

Thermoplastic elastomer ·  
Thermal degradation · Nitrile rubber ·  
ABS terpolymer · Solvent swelling ·  
Diffusion coefficient · Oil resistance

Thermoplastic elastomeric blends of nitrile rubber (NBR)/poly(styrene-co-acrylonitrile) (SAN) and NBR/scrap computer plastics (SCP) based on acrylonitrile-butadiene-styrene terpolymer (ABS) were prepared. Thermoplastic elastomeric blends of NBR/SAN containing various amounts of a model waste nitrile rubber powder (w-NBR) were also prepared. Thermogravimetric analysis of the above blends was performed in a nitrogen atmosphere. Both Friedman and Flynn-Wall-Ozawa methods were used for the evaluation of activation energies of thermal degradation of these blends. The dynamically vulcanised blends exhibit higher amount of activation energies for thermal degradation than the unvulcanised ones. Swelling studies were performed in various solvents having different solubility parameter values and maximum swelling was found to occur in a solvent having a solubility parameter that was closer to that of the blend components, i.e., around  $20 \text{ MPa}^{1/2}$ . Dynamically vulcanised blends show excellent resistance to IRM #903 oil as well as four chosen solvents possessing different solubility parameters ( $\delta$ ).

### Thermischer Abbau und Quellung von thermoplastischen Vulkanisaten aus NBR und SAN sowie NBR und thermoplastischen Computerabfällen

Thermoplastische Elastomere ·  
thermischer Abbau · Nitrilkautschuk ·  
ABS Terpolymer · Quellung ·  
Diffusionskoeffizient · Ölbeständigkeit

Thermoplastische Elastomerverschnitte bestehend aus NBR/Poly(styrol-co-acrylnitril) (SAN) und NBR/thermoplastische Computerabfälle (SCP), basierend auf ABS, wurden hergestellt. Thermoplastische Elastomerblends NBR/SAN mit einem variablen Anteil an NBR-Altgummigranulat wurden ebenfalls hergestellt.

Die thermogravimetrische Analyse der angeführten Verschnitte wurde in Stickstoffatmosphäre durchgeführt. Sowohl die Friedman als auch die Flynn-Wall-Ozawa Methode wurde zur Bestimmung der Aktivierungsenergie des thermischen Abbaus eingesetzt.

Figures and Tables:  
By a kind approval of the authors

# Thermal Degradation and Swelling of Thermoplastic Vulcanizates from NBR/SAN and NBR/Scrap Computer Plastics Blends

Oil-resistance character of nitrile rubber (NBR) makes it useful in a number of applications such as oil seals, hoses, print roller covers, etc [1]. Poly(styrene-co-acrylonitrile) (SAN) is a thermoplastic with high transparency, excellent gloss, high mechanical strength, and good chemical resistance [2]. Acrylonitrile-butadiene-styrene terpolymer (ABS) is also oil-resistant due to the presence of polar nitrile groups. Thermoplastic elastomers were developed from dynamically vulcanised blends of NBR/SAN, NBR/waste NBR/SAN and NBR/ABS-based scrap computer plastics (SCP), and their properties were reported earlier by the authors [3-6]. It was found that mechanical properties of these blends were improved by dynamic crosslinking with a sulphur-accelerator system. Dynamic vulcanisation is the crosslinking of one polymer during its molten-state mixing with another polymer or with other polymers [7]. The aforementioned dynamically vulcanised blends exhibit a phase-separated microstructure in which dynamically crosslinked NBR particles are dispersed in SAN and ABS matrices respectively, in the appropriate blends [3-6]. Thermal degradation of NBR and its vulcanizates was studied by Sircar and Lamond, and they observed a single degradation step for NBR [8]. Rajeev *et al.* found out that the thermal stability of NBR-based composites was better than that of virgin NBR [9]. Thermal degradation of ABS using thermogravimetry (TGA)/Fourier transform infrared (FTIR) spectroscopy was reported by Suzuki and Wilkie [10]. Thermal degradation of ABS under different gaseous atmospheres was reported by Yang [11]. Though thermal degradation of many single poly-

mers has been extensively studied, degradation behaviour of many polymer blends is yet to be studied in detail [12-15]. One of the main objectives of the present work was the study of thermal degradation behaviours of NBR/SAN, NBR/waste NBR/SAN and NBR/SCP blends, whose mechanical properties and morphology were reported earlier by the authors [3-6].

The performance of polymers, in general, can be improved by blending them with various other suitable polymers [16-19]. Swelling resistance of rubbers can be improved in many ways including blending and crosslinking. For example, blending of natural rubber with NBR improves its swelling resistance to various aromatic solvents [16]. Dynamic vulcanisation is a proven method for improving the swelling resistance of rubber/plastic and rubber/rubber blends [7]. Jha and Bhowmick investigated the influence of dynamic vulcanisation on

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the transport of various solvents in nylon-6/acrylate rubber (ACM) blends [20]. They reported that dynamic vulcanisation improved the swelling resistance of those blends. Kader and Bhowmick studied the thermal degradation and swelling behaviour of fluororubber/ACM blends [21]. Since NBR and its blends are used in oil-resistant applications, study of their swelling characteristics is necessary, while recommending their use in such applications. Hence, we studied the swelling behaviour of our NBR/SAN, NBR/waste NBR/SAN and NBR/SCP blends in various solvents and report the results here along with that of thermogravimetric analysis.

## Experimental

### Materials

The details of materials used in this study are given in Table 1.

### Preparation of waste nitrile rubber vulcanizate powder

A model waste nitrile rubber vulcanizate powder (designated as w-NBR) was prepared in the laboratory following the procedure that was described in one of our earlier publications [6]. The following standard oil seal formulation was used to prepare the precursor nitrile rubber vulcanizate sheet: NBR, 100; carbon black N 770, 50; DOP (dioctyl phthalate), 5; zinc oxide, 5; stearic acid, 1; IPPD (N-isopropyl p-phenylene diamine), 1; MBTS (mercapto benzothiazole), 1.5; TMTM (tetramethyl thiuram monosulfide), 0.1; sulphur, 1.5; the figures are in phr (that is, parts per hundred parts of rubber, by weight).

### Preparation of Blends

Blends were prepared by mixing NBR and the thermoplastic (namely, SAN or SCP) in an internal mixer (Brabender Plasticorder PLE 330, Germany) at 180 °C and 60 rpm with cam-type rotors. After mixing, the blends were removed in hot condition and sheeted out in a water-cooled two-roll mill (Schwabenthan, Germany) at 25 °C. 70/30 (w/w ratio) NBR/SAN blend along with its dynamically vulcanised counterpart was prepared. Dynamically vulcanised 70/30 NBR/SAN blends in which the virgin NBR was replaced partially with 20%, 30% and 45% of the rubber present in w-NBR, were also prepared. These dynamically vulcanised compositions possess thermoplastic elastomeric character [3-6]. Following compositions of NBR/SCP blends were prepared: 60/40, 70/30 and 80/20.

The dynamically vulcanised counterparts of the 60/40, 70/30, and 80/20 NBR/SCP blends were also prepared, and these were shown to possess thermoplastic elastomeric character [4].

For dynamic vulcanisation, a sulphur based cure system of the following composition was used: Zinc oxide, 3; stearic acid, 2; mercapto benzothiazole (MBT), 1; tetramethyl thiuram disulfide (TMTD), 0.5; sulphur, 0.75; the amounts are given in parts per hundred parts of NBR (phr). A rubber-curative masterbatch was prepared first, which was then

mixed with molten thermoplastic (Table 2). Sheeted out blends were compression moulded between polyester sheets at 210 °C in a hydraulic press (Moore Press, Birmingham, England) using a frame and plate mould at a pressure of 5 MPa for 2 minutes. Then, the platens were cooled under pressure.

### Thermogravimetric analysis of blends

Dynamic thermogravimetric analysis was done using TA Instruments (Luken's Drive, New Castle, DE, USA) TGA model Q 50. Samples ( $8 \pm 0.2$  mg) were heated from ambient

## 1 Details of Materials

Material	Supplier/Manufacturer
NBR Grade: N553NS ACN content: 34 % Mooney Viscosity @ $ML_{1+4}$ at 100 °C: 46 $M_v$ : $2.39 \times 10^5$ (viscometry)	Apar Industries Ltd. Mumbai, India.
SAN Grade: Lustron Sparkle ACN content: 27 % $M_w$ : $1.65 \times 10^5$ (GPC) MFI: 1.91g/10 minutes at 200 °C under a load of 2.16 kg.	Monsanto, St. Louis, MO, USA
Scrap Computer Plastics from computer cabinet, and printer	Obtained from Computer Science Centre, Indian Institute of Technology, Kharagpur.
Zinc Oxide <sup>a</sup>	E-Merck, Mumbai, India
Stearic acid <sup>a</sup>	Local supplier
IPPD <sup>a,b</sup>	ICI Ltd, Rishra, India
N 770 black	Philips Carbon Black Ltd., Durgapur, India
Dioctyl phthalate	Ranbaxy Ltd., Mumbai, India
MBT <sup>a,c</sup>	ICI Ltd., Rishra, India
MBTS <sup>a,d</sup>	ICI Ltd., Rishra, India
TMTM <sup>a,e</sup>	ICI Ltd., Rishra, India
TMTD <sup>a,f</sup>	ICI Ltd., Rishra, India
Sulphur	Qualigens, Mumbai, India

<sup>a</sup> rubber grade

<sup>b</sup> N, N'-isopropyl parphenylene diamine (antioxidant)

<sup>c</sup> Mercapto benzothiazole (accelerator)

<sup>d</sup> Mercapto benzothiazole disulfide (accelerator)

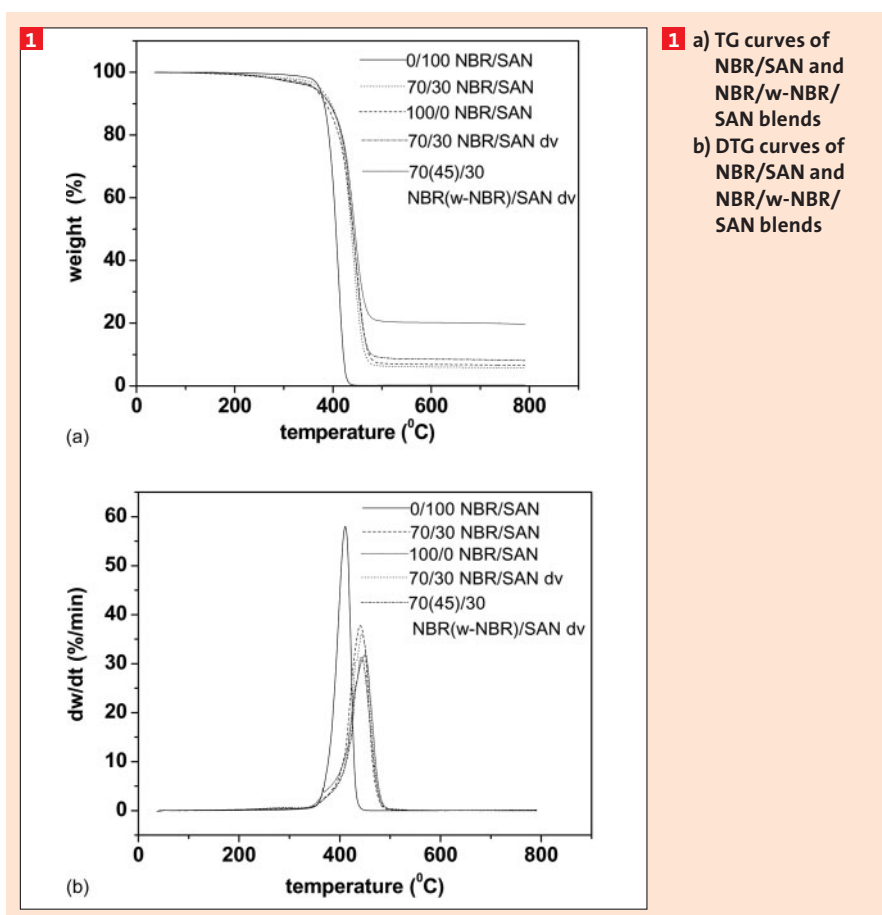
<sup>e</sup> Tetramethyl thiuram monosulfide (accelerator)

<sup>f</sup> Tetramethyl thiuram disulfide (accelerator)

## 2 Procedure for the preparation of blends

Description	Mixing equipment and temperature	Mixing time and rpm
(i) NBR charged	Brabender Plasticorder at 70 °C	1 minute at 45 rpm
(ii) Sulphur, zinc oxide, stearic acid (and w-NBR) <sup>a</sup> added	Brabender Plasticorder at 70 °C	2 minutes at 60 rpm
(iii) Accelerators added.	Two roll mill at 25 °C	2 minutes
(iii) Rubber compound sheeted out and cut to strips	Two roll mill at 25 °C	2 minutes
(iv) SAN/SCP softened	Brabender Plasticorder at 180 °C	2 minutes at 30 rpm
(v) Strips of rubber masterbatch added.	Brabender Plasticorder at 180 °C	4 minutes at 60 rpm.
(vi) Blend sheeted out.	Two roll mill at 25 °C	-----

<sup>a</sup> for the preparation of thermoplastic elastomeric 70/30 NBR/SAN blends containing w-NBR.



1 a) TG curves of NBR/SAN and NBR/w-NBR/SAN blends  
b) DTG curves of NBR/SAN and NBR/w-NBR/SAN blends

temperature to 800 °C in the furnace of the instrument under a dynamic nitrogen atmosphere flowing at 60 mL/min. In order to study kinetics of decomposition of blends, experiments were performed at four heating rates of 5, 10, 15 and 20 °C/min and data of weight loss versus temperature were recorded online in TA instruments' Q series Explorer software. Analysis of thermogravimetric (TG) and derivative (DTG) curves was done using TA Instruments Universal Analysis 2000 software version 3.3B. In the present study, onset temperature of degra-

dation ( $T_0$ ), weight loss at major degradation steps, temperatures corresponding to the maximum value in the derivative thermograms ( $T_{max}$ ) and weight of residue at 800 °C were recorded.

### Determination of activation energy of decomposition

(a) *Friedman method* Activation energy of decomposition of the blends was calculated by using Friedman method [22]. The following equation was used to calculate the activation energy of decomposition:

$$\ln(d\alpha/dt) = \ln Z + n \ln(1-\alpha) - E/RT \quad (1)$$

Where,  $\alpha$  is weight loss of the polymer undergoing degradation at time  $t$ ,  $R$  is the universal gas constant and  $T$  is absolute temperature. A linear plot of  $\ln d\alpha/dt$  as a function of  $1/T$  provides a slope that is equal to  $E/R$ .

(b) *Flynn-Wall-Ozawa method* Activation energy of decomposition was also determined by using TA Instruments' Specialty Library software version 1.4. The analysis was based on ASTM method E 1641, which follows the well known Flynn-Wall-Ozawa isoconversional method [23]. This method uses Doyle's approximation of temperature integral. This method is based on the following equation:

$$\log \beta = \log \frac{AE}{Rg(\alpha)} - 2.315 - \frac{0.457E}{RT} \quad (2)$$

Where,  $\beta$  is heating rate in °C/min,  $A$ , the pre-exponential factor,  $E$ , activation energy of decomposition in kJ/mole,  $R$ , the universal gas constant,  $\alpha$ , degree of conversion,  $T$ , absolute temperature to reach the conversion and

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} \quad (3)$$

is the integral conversion function. The procedure involved plotting logarithm of  $\beta$  (heating rate) versus  $(1/T)$  for fixed values of conversion,  $\alpha$ . For a constant  $\alpha$ , the plot of  $\log \beta$  versus  $(1/T)$  obtained from the thermograms recorded at several heating rates, should be a straight line whose slope allows evaluation of activation energy,  $E$ . To apply this isoconversional method, heating rates of 5, 10, 15 and 20 °C/min were chosen, as were conversions of 2.5, 5, 10, 15, 20, 30, 40, 50, 60 and 80% which would give  $\alpha$  values 0.025, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 respectively. Inputs for the automatic calculation of activation energy of decomposition using the software were percent conversion and temperature limit covering the major degradation steps in thermograms for each heating rate.

### Swelling studies

Swelling studies were carried in toluene ( $\delta = 18.2$ ), methyl ethyl ketone ( $\delta = 19.0$ ), 1,4-dioxan ( $\delta = 20.4$ ), dimethyl formamide ( $\delta = 24.7$ ). The values in parentheses indicate solubility parameter ' $\delta$ ' in  $\text{MPa}^{1/2}$ . For oil-resistance testing, IRM oil #903 was used and the tests were carried out at 25° and 100 °C. Circular test specimens of

### 3 Results of TG studies of NBR/SAN and NBR/w-NBR/SAN blends

Composition of Blends	$T_0$ (°C)	Wt. loss in the major step of degradation (%)	$T_{max}$ (°C)	dw/dt (%/min)	Char residue at 800 °C (%)	E (kJmol <sup>-1</sup> )
<b>NBR/SAN</b>						
0/100	367	96	411	58.0	0.3	284(281)
70/30	374	87	440	37.8	5.8	152(153)
70/30 dv	370	84	443	36.3	8.1	211(211)
100/0	358	88	451	31.6	6.5	145(143)
<b>NBR(w-NBR)/SAN</b>						
70(20)/30 dv	366	80	440	35.5	12.8	241(243)
70(30)/30 dv	366	77	439	33.1	15.9	266(264)
70(45)/30 dv	369	73	443	31.3	19.6	278(282)

Note: Activation energy values were calculated by Friedman and Flynn-Wall-Ozawa methods; the values calculated by the latter are shown in parentheses.

20 mm (approx.) radius were punched out from moulded sheets. These specimens were weighed accurately by using an electronic balance before immersing them into solvents kept at 25 °C. Swelling studies were also performed at 40 °C and 50 °C. The specimens were weighed at regular time intervals after wiping out the solvents sticking to the surface with a soft tissue paper. Also, thickness of the swollen samples was measured simultaneously. Volume swelling in percentage was calculated by using the following equation: [ 24]

$$q-1 = \left\{ \left( \frac{w_2}{w_1} \right) - 1 \right\} \cdot \rho_c / \rho_f \quad (4)$$

Where,  $q$  = ratio of swollen volume to original unswollen volume  
 $q-1$  = % of volume swell/100  
 $w_2$  = swollen weight  
 $w_1$  = unswollen weight  
 $\rho_c$  = density of the composition  
 $\rho_f$  = density of the fluid

Diffusion coefficients (D) of solvents were calculated by using the simplified expression given below [21].

$$M_t / M_\infty = \frac{4}{l} \sqrt{\frac{Dt}{\pi}} \quad (5)$$

Where,  $M_t$  and  $M_\infty$  are the weight fraction of the solvent absorbed at time 't' and at equilibrium swelling respectively and 'l' is initial sample thickness. Thus, D can be calculated from the initial slope of the linear portion of a sorption curve obtained by plotting  $M_t / M_\infty$  versus  $(t^{1/2}/l)$ .

Activation energy of diffusion was calculated from its temperature dependence expressed by an Arrhenius type equation [21]

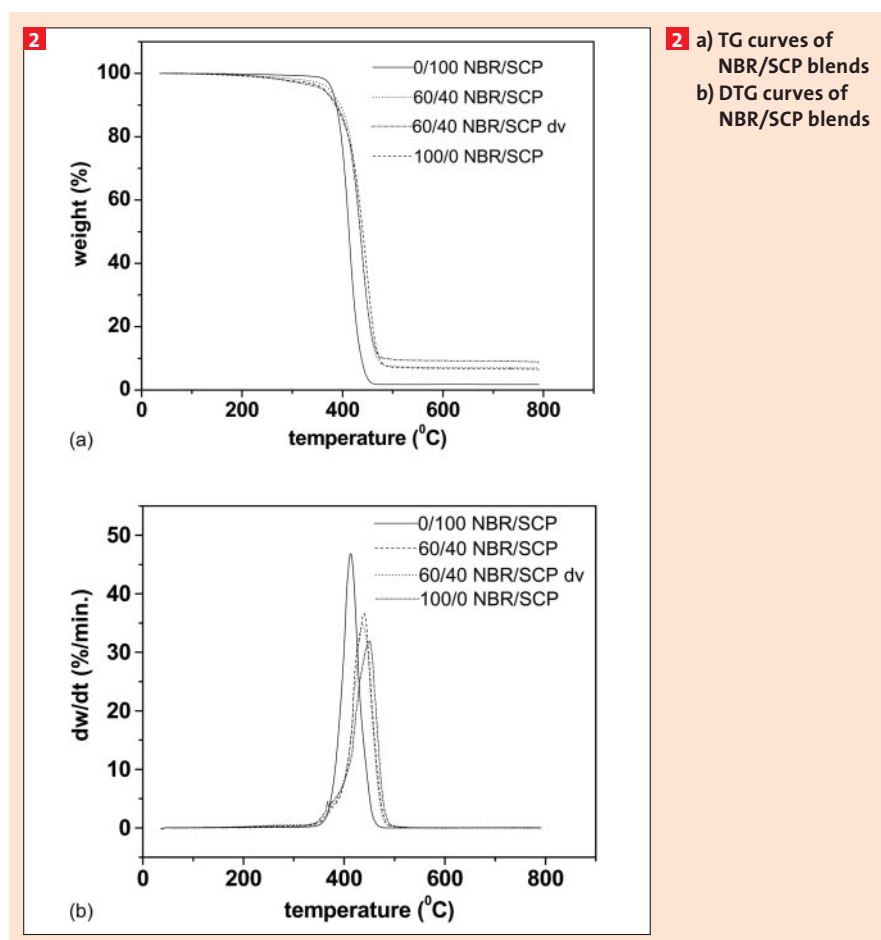
$$\log D = \log D_0 - (E_d / 2.303RT) \quad (6)$$

Where,  $D_0$  is a constant,  $E_d$  is activation energy of diffusion, R is the universal gas constant and T is absolute temperature. The value of  $E_d$  can be estimated from a plot of  $\log D$  versus  $1/T$ .

## Results and discussion

### Thermogravimetry (TG) of Blends

(a) *NBR/SAN blends* TG and DTG curves of neat SAN, NBR, 70/30 NBR/SAN blend (both unvulcanised and dynamically vulcanised) and the dynamically vulcanised 70/30 NBR/SAN blend containing 45 % of w-NBR are shown in Figures 1(a) and (b), respectively. The important parameters like  $T_0$ ,  $T_{max}$ , and activation energy of degradation, which were obtained from the thermograms re-



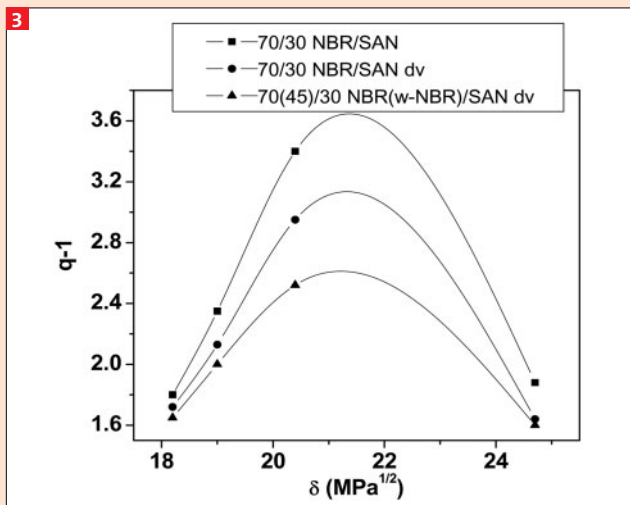
corded in  $N_2$  at a heating rate of 20 °C/min, are given in Table 3.

The thermograms of all samples show a single degradation step. The DTG curve of SAN shows a sharper peak than the others, indicating that its rate of degradation is faster than that of NBR and the other blends. The DTG curves of neat NBR and the other blends (70/30 NBR/SAN blend, dynamically vulcanised 70/30 NBR/SAN blend and dynamically vulcanised 70/30 NBR/SAN blend containing 45 % w-NBR) exhibit broader peaks. Suzuki and Wilkie observed that SAN degrades in a single step [10]. Grassie and Bain found out that the degradation mechanism of SAN is similar to that of polystyrene and moreover, it occurs by end-chain and random scission and produces styrene monomer, oligomers, benzene, toluene and acrylonitrile [25-27].

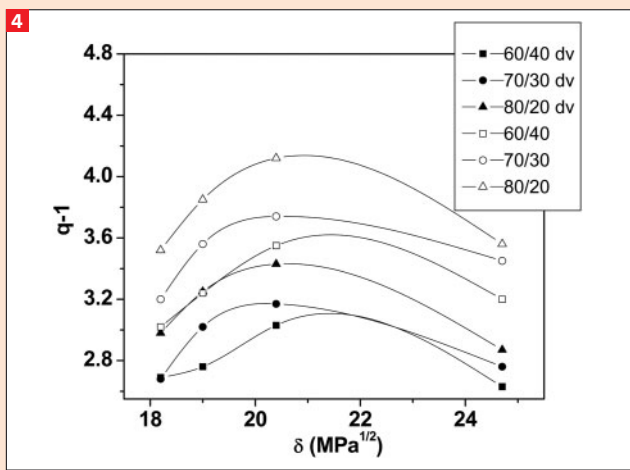
The onset temperature of degradation ( $T_0$ ) of SAN is higher than that of NBR. 70/30 NBR/SAN blends (both unvulcanised and dynamically vulcanised) exhibit slightly higher  $T_0$  values when compared to both NBR and SAN. The onset temperatures of degradation of the dynamically vulcanised 70/30 NBR/SAN blends containing 20 %,

30 % and 45 % of w-NBR show marginal variations from that of SAN. From these results, it is obvious that the thermal stability of NBR is slightly improved by blending it with SAN. This is due to the grafting of SAN onto NBR molecules during blending, which makes the liberation of butadiene from NBR molecules less facile and hence degradation of the blend starts at a slightly higher temperature [10].

The peak maximum temperature ( $T_{max}$  or the temperature corresponding to maximum rate of decomposition) of SAN is lower than that of NBR and the blends. The rate of degradation ( $dw/dt$ ) at  $T_{max}$  is the highest for SAN. SAN produces a very small amount of residue of degradation at 800 °C, while NBR produces more char residue than SAN due mainly to cyclisation of the nitrile component of NBR [8]. The 70/30 NBR/SAN blends (both unvulcanised and dynamically vulcanised) and the dynamically vulcanised 70/30 NBR/SAN blends containing 20 %, 30 % and 45 % of w-NBR produce a considerable amount of char residue. All these dynamically vulcanised blends give rise to higher amount of char residue than the unvulcanised blend, because of the formation



**3** Swelling index of NBR/SAN and NBR/w-NBR/SAN blends versus solubility parameter of solvents



**4** Swelling index of NBR/SCP blends versus solubility parameter of solvents

of stable products during dynamic vulcanisation. The char residue for the thermoplastic elastomeric NBR/SAN blend containing w-NBR is higher than that of the control and it increases with the amount of w-NBR. This is due to the fact that w-NBR contains carbon black as well as unreacted curatives (mainly ZnO) along with NBR. The activation energies of degradation ( $E$ ) (calculated by Friedman and Flynn-Wall-

Ozawa methods) of neat NBR, SAN along with those of their blends are given in Table 3. The activation energy for the degradation of SAN is higher than that of NBR. The 70/30 NBR/SAN blend has an intermediate value of activation energy; meanwhile, its dynamically vulcanised counterpart has higher activation energy. The activation energies of degradation of the thermoplastic elastomeric 70/30 NBR/SAN

blends containing w-NBR are directly proportional to the wt% of w-NBR. This might be due to the presence of carbon black and unreacted curatives (mainly ZnO) in w-NBR. (b) NBR/SCP blends TG and DTG curves of some representative NBR/SCP blends at a heating rate of 20 °C/min. in nitrogen are shown in Figures 2 (a) and (b), respectively, and the different parameters obtained from the thermograms are given in Table 4. The thermograms of NBR/SCP blends (60/40, 70/30 and 80/20 compositions and their dynamically vulcanised counterparts) exhibit a single degradation step. The onset temperature of degradation ( $T_0$ ) of SCP is higher than that of neat NBR and NBR/SCP blends.  $T_0$  of NBR is increased by blending it with SCP. DTG curve of neat SCP shows a sharp peak indicating faster rate of decomposition than NBR and NBR/SCP blends (both unvulcanized and dynamically vulcanised). The degradation mechanism of ABS (which is the major constituent of SCP used in this study) is similar to that of SAN [10]. Styrene, benzene, toluene, butadiene and acrylonitrile are formed during the degradation of ABS in a nitrogen atmosphere. The amount of char residue produced by SCP is higher than that produced by SAN. This is due to the presence of butadiene part in ABS (which in turn is present in SCP) [10].

$T_{max}$  of SCP is lower than those of the NBR/SCP blends and NBR. Weight loss in the major step of degradation is less for the dynamically vulcanised NBR/SCP blends than their unvulcanised counterparts. Activation energy values of degradation ( $E$ ) (calculated by Friedman and Flynn-Wall-Ozawa methods) of the NBR/SCP blends are given in Table 4. The  $E$  of SCP is higher than those of NBR and the NBR/SCP blends. The  $E$  values of these blends are directly proportional to the wt% of SCP in these blends. The dynamically vulcanised blends have higher  $E$  than the unvulcanised ones. This might be due to stable morphology and fineness of the dispersed NBR particles in the dynamically vulcanised blends.

The  $E$  values calculated by Friedman method for the NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends (Tables 3 and 4 respectively) are well in agreement with those calculated by Flynn-Wall-Ozawa method.

#### Swelling behaviour of blends in various solvents at 25 °C

(a) Swelling index of blends Figure 3 shows the plots of swelling index ( $q-1$ ) of some representative NBR/SAN and NBR/w-NBR/SAN blends in various solvents of different solubility parameters at 25 °C. Maximum swell-

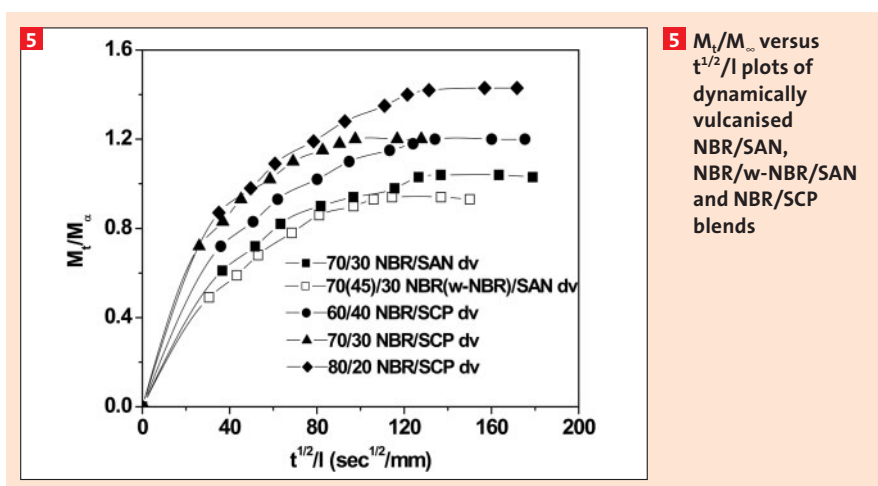
#### 4 Results of TG studies of NBR/SCP blends

Composition of Blends	$T_0$ (°C)	Wt. loss in the major step of degradation (%)	$T_{max}$ (°C)	dw/dt (%/min)	Char residue at 800 °C (%)	$E$ (kJmol <sup>-1</sup> )
NBR/SCP						
0/100	376	94	413	46.9	1.8	254(259)
60/40	368	88	440	36.7	7.0	204(205)
70/30	373	88	441	36.5	6.3	196(199)
80/20	359	88	443	32.8	6.2	183(186)
60/40 dv	374	83	437	34.7	8.9	226(233)
70/30 dv	364	84	441	33.7	8.1	212(215)
80/20 dv	368	82	443	32.5	9.3	194(197)
100/0	358	88	451	31.6	6.5	145(143)

Note: Activation energy values were calculated by Friedman and Flynn-Wall-Ozawa methods; the values calculated by the latter are shown in parentheses.

ing occurs in 1,4-dioxan ( $\delta = 20.4$ ). The blend components NBR and SAN have solubility parameter values very close to that of 1,4-dioxan ( $\delta_{\text{NBR}} = 19.9 \text{ MPa}^{1/2}$  and  $\delta_{\text{SAN}} = 20.3 \text{ MPa}^{1/2}$ ) and hence these blends exhibit maximum swelling index values in 1,4-dioxan. The swelling index of the unvulcanized 70/30 NBR/SAN blend is the highest followed by its dynamically vulcanised counterpart and the dynamically vulcanised 70/30 NBR/SAN blend containing 45% of w-NBR. This is due to the fact that crosslinks present in the rubber phase of the dynamically vulcanised blends restrict the transport of solvent molecules into the blend. w-NBR contains carbon black and hence the swelling index of the dynamically vulcanised 70/30 NBR/SAN blend containing w-NBR is the lowest among these three blends.

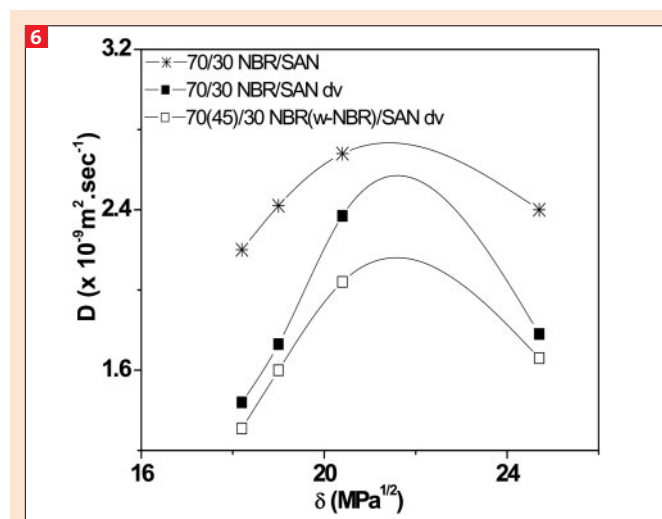
Figure 4 shows plots of swelling index ( $q-1$ ) of the 60/40, 70/30 and 80/20 NBR/SCP blends along with their dynamically vulcanised counterparts in various solvents of different solubility parameters at 25 °C. The swelling index values increase as a function of wt% of NBR. This is due to the fact that the harder ABS phase undergoes minimum swelling and hence swelling occurs to the maximum extent in the NBR phase. Swelling index values of the dynamically vulcanised blends are less than those of the unvulcanised ones. This is due to the presence of crosslinks in the NBR phase which restricts the transport of the solvent molecules. The blend components (NBR and ABS) have solubility parameter values that are close to that of 1,4-dioxan ( $\delta_{\text{NBR}} = 19.9 \text{ MPa}^{1/2}$  and  $\delta_{\text{ABS}} = 22.7 \text{ MPa}^{1/2}$ ) and hence swelling index is maximum in this solvent.



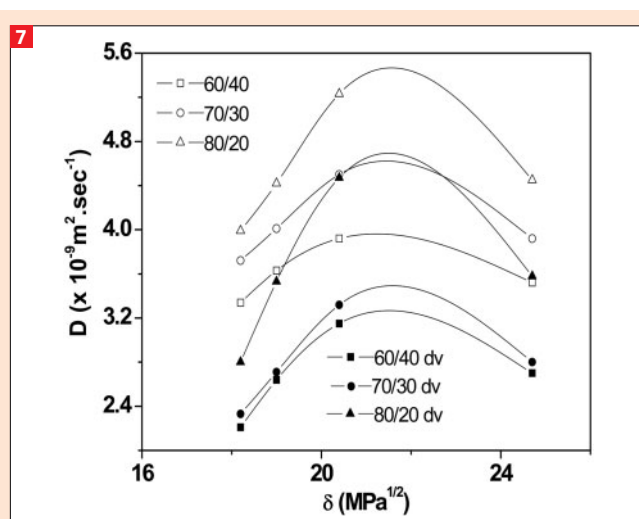
(b) Diffusion coefficients and activation energy of diffusion of solvents in blends Figure 5 shows the  $M_t/M_\infty$  versus  $\sqrt{t}/l$  plots for some representative dynamically vulcanised NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends in 1, 4-dioxan at 25 °C. Diffusion coefficients ( $D$ ) of 1,4-dioxan in these blends were calculated from the slope of the initial linear portion of the plots by using equation 5. Similar plots were obtained for all the blends in the other solvents (not shown here). The diffusion coefficients of all these blends at 40° and 50 °C were also determined in a similar manner.

The diffusion coefficients ( $D$ ) were plotted as a function of the solubility parameter of the solvents. Figures 6 and 7 show the plots of  $D$  versus solubility parameter for the NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends. Diffusion coefficient of solvents is high when the solubility parameters of blend components and solvent are closer.

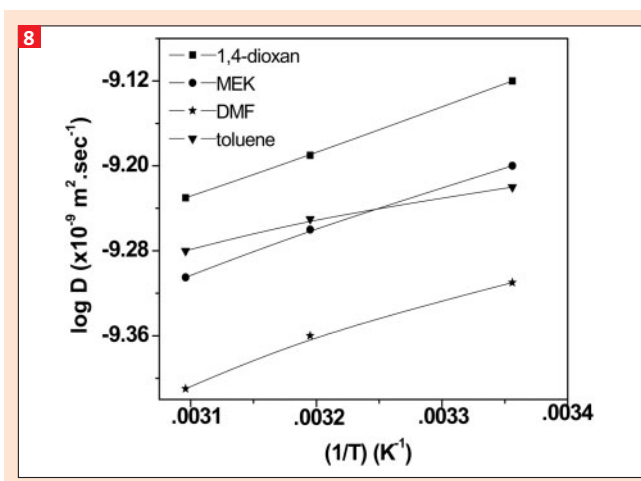
Diffusion coefficients of solvents are higher in the unvulcanised 70/30 NBR/SAN blend when compared to those in its dynamically vulcanised counterpart. This can be explained on the basis of their morphology as well as dynamic vulcanisation. The unvulcanised blend has a co-continuous morphology, whereas the dynamically vulcanised one has SAN as the continuous matrix and NBR as the dispersed phase [3]. The SAN matrix as well as crosslinks in the dispersed NBR phase restrict diffusion of the solvent molecules and hence the diffusion coefficient in the dynamically vulcanised blend is less for the solvents. The diffusion coefficients of solvents in the dynamically vulcanised 70/30 NBR/SAN blend containing w-NBR are much lower than those in the dynamically vulcanised 70/30 NBR/SAN blend. This is due to the presence of carbon black filler in the w-NBR which offers additional restriction to diffusion of solvent molecules.



6 Diffusion coefficients versus solubility parameter of solvents in NBR/SAN and NBR/w-NBR/SAN blends



7 Diffusion coefficients versus solubility parameter of solvents in unvulcanised and dynamically vulcanised NBR/SCP blends



**8** Arrhenius plots used for evaluation of the activation energy of diffusion of various solvents in the dynamically vulcanised 70/30 NBR/SAN blend

higher value of activation energy means a higher resistance to diffusion.

Activation energies of diffusion of solvents in the 70/30 NBR/SAN blend, its dynamically vulcanised counterpart and the dynamically vulcanised 70/30 NBR/SAN blend containing 45% of w-NBR are in the following order: 70/30 NBR/SAN blend > dynamically vulcanised 70/30 NBR/SAN blend > dynamically vulcanised 70/30 NBR/SAN blend containing 45% of w-NBR. This is due to the fact that the dynamically vulcanised 70/30 NBR/SAN blend, which contains 45% of w-NBR, contains carbon black in addition to crosslinks. The activation energy of diffusion of solvents in the NBR/SCP blends decrease as a function of NBR content of these blends; meanwhile, activation energy values are higher for the dynamically vulcanised blends. This is because of the increased restriction to diffusion of solvent molecules by the thermoplastic phase and crosslinks that are present in the NBR phase of the dynamically vulcanised NBR/SCP blends.

(d) *Swelling in IRM #903 oil* The % volume swelling of some representative NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends were studied at 25° and 100 °C in IRM #903 oil and the values are shown in Table 6. The % volume swelling of 70/30 NBR/SAN blend, its dynamically vulcanised counterpart and the dynamically vulcanised 70/30 NBR/SAN blend containing 45% of w-NBR at both temperatures are in the following order: 70/30 NBR/SAN blend > dynamically vulcanised 70/30 NBR/SAN blend > dynamically vulcanised 70/30 NBR/SAN blend containing 45% of w-NBR. The reason given in the previous section also holds here. % volume swelling of the NBR/SCP blends increases as a function of the NBR content of these blends. Dynamically vulcanised blends exhibit less swelling than unvulcanised ones.

D values of the NBR/SCP blends increase as a function of NBR content of the blends. This is due to the fact that the harder ABS phase (which in turn is present in SCP) restricts diffusion of the solvent molecules. The diffusion coefficients of solvents in the dynamically vulcanised NBR/SCP blends are lower than those in their unvulcanised counterparts.

In contrast to the thermodynamic nature of swelling, diffusion is a kinetic phenomenon. However, both of these processes often show similar trends giving an idea about the nature of the interaction of solvents with polymers and their blends. The diffusion coefficient versus solubility parameter plots show similar trend as that of the swelling index versus solubility parameter plots of the NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends with the maximum value in 1,4-dioxan having a solubility parameter of 20.4 MPa<sup>1/2</sup>.

(c) *Effect of temperature on swelling* The effect of temperature on diffusion process of various solvents in the dynamically vul-

canised 70/30 NBR/SAN blend was studied by carrying out swelling at three different temperatures, viz., 25, 40 and 50 °C (Fig. 8). It is found that the diffusion coefficient increases slightly with an increase in temperature. The molecular motion associated with chain flexibility allows solvent molecules to penetrate the polymer. Also, solvent molecules acquire more kinetic energy as the molecular vibrations increase proportionally with temperature. As temperature increases, segmental motion in polymers also increases resulting in diffusion of a higher amount of solvent. However, the molecular network prevents free diffusion of solvent. The swelling of crosslinked polymer is a result of a compromise between the osmotic swelling pressure and elastic force of the macromolecular chain of the network opposing it [28]. The net result is migration of solvent molecules, which is temperature-dependent. The calculated activation energy values of diffusion of solvents in NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends are displayed in Table 5. A

**5** Activation energies of diffusion of solvents in NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends

Blend composition	$E_d$ (kJmol <sup>-1</sup> )			
	Toluene	MEK	1,4-dioxan	DMF
NBR/SAN				
70/30	4.3	5.1	5.8	4.9
70/30 dv	7.5	8.3	8.3	7.5
NBR(w-NBR)/SAN				
70(45)/30 dv	9.6	10.2	10.9	10.7
NBR/SCP				
60/40	4.5	4.9	5.6	3.7
70/30	4.1	4.5	5.0	2.5
80/20	3.5	4.0	4.0	2.1
60/40 dv	8.1	9.4	12.6	10.5
70/30 dv	7.5	8.5	11.6	10.0
80/20 dv	5.9	6.8	9.5	9.1

**6** Volume swelling of NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends in IRM oil # 903

Blend composition	IRM oil # 903	
	25 °C	100 °C
NBR/SAN		
70/30	8	20
70/30 dv	5	12
NBR(w-NBR)/SAN		
70(45)/30 dv	4	9
NBR/SCP		
60/40	8	24
70/30	15	42
80/20	22	54
60/40 dv	2	4
70/30 dv	3	4
80/20 dv	3	4



## Conclusions

- 1) NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends degrade in a single step in a nitrogen atmosphere. The thermal stability of NBR is improved by blending it with SAN.
- 2) Dynamically vulcanised NBR/SAN and NBR/SCP blends exhibit higher amount of activation energies of thermal degradation than their unvulcanised counterparts.
- 3) Swelling of the blends studied depends on diffusivity as well as solubility parameter of solvents and moreover, it is a rate dependent process.
- 4) The solvents exhibit higher amount of activation energies of diffusion in dynamically vulcanised blends, indicating the resistance of the dynamically vulcanised blends to the diffusion of the solvent molecules.
- 5) Dynamically vulcanised NBR/SAN, NBR/w-NBR/SAN and NBR/SCP blends show excellent swelling resistance in IRM #903 oil.

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Note: 'dv' in tables and figures denote dynamically vulcanised blends.