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The effect of different types of carbon blacks on the rheological and thermal properties of acrylonitrile butadiene rubber

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Abstract The influence of two types of carbon black filler N330 and N990 (primary particle size 46 nm and >230 nm) on elastomeric composites based on acrylonitrile-butadiene rubber (NBR) have been investigated. The activation energy (E_a) were determined from two high temperature rheokinetic curves (T_1 = 180 °C and T_2 = 190 °C). For tensile testing, the compounds with different content of carbon black were vulcanized in a hydraulic press at 150 °C. The stress-strain experiments were performed before and after ageing the specimens in an air-circulating oven at 100 °C for 168 h. The thermal degradation and thermal stability of carbon black filled NBR rubber was investigated by thermogravimetric analysis in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Keywords Acrylonitrile butadiene rubber · Cross-linking density · Mechanical properties · N330 and N990 type carbon black · Swelling properties · Thermal stability

Introduction

The rubber industry began when Goodyear developed the first useful rubber compound: natural rubber plus sulfur. The concept of mixing materials into rubber to improve performance is still of primary importance today. Without compounding, few rubber goods would be of any commercial value. The curing process is the final step in tire manufacturing whereby green rubber goods is formed to the desired shape in a press. In curing press, heat is transferred to the tire from the surfaces, which are maintained at high temperatures, inducing the curing reaction of the rubber compounds, thereby converting them to a strong elastic material. The vulcanization process is optimized to achieve an optimal curing state for the rubber goods, which ensure the mechanical properties, required of each component. The prediction of the curing state is usually determined by employing a rheometer, in which the kinetics is described by the torque variation during curing [1–3].

Many authors have investigated the role of filler networking in the elastic properties of elastomer composites [4–7]. Filler–filler interactions are a primary mechanism in reinforcement, especially at high filler loading. These interactions depend on chemical interactions between the filler particle surfaces (filler–filler, filler–rubber), physical interactions (van der Waals forces, hydrogen bonding), morphology of the filler network, and filler volume fraction. The reinforcement of elastomers by fillers has been studied in depth in numerous investigations [8] and it is generally accepted that this phenomenon is dependent, to a large extent, on polymer properties, filler properties and processing [9, 10]. Generally speaking, the primary filler factors influencing elastomer reinforcement are:

- The primary particle size or specific surface area, which, together with loading, determines the effective contact area between the filler and polymer matrix.

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- The structure or the degree of irregularity of the filler unit, which plays an essential role in the restrictive motion of elastomer chains under strain.
- The surface activity, which is the predominant factor with regard to filler–filler and filler–polymer interaction.

The size of spherical particles is called “particle size,” and the size of the particle chain is called “structure.” Various functional groups such as the hydroxyl or carboxyl group are found in the surface of carbon black, and their amount or composition is called “surface chemistry.” These three—“particle size,” “structure,” and “surface chemistry”—are the basic properties of carbon black, and together are called the three main characteristics (Fig. 1). The three main properties have a large effect on practical properties such as blackness and dispersibility when they are mixed with inks, paints, or resins.

Nitrile rubber (NBR) is used in automobiles because of its resistance to fuels, a variety of oils and other fluids over a wide range of temperatures. However, nitrile rubber, as such cannot be used in specific applications requiring high heat and ozone resistance. The poor ozone resistance and heat ageing properties of NBR (which is a random copolymer of acrylonitrile and butadiene) are believed to be the result of unsaturation in the backbone of the polymer which permits scission of the polymer chain to occur under certain adverse conditions.

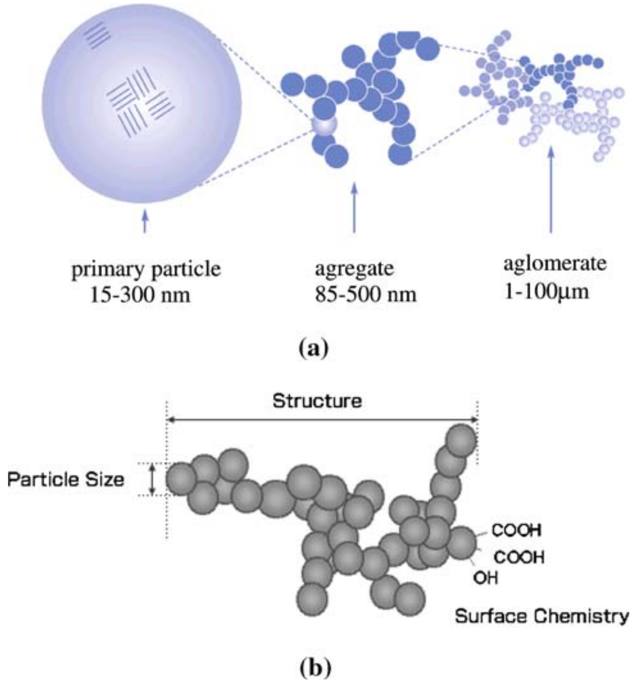

Fig. 1 **a** Dimension of carbon black primary particle size and dimension of aggregate and agglomerate which have been made in cross linking reaction of elastomer and filler. **b** Basic properties of carbon black

In this study, an experimental work was designed to measure the properties of rubber compounds by using NBR rubber filled with N990 type of carbon black and compared with NBR rubber filled with N330 type of carbon black [11]. So the different compounds based NBR rubber were prepared with various carbon black and made vulcanization tests according to standard test methods. The test results were discussed to determine the suitable type of carbon black for the desired properties of rubber compound.

Experimental

Materials

The following materials were employed in the study reported here.

Rubber

1. Nitrile rubber (NBR Kraynac 34-50, “Polysar” Canada) with acrylonitrile content 33, 2%: Moony viscosity at 100 °C, 50; specific gravity 1.17 g cm^{-3}; ash content 0.5%.

Filler

1. High abrasion furnace carbon black, N330 (“Degussa”): Black granulated powder has a particle size of 46 nm and specific gravity 1.78–1.82 g cm^{-3}. CTAB surface area 83 ± 6 m^2/g. DBP absorption number 102 cm^3/100 g.
2. Thermal carbon black, N990 (“Degussa”): Black granulated powder has a particle size of high 230 nm and specific gravity 1.80–1.85 g cm^{-3}. CTAB surface area 7 m^2/g. DBP absorption number 40 ± 5 cm^3/100 g.

Accelerators

1. *N*-cyclohexyl-2-benzothiazole sulfonamide (Vulkacit CZ): pale grey; non hygroscopic powder; melting point 95–100 °C and specific gravity 1.27–1.31 g cm^{-3}.
2. 1,3 diphenylquanidine (Vulkacit D): non hygroscopic white to light pinkish powder; melting point 140 °C, specific gravity 1.13–1.15 g cm^{-3}.

Antioxidants

1. *N*-isopropyl-*N*-phenyl-*p*-phenylendiamine (Vulkanox 4010 NA): specific gravity 1.14–1.18 g cm^{-3}.

Curing agent

1. Sulphur: Pale yellow powder of sulphur element; purity 99.9%; melting point 112 °C; specific gravity 2.04–2.06 g cm^{-3}.

Activator

1. Zinc oxide: fine powder; purity 99%; specific gravity 5.6 g cm^{-3}.
2. Stearic acid: melting point 67–69 °C; specific gravity 0.838 g cm^{-3}.

Plasticizer

1. Naftolen 40/2: naphthenic oil light yellow; specific gravity 0.936 g cm^{-3}; viscosity at 50 °C 5, 5–6°E; flash point 175 °C.

Methods of preparations

Mixing

The compounds (Table 1) were prepared using a laboratory mixing roll mill of dimensions 400 × 150 mm at a speed ratio of the rollers $n_1/n_2 = 28/22$, at a roller temperature of 40–50 °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 (CB) should be added after a few minutes, as well as plasticizer (Naftolen 40/2). The compound rubber was allowed to stand over night before vulcanization. After mixing, the elastomer compounds were molded into 2 mm thick slabs to be used for determination of the original and aged properties. The slabs were molded in a hydraulic press using molding 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.

Table 1 The NBR/CB compounds formulations with N990 type of carbon black content

Components (phr)	Sample					
	1	2	3	4	5	6
NBR	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
ZnO	5	5	5	5	5	5
Naftolen 40/2[a]	30	30	30	30	30	30
Resin	3	3	3	3	3	3
N990	20	40	50	60	80	100
4010 NA[b]	2	2	2	2	2	2
Vulkacit CZ[c]	1	1	1	1	1	1
Vulkacit D[c]	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

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

Vulcanization

The vulcanizates were prepared by curing at 150 °C for optimum cure time using an electrical press under a pressure of about 60 MPa.

Methods of characterization

Rheometric characteristic

The cure characteristics: *Ml* (minimum torque), *Mh* (maximum torque), t_{c90} (optimum cure time) and t_{s2} (scorch time) were determined with a Monsanto Rheometer model 100C at 150 °C in accordance with ASTM method D-2084.

Curing kinetics

The kinetic parameters of the cross linking process, such apparent activation energy of cross linking (E_{ac}) and reversion (E_{ar}) were calculated from the torque-time curves taken from experiments performed on accelerated-sulfur curing systems using oscillating disk rheometer (Monsanto Rheometer model 100C) at two temperature (180 °and 190 °C).

Measurement of mechanical properties

For the tensile experiment, dumbbell samples were cut from a 2 mm thick molded sheet. Mechanical properties: tensile strength and elongation at break were measured at room temperature on an electric tensile testing machine (Zwick 1425) according to ASTM D 412. Hardness was measured using an indentation hardness tester according to ISO7619. To investigate the influence of thermal aging on the mechanical properties, the vulcanizates were performed in an air circulating oven operated at 100 °C for 168 h. The retained value of percentage in tensile strength and elongation at break were calculated.

The compounds formulations (Table 1) expressed in part per hundred parts of rubber, phr.

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 mass before and after swelling, W and W', and the densities of solvent and polymer q_l and q_p.

$$r_V = 1 + \left(q_p/q_l\right)\left(W'/W - 1\right) \quad (1)$$

$$r_W = W'/W \quad (2)$$

$$v_{2g} = 1/r_V \quad (3)$$

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

$$\left[-\ln(1 - v_{2g}) + v_{2g} + \chi(v_{2g})^2\right] = \left(V_s q_p/M_c\right)\left[(v_{2g})^{1/3} - v_{2g}/2\right] \quad (4)$$

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}).

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

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

Results and discussions

Cure characteristics

Table 2 show the cure characteristics, (maximum and minimum torque (Mh and Ml), delta torque (ΔM) (difference between the maximum and minimum torques), scorch time (t_{s2}), and optimum cure time (t_{c90}), of the N990 filled NBR compounds at 150 °C. As the carbon black loading ratio increase, Mh and ΔM values are decrease up to 60 phr of carbon black content and then increase. The values of Ml are range to 3.1–3.6 daNm. Maximum values of t_{s2} and t_{c90} are obtained with 60 phr for both, N330 [11] and N990 filled compounds.

Table 2 The cure characteristics of NBR/CB compounds with N990 type of carbon black content

Cure characteristics	Sample					
	1	2	3	4	5	6
Mh (daNm)	10.9	5.05	6.0	4.8	7.7	10.8
Ml (daNm)	3.6	3.1	3.2	3.4	3.5	3.4
ΔM (daNm)	7.3	1.95	2.8	1.4	4.2	7.4
t_{s2} (min)	5.06	5.80	5.57	6.65	3.66	3.80
t_{c90} (min)	7.32	–	6.70	7.43	4.40	5.70

As the structure of carbon black develops (Fig. 1, from N990 to N330), Mh, Ml, ΔM, t_{s2} and t_{c90} values increase. The delta torques depends mainly on the amounts of free curatives in the compounds. The difference between Mh and Ml could be used as an indirect indication of the crosslink density of the rubber compound.

Mechanical properties

The addition of fillers to polymeric materials leads to improvement in the mechanical properties of the polymer matrix. The reinforcement effect is directly related to the properties of the interphase and depends on the nature of the specific interactions between polymer and reinforcing fillers [24]. The incorporation of filler into elastomers imparts many interesting and useful properties to the particle filled composite material. It is well known that the properties mainly depend on the dispersion condition of filler particles and their principal relevant properties: particle size, surface area, aggregate structure, surface activity and on rubber-filler interactions [25]. The surface chemistry of carbon black has a significant effect only on the vulcanization behavior of filled compounds. Optimal reinforcing power can be achieved only if the filler is well dispersed in the rubber matrix. The chemical or physical interaction between the filler and the rubber is a further important factor in the reinforcing effect [26]. In the case of carbon black the filler–polymer interaction is mainly of physical nature (physisorption) [27].

Test results of prepared compounds in the experimental study which are given in Table 3, showed that carbon black type and loading ratio changed the mechanical properties of compounds.

As the carbon black loading increase in the both N330 and N990 filled compounding formulation, tensile strength and hardness of cured compound are increase to a maximum value then decrease, but elongation at break decrease for both carbon blacks. The compound properties depend on carbon black loading as well as surface area and

Table 3 Some mechanical properties of NBR compounds filled with N330 and N990 type of carbon black content

Characteristics	Sample					
	N330* 1	N330 2	N330 3	N330 4	N330 5	N330 6
Tensile strength (MPa)	3.34	4.51	4.75	7.10	7.06	10.3
	0.88	3.09	5.04	5.05	5.10	5.15
Elongation at break (%)	350	315	280	285	205	200
	185	445	560	545	425	355
Hardness shore A	41	52	54	62	73	83
	41	42	47	48	57	60

*The samples were prepared according to compound formulation [11]

structure. These carbon black types have different surface area and structure.

Maximum tensile strength values were obtained with 100 phr content, for both, N330 and N990, carbon black filled NBR rubber. Higher tensile strength was obtained with N330 type which has finer particle size than N990 in this compounding study.

Percentage of elongation at break values decrease and hardness values (shore A) increase with loading ratio (phr) for both carbon blacks.

As the carbon black loading is increased, it makes additional black surface available for polymer attachments. When the loading level is reached to a limit value, the carbon black does not act as reinforcing filler [28].

As the structure of carbon black develops (from N990 to N330), elongation at break values decrease, but tensile strength and hardness values are increase.

The resistance of the rubber vulcanizate to thermal ageing is considered as an essential requirement for the long service life of products. It can be seen that after aging at 100 °C for 168 h (Table 4) the change in tensile strength and elongation at break values decrease with carbon black content increase for both type of carbon black. As the structure of carbon black develops (from N990 to N330), the change in tensile strength and elongation at break values two times increase.

The change of hardness values increase with carbon black loading increase which can be attributed to the crosslink density being increased after thermal aging. The tensile strength is a complex function of the nature and type of crosslink's, crosslink densities, the chemical structure of the used elastomers and the changes associated with degradation. It can also be seen that sample with 60 phr of N330 and sample with 100 phr of N990 type of carbon black show better ageing resistance than that of other samples. The change of elongation at break values decrease with carbon black increase and those are lower with the structure of carbon black develops (N330 filled compounds).

Curing kinetics

During sulphur vulcanization of rubber compound sulphur cross links form between rubber polymer chains (cure), while in the meantime some links decay (reversion). Thresholds for these two reactions, the activation energies of cure (E_{ac}), and reversion (E_{ar}) are the characteristic parameter of the cure properties of a given rubber compounds and can be used as criteria for energy compatibility of several rubber compound, composing the product. The prediction of the curing state is usually determined by employing a rheometer, in which the kinetics is described by the torque variation during curing [29, 30].

Table 5 show values of the E_{ac}, E_{ar} and relation E_{ar}/E_{ac} of NBR compounds filled with CB content. E_{ac} decreases with increasing CB loading filler in the NBR/CB cross linking systems up to 50 phr, above which it tends to increase. NBR compound with 50 phr content of N990 (sample 3) has minimum value of E_{ac} and maximum value of relation E_{ar}/E_{ac}. The kinetic results obtained by rheometer showed that N330 type carbon black [11] as filler reduces activation energy for all rubber compounds and increases overall curing rate more than N990 type carbon black.

Table 4 The change of some mechanical properties of NBR compounds filled with N330 and N990 type of carbon black content after thermal aging at 100 °C for 168 h

Characteristics	Sample					
	N330 1	N330 2	N330 3	N330 4	N330 5	N330 6
Tensile strength (MPa)	−0.2	−0.3	−1.6	−1.61	−1.17	−2
	−0.2	−0.64	−1.03	−1.03	−1.08	−0.93
Elongation at break (%)	−90	−135	−80	+5	−45	−60
	−45	−130	−170	−165	−125	−105
Hardness shore A	+7	+9	+8	+9	+11	+2
	+6	+6	+7	+7	+9	+9

Table 5 Activation energy of cross linking (E_a) and reversion (E_{ar}) and E_{ar}/E_{ac} ratio of NBR compounds filled with N990 type of carbon black content

Kinetic parameters	Sample					
	1	2	3	4	5	6
E_{ac} (kJ mol^{-1})	199	162	18	56	150	–
E_{ar} (kJ mol^{-1})	385	343	214	396	301	–
E_{ar}/E_{ac}	1.9	2.1	11.7	7.12	2.0	–

Cross-linking density

The calculated values of the cross-linking density and number average molecular mass of the chain between effective crosslink's, M_c, of the rubber vulcanisates are given in Table 6.

The values of r_W and r_V decrease with increasing amount of both N330 [11] and N990 types of carbon black. The polymer volume ratio v_{2g} increased with increasing carbon black content and was the largest for the sample containing a carbon black amount of 100 phr. The smallest chain molecular mass was obtained for both N330 [11] and N990 types of carbon black with the highest amount.

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 [31]. 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.

The polymer volume ratio v_{2g} in the swelled samples increase with the amount of carbon black increase and reached a maximum in the case samples with 100 phr of both N990 and N330 [11] (sample 6). The increase carbon black content 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.

Thermal stability of the NBR/CB compounds

The thermal stability of the NBR/CB rubber compounds filled by N990 type carbon black has been discussed.

The analyses were based on:

- dynamic TG curve (mass loss as a function of temperature), the shape of the curve and especially its initial part,
- the temperature values for certain mass loss, namely 0.5%, 10%, and 30% (the temperature for 0.5% mass loss was considered as the initial decomposition temperature—IDT),
- total mass loss (%) at 750 °C,
- the rate of mass loss change as a function of temperature followed by temperature and mass loss rate at peak maxima (first derivative of dynamic TG curve).

The date for the initial decomposition temperature (IDT) (0.5% mass loss), 10 and 30% mass loss temperatures are given in Table 7. It can be seen that according to the IDT ($T_{0.5\%}$) NBR/CB compound with 80 phr N990 has the best stability (274 °C). Compared with N330 [11] filled NBR rubber, N990 filled rubber has lower IDT values. In the next step (at 10% mass loss) NBR/N990 rubber with 100 phr and NBR/N330 [11] with 60 phr have maximum temperature values (381 ° and 373 °C) than other samples. But at 30% mass loss of NBR/N330 [11] rubber with 50 phr and NBR/N990 rubber with 100 phr are the most stable than other compounds.

Among the most important factors that can influence the initial TG behavior 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.

The thermal decomposition of NBR/CB rubber compounds filled by N330 [11] and N990 types CB occurs generally in two main stages (Fig. 2 and Table 7). 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 range to 14.74–22.37 [11] and 13.1–23.83% (depending on the type and amount of CB in NBR rubber) most probably indicating the

Table 6 The cross-linking density of NBR compounds filled with N990 type of carbon black content

Parameters	Sample					
	1	2	3	4	5	6
ρ_p (gcm^{-3})	1.08	1.09	1.11	1.13	1.16	1.17
r_w	3.00	2.46	2.33	2.28	2.02	1.94
r_v	3.49	2.83	2.70	2.67	2.37	2.27
v_{2g}	0.285	0.352	0.369	0.374	0.422	0.440
M_c (g mol^{-1})	2508	2276	1967	1885	1358	1222

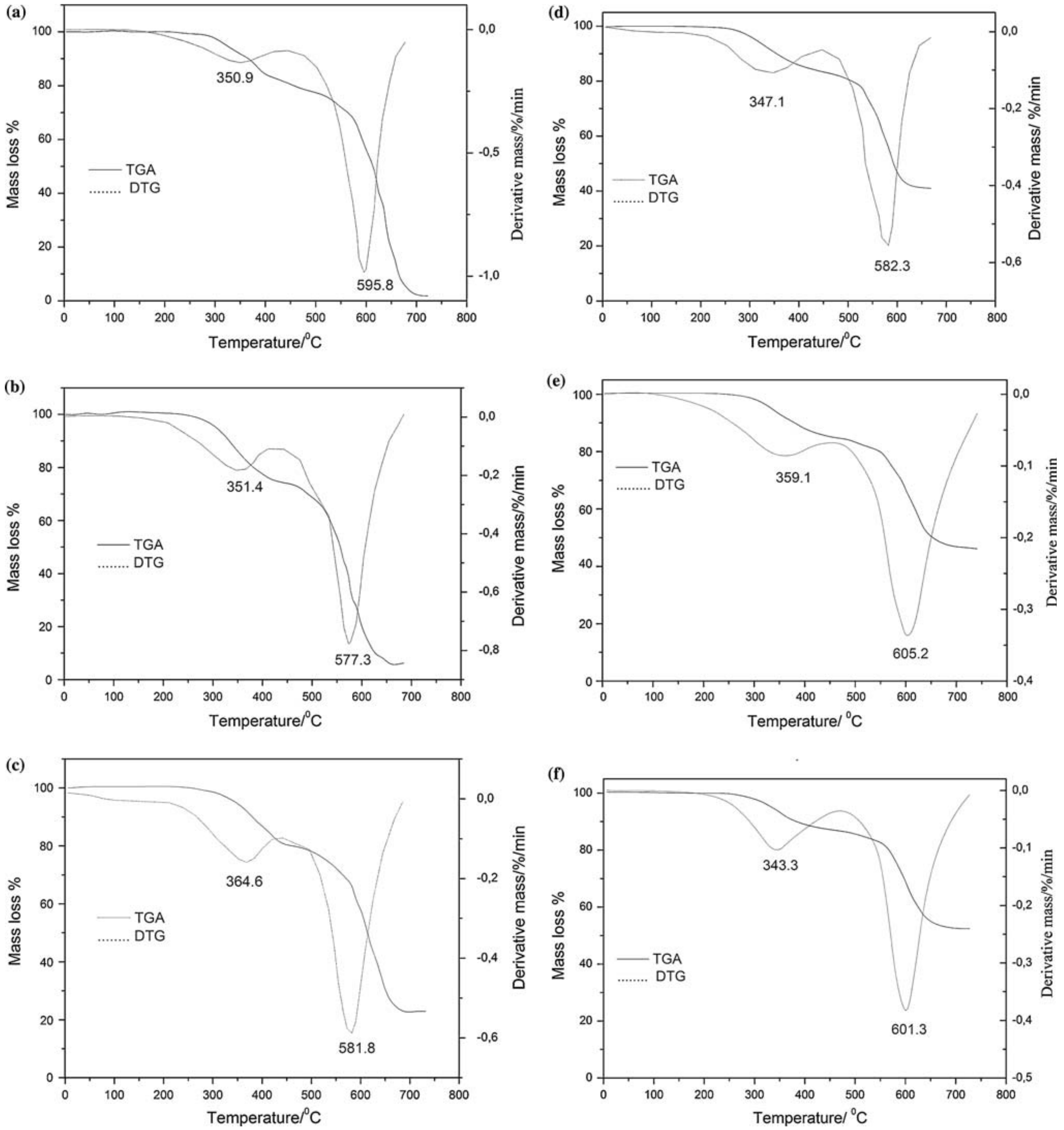

Fig. 2 Thermal decomposition of NBR/CB rubber. **a** NBR/N990 (100/20). **b** NBR/N990 (100/40). **c** NBR/N990 (100/50). **d** NBR/N990 (100/60). **e** NBR/N990 (100/80). **f** NBR/N990 (100/100)

evaporation of oil (naftolen 40/2). The second-step degradation starts at 600 °C and ends at 700 °C, and at 580°C and ends 605 °C for samples with N330 [11] and N990, respectively.

The percent of mass loss at regions of 600–700 °C is range to 40.01–79.06 and at regions of 580–605 °C is 34.46–83.9% for N330 [11] and N990, respectively, indicating polymer degradation. The large flexible polysulfidic linkages undergo chain scission and convert into monosulfidic and disulfidic linkages. Synthetic rubber decomposes by random-chain scission with intramolecular hydrogen transfer [32]. Table 7 presents the DTG peak values of N990 filled NBR rubber compounds. The shift of values of the DTG peaks to a high temperature indicating

Table 7 The temperature values of NBR compounds filled with N990 type of carbon black content for selected mass loss (0.5; 10 and 30%)

Compound	Sample					
	1	2	3	4	5	6
Mass of sample (mg)	24.9	24.15	19.0	21.45	20.5	19.55
DTG peak values (°C)	350.9	351.4	364.6	347.1	359.1	343.3
	595.8	577.3	581.8.	582.3	605.2	601.3
Mass loss (%)	14.9	23.83	19.49	17.86	15.24	13.1
	83.9	69.9	57.65	40.86	37.99	34.46
Total mass loss (%)	98.8	93.73	77.14	58.72	53.23	47.58
Temperature values for selected mass loss						
$T_{0.5\%}$ (°C)	225	254	247	252	274	262
$T_{10\%}$ (°C)	343	356	332	321	378	381
$T_{30\%}$ (°C)	527	529	492	477	593	597

increased thermal stability with 50 phr and 80 phr content of N330 [11] and N990 filled NBR rubber, respectively.

Conclusion

The results obtained allowed for the following conclusions to be made concerning the cure and kinetic characteristics, mechanical properties, cross-linking density and thermal stability of the NBR/CB rubber compounds:

1. As the carbon black loading ratio increase, *Mh*, and ΔM values decrease up to 60 phr of carbon black content and than increase. The values of *Ml* are range to 3.1–3.6 dNm. Maximum values of t_{s2} and t_{c90} are obtained with 60 phr for both, N330 [11] and N990 filled compounds. N330 type of carbon black activated the vulcanizing process through the promotion of hydrogen sulfide formation and the rapture of S–N linkage when heated with sulfonamides in rubber either in the present or absence of other compounding ingredients more than N990 type resulting as their primary structure. Higher t_{c90} values have NBR/N330 [11] than NBR/N990 compounds;
2. The kinetic results obtained by rheometer showed that N330 [11] type carbon black as filler reduces activation energy for all rubber compounds and increases overall curing rate more than N990 type carbon black.
3. As the carbon black loading increase in the both N330 [11] and N990 filled compounding formulation, tensile strength and hardness of cured compound are increase to a maximum value than decrease, but elongation at break decrease for both carbon black type filled compound.
4. The cross-linking density increases with increasing amount of carbon black; the values of r_V, r_W and M_c decrease but v_{2g} and the matrix forming density increase with increasing fraction of carbon black and the N330 [11] type carbon black filled NBR rubber have higher values than N990 filled NBR carbon black, also.
5. 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 rubber filled with 50 phr and 80 phr content of N330 [11] and N990 type of carbon black, respectively. NBR/N330 compounds [11] are more thermal stability than those NBR/N990 compounds.

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