THE PROPERTIES OF GAMMA IRRADIATED ELASTOMERIC NANOCOMPOSITES BASED ON CHLOROSULFONATED POLYETHYLENE

Jaroslava Budinski-Simendić1*, Gordana Marković2, Jelena Tanasić1, Milena Marinović-Cincović3, Ayse Aroguz4, Vesna Teofilović1, Ljiljana Korugic Karasz5

1 Faculty of Technology, University of Novi Sad, Bulevar cara Lazara 1, Novi Sad, Serbia
2 Tigar A.D., Nikole Pašića 213, Pirot, Serbia
3 University of Belgrade, Institute of Nuclear Science Vinča, PO Box 522, Belgrade, Serbia
4 Istanbul University, Faculty of Engineering, Chemistry Department, Avcilar Campus, Turkey
5 University of Massachusetts, Amherst, USA

Abstract: In the case of irradiation of polymeric materials, the progress in oxidative degradation depends on absorbed dose, dose rate, exposure environment, energy of irradiation, chemistry of material, and previous state of ageing. It is known that the main effect of the interactions between gamma rays and rubber macromolecules is the formation of free radicals, whose further evolution can cause crosslinking with increase in the crosslinking density or chain scission. Chlorosulfonated polyethylene is specifically recommended for sheeting of cables in nuclear energetic plants. Elastomers based on this network precursor are resistant to wear and repeated deformation and have excellent irradiation resistance. The goal of the current work was to study the effects of γ-ray radiation for elastomers based on chlorosulfonated polyethylene in combination with nitrile rubber. The reinforcing filler was nano-silica. The irradiation was performed in the Co60 radiation sterilization unit. The level of ageing was evaluated using the hardness and swelling measurement. The use of silica nano-particles improved the swelling resistance in toluene after irradiation ageing.

Keywords: rubber, polymer network, ageing, composite materials.

1. INTRODUCTION

Elastomers are polymers with viscoelasticity and very weak inter-molecular forces, generally having low Young's modulus and high failure strain compared with other materials. Under normal conditions, the macromolecules making up an elastomeric material are irregularly coiled. With the application of force, however, the molecules straighten out in the direction in which they are being pulled. Upon release, the molecules spontaneously return to their normal compact, random arrangement. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibility, elastomers can reversibly extend from 5 to 700%, depending on the specific material. Without the cross-linkages or with short, uneasily reconfigured chains, the applied stress would result in a permanent deformation. Elastomers are rarely applied in their pure form. They are “too weak” to fulfil practical requirements because of lack of hardness, strength properties and wear resistance.

Fillers are used in order to improve the properties. Based on the dimensions of fillers, it can be macro, micro, and nano sized. Elastomer-based nano-composites have been recognized as convenient materials for the fabrication of technologically important products. The nuclear power plants are using rubbers for many sealing applications such as airlock doors, hatches, vibration damping, pool gates. Elastomeric seals are a frequently favoured method of sealing radioactive material transport. The designer of a package with a twin elastomeric sealing system should also be aware of the possibility of high pressure arising in the interspace between those seals, due to thermal expansion of fluids trapped in that interspace. Irradiation of elastomer seals can result in increased compression set, and hence a reduction in sealing performance. The resistance of a seal to irradiation depends on the seal material and the environment it is in. Made from macromolecules from which they derive their names, rubbers also contain other materials and various additives. For selecting a network precursor for seal recipes without understanding the
The degradation of materials always takes place during exposure. The action of ionizing radiation is the most important aspect concerned for the materials usage in various components of nuclear equipment. Polymer materials in cables and accessories for nuclear engineering applications must typically be designed to withstand extreme environmental conditions. The progress in oxidative degradation of materials depends on absorbed dose, dose rate, exposure environment, energy of incidental radiation, chemistry of material, and previous state of ageing. The minimization of degradation can be accomplished by the addition of stabilizing components. The action of stabilizers is a preventive activity through which free radicals formed during exposure are generated. The scavenging action of additives blocks the reaction of hydrocarbon fragments with the molecular oxygen diffused inside the material from surrounding environment. These components protect reactive radicals, which can survive for long period or they can react to each other for achieving a higher cross-linking [1]. As a method for sterilizing medical devices, irradiation with gamma-rays has been widely employed in recent years. The gamma-rays are exciting the oxygen to yield ozone, an allotrope of oxygen, and, hence, generating the so-called gamma odor which is considered to be associated with ozone. Nitrile rubber (NBR) is a family of unsaturated copolymers of 2-propenenitrile and butadiene monomers (1,2-butadiene, 1,3-butadiene). Although its physical and chemical properties are dependent on the composition, this synthetic rubber is unusual in being generally resistant to oil, fuel, and other chemicals. The ability of NBR to withstand a temperature range from −40 to 108°C makes it an ideal material for oil, fuel, and other chemicals [2,3] for aeronautical applications. Different part of macromolecules provide very specific advantages for NBR gloves: the acrylonitrile enhances the chemical resistance, while butadiene creates flexibility and tear resistance.

Gamma ray irradiation is widely used as a means of medical device sterilization. Medical grade is a term used to designate rubber materials that will be put to use in diagnostic devices and medical equipment and are non-contaminating to the surrounding media. Materials based on NBR have superior strength, but has inferior flexibility. It is used in the nuclear industry to make protective gloves. Seals prepared from NBR are one of the classified materials used in nuclear facilities. At higher radiation doses, the physical properties of materials based on NBR are adversely affected due to the degradation and hence affect the sealing performance reducing material service life. NBR is the standard material for hydraulics and pneumatics products. There are also special low-temperature systems available for mineral oil-based fluids. Rubber medical seals are used in process equipment, pumps, pipes, couplings, valves, reactors and containers and must be able to cope with a wide
range of process media, active pharmaceutical compounds and aggressive sterilizing processes. By hydrogenation and the addition of carboxylic acid, the nitrile polymer can reach a more specified range of requirements. In order to improve the NBR sealing performance, this network precursor can be blended with other rubbers. Blending of two or more types of rubber is a useful technique for preparing materials with properties superior to those of individual constituents [4−7]. Moreover, each kind of network precursor in the blend has its own advantages and specific application due to its chemical configuration. Hence, it is economically easier to blend more than one type of rubber having the desired properties rather than chemically create a new elastomer. Chlorosulfonated polyethylene (CSM) is appropriate for advanced rubber blend preparation. It is superior to other rubbers in its resistance to the ozone and inorganic acids, such as chromic, nitric, sulfuric, and phosphoric acids, as well as to the effects of concentrated alkalis, chlorine dioxide, and hydrogen peroxide. Properly formulated elastomer based on this network precursor offer good dynamic properties and strong adhesion to various substrates, but due to its poor compression set, thus the dynamic sealing applications are not recommended. It is specifically recommended for sheeting of cables in nuclear energy plants.

Elastomers based on CSM are used for dry box gloves, inflatable and folding kayaks, as roofing materials, for the decking of modern snowshoes, and is widely practiced in exteriors or outer protective jackets in high-voltage applications due to its outstanding weather-resistant property. CSM is also applied in the preparation of composites to minimize the influence of radiation pollution emitting uncontrollably from electronic devices. The temperature range for the most efficient use is from –60° to 180°C. Elastomers based on CSM are resistant to wear and repeated deformation and have excellent irradiation resistance needed in nuclear power stations. Owing to the chlorine, it is resistant to oil, fire, the action of microorganisms, and exhibits good adhesion to various surfaces. The synergy effects of irradiation and temperature on degradation of CSM was investigated by Foucault et al [8]. The main effect of dose rate, temperature and atmosphere on molecular changes was the formation of trans-vinylene groups and in the presence of oxygen formation of oxidation products. Ivan [9] studied the influence of gamma irradiation on the behavior of CSM in the range of total absorbed dose of 5 to 550 kGy by infrared spectroscopy. The exposure to irradiation leads to cleavage of chlorine and chlorosulfonyl groups with formation of hydrochloric acid and sulfur dioxide accompanied by the formation of free macro-radicals and unsaturated C=C units. The structural group —SO2Cl and labile chlorine atoms participate in the cross-linking of this rubber. The enormous improvement in mechanical properties as well as electrical and thermal conductivity of the composites based on CSM can be obtained by the addition of the filler particles including conductive fillers. The physical behavior of composites is quite captivating with respect to other rubber composites in a wide temperature range from –80 to 160 °C. In our earlier works, we studied the thermal stability of CSM/ NBR rubber blends [10]. The goal of this work was to study gamma irradiation ageing of silica reinforced rubbers based on two network precursors (NBR and CSM). In our earlier work, we estimated using DSC method that CSM/NBR blend is thermodynamically immiscible. This is concluded by the existence of two glass transitions, corresponding to pure CSM and NBR rubbers. [11]

2. EXPERIMENTAL PART

Nitrile rubber (NBR) (Kynac 3950F, was supplied by Lanxess, Germany (In the figure 1 is given the chemical structure of NBR). Chlorosulfonated polyethylene (Its structure is given in the Figure 2), Hypalon 40S with 35% chlorine and 1% sulfur was obtained from du Pont de Nemours. The system for crosslinking was tetramethyl thiram disulfide (1phr), N-cyclohexyl 2benzothiazosulfon amide (1 phr), magnesium oxide (4 phr) and sulfur (1.5 phr). Content of zinc oxide was 5 phr. The stearic acid content was 2 phr. The naphthenic oil content was 10 phr.

![Figure 1. The chemical structure of nitrile butadiene rubber.](image)

The reinforcing filler was silica (Ultrasil VN3, Degussa) with primary particles size 22 nm. This filler has a high reinforcing potential and imparts to rubber compounds high Shore hardness, tensile strength, tear
resistance and abrasion resistance. In order to achieve optimum rubber-technical data, the addition of activators like glycols, amines or other alcaline accelerators is necessary. On account of its high specific surface area (180m²/g), it can provide elastomers of excellent transparency.

\[
\text{Figure 2. The chemical structure of chlorosulfonated polyethylene rubber.}
\]
dominant in correlation with additional cross-linking during irradiation. Moreover, the network architecture of the material becomes very irregular. After degradation, the network contains more and more weakened zones, which deteriorate the material ultimate properties. It was observed that the hardness is increasing with the increase of silica content. For composites based on polar rubbers such as CSM, the occurrence of chemical reactions with silica surface functional groups is more probable. The volume swell ratio was measured by immersing in toluene to characterize the cross-linking degree. The low value refers to high cross-linking degree. In the Figure 4, given is the effect of irradiation doses on the swelling degree for blends with different content of nanoparticles. In the case of unfilled elastomer, the swelling restriction is due to cross-links connecting the polymer chains, which avoid their extension and their diffusion. Because of the filler–rubber interactions, the addition of silica nano fillers is equivalent to the additional cross-links, which perturb the network swelling. The decrease of the volume swelling degree for rubber blends exposed to higher irradiation dose is explained by an additional bonding between the filler and rubber due to the large number of free radicals formed under irradiation.

Table 1. The obtained curing data for elastomeric nano-composites with different content of silica nano particles assessed by oscillating disc rheometer

| Sample          | Silica content phr | $M_{1}, \text{dNm}$ | $M_{99}, \text{dNm}$ | $\Delta M, \text{dNm}$ | $t_{90}, \text{min}$ | $t_{90}, \text{min}$ |
|-----------------|--------------------|---------------------|---------------------|-----------------------|----------------------|----------------------|
| NBR/CSM/0       | 0                  | 8                   | 25                  | 17                    | 5                    | 23                   |
| NBR/CSM/20      | 20                 | 7                   | 28                  | 21                    | 6                    | 24                   |
| NBR/CSM/40      | 40                 | 7                   | 30                  | 23                    | 8                    | 26                   |
| NBR/CSM/60      | 60                 | 6                   | 36                  | 30                    | 11                   | 26                   |
| NBR/CSM/80      | 80                 | 6                   | 36                  | 30                    | 11                   | 27                   |
| NBR/CSM/100     | 100                | 5                   | 36                  | 29                    | 14                   | 30                   |

Figure 3. The effect of irradiation dose on hardness (as Shore A) of composites based on CSM and NBR network precursor and different content of silica nanoparticles (in phr).
4. CONCLUSION

It is known that the main effect of the interactions between gamma rays and rubber macromolecules is the formation of free radicals, whose further evolution can cause crosslinking with increase in the cross-linking density or chain scission. Usually all these phenomena co-exist, the prevalence of each depends on many factors which can affect the concentration of the reactive species. The study was initiated to investigate the aging performance of silica reinforced CSM/NBR blends after gamma irradiation. Prepared samples were evaluated before and after ageing according to traditional essays, such as: hardness measurements and swelling in organic solvent. As a consequence of gamma irradiation, the values of hardness increased with increasing irradiation dose. It was observed that the samples hardness is increasing also with the increase of silica content. The decrease of the volume swelling degree for rubber blends exposed to higher irradiation dose is explained by an additional bonding between the filler and rubber due to the large number of free radicals formed under irradiation. For composites based on polar rubbers such as CSM, the occurrence of chemical reactions with silica surface functional groups are more probable. The use of nanoparticles improved the swelling resistance in toluene after irradiation of elastomeric materials. At higher irradiation dose chain scissions become the major degradation process. Moreover, the network architecture of the material becomes very irregular. After degradation, the network contains more and more weakened zones, which deteriorate the material ultimate properties.

5. ACKNOWLEDGEMENT

Financial support for this study was granted by the Ministry of Science and Technological Development of the Republic of Serbia (Projects Numbers 45022 and 45020).

6. REFERENCES

[1] M. Abou Zeid, S. Rabie, A. Nada, A. Khalil, R. Hilal, Effect of gamma and UV radiation on properties of EPDM/GTR/HDPE blends, Polymer-Plastics Technology and Engineering, Vol. 47–6 (2008) 567–575.
[2] M. Hassan, R. Aly, A. El-Ghandour, H. Abdelnaby, Effect of gamma irradiation on some properties of reclaimed rubber/nitrile-butadiene rubber blend and its swelling in motor and brake oils, Journal of Elastomer and Plastics, Vol. 45–1 (2013) 77–94.
[3] G. Marković, B. Radovanović, M. Marinović-Cinčović, O. Veljković, J. Budinski-Simendić, High energy radiation resistance of composites based on NR/CSM rubber blend, Kautschuk Gummi Kunststoffe Vol. 6–7 (2008) 363–3677.
[4] G. Marković, B. Radovanović, M. Marinović-Cincović, J. Budinski-Simendić, Investigations of SBR/CSM blends reinforced by carbon black. Kautschuk Gummi Kunststoffe, Vol. 5 (2006) 251–255.

[5] S. Samaržija-Jovanović, V. Jovanović, G Marković, S. Konstantinović, M. Marinović-Cincović, Nanocomposites based on silica-reinforced ethylene–propylene–diene–monomer/ acrylonitrile–butadiene rubber blends, Composites: Part B, Vol 42 (2011) 1244–1250.

[6] G. Marković, S. Samaržija-Jovanović, M. Jovanović, M. Marinović-Cincović, Thermal stability of CR/CSM rubber blends filled with nano and micro-silica particles, Journal of Thermal Analysis and Calorimetry, Vol 100 (2009) 881–888.

[7] R. Mohamed, M. Khatta, M. Abdel-Aziz, Effect of gamma-irradiation on the physico mechanical properties of synthetic rubber-based silica composites, Advances in polymer Technology, Vol. 30 (4), (2011) 301–311.

[8] F. Foucault, S. Esnouf, A. Moel, Irradiation/temperature synergy effects on degradation on degradation and ageing of chlorosulpho-ated polyethylene, Nuclear Instruments and Methods in Physics Research, Vol. 183, (2001) 311–317.

[9] G. Ivan, M. Giurginca, T. Zaharescu, Behaviour of chlorosulfonated polyethylene under gamma irradiation, Macromolecular Symposia, Vol. 129, (1998)163–172.

[10] G. Marković, B. Radovanović, V. Vodnik, M. Marinović-Cincović, J. Budinski-Simendić, Investigation of chemical interactions between CSM and NBR, Kautschuk Gummi Kunststoffe, Vol. 31 (2009) 103–107.

[11] G. Marković, B. Radovanović, V. Vodnik, M. Marinović-Cincović, J. Budinski-Simendić, O. Veljković, Thermal stability of acrylonitrile/ chlorosulphonated polyethylene rubber blend, Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 999–1006.

СВОЈСТАВА ЕЛАСТОМЕРИХ НАНОКОМПОЗИТА НА ОСНОВУ ХЛОРОСУЛФОНОВАНОГ ПОЛИЕТИЛЕНА ОЗРАЧЕНХ ГАМА ЗРАЦИМА

Сажетак: У случају озрачивања полимерних материјала, напретовање оксидативне деградације зависи од абсорбоване дозе, брзине зрачења, изложености специфичној околнини, енергији зрачења, хемијској структури материјала, као и претходног нивоа старења. Познато је да је главни ефекат интеракције између гама зрака и макромолекула еластомерног материјала настањање слободних радикала који узрокују додатно умрежавање или разарање ланца. Хлоросулфоновани полиетилен се специфично препоручује за облоге каблова у постројењима нуклеарних електрана. Еластомери на основу овог прекурсора су резистентни на старење и понављајуће деформације и имају одличну отпорност на дејство зрачења. Циљ овог рада је био да се испита старење еластомера на основу хлоросулфонованог полиетилен са нитрилним каучуком при дејству гама зрачења. Ојачавајуће пунило је био нано спицијум-диоксид. Озрачивање материјала је остварено у Кобалт60 инструменту за стерилизацију. Ниво старења на основу зрачења је одређиван мерњем тврђења и бубрења. Установљено је да додатак наночестица побољшава отпорност озрачених узорака према бубрењу у толуену.

Кључне речи: гума, полимерна мрежа, старење, композитни материјали.