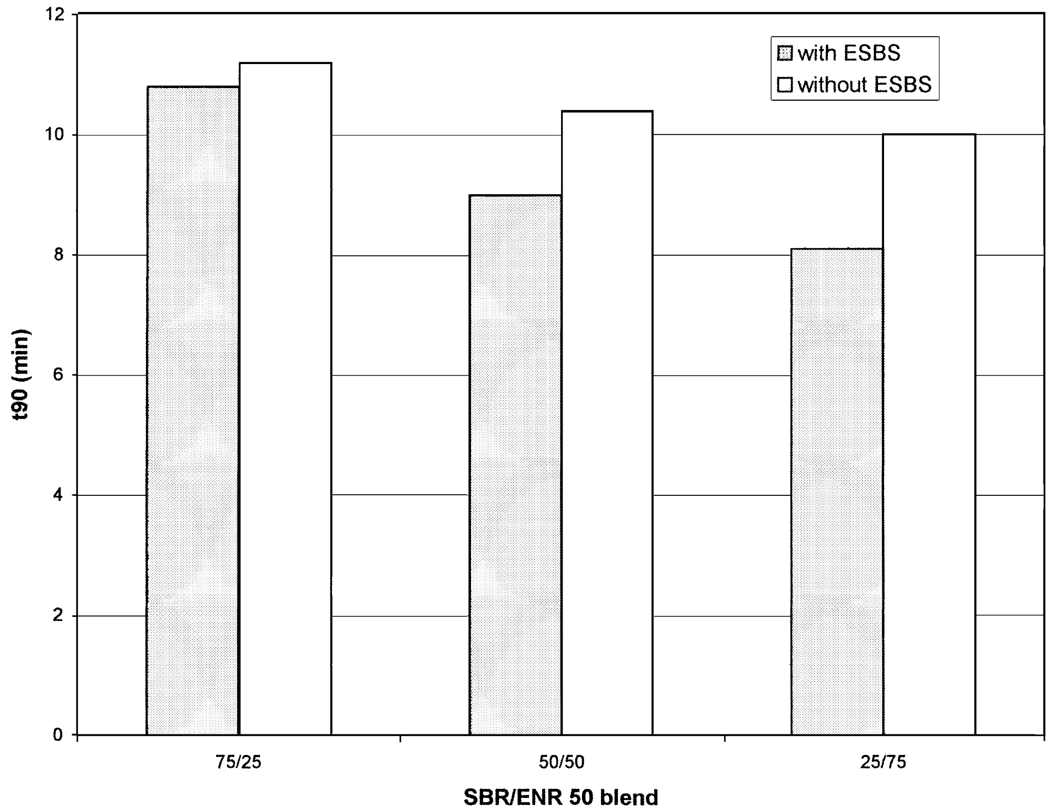


FIGURE 5 Variation of t_{90} and SBR/ENR 50 blend ratio with and without ESBS as a compatibilizer.

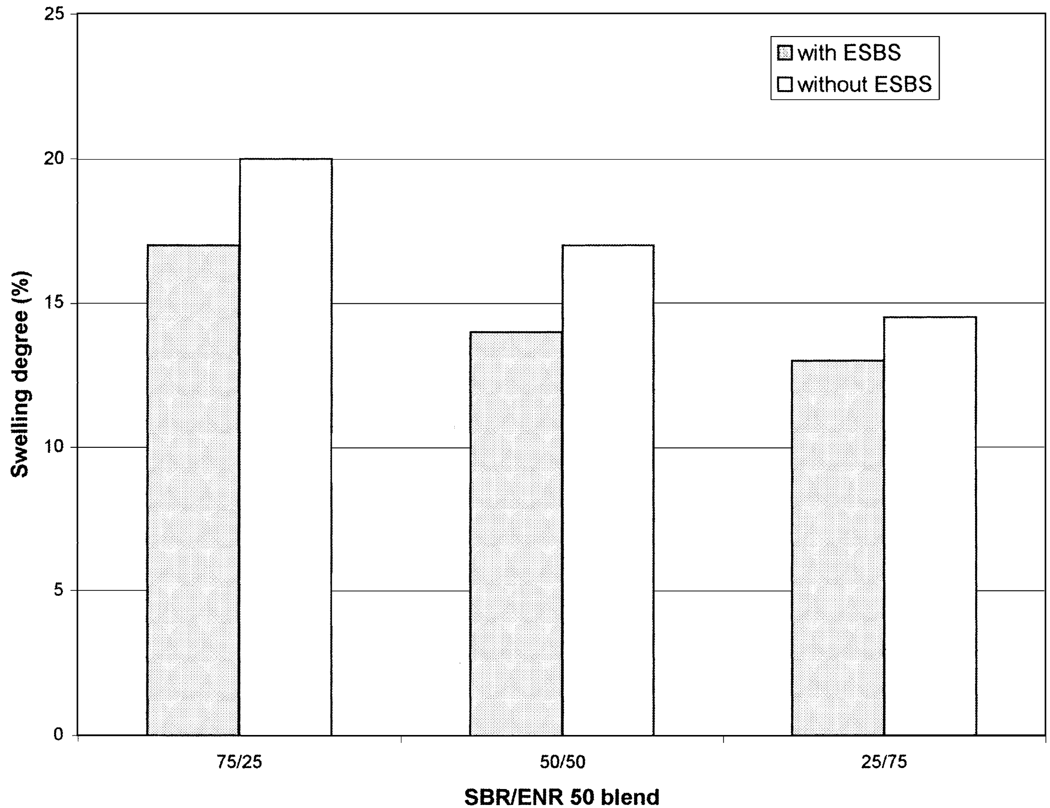


FIGURE 6 Variation in swelling degree and SBR/ENR 50 blend ratio with and without ESBS as a compatibilizer at room temperature.

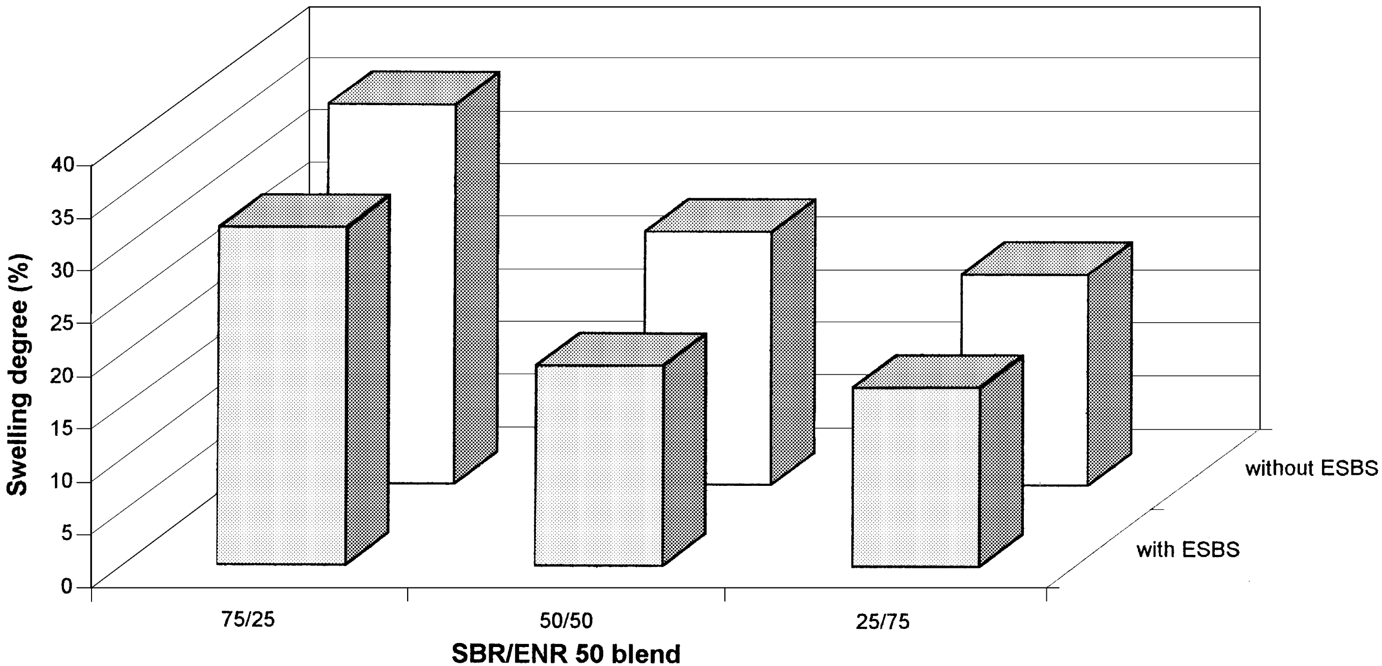


FIGURE 7 Comparative effect of a compatibilizer, ESBS on swelling degree of SBR/ENR 50 blends at 100°C.

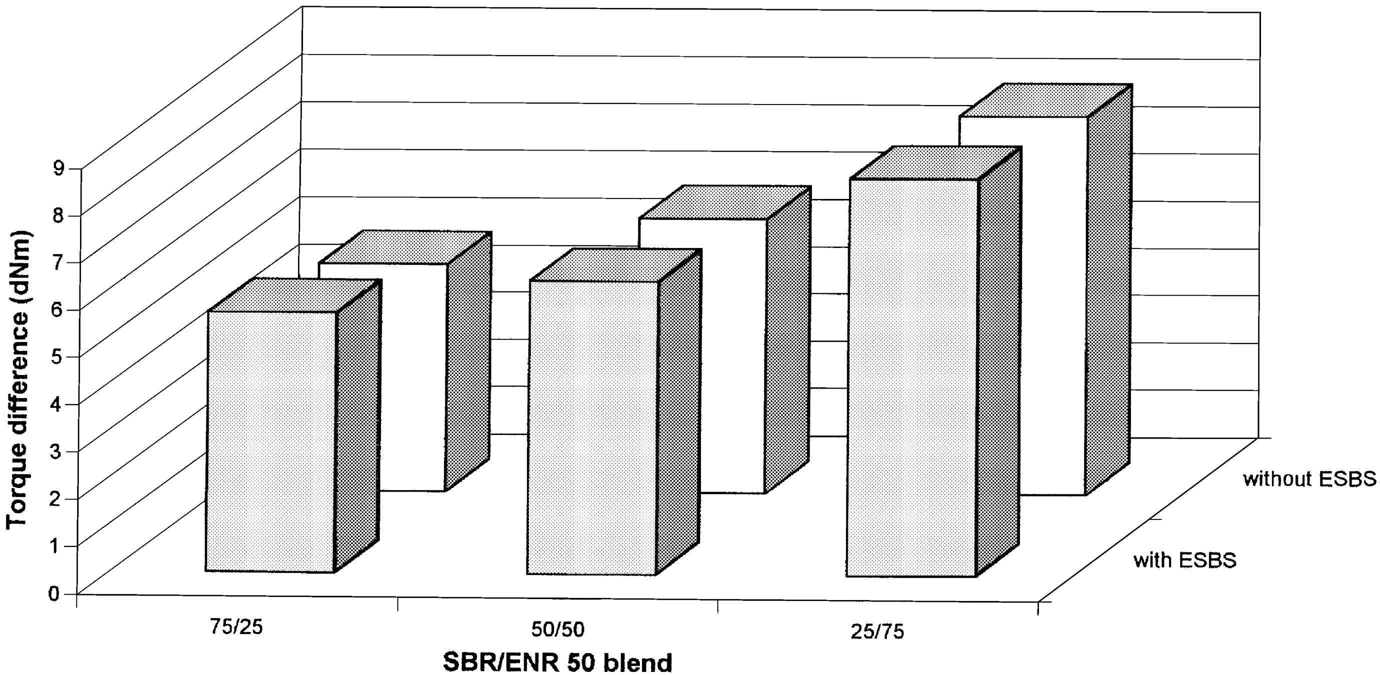


FIGURE 8 Comparative effect of a compatibilizer, ESBS on torque difference of SBR/ENR 50 blends.

the t_{90} value also decreases with increasing ENR50 content in the blends. However at a similar blend ratio in contrast to the scorch time, the incorporation of ESBS reduced the cure time of the SBR/ENR 50 blends which again indicates the beneficial effect of ESBS.

Figure 6 shows the effect of blend ratio on the degree of swelling at room temperature (23°C) for SBR/ENR 50 blends with and without ESBS. It can be seen that the degree of swelling decreases with increasing ENR 50 content in the blends. As the natural rubber is epoxidized, its chemical and physical properties change according to the extent to which the mole % of modification is introduced. According to Baker et al. [12] as the degree of epoxidation is increased, the ENR 50 becomes more oil resistant and impervious to gases. Gelling [13] found that as the fraction of the epoxide group in ENR 50 increases, the swelling resistance in oil increases and the oil resistance of ENR 50 is comparable to some of the speciality synthetic elastomers such as NBR. It can be seen also that at a similar blend ratio, SBR/ENR 50 blends with ESBS exhibit lower percentage swelling than the similar blends without ESBS.

The similar trend can be seen in Figure 7 which shows the effect of blend ratio on the degree of swelling at 100°C. Blends with larger ENR 50 content and ESBS exhibit better swelling resistance. However the percentage swelling at 100°C was higher than at 23°C for similar blend ratios. The temperature increase from room temperature to 100°C has increases the mobility of the polymer chains and consequently oil penetration become easier and faster [14].

The improved interfacial adhesion or interaction between SBR and ENR 50 in the presence of ESBS explains the better oil swelling resistance of the SBR/ENR 50 blends with ESBS compared to similar blends without ESBS. Another evidence that interactions occurred between the ESBS and these two rubbers is shown in Figure 8. It can be seen that at a similar blend ratio, the torque difference (elastic torque at maximum value (MH) – elastic torque at minimum value (ML)) of SBR/ENR 50 blends with ESBS is higher than for similar blends without ESBS. Since the torque difference indirectly shows the crosslink density [15], this results indicates that ESBS has improved the interfacial adhesion between the SBR and ENR 50 by acting as a compatibilizer.

CONCLUSIONS

From this study, the following conclusions may be drawn.

1. The processability of the SBR/ENR 50 blends improved with increased content of ENR 50 in the blends and the presence of a compatibilizer, ESBS.

2. The scorch time, t_2 and cure time t_{90} decrease with increased content of ENR 50 in the blends. At a similar blend ratio, the ESBS shows beneficial effect by increasing the scorch time and decreasing the cure time of the SBR/ENR 50 blends.
3. Oil resistance of the SBR/ENR 50 blends was improved by increased content of ENR 50. At a similar blend ratio, the presence of ESBS further enhanced the oil resistance of the blends.

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