ELASTOMERIC NANOMATERIALS BASED ON NATURAL RUBBER FOR THE FOOD INDUSTRY

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This paper presents the obtaining and characterization of new elastomeric nanocomposites based on natural rubber reinforced with plasticized starch, precipitated silica and layered clay, for obtaining consumer goods for the food industry. Obtaining nanocomposites was carried out by the technique of mixing and melt interleaving. The mixtures were vulcanized in the press, at high temperatures, using peroxides as vulcanizing agents, and triallyl cyanurate as vulcanizing coagent. In order to obtain products with improved characteristics, the influence of the amount of modified organic montmorillonite layered clay (OMMT) Nanomer I31PS and the adhesion promoter between mineral filler and polymer - bis-[3-(triethoxysilyl)-propyl]-tetrasulfane (TEPS) on the characteristics of the mixtures, was analysed. The rheological characteristics of the samples show an increase of the minimum torque at the increase in the amount of OMMT type nanofiller and a decrease in the optimal vulcanization time by adding the adhesion promoter between the rubber and the filler. An improvement of the mechanical characteristics of the samples was observed at the introduction of both OMMT and TEPS. These changes may be due to both the nanofiller reinforcement effect and the changes in the morphology of the mixture. The samples showed a good behaviour after immersion in different environments specific to the food industry (water, ethyl alcohol, 10% glucose solution, 0.9% sodium chloride solution and sunflower oil). SEM analyses indicate that the starch particles, together with the other ingredients of the mixture, are quasi uniform distributed in the elastomer matrix. Several superficial microcracks are observed, on the surface of the analysed material, without structural discontinuities or other defects.

Keywords: elastomeric nanocomposites, plasticized starch, OMMT

INTRODUCTION

Currently, in the production of elastomeric materials, the goal is to replace inorganic fillers (which are generally toxic) with different types of natural fibers or organic fillers. (Carvalho *et al.*, 2003; Shey *et al.*, 2006). These materials can be used for various applications, such as: NR / coconut fiber composites - used for Mercedes A-class seats, Cordenka cellulose fibers are used to reinforce tires, starch is added as a rubber mixture filler used in obtaining the tires for Ford Fiesta etc. (Shinoj *et al.*, 2011; Mohammed *et al.*, 2015; Wu *et al.*, 2006). In general, the use of organic fillers as a filler in the polymer matrix offers several advantages over conventional inorganic ones, especially in terms of biodegradability and non-toxicity, but has inadequate adhesion to the elastomeric matrix, has low water resistance and dimensional stability (Wang *et al.*, 2009; Wu *et al.*, 2006). To remedy these problems, in this paper was used a small amount of organic modified montmorillonite layered clay (OMMT) nanofiller and an adhesion promoter bis-[3-(triethoxysilyl)-propyl]-tetrasulfane (TEPS) type, between mineral filler and polymer, to improve physical-mechanical characteristics and behaviour to various mediums for an elastomeric composite based on natural rubber reinforced with plasticized starch and precipitated silica.

MATERIALS AND METHODS

Materials

The following materials were used for rubber mixtures: natural rubber (NR) Crep from Sangtvon Rubber Ltd, starch - produced by Lach-Ner - soluble potato starch, glycerine from SC Chimreactiv SRL, organic modified montmorillonite layered clay Nanomer I31PS produced by Nanocor, amorphous precipitated silica - BM30 Egesil, antioxidant 2,2,4 trimethyl 1,1, dihydroquinone TMQ, polyethyleneglycol PEG 4000, adhesion promoter between mineral filler and polymer, bis-[3-(triethoxysilyl)-propyl]-tetrasulfane Luvomaxx TESPT DL50/L (50% active substance), benzoyl peroxide Luperox A75, di(2-tert-butylperoxyisopropyl)benzene Perkadox 14-40B (40% active substance), triallyl cyanurate Vulcofac TAC – 70 (70% active substance).

Methods

Specimen Obtaining

The starch is dried at 80°C for 24 hours and then plasticized by mixing 2 parts starch with one part glycerine for 7-10 minutes at 70°C and 50-100 rotations per minute until a homogeneous mixture is obtained. For an efficient compounding, the mixtures based on natural rubber, plasticized starch, precipitated silica, and OMMT were obtained by the mixing technique on an internal Brabender type mixer. The processing parameters were: rotation speed 12-80 rpm, temperature 45-110°C, total time 12'. The compositions of the rubber mixtures expressed in parts per 100 parts rubber (phr) are shown in Table 1. Vulcanizing agents were incorporated into the mixture on a laboratory roller with a heating-cooling system, at a temperature of max 90°C for 4' and a 1: 1 friction. After homogenization for 3', the mixtures were removed from the roller in the form of sheets with a thickness of about 2 mm. From these sheets, the test specimens were obtained for characterizing the material, by the compression method using a hydraulic press. Processing parameters: 165°C, 300 kN press force, 8' cooling time until it reaches a temperature of 35°C and the optimum curing time (t_{90}) is determined using the Monsanto rheometer.

Table 1. Formulation of rubber mixtures

Ingredients	Mixture symbol				
	S0	S3	S3t	S6	S6t
<i>Internal mixer</i>					
Natural rubber (g)	100	100	100	100	100
Starch plasticized with glycerine (g)	30	30	30	30	30
Egesil BM30 (g)	20	20	20	20	20
PEG 4000 (g)	3	3	3	3	3
Antioxidant TMQ (g)	1	1	1	1	1
TESPT DL 50/L (g)	-	-	3	-	3
OMMT I31PS (g)	0	3	3	6	6
<i>Laboratory two-roll mill machine</i>					
Luperox A75 (g)	3	3	3	3	3
Perkadox 14-40B (g)	6	6	6	6	6
Vulcofac TAC (g)	4	4	4	4	4

Specimen Characterization

Curing Characteristics

Curing characteristics were determined by an oscillating disk rheometer (Monsanto), at 165°C for 30 min, according to the ISO 3417/2008. 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.

Physical-Mechanical Characteristics

Tensile strength and tearing strength tests were carried out with a Schopper strength tester with testing speed 500 mm/min, using dumb-bell shaped specimens according to ISO 37/2012 and angular test pieces (Type II) according to EN 12771/2003, respectively. 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.

Swell Determination

Swell Determination was performed according to ISO 1817/2015 and the action of the following liquids was tested: water, ethyl alcohol, 10% glucose solution, 0.9% sodium chloride solution and sunflower oil. The specimens of known weight, m_0 , were immersed in various solvents in test bottles and kept at room temperature for 22 hours. After immersion the samples were taken out from the solvents and the wet surfaces were quickly dried using a tissue paper and re-weighted, m_i . To calculate the percentage change in mass Δm_{100} the following formula was used:

$$\Delta m_{100} = \frac{m_i - m_0}{m_0} \times 100 \quad (1)$$

where m_0 is the initial mass of the test piece and m_i is the mass of the test piece after immersion.

To calculate the percentage change in volume ΔV_{100} the following formula was used:

$$\Delta V_{100} = \left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100 \quad (2)$$

where:

- $m_{0,w}$ is the initial mass of the test piece (plus sinker if used) in water;
- $m_{i,w}$ is the mass of the test piece (plus sinker if used) after immersion in water;
- $m_{s,w}$ is the mass of the sinker, if used, in water.

The result was reported as the median value for the three test pieces.

SEM and EDAX Analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDAX) analysis were carried out by Quanta 250 electronic microscope. SEM analysis was performed on a square shaped sample of 10×10 mm, with a magnification between 100÷10.000. EDAX analyse was used to determine the elemental composition of the materials.

RESULTS AND DISCUSSIONS

Rheological Characteristics

The rheological characteristics of the mixtures are presented in Table no. 2. It is observed that with the introduction of OMMT, there is an increase in the minimum torque, showing an increase in the rigidity of the unvulcanized material. The optimum vulcanization time increases for mixtures containing nanofillers and decreases for the mixtures containing promoter adhesion between mineral filler and polymer. This shows an increase in vulcanization rate due to improved filler dispersion in the elastomeric matrix.

Table 2. Rheological characteristics of blends

Rheological characteristics	Mixture symbol				
	S0	S3	S3t	S6	S6t
The minimum torque (ML) (dNm)	7.8	12.7	13.6	12.6	13.9
The maximum torque (MH) (dNm)	74.3	74.7	74.3	72.2	74.6
$\Delta M = MH - ML$ (dNm)	67	62	60.7	59.6	60.7
Optimum cure time (t_{90}) (minute)	8.6	13.08	9	11.05	10.87

Physical-Mechanical Characteristics

Physical-mechanical characteristics of obtained samples are presented in Table 3. Hardness increase with 1-6°Sh A by adding OMMT into mixtures, as a result of reinforcing the mixtures, as the amount of filler increases. Elasticity and elongation at break vary unevenly and have very good values for all samples, over 38% and over 500%, respectively. Improvements are observed in the modulus, tensile, and tear strength for samples with different amounts of nanofiller, and which also contain an adhesion promoter between rubber and filler, namely S3t and S6t mixtures. These mixtures presented the best characteristics and were selected to be tested and observe the effect of different mediums used in the food industry on them.

Table 3. Physical-mechanical properties of blends

Physical-mechanical properties	Mixture symbol				
	S0	S3	S3t	S6	S6t
Hardness, °Sh A	56	62	57	57	59
Elasticity, %	40	46	42	38	39
Modulus 100%, N/mm ²	0.89	1.3	1.1	1.1	1.2
Modulus 300%, N/mm ²	1.9	2.6	2.3	2.2	2.45
Tensile strength, N/mm ²	8.9	8	10	10	11
Elongation at break, %	580	500	560	600	590
Tear strength, N/mm	23	24	25.5	21	26

Analysis of the Variation of Mass and Volume in Different Liquids

The analysis of the variation of mass and volume in different liquids specific to the food industry was performed at room temperature for 22 h. From the results obtained (presented in Table no. 4), it is observed that for immersions in liquids containing a large amount of water (distilled water, 10% glucose solution and 0.9% NaCl solution) or in ethyl alcohol, good values were obtained for both analyzed mixtures: less than 9.24% mass variation and less than 15.9% volume variation. It is known that natural rubber is water-resistant (hydrophobic) but starch is hydrophilic - absorbs water (Stelescu *et al.*, 2017). The good results obtained are due both to the use in mixtures of the OMMT nanofiller, and to the fact that the starch is embedded in the elastomeric matrix, according to the morphological analyses presented in section 3.4, and does not come into contact with the immersion medium except at the sample surface. Similar aspects have been presented by other existing studies in the literature (Manaila *et al.*, 2018). The variation of mass and volume when immersed in sunflower oil has higher values and decreases with increasing amount of OMMT, and the obtained values (below 14%, respectively below 24.1%) allow the use of new materials to produce elastomeric consumer goods for the food industry.

Table 4. Variation of mass and volume after immersion 22 h in different mediums

Immersion medium	Mixture S3t		Mixture S6t	
	Δ mass, %	Δ volume, %	Δ mass, %	Δ volume, %
Distilled water	9.24	15.9	7.74	13.5
Ethyl alcohol	6.39	11.1	6.8	11.9
10% glucose solution	7.68	12.8	7.15	12.4
0.9% NaCl solution	9.04	15.07	7.48	12.9
Sunflower oil	14	24.1	12.5	21.7

SEM and EDAX Analyses

The phase morphology of some rubber mixtures depends on the composition of the mixture, the processing technology, method, the interfacial stresses between the phases, etc. All microscopic images were registered in the fracture area of samples. The surface morphology of the S6t sample shown in Figure 1 shows that the starch particles have a typical granular shape about 5-60 μm in size. These, together with the other ingredients of the mixture, are uniformly dispersed in the elastomer matrix. This quasi-uniform distribution led to good physical and mechanical properties. Several superficial microcracks are observed on the surface of the analysed material, without structural discontinuities or other defects. The EDAX spectra for the S6t sample (Figure 2) confirm the presence of Al (1.95%w) and Si (4.97%w) from OMMT, a high amount of oxygen (21.73%w) which comes from plasticized starch, the basic element being C (71.3% w), which exists in both elastomer and plasticized starch.

Figure 1. SEM micrographs of S6t sample

Figure 2. EDAX spectrum for 6St sample

CONCLUSIONS

From the data presented it can be concluded that by introducing small quantities of OMMT in composites based on natural rubber, plasticized starch and precipitated silica, the following occurs: (1) an increase in the minimum torque, showing an increase in the rigidity of the unvulcanized material with increase of filler amount, (2) increase of hardness by 1-6°ShA and an improvement in 100% and 300% elongation modulus.

By adding the adhesion promoter between the rubber and the filler, an improvement of tear and tensile strength is observed and a decrease of the optimal vulcanization time. These changes may be due to both the nanofiller reinforcement effect and the changes in the morphology of the mixture.

Samples S3t and S6t show a very good behavior after immersion 22 hours at 23°C in: distilled water, ethyl alcohol, 10% glucose solution and 0.9% NaCl solution, due to the polymer matrix of natural rubber is hydrophobic.

Obtaining good physical-mechanical and chemical properties is determined both by the composition of the mixtures and by the technology and methods used in processing the mixtures that led to the obtaining of materials in which the starch particles and other ingredients of the mixture have a quasi-uniform distribution in elastomer matrix (according to SEM and EDAX analyses), without structural discontinuities or other defects.

New elastomeric nanomaterials can be used to obtain rubber consumer goods for the food, pharmaceutical, the footwear industry etc.

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