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THERMAL AND VULCANIZATION KINETIC BEHAVIOUR OF ACRYLONITRILE BUTADIENE RUBBER REINFORCED BY CARBON BLACK

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The present paper discusses the results of assessing thermal properties, vulcanization kinetic and swelling properties of acrylonitrile butadiene rubber (NBR) reinforced by carbon black (N-330) with mass ratio 0 to 100 phr. The kinetic parameters were determined from two high temperature rheokinetic curves (T_1=180°C and T_2=190°C). The cross-linking density was calculated using swelling measurements. Thermal stability of the samples was measured in the temperature range between 25 and 750°C.

Keywords: *acrylonitrile butadiene rubber, carbon black, cross-linking density, swelling properties, thermal stabilty*

Introduction

Elastomer macromolecules must have double bonds in order for sulphur vulcanisation to take place. Sulphur addition causes adjoining macromolecular chains to link resulting in sulphur links (cross-linking) of the cyclic or –C–S_x–C-type [1, 2]. A simultaneous action of decay in the same links is seen to take place [3]. Active fillers are known to affect the cross-linking process during vulcanisation, resulting in mobile links different from sulphur bridges and covalent –C–C– links [4–6]. The most popular and practical measure method of the curing conversion is based on mechanical dynamical measurement of the isothermal torque *vs*. time at a given strain using a die rheometer [7]. The rheometric technique is usually employed in the examination of the filler effect on the cross-linking rate. Rheometer provides the effective cross-linking time across all types of links [8]. Scheel [9] was investigated and systematised kinetic curves on the basis of the mechanical properties of the rubber. Kinetic curves with maxim are explained in the following way: cross-linking and reversion reactions are first order reactions. They are simultaneous reactions. The intermediary product or cross-linking with a sulphur link concentration of c_{ln} is subject to decomposition resulting in a final product with a concentration of sulphur links c.

It follows from the above, that:

$$\mathrm{d}c_{in}/\mathrm{d}t=k_1(c_0-c_{in}) \qquad (1)$$

where c_0 is the initial concentration of the vulcanisation agent. The final concentration of the sulphur links can be obtained from the equation:

$$c=k_1c_0/(k_2-k_1)[\exp(-k_1t)-\exp(-k_2t)] \qquad (2)$$

where k_1 and k_2 are the cure rate constants of cross-linking and reversion, respectively, and t is the time. Eckelmann *et al*. [10, 11] demonstrated that the rheometric obtained resistance moment F measured during vulcanisation could be written in the form of the equation:

$$(F-F_a)=k_1(F_\infty-F_a)/(k_2-k_1)[\exp(-k_1t)-\exp(-k_2t)] \qquad (3)$$

This is, in turn, seen to be analogous to Eq. (2). F_a is the turning moment of the examined material, preceding the onset of vulcanisation, and F_∞ is the maximum turning moment providing the cross-linking reaction is the only ongoing process. The experimental maximum of the turning moment F_{max} is lower than F_∞ and is depends on temperature.

Equation (3) is simple to solve if $\omega=k_2/k_1$ and represent the time necessary to attain F_{max}:

$$k_1t_{max}=\frac{\ln\omega}{\omega-1} \qquad (4)$$

$$\frac{F_{max}-F_a}{F_\infty-F_a}=\omega^{\omega/(1-\omega)} \qquad (5)$$

The value of F_∞ evaluated from the kinetic curve in which reversion is not noticeable, and the values of F_{max}, F_a and t_{max} are evaluated from the curves registered by a rheometer at high temperatures (T_1=180°C and T_2=190°C).

The aim of this study was to investigate the effect of the mass ratio of carbon black on the thermal stability, vulcanization kinetics and swelling behaviour of acrylonitrile butadiene rubber compounds.

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Experimental

Materials

The elastomer used in this investigation was: acrylonitrile-butadiene rubber (NBR), type NBR-35 (‘Polysar’), containing 35% acrylonitrile. The reinforcing filler was carbon black (CB), type N-330 (‘Degussa’). The cure system included Vulkacit CZ (‘Bayer’), Vulkacit D (‘Bayer’), Sulphur (‘Zorka’). The compound formulations (Table 1) expressed in part per hundred parts of rubber, phr.

Mixing procedure

The compounds were prepared on a laboratory two-roll mixing mill, 152×300 mm, at a ratio rollers speed of n_1/n_2=21/28 at 50°C. The NBR rubber should be masticated for a few minutes. The activators, zinc oxide, stearic acid, resin and sulphur were then added, as well Vulkacit CZ and Vulkacit D together with an anti-ageing agent (4010 NA). Carbon black should be added after a few minutes, as well as plasticizer (Naftolen 40/2).

Sample preparation

After mixing, the elastomer compounds were moulded into 2 mm thick slabs to be used for determination of the original and aged properties. The slabs were moulded in a hydraulic press using moulding conditions previously determined from the torque data, obtained by a Monsanto Rheometer 100 S at 160°C. The cure time for each compound was defined as the time interval at which 90% of its maximum torque was reached. The test specimens were dying cut from test slabs.

Methods

Rheometric characteristic

The cure characteristics: M_l (minimum torque), M_h (maximum torque), t_{c90} (optimum cure time) and t_{s2} (scorch time) were determined with Monsanto Rheometer model 100C at 160°C in accordance with ASTM method D-2084.

Swelling measurement and determination of cross-linking density [12–15]

The samples (about 1 g) were accurately weighed (W) and immersed in about 30 mL of toluene in closed sample bottles and taken out after 8 days. The surfaces were dried with filter paper and the samples placed in a previously weighed bottle and quickly weighed (W’).

The volume swelling ratio (r_V) or the mass swelling ratio (r_W) was calculated using the sample masses before and after swelling, W and W’, and the densities of solvent and polymer q_l and q_p.

$$r_V = 1 + \frac{q_p}{q_1}\,\frac{W'}{W-1} \tag{6}$$

$$r_W = \frac{W'}{W} \tag{7}$$

$$\nu_{2g} = \frac{1}{r_V} \tag{8}$$

where ν_{2g} is the volume fraction of polymer in the swollen gel. From the value of ν_{2g} thus obtained, M_c was then calculated using Eq. (9) [12, 16–18].

$$\begin{aligned}&-[\ln(1-\nu_{2g}) + \nu_{2g} + \chi(\nu_{2g})^2] = \\ &= \frac{V_s q_p}{M_c}\left((\nu_{2g})^{1/3} - \frac{\nu_{2g}}{2}\right)\end{aligned} \tag{9}$$

where χ is the Flory–Huggins (rubber–toluene) interaction parameter and was taken as 0.435 for the NBR–toluene system in this calculation. V_s are the molar volume of toluene (106.4 cm^3 mol^{-1}).

Table 1 The NBR/CB compound formulations

Component/phr	Sample						
	1	2	3	4	5	6	7
NBR	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1
ZnO	5	5	5	5	5	5	5
Naftolen 40/2[a]	30	30	30	30	30	30	30
Resin	3	3	3	3	3	3	3
N330	0	20	40	50	60	80	100
4010 NA[b]	2	2	2	2	2	2	2
Vulkacit CZ[c]	1	1	1	1	1	1	1
Vulkacit D[c]	0.3	0.3	0.3	0.3	0.3	0.3	0.3
S	2.4	2.4	2.4	2.4	2.4	2.4	2.4

[a]Plasticizer, [b]anti-ageing agent, [c]accelerator

Table 2 The cure characteristics of NBR/CB compounds

Cure characteristics	Sample						
	1	2	3	4	5	6	7
M_h/daNm	68.1	3.7	4.2	6.1	11.4	24.8	33.7
M_l/daNm	7.5	2.9	3.2	3.5	3.7	5.9	9.1
ΔM/daNm	60.6	0.8	1	2.6	7.7	18.9	24.6
t_{s2}/min	3.47	–	22.43	6.68	3.16	2.60	2.28
t_{c90}/min	10.18	3.93	19.7	8.73	6.23	8.93	7.65

Thermal stability of the carbon black reinforced NBR rubber [19–23]

Thermogravimetric (TG) measurements have been performed on the Perkin Elmer TGS-2 instrument. Rubber samples were heated from 25 to 750°C at the heating rate of 10°C min^{-1} in nitrogen atmosphere with the gas flow rate of 50 $\text{cm}^3\ \text{min}^{-1}$. The mass of the samples ranged from 17 to 25 mg.

Results and discussion

Cure characteristics

Table 2 shows the cure characteristics, such as delta torque (ΔM) (difference between the maximum and minimum torques), scorch time (t_{s2}) and optimum cure time (t_{c90}), of the compounds at 160°C. The values of maximum and minimum torque (M_h and M_l) and delta torque (ΔM) are increased with the increase of the CB loading filler of the NBR cross-linking systems. They are shown significant lower values than unfilled NBR compounds. The values of delta torques depends on the amounts of free curatives in the compounds mainly, and could be used as an indirect indication of the cross-link density of the rubber compound. As can be seen, the values of ΔM and cross-linking density ρ_p (Table 4) are increased continuosly with increasing CB loading. Both, t_{s2} and t_{c90} are found to decrease noticeably with CB loading increasing.

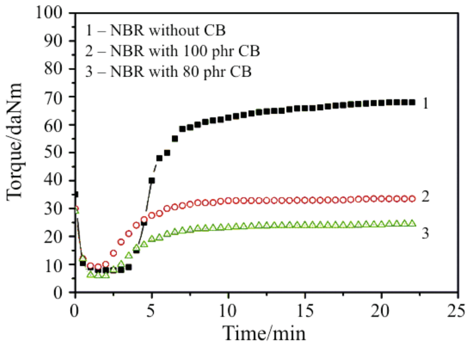

Fig. 1 Torque *vs.* time during curing of NBR compounds filled with and without CB

According to the data obtained from the rheometric curves (Fig. 1) of the examined compounds with different mass ratio of carbon black (Table 2) it appears, that sample 5 with 60 phr carbon black has the same values of t_{s2} as sample 1 (without filler). t_{c90} of sample 5 is shorter than the values of samples 1–4 and 6–7.

Kinetic characteristics and cross-linking and reversion activation energy

The kinetic parameters, activation energies of cross-linking (E_{ac}) and the reversion (E_{ar}), are given in Table 3, and they were calculated by applying Eqs (3)–(5).

Table 3 Activation energy of cross-linking (E_{ac}) and reversion (E_{ar}) and E_{ar}/E_{ac} ratio of NBR/CB compounds

Kinetic parameters	Sample						
	1	2	3	4	5	6	7
E_{ac}/kJ mol^{-1}	102	36	14	32	10	91	15
E_{ar}/kJ mol^{-1}	506	135	186	420	156	120	343
E_{ar}/E_{ac}	4.9	3.8	13.6	13.1	16.3	1.4	2.2

With the carbon black ratio increase in the elastomer matrix initiates the formation of points with different local carbon black concentration and causes and increase of the E_{ar}/E_{ac} ratio, which has a maximum in sample 5. Further increase of the amount of carbon black does not only indicate filler–elastomer interaction, but also filler–filler interaction and even the formation of a three-dimensional filler matrix. Increasing fraction of the filler causing contact between some filler particles and when the concentration reach certain value it is forming three-dimensional network. Since the activation energies of both, cross-linking and reversion process can be taken as criteria for energy compatibility of the examined compounds. Since the tendency is to make a type with the smallest possible E_{ac} and at the same time, retain the basic physical and mechanical characteristics, it can be seen from the results that sample 5 meets the criteria. According to the calculated values for E_{ac} and E_{ar}, the correct choice of filler can be made, if it is known that all the changes are correlated with the mass ratio of carbon black.

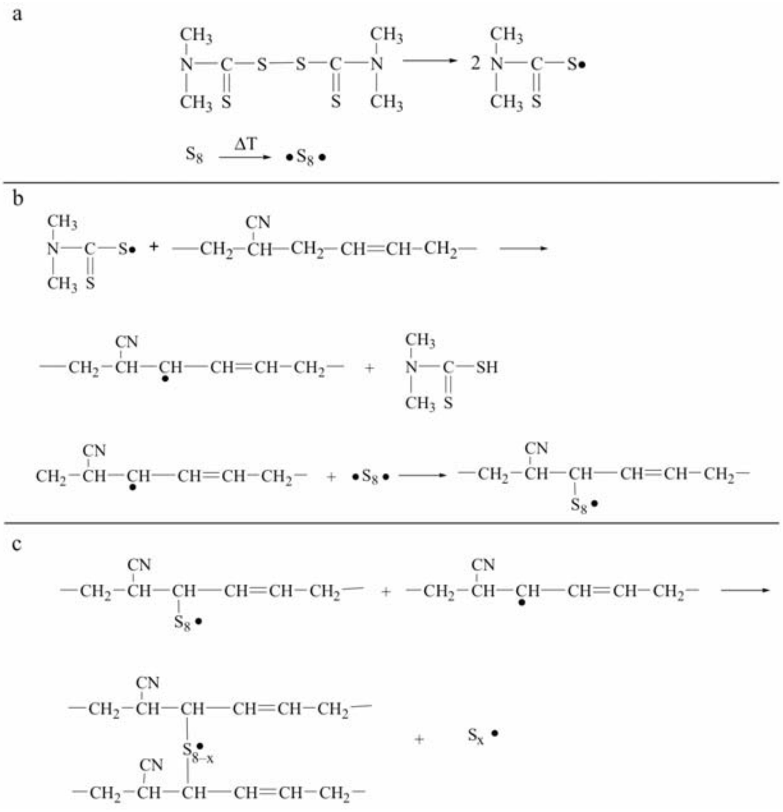

Fig. 2 Reaction scheme of NBR sulphur cross-linking: a – radical formation, b – propagation and c – cross-linking

Cross-linking density

In Fig. 2 reaction scheme of NBR sulphur cross-linking is shown.

The calculated values of the cross-linking density and number average molecular mass of the chain between effective cross-links, M_c, of the rubber vulcanisates are given in Table 4.

The values of r_W and r_V decrease with increasing amount of carbon black. The polymer volume ratio ν_{2g} increased with increasing carbon black concentration and was the largest for the sample containing a carbon black amount of 100 phr. The largest chain molecular mass was obtained for sample 1 (unfilled) and the smallest for the sample 7 with the highest amount of carbon black.

The swelling degree decrease can be explained by linkage combination between polymer chains and functional groups on the carbon black surface, and by a possible increase in cross-linking bonds in the polymer matrix because of filler influence on the vulcanization reaction [24]. Even with low carbon black concentrations, the observed vulcanizates developed a three-dimensional structure. The filled vulcanizates always has higher link concentrations of the vulcanization matrix than their unfilled analogues [25].

The polymer volume ratio ν_{2g} in the swelled samples increased with the amount of carbon black and reached a maximum in the case of sample 7. The increase carbon black concentration caused a decrease in M_c, i.e., a decrease of the fraction, as well as the degree of elastomer interaction with solvent due to the matrix forming effective density. The increase of polymer volume ratio in the swollen samples, as well as the decrease in M_c, can be explained by the formation of a filler matrix structure.

Table 4 The cross-linking density of NBR/CB compounds

Kinetic parameters	Sample						
	1	2	3	4	5	6	7
ρ_p/g cm^{-3}	1.04	1.06	1.09	1.11	1.13	1.17	1.21
r_W	3.19	2.67	2.40	2.33	2.19	2.01	1.86
r_V	3.53	3.04	2.76	2.72	2.55	2.36	2.20
ν_{2g}	0.283	0.328	0.361	0.367	0.391	0.422	0.453
M_c/g mol^{-1}	3930	2574	2121	1981	1696	1369	1144

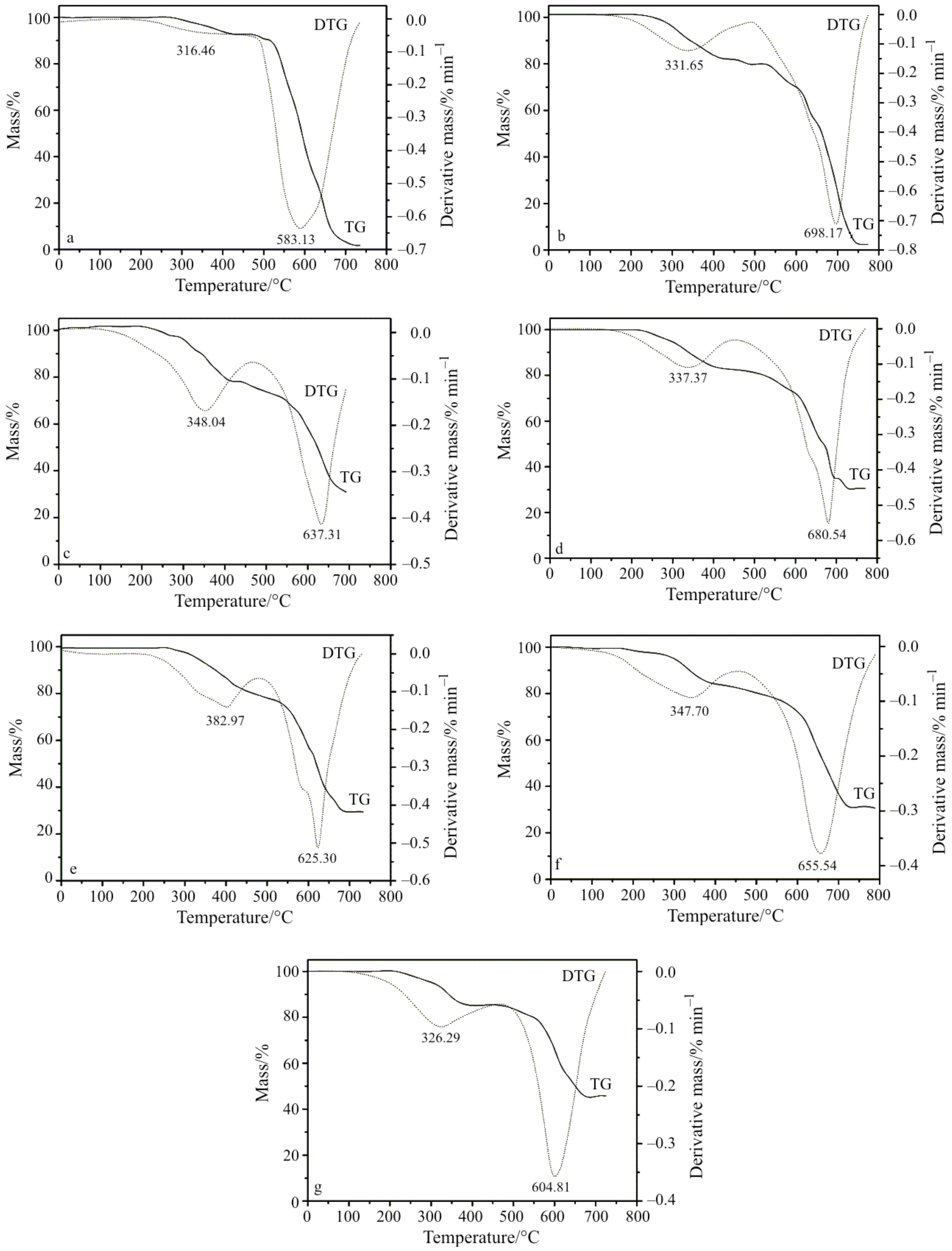

Fig. 3 Thermal decomposition of NBR/CB reinforced rubber: a – NBR/CB (100/0), b – NBR/CB (100/20), c – NBR/CB (100/40), d – NBR/CB (100/50), e – NBR/CB (100/60), f – NBR/CB (100/80), g – NBR/CB (100/100)

Table 5 The temperature values of NBR/CB compounds for selected mass loss (0.5, 10 and 30%)

Compound	Sample						
	1	2	3	4	5	6	7
Mass of sample/mg	22.2	17.8	23.9	20.35	21.3	24.5	18.45
DTG peak/°C	316.46 583.13	331.65 698.17	348.04 637.31	337.37 680.54	382.97 625.89	347.70 655.54	326.29 604.81
Mass loss/%	7.01 90.54	18.49 79.06	21.38 46.65	16.64 53.16	22.37 47.43	15.69 53.34	14.74 40.01
Total mass loss/%	97.55	97.55	68.03	69.8	69.8	69.03	54.75
Temperature values for selected mass loss							
$T_{0.5\%}$/°C	377	307	307	287	327	297	299
$T_{10\%}$/°C	489	345	345	339	373	339	341
$T_{30\%}$/°C	514	602	546	612	568	610	588

Thermal stability of the NBR/CB compounds

The data for the initial decomposition temperature (IDT) (0.5% mass loss), 10 and 30% mass loss temperatures are given in Table 5. It can be seen that according to the IDT unfilled NBR compounds has the best stability (377°C) than carbon black reinforced compounds. In the next step (at 10% mass loss) the order is the same, but at 30% mass loss the NBR/CB (100/50) compounds (sample 4) is the most stable than other compounds.

Figure 3 shows that unfilled NBR compounds initially more stable than other samples. Among the most important factors that can influence the initial TG behaviour are the strength of the bonds in the main polymer chain, the cross-linking density, i.e. concentration of free chain ends whose extraction would lead to mass loss and polymer chain flexibility which is affected by polymer structure and cross-linking density.

In the NBR/CB rubber compounds (Fig. 3 and Table 5) the degradation takes place in two stages. Up to 300°C, there is no change and hence no mass loss. The first-step degradation occurs in the temperature region 300–400°C and the mass loss is ranged to 7.01–22.37% (depending on the amount of CB in NBR rubber) most probably indicating the evaporation of oil (naftolen 40/2). The second-step degradation starts at 580°C and ends at 700°C. The percent of mass loss at this region is ranged to 40.01–90.54% indicating polymer degradation. The large flexible polysulfidic linkages (Fig. 2) undergo chain scission and convert into monosulfidic and disulfidic linkages. Synthetic rubber decomposes by random-chain scission with intramolecular hydrogen transfer [26]. Table 5 presents the DTG peak values of NBR/CB rubber compounds. The shift of values of the DTG peaks to a high temperature indicating increased thermal stability.

Conclusions

The results obtained allowed for the following conclusions to be made concerning the cure and kinetic characteristics, thermal stability and cross-linking density of the NBR/CB rubber compounds: The M_l and M_h increase, but t_{s2} values decrease with carbon black increasing. Carbon black activated the vulcanizing process through the promotion of hydrogen sulfide formation and the rapture of S–N linkage when heated with sulfhenamides in rubber either in the present or absence of other compounding ingredients. The t_{c90} values remain quasi constant for samples no. 4–7; the cross-linking density increases with increasing amount of carbon black; the values r_V, r_W and M_c decrease but ν_{2g} and the matrix forming density increase with increasing fraction of carbon black. Organic functional groups of carbon black surface lead to an increase of the adhesion at interface between carbon black and the rubber matrix, resulting thermal stability and mechanical interfacial properties of the NBR/CB (100:50) compounds.

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