

## Curing characteristics of chlorosulphonated polyethylene and natural rubber blends

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**Abstract:** The dependence of the Mooney scorch time and cure index on the blend ratio of chlorosulphonated polyethylene/natural rubber (CSM/SMR 20 CV) and chlorosulphonated polyethylene/chlorinated natural rubber (CSM/Pergut S 40) blends were determined in the temperature range from 120 °C to 160 °C using a Monsanto Mooney viscometer. Semi-efficient vulcanization systems were used for the study. The morphology of the fracture surface of the crosslinked systems was determined by Scanning Electron Microscopy (SEM). The results showed that the scorch time decreased with increasing SMR 20 CV and Pergut S 40 contents. This observation is attributed to the increasing solubility of sulfur, as the content of SMR 20 CV and Pergut S 40 in the composition increased. For temperatures greater than 140 °C, the dependence of the scorch time on blend ratios diminishes, as enough thermal energy is available to overcome the activation energy of vulcanization. The differing curing characteristics of the two blends is explained by the compatibility factor of the respective blend. Morphological analysis of the blends shows a very satisfactory agreement.

**Keywords:** Chlorosulphonated polyethylene/natural rubber blends, chlorosulphonated polyethylene/chlorinated natural rubber blends, curing characteristics, surface morphology.

### INTRODUCTION

In recent years, economic, technological, and other regulatory pressures have gradually narrowed the further development of new chemical varieties of polymers.<sup>1,2</sup>

A blend can offer a set of properties that may give it the potential of entering application areas not possible with either of the polymer comprising the blends. Among authors investigating rubber blends, Baker<sup>3</sup> reported that replacement of polychloroprene by a 20/80 natural rubber/Neoprene GRT blend could be accept-

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able for many applications where Neoprene GRT is used; Patra and Das<sup>4</sup> studied the flame retardancy and heat shrinkability of polyolefin/elastomer blends. The blending together of natural rubber (NR) and chlorosulphonated polyethylene rubber (CSM) is intended to produce a vulcanizate with the best properties from each component, *i.e.*, the good strength properties of NR and the good weather resistance, color stability and high extension values of CSM.<sup>5</sup>

The most commonly used crosslinking system consists of a metallic oxide, an organic acid and an accelerator. The crosslinking of chlorosulphonated polyethylene is initiated by hydrolysis of the sulphochloride group contained in the polymer.<sup>6</sup> Natural rubber, which are non-polar substances, are crosslinked by tetramethylthiuram disulfide with a little sulfur.<sup>7</sup>

In this preliminary study, the curing characteristics of chlorosulphonated polyethylene and natural rubber blends are reported. In order to understand the curing characteristics of CSM/SMR 20 CV and CSM/Pergut S 40, the Mooney scorch time and the cure index of the blends were determined. The morphology of the fracture surface of the crosslinked systems was investigated by Scanning Electron Microscopy (SEM).

#### EXPERIMENTAL

In this study, natural rubber (NR), *i.e.*, SMR 20 CV and chlorinated natural rubber (CNR), *i.e.*, Pergut S 40, were blended with CSM at different ratios. SMR 20 CV was supplied by Lee rubber (Malaysia) and Pergut S 40 was supplied by Bayer (Denmark). The chlorosulphonated polyethylene rubber (CSM) was Hypalon-40 and supplied by Du Pont, USA. The chlorine content was 35 % and the sulfur content was 1-1.5 % by weight as  $-SO_2Cl$  units. Sulfur, magnesium oxide and tetramethylthiuram disulfide (TMTD) were used as the vulcanizing agent and accelerator, respectively, throughout this study. Commercial grade rubber chemicals, such as zinc oxide and stearic acid were also used. For each of the two types of NR, various ratios of CSM were incorporated into the cure system. The details of the blend ratios are shown in Table I.

TABLE I. Blend formulations of NR and CNR with CSM rubber<sup>a</sup>

CSM (pphr) <sup>b</sup>	NR/CNR (pphr) <sup>b</sup>
100	0
80	20
50	50
20	80
0	100

<sup>a</sup>Cure system: zinc oxide, 5; stearic acid, 2; sulfur 1.5; tetramethylthiuram disulfide (TMTD), 2; magnesium oxide, 4'; <sup>b</sup>Part per hundred rubber

#### Compounding

The compounds (Table I) were prepared using a laboratory mixing roll mill of dimensions 400 × 150 mm at a speed ratio of the rollers  $n_1/n_2 = 28/22$ , at a roller temperature of 40-50 °C.<sup>8</sup>

The time of the preparation of the blends was *ca* 20 min. Curing was performed at 160 °C up to the optimum cure time ( $t_{c90}$ ), which was determined from the rheograph obtained using a Monsanto R-100 model.

### Testing

The Mooney scorch time and cure index were determined using a Monsanto Mooney viscometer (MV 2000) and average values were obtained from three scalings of the Mooney viscosity. The boundary error was  $\pm 1$ . The testing procedure was conducted according to the method described in ASTM D 1646-94. The Mooney scorch time ( $t_5$ ) is defined as the time required for an increase of 5 units above the minimum viscosity, as determined from a plot of the Mooney viscosity versus time. The cure index is defined as the difference in time required for an increase of 35 units ( $t_{35}$ ) above the minimum viscosity, *i.e.*,

$$\Delta t = t_{35} - t_5$$

The cure index defines the overall cure rate.

### Scanning electron microscopy studies

Examination of the fracture surface was carried out using a scanning electron microscope (SEM) model JEOL JSM 5300. The aim was to obtain some information on the model of fracture and the condition of the matrix. The fracture ends were sputter-coated with a thin layer of gold in a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Scorch time

The variation of the Mooney scorch time,  $t_5$  of the CSM/SMR 20 CV and CSM/Pergut S 40 blends with the blend ratio of SMR 20 CV and Pergut S 40, are shown in Figs. 1 and 2, respectively.

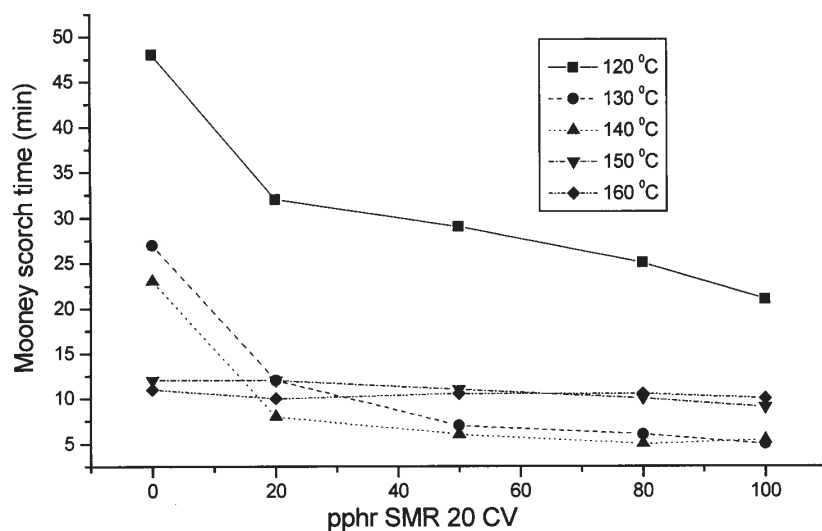


Fig. 1. Variation of the Mooney scorch time with blend ratio of SMR 20 CV (pphr) in the CSM/SMR 20 CV blend for various vulcanization temperatures.

It can be seen that the  $t_5$  of the blends decreases with increasing SMR 20 CV and Pergut S 40 content. CSM is a polar rubber. As the content of CSM in the

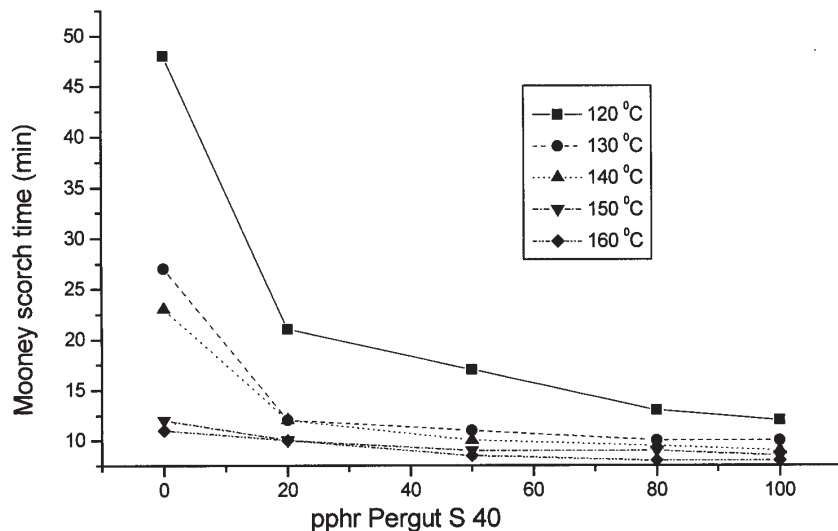


Fig. 2. Variation of the Mooney scorch time with blend ratio of Pergut S 40 (pphr) in the CSM/Pergut S 40 blend for various vulcanization temperatures.

blends decreases, the curing agents, *i.e.*, sulfur, magnesium oxide and tetramethylthiuram disulfide, become more soluble in the SMR 20 CV and Pergut S 40 than in the CSM. Consequently, the cure rate of the blend increases with decreasing content of CSM. According to Lewan,<sup>9</sup> for blends with two rubbers differing in polarity, such as SMR 20 CV or Pergut S 40 with CMS, a distribution of crosslinks can arise through preferential solubility of the curing agents and vulcanization inter-

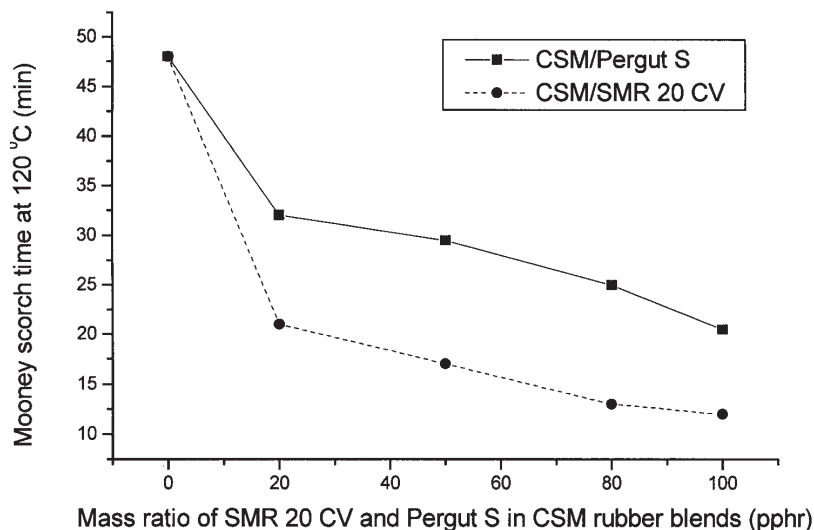


Fig. 3. Variation of the Mooney scorch time at 120 °C with the ratio of Pergut S 40 and SMR 20 CV (pphr) in the CSM/Pergut S 40 and CSM/SMR 20 CV rubber blends.

mediates. Both figures also indicate that the reduction of  $t_5$  with blend ratio of SMR 20 CV and Pergut S 40 is more pronounced at temperatures lower than 130 °C. At higher temperatures, *i.e.*, higher than 140 °C,  $t_5$  does not show a significant dependence on the blend ratio because enough thermal energy is available to overcome the activation energy of vulcanization.

A comparison of  $t_5$  for CSM/SMR 20 CV and CSM/Pergut S 40 blends at 120 °C is shown in Fig 3. It can be seen that with a similar blend ratio, the  $t_5$  of the CSM/SMR 20 CV blend is shorter than that of the CSM/Pergut S 40 blend. According to Poh and Wong,<sup>10</sup> more activated precursors to crosslinks are formed which accelerate the vulcanization process.

#### *Cure index*

The dependence of cure index of the CSM/SMR 20 CV blend on the blend ratio of SMR 20 CV for the various temperatures investigated in this study is shown in Fig. 4. For temperatures lower than 140 °C, the cure index is significantly dependent on the blend ratio of SMR 20 CV. It passes through a maximum at 20 pphr of SMR 20 CV in the blend. This observation is attributed to the incompatibility between CSM (a polar rubber) and SMR 20 CV (a nonpolar rubber), the respective solubility parameters of which are 9.5 and 8.1.<sup>11</sup> Also, owing to the higher unsaturation in SMR 20 CV, it cures faster than CSM, resulting in uneven vulcanization of the blend. For instance, at 120 °C, the cure index of CSM and of SMR 20 CV are 7.2 and 8 min, respectively. As the SMR 20 CV content in the blend is increased from 0 to 20 pphr, more sulfur reacts with the SMR 20 CV rubber than with CSM. This means that less sulfur and magnesium oxide is available for the vulcanization of CSM, which is the dominant rubber component in the blend. However, beyond 20 pphr of SMR 20 CV, the role of SMR 20 CV becomes more significant and results in a drop of the cure index of the blend. For the temperatures greater than 140 °C, the cure index shows less dependence on the blend ratio of SMR 20 CV, a phenomenon that is associated with the increase in cure rates for both rubbers resulting from an ample supply of thermal energy to overcome the activation of vulcanization for both rubbers, *i.e.*, even vulcanization of the blend is obtained. In fact, above 150 °C, the cure index is almost independent of the blend ratio of SMR 20 CV.

The effect of blend ratio of Pergut S 40 on the cure index of CSM/Pergut S 40 blend is shown in Fig. 5. Generally, a gradual drop of cure index is observed as the pphr of Pergut S 40 is increased, although a slight maximum is displayed in some cases. This finding is attributed to the better compatibility between CSM and Pergut S 40, both of which have a polar nature. The respective solubility parameters are 9.5 and 9.2,<sup>9</sup> which are closer than the corresponding values for CSM and SMR 20 CV, as discussed earlier. As in the case of the CSM/SMR 20 CV system (Fig. 5), the cure index of the blend was less dependent on the blend ratio of Pergut

S 40 at higher vulcanization temperature, *i.e.*, greater than 140 °C. Again, this is attributed to the availability of thermal energy to overcome the activation energy of vulcanization.

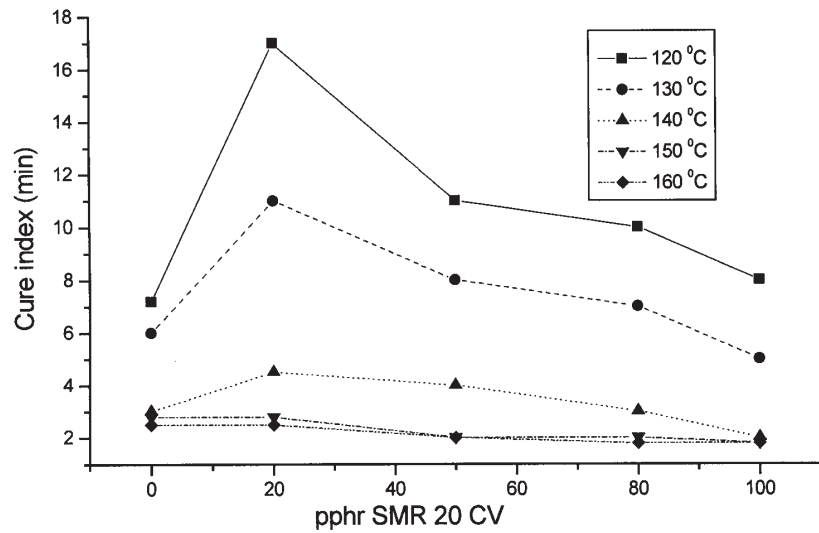


Fig. 4. Variation of the cure index with blend ratio of SMR 20 CV (pphr) in the CSM/SMR 20 CV blend for various vulcanization temperatures.

In order to compare the cure index of both blends, the cure index was plotted against the cure temperature for blends, containing either 20 pphr SMR 20 CV or

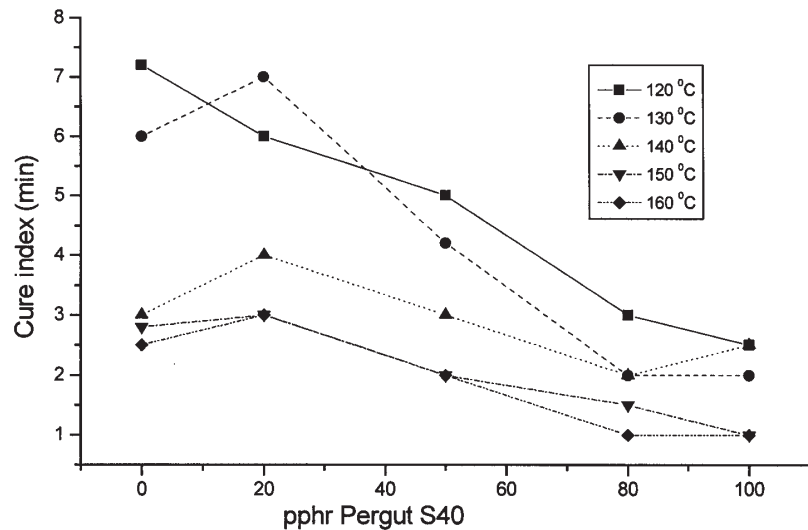


Fig. 5. Variation of the cure index with blend ratio of Pergut S 40 (pphr) in the CSM/Pergut S 40 blend for various vulcanization temperatures.

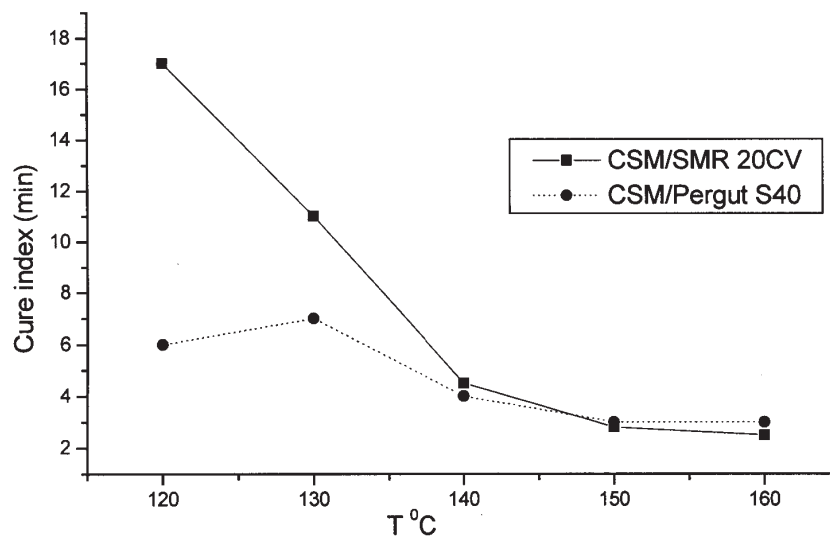
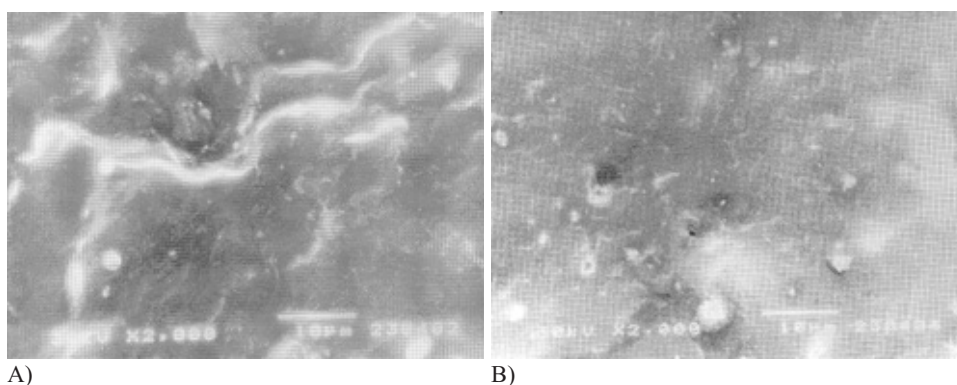


Fig. 6. Temperature dependence of the cure index at 20 pphr of SMR 20 CV or Pergut S 40 for both blends.

Pergut S 40 (Fig. 6). The cure index decreases with increasing temperature for both blends. The crosslinking of CSM takes place according to a completely different mechanism from those involved in the crosslinking of natural rubber *i.e.*, the activation energy is different.

#### *Morphology microscopic studies*

Scanning electron microscopic (SEM) studies of fracture surface were performed in order to gain a better insight into the compatibility of the rubber blends. When the polarity of the natural rubber increases, the compatibility with CSM rubber is increased. The SEM microphotographs at 2000 x magnification of the frac-



A) B)  
Fig. 7. SEM microphotograph at 2000 x magnification of CSM/Pergut S 40 (A) and CSM/SMR 20 CV (B) rubber blends.

ture surfaces of CSM/SMR 20 CV (80:20) rubber blends are less homogeneous (Fig. 7B) than those of CSM Pergut S 40 (80:20) (Fig. 7A). The domain size (5-10  $\mu\text{m}$ ) in CSM/SMR 20 CV (80:20) rubber blends (Fig. 7B) were determined by morphology microscopic studies.

#### CONCLUSION

The Mooney scorch time,  $t_5$  of CSM/SMR 20 CV and CSM/Pergut S 40 blends decreases with increasing SMR 20 CV and Pergut S 40 content in the blends. The reduction is more pronounced at lower temperatures, *i.e.*, below 130 °C.

For CSM/SMR 20 CV blend, the cure index shows a maximum at 20 pphr of SMR 20 CV in the blend at lower vulcanization temperature, an observation which is attributed to the incompatibility between CSM and SMR 20 CV and the faster cure rates of the latter. In the case of CSM/Pergut S 40 blends, the cure rate virtually decreases with increasing Pergut S 40 content, as a result of the better compatibility between CSM and Pergut S 40, both of which are polar in nature. For temperature greater than 140 °C, the cure index for both blend systems exhibits less dependence on the blend ratio due to the availability of thermal energy to overcome the activation energy of vulcanization.

Based on the morphological investigations, the fracture surfaces of CSM/SMR 20 CV (80:20) rubber blends are less homogeneous than those of CSM/Pergut S 40 (80:20).

#### ИЗВОД

#### КАРАКТЕРИСТИКЕ ПРОЦЕСА УМРЕЖАВАЊА БЛЕНДИ КАУЧУКА НА БАЗИ ХЛОРОСУЛФОНОВАНОГ ПОЛИЕТИЛЕНСКОГ И ПРИРОДНОГ КАУЧУКА

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Зависност времена Моонеу скорчинга и индекса умрежавања од састава бленди хлоросулфоновани полиетиленски каучук/природни каучук (CSM/SMR 20 CV) и хлоросулфоновани полиетиленски каучук/хлоровани природни каучук (CSM/Pergut S 40) у температурном опсегу од 120 °C до 140 °C одређивана је Monsanto Моонеу вискозиметром. За умрежавање су коришћени полуефикасни системи. Морфологија површинског прелома умрежених система одређивана је сканирајућом електронском микроскопијом (SEM). Резултати су показали да са повећањем садржаја SMR 20 CV и Pergut-a S 40 време скорчинга опада. Ово се приписује повећању растворљивости сумпора у умреженим материјалима са повећаним садржајем SMR 20 CV и Pergut-a S 40. При температурама већим од 140 °C, зависност времена скорчинга од састава бленди је незнатна, што се објашњава тиме да је расположива топлотна енергија већа од енергије активације процеса умрежавања. Разлика у вредностима карактеристика процеса умрежавања за два типа бленди каучука објашњава се фактором компатибилности каучука. Морфолошка испитивања прелома површине бленди каучука то потврђују.

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## REFEERENCES

1. S. Ray, C. K. Das, *Polym.-Plast. Technol. Eng.* **40** (2001) 23
2. D. J. Zanzing, *Rubber Chem. Technol.* **66** (1993) 456
3. C. S. L. Baker, *Rubber Chem. Technol.* **5** (1974) 5
4. P. K. Patra, C. K. Das, *J. Appl. Polym. Sci.* **68** (1998) 597
5. R. E. Fuller, K. S. Macturk, *Kautsch. Gummi Kunsts.* **7** (2001) 357
6. W. Hofmann, *Vulcanization and vulcanizing agents*, Maclaren & Sons LTD, London, 1967, p. 270
7. W. Hofmann, *Vulcanization and vulcanizing agents*, Maclaren & Sons LTD, London, 1967, p. 211
8. P. K. Pal, S. K. De, *Rubber Chem. Technol.* **55** (1982) 1370
9. M. V. Lewan, *Blends of natural rubber*, Chapman & Hall, London, 1998, p. 52
10. B. T. Poh, K. W. Wong, *J. Appl. Polym. Sci.* **69** (1998) 1301
11. J. A. Bridson, *Rubber Chemistry*, Applied Science Publishers, London, 1978, p. 83.