

# High-temperature and ageing properties of high-crystalline TOR-filled SBR vulcanizates

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The influence of a co-cross-linkable processing aid, *Trans*-polyoctenylene (TOR), on high-temperature stress–strain properties and ageing of filled styrene butadiene rubber (SBR) vulcanizates, was studied. Three different cross-linking systems, conventional (CV), semi-efficient (SEV) and efficient (EV), with respect to SBR were included. A linear regression equation has been obtained between vulcanizate modulus (200%), TOR dosage and sulphur/accelerator ratio at different test temperature. A similar equation has also been found with tensile strength at 120 °C. Thermal analysis, Fourier transform-infrared spectroscopy and a few solid-state <sup>13</sup>Carbon nuclear magnetic resonance spectroscopic techniques were performed to get insight into the structural changes that occur between TOR and SBR during cross-linking. A plausible mechanism of the interaction between TOR and SBR has been suggested. Based on the property retention of the vulcanizates at room as well as at high working temperature, an optimization of properties between the CV and EV systems has been attempted by the modification of the CV system using TOR.

## 1. Introduction

In service, rubber products develop gradual temperature rise under dynamic conditions. Because rubber is a poor conductor of heat, a considerable difference in temperature is found over the entire cross-section of the product. Temperature build-up leads to ageing and thus a change in the properties of the cured rubber product [1]. However, temperature developed on the surface may dissipate, whereas the temperature developed inside the product is retained, which is detrimental to the life of the product. Use of special chemicals can alleviate this problem on the surface of a product, whereas cross-linking system plays a vital role in the bulk of the product. Thus a judicious choice of compounding formulation is necessary for products requiring high strength at elevated temperature [2]. An ageing study alone can partly indicate the performance of the product in service. Hence, study of the actual strength property at high working temperature [2] is significant. This study will elucidate the vulcanizate property at high temperature as well as property optimization, which is correlated with the structural changes, as indicated from advanced analytical techniques.

## 2. Experimental procedure

### 2.1. Materials used

Details of the materials used are given in Table I.

### 2.2. Mixing and curing

Mixing (formulation given in Table II) was performed in a Laboratory Banbury (1.6 l capacity) as reported previously [3]. Gum polymer blends were mixed in a Brabender Plasticorder PL 2000-3 as reported earlier [3]. Filled compounds were cured at  $140 \pm 2$  °C for 50 min for high-temperature property and ageing studies. Gum samples for Fourier transform-infrared (FT-IR) and nuclear magnetic resonance (NMR) study were cured in a compression mould at  $140 \pm 2$  °C for 50 min, between cellophane papers on both sides.

### 2.3. Vulcanizate testing

Stress–strain properties at high temperature were measured as per ASTM D-412, die C (tensile strength) and ASTM D-624, die C (tear) using a Zwick UTS-1445 with an optical extensometer and a heating chamber (temperature accuracy  $\pm 1$  °C). Test pieces were allowed to equilibrate in the chamber for 5 min before testing. No detectable ageing took place during this time. The temperature of the test ranged from 23–120 °C. Three tests were carried out at each temperature, the quoted tensile strength (TS), modulus and other values, were median values. Ageing was performed in an ageing oven at 105 °C for 3 days. To

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TABLE I Details of materials used

Material	Characteristics	Source
Styrene-butadiene rubber (SBR)	1502 grade, ML <sub>1+4</sub> at 100 °C = 49 <i>cis</i> 9.5%, <i>trans</i> 55% and vinyl 12%	Nippon Zeon Co. Tokyo, Japan
<i>Trans</i> -polyoctenylene (TOR)	8012 grade, m.p. = 54 °C <i>T<sub>g</sub></i> = -65 °C <i>cis</i> 20%, <i>trans</i> 80%	HÜLS, Germany
High-abrasion furnace black (HAF)	N 330, Surface area = 80 m <sup>2</sup> g <sup>-1</sup>	Thai Carbon Ltd, Thailand
<i>N</i> -cyclohexyl benzothiazyl sulphenamide (CBS)	Rubber grade	Bayer (I) Ltd, India
Sulphur, ZnO, stearic acid, etc.	Rubber grade	Standard suppliers of India

TABLE II Compound formulation

Ingredients <sup>a</sup>	Curing system											
	Conventional				Semi-EV				EV			
	1	2	3	4	5	6	7	8	9	10	11	12
TOR	0	5	10	20	0	5	10	20	0	5	10	20
Sulphur	2	2	2	2	1.2	1.2	1.2	1.2	0.5	0.5	0.5	0.5
CBS	1	1	1	1	2.5	2.5	2.5	2.5	5.0	5.0	5.0	5.0

<sup>a</sup> All formulations contain (p.h.r.): SBR-1502, 100; ZnO, 4; steric acid, 2; HAF (N 330), 50.

measure the volume fraction  $V_r$ , experimental samples after testing at high temperature were allowed to return to room temperature and then put in toluene to attain equilibrium swelling (72 h at room temperature). The changes which occurred due to high temperature on the sample were studied in relation to the volume fraction,  $V_r$ , as given elsewhere [4].

Thermal analysis was performed in a 7 series Perkin-Elmer thermal analyser system. Thermogravimetric analysis (TGA) was carried out in nitrogen and oxygen atmospheres at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) of filled compounds was carried out in a nitrogen atmosphere at 10 °C min<sup>-1</sup> heating rate.

#### 2.4. Spectroscopic measurements

FT-IR spectra were recorded on a Perkin-Elmer FT-IR-2000 spectrometer. A minimum of five scans were signal averaged at a resolution of 4 cm<sup>-1</sup>. Gum vulcanizate thickness was 1.5 mm for the study. The spectra of the vulcanizates were taken by mounting an attenuated total reflectance (ATR) attachment. The internal reflection element (IRE) chosen was 45°. The solid state <sup>13</sup>C NMR measurements of gum vulcanizates were performed using a Bruker MSL-300 pulsed NMR spectrometer at room temperature with CP/MAS and gated high-power decoupling. The operating carbon frequency was 75.47 MHz and the

sample spinning speed was 1 KHz. Chemical shifts of <sup>13</sup>C spectra are reported in p.p.m. relative to TMS as standard.

### 3. Results and discussion

Table III shows that the modulus (200%) of all vulcanizates, is more at high temperature in the CV system followed by the SEV and EV systems for SBR. The modulus (100%) is comparable in CV and SEV, followed by the EV system. Tensile strength decreases down the series from CV to SEV for all vulcanizates at high temperature. This may be because of more polysulphidic cross-links in the CV system compared to the other two. However, the tensile strength in the EV system was found to be more than SEV, both at room and high temperature. The modulus (200%) also decreases with incorporation of TOR in SBR at high temperature, irrespective of the curing system (Table III). This is probably because of the simultaneous cross-linking reaction that takes place in the TOR phase in addition to the SBR phase [5]. As the total sulphur and accelerator is the same in the compound, the available sulphur and accelerator decreases in the SBR phase of compounds with TOR during curing. This results in a change in the degree of cure in the SBR phase and also the cross-link structure of TOR-filled vulcanizates which ultimately affect the modulus. Details were explained earlier [3].

TABLE III Physical properties (unaged)

Compound	Modulus (100%) (MPa)		Modulus (200%) (MPa)		Tensile strength (MPa)		Elongation at break (%)		Fracture energy ( $10^{-5} \text{ J m}^{-2}$ )	
	RT <sup>a</sup>	120 °C	RT <sup>a</sup>	120 °C	RT <sup>a</sup>	120 °C	RT <sup>a</sup>	120 °C	RT <sup>a</sup>	120 °C
1	3.6	2.6 (72) <sup>b</sup>	10.6	6.2	21.0	8.0 (38)	307	241 (79)	6.6	2.1 (32)
2	3.4	2.3 (67)	9.9	5.5	19.5	7.0 (36)	309	240 (78)	6.1	1.9 (31)
3	3.0	2.3 (76)	8.8	5.3	17.2	6.4 (37)	303	231 (76)	5.2	1.7 (33)
4	2.9	1.8 (62)	7.3	4.0	18.1	5.3 (29)	361	249 (69)	6.7	1.5 (22)
5	3.1	2.4 (77)	9.5	–	17.6	5.6 (32)	295	188 (64)	5.2	1.2 (23)
6	2.9	2.4 (83)	8.5	–	19.5	5.0 (26)	334	178 (53)	6.6	1.1 (17)
7	3.0	2.2 (73)	8.4	–	18.5	4.6 (25)	330	180 (55)	6.4	1.0 (16)
8	2.9	1.9 (65)	7.4	4.2	17.4	4.5 (26)	363	213 (59)	6.7	1.1 (16)
9	2.4	1.8 (75)	6.9	4.2	20.5	6.2 (30)	408	259 (63)	8.4	1.7 (20)
10	2.2	1.7 (77)	6.3	4.6	20.9	5.4 (26)	431	224 (52)	9.7	1.4 (14)
11	2.4	1.5 (62)	6.2	3.9	20.6	5.4 (26)	440	242 (55)	9.8	1.4 (14)
12	2.6	1.3 (50)	5.9	3.3	18.7	4.7 (25)	470	255 (54)	9.5	1.4 (15)

<sup>a</sup> RT = room temperature,  $23 \pm 2^\circ\text{C}$ .

<sup>b</sup> Values in parentheses are percentage retention.

Vulcanizate modulus (200%) at room and high temperature are found to exhibit the following relations, obtained by multi-variable linear regression analysis using Linpack routines.

$$23^\circ\text{C} \quad M_{200} = 7.97 - 0.0865f_1 + 1.06f_2 - 0.00403f_1/f_2 \quad R^2(\text{adj}) = 61.1\% \quad (1)$$

$$40^\circ\text{C} \quad M_{200} = 6.24 - 0.0696f_1 + 0.38f_2 - 0.00725f_1/f_2 \quad R^2(\text{adj}) = 58.1\% \quad (2)$$

$$80^\circ\text{C} \quad M_{200} = 5.70 - 0.0662f_1 + 0.29f_2 - 0.00796f_1/f_2 \quad R^2(\text{adj}) = 50.6\% \quad (3)$$

$$120^\circ\text{C} \quad M_{200} = 5.22 - 0.0739f_1 + 0.39f_2 - 0.00289f_1/f_2 \quad R^2(\text{adj}) = 59.9\% \quad (4)$$

where  $M_{200}$  is the modulus at 200% elongation,  $f_1$  the TOR dosage in the vulcanizate,  $f_2$  the sulphur/accelerator ratio.

At high temperature ( $120^\circ\text{C}$ ), the tensile strength also follows a similar equation

$$\text{TS}_{120} = 5.50 - 0.116f_1 + 1.06f_2 - 0.00766f_1/f_2 \quad ; \quad R^2(\text{adj}) = 84.2\% \quad (5)$$

where  $\text{TS}_{120}$  is the tensile strength at  $120^\circ\text{C}$ ,  $f_1$  and  $f_2$  are the same as in Equations 1–4.

Fracture energy decreases with TOR dosage during high temperature in the CV system (Table III) whereas, it remains almost the same for TOR-filled vulcanizates in the SEV and EV systems. Moreover, the fracture energy in the CV system is slightly more than in the EV and SEV for all vulcanizates. Tearing energy decreases with increase in test temperature irrespective of the TOR dosage in all curing systems. Fig. 1 shows a representative tearing energy for all other systems.

Retention of modulus (200%) and tensile strength at high temperature in the presence of TOR is slightly better in the CV system compared to the SEV and EV

systems (Figs 2–4). It has been previously reported that SBR with regular sulphur/accelerator dosage in the CV system contains much less polysulphidic cross-links compared to the natural rubber (NR) CV system

[6]. Cross-links from cured TOR are more of the monosulphidic type because TOR on curing, with regular sulphur/accelerator dosage, gives an enthalpy which closely resembles that of the EV system of NR. This has been explained in detail earlier [7]. Thus TOR when present in SBR, induces a change of cross-links of the SBR phase towards more monosulphidic/disulphidic type. The greater the polysulphidic linkage in the vulcanizate, the greater is the change-over from polysulphidic to monosulphidic/disulphidic type. Therefore, the CV system, having a high proportion of polysulphidic cross-links compared to SEV and EV, is influenced more by TOR which helps to improve the retention of properties in the CV system.

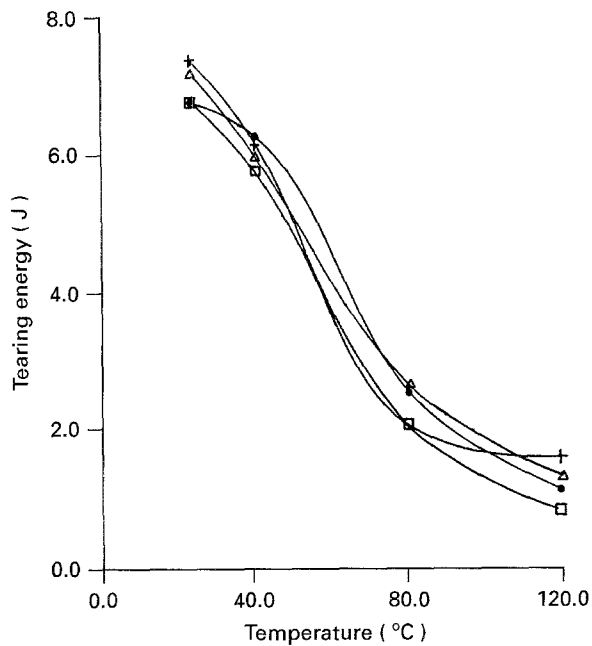


Figure 1 Tearing energy at different temperature (EV system) (●) No TOR, (+) 5 parts TOR, (Δ) 10 parts TOR, (□) 20 parts TOR.

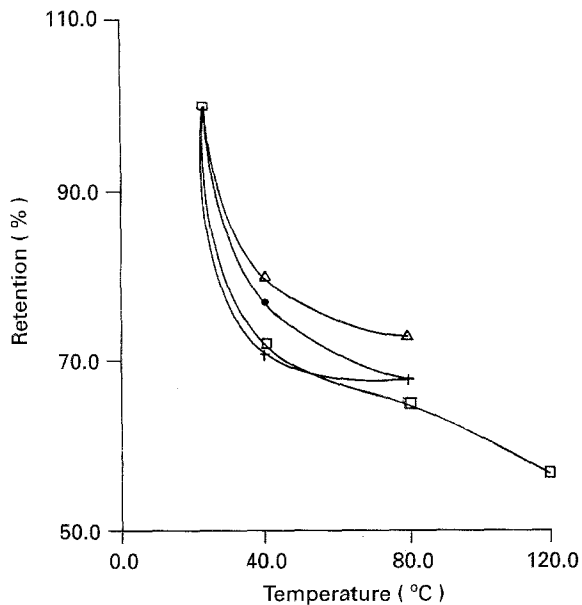


Figure 3 Per cent retention of modulus (200%) in the SEV system. For key, see Fig. 1.

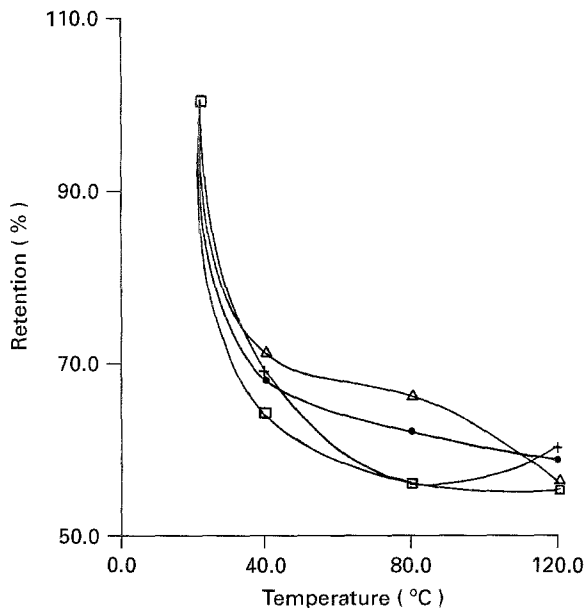


Figure 2 Per cent retention of modulus (200%) in the CV system. For key, see Fig. 1.

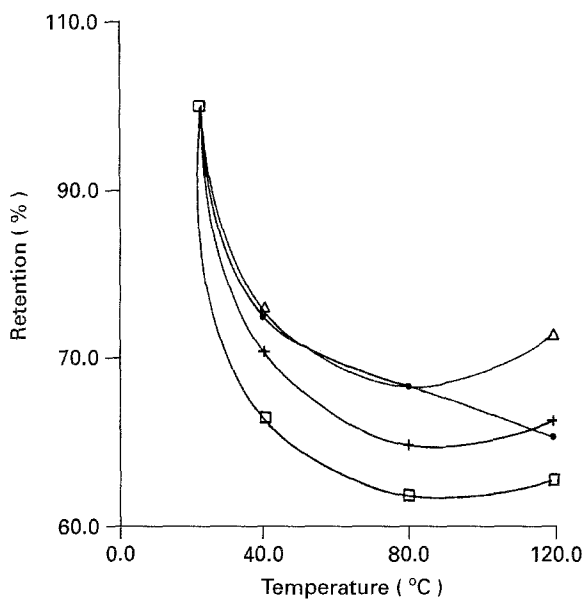


Figure 4 Per cent retention of modulus (200%) in the EV system. For key, see Fig. 1.

Modulus (200%) retention has not been reported at 120°C (Fig. 3) because of early failure of the sample (elongation at break < 200%).

It has also been observed that retention (Table III) is more in the case of 5 and 10 parts TOR-filled vulcanizate compared to 20 parts TOR-filled vulcanizate. This may be because TOR has two effects: one is reinforcement and the other is plasticization. There is an optimum dosage of TOR below which it will have a reinforcing action and above which it acts more as a plasticizer. Thus 5 and 10 parts have better reinforcing action, whereas beyond 10 parts, TOR has more plasticizing effect [8]. This results in high elongation at break (%) at room and high temperature with 20 parts TOR-filled vulcanizate compared to 5 and 10

parts TOR-filled vulcanizate. This is true for all curing systems (Table III). Retention of the properties is also exhibited in the volume fraction of vulcanizates,  $V_r$ . At high temperature,  $V_r$  decreases with TOR as at room temperature (Table IV). However, retention of  $V_r$  at 120°C (compared to room temperature) is comparable for TOR-filled vulcanizate in the CV system. Such retention of  $V_r$  indicates a less destructive change in the network in the presence of TOR in the CV system. Figs 5–7 show the retention of cross-link density of the vulcanizates which is measured according to Prime's method [9]. This supports modulus retention as obtained earlier.

In order to explain the property improvement in the CV system with the help of TOR, infrared spectra of SBR gum vulcanizates in the CV and EV systems are presented in Fig. 8. TOR contains one double bond

TABLE IV DSC and volume fraction results

Compound	$T_{o_1}$ , onset temp. (°C)	$T_{p_1}$ , peak temp. (°C)	$V_r$ at		Enthalpy change, $\Delta H$
			RT <sup>a</sup>	120 °C	
1	168	198	0.248	0.229 (92)	14.7
2	172	195	0.248	0.230 (93)	14.3
3	180	195	0.241	0.220 (91)	13.1
4	183	199	0.234	0.215 (92)	9.6
5	145	173	0.237	0.223 (94)	12.0
6	154	177	0.235	0.211 (89)	9.9
7	154	183	0.232	0.204 (88)	10.0
8	160	183	0.223	0.196 (88)	8.9
9	158	169	0.215	0.198 (92)	7.0
10	156	172	0.205	0.180 (88)	6.8
11	157	172	0.202	0.173 (86)	6.6
12	156	172	0.189	0.165 (85)	6.3

<sup>a</sup> RT = room temperature,  $23 \pm 2^\circ\text{C}$

<sup>b</sup> Values in the parentheses are percentage retention.

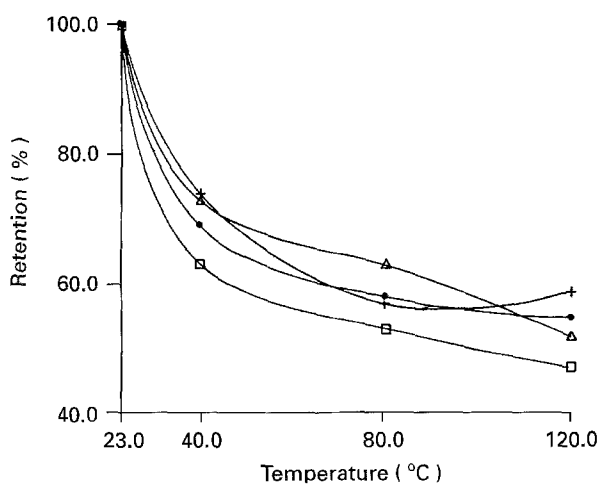


Figure 5 Per cent retention of cross-link density in the CV system. For key, see Fig. 1.

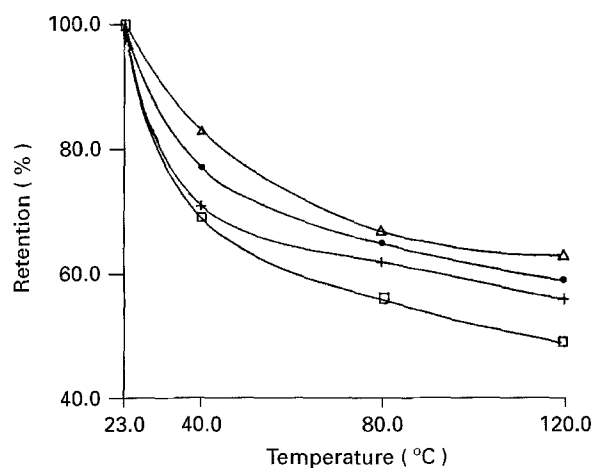


Figure 6 Per cent retention of cross-link density in the SEV system. For key, see Fig. 1.

for every eight carbon atoms in its structure. The two strong absorption bands at  $720$  and  $967\text{ cm}^{-1}$  in the infrared spectrum of TOR are assigned [10] to *cis* and *trans* isomers of the double bond. Similarly, the strong absorption bands at  $699$ ,  $758$ ,  $910$  and  $964\text{ cm}^{-1}$  of SBR gum vulcanizate in the CV system are assigned to "styrene" and *cis*, "vinyl", *trans* isomers of butadiene structure [10]. When TOR is present with SBR (10 parts), the particular peak at  $720\text{ cm}^{-1}$  (corresponding to the *cis* isomer) of TOR, disappears totally. In addition, the *cis* peak ( $758\text{ cm}^{-1}$ ) of the butadiene part of SBR is also significantly reduced. This suggests that there is an interaction between two *cis* counterparts (a certain portion of the microstructure, not total)

of TOR and butadiene of SBR. The possibility of *trans-trans* or *cis-trans* interaction is ruled out, as there is no change in the *trans* ( $964\text{ cm}^{-1}$ ) peak of SBR. There is also a small diminution in the "vinyl" peak ( $910\text{ cm}^{-1}$ ) of the butadiene part of SBR in the CV system of TOR-filled SBR vulcanizate. This further suggests the mild interaction between *cis* and "vinyl" isomers of TOR and butadiene parts, respectively. Because the *cis-cis* interaction is conformationally more favourable compared to *cis-vinyl* interaction, the former may be the reason for improvement of properties in the CV system in the presence of TOR. A similar *cis-cis* interaction has also been identified in a  $^{13}\text{C}$  CP/MAS spectra of a gum vulcanizate

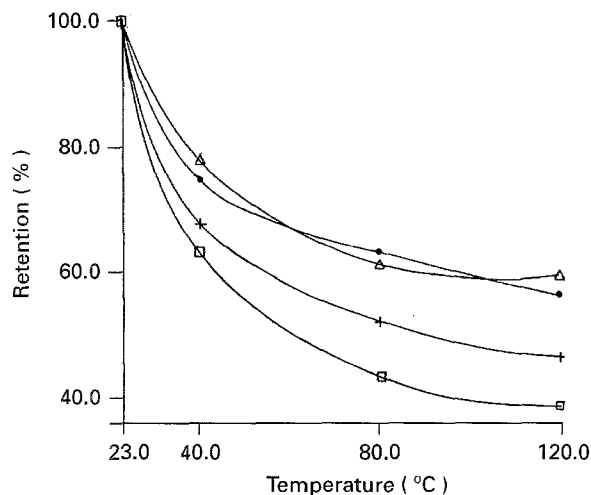
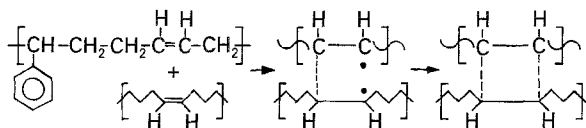


Figure 7 Per cent retention of cross-link density in the EV system. For key, see Fig. 1.

with 10 parts TOR in the CV system (Fig. 9). The signals at 26.1, 33.9, 130.4 p.p.m. are assigned to *cis*, *trans* and "styrene" structure, respectively, of SBR in gum vulcanizate [11]. When TOR is added to SBR in the CV system, the signal corresponding to the *trans* part of butadiene remains the same. However, the singlet corresponding to the *cis* isomer turns into multiplets. This is certainly because of the interaction that takes place with the *cis* part of butadiene. Detailed study is in progress. A plausible diradical mechanism



Diradical mechanism

[12] to this *cis-cis* interaction may be suggested as Interaction on gum vulcanizates has been taken as representative of the corresponding filled vulcanizates.

For the EV system, these two interactions, namely *cis-cis* and *cis-vinyl* are also present (Fig. 8) in TOR-filled gum vulcanizate. However, the *cis-cis* interaction is not as strong as in the CV system because the *cis* peak of TOR has not disappeared totally in the case of 10 parts TOR-filled vulcanizate in the EV system. In addition, the "vinyl" peak of butadiene is more reduced in the gum vulcanizate with TOR, unlike the CV system. This reveals that the *cis-cis* interaction is less compared to the *cis-vinyl* in gum vulcanizate with TOR in the EV system. *cis-vinyl* interaction is not a favoured conformation, TOR probably does not help to improve properties in the EV system.

Besides property retention, Table III also shows that at high temperature (120°C) the absolute values of modulus and tensile strength of 10 parts TOR-filled SBR vulcanizate in the CV system are equal to or somewhat greater than the average values of modulus and tensile strength of SBR vulcanizates without TOR in the SEV and EV systems, respectively. This is also observed in the case of the room-temperature study. Therefore, it appears possible to achieve the properties of the SEV and EV systems in the CV system itself, by suitably optimizing TOR dosage in the CV system.

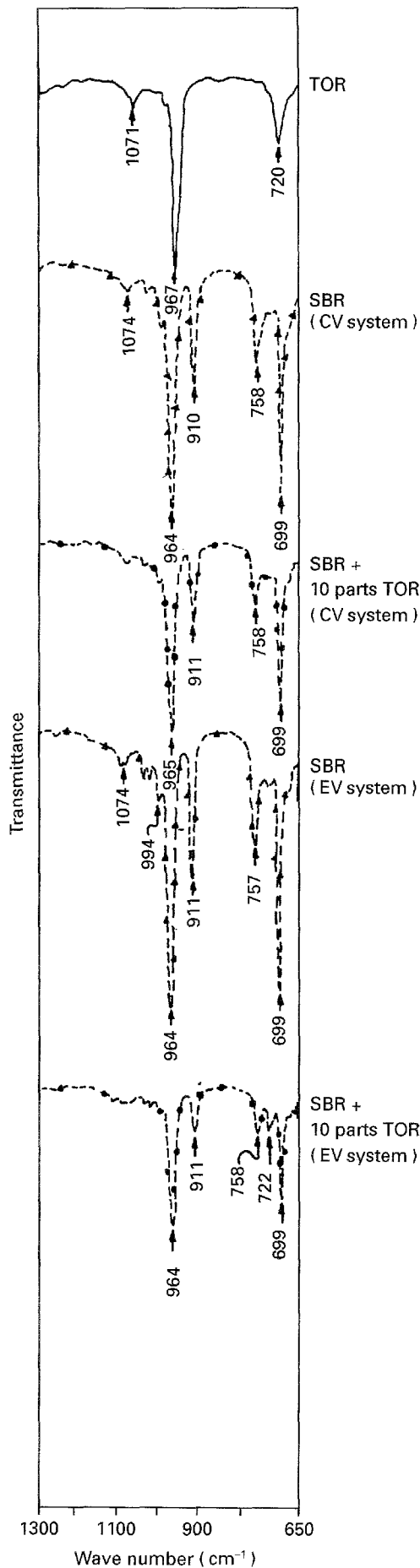


Figure 8 Infrared spectra of gum vulcanizates.

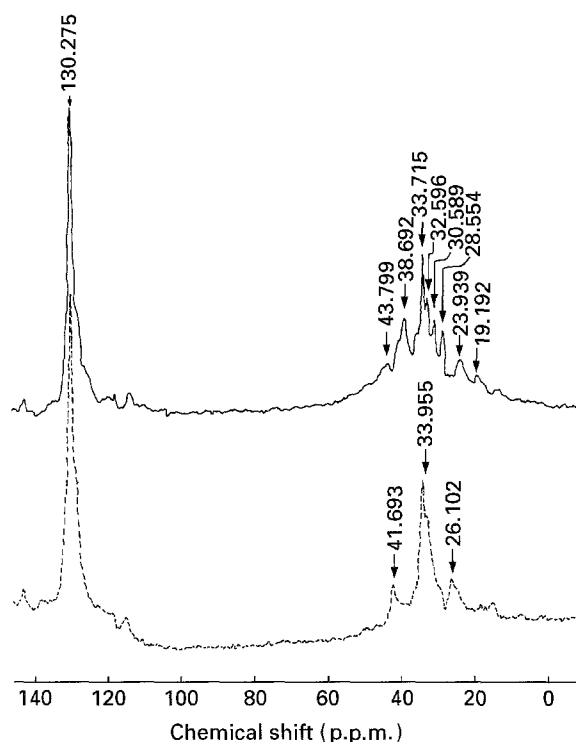


Figure 9 Solid-state  $^{13}\text{C}$  NMR spectra; (—) SBR + 10 parts TOR, (---) SBR.

### 3.1. Ageing study

Retention of tensile strength and elongation at break after ageing is better in the EV system followed by the SEV and CV systems for TOR-filled vulcanizates (Table V). Thus TOR does not change the system effect (i.e. EV > SEV > CV) after ageing. However, retention of tearing energy after ageing is better in the CV system with a higher dosage of TOR.

### 3.2. Thermal analysis

Brazier [13] has reported that the overall vulcanization enthalpy,  $\Delta H$ , generally decreases with addition of accelerator (i.e. from CV to SEV to EV systems). Similarly, vulcanization enthalpy also decreases with incorporation of TOR in SBR vulcanizates (Table IV). Change in the  $\Delta H$  value from the CV to EV system can be taken as the change in the nature of cross-links ( $\Delta H$  value is more in the CV system because of greater polysulphidic linkage and is less in EV as polysulphidic linkage is less). Thus, because of change in the polysulphidic cross-links to more stable monosulphidic/disulphidic type, the  $\Delta H$  value of vulcanizates with TOR decreases. The decrease in enthalpy value correlates with a change in cross-links from polysulphidic to more stable mono/disulphidic type in TOR-filled SBR vulcanizates. This reduction of the  $\Delta H$  value in the presence of TOR is greater in the CV than the SEV and EV systems. Therefore, the properties improve more in the CV system. Details have been reported earlier [3].

Markov *et al.* [14] also noted that plasticizers affect the vulcanization enthalpy. Aliphatic plasticizers reduce the enthalpy more. Because TOR is a plasticizer, it reduces the enthalpy value of TOR-filled SBR vulcanizates (Tables IV).

TGA study was carried out to determine whether or not the polymers (SBR and TOR) when blended together, have enhanced thermal stability, because it may influence the cured properties of filled vulcanizates. In a nitrogen atmosphere, Fig. 10, SBR blended with 10 and 20 parts TOR shows no increase of  $T_{\text{max}}$  (the temperature at which maximum degradation takes place) of pure SBR. Even in an oxygen atmosphere (Fig. 11),  $T_{\text{max}}$  of SBR remains the same for

TABLE V Physical properties after ageing (at 105°C for 3 days)

Compound	Modulus (100%) (MPa)	Tensile strength (MPa)	Elongation at break (%)	Fracture energy ( $10^{-5} \text{ J m}^{-2}$ )	Tearing energy (J)
1	6.9 (191) <sup>a</sup>	14.2 (68) <sup>a</sup>	160 (52) <sup>a</sup>	2.3	0.8 (17) <sup>a</sup>
2	6.5 (191)	12.5 (64)	152 (49)	2.0	0.9 (20)
3	5.7 (190)	13.5 (78)	178 (59)	2.6	0.9 (23)
4	4.9 (169)	10.8 (60)	167 (46)	1.9	1.6 (34)
5	5.0 (161)	14.8 (84)	200 (68)	3.0	0.9 (16)
6	4.9 (169)	13.4 (69)	190 (57)	2.7	0.7 (13)
7	4.5 (150)	14.0 (76)	207 (63)	2.9	0.6 (13)
8	4.2 (145)	14.0 (80)	227 (63)	3.4	0.8 (15)
9	3.0 (125)	19.6 (96)	353 (87)	7.2	1.2 (18)
10	2.7 (123)	19.9 (95)	389 (90)	8.1	1.4 (19)
11	2.9 (121)	18.9 (92)	380 (86)	7.7	1.7 (23)
12	3.1 (119)	18.8 (101)	409 (87)	8.5	0.9 (13)

<sup>a</sup> Values in parentheses are percentage retention.

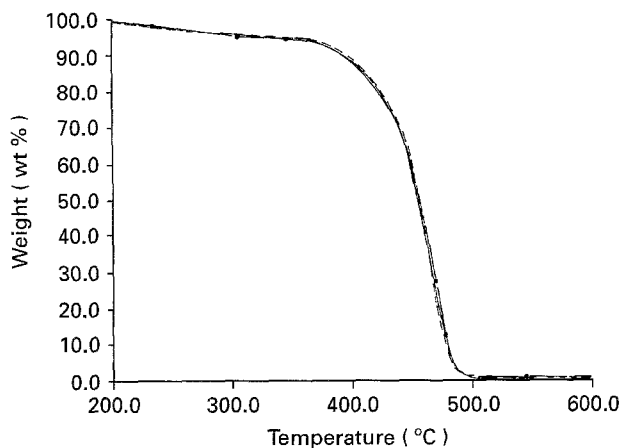


Figure 10 TGA curve of polymer blends in a nitrogen atmosphere: (—) SBR, (---) SBR + 10 parts TOR, (●) SBR + 20 parts TOR.

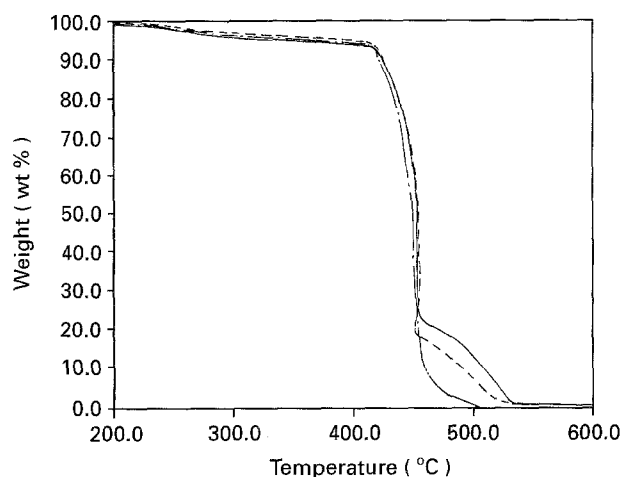


Figure 11 TGA curve of polymer blends in an oxygen atmosphere: (—) SBR (gum), (---) SBR + 10 parts TOR, (---) SBR + 20 parts TOR.

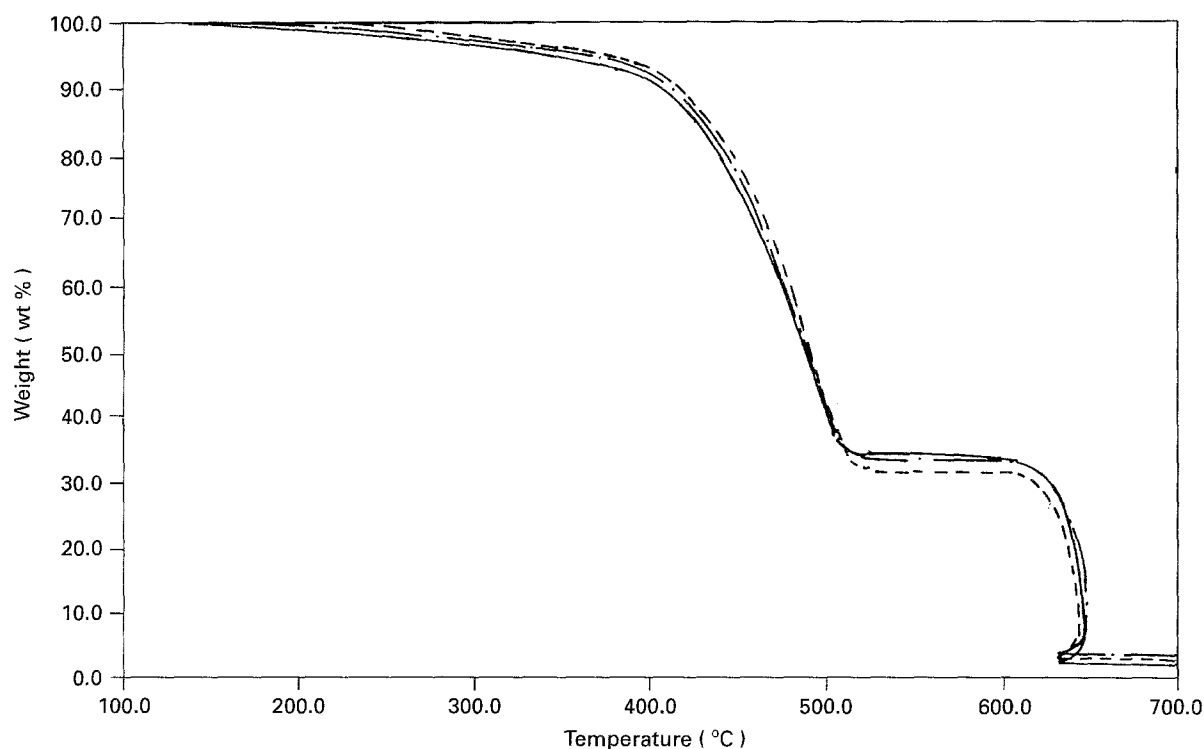


Figure 12 TGA curve of filled SBR vulcanizates. (—) SBR, (---) SBR + 10 parts TOR, (---) SBR + 20 parts TOR.

SBR/TOR blends. This reveals that in an inert as well as in an oxygen atmosphere, TOR does not influence the thermal stability of SBR in uncured gum blends.  $T_{max}$  of SBR also remains unaffected for the corresponding filled compounds (Fig. 12) in TGA.

Table IV shows that the onset temperature,  $T_o$ , of curing increases with increased dosage of TOR in the CV system because of the slow curing behaviour of TOR-filled compounds [7, 8]. However, the change in the onset temperature,  $T_o$ , of TOR-filled compounds in the SEV and EV systems is minimum.  $T_o$  is the first noticeable departure from the baseline and  $T_p$ , the peak temperature, is the maximum departure from the base line [15]

#### 4. Conclusions

1. At high temperature (120°C), modulus and tensile strength of the vulcanizate with 10 parts TOR in the CV system are equal to the average modulus and tensile strength of vulcanizates without TOR in the SEV and EV systems. This is also seen in the properties at room temperature. Thus the CV system can be modified by incorporation of 10 parts TOR to optimize the original properties of CV and retain the properties of the EV system.

2. Improvement in properties in the CV system by TOR has been found to be due to *cis-cis* interaction as well as change in the cross-link structure, as explained from FT-IR/NMR/ thermal studies.

3. Under aerobic ageing, TOR cannot change the usual trend of the curing system with respect to property retention, e.g. EV > SEV > CV.



## References

1. W. HOFMANN, "Vulcanization and vulcanizing agents" (Maclaren, London, 1967).
2. D. J. ELLIOTT, *NR Technol.* **2** (1971) 1.
3. P. P. CHATTARAJ, A. K. KALIDAHA, R. MUKHOPADHYAY and D. K. TRIPATHY, *J. Elastomers Plast.*, in press.
4. B. ELLIS and G. N. WELDING, "Techniques of polymer science" (Society of the Chemical Industry, London, 1964).
5. HÜLS, "An unusual rubber with versatile possibilities", 2nd Edn, October 1991.
6. A. WHELAN and K. S. LEE, "Developments in rubber technology-1" (Applied Science, London, 1979).
7. P. P. CHATTARAJ, R. MUKHOPADHYAY and D. K. TRIPATHY, *J. Elastomers Plast.* **26** (1994) 74.
8. P. P. CHATTARAJ, D. N. TIWARI, R. MUKHOPADHYAY and D. K. TRIPATHY, *Kaustschuk Gummi Kunststoffe* **7** (1993) 534.
9. R. B. PRIME, *Thermochem. Acta* **26** (1978) 165.
10. D. GROSS, *Rubb. Chem. Technol.* **48** (1974) 289.
11. J. SCHAEFER, *ibid.* **46** (1972) 359.
12. I. L. FINAR, "Organic chemistry", Vol. 1 (English Language Book Society/Longman, Harlow, 1973).
13. D. W. BRAZIER, *Rubb. Chem. Technol.* **53** (1980) 437.
14. V. V. MARKOV, N. P. PRIVALIKHINA and N. A. ZANEMONETS, *J. Polym. Sci. Polym. Symp.* **42** (1973) 633.
15. D. W. BRAZIER and G. H. NICKEL, *Rubb. Chem. Technol.* **48** (1975) 26.

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