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THE INFLUENCE OF CARBON BLACK ON CURING KINETICS AND THERMAL AGING OF ACRYLONITRILE-BUTADIENE RUBBER*

Elastomers based on a copolymer of butadiene and acrylonitrile (NBR) have excellent oil resistance but are very sensitive for degradation at very high temperatures. The aim of this applicative contribution was to determine the effect of high abrasion furnace carbon black with primary particle size 46 nm on aging properties of elastomeric materials based on NBR as network precursor. The curing kinetics was determined using the rheometer with an oscillating disk, in which the network formation process is registered by the torque variation during time. The vulcanizates were obtained in a hydraulic press at 150 °C. The mechanical properties of elastomeric composites were determined before and after thermal aging in an air circulating oven. The reinforcing effect of the filler particles was assessed according to mechanical properties before and after aging.

Key words: elastomer; active filler; carbon black; curing; elastomer; aging properties.

Elastomers are cross-linked polymers with a low modulus of elasticity and the capability to reverse large deformations at their service temperatures. The low modulus of elastomers, combined with their high deformation reversibility, allows their use in a wider range of applications [1]. For more than a century, elastomer and carbon black (CB) have played a central role in tire technology as active filler. At the onset, the usages of regular industrial soot and natural rubber have opened the way to an industry in the continuous evolution. The rubber industry began when Goodyear developed the first useful rubber compound of natural rubber with sulphur. The concept of mixing materials into rubber to improve performance is still of primary importance today. Without fillers, few rubber goods would be of any commercial value. The curing

process is the final step in the elastomeric material manufacturing whereby rubber goods are formed to the desired shape. In press, heat is transferred to the compounds from the surfaces which are maintained at high temperatures, inducing the network formation i.e. obtaining the strong elastic material. The progress in car industry and tire industry was paralleled by a substantial progress in carbon black technology and production facilities as well. As far as CB is concerned, quite a lot of characterizations came from other industries where this material was used [2]. The incorporation of filler into polymer networks based on rubber macromolecules imparts many useful properties to the particle filled composite material. Nitrile butadiene rubber (NBR) is a copolymer of butadiene and acrylonitrile and it comes under „special purpose“ synthetic rubbers. Elastomeric materials based on NBR as network precursors are used in automobile industry because of its resistance to fuels, a variety of oils and other fluids over a wide range of temperatures [3]. However, NBR cannot be used in specific applications requiring high heat and ozone resistance [4]. It is widely used in products like oil seals, water pump seals, blow out preventors, fuel lines, hoses, fuel pump diaphragms, etc., because of its high oil, solvent and fuel resistance and gas impermeability.

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Thus the unfilled vulcanizates have very low tensile strength but when used in combination with reinforcing fillers, vulcanizates with excellent mechanical properties can be obtained [5]. NBR use is dominant in the oil field used in blown out preventors packers. The other major use is in the automotive sector.

The reinforcement with the addition of active fillers has been well-known for a long period of time [6,7] and it is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus [8,9]. The recognition of the role of the main factors influencing interfacial adhesion and proper surface modification may lead to significant progress in many fields of research, as well as in related technologies [10]. As compared to micron size filler particles the nano-sized filler particles are able to occupy substantially greater number of sites in the polymer matrix. The network formation implies that the rubber molecules are selectively confined into the void of carbon black agglomerates during mixing. A detailed understanding of the general mechanism of rubber reinforcement is one key to develop new systems providing the performance enhancement needed [11]. Carbon black is the predominant reinforcing filler used in rubber compounds. During the manufacture of carbon black the primary particles fuse to form aggregates. The shape and degree of aggregate branching is referred to as structure. The increasing structure typically increases modulus, hardness, electrical conductivity and compound viscosity. Typical carbon black primary particle size ranges from 8 nanometers for furnace blacks to 300 nanometers for thermal blacks. Carbon black surface chemistry is a function of the manufacturing process and the heat history of the carbon black. The surface chemistry can affect the abrasion resistance, tensile strength, hysteresis and modulus. Higher porosity allows compounders to increase carbon black loading, while maintaining compound specific gravity. Carbon black, generally supplied as pellets has to be dispersed during mixing into smaller entities (such as agglomerates and aggregates). Large particle-particle interactions result in inhomogeneous dispersion and distribution of the filler, processing problems, poor appearance and inferior properties. Highly sophisticated process technology was the key to enhance the surface activity of these carbon black grades. This progress in the process technology resulting in the nanostructuring of carbon black particles was used to generate special carbon blacks for different applications. The effect of added carbon black is directly related to the properties of the inter phase and due to the specific interactions between rubber macromolecules and ac-

tive filler surfaces [12]. 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 [13]. The surface chemistry of carbon black has a significant effect only on the vulcanization behavior of compounds. The chemical or physical interaction between the filler and the rubber is a further important factor in the reinforcing effect [14,15]. Processability and final properties of elastomeric products could be obtained through a series of experiments that vary the ratios of additives and measure the effects over different temperatures and time. It is obvious that, to obtain as many interactions as possible, the polymer active segments must have access to the majority of the carbon black active sites. Since the mono-unit of CB is the aggregate the most possible isolated aggregate must be made available to be in contact with the polymer chains and their unsaturation domains. Networking of fillers depends on its attractive potential and the distance between aggregates. Since, with regard to surface energy, the attractive potential is almost the same for all furnace blacks in hydrocarbon elastomers, the distance between aggregates becomes the controlling factor for compounds processability. At elevated temperatures polymer chains possess a higher thermal energy and are in a mobile condition. The cross-linked networks respond rapidly to the imposed stress as it go to a new equilibrium position. Consequently, there is deterioration of physical properties at elevated temperature. The heat resistance of NBR elastomer is directly related to the increase in ACN content in rubber macromolecules. However, the presence of double bond in the polymer backbone make it more susceptible to resistance to heat ozon and light. Several strategies have been adopted recently to improve the aging resistance of elastomeric materials based on NBR rubber as a network precursor. The most important is the proper choice of fillers and a cure system in compound formulation. The aim of this contribution was to assess the effect of high abrasion furnace carbon black on curing kinetics of acrylonitrile-butadiene rubber and to compare mechanical properties of original and aged reinforced elastomeric materials.

EXPERIMENTAL

Materials

The industrial grade of random copolymer acrylonitrile and butadiene, NBR (Kraynac 34-50, „Polysar“, Canada), with acrylonitrile content 33,2% was

used. Moony viscosity at 100 °C was 50, specific gravity 1.17 g cm⁻³, ash content: 0.5%. High abrasion furnace carbon black: N-330 („Deggusa“, Germany), with nominal particle size of 46 nm and density 1.78–1.82 g cm⁻³, CTAB surface area 83±6 m²/g, (0, 20, 40, 60 and 80 phr). *N*-Cyclohexyl-2-benzothiazole sulphenamide (CBS): pale grey, non hygroscopic powder; melting point 95–100 °C and density 1.27–1.31 g cm⁻³ (1.5 phr). Tetramethylthiuram disulfide (TMTD): non-hygroscopic white powder, melting point 140 °C, specific gravity 1.33–1.40 g cm⁻³. *N*-Isopropyl-*N*-phenyl-*p*-phenylenediamine (Vulkanox 4010 NA): density, 1.14–1.18 g cm⁻³. Sulphur: pale yellow powder, purity 99.9%; melting point, 112 °C; density, 2.04–2.06 g cm⁻³ (1 phr). Zinc oxide: fine powder; purity, 99%; density, 5.6 g cm⁻³ (5 phr). Stearic acid: melting point, 67–69 °C, density, 0.838 g cm⁻³ (1 phr).

Compound preparation

Rubber ingredients were accurately weighed and mixed on a laboratory size two-roll mill (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 mixing time was 20 min. The sheeted rubber compounds were conditioned at 23±2 °C during 24 h before cross-linking.

Curing assessment

The curing were assessed by using a Monsanto Oscillating Disc Rheometer R-100, at 160±1 °C, according to ASTM D2084-95. The mixing energy of each compound was recorded. The cure characteristics: *Ml* (minimum torque), *Mh* (maximum torque), t_{c90} (optimum cure time), t_{s2} (scorch time) were registered and *CRI* (cure rate index) was calculated according Eq. (1) [16,17]:

$$CRI = \frac{100}{t_{c90} - t_{s2}} \quad (1)$$

The crosslinking apparent activation energy (E_a) and reversion activation energy (E_{ar}) were calculated from the torque-time curves taken from experiments performed using oscillating disk rheometer (Monsanto Rheometer, model 100C) at two temperatures (180 and 190 °C). The rheometer torque is directly related to the crosslinking density. If the crosslinking process is a first-order reaction, the kinetic expression for the reaction can be shown in terms of torque as Eq. (2). Eckelmann *et al.* [18,19] demonstrated that the obtained resistance moment, M , measured during cross-linking could be written in the form of the equation:

$$(M - M_a) = k_1(M_\infty - M_a)/(k_2 - k_1)[\exp(-k_1 t) - \exp(-k_2 t)] \quad (2)$$

M_a is the the torque at a given time t , preceding the onset of vulcanisation, and M_∞ is the maximum torque providing the cross-linking reaction is the only ongoing process, k_1 and k_2 are the rate constants for crosslinking and reversion, respectively, and t is the time. The torque maximum, M_{max} , is lower than M_∞ and it is dependent on temperature. Eq. (2) is simple to solve if $\omega = k_2 / k_1$, and thus we can obtain the time necessary to attain M_{max} :

$$k_1 t_{max} = \frac{\ln \omega}{\omega - 1} \quad (3)$$

$$\frac{M_{max} - M_a}{M_\infty - M_a} = \omega^{\omega(1-\omega)} \quad (4)$$

The value of M_∞ evaluated from the curve in which reversion is not noticeable, and the values of M_{max} , M_a and t_{max} are evaluated from the curves registered at temperatures of 180 and 190 °C. The activation energy is calculated using of Arrhenius as:

$$E_a = \frac{RT_1 T_2}{(T_2 - T_1)} \ln \frac{k_2}{k_1} \quad (5)$$

The value of the gas constant, R , is 8.31 J K⁻¹ mol⁻¹.

Elastomeric materials preparation

To perform a systematic study, rubber compounds without and with filler were prepared and cross-linked under similar experimental conditions. A cross-linking procedure has been performed in a hydraulic press during earlier determined optimal curing time (t_{c90}). Compounds were also molded into 2-mm thick slabs for later determination of mechanical properties of cross-linked materials. The molded samples were taken out after cooling them to room temperature under pressure by circulating cold water through the platens of the press.

Mechanical properties measurements

For the tensile experiment, dumbbell samples were cut from a 2-mm thick molded sheet. Dumbbell-shaped specimens were cut from the molded sheets with a width of 6.3±0.1 mm. Mechanical properties: tensile strength, elongation at break, 200 and 300% modulus, were measured at room temperature on an electric tensile testing machine (Zwick 1425) according to ASTM D 412. The tensile strength and elongation at break were recorded. At least, three measurements have been taken and average values were reported. The hardness test of a rubber is the relative resistance of the surface to indentation by an indenter of a defined dimension, under a defined load. Hardness of the elastomer samples was determined by the

standard method using a Shore A type durometer. Hardness was measured using an indentation hardness tester according to ISO7619.

Thermal aging of elastomeric composites samples

To investigate the influence of thermal aging on the mechanical properties, the obtained reinforced elastomeric materials were performed in an air circulating oven operated at 100 °C during 50 h. The retained percentage value of tensile strength and elongation at break were calculated.

RESULTS AND DISCUSSION

During cross-linking sulphur is forming the cross-links between rubber macromolecules, while in the meantime some links decay and this opposite process is called reversion. In Fig. 1 the changes of torque during cross-linking of rubber compounds filled with different content of carbon black are shown. With the ever increasing rubber technology development costs

and complexity, it became mandatory to replace the trial and error development approach with a more rational way of obtaining competitive products. It then became obvious that a better and fundamental understanding and knowledge of curing process is required.

In Table 1 the obtained curing characteristics, such as delta torque (difference between the maximum and minimum torques), scorch time (t_{s2}), and optimum cure time (t_{c90}), for the compounds with different carbon black loading are summarized. The maximum and minimum torque (Mh and MI) and delta torque (M) increases with the increase of the carbon black loading for all samples. The difference between Mh and MI could be used as an indirect indication of the network formation in the crosslinking system. Both scorch time and optimum curing time are decreasing noticeable with increasing the active filler content. The kinetic parameters, activation energies of cross-linking (E_{ac}) and the reversion (E_{ar}), are given in Table 2, and they were calculated by applying Eqs. (3)–(5). Thresholds for the cure activation energy and rever-

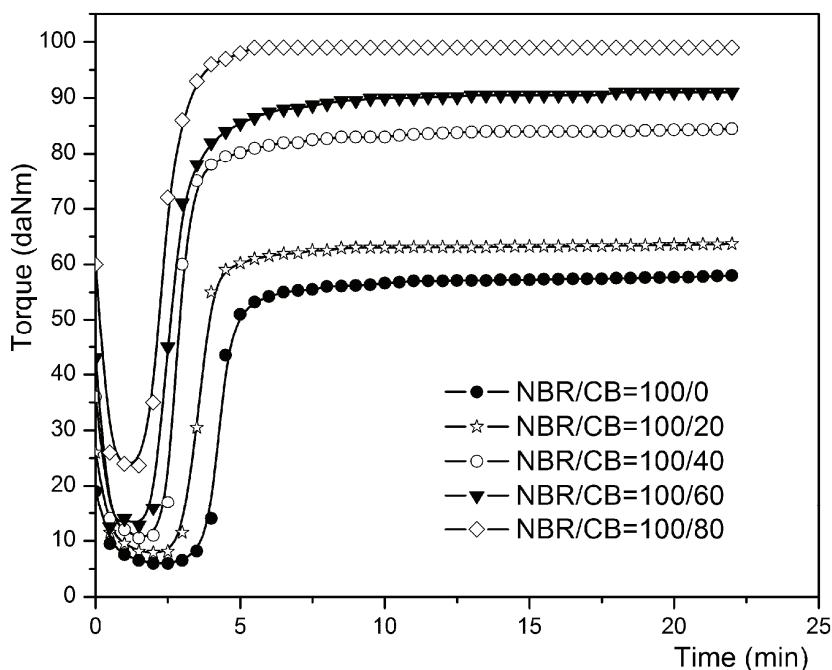


Figure 1. Torque vs. time during cross-linking of rubber compounds filled with different content of carbon black (CB) (0; 20; 40; 60; 80 phr) at 150 °C.

Table 1. Curing characteristics of NBR compounds filled with carbon black

Compound	NBR/CB (phr)	Mh (N m)	MI (N m)	M (N m)	t_{s2} (s)	t_{c90} (s)	CRI (s ⁻¹)
1c	100/0	6.55	0.68	5.87	156	270	0.88
2c	100/20	7.23	0.90	6.33	120	210	1.11
3c	100/40	9.54	1.18	8.36	90	180	1.11
4c	100/60	10.28	1.41	8.87	66	168	0.98
5c	100/80	11.18	2.59	8.59	54	150	1.04

sion activation energy are the important parameters for a rubber compounds. Fig. 2 shows the determined values of E_{ac} , E_{ar} and E_{ar}/E_{ac} for samples with different filler content. E_{ac} increases with increasing carbon black loadings up to 40 phr (267.8 kJ/mol), above which it tends to decrease. Minimum value of E_{ac} (16.8 kJ/mol) and maximum value of relation E_{ar}/E_{ac} (10.26) was obtained for the sample with 80 phr carbon black.

Not so long ago, the compounder had a multitude of tests to do in order to decide which compound would be best suitable for a given elastomers application. To mention only a few: the 300% modulus, tensile, elongation at break, multiple tear tests, rebound, abrasion etc., are tests not based on relevant elastomer operating conditions but often on the past history and approximate guesses. Optimal filler

reinforcing power can be achieved only if the particles are well dispersed in the rubber matrix. Since no methodologies exist today to quantify that “ultimate” dispersion, one rough approach is to suppose that by increasing the compound mixing time the number of interactions between the filler and the macromolecules are increasing [19]. Of course, this is easy to do in a laboratory but may not be so easy in a production facility. In Table 3 the values of tensile properties and hardness for obtained elastomeric materials with different filler loading are summarised. It is obvious that the tensile strength increases with increasing carbon black loading. The resistance of the rubber vulcanizate to thermal aging is considered as an essential requirement for the long service life of products. The percentages of decrease in tensile strength and elongation at break due to aging at 100 °C during

Table 2. The data for calculated kinetic parameters for the crosslinking activation energy (E_{ac}) and the reversion activation energy (E_{ar})

Compound	NBRI/CB(phr)	Activation energy (kJ mol ⁻¹)		E_{ar}/E_{ac}
		E_{ac}	E_{ar}	
1	100/0	173.5	383.0	2.21
2	100/20	124.6	433.1	3.46
3	100/40	267.8	417.1	1.56
4	100/60	81.0	197.0	2.43
5	100/80	16.8	172.3	10.26

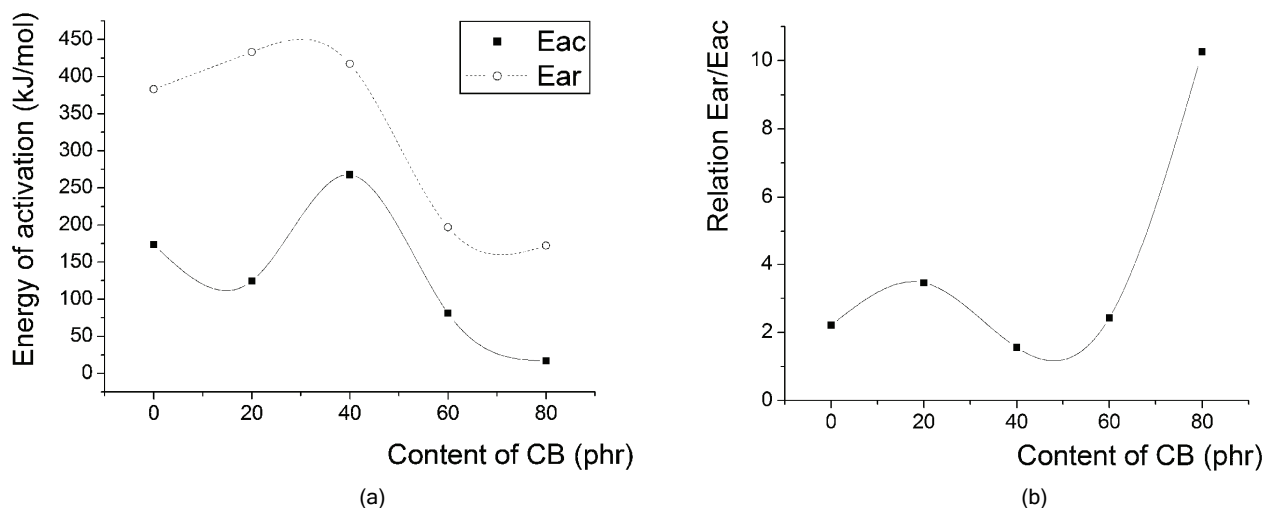


Figure 2. The values a) of curing and reversion activation energy and b) its ratio, E_{ar}/E_{ac} .

Table 3. Mechanical properties of NBR elastomers reinforced with different carbon black content

Sample	NBRI/CB (phr)	Modulus 200% (MPa)	Modulus 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness Shore A
1	100/0	0.64	0.78	0.98	420	48
2	100/20	1.08	2.06	6.28	485	57
3	100/40	3.83	8.20	15.70	440	67
4	100/60	6.87	13.73	18.88	375	75
5	100/80	10.79	18.64	20.16	340	85

50 h are presented in Table 4. It can be seen that after aging, the tensile strength and elongation at break are decreased with increasing of CB loading. The values of hardness increase with increasing the CB content. Thus the poor heat aging resistance of NBR rubber is the result of unsaturations in the macromolecule back-

bone which permits scission of the chains to occur under certain adverse conditions.

In Figs. 3 and 4 the data of mechanical properties for filled elastomers (hardness, tensile strength, and elongation at break) before and after thermal aging at 100 °C during 50 h are summarised. The

Table 4. Mechanical properties of NBR elastomers filled with carbon black after aging

Sample	NBR/CB (phr)	Tensile strength (%)	Elongation at break (%)	Hardness Shore A
1a	100/0	79.59	69.04	+7
2a	100/20	79.61	70.10	+9
3a	100/40	80.00	70.45	+10
4a	100/60	78.97	72.00	+9
5a	100/80	83.68	70.59	+8

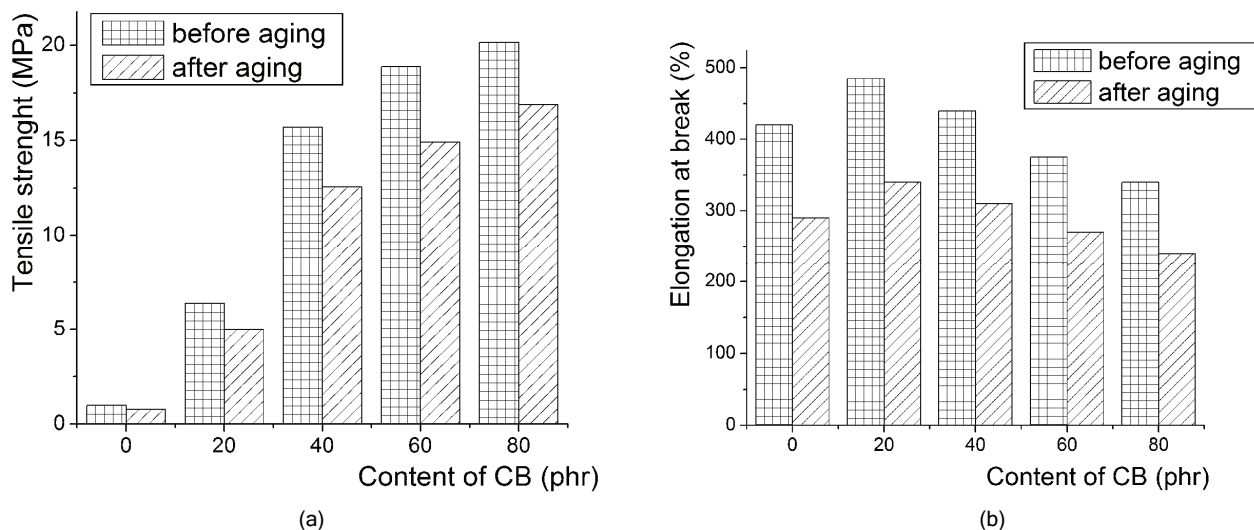


Figure 3. Mechanical properties before and after aging for elastomers with different carbon black content, a) the tensile strength and b) elongation at break.

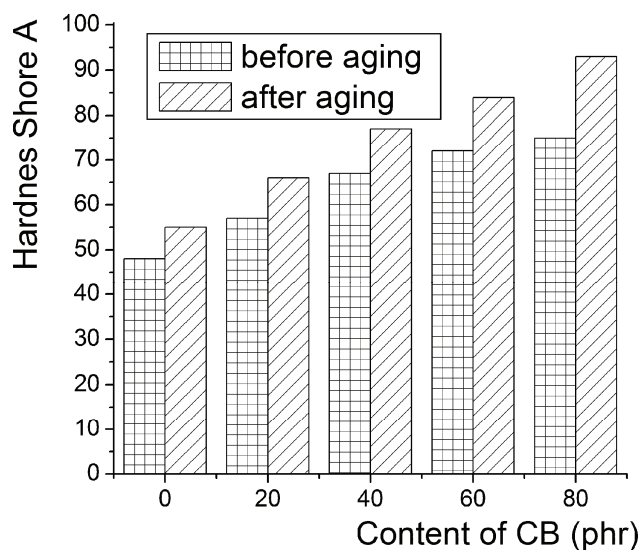


Figure 4. The influence of carbon black content on elastomeric material hardness before and after aging.

hardness of the samples increases with increasing the filler content, as it is shown in Fig. 4. This statement can be attributed to the increase of cross-linking density after thermal aging. The tensile strength after aging is a function of the crosslink's type, cross-linking density, the chemical structure of the rubber macromolecule and a chain scission associated with degradation. A sample with 80 phr carbon black has the maximum value of tensile strength, before and after aging (Fig. 3). The values of elongation at break decrease with the carbon black loading increase.

CONCLUSION

The unfilled NBR vulcanizates have a very low tensile strength because of no self-reinforcing effect but when used in combination with reinforcing carbon black nanoparticles the elastomeric materials with excellent mechanical properties were obtained. The hardness of the samples increases with increasing the filler content. Our investigation indicated that the content of carbon black nanosized particles has a significant influence on the aging properties of the obtained composite materials. The vulcanizates filled with 80 phr of carbon black have the best aging resistance. The poor thermal aging properties of random copolymer of acrylonitrile and butadiene are the result of unsaturations in the rubber macromolecules backbone which permits a chain scission to occur under certain adverse conditions.

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