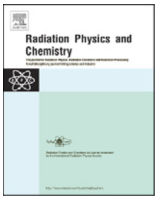
Radiation Physics and Chemistry ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Evaluation of “Payne effect” in radiation-induced modification of chlorobutyl rubber

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ARTICLE INFO

Article history:
Received 1 January 2011
Accepted 1 January 2012

Keywords:
Chlorobutyl rubber
Degradation
Gamma radiation
DMA
Payne effect

ABSTRACT

The major effect of high energy photon, such as gamma rays, in organic polymers is the generation of free radicals, causing changes in electrical, optical and mechanical properties. This work aims to the study of a controlled degradation of a chlorobutyl rubber compound after irradiation at: 25, 100 and 200 kGy doses. Effects of irradiation on a rubber compound were investigated via DMA (Dynamic Mechanical Analysis) tests using the so-called Payne effect, which is directly related to the dynamic properties of the vulcanized rubber. The test begins in a low strain excitation upwards to a maximum programmed strain, and then downwards to a minimum strain at room temperature. The dependency of the material related to the strain amplitude is illustrated by Payne effect. Material behavior presents a non linear evolution on both modulus and Tan when increasing the strain (Payne effect). A difference on G' and tangent δ values at low strain can be observed between the sweeping ways up and down. The difference between new and irradiated material at 25 kGy dose material is not very significant. Nevertheless, the chain scission for higher irradiation doses ($\geq$ 25 kGy) is verified, as observed by Payne effect. Another interest in strain sweep is to facilitate the detection of strong breaking in materials linkage at high strain amplitude as illustrated by Mullins effect.

1. Introduction

Butyl rubber (isobutylene and isoprene copolymer) is provided with good properties, including low permeability to gases, 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 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), besides natural rubber compositions (Parra and Matos, 2002).

At the end of XX century, researches on polymers chemical radiation had a considerable increase and further more new applications were discovered toward polymers modification and improvement of their properties via radiation (Bradley, 1984). Aliphatic halides, with exception to fluorates, are among the organics compounds, the most radiation sensitive. In these compounds, carbon–halogen bonds are weaker when compared to carbon–carbon and carbon–hydrogen bonds, the major effect of radiation is a scission in carbon–halogen bond in order to create a free organic radical and an halogen radical (Hill et al., 1995). Besides, halogen atoms show a significant reduction in reactivity, for example, chlorine atoms are able to subtract hydrogen from organic molecules, while bromine atoms perform this reaction more slowly. Consequently, initial radiolysis of chlorine compounds products show a tendency to include hydrogen chloride, while bromides include bromine, as well as hydrogen bromide (Takehisa et al., 1966).

The irradiation of given alkyl chlorides and bromides can impart isomerism (Martin and Willians, 1970), where halogen atom site is changed and carbon chain backbone remains unchanged. For example, irradiation of n-butyl bromide gives high yields of the secondary isomer and irradiation of isobutyl chloride gives tertiary butyl chlorides. The isomerism is attributed to free radical chain reactions (Hill et al., 1995).

The irradiation causes effects in vulcanized chlorobutyl rubber properties, especially shown in Dynamic Mechanical analyses accomplished by DMA apparatus (Dynamic Mechanical Analysis), a technique used to study and to characterize materials including polymers viscoelasticity behavior. Senoidal stress is applied and the strain in material is evaluated making feasible the determination of complex modulus (Agrawal et al., 2008).

The dependency of the material related to the strain amplitude is illustrated by Payne effect, which is directly related to the dynamic properties of vulcanized rubber. The effect is observed under cyclic loading conditions with small strain amplitudes, meaning a dependence of the viscoelastic storage modulus on the amplitude of the applied strain (Pan and Kelley, 2003).

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http://dx.doi.org/10.1016/j.radphyschem.2012.06.047

Please cite this article as: Scagliusi, S.R., et al., Evaluation of “Payne effect” in radiation-induced modification of chlorobutyl rubber. Radiat. Phys. Chem. (2012), http://dx.doi.org/10.1016/j.radphyschem.2012.06.047

For higher values than 0.1% strain amplitude, the storage modulus decreases rapidly with increasing amplitude. At sufficiently large strain amplitudes (about 20%), the storage modulus approaches to a lower bound. In region where the storage modulus decreases and the loss modulus shows a maximum, the Payne effect will depend on material filler content and will vanish for unfilled elastomers. Physically, the Payne effect can be attributed to deformation-induced changes in the materials microstructure, i.e. to breakage and recovery of weak physical bonds adjacent to filler clusters (Payne, 1962; VKRT Meeting, 2009).

The stress softening phenomenon, which arises in many rubberlike materials subject to cyclic loading, is widely known as the Mullins effect. When fine filler particles, for example, carbon black, are dispersed in a rubbery polymer, there is a significant physical–chemical interaction between the filler and the polymer, and the details of such interactions when associated to the damage process become very important for the Mullins effect. (Tommasi and Puglisi, 2006).

This work aims to the study of a controlled degradation of a chlorobutyl rubber compound after irradiation at: 25, 100 and 200 kGy doses. Irradiation effects on rubber compounds were investigated via DMA (Dynamic Mechanical Analysis) tests, by using the so-called Payne and Mullins effects.

2. Experimental

2.1. Materials

The elastomer employed for this study was chlorobutyl rubber (EXXON Chlorobutyl Grade 1066). The rubber was blended with 75 phr (parts per hundred rubber) of a reinforcing carbon black and other ingredients. Sulfur was used as bonding agent, as the usual practice for achieving a good mixing. The sample was cured in an electrically heated HIDRAUL-MAQ, at 5 MPa pressure and 165 °C temperature to their optimum cure times (determined from a rheometer Monsanto R-100). The samples correspond to the same material before and after radiation doses (Fig. 1).

2.2. Irradiation process

Samples of 11.5 × 11.5 × 0.1 cm^3 cured sheets were cut into small pieces at about 1 cm × 1 cm, mass of 250 g total weight. They are irradiated at 25, 100 and 200, in a Cobalt-60 source with kGy, 5 kGy h^{-1} dose rate.

2.3. Dynamic mechanical analysis (DMA)

Dynamic Mechanical Analysis determines elastic modulus (or storage modulus, G′), viscous modulus (or loss modulus, G″) and damping coefficient ($\tan\delta = G''/G'$), in function of temperature, frequency or time. Results are typically provided in a graphical plot of G', G'', and $\tan\delta$ versus temperature. Tests accomplished in this work have been performed in a METRAVIB DMA 50 (Fig. 2) equipment, and showed G' and $\tan\delta$ in function of strain amplitude.

2.3.1. Tests conditions

- *Test mode*: Shear (one gap)
- *Specimens dimensions*:
  - 0 kGy: height 13 × gap 2.7 × width 7.7 mm
  - 25 kGy: height 13 × gap 2.8 × width 7.7 mm
  - 100 kGy: height 12.3 × gap 3.2 × width 6.4 mm
  - 200 kGy: height 11 × gap 2.8 × width 5.8 mm
- *Dynamic strain*: from 1E−3 up to 0.5
- *Frequency*: 10 Hz
- *Temperature*: room temperature (RT)
- *Software*: DYNATEST 6.82

2.3.2. Test description

The test begins with a low strain excitation upwards to a maximum programmed strain, and then, downwards, to a minimum strain at room temperature and 10 Hz frequency.

Fig. 2. Metravib DMA 50.

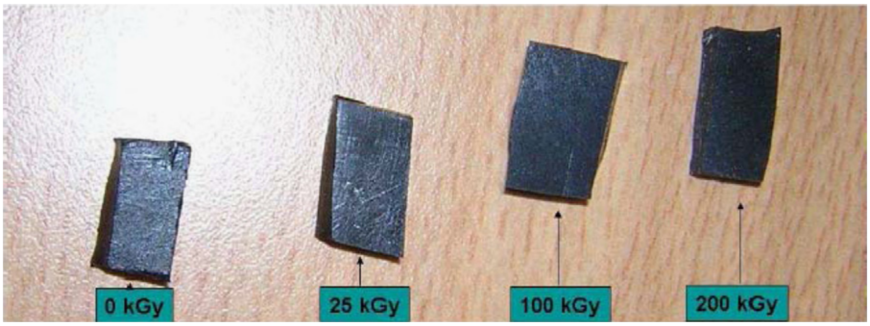

Fig. 1. The samples after e before irradiation.

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2.3.2.1. G′ and G″ properties. Elastic Modulus (G') strain and Viscous Modulus (G'') strain are plotted versus temperature. The Damping Coefficient (tan δ) is investigated versus temperature. And Results of Elastic Modulus Variation ($G'_0 - G'_\infty$) are reported versus irradiation dose.

tan δ, from the storage and loss modulus, is calculated for the ratio between G'' and G'—relative degree of material damping. It is an indicator of how efficient a material loses energy to molecular rearrangements and internal friction.

Complex Modulus in Torsional Mode: G^* (Complex Shear Modulus), is the complex response of the material to an applied strain (or stress) and is, in simplistic terms, the vector sum of the storage (Elastic) G' and loss (viscous) G'' components.

3. Results and discussions

In Fig. 3 it can be noticed a difference in G' and tan δ values, at low strain, between sweeping up and down, a characteristic of the Mullins effect.

A theoretical model of the Mullins effect should consider a constitutive structure which includes at least highly nonlinear deformations, hysteresis, and stress softening. Moreover, it is important to recognize that there is a great technological interest centered on the fact that the Mullins effect is one of the main sources of dissipation for rubber under quasistatic or low-frequency loading. Rubber softening effect is less evident at high doses, once inelastic answer is less emphasized due to the initial

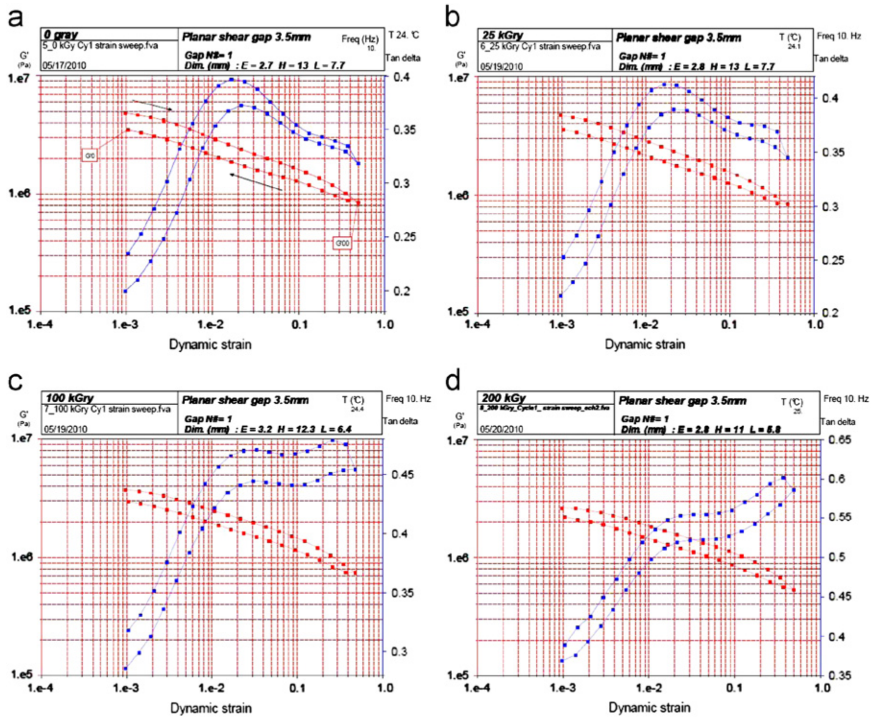

Fig. 3. Storage shear modulus G' and tan δ vs. strain at RT: (a) for the pristine; (b) irradiated 25 kGy; (c) irradiated 100 kGy and (d) irradiated 200 kGy.

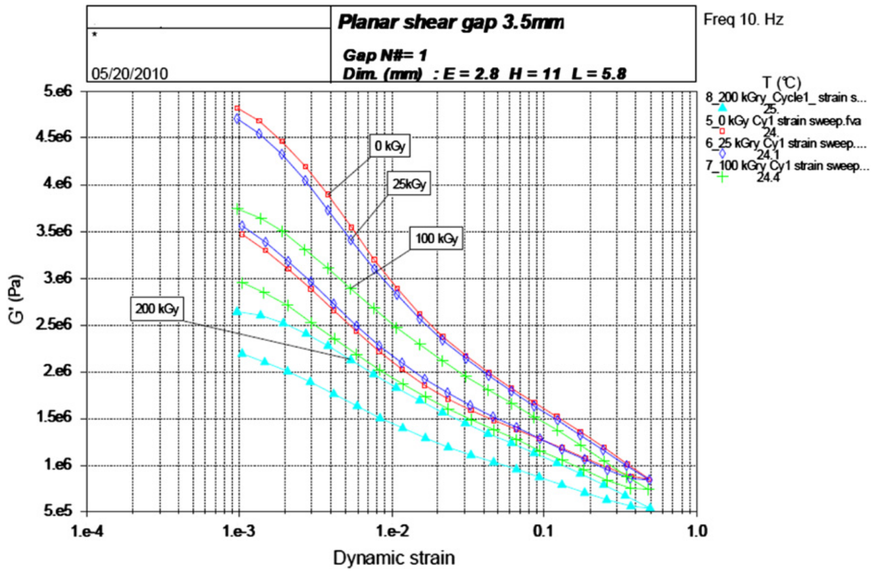

Fig. 4. Superimposition of 4 specimens–storage shear modulus G' vs. strain at RT.

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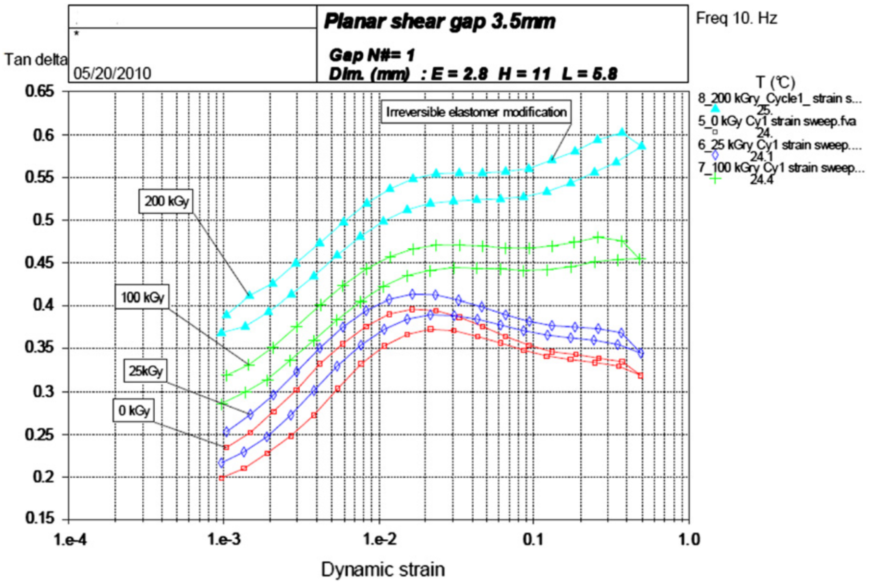

Fig. 5. Superimposition of 4 specimens–storage shear tan δ vs. strain at RT.

degradation state for samples irradiated above 25 kGy. About the elastic modulus there is no difference in curves shape but there is a decrease at low strain (downwards the sweeping) from initial modulus value of 4.7 MPa for pristine and 25 kGy, to 3.7 MPa for 100 kGy and 2.7 MPa for 200 kGy, the low value for initial modulus points out a sample degradation otherwise higher the dose, higher the degradation (Dubey et al., 1995). The same is observed for limit elastic strain obtained values, the effect is probably due to chain scission.

Weak interactions between halogenated radicals for rubber compounds and filler are easily destroyed at high irradiation doses, and it means that since analysis start-up at low strains the damage process was already initiated, making less severe the Mullins effect.

In order to make a comparison between these results we have plotted the curves together in Fig. 4 for storage modulus vs. strain, by observing more clearly Mullins and Payne effects, in irradiated samples.

With respect to tan δ, the curves are plotted together in Fig. 5, by noticing that the values increase in function of strain value 0.4 for the pristine, 0.45 for 25 kGy, 0.48 for 100 kGy and 0.55 for 200 kGy. This phenomenon is more sensitive at high strain (strain=50%) due to a breaking in linkage for highly irradiated ($\geq$100 kGy) material. Samples irradiated at 100 and 200 kGy showed for tan δ a maximum at about 3% strain. Above 10% strain, tan δ increases again.

The Payne effect can be measured by the storage shear modulus variation as $\Delta G' = G'_0 - G'_\infty$ vs. radiation dose (Fig. 6). Notice that G'_0 corresponds to the magnitude at sweeping down (Fig. 3a). Payne effect is lower for higher irradiation doses, due to its degradation degree, once it presents a lower G'_0 at lower strains.

The difference between pristine material and irradiated material at 25 kGy is not very significant, however for high irradiation dose ($\geq$25 kGy), a different behavior due to a polymer backbone modification caused by radiation is observed, in conditions of higher chain-scission and consequently, an easier strain. This effect is related to tertiary carbon present in butyl-elastomer chain, provided with a weaker C–Cl bond and much easily ruptured by irradiation (Hill et al., 1995).

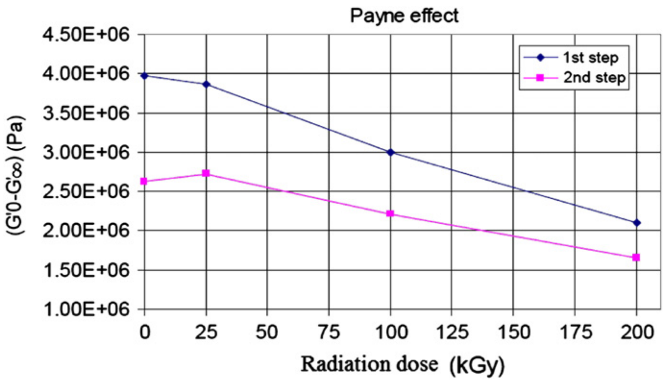

Fig. 6. Payne effect—storage shear modulus variation ($G'_0 - G'_\infty$) vs. radiation dose.

4. Conclusion

Payne effect in chlorobutyl rubber for irradiated measurements is very significant; degradation degree caused by irradiation is inversely proportional to Payne effect, when increasing irradiation dose $\geq$100 kGy, the effect will diminish ($\Delta G' = G'_0 - G'_\infty$).

A difference can be observed in G' and tan δ values, at low strain, between the up and down sweeping, a characteristic of Mullins effect. Another interest of strain sweep is to facilitate the detection of strong rupture in backbone material at high strain amplitude.

Acknowledgments

The authors thank Dr. Arnaud Favier (Metravib) for Dynamic Mechanical Analysis (DMA) tests, Embrarad/CBE for irradiation process, Pirelli for elastomers, Basile Chemistry for raw-material, IPEN/CNEN-SP agencies for financial support.

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