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Dynamic mechanical properties of hydrogenated nitrile rubber: effect of cross-link density, curing system, filler and resin

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The effect of cross-link density, curing system, filler and resin on dynamic mechanical properties of hydrogenated nitrile rubber (HNBR) is reported. The storage modulus, G', increases and the loss angle, tan δ, decreases in the plateau zone with cross-link density. At equal cross-link density, the tan δ peak value at the transition zone of sulphur cured system, is less than that of peroxide cured system. Tan δ decreases from 90 to 180 °C and increases beyond 180 °C due to post vulcanization reaction and sulphidic linkage cleavage, respectively. The ZSC 2295 resin increases G' and decreases tan δ, and is found to be compatible with HNBR. The plateau modulus, G', increases with carbon black loading. The tan δ is lower for high structure carbon black in the transition zone and higher in the plateau zone when the surface area is high.

1. Introduction

In recent years hydrogenated nitrile rubber (HNBR) because of its improved heat and oil resistance, is finding an increasing number of applications starting from small and highly critical products like automotive shaft seals, oil well packers, hoses, power transmission and timing belts to solid tyres and tank track pads. It has a distinct advantage such as ageing and oil resistance even at high temperatures (150 °C) and an 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 a resin (ZSC 2295) [4].

In order to use HNBR in different engineering applications, particularly in the areas where the product is subjected to high vibration and pulsating loads, like power transmission and timing belts, tank track pads, etc., one should understand its mechanical properties under rapidly varying stress conditions. Though the physical properties of HNBR have been extensively studied, its dynamic mechanical properties like storage shear modulus, G', loss shear modulus, G'' and loss angle, tan δ, under rapidly varying stress conditions as a function of temperature have not yet been reported.

The dynamic mechanical properties at different frequencies, amplitudes and temperatures for natural rubber (NR), styrene butadiene (SBR), ethylene propylene rubber (EPDM) [5] have been widely reported. Medalia [6] has reviewed the effects of carbon black on the dynamic mechanical properties of rubber vulcanizates. Payne *et al.* [7] reported the effects of curative levels at different amplitudes and at different levels of carbon black loading on the elastic modulus, G', of NR. Payne observed that $\Delta G'$ ($\Delta G' = G'_0 - G'_\infty$, where G'_0 and G'_∞ are low strain and high strain plateau values of shear modulii) was independent of curative level. Sommer and Meyer [8] reported that increasing the curing time from 75 to 100 to 125% of optimum cure time caused significant increase in both elastic modulus, G', and loss modulus, G'', of oil extended NR. Class and Chu [9] have reported the effect of resin on the viscoelastic properties of NR and SBR and observed that the tan δ transition peak temperature is affected by nature and concentration of resin in the rubber resin blends.

Observations on the effects of cross-linking system and cross-link density, nature and level of filler and resin on storage modulus, G', and loss angle, tan δ of HNBR are reported.

2. Experimental procedure

2.1. Materials

HNBR (ZETPOL 1020) and resin (ZSC 2295) used in this study were obtained from M/s. Nippon Zeon Co., Ltd, Japan. The carbon black (N110 and N660) were obtained from M/s. Philips Carbon Black Ltd, India. The conductive grade carbon black 'Vulcan P' was supplied by M/s. Cabot Corporation, USA. The dicumyl peroxide 'Di-Cup R' was obtained from M/s. Hercules Incorporated, USA. Other materials like zinc oxide, stearic acid, sulphur etc. were of chemically pure and rubber grade.

2.2. Preparation of samples

The formulations of the mixes are given in Table I, and the physical properties of the vulcanizates are given in Table II. The rubber and other ingredients were mixed in a laboratory size two roll mixing mill (330 mm

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TABLE I Formulation of compounds

Ingredients	Compound Reference (p.h.r.)[a]														
	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13	D14	D15
ZETPOL 1020[b]	100	100	100	100	90	80	70	60	100	100	100	100	100	100	100
ZSC 2295[c]	–	–	–	–	10	20	30	40	–	–	–	–	–	–	–
Zinc oxide	2	2	2	5	2	2	2	2	2	2	2	2	2	2	2
Stearic acid	–	–	–	1	–	–	–	–	–	–	–	–	–	–	–
Sulphur	–	–	–	0.5	–	–	–	–	–	–	–	–	–	–	–
Carbon black N110	50	50	50	50	30	30	30	30	–	10	20	30	40	–	–
Vulcan P	–	–	–	–	–	–	–	–	–	–	–	–	–	50	–
Carbon black N660	–	–	–	–	–	–	–	–	–	–	–	–	–	–	50
TMTD[d]	–	–	–	2	–	–	–	–	–	–	–	–	–	–	–
MBT[e]	–	–	–	0.5	–	–	–	–	–	–	–	–	–	–	–
Di-Cup R	4.5	3.0	1.5	–	3.0	3.0	3.0	3.0	3	3	3	3	3	3	3
Total	156.5	155.0	153.5	159.0	135.0	135.0	135.0	135.0	105	115	125	135	145	155	155

[a] Parts per hundred parts of rubber

[b] Hydrogenated nitrile rubber with 44% acrylonitrile content and 25 (g/100g) iodine number

[c] Commercially available blend of zinc polymethylmethacrylate

[d] Tetramethylthiuram-disulphide

[e] Mercaptobenzothiazole

TABLE II Physical properties of compounds

Properties	Compound reference														
	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13	D14	D15
Optimum cure time @ 160 °C (Mint)	16	16	16	8	16	15	15	15	16	16	16	16	16	16	16
Specific gravity	1.15	1.15	1.15	1.17	1.13	1.15	1.18	1.18	0.99	1.04	1.08	1.12	1.14	1.15	1.15
Hardness (Shore A)	79	77	72	77	70	75	80	85	51	56	62	65	71	77	72
Tensile strength (MPa)	35.7	32.4	30.1	31.3	34.6	37.2	38.7	39.4	11.2	24.5	28.7	30.1	31.5	29.3	27.4
300% Mod. (MPa)	34.2	26.1	14.5	19.5	20.5	27.3	30.3	36.2	2.5	5.3	13.5	21.2	25.0	26.3	27.4
Elongation @ break (%)	320	400	600	500	450	400	350	320	600	500	450	400	400	350	300
Tear strength (N cm^{-1})	920	855	800	830	960	980	1010	1090	350	430	480	710	770	830	820
Volume fraction of rubber (V_r)	0.46	0.42	0.34	0.42	0.47	0.49	0.5	0.51	0.42	0.44	0.44	0.44	0.45	0.45	0.41

× 152 mm) according to ASTM D 3182–1984. Slabs were prepared by vulcanizing the mixes in a single day-light electrically heated press at 160 °C to its optimum cure time as determined from a Monsanto Rheometer (R-100S) Chart. The specimens for dynamic mechanical tests were punched out from the slabs and conditioned at room temperature for 48 h before commencing the test. The specimens of circular form having diameter 7 mm and thickness 1.5 mm were used.

2.3. Test procedure

The dynamic mechanical properties were measured using a Polymer Laboratories' PL–DMTA unit in the shear mode of deformation with double strain amplitude of 64 µm at a frequency of 10 Hz and a heating rate of 1 °C min^{-1}. The data acquired were analysed using a COMPAQ computer.

The cross-link density was measured in terms of volume fraction of rubber, V_r, in swollen gel in ethyl acetate solvent [10].

3. Results and discussion

3.1. Effect of cross-link density and cure system

Figs 1 and 2 show the effect of cross-link density on tan δ and storage modulus, G', respectively, for compounds D1, D2 and D3 which have a cross-link density in the order D1 > D2 > D3 (Table II). From Fig. 1 it is clear that the glass–rubber transition temperature is not influenced by the cross-link density. The tan δ remains same for all the compounds in the glassy and transition zone. In the plateau zone tan δ increases with decreasing cross-link density and then decreases in the high temperature zone. The storage modulus, G', remains the same for all the compounds in the glassy and transition zones and it decreases with decreasing cross-link density in the plateau zone. Similar results were reported [5] for EPDM with sulphur cure system. This could be explained as follows: if the cross-linking process is not accompanied by side reactions which significantly alter the chemical nature of the polymer, the effects on the monomeric friction coefficient and the position of the viscoelastic functions are extremely slight [11]. Since the peroxide curing forms carbon–carbon cross-links between two chain atoms which is not altering the chemical nature of the polymer, the values of tan δ and G' are unaffected in the glassy and transition zones. However, in the plateau zone tan δ is increasing with decreasing cross-link density which is attributed to the relaxation and slippage of dangling free ends and untrapped entanglements which are increasing with decreasing cross-link density [11].

Figs 3 and 4 show the effect of curing system on tan δ and G' for compounds D2 (peroxide cured) and D4 (sulphur cured) having a similar degree of cross-link density. In the glassy state no difference in tan δ and G'

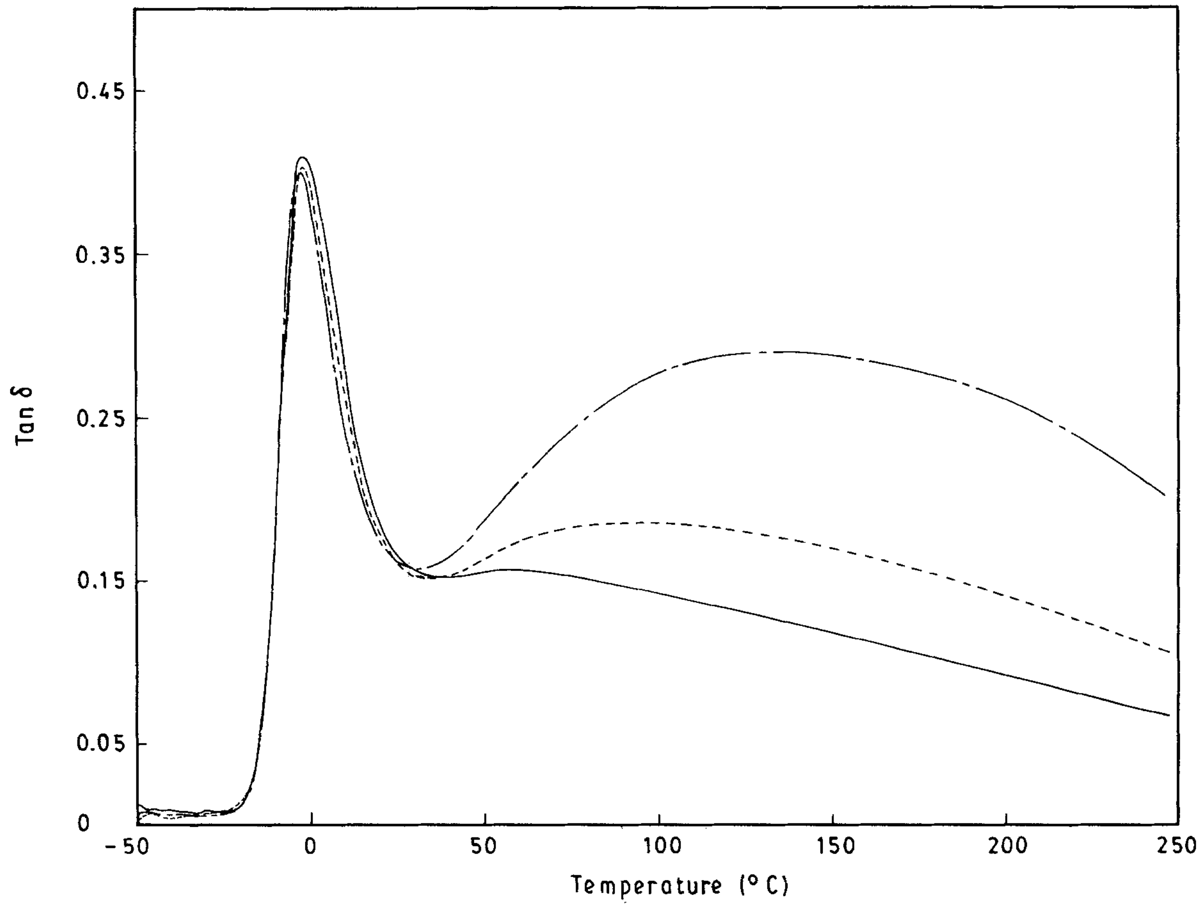

Figure 1 Tan δ as a function of temperature for the compounds having different degrees of cross-link density (D1 > D2 > D3): (——) D1; (– – –) D2 and (— - —) D3.

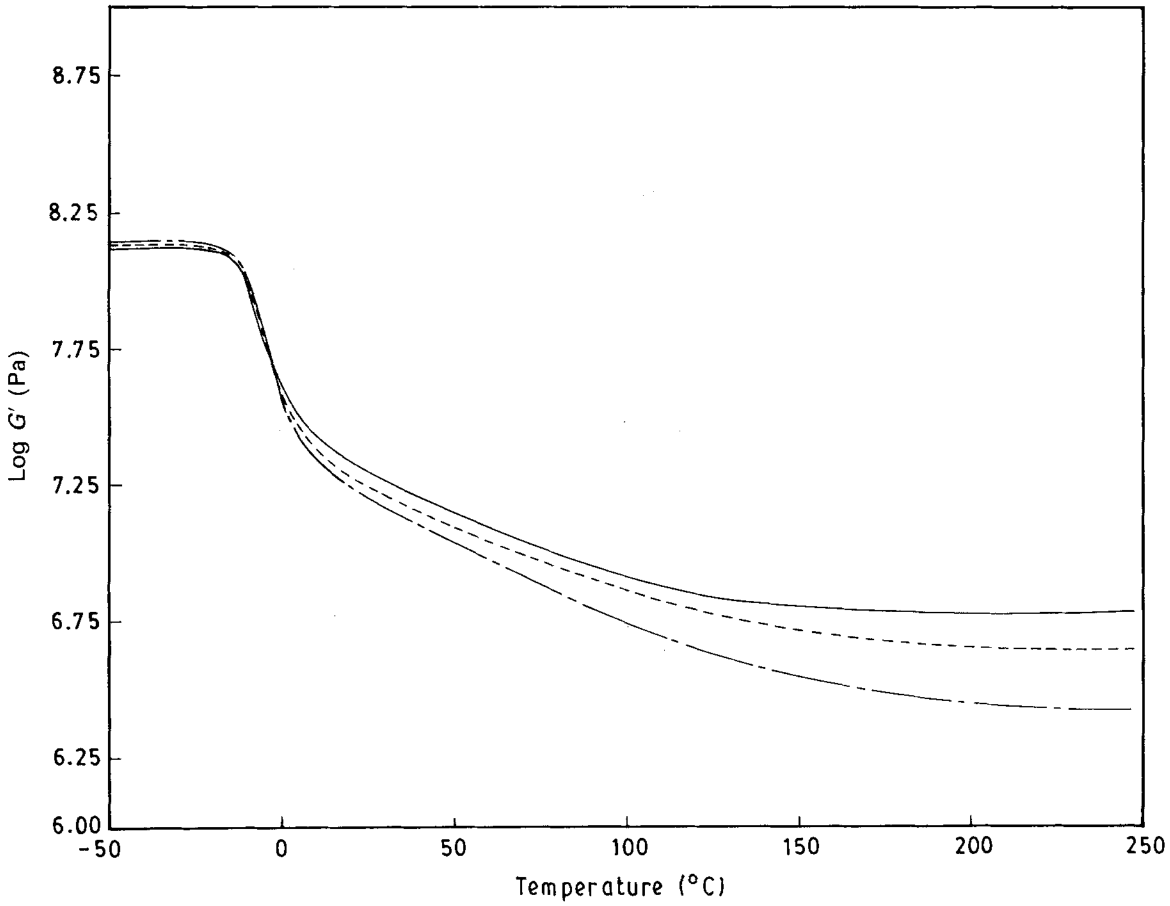

Figure 2 Storage modulus, G', as a function of temperature for the compounds having different degrees of cross-link density: (——) D1; (– – –) D2 and (—·—) D3.

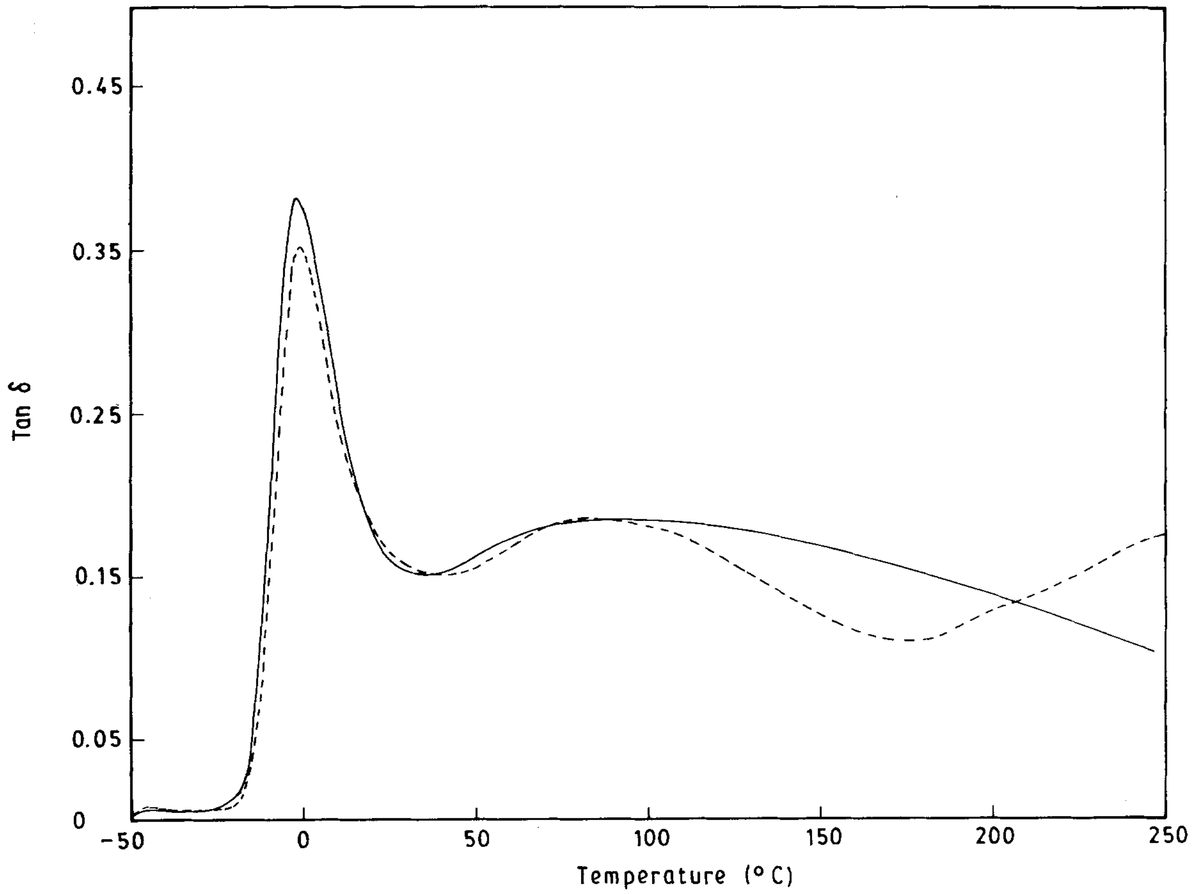

Figure 3 Tan δ as a function of temperature for the compounds cured with different curing systems: (—) D2 (peroxide cured) and (– – –) D4 (sulphur cured).

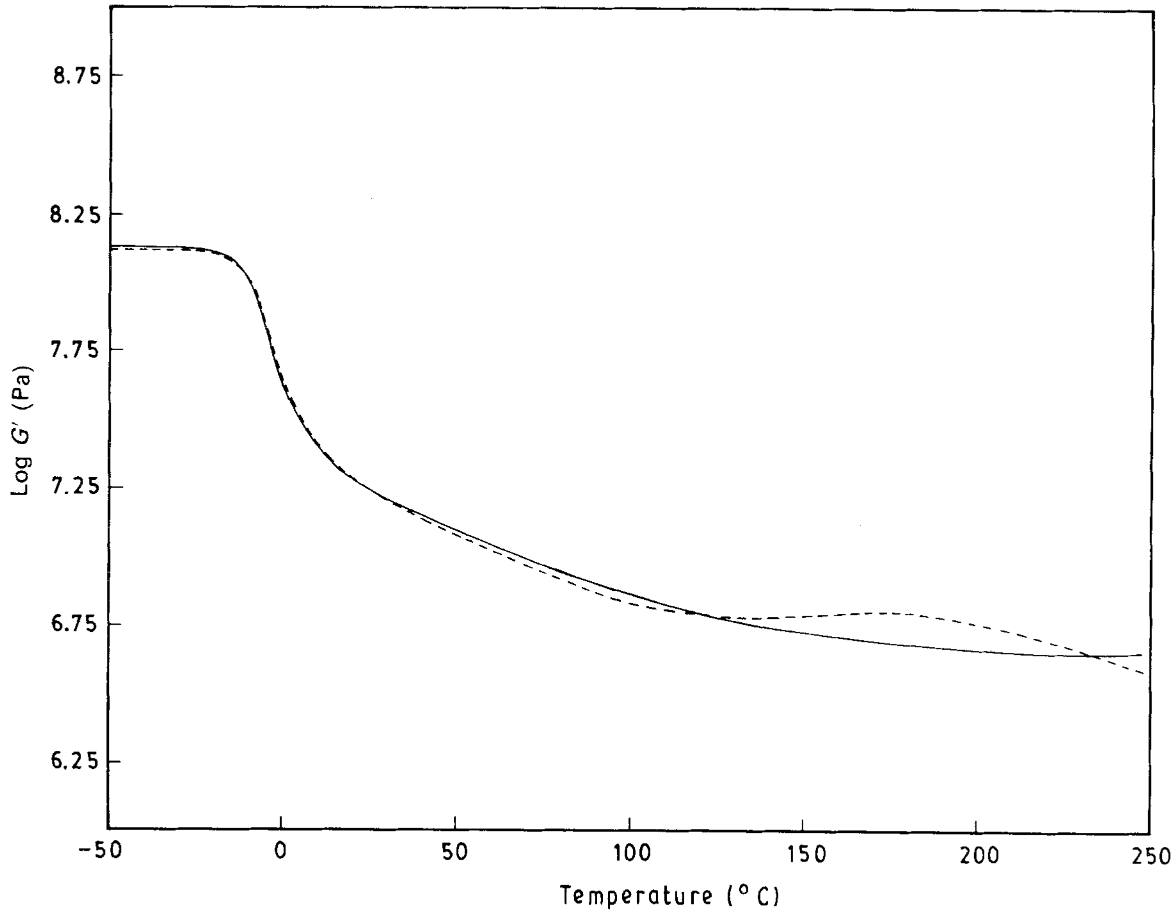

Figure 4 Storage modulus, G', as a function of temperature for the compounds cured with different curing systems: (——) D2 (peroxide cured) and (– – –) D4 (sulphur cured).

is observed, but in the transition zone tan δ peak height is reduced for the sulphur cure system (D4). The tan δ in the plateau zone increases upto 90 °C and then decreases with temperature for both the compounds. But in the sulphur cured system, from 90–180 °C the tan δ decreases drastically and then increases continuously with temperature. Similarly the G' value decreases continuously with temperature for the peroxide cured system (D2) while for the sulphur cured system (D4) G' decreases upto 90 °C then increases upto 180 °C and above that it decreases continuously with temperature. The observations could be explained as follows: the sulphur cross-linking reaction may modify the chemical nature of the polymer through sulphur cross-link formation, which increases the monomeric friction co-efficient substantially as in the case of NR [11]. Also the combined sulphur increases the cohesive energy density of the polymer and hence there is slight shift in the transition peak position (no apparent change in the glass transition temperature) and the tan δ transition peak height is reduced due to the perturbed relaxation of the molecules [11]. The increase in tan δ upto 90 °C is attributed to the relaxation of the dangling free ends and untrapped entanglements. The decrease in tan δ and increase in G' from 90–180 °C and the reverse in the high temperature zone was assumed to be post vulcanization reaction and cleavage of sulphidic linkage, respectively. In order to confirm this assumption one experiment with D4 was carried out upto 170 °C, then repeated upto 200 °C and again the experiment was repeated from 150–200 °C with the same sample. The storage modulus, G', of second run was more than the first run while the third run was less than the second run which supports the above assumption. The increase in volume fraction of rubber, V_r, of sample tested upto 170 °C also confirms the above assumption (V_r (initial) = 0.42, V_r (tested up to 170 °C) = 0.47).

3.2. Effect of resin

Figs 5 and 6 show the effect of resin concentration on tan δ and G' of compounds D5, D6, D7, D8 and D12. The resin concentration decreases in the order D8 > D7 > D6 > D5. Compound D12 is without resin. From Fig. 5 it is observed that the glass transition temperature is not much affected but the peak tan δ value is decreasing with increasing concentration of resin in the transition zone. Single tan δ peak maxima indicates the compatibility of the resin with rubber. Tan δ also converges at the middle of the plateau zone (130 °C) and then reverses. This is due to the fact that a post vulcanization reaction takes place in the compounds blended with resin and its rate increases with resin concentration. Above 150 °C decomposition of the polymer starts, rate of which decreases wih resin concentration. The storage modulus, G', from the transition zone increases with resin concentration at all the temperatures reported here. This indicates that resin ZSC 2295 reinforces the polymer matrix. This could be explained with the help of theory postulated

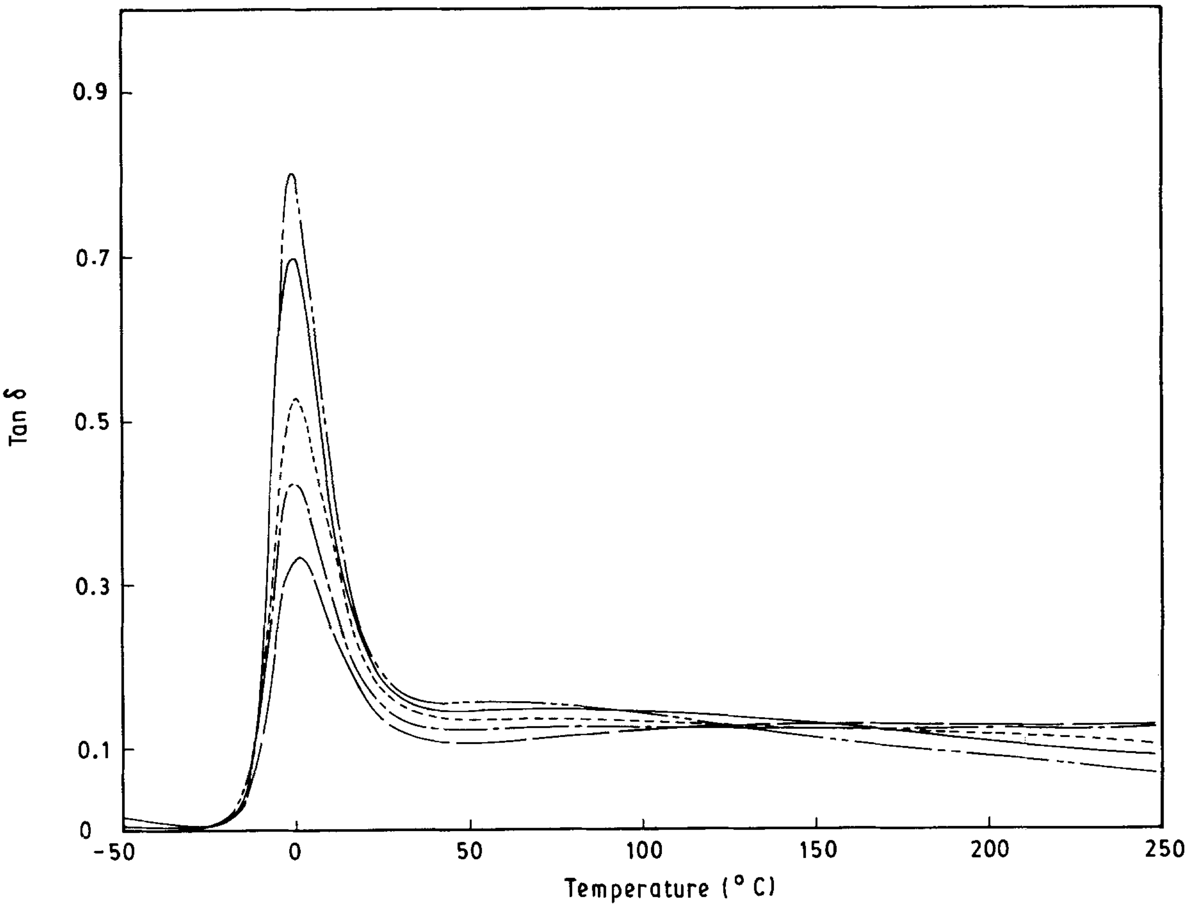

Figure 5 Variation of tan δ as a function of temperature for the compounds D5–D8 and D12: (—) D5; (- - - -) D6; (—-—) D7; (— —) D8 and (– – – –) D12.

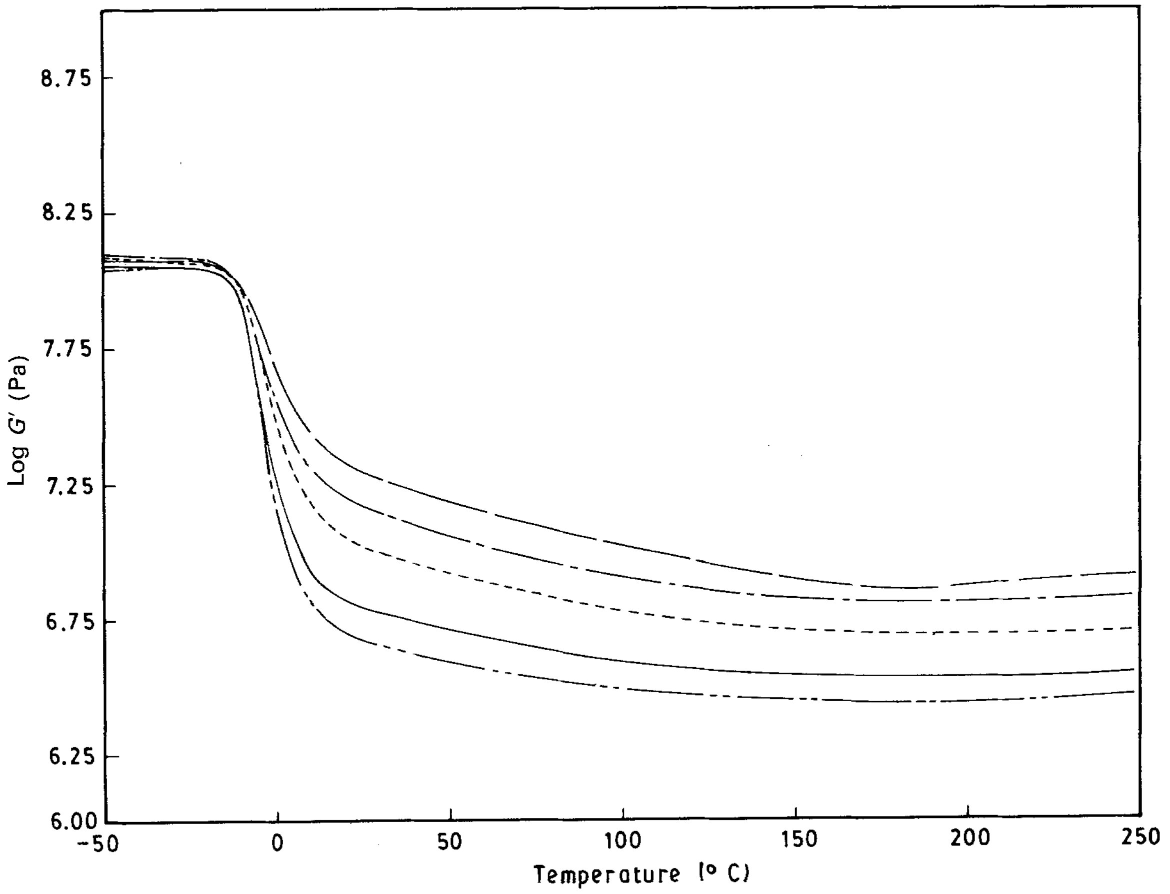

Figure 6 Variation of storage modulus, G', as a function of temperature for the compounds D5–D8 and D12: (——) D5; (- - - -) D6; (—-—) D7; (— —) D8 and (—-—) D12.

by Anfimov and Dontsove [12] for SBR–PMMA system that the ZSC 2295 reinforces the HNBR due to the formation of microcrystallites of zinc salt of polymethyl methacrylic acid polymer which graft on to the HNBR elastomer chain as shown in Fig. 7.

The effect of resin concentration on tan δ and G' for NR and SBR systems has been reported by Class and Chu [9]. Within the range of compatibility, temperature scan of rubber–resin systems showed a progressive increase in the temperature at which tan δ reached a peak and a progressive decrease in the modulus, G', of the rubbery plateau as the concentration of the resin was increased. But in this study tan δ peak temperature is not affected and a progressive increase in modulus, G', in the plateau zone with resin concentration is observed. This is due to the fact that in the investigation by Class and Chu [9], the resin in the rubber–resin system acted merely as physical blend and also as a diluent. Hence the tan δ peak temperature increased and modulus, G', progressively decreased with resin concentration. But in HNBR–ZSC 2295 system the resin is grafted on to elastomer chain and hence modulus, G', increased with resin concentration. The decreasing tan δ peak values may be due to perturbed relaxation caused by ZSC 2295 crystallites.

The plateau modulus of rubber–resin system, G', is related to that of rubber, G^0, by the following equation [9]:

$$G' = (V_p)^n G^0 \qquad (1)$$

where V_p is the volume fraction of the polymer.

Raju *et al.* [13] reported a value of 2.26 for the exponent n for polybutadiene in different oils and 2.22 for hydrogenated polybutadiene in waxes. In this study the value of n is negative and decreases with increasing V_p. The value of n lies between -6 to -1 corresponding to range of V_p values 0.799–0.832. It is also sensitive to the small changes in V_p.

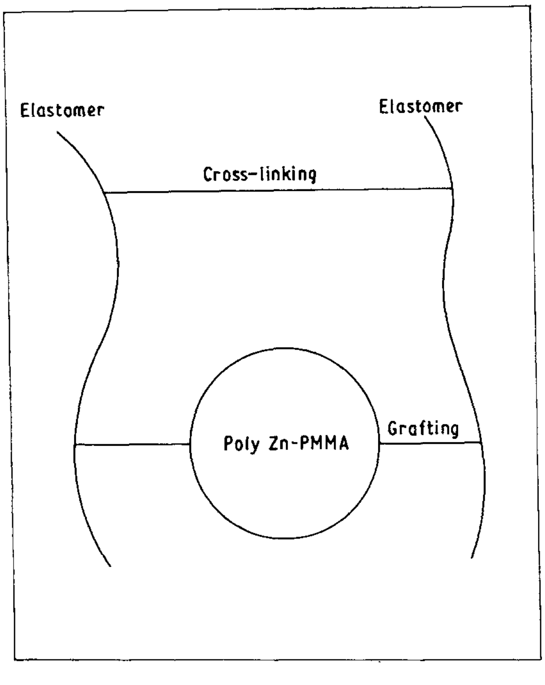

Figure 7 The probable reaction of ZSC 2295 with HNBR.

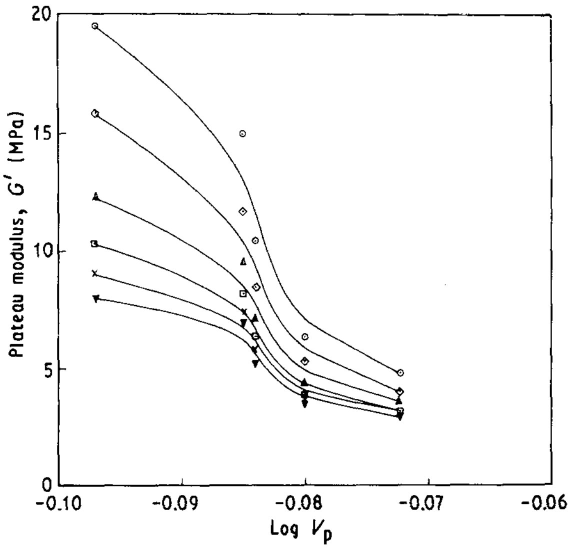

Figure 8 Variation of the plateau modulus, G', with log (V_p) at different temperatures: (○) 25; (◇) 50; (△) 75; (□) 100; (X) 125 and (▽) 150 °C.

The plateau modulus, G', is also plotted against log (V_p) as shown in Fig. 8. Class and Chu [9] have made a similar plot for NR and SBR with different resin systems where the G' increases with V_p. This observation clearly indicates that ZSC 2295 reinforces the HNBR matrix and hence the exponent n is negative.

3.3. Effect of carbon black

Figs 9 and 10 show the effect of carbon black on tan δ and G' as a function of temperature for compounds D9–D13 and D2. From Fig. 9 it is clear that in the glassy region tan δ is independent of carbon black loading. The tan δ peak value is progressively decreasing with filler loading and in the plateau zone it reverses and decreases in this order D9 > D10 > D11 > D12 > D13 > D2. But G' in all the regions increases with filler loading. The above observations could be explained as follows: investigations by Medalia [14] and Kraus [15] have shown that rubber occluded within the voids of primary aggregates of carbon black is not free to fully share in the microscopic deformation of a carbon black filled rubber. Some investigators [16] identified this immobilized rubber with bound rubber whereas, others through microscopic study [17], modulus and tensile measurements [18, 19] indicated the existence of a shell of immobilised rubber of definite thickness around vulcanizates. Medalia [20] suggested that due to their independent nature, occluded rubber, bound rubber and shell rubber can overlap each other and can form a complicated interlinked system. This adsorbed hard immobilized rubber fraction increases with carbon black loading. Since the adsorbed rubber perturbs the relaxation responses of matrix, a diffused maxima in tan δ value at the glass–rubber transition region (which decreases progressively with carbon black loading) is observed. The diffused maxima may be attributed to the superposition of different relaxation processes. In the glassy state the increase in G'

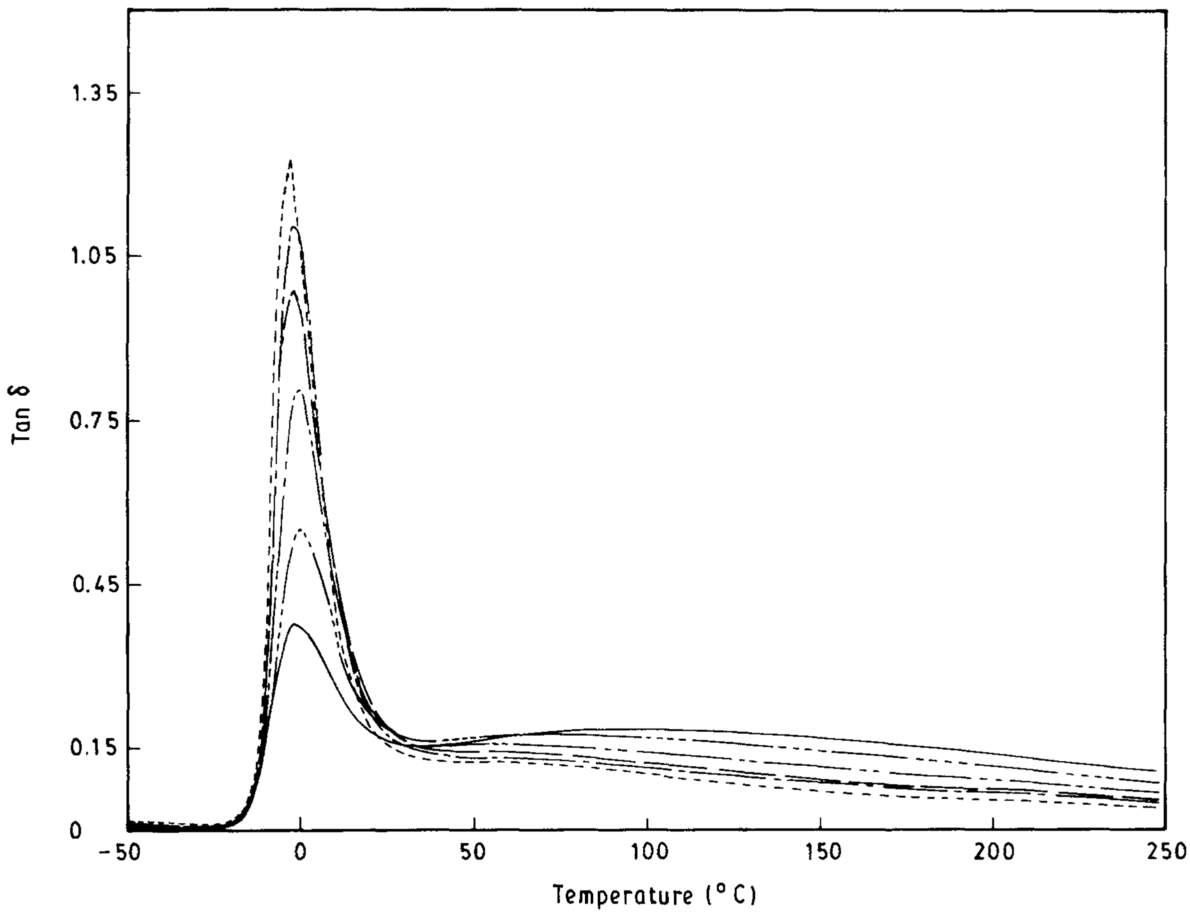

Figure 9 Variation of tan δ as a function of temperature for the compounds D9–D13 and D2: (—) D2; (- - -) D9; (— - —) D10; (— —) D11; (— - - - —) D12 and (— - - - - - —) D13.

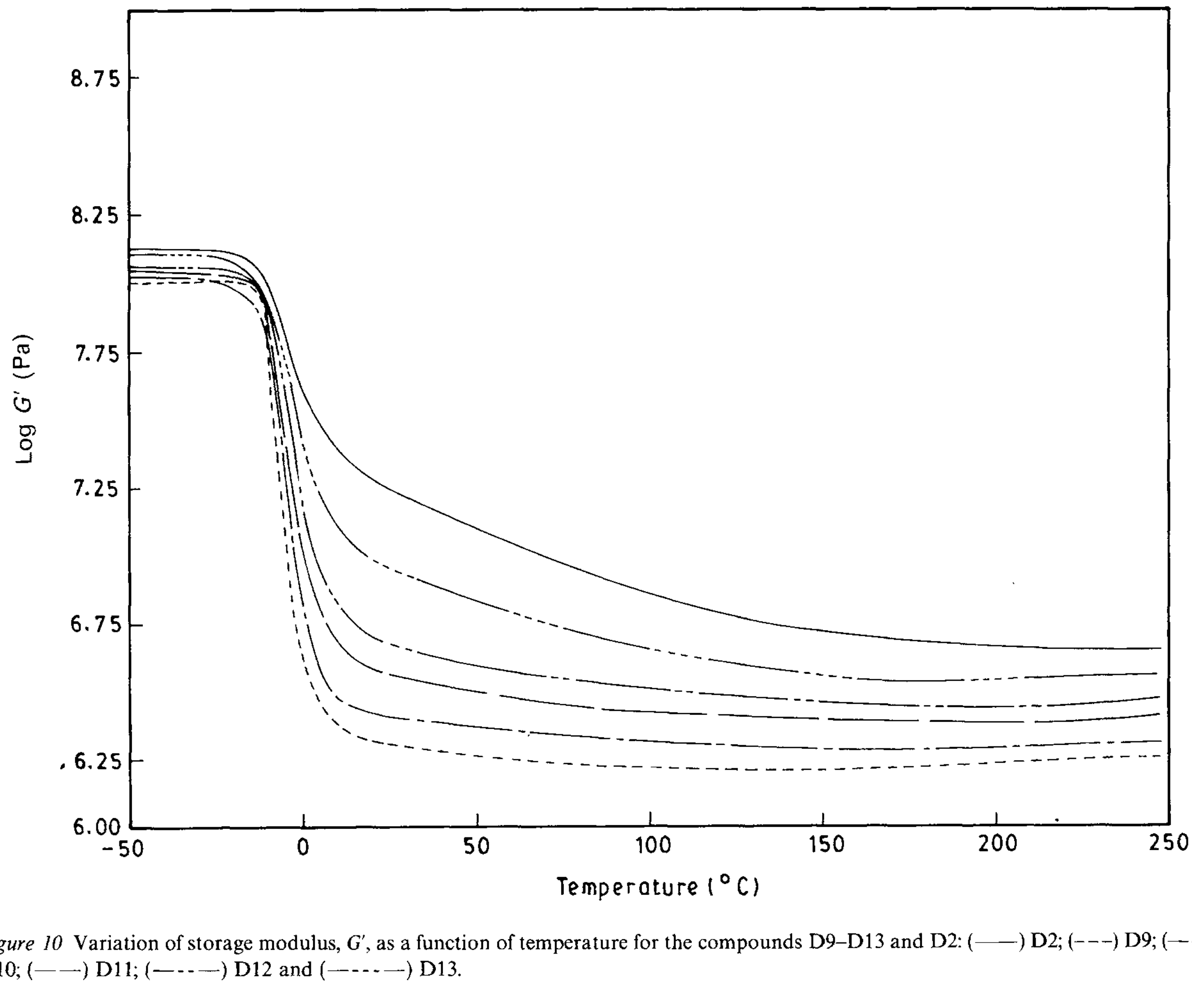

Figure 10 Variation of storage modulus, G', as a function of temperature for the compounds D9–D13 and D2: (——) D2; (- - -) D9; (— - —) D10; (— —) D11; (— - - —) D12 and (— - - - —) D13.

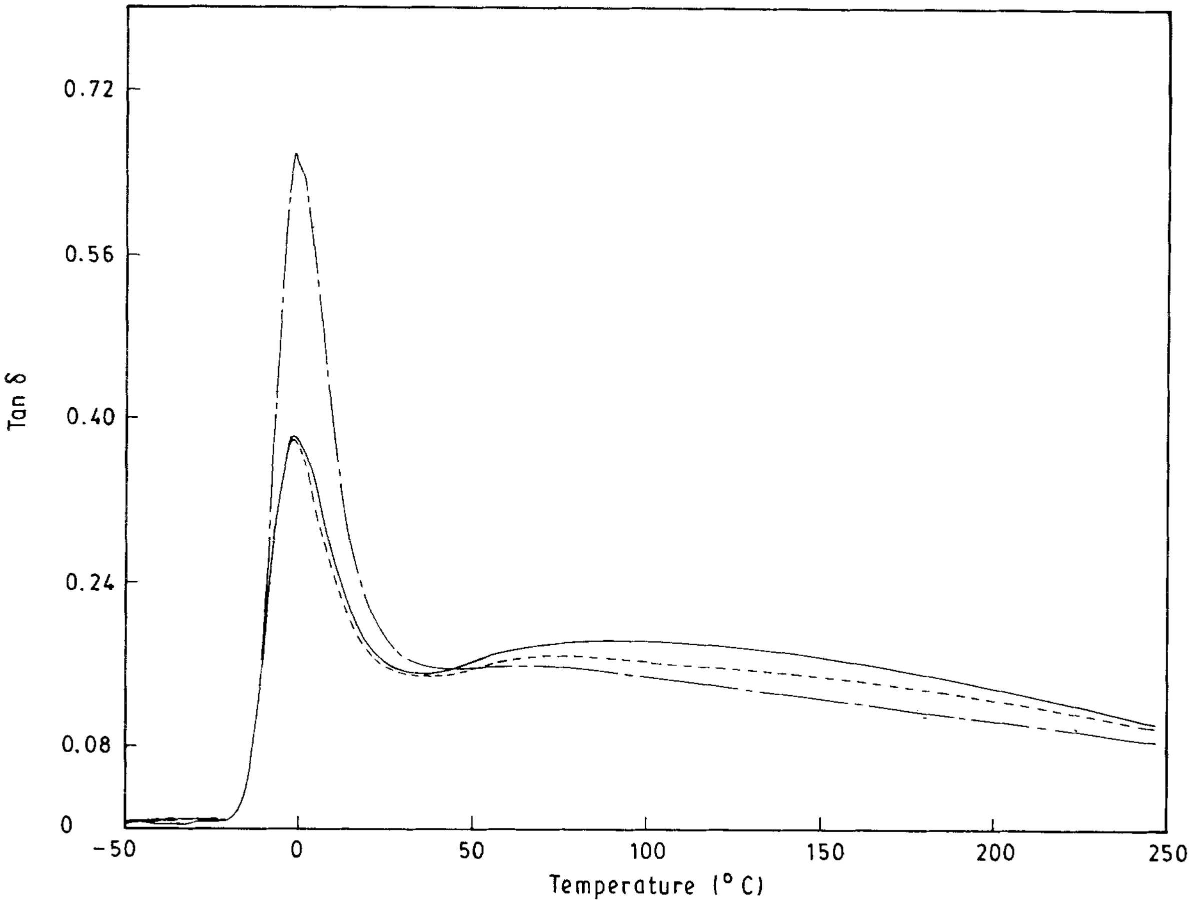

Figure 11 Variation of tan δ as a function of temperature for the vulcanizates having different types of carbon black at 50 phr loading: (—) D2 (N110); (– – –) D14 (Vulcan P) and (— – —) D15 (N660).

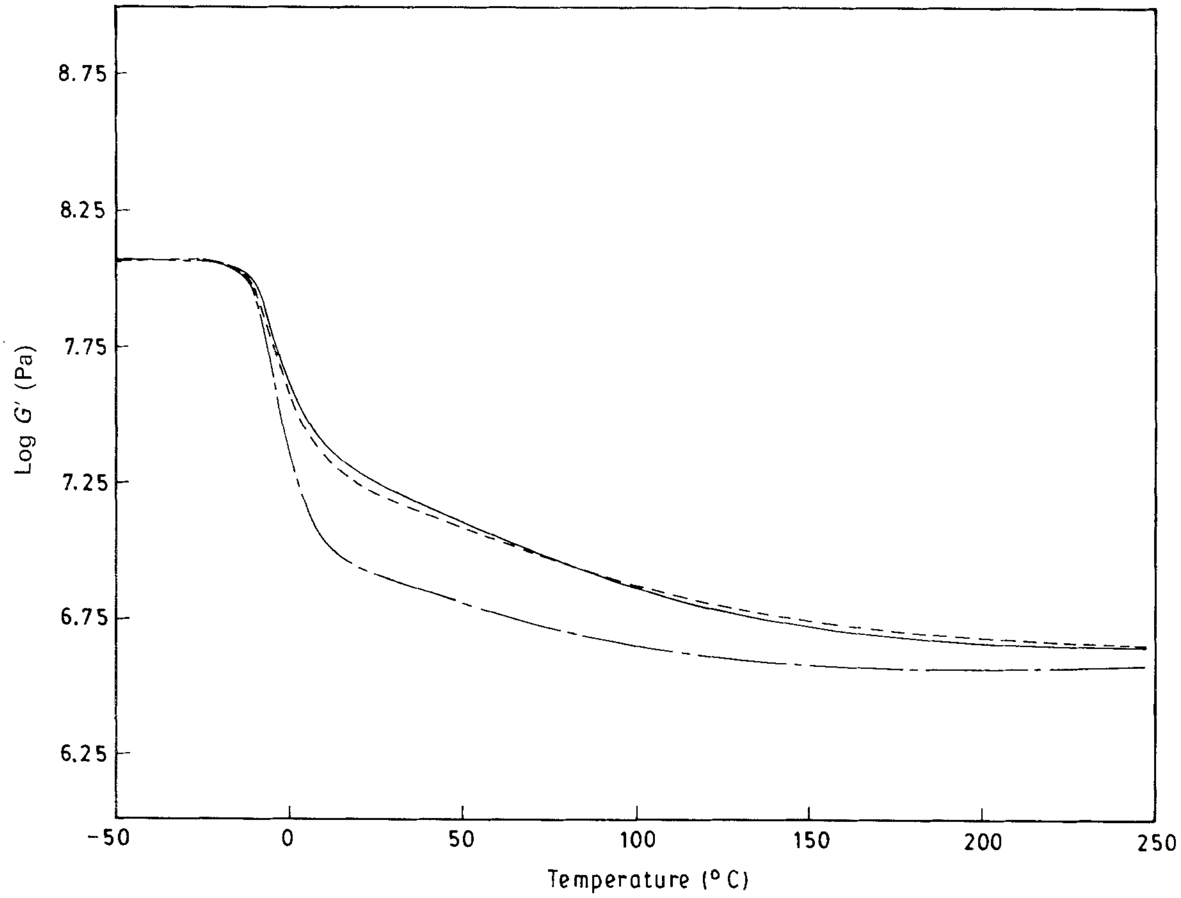

Figure 12 Variation of storage modulus, G', as a function of temperature for the compounds having different types of carbon black at 50 phr loading: (——) D2 (N110); (– – –) D14 (Vulcan P) and (— - —) D15 (N660).

TABLE III Properties of carbon black

PROPERTIES	SAF (N110)	Vulcan P	GPF (N660)
Nitrogen surface area ($m^2 g^{-1}$)	148	143	60
Dibutylphthalate absorption (cc $100 g^{-1}$)	113	118	90
Volume fraction of occluded rubber	0.270	0.295	0.202
Volatile content (% Max)	3.0	1.0	1.0

with filler loading may be attributed to the hydrodynamic effect of the carbon black particles embedded in the polymer continuum. Other factors like stronger filler–rubber interaction [21], tightening of the network associated with a shell of hindered rubber at the filler surface which increases the viscoelastic response of the elastomer [22] and the concept of occluded rubber could well explain the increase in G' with carbon black loading in the plateau zone.

Figs 11 and 12 show the effect of types of carbon black on tan δ and G' for compounds D2 (SAF), D14 (conductive carbon black) and D15 (GPF) as a function of temperature. The tan δ is not affected in the glassy region, but tan δ peak value is decreasing in the order D15 > D2 > D14 and in the rubbery plateau zone, tan δ value decreases in the reverse order. A similar explanation as mentioned above can be ascribed here also.

The volume fraction of occluded rubber $(\phi' - \phi)$ could be calculated from the dibutylphthalate absorption [23] (DBPA in cc per 100 g) by [14]

$$(\phi' - \phi)/\phi = [0.02139(\text{DBPA}) - 0.46]/1.46 \quad (2)$$

where ϕ is the volume fraction of filler and ϕ' is the volume fraction of filler plus occluded rubber.

The volume fraction of occluded rubber and the properties of carbon blacks are given in Table III.

It has been calculated that the storage modulus, Gm', of the filled compound from the experimental values of gum compound Gg' by modifying the Guth–Gold equation [24] as

$$Gm' = (1 + 2.5V + 14.1V^2)Gg' \quad (3)$$

where V is the effective volume fraction of carbon black, determined by taking an effectiveness factor [25] of 0.5 for the immobilized occluded rubber.

$$V/\phi = 0.5(1 + [1 + 0.02139(\text{DBPA})]/1.46) \quad (4)$$

In our experiment the calculated and the experimental values are in good accord with a value of 0.5 as an effectiveness factor upto 0.135 volume fraction of carbon black (30 PHR). Above this the calculated value is less. This is due to the fact that the carbon black aggregate network may also contribute to the storage modulus in addition to the occluded rubber.

4. Conclusions

1. HNBR vulcanizates having different degrees of cross-link density (D1 > D2 > D3) show the same tan δ, G' and glass–rubber transition temperature for peroxide curing system in the glassy region. In the rubbery plateau zone G' increases and tan δ decreases with increasing cross-link density. This is due to the relaxation and slippage of dangling free ends and untrapped entanglements which are increasing with decreasing cross-link density.

2. Vulcanizates with different cure systems (D2 (peroxide cured) and D4 (sulphur cured)) having the same degree of cross-link density show same value of tan δ and G' in the glassy state. But tan δ peak value at the transition zone is less for sulphur system. Also the tan δ decreases while G' increases from 90 to 180 °C due to post-vulcanization reaction. An opposite trend in tan δ and G', due to sulphidic link cleavage, is observed beyond 180 °C.

3. The blend of HNBR and ZSC 2295 (resin) has shown only one tan δ peak which indicates that the resin is compatible with HNBR in all the concentrations studied.

4. Blending HNBR with ZSC 2295 progressively increases the storage modulus, G', and reduces the tan δ without affecting the glass–rubber transition temperature.

5. The values of tan δ at the transition region decreases and that of G' in all the regions increases with filler loading. The vulcanizates with different types of carbon black (D2 (N110), D14 (conductive black) and D15 (N660)) at equal loading show lower tan δ values for high structure carbon black in the transition zone and higher values for high surface area carbon black in the plateau zone. The storage modulus is also increasing with surface area of carbon black.

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