Studies on gamma irradiated rubber materials

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Abstract. Due to the increase in use and production of polymer materials, there is a constant pressure of finding a solution to more environmental friendly composites. Beside the constant effort of recycling used materials, it seems more appropriate to manufacture and use biodegradable and renewable row materials. Natural polymers like starch, cellulose, lignin etc are ideal for preparing biodegradable composites. Some of the dynamic markets that use polymer materials are the food and pharmaceutical industries. Because of their desinfastation and sometimes sterility requirements, different treatment processes are applied, one of it being radiation treatment. The scope of this paper is to analyze the mechanical behaviour of rubber based materials irradiated with gamma rays at four medium doses, 30.1 kGy, 60.6 kGy, 91 kGy and 121.8 kGy. The objectives are the following: to identify the optimum radiation dose in order to obtain a good mechanical behaviour and to identify the mechanical behaviour of the material when adding different quantities of natural filler (20 phr, 60 phr and 100 phr).

1. Introduction

The elastomeric materials have a wide spread of usage, including medical, pharmaceutical and food domain. They are used in manufacturing of seal gaskets, vibration cushioning, protection equipment, medical devices, etc. [1], [2]. Beside the constant effort of recycling used materials, it seems more appropriate to manufacture and use biodegradable and renewable row materials. Natural polymers like starch, cellulose, lignin, etc. are ideal for preparing biodegradable composites. Lately, the beneficiary market and also the producers became more interested in using biodegradable materials.

In this paper it is studied the effect of ionizing gamma radiation over natural rubber materials regarding its mechanical behaviour. Natural rubber is the most ancient and important elastomer which was the model of the first synthesis trials of synthetic rubbers. Natural rubber is widely used in tire industry, and, at least by now, it cannot be replaced entirely with other type of synthetic rubber [2], [3].

In order to obtain products, are used mixes of rubber which include batches, cross-linking agents, plasticizers, oxidants etc. The most important step in the manufacturing technology of rubber is represented by vulcanization or cross-linking. Vulcanization represents the process in which the rubber is transformed from a plastic material in an elastic material. Conventionally, it is given the term “cross-linking” (vulcanization) to all processes in which there are created bridges between macromolecules.
There are multiple possibilities of cross-linking rubber materials. Sulphur vulcanization was the first method discovered for cross-linking and by now is the most known. Other cross-linking systems, like the ones that uses peroxides, ultra-violet radiation, resins etc were discovered later and became important along with the progressive development of synthetic rubbers [2-5].

The use of gamma irradiation for cross-linking and grafting of elastomers has become more attractive along with the constant request for more cheaper, durable and resistant materials. The process is very clean, the energy consumption is small, permits high processing speeds than in other processes of curing and operates at ambient temperature [6]. Numerous polymers were studied and characterized regarding their behaviour to radiation processing. Today, this technology is very well established and used in almost every industries. The purpose of using radiation processing is to enhance the materials mechanical, chemical and temperature resistance in different environments and also to eliminate the cross-linking agents.

Regarding the use of these materials in various industries and the global tendencies in using eco-friendly and biological materials, the scope of this study to reduce and/or eliminate toxic and carcinogenic substances. So, the inorganic batch, like silica precipitate and carbon black, which are carcinogenic [7-9], were replaced with an organic, non-toxic component. Nevertheless, the material must be able to comply with requirements in the form of mechanical characteristics, both in ready to use material and also when treated with gamma radiation.

The objectives of this study are: to identify the optimum radiation dose in order to obtain a good mechanical behaviour and to identify the mechanical behaviour of the material when adding different quantities of natural filler (20 phr, 60 phr and 100 phr).

2. Experimental

2.1. Materials

The materials used in this experiment are the following: natural rubber, vulcanizing agents, batch, plasticizers, compatibilizer and other ingredients.

The following natural rubber was used: Crep from Sangtvon Rubber Ltd, in the form of white rubber sheets, Mooney viscosity 67.64 ML (1 ' + 4') 100°C, volatile matter content of 0.5%, nitrogen content 0.45%, ash content of 0.25%, impurity content of 0.026%.

The vulcanisation of NR by sulfur in presence of organic accelerators which lead to elimination of nitrosamines was replaced with another cross-linking and less toxic system, in this case, gamma radiation processing. The process was performed using low quantities of cross-linking agents. The following were used: perkadox 40 benzoyl peroxide (density 160 g/cm³, 3.8% active oxygen content, 40% peroxide content, pH 7) and polyfunctional monomer trimethylolpropane trimethacrylate Luvomaxx TMPT DL 75 (TMPT) (22 % ash, pH 9.2, density 1.36 g/cm³, 75 ± 3 % active ingredient).

The mixes contain the following proportions: 0 phr (parts per 100 parts of rubber), 20 phr (parts per 100 parts of rubber), 40 phr and 100 phr of organic filler.

The organic filler have special advantage in comparison to inorganic filler, but are hydrophilic. This leads to poor interface between organic filler and hydrophobic matrix of elastomer. In order to improve the interfacial interactions between rubber and organic filler, addition of compatibilizers is required [10], [11] in the case of maleated natural rubber (NR-g-AM). The compatibilizing agent was obtained by roll mixing NR with 5 phr (parts per 100 parts of rubber) of maleic anhydride for synthesis (produced by Merck KGaA, Germany, melting point 52°C) and 0.75 phr of Perkadox 40. The resulting mixture was kept at a temperature of 160°C for 30 minutes and then used as such.

Other ingredients used were the following: (a) antioxidant Richon IPPD (4010 NA) N-isopropyl - N-phenyl - phenylene diamine, 98% purity, molecular mass 493.6374; (b) plasticizer – glycerine, free acidity 0.02%, density 1.26 g/cm³, purity 99.5%; (c) polyethylene glycol PEG 4000 (1.128 g/cm³ density, 4-8°C melting point range), (d) zinc oxide and (f) stearic acid.
2.2. Sample preparation

Sample preparation was carried out at National R&D Institute for Textile and Leather – Leather and Footwear Research Institute – Rubber Department.

The blends were carried out using a laboratory two-roll mill machine. Formulations are presented in Table 1. First, the NR and NR-g-AM was added into two roll mills. The temperature of this machine was between 50-70°C. Afterwards, antioxidant, organic filler, plasticizer, zinc oxide, stearic acid, PEG 4000 and lastly the vulcanizing agent (peroxide and TMPT) were added into the compounding. The time taken to complete the entire process was about 18 to 30 minutes. Nip gap, the speed roll mill and the sequence of adding ingredients were kept constant for all formulations.

| Mixture symbol       | N-20 (phr) | N-60 (phr) | N-100 (phr) |
|----------------------|------------|------------|-------------|
| Natural rubber       | 95         | 95         | 95          |
| NR-g-AM              | 5          | 5          | 5           |
| Organic filler       | 20         | 60         | 100         |
| Plasticizer          | 10         | 30         | 50          |
| Peroxide             | 2          | 2          | 2           |
| TMPT                 | 3          | 3          | 3           |
| Zinc oxide           | 1          | 1          | 1           |
| Stearic acid         | 0.1        | 0.1        | 0.1         |
| PEG 4000             | 3          | 3          | 3           |
| Antioxidant 4010     | 1          | 1          | 1           |

Table 1. Formulations

The test specimen sheets of all compounds were produced using compression moulding at 165°C, 5 minutes duration and pressure of 300 MPa.

2.3. Sample irradiation treatment

The radiation treatment was carried out at IRASM department using the SVST Co60 gamma irradiator. The materials were irradiated at four medium doses of 30.1 kGy, 60.6 kGy, 91 kGy and 121.8 kGy. For the first medium dose (30.1 kGy), the minimum/maximum values were 29.3 kGy respectively 30.9 kGy with a dose uniformity ratio of 1.054. For the second medium dose (60.6 kGy), the minimum/maximum values were 58.8 kGy respectively 62.3 kGy with dose uniformity ratio of 1.059. The third medium dose (91 kGy), the minimum/maximum values were 88.9 kGy respectively 93 kGy with dose uniformity ratio of 1.046. The forth medium dose (121.8 kGy), the minimum/maximum values were 119.2 kGy respectively 124.4 kGy with dose uniformity ratio of 1.043. The dose debit was approximately 2.3 kGy/hour. The radiation treatment was carried out at room temperature.

2.4. Mechanical testing

The mechanical tests were performed on a Zwick Roell Z005 testing machine equipped with a 5 kN cell force. The tests were conducted according to ISO 37 with a constant load speed of 200 mm/min and all measurements were repeated for minimum five times. The samples were cut in a bone shape specimen, type 4: 35 mm in length, 6 mm shoulder width, 12 mm gage length, 2 mm specimen width.

Tearing strength tests were carried out with a Schopper strength tester with testing speed 460 mm/min, using angular test pieces (Type II) in according to SR EN 12771/2003.

Hardness was measured by using a hardener tester according to ISO 7619-1/2011 using 6-mm thick samples.

Elasticity was evaluated with a test machine of type Schob using 6-mm thick samples, according to ISO 4662/2009.
3. Results and discussions
The following mechanical tests were carried out: tensile strength determination, elongation, hardness, elasticity and tearing strength.

3.1. Tensile strength
Figure 1 shows the dependence of the tensile strength depending on the amount of organic filler introduced in the mixture and irradiation dose. Complementary to the mean value, there are also shown the values for error of the mean.

![Figure 1. Tensile strength variation depending on the amount of organic filler introduced in the mixture and irradiation dose](image)

The highest values are obtained for N-20 mix with two peaks, at 30.1 kGy and 91 kGy while N-100 obtained the lowest values, its highest peak being obtained at 30.1 kGy. For N-60, the highest peak value was obtained at 121.8 kGy. Per all, the tensile strength shows an increase in value to a maximum value which differs from the irradiation dose and the quantity of filler introduced in the mixes and after it decreases. This behaviour is consistent with reports from the scientific literature regarding tensile strength variation depending of the cross-linking degree [12-14].

3.2. Elongation at break
Figure 2 shows the dependence of elongation at break depending on the amount of organic filler introduced in the mixture and irradiation dose.

Elongation is most effected for N-20 mix, which scored higher at the tensile strength. For N-60 and N-100, the radiation dose does not effect significantly the elongation behaviour. This information is used when elongation is regarded as a significat parameter for the use of the material.

3.3. Hardness
Figure 3 shows the dependence of elongation at break depending on the amount of organic filler introduced in the mixture and irradiation dose.
Figure 2. Elongation at break variation depending on the amount of organic filler introduced in the mixture and irradiation dose

Figure 3. Hardness variation depending on the amount of organic filler introduced in the mixture and irradiation dose

It can be observed that increasing the filler quantity with 40 phr organic filler, from N-20 to N-60 leads to an increase in hardness between 29-53%, respectively 71-100% when adding 80 phr organic filler, from N-20 to N-100.
This means that organic filler leads to reinforcement of NR, therefore it can replace active fillers such as carbon black or precipitated silica which are harmful and may lead to occupational illnesses of employees of the rubber processing industry [7], [8].

Using radiation processing there is a 4-15°ShA increase in hardness due to the increase of cross-linking.

### 3.4. Elasticity

Elasticity variation depending on the amount of organic filler introduced in the mixture, respective irradiation dose is presented in Figure 4.

Elasticity tends to decrease along with the addition of the organic filler. An addition of 40 phr organic filler, from N-20 top N-60 decreases elasticity between 16.6-25% and an addition of 80 phr organic filler from N-20 top N-100 decreases elasticity between 18.23-38.5%.

Radiation processing using the above doses determines, per all, a decrease till 15.4% which can be due to modification of materials’ surfaces or cross-linking.

![Figure 4](image.png)

**Figure 4.** Elasticity variation depending on the amount of organic filler introduced in the mixture and irradiation dose

### 3.5. Tearing strength

Tearing strength variation depending on the amount of organic filler introduced in the mixture, respective irradiation dose is presented in Figure 5.

It can be observed that the tearing strength decreases along with the addition of 40 phr organic filler, from N-20 to N-60, between 26.9-38.5% and 23.1-61.5% with the addition of 80 phr organic filler from N-20 to N-100. Radiation processing induces an non-uniform variation in tearing strenghts, with tendencies of ageing. These results follow the characteristics needed in a wide range of applications.
4. Conclusions
It has been shown that gamma radiation processing for natural rubber mixed with different quantities of organic fillers has a positive effect on the material. The mechanical behaviour varies between accepted intervals of values needed for various industries, especially for medical and pharmaceutical markets where radiation processing is mostly used. An important aspect showed by the results is that relatively low doses of radiation increase some of materials’ characteristics like, tensile strength, elasticity and tearing strength starting from 30.1 kGy for N-20. Increase in hardness is achieved for N-100 starting also from low doses like from 30.1 kGy.

Independent of application, a good result can be considered when using a low radiation dose, which can be translated in shorter processing time and low cost and high quantity of natural material which makes the final product more eco-friendly and less toxic for manufacturing workers.

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