Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 749–763

THERMOGRAVIMETRIC ANALYSIS AND THERMAL AGEING OF CROSSLINKED NITRILE RUBBER/POLY-(ETHYLENE-CO-VINYL ACETATE) BLENDS

H. Varghese[1], *S. S. Bhagawan*[2] *and S. Thomas*[2*]

[1]School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam 686 560, Kerala, India
[2]Propellant Engineering Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695 022, Kerala, India

(Received March 18, 1999; in revised form September 4, 2000)

Abstract

The thermal behaviour of nitrile rubber (NBR)/poly(ethylene-co-vinyl acetate) (EVA) blends was studied by thermogravimetry. The effects of blend ratio, different crosslinking systems (sulphur, peroxide and mixed), various fillers (silica, clay and carbon black) and filler loading on the thermal properties were evaluated. It was found that the initial decomposition temperature increased with the addition of NBR to EVA. Among the various crosslinking systems studied, the peroxide cured system showed the highest initial decomposition temperature. This is associated with the high bond dissociation energy of C–C linkages. The addition of fillers improved the thermal stability of the blend. The mass loss at different temperatures and activation energy of degradation were also studied. The thermal ageing of these blends was carried out at 50 and 100°C for 72 h. It was seen that the properties are not affected by the mild ageing condition. Also, the peroxide cured system was found to exhibit better retention in properties, than other crosslinking systems.

Keywords: nitrile rubber and poly(ethylene-co-vinyl acetate), thermal ageing, thermogravimetric analysis

Introduction

The thermal degradation of polymers is an important subject as it covers a broad field, ranging from the development of thermoresistant polymers and ablation problems to the stabilisation of thermolabile polymers. Thermogravimetric analysis (TG) has proved to be a successful technique in determining the thermal stability of polymers and polymer blends. The knowledge of how polymers breakdown on heating takes place is important when these materials are processed and produced for use. The threshold temperature for the breakdown determines the upper limit of tempera-

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* Author to whom all correspondence should be addressed.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ture in their production [1]. Under different environmental conditions most polymers and their products gradually lose their useful properties as a result of polymer chain degradation. Heat is one of the degrading agents and its effect can be studied by thermal ageing.

The thermal stability of individual polymers is greatly influenced by blending. It strongly depends on the interactions of the component polymers. The thermal stability of poly(vinyl chloride)/epoxidised natural rubber (PVC/ENR) blends is greatly influenced by the interaction between PVC and ENR, which is a miscible system [2, 3]. A comparison of thermal behaviour of miscible and immiscible blends was reported from this laboratory by Lizymol and Thomas [4]. In the case of completely miscible PVC/EVA system, the thermal stability of PVC is considerably improved by the addition of EVA. But in the case of partially miscible PVC/SAN and completely immiscible EVA/SAN blends, the decomposition behaviour of individual polymers is retained in the blend. The thermal property of a blend of PVC/EVA/SAN is also reported by them [5]. In this ternary system there is a thermodynamically miscible region in which PVC acts as an interfacial agent for the immiscible SAN/EVA system and the overall thermal stability of the ternary blend is superior to the homopolymers and PVC/SAN and SAN/EVA blends.

Nando and co-workers reported on the thermal behaviour of blends of poly(ethylene-co-acrylic acid)/epoxidised natural rubber [6] and ethylene methyl acrylate (EMA) copolymer/poly(dimethyl siloxane) (PDMS) rubber, which exhibited synergism in thermal and physicochemical properties [7]. Thermogravimetric analysis of aromatic polyoxadiazole/polyamide-6 shows that the temperature of degradation of PA-6 in the blends decreases with the addition of more than 10 mass% of polyoxadiazole [8]. Amraee *et al*. [9] used thermogravimetric analysis for the quantitative and qualitative identification of SBR/BR blends. They also checked the uniformity of mixing and differentiated oil extended SBR from non-extended SBR.

During thermal ageing main chain scission, crosslink formation and crosslink breakage can take place. It is also possible that the existing crosslinks may break and a more stable type of crosslink can be formed. The extent of change in property is governed by the relative ratios and magnitudes of such reactions. Recently, Thomas and co-workers have reported the ageing of polymer blends and composites [10–12]. The addition of poly(vinyl chloride) to nitrile rubber yielded advantages in thermal ageing, ultraviolet and ozone resistance [13]. Noland *et al*. [14] noted that the ultraviolet degradation of the poly(methyl methacrylate)/poly(vinylidene fluoride) blends are consistent with that of the two components considered separately. Weatherable film applications of this blend are possible because of the high resistance of both the components to UV degradation. Blending of natural rubber and polybutadiene has shown various advantages including heat stability and abrasion resistance [15]. The photodegradation of ethylene vinyl acetate copolymer/poly(vinyl chloride) and nitrile rubber/poly(vinyl chloride) blends has been studied by Skowronski *et al.* [16]. The thermo-oxidative ageing of rubbers is reported by several authors [17, 18].

Acrylonitrile butadiene rubber has excellent oil resistance and abrasion resistance but poor ozone resistance. Poly(ethylene-co-vinyl acetate) offers excellent ozone resistance, weather resistance and mechanical properties. The morphology, mechanical properties, viscoelastic response, reprocessability, tear resistance, melt flow behaviour and swelling resistance of NBR/EVA blends have been reported earlier [19–22]. The aim of the present work is to study the effect of blend ratio, crosslinking systems, and fillers on the thermal degradation of NBR/EVA blends. The influence of these parameters on the thermal ageing of the blends is also investigated.

Curing systems were carefully selected to generate semi and full interpenetrating polymer structures. A full interpenetrating polymer network consists of an interwoven crosslinked polymer network while in a semi-interpenetrating network only one of the polymer is crosslinked [23]. Dicumyl peroxide can be used for the crosslinking of both NBR and EVA. Hence in the peroxide cured system, both NBR and EVA phases are crosslinked. This results in the formation of a full interpenetrating network. But sulphur can crosslink only NBR and not EVA due to its saturated backbone structure. So in the sulphur cured system only one phase, i.e., NBR is crosslinked and results in the formation of a semi-interpenetrating network. A mixed cure system, containing both peroxide and sulphur, was also selected for an effective curing of both the phases. The mixed cure system results in the formation of a full interpenetrating network.

Experimental

Materials

NBR (Aparene N 553 NS) having 34% bound acrylonitrile content was supplied gratis by Gujarat Apar Polymers Ltd., Mumbai. EVA (Pilene-1802) having 18% VAc content was procured from PIL, Chennai. The basic characteristics of NBR and EVA are given in Table 1. The rubber chemicals such as dicumyl peroxide, zinc oxide, stearic acid, mercaptobenzothiazyl disulphide (MBTS), sulphur and fillers such as high abrasion furnace black (HAF), semi-reinforcing furnace black (SRF) etc. are of commercial grade.

Blend preparation

The blends of NBR/EVA with different crosslinking systems and blend ratio were prepared on a two-roll mixing mill having a fraction ratio 1:1.4. The compounding recipes of the blends are given in Table 2. The different crosslinking systems used, *viz.*, peroxide system (DCP), sulphur system (S) and mixed system (DCP+S) are indicated using P, S and M respectively. The compounds with peroxide cure systems are designated as N_0P, $N_{30}P$, $N_{50}P$, etc. The subscripts indicate the mass percentage of NBR in the blend, i.e., N_0 is pure EVA, N_{30} is 30/70; NBR/EVA and so on. The peroxide cured 50/50; NBR/EVA blend (i.e., $N_{50}P$) was selected to study the effect of fillers. The different fillers used such as HAF, SRF, silica and clay are designated as BH, BS, S and C, respectively. The loading is indicated by prefixing numbers. The compounded blends were then compression moulded at 160°C for optimum cure.

Table 1 Details of materials used

Materials	Characteristics	Value	Source
Nitrile rubber	volatile matter/%	0.130	Gujarat Apar
Aparene N553NS	antioxidant/%	1.400	Polymers Ltd.,
	organic acid/%	0.250	Mumbai
	soap/%	0.004	
	mooney viscosity/ML_{1+4} 100°C	40.000	
	bound acrylonitrile/%	34.000	
	intrinsic viscosity/dl g^{-1}	1.527	
Poly(ethylene-co-	melt flow index/g 10 min^{-1}	2.000	Polyolefins
vinyl acetate)	density/g $(cm^3)^{-1}$	0.937	Industries Ltd.
Pilene (1802)	vicat softening point/°C	59.000	Chennai
	vinyl acetate/%	18.000	
	intrinsic viscosity/dl g^{-1}	0.170	

Table 2 Compounding recipe for NBR/EVA blends

Ingredients/ phr[a]	Peroxide system	Sulfur system	Mixed system	10	10	10	10	20	30
	(P)	(S)	(M)	S	C	BS	BH	BH	BH
Polymer	100	100	100	100	100	100	100	100	100
Zinc oxide	–	5.0	5.0	–	–	–	–	–	–
Stearic acid	–	1.5	1.5	–	–	–	–	–	–
MBTS[b]	–	1.5	1.5	–	–	–	–	–	–
Sulfur	–	1.5	1.5	–	–	–	–	–	–
DCP[c]	4.0	–	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Silica	–	–	–	10.0	–	–	–	–	–
Clay	–	–	–	–	10.0	–	–	–	–
SRF	–	–	–	–	–	10.0	–	–	–
HAF	–	–	–	–	–	–	10.0	20.0	30.0

[a]Parts per hundred rubber by mass; [b]mercaptobenzo thiazyl disulfide; [c]dicumyl peroxide

Thermogravimetric analysis

A delta series-TG 7 was used to obtain the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves. Samples were scanned from 30–750°C at a heating rate of 10°C min^{-1}.

Thermal ageing

Test samples were heated at 50 and 100°C in an air-circulating oven for 72 h. After being cooled down and conditioned at room temperature, the dimensions of each specimen were measured. The tensile properties of these samples were determined according to ASTM D412-87 using an Instron Universal Testing Machine (model 1121) at a crosshead speed of 500 mm min^{-1}.

Crosslink density determination

The crosslink density of the unaged and aged samples was determined by the swelling method. The samples were allowed to swell in cyclohexanone and the equilibrium uptake is noted. The molecular mass between the crosslinks is calculated using the following equation:

$$M_c = \left[\frac{\rho_p V_s \phi^{1/3}}{\ln(1-\phi)+\phi+\chi\phi^2} \right] \tag{1}$$

where ρ_p – density of polymer, V_s – molar volume of solvent, ϕ – volume fraction of polymer in the swollen mass, x – interaction parameter. ϕ and χ are given by the following equations.

$$\phi = \frac{\frac{W_1}{\rho_1}}{\left(\frac{W_1}{\rho_1} + \frac{W_2}{\rho_2} \right)} \tag{2}$$

where W_1 – mass of polymer, ρ_1 – density of polymer, W_2 – mass of solvent at equilibrium, ρ_2 – density of solvent.

$$\chi = 0.34 + \frac{V_s}{RT}(\delta_A - \delta_B)^2 \tag{3}$$

where δ_A, δ_B – solubility parameter of solvent and polymer, respectively.

From the molecular mass between crosslinks, the crosslink density, is calculated using the following equation

$$\nu = 1/2M_c \tag{4}$$

Results and discussion

Thermogravimetry

Effect of blend composition

The thermogravimetric plots of peroxide cured EVA and NBR are given in Figs 1 and 2 respectively. Two regions of degradation of EVA are evident (Fig. 1). The first

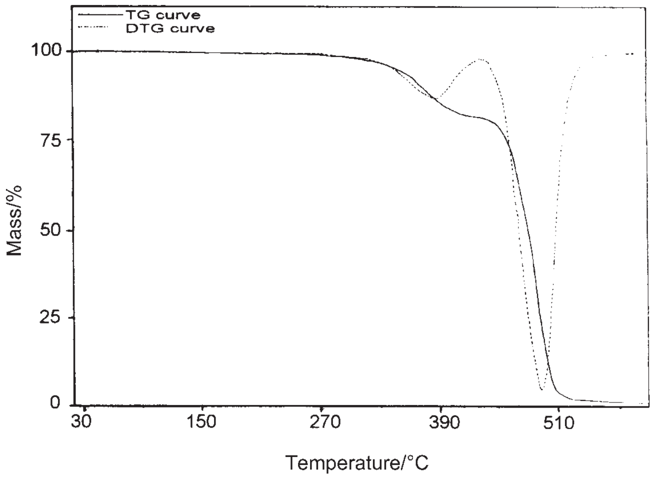


Fig. 1 TG and DTG curves of peroxide cured EVA

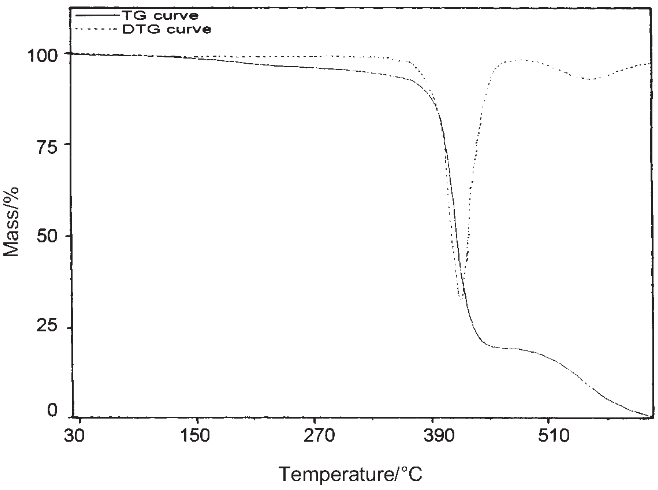
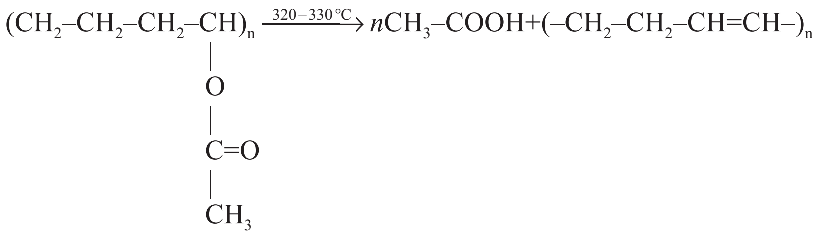


Fig. 2 TG and DTG curves of peroxide cured NBR

step degradation starts at about 310 and is completed at 427°C. The second stage degradation occurs in the region 446–538°C. The former stage of the degradation is due to the elimination of acetic acid from the vinyl acetate sections of the chain and degradation of polyethylene segments. The degradation of polyethylene segments is sensitive to the presence of branches and oxidised structures. Even at temperature much lower than the onset of volatilisation (occurs at about 370°C), polyethylene segment in ethylene-vinyl acetate segment shows a decrease in molecular mass due to scission at these structures which provide weak links. The later stage of degradation is due to scission of polyene left after the first stage of degradation [1].



$$\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{CH_3}}}{(\mathrm{CH_2{-}CH_2{-}CH_2{-}CH})_n} \xrightarrow{320-330^\circ\mathrm{C}} n\mathrm{CH_3{-}COOH}+(\mathrm{-CH_2{-}CH_2{-}CH{=}CH-})_n$$

$$(\mathrm{-CH_2{-}CH_2{-}CH{=}CH-})_n \xrightarrow[\text{scission}]{440-450^\circ\mathrm{C}} \text{hydrocarbons}$$

The mass loss observed during the first and second stages are 18.7 and 79.4% respectively. About 1.9% remains as residue above 538°C. The mass loss observed at 350°C is 4.81% and that at 475°C is 43.5%. In the DTG curve (dotted line), the major peak is observed at 493°C which corresponds to the scission of conjugated polyene left after the first stage of degradation. A small peak corresponding to the deacetylation and degradation of polyethylene is observed at 387°C.

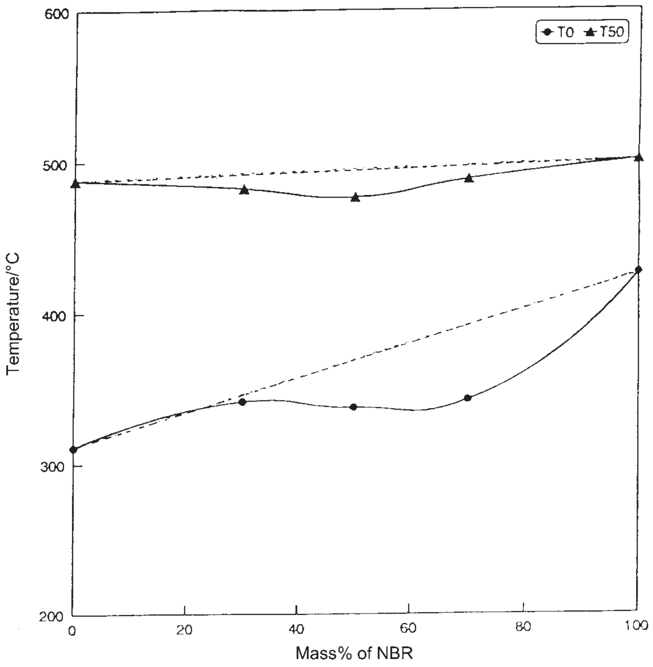


Fig. 3 Variation in T_0 and T_{50} with mass% of NBR

In the case of nitrile rubber (NBR) also a two-step degradation is observed (Fig. 2). Due to the presence of acrylonitrile and butadiene units in nitrile rubber, degradation occurs via a two-stage mechanism [9]. The first step degradation is from 427 to 536°C and the second step from 584 to 706°C. A mass loss of 80.5 and 18% are observed during the first and second steps of degradation respectively. About 1.5% remains as residue above 692°C. The mass loss observed at 350°C is 4.8% and that at 475°C is 33.1%. In the DTG curved (dotted line), a major peak at 488 and minor peak at 638°C is observed. The peak at 488°C is mainly due to the degradation of butadiene segments which will be completed around 500°C and the peak at 638°C corresponds mainly to the degradation of acrylonitrile segments. In general, the degradation behaviour of the blends is marginally different from that of the individual components. It has been reported that the thermal stability can be improved by the incorporation of a second polymer [24]. The initial and final decomposition temperatures and mass loss at different temperatures of the blends are given in Table 3. As the NBR content increases, the initial and final decomposition temperatures increase slightly. The initial decomposition temperature (T_0) and the temperature of 50% decomposition (T_{50}) is plotted as a function of blend composition in Fig. 3. Both T_0 and T_{50} show a negative deviation from the additivity. In Fig. 4, the residue mass at different temperatures is plotted as a function of blend composition. At 350°C, the residue mass of the pure components as well as the blends are nearly same. At 450 and 500°C, a slight increase in the residue mass is observed with the increase in the mass per cent of NBR.

Table 3 Decomposition temperatures and mass loss of different NBR/EVA blends

Sample		Decomposition temperature/°C		Mass loss/%		
		initial	final	at 350°C	at 475°C	total
Blend ratio	N_0P	311	537	4.83	43.45	98.11
	$N_{30}P$	341	544	4.81	33.79	93.85
	$N_{50}P$	337	538	5.52	38.91	89.44
	$N_{70}P$	342	655	4.14	42.07	98.22
	$N_{100}P$	426	705	4.83	33.11	98.45
Crosslinking systems	$N_{50}S$	321	541	6.21	42.76	96.14
	$N_{50}M$	334	554	6.21	39.31	86.49
Fillers	10S	334	544	5.52	33.11	91.31
	10C	340	541	4.82	32.41	91.43
	10BS	342	560	4.14	31.72	85.29
	10BH	320	558	4.14	27.59	98.83
	20BH	328	559	4.82	25.52	98.84
	30BH	333	567	3.75	25.00	72.01

Effect of crosslinking systems

For the different crosslinking systems the initial decomposition temperature is 321, 337 and 334°C for the sulphur (S), peroxide (P) and mixed (M) cure systems, respectively (Table 3). Here the peroxide cured systems shows the highest initial decomposition temperature indicating a good thermal stability. This can be explained on the basis of the structure of networks (Fig. 5) formed during vulcanisation. The C–C link-

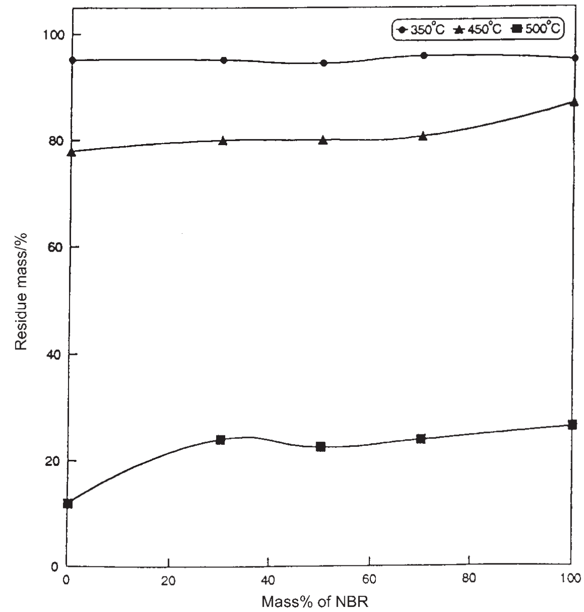
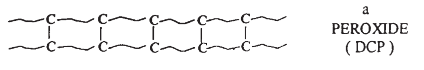
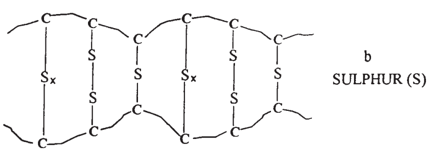


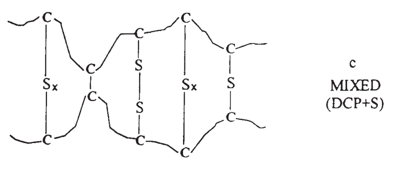
Fig. 4 Variation in residue mass with mass% of NBR



C-C linkages



Mono, di and polysulphidic linkages
(Predominantly polysulphidic x>3)



Mixed linkages (x>3)

Fig. 5 Schematic representation of the nature of crosslinks ages in the peroxide cured system are less flexible with the highest bond energy (85 kcal mol^{-1}). The mass loss observed at 350 and 475°C is given in Table 3. Here also the peroxide cured system shows the lowest mass loss at a particular temperature.

Effect of fillers

In the case of filled NBR/EVA ($N_{50}P$) system, the initial decomposition temperature of silica (10S) and HAF (10, 20 and 30 BH) filled systems decrease and that of clay (10C) and SRF (10 BS) filled system increase. But there is increase in the final decomposition temperature on addition of filler in all cases. With increase in filler loading (10, 20 and 30 BH) there is an improvement in the initial as well as final decomposition temperatures. In the case of all the filled systems DTG curves exhibit two peaks – a minor one around 390°C and a major one around 500°C. From Table 3, it can be seen that the mass loss at 350 and 475°C is low for all the filled systems compared to the unfilled one ($N_{50}P$). This indicates the improvement in the thermal stability of the system with the addition of fillers.

Activation energy of degradation

The activation energy for the degradation process (temperature range 350–500°C) was calculated from the Arrhenius relationship.

Table 4 Activation energy for degradation and property retention after ageing for NBR/EVA blends

Samples	Activation energy E_x/kJ mol^{-1}	Retention in tensile strength after ageing at 100°C for 72 h/%
N_0P	2.47	91
$N_{30}P$	3.01	92
$N_{50}P$	3.60	97
$N_{70}P$	4.21	94
$N_{100}P$	3.19	90
$N_{50}S$	2.94	80
$N_{50}M$	2.91	85
10S	3.20	81
10C	2.79	74
10BS	2.82	76
10BH	2.94	79
20BH	2.33	80
30BH	1.85	84

$$X = X_0 \exp\left(-\frac{E_x}{RT}\right) \tag{5}$$

where X is the mass loss at a particular temperature, X_0, a constant, E_x, the activation energy; R, the universal gas constant and T, the absolute temperature. The activation energy for the degradation process of all the systems is given in Table 4. It is seen that the blends exhibit higher activation energy than the pure components indicating the thermal stability achieved by blending. Among the various crosslinking systems, the peroxide cured system shows the highest activation energy for the process. This is due to the nature of networks (Fig. 5) and its respective bond length and bond energy as explained earlier. In the mixed cure system, both types of linkages are present and its activation energy is close to that of the sulphur cured system. Among the various fillers used, the silica filled system shows the highest activation energy.

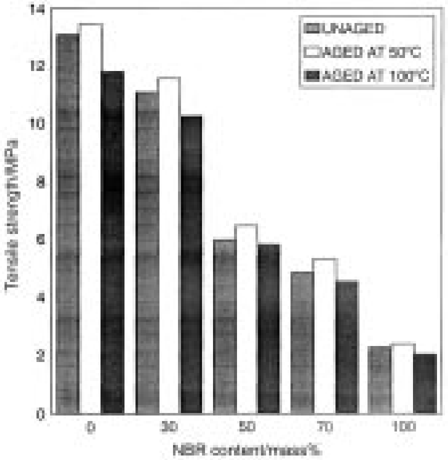


Fig. 6 Effect of blend composition on the tensile strength of unaged and aged samples

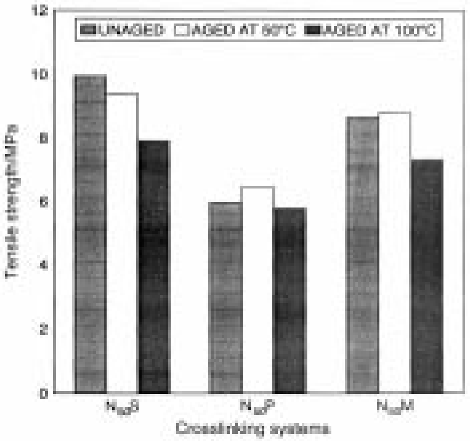


Fig. 7 Effect of crosslinking systems on the tensile strength of unaged and aged samples

Thermal ageing

The results of thermal ageing of NBR/EVA blends as a function of blend composition, crosslinking systems, filler type (at 10 phr loading) and filler loading (HAF) are presented in Figs 6–9 respectively. In all the cases except sulphur cured system (Fig. 7) a marginal increase in the property is observed after ageing of the samples at 50°C. This is due to the additional crosslinks formed during thermal ageing as evidenced by the crosslink density values given in Table 5.

Table 5 Crosslink density values of NBR/EVA blends

Samples	Crosslink density·10^4/mol cm^{-3}		
	Unaged	Aged at 50°C	Aged at 100°C
N_0P	16.88	16.97	16.69
$N_{30}P$	5.21	5.32	5.20
$N_{50}P$	2.84	3.02	2.84
$N_{70}P$	0.60	0.69	0.56
$N_{100}P$	0.95	1.07	0.89
$N_{50}S$	3.01	2.94	2.84
$N_{50}M$	3.25	3.37	3.02
10S	4.12	4.23	3.98
10C	4.02	4.19	3.94
10BS	4.28	4.33	4.15
10BH	4.55	4.62	4.42
20BH	5.01	5.09	4.97
30BH	5.07	5.14	5.03

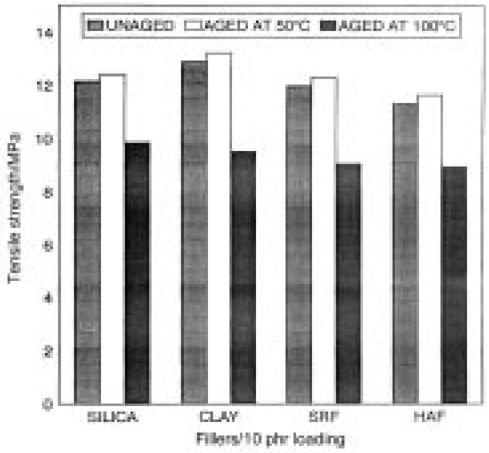


Fig. 8 Effect of fillers on the tensile strength of unaged and aged samples

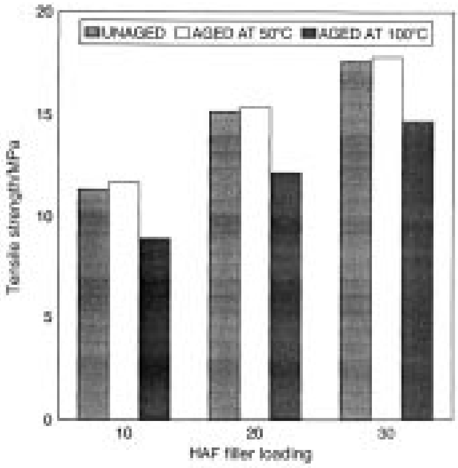


Fig. 9 Effect of filler loading on the tensile strength of unaged and aged samples

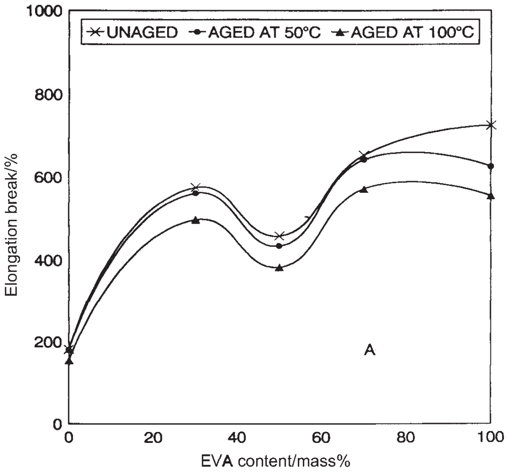


Fig. 10 Effect of blend composition on the elongation at break of unaged and aged samples

There is an increase in crosslink density of the samples, except sulphur cured system ($N_{50}S$), after ageing at 50°C. In the case of sulphur system, the S–S crosslinks are more flexible with the lowest bond energy (57 kcal mol^{-1}). They can be easily dissociated by thermal energy. Therefore in sulphur cured system, the property decrease as a result of ageing. It is important to notice that in all cases, the properties decrease after ageing at 100°C. This is due to the disintegration of crosslinks at an elevated temperature. The crosslink density also decreases after ageing at 100°C (Table 5). After severe ageing condition at 100°C, the sulphur cured system retains only 80% of the property. For the peroxide and mixed cure systems, the retention in property was 97 and 85% respectively. This implies that, among the different crosslinking systems, peroxide cured system exhibits the best retention in property even after severe ageing

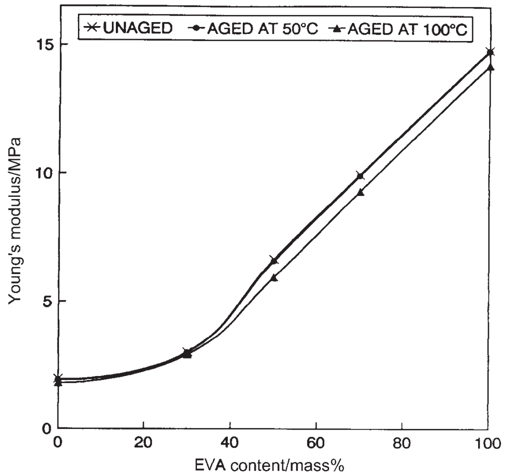


Fig. 11 Effect of blend composition on the Young's modulus of unaged and aged samples

condition. This is due to the thermal stability of the peroxide cured system as evident from the TG studies discussed above.

The retention in property of all the blends is given in Table 4. The effect of blend composition and ageing on the mechanical properties of NBR/EVA blends is given in Figs 10 and 11. In Fig. 10, the elongation at break shows an initial increase followed by a decrease at 50/50 : NBR/EVA blend composition. After 50/50 composition it again shows an increase. The decrease in elongation at break of 50/50 composition is associated with the co-continuity of the two phases at this composition [19]. Since the two phases are co-continuous the interfacial interaction is higher at this composition leading of a decrease in extensibility. The Young's modulus increases with increase in EVA content (Fig. 11). The sample aged at 100°C exhibits a lower Young's modulus than those aged at 50°C and unaged samples. However, the property is not much affected by the mild ageing condition.

Conclusions

The thermogravimetry and thermal ageing of NBR/EVA blends have been carried out with special reference to the effect of blend ratio, crosslinking systems, fillers and filler loading. Both NBR and EVA exhibited a two-step degradation process. As the NBR content in the blend increases, an increase in the initial and final decomposition temperatures is obtained. Among the various crosslinking systems, the peroxide cured system shows the highest initial decomposition temperature indicating a better thermal stability. The activation energy of degradation for the blends was higher than that of the pure components indicating the enhanced thermal stability by blending. Among the various filled systems, the silica filled system showed highest thermal stability. After mild ageing condition (50°C for 72 h) properties are not affected, for all the systems. However, under severe ageing condition (100°C for 72 h) a deterioration in property was observed due to the degradation of the crosslinks. The crosslink density values are in accordance with the above observation. The peroxide cured system exhibited a better retention in property even after severe ageing condition.

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One of the authors (H. V.) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for financial assistance.

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