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SCIENTIFIC PAPER

THE EFFECT OF GAMMA RADIATION ON THE AGEING OF SULFUR CURED NR/CSM AND NBR/CSM RUBBER BLENDS REINFORCED BY CARBON BLACK*

In this work the effect of the γ-radiation dose on ageing of carbon black reinforced elastomeric materials was studied. The compounds based on natural rubber/chlorosulfonated rubber blend (NR/CSM) and butadiene acrylonitrile rubber/chlorosulfonated rubber blend (NBR/CSM) (50:50, w/w) with different loadings (0, 20, 40, 50, 60, 80 and 100 phr) of the filler with the average particle size of 40 nm were cured by sulfur. The obtained elastomeric composites were subjected to radiation doses (100, 200, 300 and 400 kGy) in the presence of oxygen. The changes of material mechanical properties were estimated after radiation accelerated ageing. By using Fourier transform infrared measurements (ATR-FTIR) it was assessed that after exposure to doses of 100 kGy alcohols, ethers, lactones, anhydrides, esters and carboxylic acids are formed in materials. The formation of shorter polyene sequences and aromatic rings in aged samples are assumed on the basis of the obtained spectra.

Key words: NR/CSM; blend; NBR/CSM; FTIR; gamma radiation; rubber reinforcement.

The physical properties of elastomeric materials are influenced by filler distribution or cross-linking procedure. Normally, rubbers are crosslinked with systems based on sulfur or peroxide. The extremely high curing temperatures (150-180 °C) have a disadvantage that the final properties of the products may be affected by uncontrolled side reactions. On the other hand, radiation curing is a process that differs from thermal curing because the curing is carried out at ambient temperature under closely controlled conditions, such as, radiation dose, dose rate, etc. The type of crosslink formed with radiation curing (-C-C-) gives rise to better mechanical properties at higher temperatures.

During a long period of service most polymers and their products gradually lose their useful properties as a result of polymer chain degradation. This is due to the action of degrading agents such as oxygen, heat and high energy radiation. The effects of these degrading agents depend mainly upon a chemical structure of the polymer chain. The thermo-oxidative degradation of rubber has been discussed in the literature [1]. Ungar [2] has been studied the degradation of polymers in the presence of ozone. Mechanical properties of polymers are changed considerably by high energy radiation. This may be result of either crosslinking or scission of the polymer chains. Properties such as tensile strength, hardness, modulus and elongation at break are decreased as a result of chain scission. The effects of radiation on polymeric materials and their blends have been reported by several research groups [3]. Koshy et al. [4] have studied the effect of blend ratio and cure systems on the degradation of blends of natural rubber and ethylene-vinyl acetate rubber. The cross-linking of ethylene-vinyl acetate rubber by high-energy radiation has been reported by Sweet [5]. Skowronski et al. [6] have studied the photo-degradation of PVC/EVA and PVC//nitrile rubber blends. De and his coworkers [7] have reported on the effect of γ-radiation on the mechanical properties and failure properties of polyether/PVC and NR/PE blends. The changes induced by radiation of the blends based on polyethylene (PE), butyl rubber, and polyisoprene have been studied by Ivehenko et al. [8].The degradation of NR by radiation is a serious

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problem, mainly the one by gamma ray radiation, which is usually used in sterilization. With gamma ray radiation, a high molecular weight macromolecular chain may decompose. The mechanism of gamma ray radiation ageing of polymer has been studied by Akhtar [9]. The introduction of fillers into polymers leads to a wide range of interactions arising at the polymer-filler interface. These dispersed fillers considerably influence the properties of the polymer composites, including their degradation and stability. The major factors that control these properties are the filler surface chemistry, the nature, shape and size of primary particles, and a specific surface area etc. [10]. The reinforcing agents are added to rubber compounds in order to improve final elastomer properties that meet a given service application or sets of performance parameters. In rubber products carbon black is often added not only as filler for cost reduction, but also an important ingredient for reinforcement. There is evidence that both physical and chemical attachments of the molecular polymer chains to the filler surface contribute to the reinforcing effect. By the use of carbon black a degree of interaction with rubber mainly depends on the primary particle size, a degree of aggregation and the surface energy. In our earlier investigation we studied high energy radiation resistance of composites based on NR/CSM rubber blends [11] for industrial application. The aim of this project was to investigate chemical changes induced by γ-radiation in carbon black reinforced elastomeric materials based on NR/CSM and NBR/CSM rubber blends by using FTIR method.

EXPERIMENTAL

Materials

Polyisoprene rubber, NR, produced by Indian Standard Natural Rubber, grade 5 (ISNR-5). Acrylonitrile butadiene rubber, NBR, Krynac-3345, produced by Polysar Canada, containing 33%, mass of acrylonitrile). Chlorosulphonated polyethylene, CSM, Hypalon-40, with 35% chlorine and 1% sulfur by weight was obtained from E. I. duPont de Nemours and Co., Inc., U.S.A, 1.18 g/cm^3); its content was 1.8 phr. The prosessed Tephil naphtene PO100 oil (10 phr) was used as plastificator. The content of zinc oxide was 4 phr. A carbon black active filler (N550) produced by Degussa, Italy (dibuthyl phthalate number DBP = 121 cm^3/100g and the average size of primary particles 40 nm [10]). The content of filler was 0, 20, 40, 50, 60, 80 and 100 phr.

Compounding and curing

The rubbers were separately premasticated for about 1 min each, keeping a tight nip gap (0.8 mm), and subsequently blended for 3 min. The mixing of the rubber blends (50:50, w/w) and filler particles was performed on a two-roll mill at 50 °C, according to the compounding procedure [12]. The compounds were conditioned at nearly 25 °C for 24 h before the investigations. The curing properties of the compounds were carried out by an oscillating disc rheometer (Monsanto 100) at 160 °C. The cross-linking was carried out in an electrically heated laboratory hydraulic press under the pressure of 4 MPa (platen size 300×300 mm). The scorch time (t_{s2}), optimum curing time (t_{90}), and torque (*Mmax* and *Mmin*) was estimated from rheometer data.

Mechanical measurements

Tensile tests were performed on dumbbell samples that were cut from a 2 mm thick molded rubber sheet. The tensile strength, σ_b, and the ultimate elongation, E_b (%), were determined at the room temperature by using a Zwick 1425 universal tensile testing machine [13]. The tests were performed according to ASTM D412-98a. The given results are the mean value of three separate specimens. The error in these measurements is ±0.5%. Samples with flat surface were used for hardness test. The measurement was done using Durometer Model 306L Type A [14].

Gamma radiation ageing

Radiations of elastomeric materials have been performed in air in the Co-60 radiation sterilization unit with the dose rate of 10 kGy h^{-1} and total absorbed dose of 100, 200, and 400 kGy. The radiation dose of 400 kGy can be considered as the relatively big dose which exceeds the doses for degradation of radiation degradable polymers many times and is also above the typical doses used in practice for radiation modification of polymer based products.

Scanning electron microscopy

The scanning electron microscopy images of the rubber blends fractured surfaces were taken in a JEOL JSM-5400 model. The samples were sputter coated with gold for 3 min under high vacuum with image magnifications of 2000×.

Fourier transform infrared analysis (FTIR-ATR)

Fourier transform infrared spectra (FTIR) were recorded on a Bruker IFS-66 spectrometer with an attenuated total reflection (ATR) attachment. A minimum of 500 scans was signal-averaged at a resolution of 4 cm^{-1}. For measurements, the spectrometer

was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The internal reflection element (IRE) chosen was a 45-degree KRS-5. The samples were approximately 0.3 mm thick sheets, prepared by compression molding between two teflon films at the temperature of 100 °C.

RESULTS AND DISCUSSION

Cure characteristics

The obtained rheomether curves for curing of filled and unfilled rubber blend compounds are given in Fig 1. The cure characteristics for NR/CSM and NBR/CSM rubber blends are summarized in Table 1 as the function of the carbon black content together with some other experimental data. The values for curing data depend mainly on the combination of network precursor. The maximum torque, which is a measure of the stiffness of the compound, is directly related to the modulus of the compounds. The value of the cure time, t_{c90}, is systematically decreased with increasing the carbon black content for both rubber blend compounds. The NR/CSM rubber blends have considerably shorter t_{s2} and t_{c90} values than those of
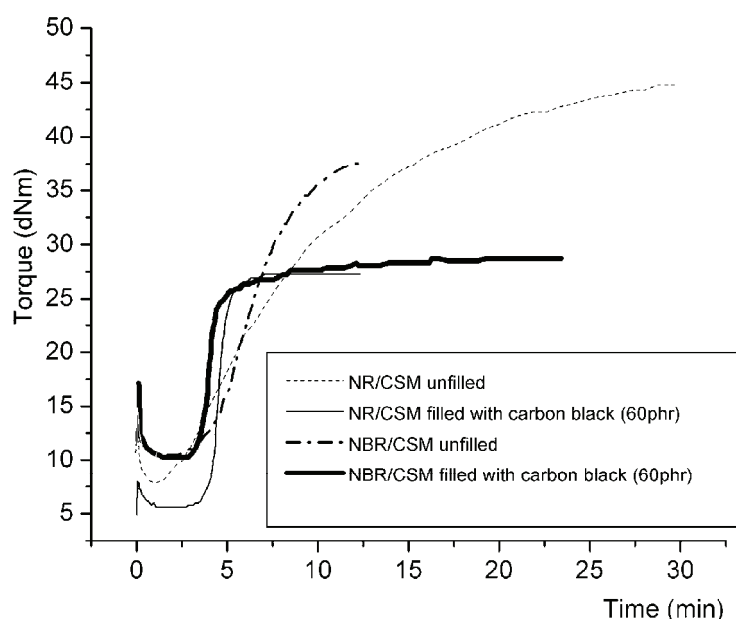

Figure 1. Rheometric curves for curing of unfilled and filled rubber blends.

Table 1. The obtained data for mechanical properties of cured rubber blends and curing data for compounds with a different content of carbon black

Blend	No.	Filler (phr)	$[Tb]^a$, MPa	Eb^b, %	Torque (dNm)		t_{s2}^c (min)	t_{c90}^d (min)
					Mmin	Mmax		
NR/CSM	1	0	20	573	3.05	25.6	2.1	11.3
	2	20	23	529	2.6	23.6	2.3	9.3
	3	40	24	442	3.3	27.5	2.1	8.1
	4	50	26	412	4.1	32.2	1.9	9.7
	5	60	28	343	5.2	37.3	1.8	7.2
	6	80	25	280	6.7	40.8	1.8	6.6
	7	100	24	220	9.1	46.5	1.6	6.5
NBR/CSM	8	0	14	343	5.8	46.6	8.1	15.2
	9	20	15	361	5.1	45.7	6.3	13.1
	10	40	16	383	5.8	46.6	5.6	13.1
	11	50	20	427	7.1	50.8	4.6	11.9
	12	60	20	381	7.7	58.6	3.7	5.9
	13	80	19	373	8.7	62.7	3.3	9.4
	14	100	18	335	9.8	62.7	3.2	9.6

[a]Tensile strength; [b]elongation at break; [c]scorch time; [d]cure time

NBR/CSM rubber blend. This result can be primarily related to the fact that the cure process of NBR macromolecules is slower compared to the NR macromolecules and needs a higher activation for cross-link point formation *via* sulfur. In addition, a limited efficiency of the accelerators used in the compound formulations can play a decisive role [15,16].

Mechanical properties

The mechanical properties that have been followed up for unfilled and filled rubber blends (50/50), as a function of radiation dose were the tensile strength (*TS*), modulus at 100% elongation (*M*100), elongation at break (*Eb*%) and hardness.

Figure 2 illustrates the variation of *TS* as a function of the radiation dose for unloaded as well as loaded NR/CSM rubber blends. Te dependences for NBR/CSM rubber blend reinforced with a different content of carbon black are in Figure 3. The TS values for blend without radiation and unfilled blend are also given. It can be seen that not-radiated blend have attained comparatively low TS values that extend over a limited range. On the other hand, the tensile values attained for unloaded as well as loaded blends increased with the irradiation dose reaching its maximum value at 200 kGy and then they decreased over any further increase in dose. Moreover, it may be observed that unloaded blend has attained the lowest *TS* value over the whole range of irradiation and that the values attained by loaded composites increase with the degree of loading with the filler. Besides, comparatively high TS values have been attained by composites loaded with 50 phr or more of the filler.
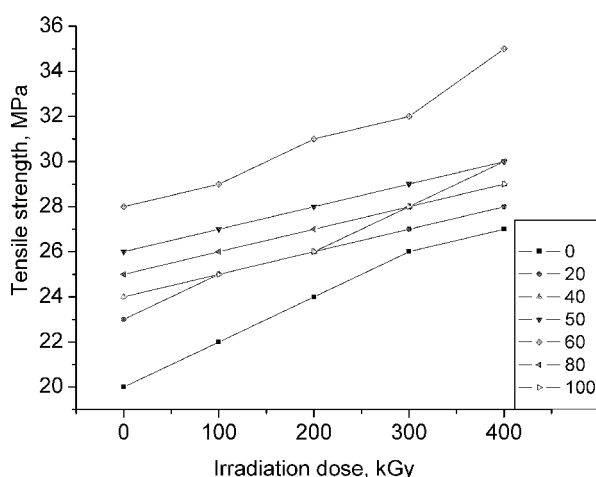
Figure 2. The effect of the radiation dose on the tensile strength of NR/CSM rubber blend reinforced with a different content of carbon black.
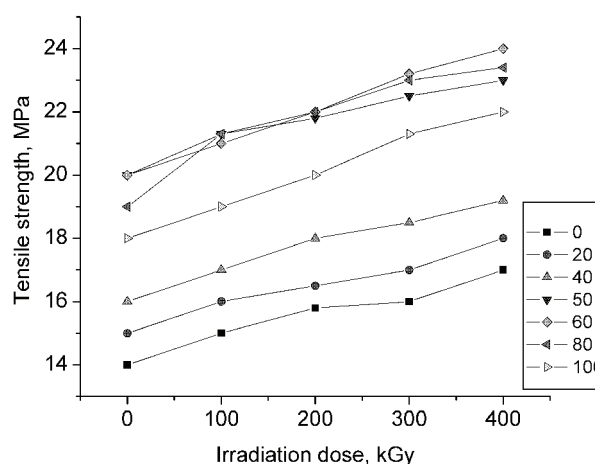
Figure 3. The effect of the radiation dose on the tensile strength of NBR/CSM rubber blend reinforced with a different content of carbon black.

These data indicate clearly that carbon black has acted effectively in raising up the TS value of radiation vulcanized NR/CSM and NBR/CSM blends, especially for a degree of loading 50 phr. NR, NBR and CSM rubbers are categorized as predominantly radiation cross-linkable type of polymers [17] which would account for the increase in TS values with the radiation dose up to 200 kGy. Apparently, the degradation may then predominate, accompanied with the restriction in reorientation, for doses higher than 200 kGy [18]. The TS measurements were carried out at comparatively large elongations and it would be expected that carbon black filler exists in its particle form, that is, in its almost accessible area. A high stress transfer between the rubber matrix and filler particles would then be expected to take place. Moreover, the different type of groups that exist on its surface such as carboxylic, phenolic, hydroxylic, aldehydic and ketonic, would then participate in physical as well as chemical bond formation at the interface between the filler and rubber matrix, on irradiation [19]. These two parameters would account for the role played by carbon black filler in increasing the TS values of the radiation induced loaded rubber composites. The data obtained for the variation of tensile modulus at 100% elongation, M100 as a function of radiation dose for unfilled and filled NR/CSM and NBR/CSM (50/50) blends are depicted in Figs. 4 and 5, respectively. The data for corresponding compositions without radiation are also given. Here again, the values obtained for M100 for latter compositions are relatively small with respect to corresponding radiated ones. Moreover, it may be observed that the values of M100 for different samples are directly proportional to the radiation dose up to 400 kGy. In addition, a degree of loading with

carbon black filler of 50 phr or more has resulted again in a noticeable increase in the rate of variation of M100 value with respect to the irradiation dose. These results may be attributed not only to the radiation induced cross-linking, as well as different interphase linking, but also to the role played by the carbon black filler as a separate phase. In this respect and under a limited extension of 100% elongation, the carbon black filler would be expected to exist predominantly in its "structure" state, according to particles aggregated solid and separate form [20]. The effective contribution to the M100 value of vulcanized composites from this solid phase of the filler would then be expected, when taking into consideration that the tensile modulus parameter is an additive in character. The obtained results are in accordance with the comparable results reported before for other rubber composites [21].
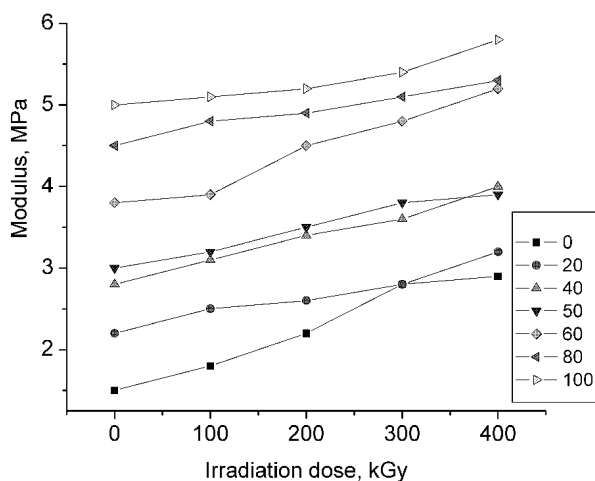

Figure 4. The effect of the radiation dose on the modulus of NR/CSM blend reinforced with a different content of carbon black.
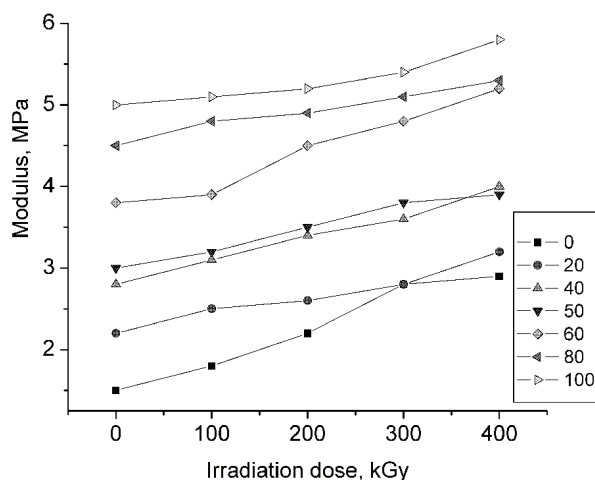

Figure 5. The effect of the radiation dose on the modulus of NBR/CSM blend reinforced with a different content of carbon black.

The variation of the values of elongation at break percent, *Eb* %, as a function of irradiation dose for unloaded as well as carbon black loaded NR/CSM and NBR/CSM blends is depicted in Figs. 6 and 7, respectively. As expected, the values of *Eb* for both reinforced blends decrease with increasing the irradiation dose. This systematic decrease in *Eb* values may be attributed to the induced cross-linking by gamma irradiation. On the other hand, the *Eb* values decreased with the increase in a carbon black filler loading. This reduction is due to stiffening of the matrix by carbon black filler particles [22]. In fact, with any further increase in filler loading the molecular mobility decreased due to the formation of a physical bonding between the filler particles and the rubber chain. The decrease of *Eb* values for blends loaded with the increasing radiation dose may be explained as an additional bonding between the filler and rubber due to the large number of free radicals formed under radiation. Therefore, an increased radical recombination is likely to generate strong chemical linkage with an increase of the irradiation dose.
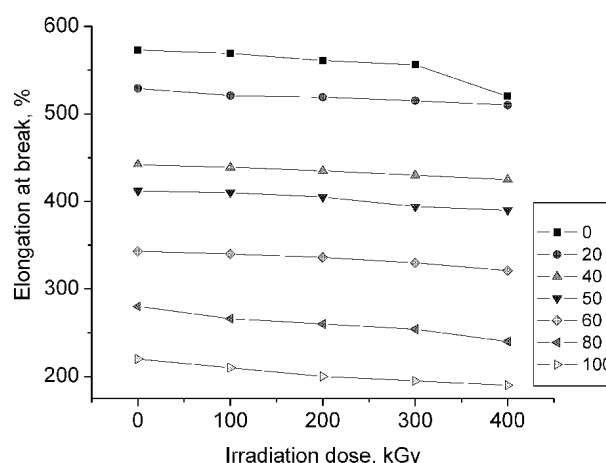

Figure 6. The effect of the radiation dose on the elongation at break of NR/CSM rubber blend reinforced with a different content of carbon black.

The changes of hardness of loaded and unloaded NR/CSM and NBR/CSM rubber blend as a function of the radiation dose is illustrated in Figs. 8 and 9, respectively. Also, the data for loaded rubber without irradiation were introduced in the same figure for comparison. It may be observed that the values of hardness of the latter composition have increased effectively with increasing the degree of loading with the filler. A similar behavior has been attained for the radiation vulcanized composites when comparing its hardness values at the same irradiation dose. On the other hand, a comparatively limited increase has been

attained in the value of hardness for one and the same composition, whether loaded or unloaded, with increasing the irradiation dose from 100 to 400 kGy. These data indicate clearly that the contribution to hardness values from the radiation-induced cross-linking that has taken place in the totally amorphous rubber matrix of NBR/CSM blend is a limited one. On the other hand, the main contribution to the hardness value is affiliated with the occurrence of the filler in its aggregated solid and distinct phase, that is, its "structured" form as mentioned before.
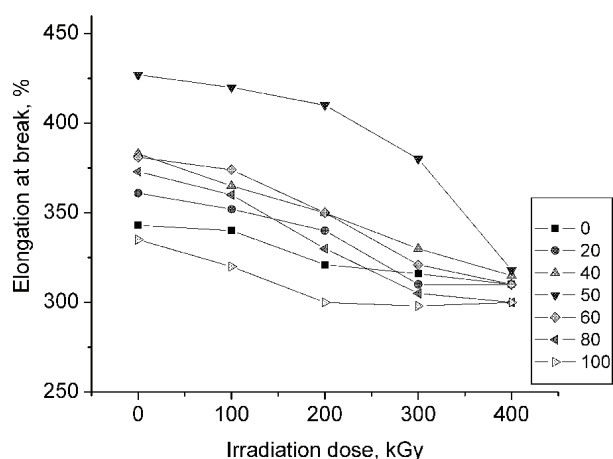

Figure 7. The effect of the radiation dose on the elongation at break of NBR/CSM rubber blend reinforced with a different content of carbon black.
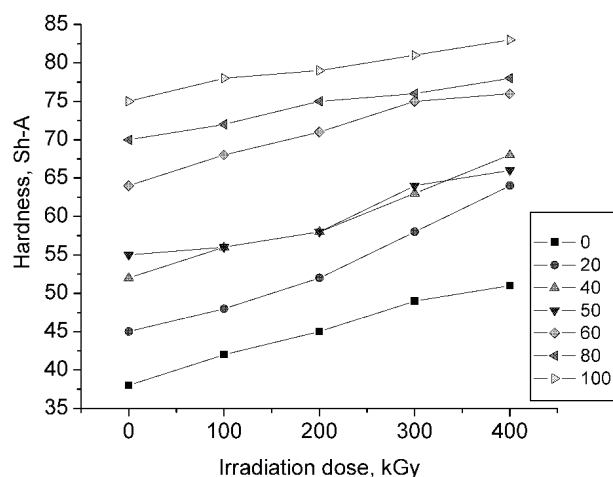

Figure 8. The effect of radiation dose on the hardness of NR/CSM rubber blend filled with different content of carbon black.

Electron scanning microscopy

　　SEM micrographs of fractured surfaces for NR/ /CSM and NBR/CSM rubber blend filled with 60 phr are shown in Fig. 10 and Fig 11, respectively. The formation of small micro-craters was observed in

NBR/CSM rubber blends. A detachment of small micro-craters from the fractured surface is a result of poor polymer-filler adhesion. A comparatively good polymer-filler interaction with carbon black and NR/CSM blend increases the resistance to fracture [22]. Filler distribution in the blend affects the properties of the obtained elastomeric materials.
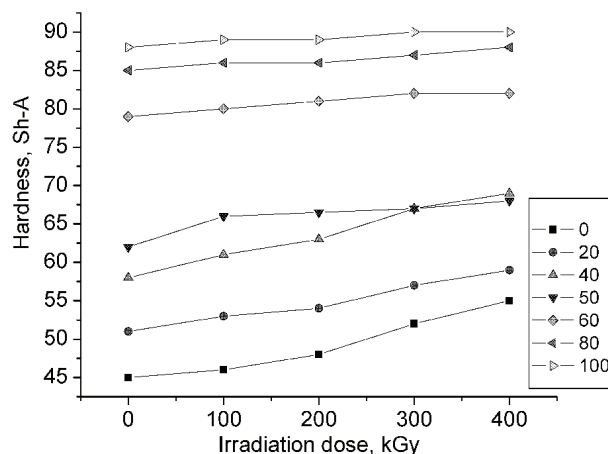

Figure 9. The effect of the radiation dose on the hardness of NBR/CSM rubber blend filled with a different content of carbon black.
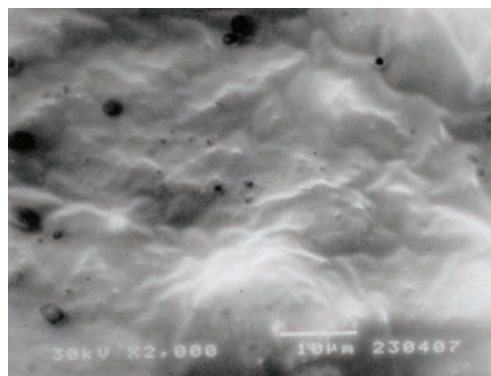

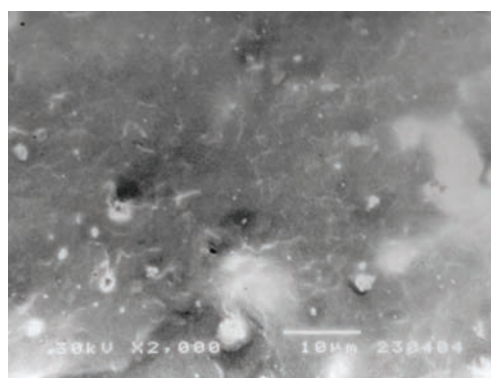Figure 10. SEM of radiated NR/CSM rubber blend filled with carbon black (60 phr).

Figure 11. SEM of radiated NBR/CSM rubber blend filled with carbon black (60 phr).

FTIR spectra measurements

Gamma radiation leads to significant changes in the FTIR spectra of carbon black reinforced elastomers based on NBR/CSM (fig 12 a and 12b) and NR/CSM (fig 13a and 13b) rubber blend. The broad increase in absorption can be found in C=O, O-H, and C-O stretching vibration domains for both blends. Significant changes appeared in the region of conjugated double bonds, too. Several oxidation products contribute to band at the hydroxyl region, *i.e.* alcohols (band at 1028-1075 cm^{-1}), ethers and small amounts of lactones, anhydrides, esters and carboxylic acids. Due to the formation of oxidation products, the bands related to CH_2, CH_3, =C-H and C=C vibrations decrease. CH_2 deformation band at 1458 cm^{-1}, CH_3 asymmetric deformation at 1372 cm^{-1}, and =C-H wagging at 831 cm^{-1} show a significant increase in the spectra of irradiation reinforced rubber blend.

A decrease in absorption at 1660 cm^{-1} is related to the loss of C=C bonds in 1,4-*cis* units. 1,4-*Cis* units also absorb at 831 cm^{-1}. Besides the oxidation of C=C bonds in 1,4-*cis* units, *cis-trans* the isomerization can take place. The band at 2956 cm^{-1} related to methyl groups decreases, especially at the highest doses 200, 300 and 400 kGy. Researchers in the field elastomers based on polyisoprene, acrylonitrile and chlorosulphonated polyethylene rubbers [23] did not report the appearance of new bands related to these processes in the conjugated double bonds region of radiated NR/CSM and NBR/CSM FTIR spectra. In thermally degraded NR/CSM and NBR/CSM rubber blends there have been identified di pentene, two isomeric forms of dimethylvinylcyclohexene, isoprene, and some aromatic compounds formed via the Diels-Alder reactions. Coran [24] reported that during thermal degradation of 1,4-*cis*-polyisoprene, the chains with conjugated C=C bonds are also formed. Chan-
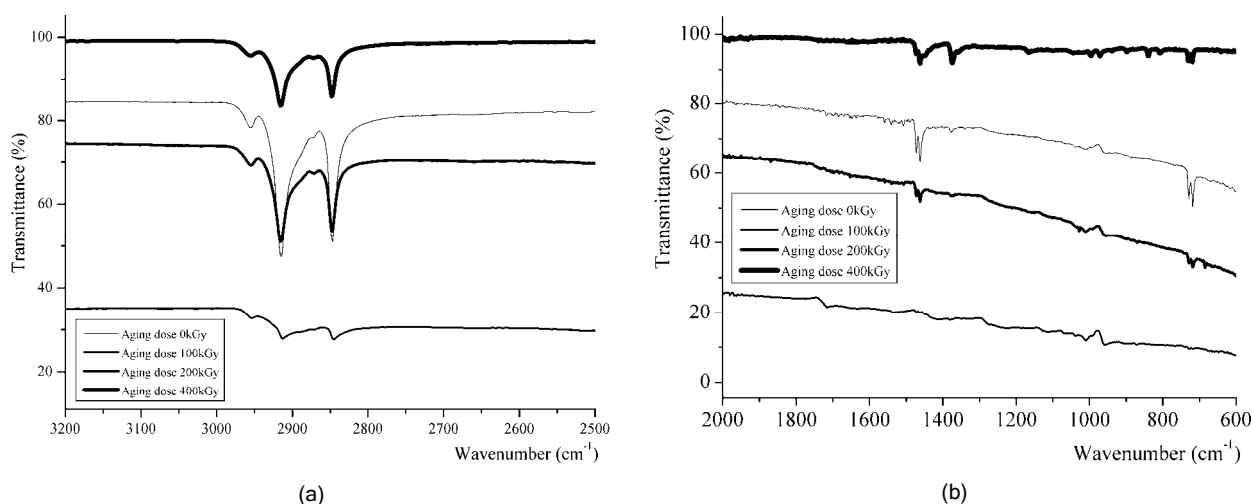

Figure 12. FTIR spectra (a and b) of elastomers aged under different doses for NR/CSM rubber blend filled with carbon black (60 phr).
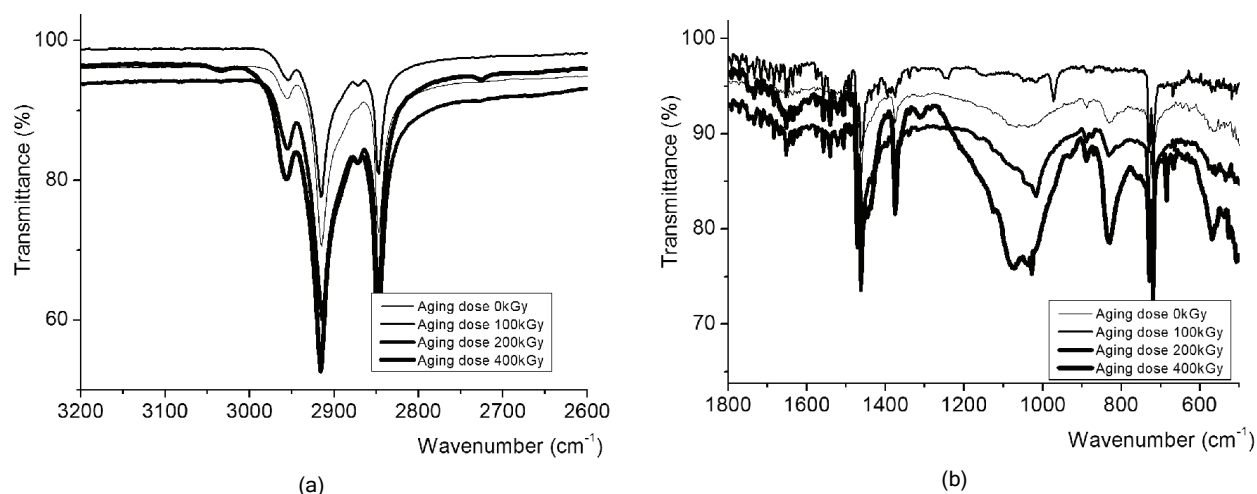

Figure 13. FTIR spectra (a and b) of elastomers aged under different doses for NBR/CSM rubber blend filled with carbon black (60 phr).

ges corresponding to similar processes are also present in the region 1620-1450 cm $^{-1}$ of the irradiated polyisoprene and acrylonitrile spectra, where no oxidation product absorbs. Polyenes and polyenals show several bands in the 1500-1650 cm $^{-1}$ range. Benzene C=C stretching vibrations bands are located between 1600-1450 cm $^{-1}$; hydrogen bond can cause the reduction of the stretching vibration frequency. The subtraction spectra reveal the occurrence of the broad band with a significant increase in absorption at 1470 cm $^{-1}$. This band can be assigned to aromates and shorter polyene structures. Absorption at 1470 cm $^{-1}$ remains the same (the maximum is slightly shifted to higher wave numbers) for highest doses, absorption at 1461 cm $^{-1}$ was lowered in the case of the sample irradiated with the highest dose (Figs. 7 and 8). It implies that formed species are a subject of consecutive reactions. It can be concluded that radiation induces serious changes in NR/CSM and NBR/CSM rubber blends backbone - chain scissions and various consecutive reactions take place. These changes are noticeable in the 1470-1450 cm $^{-1}$ region that indicates the occurrence of the polyene sequences and aromatic rings. Contrary to the chain scission reactions [25], the formation of cross-links is difficult to detect by using IR spectroscopy due to the overlap of many bands in the region of C-C stretching vibrations. Doses exceeding 200, 300 and 400 kGy caused serious modification of the polymer structures.

CONCLUSION

The influence of carbon black (with an average particle size of 40 nm) on gamma-radiation resistance of rubber blends was investigated. The mechanical properties of elastomer depend mainly on the carbon black loading. Tensile strength, modulus at 100% elongation and hardness were increased with increasing the radiation dose, as well as carbon black loading, but the elongation at break values decreases with increasing the radiation dose and carbon black content. The FTIR spectra of aged samples confirmed the formation of various oxidation products, *i.e.* alcohols, ethers and small amounts of lactones, anhydrides, esters and carboxylic acids during radiation. Significant changes in spectra are induced by chain scission which was registered in the 1620-1450 cm $^{-1}$ region. The formation of shorter polyene sequences and aromatic rings are assumed. The radiation doses lower than 100 kGy influenced only small changes in

the rubber macromolecules structure if we consider the development of the bands in carbonyl and conjugated C=C bonds regions. On the other hand, 200, 300 and 400 kGy doses caused a serious chemical modification of the prepared rubber blend samples.

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