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The effect of crosslink density, curing system, filler and resin on the decomposition of hydrogenated nitrile rubber and its blends

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Abstract

The decomposition behaviour and kinetics of oxidative decomposition of hydrogenated nitrile rubber (HNBR), zinc–poly(methyl methacrylate) resin (ZSC-2295) and the tank track pad compositions developed from their blends have been studied by thermogravimetry in air and compared with those of natural rubber (NR) and styrene–butadiene rubber (SBR) based compositions. The effect of crosslink density, curing system and carbon black on the degradation characteristics of HNBR have also been investigated. HNBR undergoes first order and ZSC-2295 undergoes second order degradation with an activation energy (ΔE_a) of 330 ± 10 and 400 ± 10 kJ mol^{-1} respectively. The degradation characteristics and kinetics are not influenced by the crosslink density, the curing system or the carbon black loading. The ΔE_a of the degradation reaction of HNBR based compositions increases slightly on the addition of the resin ZSC-2295. Degradative stability in terms of onset and peak temperature of degradation and ΔE_a of degradation of the tank track pad compositions follow the order HNBR > SBR > NR.

INTRODUCTION

Recently, hydrogenated nitrile rubber (HNBR) has found wide application in tank track pads, oil well packers, automotive shaft seals etc. because of its improved heat resistance and good oil resistance. The distinct advantages of HNBR are its excellent ageing properties and oil resistance, even at high temperature (150°C), and its outstanding abrasion resistance, even under extremely adverse conditions [1–3]. Its properties could be further enhanced over conventional filled rubber vulcanizates by blending it with the resin zinc–poly(methyl methacrylates) (ZSC-2295) [4].

We have developed suitable compositions based on hydrogenated nitrile rubber (HNBR), natural rubber (NR) and styrene–butadiene rubber (SBR) for the main battle tank track pad. As the tank is heavy and often

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operated in hilly and rough terrain, the track pad fails frequently owing to heat build-up, leading to rubber-to-metal bond failure, excessive wear, chipping and loss of large pieces of rubber, as well as thermal degradation [5]. Computer modelling of the track pad indicated that the surface temperature of the pads during operation could exceed 100°C [6]. The track pad composition should thus have high resistance to thermal decomposition. Our field test results indicated that the performance of a HNBR pad was excellent despite high heat generation [7]. It is apparent that the thermal stability plays an important role in deciding the mechanical properties in the field. In order to predict the service performance of HNBR based compositions, it is essential to know their degradation behaviour. Although the physical properties of HNBR compositions have been studied, degradation studies have not received much attention until now. Recently the authors reported the dynamic mechanical properties of HNBR based compositions under rapidly varying strain conditions as a function of temperature [8]. Brazier has reviewed the application of thermal analysis techniques to the study of elastomer systems [9]. The ageing and degradation behaviour of various rubbers has been reported from this laboratory [10–12].

The present work is concerned with thermogravimetric studies in air on the influence of crosslink density, curing system, resin and filler on the degradation behaviour of HNBR vulcanizates. The degradation of tank track pad compositions has also been investigated. The decomposition and oxidative decomposition kinetics of HNBR based compositions have been compared with those of NR and SBR based compositions.

EXPERIMENTAL

Materials

The HNBR (Zetpol 1020) and zinc–poly(methyl methacrylate) resin (ZSC-2295) used in this study were obtained from Nippon Zeon Co. Ltd., Japan. The carbon black N-110 was obtained from Phillips Carbon Black Ltd., India. The conductive grade carbon black Vulcan P was supplied by Cabot Corporation, USA. Di-Cup R dicumyl peroxide (DCP) was obtained from Hercules Inc., USA. Other materials such as zinc oxide, stearic acid, sulphur etc. were chemically pure.

Preparation of samples

The formulations of the mixes are given in Tables 1 and 2. The rubber and other ingredients were mixed in a laboratory size two-roll mixing mill (330 mm × 152 mm) according to ASTM D 3182-80. Samples were prepared by curing the mixes in a single daylight (space between top and bottom plates) electrically heated press at 160°C for the optimum cure time as determined with a Monsanto rheometer (R-100S).

TABLE 1

Formulation of rubbers (phr)[a]

Ingredients	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{12}
Zetpol 1020	100	100	100	100	90	80	70	60	100	100
ZSC-2295[b]	–	–	–	–	10	20	30	40	–	–
Zinc oxide	2	2	2	5	2	2	2	2	2	2
Stearic acid	–	–	–	1	–	–	–	–	–	–
Sulphur	–	–	–	0.5	–	–	–	–	–	–
Carbon black N-110	50	50	50	50	30	30	30	30	–	30
TMTD[c]	–	–	–	2	–	–	–	–	–	–
MBT[d]	–	–	–	0.5	–	–	–	–	–	–
Di-cup R	4.5	3.0	1.5	–	3.0	3.0	3.0	3.0	3.0	3.0
Total	156.5	155.0	153.0	159.0	135.0	135.0	135.0	135.0	105.0	135.0

[a] phr means parts per hundred parts of rubber. [b] ZSC-2295 is a commercially available blend of zinc–poly(methyl methacrylate). [c] TMTD is tetramethylthiuram disulphide. [d] MBT is mercaptobenzothiazole.

TABLE 2

Formulation of tank track pad rubbers (phr)

Ingredient	T_6	T_{20}	T_{23}
NR	100	–	–
SBR-1502	–	–	100
Zetpol-1020	–	70	–
ZSC-2295	–	30	–
Zinc oxide	5	2	5
Stearic acid	6	1	6
TMQ[a]	0.5	1.0	0.5
Pilflex-13[b]	3.0	1.0	3.0
Carbon black N-110	50	25	55
Conductive carbon black (Vulcan P)	–	10	–
CBS[c]	0.8	–	0.8
TMTD	–	2.0	–
MBT	–	0.5	–
Di-cup R	–	1.5	–
Sulphur	2.0	0.5	2.0
PVI[d]	0.5	–	0.5
Total	167.8	147.5	172.8

[a] TMQ is 1,2-dihydro-2,2,4-trimethylquinoline. [b] Pilflex-13 is *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine. [c] CBS is cyclohexylbenzothiazyl sulphenamide. [d] PVI is pre-vulcanization inhibitor.

Thermal analysis

Thermogravimetric analyses were carried out in a Mettler TG-50 of the TA-3000 system interfaced to a TC-10A microprocessor. The heating rate was 20°C min^{-1}. The flow rate (100 $\mathrm{cm}^3\,\mathrm{min}^{-1}$) of air was kept constant throughout the study. The first derivative of the thermogravimetric (TG) curves and the kinetic parameters were calculated using the in-built software.

RESULTS AND DISCUSSION

The effect of crosslink density and curing system on the degradation of carbon black filled HNBR rubbers

Crosslink density was varied by adjusting the level of DCP in the HNBR (Table 1). The thermogravimetric (TG) traces of rubbers D_1, D_2 and D_3, containing 4.5, 3.0 and 1.5 phr of DCP respectively, are shown in Fig. 1 (phr is parts per hundred parts of rubber). Weight loss occurs in two stages; the first is due primarily to the decomposition of HNBR, starts at 340°C and reaches a maximum rate of weight loss at 495°C, the T_{max}. About 86% of the

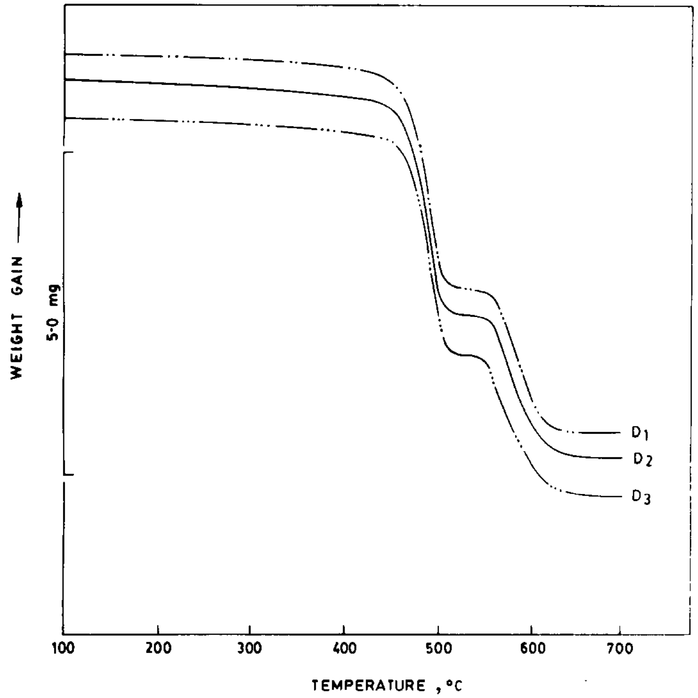

Fig. 1. TG curves of carbon black filled HNBR containing different amounts of DCP.

total HNBR decomposes in this step. The second starts at about 540°C and reaches a maximum rate of production of volatiles at 580°C. Weight loss in this second stage is due to the complete combustion of carbon black to CO_2 and the degradation of the rest of the HNBR. The residue left after the second stage is mainly ZnO, along with ash from the HNBR. The initial and the maximum rate temperatures are similar for rubbers D_1, D_2 and D_3 and are not influenced by the crosslink density.

Bhattacharjee et al. [11] reported that the degradation of raw HNBR took place in one step with a T_{max} of 495°C which is the same in the present experiment. Sircar and Lamond [13] reported that the degradation of nitrile rubber in a nitrogen atmosphere formed a thermally stable cyclized acrylonitrile product, and also that this rubber left a carbonaceous residue at high temperature. During the degradation of HNBR also, some thermally stable cyclized acrylonitrile intermediate might have formed, and hence only 86% of HNBR is decomposed in the first step.

The TGA traces of the peroxide (D_2) and sulphur (D_4) cured rubbers are presented in Fig. 2. The onset temperature for decomposition of the sulphur cured rubber is slightly lower than that for the peroxide cured rubber; this may be caused by the decomposition of the other ingredients, such as stearic acid, accelerators etc. The percentage weight loss and the residue are higher for the sulphur cured rubber because it contains more zinc oxide compared with the peroxide cured rubber. However, the peak

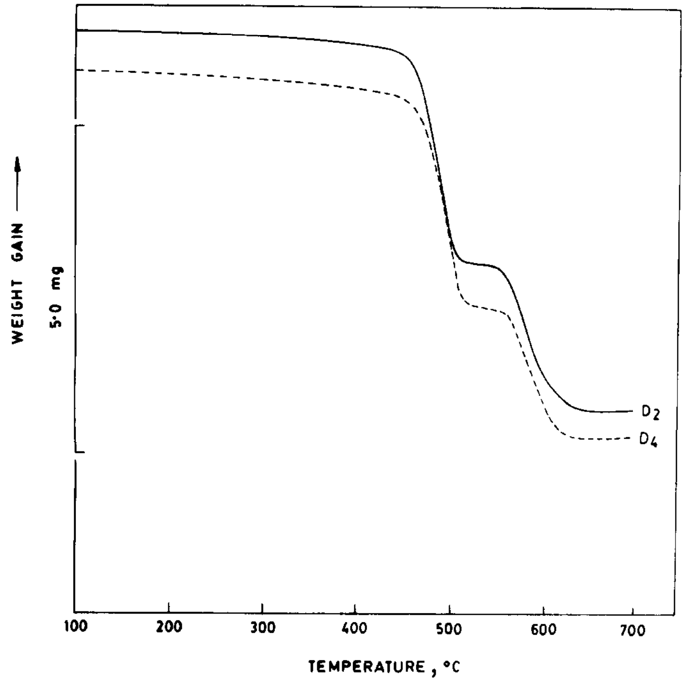

Fig. 2. TG curves of DCP and sulphur cured carbon black filled HNBR.

temperature and the percentage decomposition of HNBR remain the same for both rubbers, indicating that the decomposition of HNBR does not depend on the type of crosslinks or the network structure.

The effect of carbon black

Figure 3 shows the effect of carbon black loading on the weight loss as a function of temperature. As above, the decomposition takes place in two stages with onset at 340°C and maximum rate of evolution of volatiles at 495°C for the unfilled as well as the carbon black filled rubbers. Although the percentage weight loss decreases with filler loading, only 86% of the HNBR content in the rubber is decomposed. The decreased weight loss is due to the increase in the residue of carbon black left at the end of the first step. The second step starts at 540°C and reaches a maximum rate at 580°C. In this step, decomposition of the rest of the HNBR and combustion of the carbon take place. The residue is mainly ZnO and ash from the HNBR. It is clear from the above observation that the addition of carbon black has no effect on the decomposition behaviour of HNBR.

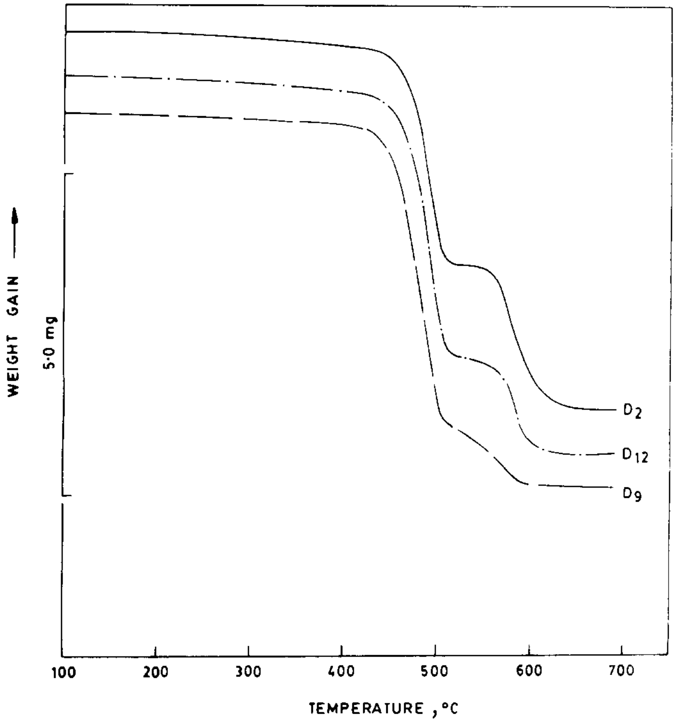

Fig. 3. TG curves of gum and carbon black filled HNBR vulcanizates containing different amounts of carbon black.

The effect of the resin ZSC-2295

The decomposition characteristics of ZSC-2295 are shown in Fig. 4. Decomposition starts at a comparatively low temperature (210°C). The peak temperature occurs at 450°C, which is 45°C lower than the peak temperature for the HNBR vulcanizate (495°C). A 66.4% weight loss occurs in stage 1. The second step starts at 496°C and reaches its peak temperature at 527°C. Both the onset and the peak temperatures are lower than those for the gum HNBR vulcanizate. About 15.6% weight loss occurs in the second step, and the 18% remaining as residue is ZnO.

The thermogravimetric traces of the blends D_5, D_6, D_7 and D_8, containing 10, 20, 30 and 40 phr of ZSC-2295, are shown in Fig. 4. Decomposition of blends D_5–D_8 occurs in two steps. The onset temperature decreases with the resin content, owing to the low thermal stability of poly(methyl methacrylate), which undergoes almost complete depolymerization to its monomer at ≈220°C [14]. The peak temperature also decreases with resin content. Decomposition of both HNBR and ZSC-2295 occurs in step 1. It is interesting to note that the percentage weight loss in both steps decreases with increasing amounts of the resin. In the second stage, combustion of carbon black takes place along with the oxidation of

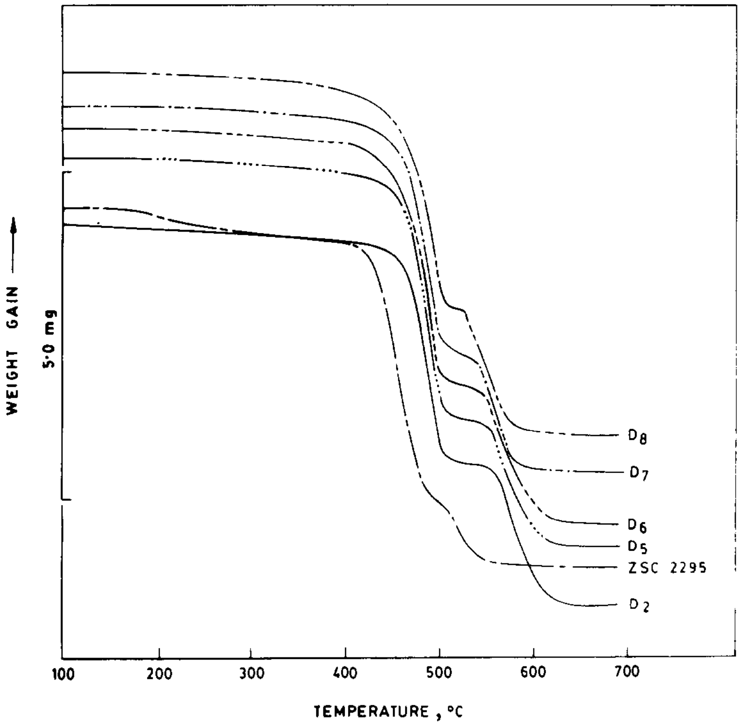

Fig. 4. TG curves of the resin ZSC-2295 and HNBR–ZSC-2295 blends.

the residue from HNBR and ZSC-2295. As expected, the amount of residue left after stage 2 increases with increasing ZSC-2295 content because of the higher residue of ZnO.

The effect of crosslink density, curing system, carbon black and resin (ZSC-2295) on decomposition kinetics

Kinetic parameters of the decomposition of the rubbers, determined by non-isothermal thermogravimetric studies in air, are listed in Table 3. The HNBR vulcanizates having different degrees of crosslink density, curing systems and loadings of carbon black undergo first order thermal degradation with activation energy ΔE_a of 330 ± 10 kJ mol^{-1}, and the pre-exponential factor ($\ln k_0$) is also the same (48 ± 2). These observations indicate that the kinetics of oxidative decomposition are not influenced by the crosslink density, the curing system or the loading of carbon black. However, the incorporation of ZSC-2295 changes the kinetics, in that ZSC-2295 resin shows second order dependence with an activation energy of 400 ± 10 kJ mol^{-1} and $\ln k_0$ of 60 ± 3. The ΔE_a of ZSC-2295 is thus higher than that of HNBR. The ΔE_a of HNBR increases on incorporation of ZSC-2295, but this increase in ΔE_a becomes apparent only for additions of 30 and 40 phr. However, the order of the reaction and the $\ln k_0$ value remain unaltered. Bhattacharjee et al. [11] reported a reaction order of unity for raw HNBR.

TABLE 3

Kinetic parameters from non-isothermal thermogravimetric study in air

Sample no.	Onset temp. of decomposition (°C)	Peak (max) temperature (°C)	Kinetic order	Activation energy ΔE_a (kJ mol^{-1})	Pre-exponential factor $\ln k_0$
D_1	340	495	1	330 ± 10	48 ± 2
D_2	340	495	1	330 ± 10	48 ± 2
D_3	340	495	1	330 ± 10	48 ± 2
D_4	340	495	1	330 ± 10	48 ± 2
D_9	340	495	1	330 ± 10	48 ± 2
D_{12}	340	495	1	330 ± 10	48 ± 2
ZSC-2295	210	440	2	400 ± 10	60 ± 3
D_5	330	491	1	332 ± 10	48 ± 2
D_6	325	485	1	335 ± 10	48 ± 2
D_7	319	482	1	340 ± 10	48 ± 2
D_8	308	475	1	350 ± 10	48 ± 2

Studies on tank track pad rubbers

We have developed a tank track pad composition based on HNBR. The performance of this composition, both in the laboratory and in field tests, is better than that of existing natural rubber (NR) and styrene–butadiene rubber (SBR) based compositions. Although the HNBR shows higher heat generation, its wear resistance is excellent. The thermogravimetric analysis of the HNBR tank track pad has therefore been investigated, and the results have been compared with those for similar NR and SBR pads. Sample T_{20} is based on a blend of HNBR and ZSC-2295 in 70:30 ratio, and T_6 and T_{23} are based on NR and SBR respectively; see Table 2. The TG and DTG traces of T_{20}, T_6 and T_{23} are shown in Figs. 5(a), 5(b) and 5(c) respectively. Sample T_{20} decomposes at 301°C and the peak temperature is 490°C (Fig. 5(a)). In step 1, decomposition of both HNBR and ZSC-2295 takes place, and a 58.4% weight loss is observed. If 86% of the HNBR and 66% of the ZSC-2295 resin decompose in this step, then the weight loss is little more than that expected. In step 2, a 33.1% weight loss takes place; a 22.7% weight loss in this stage involves the combustion of carbon black in the composition. The residue left is relatively higher (8.5%) owing to the formation of ZnO and ash.

The onset of decomposition for NR starts at 151°C with a peak temperature at 407°C (Fig. 5(b)). More than 85% of NR, along with other ingredients, is decomposed by 465°C. A small diffuse peak at 516°C is observed in step 2, in which $\approx$10% weight loss occurs. The decomposition of the rest of the NR, along with the other ingredients, is involved in this step. Combustion of carbon black takes place in the next stage of this second step. The weight loss is 29.9%, which correlates well with the carbon black content (29.8%). Sircar [15] reported that thermally stable products were formed by cyclization of NR and the cyclised products decomposed along with the combustion of the carbon black. Hence the decomposition of T_6 takes place in two steps.

The TG and DTG traces of the SBR based tank track pad rubber T_{23} are shown in Fig. 5(c). The DTG curve shows a very small diffuse peak at 308°C, and only 5.7% degradation corresponds to this peak. The maximum rate of decomposition is observed at 477°C and the corresponding weight loss is 53.5%. The total weight loss in step 1 is 59.2%, and almost 90% of the SBR, along with other ingredients, decomposes in this step. In the second step, 31.8% of carbon black undergoes combustion along with the remaining SBR taking the weight loss to 37.4%. The residue, 3.4%, is mainly ZnO.

It can be concluded from the above observations that the thermal stability of the track pad compounds follows the order HNBR > SBR > NR.

The kinetics of oxidative decomposition

The kinetic parameters of the oxidative decomposition of HNBR–ZSC-2295, NR and SBR based tank track pad compositions are compared in

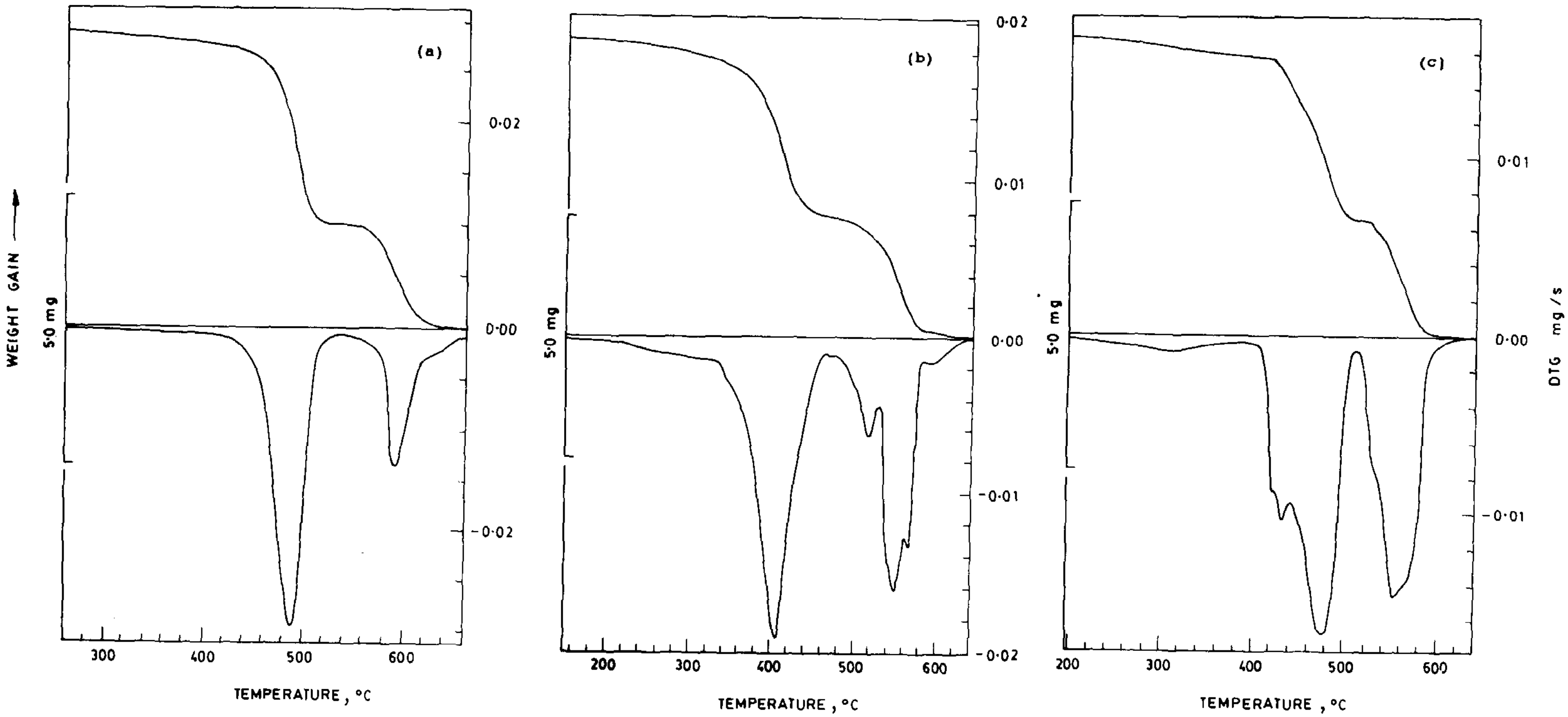

Fig. 5. TG and DTG curves: (a) HNBR–ZSC-2295 blend (70:30) based tank track rubber (T_{20}); (b) NR based tank track pad rubber (T_6); (c) SBR based tank track pad rubber (T_{23}).

TABLE 4

Kinetic parameters of the degradation of tank track pad compositions obtained from non-isothermal thermogravimetric study in air

Sample no.	Onset temp. of degradation (°C)	Peak (max) temp. of degradation (°C)	Order of degradation reaction	Activation energy ΔE_a of degradation reaction (kJ mol^{-1})	Pre-exponential factor $\ln k_0$
T_{20}	301	490	1	340 ± 10	50 ± 3
T_6	151	407	1	180 ± 10	27 ± 3
T_{23}	201	477	1	210 ± 10	32 ± 3

Table 4. First order kinetics are observed for rubber based on a 70:30 HNBR–ZSC-2295 blend, with an activation energy ΔE_a of 340 ± 10 kJ mol^{-1} and a pre-exponential factor ($\ln k_0$) of 50 ± 3. The NR based composition also undergoes first order decomposition; its ΔE_a is 180 ± 10 kJ mol^{-1} and the pre-exponential factor is 27 ± 3. In the case of the SBR based composition, first order kinetics are observed with a ΔE_a of 210 kJ mol^{-1} and $\ln k_0 = 32 \pm 3$. Hence, compared with the NR and SBR based compounds, the ΔE_a for HNBR–ZSC-2295 blend based rubber is significantly higher (by more than 1.5 times), revealing its higher thermo-oxidative stability. The high thermal stability of T_{20} may be attributed to the saturated backbone of the HNBR and ZSC-2295.

CONCLUSIONS

1. The decomposition of HNBR takes place in two steps. Most of the HNBR (86%) decomposes in step 1, and combustion of carbon black with the degradation of the remaining part of the HNBR takes place in step 2. Both unfilled and carbon black filled HNBR vulcanizates undergo first order decomposition.

2. Reaction order and ΔE_a are found to be independent of crosslink density and curing system.

3. No change in activation energy ΔE_a is observed on the addition of carbon black to HNBR.

4. ZSC-2295 resin undergoes second order decomposition with $\Delta E_a = 400$ kJ mol^{-1}. However, the addition of the resin does not alter the order of the degradation reaction of the rubber compositions except for a small increase in ΔE_a.

5. The stability of the tank track pad compositions in terms of onset and peak temperature of decomposition and energy of activation follows the order HNBR > SBR > NR.

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