Radiation-Induced degradation of Butyl Rubber Vulcanized by Three Different Crosslinking Systems

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ABSTRACT

Butyl rubber (IIR) is an isobutylene/isoprene copolymer and is provided with good properties including low permeability to gases, good thermal stability, high resistance to oxygen and ozone action, among other ones. The vulcanization is a thermo-chemical process applied to elastomeric polymers and due to it rubbers acquire physical properties which make them appropriate for various applications. In vulcanization process the rubber is heated in a sulfur and accelerators and activators environment. The major effect of ionizing radiations on butyl rubber is chain scission accompanied with a significant reduction in molar mass. This work aims to show effects of gamma radiation in properties of butyl rubbers vulcanized with sulfur, using sulfur donators and phenolic resin. Non-irradiated and irradiated samples characterization will include following properties: tensile, elongation, hardness, elasticity modulus. Gamma radiation doses used were: 25 kGy, 50 kGy, 100 KGy, 150 kGy and 200 KGy, in order to identify whether cure system is the most stable under irradiation. It was observed that doses higher than 150 kGy prejudice assessed properties for all butyl compounds, no matter the vulcanization system used, and that compounds cured with phenolic resin showed a prejudice in properties proportional to the dose.

Keywords: Butyl rubber; Degradation; Gamma radiation; Crosslinking systems; vulcanization.

1. Introduction

Butyl rubber-IIR (isobutylene and isoprene copolymer) has been used in a great variety of applications, such as tires spare parts (air chambers, tires internal coating, etc.) and various articles (lids, gaskets, etc.) due to its low insaturation (Karaagaç et al, 2007), due to their unique properties, including high gas permeability resistance, good thermal stability, high resistance to oxygen, ozone and solar radiation action and excellent resistance to humidity and to chemical substances attack (Teinov et al,2002). It besides natural rubber compositions (Parra et al, 2002).

Vulcanization is one of the most traditional chemical processes in polymer industries (Coran et al, 1994 and Chapman et al, 1988). Since the discovery of using sulfur by Goodyear in 1939, sulfur cross-linking reactions have been advanced by easeless innovation of accelerators, activators, retarders, and so on, in order to improve processability and mechanical properties (Coran et al, 2003). Like other rubbers, for most applications, butyl rubber must be compounded and vulcanized (chemically cross-linked) to yield useful, durable end use products. Grades of Butyl have been developed to meet specific processing and property needs, and a range of molecular weights, unsaturation, and cure rates are commercially available. The selection and ratios of the proper fillers, processing aids, stabilizers, and curatives also play critical roles in both how the compound will process and how the end product will behave.

Elemental sulfur and organic accelerators are widely used to cross-link butyl rubber for many applications. The low level of unsaturation requires aggressive accelerators such as thiuram or thiocarbamates. The vulcanization proceeds at the isoprene site with the polysulfidic cross links attached at the allylic positions, displacing the allylic hydrogen. The number of sulfur atoms per cross-link is between one and four or more. Cure rate and cure state (modulus) both increase if the diolefin content is increased (higher unsaturation). Sulfur cross-links have limited stability at sustained high temperature. Resin cure systems (commonly using alkyl phenol-formaldehyde derivatives) provide for carbon-carbon cross-links and more stable compounds (Vanderbilt Handbook, 1982).

The major effect of ionizing radiations on butyl rubber is chain scission accompanied with a significant reduction in molar mass (Chandra eta al., 1982). The energy transfer from the radiation to the matter does not take place selectively, but the lower the bond energy, the faster the bond scission (Zaherescu et al, 1996). The radiation chemical behaviors are determined by the presence of quaternary carbon atom in the isobutylene unit of butyl rubber macromolecules (Chapiro, 1962).

This work aims to show effects of gamma radiation in properties of butyl rubbers vulcanized with sulfur, using sulfur donators and phenolic resin. The compounds after irradiation at: 25, 50, 100, 150 and 200 kGy doses. Irradiation effects in properties of rubber compounds were investigated.

2. Materials and Methods

2.1 Materials

Butyl rubber samples used three different types of acceleration (Table 1) and reference formulations were based on standards commonly used in tire and automotive industry. Isobutylene-based polymers employ a variety of cure systems depending on requirements of the final cured product. Admixtures were prepared in an open roll-mill, each roll with a 40kg capacity. The samples were cured in an electrically heated HIDRAUL-MAQ, at 5 MPa pressure. Cured with sulfur and donors samples were vulcanized at 170 ° C for 15 min; cured phenolic resin sample was vulcanized at 190 ° C for 15 min. The samples correspond to the same material before and after radiation doses

2.1.1 Butyl Cure

A borracha butilica pode ser vulcanizada por três métodos básicos:

- Vulcanização com enxofre: A borracha butilica tem elevada insaturação e pode ser reticulado com enxofre e ativado com oxido de zinco e aceleradores orgânicos (Morton, 1989).

[insert fig.1]

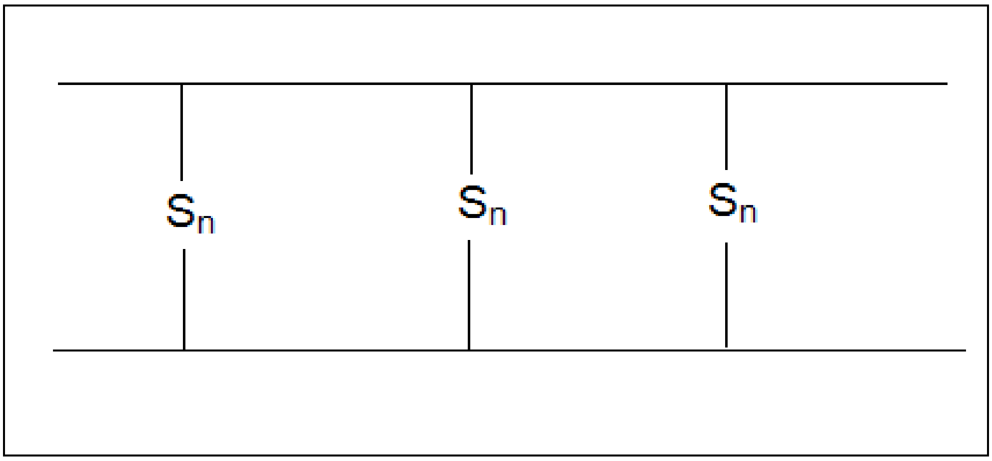

Figure 1: structure for sulfur cure

- Vulcanização com doadores de enxofre : O uso de doadores de enxofre em substituição ao enxofre elementar promove a formação de ligações monossulfídicas elementares(Morton, 1989).

[insert fig 2]

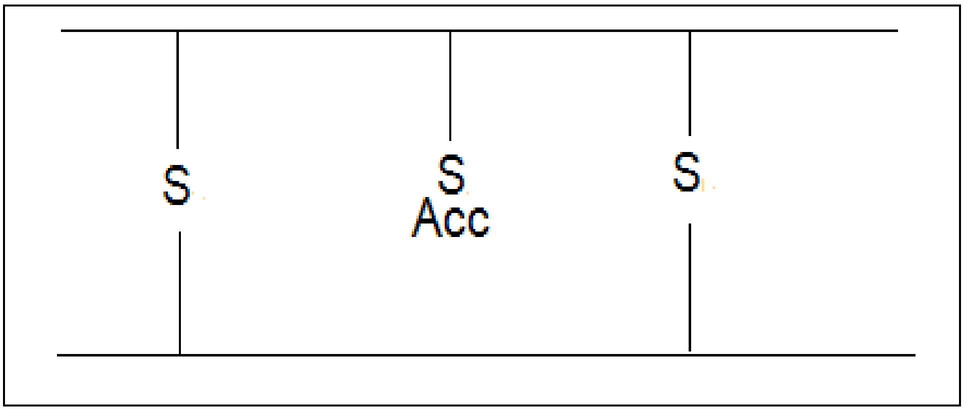

Figure 2: Structure for donor sulfur cure

• Vulcanização com resina: As resinas de fenol formaldeído, são classificadas de resols (Exxon, 2006), isto é, sistemas de resinas tridimensionais que formam uma rede de reticulação que pode servir como resina reforçante, em comparação com as resinas de estruturas lineares. A vulcanização da borracha butilica e de outros elastômeros contendo insaturação olefínica pelo metodo da “vulcanização com resina” é dependente da reatividade dos grupos fenol e metanol das resinas reativas de fenol-formaldeido (Kresge et al, 1987) .

[insert fig.3]

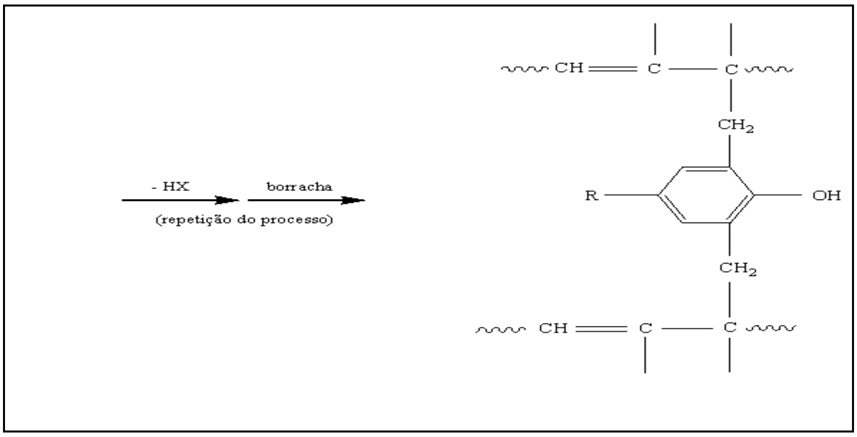

Figure 3: Structure for donor resin cure (octylphenol formaldehyde)

2.2 Irradiation Process

Samples of 11.5 x 11.5 x 0.1 cm³ cured sheets , mass of 250g total weight. They are irradiated at 25, 50, 100, 150 and 200 kGy, in a Cobalt-60 source with kGy, 5 $kGyh^{-1}$ dose rate. For the characterization of triplicate samples, there were assessed following properties, before and after radiations:

2.3 Methods

2.3.1 Rupture Tensile

It is defined as the applied force by initial area unit of a specimen, at the rupture point (ASTM D 412). Tests were accomplished in a *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.3.2 Elongation

Generally it is expressed as the percentage between two marks in uniform cross section. Ultimate elongation is the elongation at which rupture occurs in the application of continued tensile stress (ASTM D 412).

Tests were accomplished in a *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.3.3 Elasticity Modulus

O comportamento elástico segue a lei de Hook, que estabelece que sua deformação varie linearmente com a tensão aplicada (ASTM D 638). O modulo de elasticidade de um material é a medida de rigidez do mesmo (Caram, 2010). Tests were accomplished in a *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.3.4 Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240, being the Shore A, *Instrutemp,* portable digital model Dp-100 the durometer used herein. This instrument is provided with a conical needle emerging from the apparatus, kept at zero level by means of a spring.

3. Results and Discussions

Butyl rubber shows a significant degradation under ionizing radiation. The major and practically single effect of ionizing radiation on this type of rubber is the chain scission with a significant reduction in molar mass. The mechanical properties of rubber mixtures analyzed using the cure systems with resin, sulfur and sulfur donor as a function of irradiation dose.

.Results for tensile, ultimate elongation (elongation at break) and hardness at different radiation doses are presented in Figures 4, 5 and 6, respectively.

[insert fig. 4]

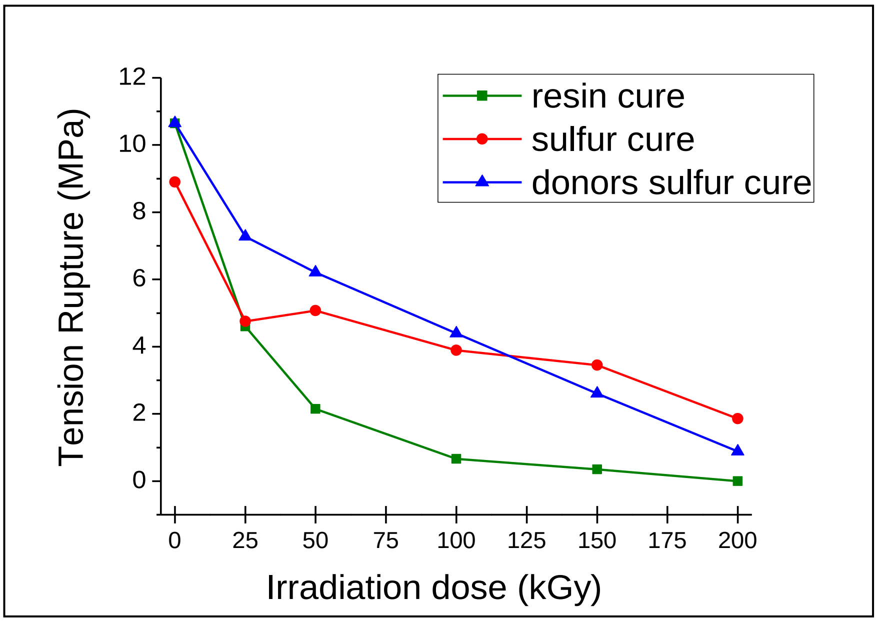

Figure 4- Tensile strength for butyl rubber cured with sulfur, resin and sulfur donators

It is observed that the cure systems of the compounds tested have different sensitivity when irradiated. The sample cured "resin and sulfur donors" showed that there is a proportional reduction property of the dose due to loss of molecular weight of irradiated polymer, indicating that occurred a scission in polymeric chain and not in the crosslinker. Since the sample cured with sulfur showed a sharp decline even at low doses, without some were proportional to dose, indicando uma flexibilidade relativamente alta da estrutura de rede tridimensional, devido a presença de polissulfetos (C-S-S_n-C), e o valor de n é maior que o da unidade (Sombatompop, 2009), enquanto que para cura com doadores a estrutura de ligação é monosulfidica (C-S-C), mais curta e menos flexivel and simple aromatic ring present in resin chemical structure is radiation resistant.

[insert fig. 5]

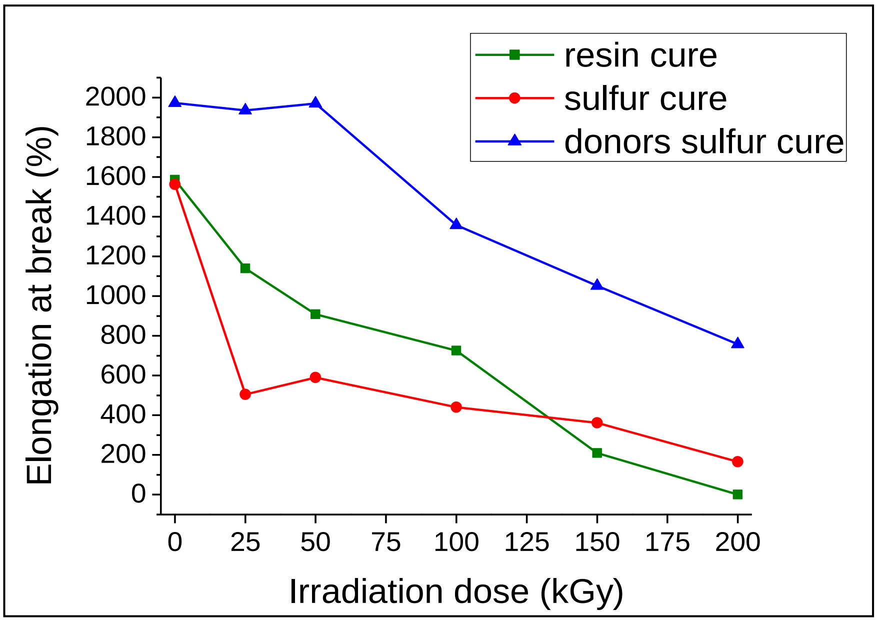

Figure 5 -Elongation at break for butyl rubber cured with sulfur, resin and sulfur donor

Figure 5 show that the sample for a “resin cure” compound there was a reduction in properties proportional to applied dose, para doses altas acima de 100 kGy observa-se uma queda acentuada de propriedades causada provavelmente pela degradação da cadeia polimerica . The sample for a “sulfur donors cure” compound occurred uma queda da pouca significativa para baixas doses; this behavior probably due to a higher selectivity in bonds rupture verified at higher doses for the crosslinker. The sample for a “sulfur cure” compound it was observed a significant reduction in elongation tests pointing toward a polymeric chain scission, decreased slightly from values without dose proportionality.

Os resultados obtidos para o teste de dureza são mostrados na Figura 6.

[insert fig.6]

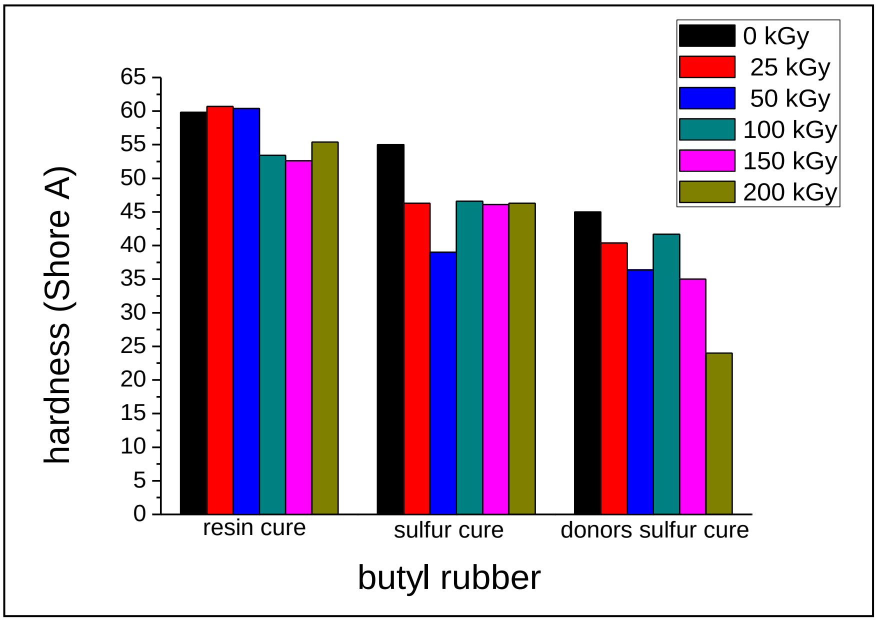

Figure 6 : Hardness for butyl rubber cured with sulfur, resin and sulfur donors

Observa-se que independente de sistema de aceleração em todas as amostras houve um decréscimo de propriedades, ou seja, ocorreu um amolecimento da borracha. Para amostras curadas com resina não houve variações significativas na dureza do composto com o aumento da dose de irradiação, para amostra curada com doador de enxofre ocorre uma perda de propriedade sem proporcionalidade a dose, porém a doses mais elevadas acima de 100 kGy nota-se uma queda brusca de valores indicando a degradação do polímero. As amostras curadas com enxofre apresentam perdas de propriedades iguais para todas as doses, provavelmente caudas pela flexibilidade da cadeia polimérica devido a presença de ligações polisulfidica.

4. Conclusion

Systems for accelerated vulcanized compounds presented quite different sensitivity when irradiated and affected material properties. Resin cure system did not protected the polymer against radiation effect. The highest degradation occurred in sulfur vulcanized compound that for low doses was kept the crosslinking and at high doses suffered degradation, then for sulfur donor compound the cure is maintained constant but at higher doses it occurred an intense degradation. It was observed that for doses higher than 100 kGy there was a prejudice in assessed properties for all butyl compounds, no matter the vulcanization system used.

It can be concluded that the systems for acceleration of vulcanized compounds have quite different sensitivity when irradiated and affect the material properties. It was observed that doses higher than 150 kGy prejudice assessed properties for all butyl compounds, no matter the vulcanization system used, and that compounds cured with phenolic resin showed a prejudice in properties proportional to the dose, according observed in results for tensile elongation.

Acknowledgments

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References

Agrawal, S.L.; Bandyopadhyay, S.; Dasgupta, S.; Mukhopadhyay, R. (2008, January 1). Prediction of dynamic mechanical properties for tire tread compounds The Free Library**.** (2008). Retrieved October 08, 2010 from http://www.thefreelibrary.com/Prediction of dynamic mechanical properties for tire tread compounds.-a0174325299 .

Bradley R., 1984 Radiation technology handbook (New York and Basel: Marcel Dekker) p. 74.

Dubey, V.; Pandey, S.K.; Rao, N.B.S.N., 1995. Research trends in the degradation of butyl rubber. Journal of Analytical and Applied Pyrolysis. 34, 111-125.

Hill, D.J.T.; O'Donnel, J.H.; Perera, M.C.S.; Pomery, P.J.,1995. High energy radiation effects on halogenated butyl rubbers. Polymer. 36, 4185-4192.

Karaagaç, B; Sen, M.; Deniz, V.; Güven, O., 2007. Recycling of gamma irradiated inner tubes in butyl based rubber compounds. Nuclear Instruments and Methods in Physics Research, B.65, 290-293.

Martin, D. H.; Willians, F., 1970. Radiation-Induced isomerization of 1-bromobutane by a free radical chain reaction. Journal of the American Chemical Society. 92, 769–774.

Pan, X-D; Kelley E.D., 2003. Enhanced apparent Payne effect in a gum vulcanizate at low temperature approaching glass transition. Polymer Engineering & Science.42, 1512-1521.

Parra, D.F., Matos, J.R., 2002, Some synergistic effects of antioxidants in natural rubber, J. Therm. Anal. Cal. 67, 287-294

Payne, A. R., 1962. The dynamic properties of carbon-black loaded natural rubber vulcanizates. Part 1. Journal of Applied Polymer Science. 6, 53-57.

Payne, A. R., 1965. Effect of dispersion on the dynamic properties of filler-loaded rubbers. Journal of Applied Polymer Science. 9, 2273-2284.

Takehisa, M.; Levey, G.; Willard, J.E., 1966. Isomerization of alkyl chlorides and bromides by radiation. Journal of the American Chemical Society. 88, 5694–5700

Teinov, A.V.; Zavyalov, N.V.; Khokhlov, Y.A.; Sitnikov, N.P,; Smetanin, M.L.; Tarantasov, V.P.; Shadrin, D.N.; Shorikov, I.V.; Liakumovich; A.L.; Miryasova, F.K., 2002. Radiation degradation of spent butyl rubbers. radiation physics and chemistry. 63, 245-248.

Tommasi, D.; Puglisi, G.,2006. A micromechanics-based model for the Mullins effect. Journal of Rheology. 50, 495-511.

Wehmeier, A. in VKRT meeting 2009. Measuring the Payne effect in filled rubber. Elastomer Research Testing B.V.

List of Figure Captions

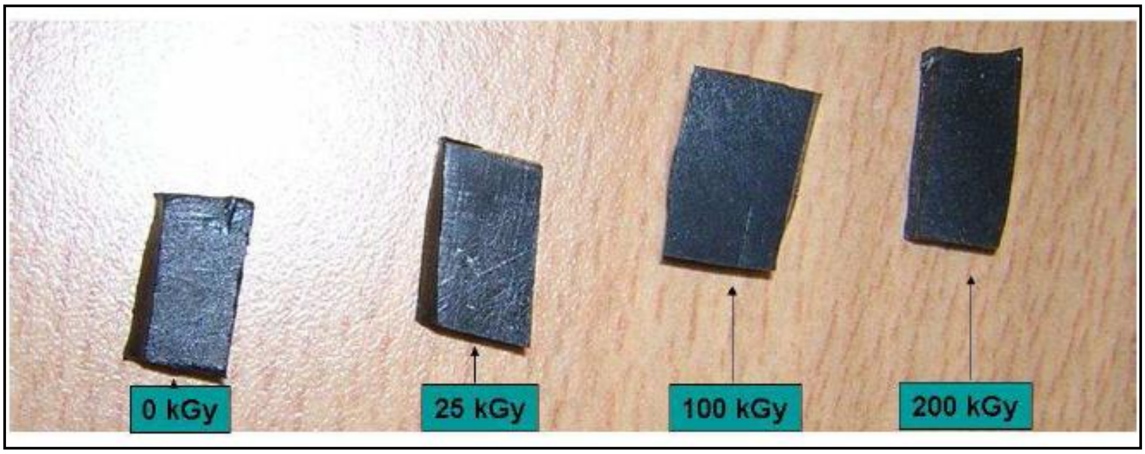

Fig. 1. The samples after e before irradiation

Fig. 2. Metravib DMA 50

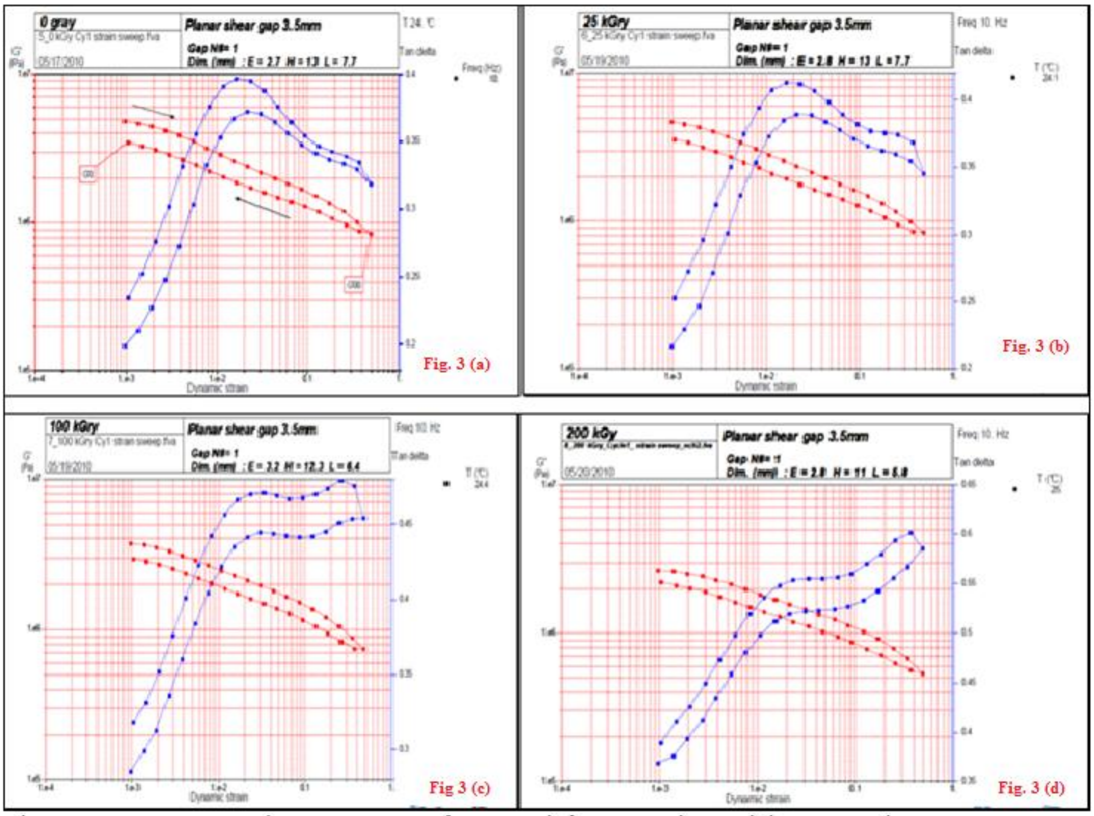

Fig. 3. Storage shear modulus G' and Tanδ vs strain at RT
(a) For the pristine; (b) irradiated 25 kGy; (c) irradiated 100 kGy and (d) irradiated 200 kGy

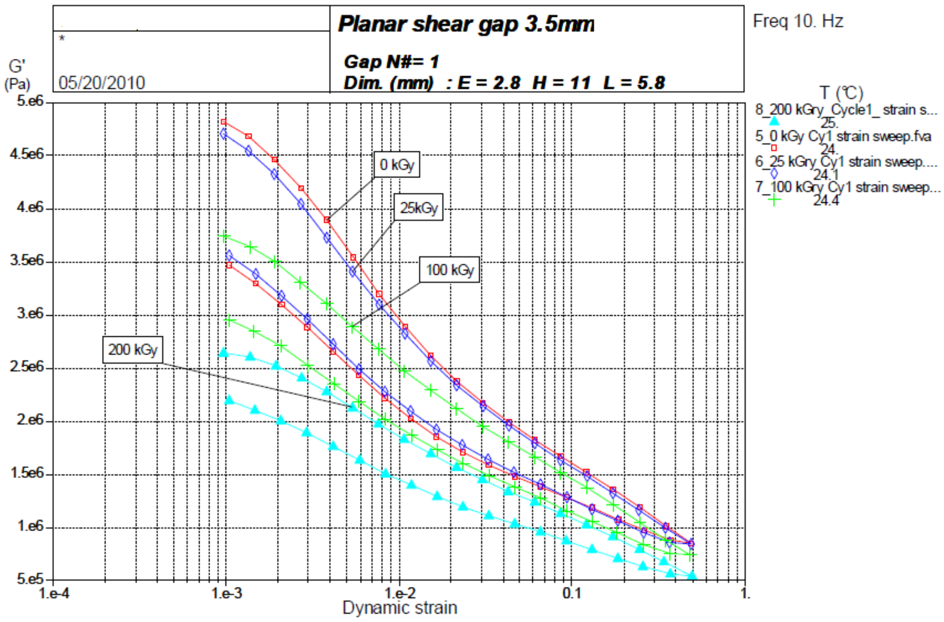

Fig. 4: Superimposition of 4 specimens - Storage shear modulus G' vs. strain at RT

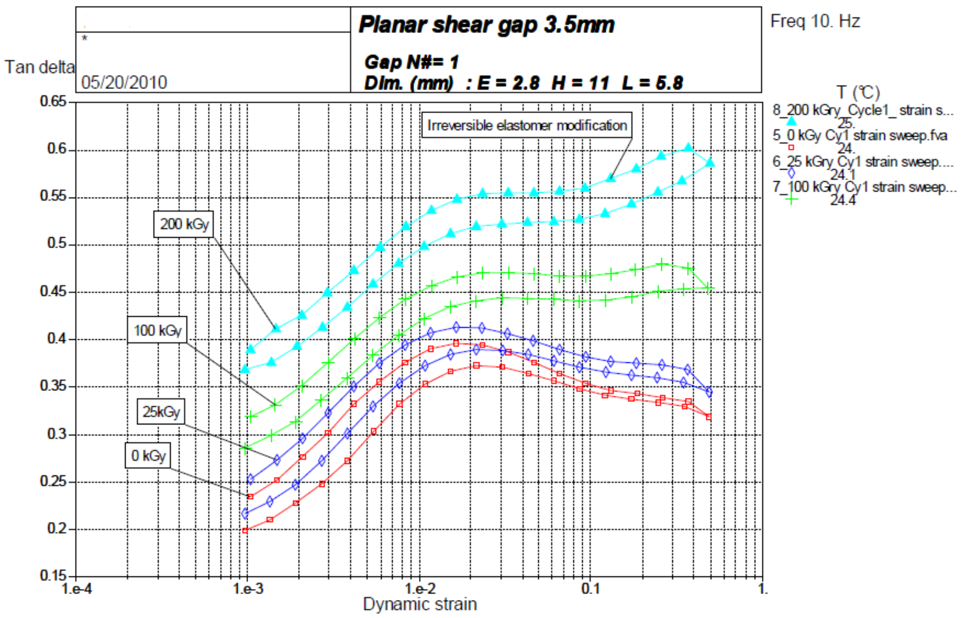

Fig. 5: Superimposition of 4 specimens - Storage shear Tan δ vs.strain at RT

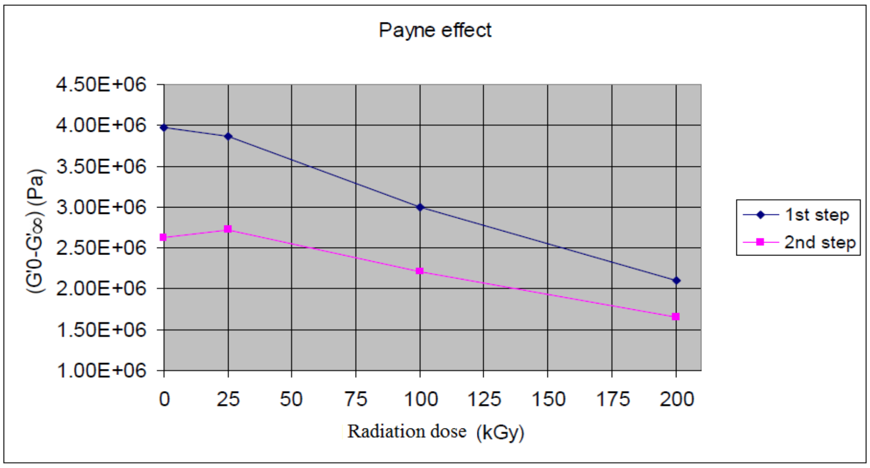

Fig. 6: Payne effect – Storage shear modulus variation (G'_0-G'_∞) vs radiation dose.