COMPARISON OF CHARACTERISTICS OF NATURAL RUBBER COMPOUNDS WITH VARIOUS FILLERS

MARIA DANIELA STELESCU[1], ELENA MĂNĂILĂ[2], MIHAELA (VÎLSAN) NIŢUICĂ[1], LAURENŢIA ALEXANDRESCU[1], DANA GURĂU[1]

[1]*INCDTP - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, Romania, dmstelescu@yahoo.com*

[2]*National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, 409 Atomistilor St, Magurele, Bucharest, Romania*

Natural rubber is the most frequently used elastomer worldwide due to its low prices, renewability, non-toxicity and excellent physical properties. Natural rubber is not used as such but in the form of mixtures which generally contain: fillers for reinforcement, plasticizers, crosslinking agents and other ingredients that confer different characteristics to the final product. Reinforcement of elastomers by incorporating fillers is a process of great practical and technological importance that greatly enhances the physical-mechanical properties of the composite material and reduces the cost price. The origin of such mechanical reinforcement has been linked to the interaction between the rubber and filler as well as the homogeneous dispersion of the filler within the polymer matrix. In natural rubber technology, knowledge of the conditions necessary to achieve more efficient natural rubber–filler interactions is improving continuously. The purpose of this article is to determine the influence of different types of mineral or organic fillers on the properties of natural rubber mixtures. The following were determined for the mixtures obtained: curing characteristics, hardness, elasticity, tensile strength, elongation at break and tear strength. The results indicate that both organic and inorganic fillers have led to improved physical and mechanical characteristics.

Keywords: natural rubber, filler, curing characteristics, physical-mechanical characteristics

INTRODUCTION

Reinforcement of a polymer matrix through the incorporation of fillers is a common industrial practice that greatly enhances the physic-mechanical properties of the composite material. The origin of such mechanical reinforcement has been linked to the interaction between the polymer and filler as well as the homogeneous dispersion of the filler within the polymer matrix. In natural rubber (NR) technology, knowledge of the conditions necessary to achieve more efficient NR–filler interactions is improving continuously. Reinforcement of elastomers with certain ingredients is a process of great practical and technological importance. The purpose of this article is to investigate the influence of different types of mineral or organic fillers on the characteristics of natural rubber compounds. Usage of natural rubber only to produce rubber products is disadvantageous in economical and environmental aspect. It will be more efficient if the rubber is reinforced with filler as its additive without affecting its properties. Moreover, the increasing interest in using natural fillers as reinforcement in natural rubber to substitute the conventional fillers has become one of the main concerns nowadays.

In this research work, the influence of the type of filler on the characteristics of some composites based on natural rubber was studied. Five types of filler used in the study were: precipitated silica, precipitated calcium carbonate, sawdust, hemp and starch. It can be seen that there are two mineral fillers, of which an active one (precipitated silica) and a semi-reinforcing one (precipitated calcium carbonate) (Evans, 2001; Franta, 1989), and three organic fillers, made of natural fibre, namely: sawdust, hemp and starch. Samples were crosslinked using peroxide and a polyfunctional monomer. Research papers have been published suggesting that

appropriate polyfunctional monomers (PFMs), also called coagents, added in polymer matrix could be used to obtain desired physical properties of the blend. Coagents are multifunctional organic molecules which are highly reactive towards free radicals. Previous studies (Stelescu *et al.*, 2014; Mănăilă *et al.*, 2014) show that the most efficient PFM in the case of natural rubber was polyfunctional monomer trimethylolpropane trimethacrylate (TMPT).

EXPERIMENTAL

Materials

To obtain rubber mixtures the following materials were used:

- Natural rubber (NR) for pharmaceutical use, 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%;
- Richon IPPD antioxidant (4010 NA) N-isopropyl - N-phenyl - phenylene diamine, 98% purity, molecular mass 493.6374;
- For crosslinking blends, the following were used: Perkadox 40 benzoyl peroxide (density 160 g/cm^3, 3.8% active oxygen content, 40% peroxide content, pH 7) and polyfunctional monomer trimethylolpropane trimethacrylate Luvomaxx TMPT DL 75 (22 % ash, pH 9.2, density 1.36 g/cm^3, 75 ± 3 % active ingredient);
- The compatibilizing agent - maleated natural rubber (NR-g-AM) was obtained by roll mixing NR with 5 phr (parts per 100 parts of rubber) of maleic anhydride for synthesis, S6855208, 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.
- Five different types of fillers were tested, of which 2 mineral fillers and 3 types of natural fibers:
    - Precipitated silica Ultrasil VN$_3$, Evonik Industries (pH=6.2, SiO_2 content 97%);
    - Chalk, Omyacarb 2T-TN, Tetravion Ltd., Thessaloniki, Greece, surface treated, very fine calcium carbonate powder with good dispersion properties (98.6% CaCO3, 1.1% MgCO3, pH=9);
    - Ground hemp (thread length of max 3 mm);
    - Sawdust;
    - Starch - produced by Lach-Ner - soluble potato starch (water insoluble substances 0.28%; loss on drying 16.9%, easily biodegradable: BOD_5 – 0.6 g/g – and COD – 1.2 mg/g) plasticized with glycerin: produced by SC CHIMREACTIV SRL (free acidity 0.02%, density 1.26 g/cm^3, purity 99.5%); the starch was dried at 80°C for 24 h. To obtain the plasticized starch, the starch (50%), water (20%) and then glycerol (30%) were mixed at 70°C for 15 minutes at 50-100 rpm until obtaining a homogeneous mixture. It was left for 1 hour at room temperature, then in an oven at 80°C for 22 h and then for 2 hours at 110°C.

Rubber Compounding

Compounding process was carried out by 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 mill. The temperature of this machine was 30-50°C. Afterwards, antioxidant, filler and lastly the vulcanizing agent were added into the compounding. The control sample, NR was also prepared by using two roll mill machine. No filler was added in the control sample (M). This sample was used to compare the properties between NR composites with different filler. The time taken to complete all process was about 18 to 20 minutes. Nip gap, the speed roll mill, time of mixing and the sequence of adding ingredients were kept constant for all formulations.

Table 1. Formulations

Mixture symbol	M (phr)	R (phr)	A (phr)	U (phr)	C (phr)	I (phr)
Natural rubber	95	95	95	95	95	95
NR-g-AM	5	5	5	5	5	5
Glycerine-plasticized starch	-	-	64	-	-	-
Sawdust	-	50	-	-	-	-
Ultrasil VN3	-	-	-	50	-	-
Chalk	-	-	-	-	50	-
Hemp	-	-	-	-	-	50
Peroxide	8	8	8	8	8	8
TMPT	3	3	3	3	3	3
Antioxidant 4010	1	1	1	1	1	1

Preparation of Tensile Test Sample

The test specimen sheets of all compounds were produced using compression moulding. The temperature of the compression moulding machine was kept constant at 165°C. The time taken to produce the specimen sheets was based on the curing time (t_{90}) from the curing testing.

Laboratory Tests

Curing Characteristics

Curing characteristics were determined by an oscillating disk rheometer (Monsanto), at 165°C for 24 min, according to the SR ISO 3417/1997. Delta torque or extent of crosslinking is the maximum torque (MH) minus the minimum torque (ML). Optimum cure time (t_{90}) is the time to reach 90 % of the delta torque above minimum. Scorch time (ts_2) is taken as the time to reach 2 % of the delta torque above minimum. Optimum cure time (t_{90}) is the time to reach 90 % of the delta torque above minimum. The cure rate index (CRI) of the recipe was calculated according to the following formula:

$$CRI = 100 : (t_{90} - ts_2) \quad (1)$$

The CRI is a measure of the rate of vulcanization based on the difference between optimum vulcanization time, t_{90}, and incipient scorch time, ts_2.

Physical-Mechanical Characteristics

Tensile strength and tearing strength tests were carried out with a Schopper strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012, respectively, angular test pieces (Type II) according to SR EN 12771/2003. Hardness was measured by using a hardness tester according to ISO 7619-1/2011 using 6-mm thick samples. Elasticity (rebound resilience) was evaluated with a Schob test machine using 6-mm thick samples, according to ISO 4662/2009. Residual elongation is the elongation of a specimen measured 1 min after rupture in a tensile test. It was calculated using the formula:

$$\text{Residual elongation}(\ ) = \frac{L - L_0}{L_0} \times 100 \quad (2)$$

where: L_0 is the initial length between two marks and L is the length between the marks 1 min after the sample broke in a tensile test.

RESULTS AND DISCUSSIONS

Cure Characteristics

The curing characteristics, expressed in terms of the optimum curing time, t_{90}, scorch time (ts_2), CRI minimum torque ML, maximum torque MH and torque value DM, (dNm) for the NR samples with different types of fillers, are reported in Table 2. A minimum torque, ML, is a measure of stiffness of the unvulcanized test specimen taken at the lowest point of the cure curve. A maximum torque, MH, is a measure of stiffness or shear modulus of the fully vulcanized test specimen at vulcanization temperature. In other words, it is also a measure of crosslink density (Lopez-Manchado *et al*., 2003; Arroyo *et al*., 2003). It is noticed that the mixture filled with starch had a different behavior than the other mixtures, that can be determined from the existence of plasticizer - glycerine, which led to a plasticized mixture, obtaining smaller values of MH and ML. For other mixtures, it was noticed that introducing the filler leads to an increase in CRI and a decrease in optimum vulcanization time (highest/lowest values were seen when using precipitated silica, followed by sawdust and hemp).

Table 2. Rheological characteristics of blends

Characteristic/ Mixture symbol	M	C	U	A	R	I
The minimum torque M_{min} (dNm)	22.5	21.3	25.4	15.3	21.1	24
The maximum torque M_{max} (dNm)	74.2	74.2	74.2	35.6	74.2	74.3
Torque value ΔM (dNm)	51.7	52.9	48.8	20.3	53.1	50.3
Scorch time,T_{s2} (minutes)	1.52	1.52	1.33	1.9	1.2	1.31
T_{50} (minutes)	5.77	5.1	3.68	5.26	3.74	3.9
Optimal curing time,T_{90} (minutes)	12.47	9.34	5.45	14.6	6.22	6.81
Cure Rate Index (CRI), min^{-1}	9.13	12.79	24.27	7.87	19.92	18.18

Physical-Mechanical Characteristics of Samples

Physical–mechanical characteristics of samples are presented in Figure 1. Hardness increases when adding the filler, thus indicating that all the filler types had a reinforcing effect on mixtures. 100% elongation modulus, tensile strength and the tear strength increased in mixtures containing filler. Elasticity and elongation at break show an

uneven variation and residual elongation shows low values, indicating a good return to its original state after applying a force, and therefore, an efficient crosslinking.

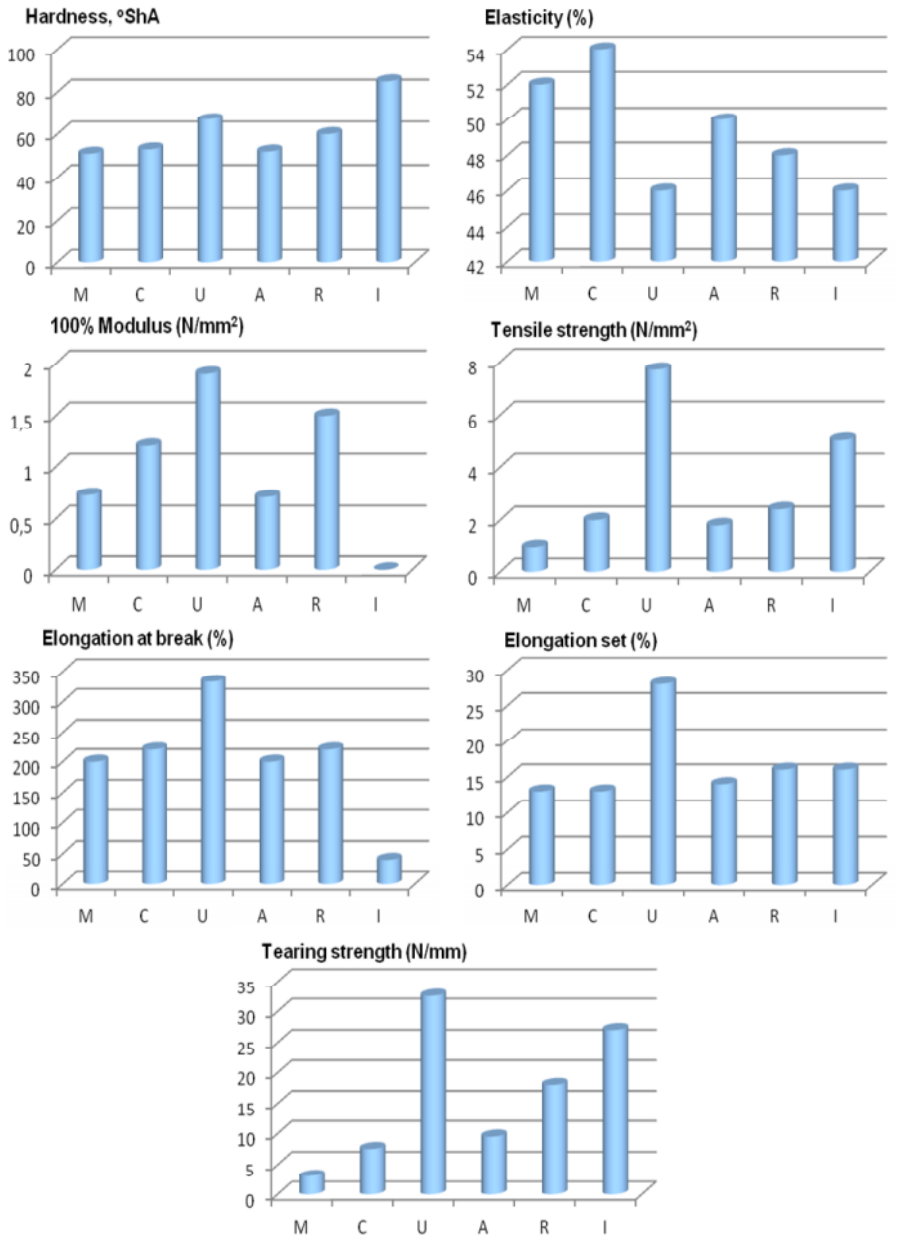

Figure 1. Physical-mechanical characterisation

CONCLUSIONS

The objective of this research is to compare the effect of different types of fillers, mineral or organic, on the characteristics of natural rubber mixtures. From the data it was observed that the mixture filled with starch had a different behavior from the other mixtures, that may be determined from the existence of the plasticizer - glycerine, which led to a plasticized mixture. For other mixtures, it was noticed that introducing the filler leads to an increase in CRI and a decrease in optimum vulcanization time (highest/lowest values were seen when using precipitated silica, followed by sawdust and hemp). The values of hardness, tensile strength and tearing strength have increased by introducing fillers in rubber mixture because the latter have a reinforcing effect on natural rubber. It is noticed that the mixtures filler with sawdust and hemp had better characteristics than those achieved for the mixture with chalk filler. The mixture filled with plasticized starch shows similar physical and mechanical characteristics to those obtained for mixtures filled with chalk and are also superior to the control mixture.

Acknowledgements

This research was financed through Nucleu Program 2016-2017 PN 16 34 01 01: "Development of biodegradable nanocomposites based on natural rubber, starch and OMMT with applications in the food and pharmaceutical industries" supported by Romanian Ministry of Education.

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