



Review

Radiation-induced degradation of butyl rubber vulcanized by three different crosslinking systems

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ARTICLE INFO

Article history:

Received 25 June 2011

Accepted 7 January 2012

Available online 28 January 2012

Keywords:

Butyl rubber

Degradation

Gamma radiation

Crosslinking systems

Vulcanization

ABSTRACT

Butyl rubber (IIR) is an isobutylene/isoprene copolymer and is provided with good properties including low permeability to gases, good thermal stability and high resistance to oxygen and ozone action, among others. It is well known that the major effect of ionizing radiations on butyl rubber is chain scission accompanied with a significant reduction in molar mass. This work aimed to study the effects of gamma radiation on the properties of butyl rubbers vulcanized by three different curing systems, such as, the ones based on sulfur, sulfur donor and phenolic resin to identify which curing system is the most stable under irradiation. The butyl rubber vulcanized by three different systems was gamma irradiated with doses of 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy. Irradiated and non-irradiated samples were characterized by the following techniques: tensile, elongation and hardness. It was observed that doses higher than 150 kGy practically destroy the assessed properties for all butyl compounds, irrespective of the vulcanization system used; however compounds cured with phenolic resin showed a decrease in properties proportional to the dose.

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1. Introduction

Butyl rubber (IIR), a copolymer of isobutylene and isoprene (IIR) has been used in a great variety of applications, such as inner tubes, internal coating of tires and various articles (lids, gaskets, etc.) (Karaagaç et al., 2007), due to their unique properties, including low gas permeability, good thermal stability, high resistance to oxygen and to ozone and solar radiation action (Teinov et al., 2002). As a result, IIR has reached a very large consumption worldwide; therefore it was necessary to develop its recycling technologies. The recycling can be troublesome due to the availability of different types of scrap IIR vulcanized with different curing systems. The curing systems are specified according to the product's final application, its specification and production restrictions, like raw materials availability and cost. Rubber must be compounded and vulcanized to yield useful and durable products. The selection and the choice of ratios for the proper fillers, processing aids, stabilizers and curing systems also play critical roles in both how the compound will be processed and how the end product will behave (Morton, 1989). Almost 90% of all sulfur vulcanizations occur in natural rubber, ethylene-propylene-diene (EPDM), butyl rubber and nitrile rubber (Hofmann, 1989; Coran, 2003).

The use of high energy radiation was already proposed as an advanced technique to allow the industrial reprocessing of scrap rubber (Landini et al., 2007; Burillo et al., 2002) and in particular IIR (Binglin et al., 1993; Yang, 1998; Yang and Liu, 2000).

Chapiro (1962) had already unraveled the radiation chemistry of IIR and understood that its main reaction was chain scission. This characteristic was explained by the presence of quaternary carbon atom in the isobutylene unit of butyl rubber macromolecules. The major effect of ionizing radiations on butyl rubber is chain scission accompanied by a significant reduction in molar mass (Chandra et al., 1982 and Hill et al., 1992). According to Zaharescu et al. (2001), the energy transfer from the radiation to the matter is not selective, but the lower the bond energy, the faster is the bond scission. Recently, the degradation induced by radiation in Chlorobutyl rubber was evaluated via Dynamic Mechanical Analysis (DMA) tests, consonant evaluations of the Payne effect. This effect reveals a particular feature of the stress-strain behavior of vulcanized rubber compounds containing carbon black and other fillers, and allows us to identify correlations with micro-deformations induced by changes in the microstructure of the sample. In other words, the dynamic deformation leads to the rupture and recovery of the weak physical bonds of the rubber with its reinforcement loads. The above deformation also breaks the agglomerate structure of the reinforcement loads and thus lowers the resistance of the rubber. The authors (Scagliusi et al., 2010) observed that the irradiation induced a severe degradation on IIR and the Payne effect was inversely

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proportional to the dose because the smaller the Payne effect the smaller is the compound's viscosity.

This work aims to study the effects of gamma radiation on the properties of vulcanized butyl rubber with sulfur, sulfur donors and phenolic resin.

2. Materials and methods

2.1. Materials

The butyl rubber used in this study was Butyl grade 268 from Exxon Mobil Chemical. Samples were prepared with three different types of vulcanization systems (see Table 1) and reference formulations were based on standards commonly used in tyre and automotive industry. Isobutylene-based polymers employ a variety of cure systems depending on requirements of the final cured product.

Parts per hundred rubber (phr) is a measurement unit used in the formulation of rubber compounds and refers to the amount of a particular compound in relation to the total amount of rubber used per 100 parts of rubber.

Admixtures were prepared in an open roll-mill, each roll of 40 kg capacity. The samples were cured in an electrically heated HIDRAUL-MAQ, at 5 MPa pressure. Samples cured with sulfur and donors were vulcanized at 170 °C for 15 min and the sample cured with phenolic resin was vulcanized at 190 °C for 15 min. Samples correspond to the same material before and after radiation doses.

2.1.1. Butyl rubber vulcanization

Vulcanization systems contain vulcanizing agents (sulfur, metal oxide and peroxide compounds) and, when necessary, accelerators, activators, retarders, etc.; all of these use to produce the desired vulcanization characteristics of the final cured product. Butyl rubber can be vulcanized by means of three basic methods:

- **Sulfur:** Butyl rubber is provided with a high level of insaturation and can be sulfur crosslinked and further activated with zinc oxide and organic accelerators (Morton, 1989).
- **Sulfur donors:** The use of sulfur donors in replacement of elemental sulfur promotes the creation of elemental monosulfide bonds (Morton, 1989).
- **Resin:** Phenol-formaldehyde resins are classified as resol (Exxon Mobil Chemical, 2006), that is, tridimensional resin systems that build a crosslinking network capable of being used as reinforcing resins, when compared to linear structured resins. Butyl rubber and other elastomers vulcanizations, containing olefinic unsaturation by “resin vulcanization”

Table 1
Formulation of butyl rubber.

Ingredients	Resin cured (phr)	Sulfur cured (phr)	Donors sulfur cured (phr)
Butyl 268	100	100	100
Chloroprene	5	–	–
Zinc oxide	5	5	5
Stearic acid	0.5	1	1.5
Plasticizer	5	25	20
Carbon black HAF 330	60	70	50
Octylphenol formaldehyde	10	–	–
Sulfur	–	2	–
TMTD	–	1	1.75
MBT	–	0.5	1

methods, are dependent on phenol and methyl groups' reactivity from phenol-formaldehyde reactive resins (Kresge et al., 1987).

The chemical structures of curing systems are shown in Fig. 1.

2.2. Irradiation process

11.5 × 11.5 × 0.1 cm³ specimens were prepared and vulcanized, within a 250 g total weight mass. Specimens were irradiated at 25, 50, 100, 150 and 200 kGy doses, in a Cobalt-60 source, at a 5 kGy h⁻¹ dose rate.

2.3. Mechanical properties

The properties of a polymer depend on the chemical structure (composition and constitution), configuration, molecular weight, its polydispersity, morphology, the processing conditions, etc. In addition, the properties of elastomers depend on other ingredients such as fillers, plasticizers and cure systems, or vulcanization also contributes to the performance of the final vulcanized product (Kuczkowski, 1988). The cured IIR's typical properties are specified at ASTM D-2000 (Table 2) and the uncured rubber's basic properties are shown in Exxon Data Sheet (2010). The product has a characteristic specific gravity of 0.92. The product form is white to light amber bales.

For the characterization of triplicate samples, tensile strength at break, elongation and hardness were assessed, before and after gamma irradiations. Tensile strength at break and elongation were accomplished using an EMIC dynamometer, model DL 300, 300 kN maximum capacity according to ASTM D 412. Hardness was conducted following ASTM D 2240, using a Shore A durometer-*Instrutemp*, portable digital model Dp-100. This instrument is provided with a conical needle emerging from the apparatus, kept at zero level by means of a spring.

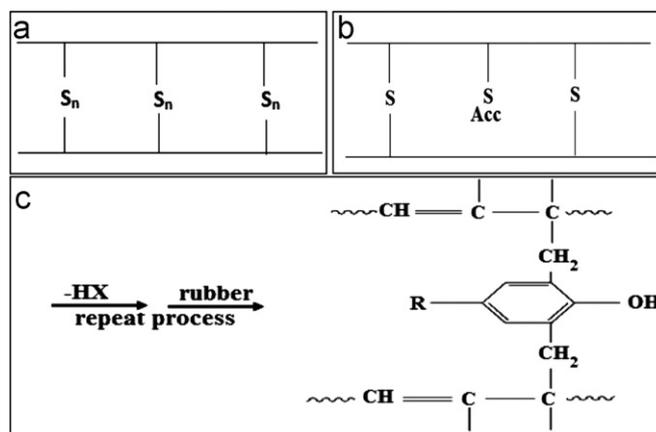


Fig. 1. Chemical structure of curing: (a) sulfur cure, (b) donor sulfur cure and (c) resin cure (octylphenol formaldehyde).

Table 2
Typical properties of unvulcanized butyl rubber (IIR).

Properties	Typical values
Density of polymer	0.92 g/cm ³
Hardness Shore A	30–90
Tensile strength (MPa)	7–17
Elongation at break (%)	800

3. Results and discussions

Mechanical properties were assessed for rubber mixtures, using vulcanizing systems with sulfur, sulfur donors and resin, as a function of irradiation dose. Results for tensile, ultimate elongation (elongation at break) and hardness at different radiation doses were presented in Figs. 2, 3 and 4, respectively.

Vulcanization systems of the tested compounds indicated different sensitivities when irradiated, as observed in Fig. 2. According to Chandra et al. (1982), the initial stages of degradation of butyl rubber generally indicate a random breaking of bonds in the polymer chain. In fact, the vulcanized samples with “resin”, “sulfur” and “sulfur donors” showed that stress rupture decreases proportionally with the increase in radiation. This decrease was caused by a loss of molecular weight in the irradiated polymers, indicating a predominance of polymer chain scission instead of crosslinking, because irradiated butyl rubber loses molecular weight even at doses, which are not that high—this loss can be proved particularly through viscosity measurements (Hill et al., 1992). The vulcanized sample with sulfur showed initially a sharp decline in stress rupture even at low doses, probably because of the high flexibility of the tridimensional network structure, due to the presence of polysulfides

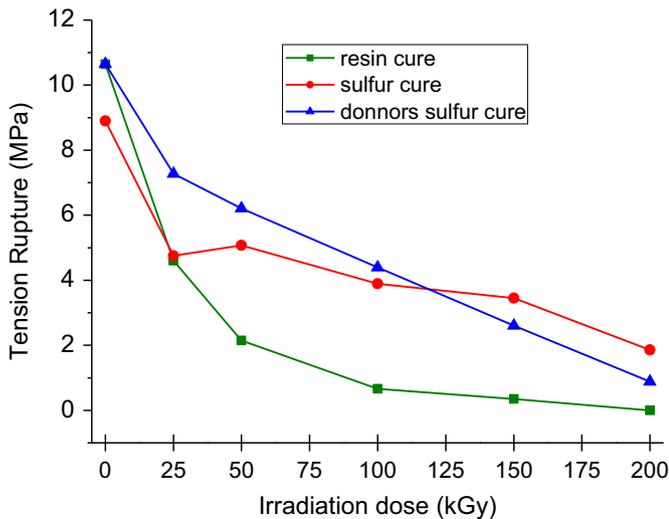


Fig. 2. Tensile strength for butyl rubber cured with sulfur, resin and sulfur donors.

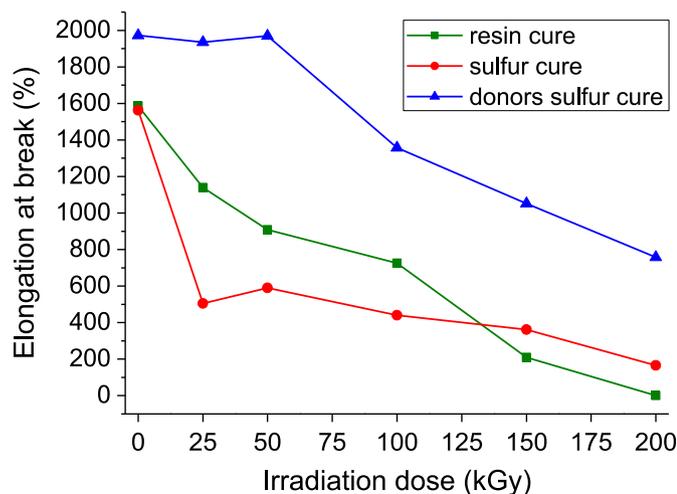


Fig. 3. Elongation at break for butyl rubber cured with sulfur, resin and sulfur donor.

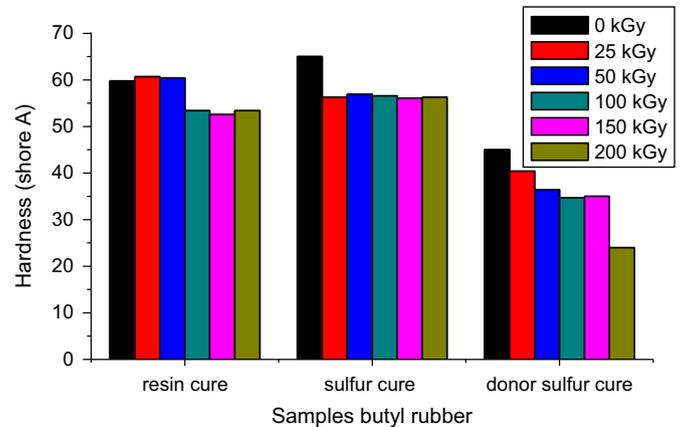


Fig. 4. Hardness for butyl rubber cured with sulfur, resin and sulfur donors samples.

(C–S–S_n–C), where $n > 1$ (Sombatsompop, 1998). For the sample cured with sulfur donor, the molecular weight loss occurred proportionally to the dose, showing that the loss in molecular mass follows the increase in the dose and more severe property losses were observed at doses above 50 kGy, probably because the crosslinked structure is monosulfide (C–S–C), shorter and less flexible. As for the resin vulcanized samples at a 25 kGy dose it was observed a marked loss in the properties, showing that even at low doses the polymer begins to suffer degradation, indicating a loss of molecular weight, because the lower the stress rupture the lower is the compound's viscosity.

Irradiation affects the elongation at break property in different ways for the three vulcanization systems, as shown in Fig. 3. “Sulfur cure” samples showed a significant reduction in elongation leading toward a polymeric chain scission, with sudden reduction at lower doses and almost leveling off for doses above 50 kGy. Changes in the vulcanized network structure are responsible for the change in the vulcanized's properties, due to the curing-system formulation (Coran, 2003). “Sulfur donor” samples experienced a non-significant reduction in properties at doses up to 50 kGy; above this dose, sudden properties' reduction have occurred, proportional to doses, probably due to a higher selectivity in bonds rupture verified for the cross linker (Coran, 2003). For “resin cure” samples there was a reduction in the properties proportional to the applied dose; for doses higher than 100 kGy a sudden reduction in properties probably imparted by very large polymeric chain degradation was observed (Hill et al., 1992).

Hardness is proportional to the entangled bonds formed during the vulcanizing process and consequently directly affected by the amount of sulfur present in vulcanizing systems. The higher the sulfur amount the higher are the hardness and the degree of crosslinking (Oliveira and Soares, 2002). This behavior was just the one obtained. Sulfur cure systems showed slightly higher hardness values, pointing to a higher degree of crosslinking of these mixtures. These samples showed equal losses in properties for all doses, as shown in Fig. 4, indicating that irradiation did not affect the compound's hardness, probably because the butyl rubber isobutylene units are practically non-reactive toward sulfur under the condition of vulcanization and only the isoprene units are involved (Popowa et al., 1985). “Sulfur donor cured” samples showed a reduction in hardness related to the dose applied, as a function of a decrease in molecular weight, because crosslinking would be expected only through the isolated isoprene units (Hill et al., 1992). For “resin cure” samples the hardness remain almost unchanged for almost all dose values, whereas for doses higher than 100 kGy, samples showed a sudden reduction in hardness values indicating polymer degradation,

because of the dose-dependent nature of chain scission (Chandra et al., 1982).

4. Conclusion

The compounds with three vulcanization systems presented quite different sensitivities when irradiated as shown by the affected material properties. Resin cure systems showed no protection of polymers against effect of radiation. The highest degradation occurred in sulfur vulcanized compounds, being observed that for low doses the crosslinking was preserved, whereas for high doses, just degradation occurred. "Sulfur donor" samples were more stable at low doses, as their properties were maintained constant, whereas at higher doses they showed severe degradation. At doses higher than 100 kGy there was a major loss observed in the assessed properties for all butyl compounds, irrespective of the vulcanization system used, except for the "sulfur cure" samples that showed no variations in hardness for all applied doses.

Acknowledgments

The authors wish to thank CBE Embrarad for the irradiation process, Pirelli for the elastomers, Basile Chemistry for the raw materials, Schenectady Chemical's for the resins and IPEN/CNEN-SP and CNPQ Process no. 140175/2010 agencies for their financial support.

References

- Binglin, W., Ziyang, X., Xingmiao, Z., Shiming, M., Yuxi, Z., Daoming, S., 1993. Study and application of the radiation reclaiming waste butyl rubber products by gamma rays. *Radiat. Phys. Chem.* 42, 215–218.
- Burillo, G., Clough, R.L., Czikovszky, T., Guven, O., Le Moel, A., Liu, W., Singh, A., Yang, J., Zaharescu, T., 2002. Polymer recycling: potential application of radiation technology. *Radiat. Phys. Chem.* 64 (1), 41–51.
- Chandra, R., Subhash, V., Verma, A.K., 1982. Changes in physical properties and molecular structure of butyl rubber during γ radiation. *Polymer* 23, 1457–1460.
- Chapiro, A., 1962. 1st Ed. *Radiation Chemistry of Polymeric Systems*. Encyclopedia of Polymer Science and Engineering, vol. 15. John Wiley and Sons, Inc., New York., pp. 66–113.
- Coran, A.Y., 2003. Chemistry of the vulcanization and protection of elastomers: a review of the achievements. *J. Appl. Polym. Sci.* 87, 24–30.
- Data Sheet, 2010. Butyl Rubber. <http://www.exxonmobilchemical.com/Chem-English/Files/Resources/butyl_068-268-269-ww_en-fps.pdf>.
- Exxon Mobil Chemical, 2006. Model vulcanization systems for butyl rubber, halobutyl rubber, and bism elastomer.
- Hill, D.J.T., O'Donnel, J.H., Senake Perera, M.C., Pomery, P.J., 1992. Determination of scission and crosslinking in gamma irradiated butyl rubber. *Radiat. Phys. Chem.* 40 (2), 127–138.
- Hofmann, W., 1989. *Rubber Technology Handbook*. Hanser Publishers, Munich, (651 pp.).
- Karaagaç, B., Sen, M., Deniz, V., Güven, O., 2007. Recycling of gamma irradiated inner tubes in butyl based rubber compounds. *Nucl. Instrum. Methods Phys. Res.: Sect. B* 65, 290–293.
- Kresge, E.N., Schatz, R.H., Wang, H.-C., 1987. 2nd edition *Isobutylene Polymers in Encyclopedia of Polymer Science and Engineering*, vol. 8. John Wiley & Sons Inc., New York., pp. 423–448.
- Kuczkowski, A., 1988. The electrical properties of polyester polymer-quinoline salt of tetracyanoquinodimethane composites. *Phys. Status Solidi (a)* 105, 61–65.
- Landini, L., Araujo, S.G., Lugao, A.B., Wiebeck, H., 2007. Preliminary analysis to BIR recovery using the microwave process. *Eur. Polym. J.* 43 (6), 2725–2731.
- Morton, M., 1989. *Rubber Technology*, 2nd Ed. Van Nostrand Reinhold, New York, ISBN: 0-442-25565-9, pp. 96–97.
- Oliveira, M.G., Soares, B.G., 2002. The influence of the vulcanizing system on curing, mechanical and ageing properties of NBR/EPDM blends. *Polímeros: Ciênc. Tecnol.* 12 (1), 11–19.
- Popowa, C., Mladenov, I., Slusarski, L., 1985. The effect of overcure on the properties of butyl rubber. *Thermochim. Acta* 93, 229–232.
- Scagliusi, S.R., Cardoso, E.C.L., Parra, D.F., Lima, L.F.C.P., Lugao, A.B., 2010. Evaluation of "Payne Effect" in radiation-induced modification of chlorobutyl rubber. In: *Proceedings of the Ionizing Radiation and Polymers Symposium (IRaP)*, Maryland, USA, pp. 25–29.
- Sombatsompom, N., 1998. Analysis of cure characteristics on cross-link density and type, and viscoelastic properties of natural rubber. *Polym. Plast. Technol. Eng.* 37 (3), 333–349.
- Teinov, A.V., Zavyalov, N.V., Khokhlov, Y.A., Sitnikov, N.P., Smetanin, M.L., Tarantsov, V.P., Shadrin, D.N., Shorikov, I.V., Liakumovich, A.L., Miryasova, F.K., 2002. Radiation degradation of spent butyl rubbers. *Radiat. Phys. Chem.* 63, 245–248.
- Yang, J., 1998. Radiation recycling of butyl rubber wastes. In: Cooper, W.J., Curry, R.D., O'Shea, K.E. (Eds.), *Environmental Applications of Ionizing Radiation*. Wiley, New York., p. 601.
- Yang, J., Liu W., 2000. In: *Technological Development of Irradiated Reclamation of Butyl Rubber Wastes*, IAEA Consultants Meeting, Saclay, France, pp. 19–21.
- Zaharescu, T., Cazac, C., Jipa, S., Setnescu, R., 2001. Assessment on radiochemical recycling of butyl rubber. *Nucl. Instrum. Methods Phys. Res.: Sect. B* 185 (1), 360–364.