

ELASTOMERIC NANOCOMPOSITES DEVELOPMENT FOR O-RINGS MANUFACTURING

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Abstract

This paper presents studies on the development and characterization of nanocomposites based on natural rubber, plasticized starch, precipitated silica and layered clay such as organically modified montmorillonite (OMMT). Mixtures were made containing 0, 3 and 6 phr (parts per 100 parts rubber) OMMT, respectively. They were obtained by melt intercalation in a Brabender mixer at 12/80 rotations/min and 100-150°C, for 10 minutes. Curing agents (sulfur and curing accelerators) were embedded on a laboratory roller at 90°C, friction 1:1.1, processing time 5 minutes. Rubber specimens were obtained by compression, using a hydraulic press at 165°C and a pressing force of 300 kN. Curing time, determined using the Monsanto rheometer, decreases with the increased amount of OMMT in the mixtures. At the same time, it was noticed that mixtures containing OMMT show improvement in physical-mechanical properties and resistance in various working environments specific to the food and pharmaceutical industry. Permanent compressive deformation 25%, 24hx70°C shows very good values for mixtures containing OMMT. The new types of nanocomposites may be used to obtain O-rings for the sugar industry or for other areas of application.

Keywords: natural rubber, nanocomposites, montmorillonite, characteristics

1. INTRODUCTION

Natural rubber is the world's most widely used elastomer due to its low price, it is renewable, it is not toxic and has excellent physical properties. Natural rubber (NR) is a diene polymer with the structure of cis-poly (isoprene) extracted as a colloidal dispersion called latex from the juice of some tropical plant varieties such as the *Hevea Brasiliensis* rubber tree. The rubber is obtained by breaking the latex with acetic acid or formic acid. The coagulate is mechanically calendered for homogenization, and then is processed into translucent and elastic yellow-brown sheets [1-3]. To prevent macromolecular chains from slipping and to improve elastic properties, natural rubber is cured. The cured rubber does not soften and keeps its elasticity at low temperatures. The rubber dissolves in hydrocarbons (benzene, petrol, turpentine) and in halogenated compounds (chloroform) but does not dissolve in polar solvents (water, alcohol, acetone). Dissolution is preceded by soaking, changing appearance and dimensions. Therefore rubber objects should not be brought into contact with liquid hydrocarbon and chlorinated solvents. Vulcanization decreases the product's soak capacity. Natural rubber is mainly used in the tire industry and, at least for now, it cannot be replaced entirely with any type of synthetic rubber.

Natural rubber is not used as such but as blends, which generally contain fillers, plasticizers, crosslinkers and other ingredients that give different characteristics to the final product [1-2]. The replacement of active fillers of rubber blends such as carbon black or silica (which has harmful effects on health) with natural fibers offers several advantages over conventional inorganic fillers, namely: lack of toxicity, drop in density and price, etc. [2-3]

In this paper we present some of our experiments on obtaining blends based on natural rubber and starch. Starch is an organic substance found in plant seeds, fruits and tubers and used in the food, chemical, and other industries. In terms of chemical composition, starch is a mixture of 2 polysaccharides: amylopectin and amylose, which differ in structure and reactivity. [4-6].

Starch is obtained from renewable resources and has the following advantages: low price, availability, is not toxic, and is widely used in many fields (food, paper making, chemical industry, packaging industry, etc.) [5-7]. The use of starch as a batch in the polymeric matrix provides several advantages

over conventional inorganic batch, particularly in terms of biodegradability and toxicity, but exhibits poor adherence to the elastomeric matrix, low water resistance and reduced dimensional stability [7-8].

Due to their commercial importance, researchers have recently focused on obtaining (nano)composites based on starch and rubber reinforced with nanodispersed layered silicates [8-10]. It is well known that stratified clay/ rubber nanocomposites have presented interest in both fundamental and applied research, in that they present a combination of properties that their individual components or classical composites do not have. Compared to the polymeric blend from which they initiated, these nanocomposites exhibit improvements in mechanical properties, water resistance, thermal stability, heat resistance, friction coefficient, chemical stability, abrasion resistance, etc. All these advantages are obtained by introducing a small amount of nanofiller (less than 7% by weight). The most commonly used clay for obtaining nanocomposites (PCN) is montmorillonite. In order to achieve a nanometric dispersion of clay in the polymer matrix, the clay is modified with alkyl ammonium or phosphonium salts, which allow the surface polarity to be changed and the distance between the clays layers to be increased. In this way, clay can be easily dispersed in the polymer matrix and nanocomposites are formed with intercalated or exfoliated structure. The intercalation and peeling of clay is the most important phenomenon, influencing the improvement of the rheological, chemical and physico-mechanical properties of the clay rubber nanocomposites [9-11].

This paper presents the obtaining and characterization of some nanocomposites based on natural rubber, plasticized starch, precipitated silica and layered clay in order to obtain O-rings for the sugar industry or other areas of application.

2. MATERIALS AND METHODS

2.1. Materials

The following materials were used for rubber mixtures:

- Natural rubber (NR) 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%;
- Starch - produced by Lach-Ner - soluble potato starch (water insoluble substances 0.28%; loss on drying 16.9%, easily biodegradable: BOD₅ – 0.6 g/g – and COD – 1.2 mg/g);
- Glycerine from SC Chimreactiv SRL (free acidity 0.02%, density 1.26 g/cm³, purity 99.5%);
- Organic modified montmorillonite layered clay, produced by Nanocor: Nanomer I44P - the clay is organically modified using dimethyl dialkyl (C₁₄-C₁₈) (34-45%), particle size 14-18 microns, density 1.9 g/cm³.
- Amorphous precipitated silica- BM30 Egesil -Turkey (surface area 155-195 m²/g).
- Antioxidant 2,2,4 trimethyl 1,1, dihydroquinone TMQ in the form of dark-colored granules (density 1.1 g/cm³, boiling point 85°C) (produced by Interquímica Comercio e Industria de Produtos Químicos Ltd.)
- Polyethyleneglycol PEG 4000 – produced by Advance Petrochemicals Ltd. (density 1.128 g/cm³, boiling point 4-8°C).
- Adhesion promoter between mineral filler and polymer, Luvomaxx TESPT DL50/L, white powder containing 50% bis-[3-(triethoxysilyl) propyl] -tetrasulfan and 50% silica.
- Other ingredients: Zinc Oxide Grade I, stearin.
- The following materials were used for crosslinking blends:
 - Sulphur – yellow powder, melting point 115°C, density 1.96 g/cm³;

- 2 mercaptobenzothiazole (MBT) - molecular weight 167.2, melting point 179°C, density 1.42 g/cm³
- N-cyclohexyl 2-benzothiazolesulfenamide (CBS) - molecular mass 264.4, melting point 101°C, density 1.31 g/cm³
- Tetramethylthiuram disulphide (TMTD) - molecular mass 240.4, melting point 156°C, density 1.43 g/cm³

2.2. Methods

2.2.1. Starch plasticization

The starch is dried at 80°C for 24 hours. Mix 2 parts starch with one part glycerin for 7 minutes until a homogeneous mixture is obtained. For each mixture, the required amount of plasticized starch was prepared.

2.2.2. Blends obtaining

The blends were obtained in the Brabender mixer, and curing agents were added on a laboratory roller with a heating-cooling system. The compositions of the rubber mixtures are shown in **Table 1**.

Ingredients	Mixture symbol		
	C0	C3	C6
Natural rubber (g)	100	100	100
Starch plasticized with glycerin (g)	30	30	30
Egesil BM30 (g)	20	20	20
Zinc oxide (g)	5	5	5
Stearin (g)	1	1	1
PEG 4000 (g)	3	3	3
Antioxidant TMQ (g)	1	1	1
TESPT DL 50/L (g)	3	3	3
OMMT I44P (g)	0	3	6
Sulphur (g)	1.5	1.5	1.5
Mercaptobenzothiazole (MBT) (g)	0.3	0.3	0.3
Tetramethylthiuram disulphide (TMTD) (g)	0.3	0.3	0.3

Table 1. Composition of natural rubber mixtures

2.2.3. Specimen obtaining

The curing for obtaining the nanocomposites specimens for the characterization is carried out by the compression method, using a hydraulic press. Processing parameters: 165°C, 300 kN press force, 8' cooling time until it reach a temperature of 35°C and the optimum curing time is determined using the Monsanto rheometer.

2.3. Specimen characterization

2.3.1. *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.

2.3.2. 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 (the precision and the uncertainties of the test are ± 0.64 for tensile strength and ± 2.95 for elongation at break), 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 (the precision and the uncertainties of the test are ± 0.05). 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 minute after rupture in a tensile test. It was calculated using the following formula (1):

$$\text{Residual elongation (\%)} = \left[\frac{L - L_0}{L_0} \right] \times 100 \quad (1)$$

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

2.3.3. Swell Determination. Determinations were 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 (2):

$$\Delta m_{100} = \frac{m_i - m_0}{m_0} \times 100 \quad (2)$$

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 (3):

$$\Delta V_{100} = \left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100 \quad (3)$$

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. The precision and the uncertainties of the test are ± 0.04 .

2.3.4. Permanent compressive deformation. The determinations were performed for a 25% compression at 70°C for 24 hours according to SR ISO 7791-67 method B. The specimens were obtained by punching rubber plates in the form of discs with a thickness of 6 mm.

2.3.5. Flexion Determination. The specimens were obtained by punching rubber plates and had the parallelepiped shape. The test was carried out with a De Mattia tester equipment observing when the first crack appears, according to ISO 7854/1995, and using a Ross Flex equipment to test the crack propagation, according to ISO 4643/2013.

2.3.6. *Accelerated ageing trial* was carried out according to ISO 188/2011 using the hot air circulation oven method. Similar samples to those used for hardness determination were used. Test duration was of 7 days and temperature of $70 \pm 1^\circ\text{C}$. The results were compared with those from samples not subjected to ageing.

2.3.7. *Behavior in sugar solution*. Place the specimens in beakers containing a volume of sugar solution of at least 15 times the volume of the rubber, and boil for 30 minutes. Remove the specimens from the beakers, allow to cool, and examine the taste, color and smell. The solution is obtained by dissolving 100 g of sugar in 1000 cm^3 of water, and adding 10 cm^3 of glacial acetic acid.

2.3.8. *The densities* of elastomer samples were measured according to ISO 2781/2010 (the precision and the uncertainties of the test are ± 0.09).

2.3.9. *Determining abrasion resistance* was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth and abrasive based on normal electrocorundum on dressed cloth substrate with granulation of $212\text{--}80\text{ }\mu\text{m}$ (PE 80), whose abrasiveness must be of $180\text{--}220\text{ mg}$ control rubber. The samples used were obtained from rolled blends and pressed by cutting with a rotating die and have cylindrical shape, with a diameter of 16mm and height of min. 6 mm. The precision and the uncertainties of the test are ± 0.15 .

3. RESULTS AND DISCUSSIONS

3.1. Cure Characteristics

The curing characteristics, expressed in terms of the optimum curing time, t_{90} , minimum torque (ML) and maximum torque (MH) for the samples, are reported in **Table 2**. It is noted that upon introduction of nanoclay there is a decrease of the optimal curing time, which indicates a more rapid curing due to OMMT nanofiller, which leads to increased crosslinking degree, an increase in ML which is a measure of the rigidity of the uncured material.

Characteristic	Mixture symbol		
	C0	C3	C6
The minimum torque $M_{\min}$ (dNm)	10	16	15.3
The maximum torque $M_{\max}$ (dNm)	53.7	48.3	43.1
Delta torque (dNm)	43.7	32.3	27.8
Optimal curing time, T_{90} (minutes)	1.43	1.09	1.13

Table 2. Rheological characteristics of blends

3.2. Physical-Mechanical Characteristics

Physical–mechanical characteristics of samples are presented in **Table 3**.

Physical-mechanical properties	Mixture symbol		
	C0	C3	C6
Hardness, °Sh A	52	55	56
Elasticity, %	50	35	33
100 % Modulus, N/mm ²	0.86	0.9	1.5
Tensile strength, N/mm ²	13.5	15.9	14.6
Elongation at break, %	700	720	647
Residual elongation, %	30	28	36
Tear strength, N/mm	32	32.5	33

Table 3. Physical-mechanical properties of blends

It can be seen that with the introduction of the nanoclay, natural rubber mixtures show an increase by 5-6°ShA of hardness, a decrease by 32.7-36.7% of elasticity, and an improvement in 100% elongation modulus, tear strength, and tensile strength. The elongation at break has a variation of $\pm 7.6\%$ and residual elongation a variation of $\pm 30\%$. These changes may be due to both the nanofiller reinforcement effect and the changes in the morphology of the mixture.

3.3. Variation of mass and volume in liquids

In general, the chemical properties of the polymeric composites obtained are additive and depend on the behavior of the mixture components in the immersion media. Thus, natural rubber is water-resistant (it is hydrophobic) but starch is hydrophilic - absorbs water. Considering the fact that the mixtures contain the same amount of starch and natural rubber, but the quantity of OMMT nanofiller is different, it can be seen from the **Table 4** that mixtures containing 6 phr OMMT showed a better behavior towards liquids - values of mass variations below 10% in water, ethyl alcohol, 10% glucose and 0.9% NaCl solution and below 30% in sunflower oil - unsaturated fatty acids.

Variation of mass and volume, %	Mixture symbol	
	C3	C6
Distilled water		
- Δ mass, %	5.9	4.66
- Δ volume, %	9.85	8.18
Ethyl alcohol		
- Δ mass, %	10.7	8.21
- Δ volume, %	18	14.3
10% glucose solution		
- Δ mass, %	6.34	3.71
- Δ volume, %	10.4	6.44
0.9% NaCl solution		
- Δ mass, %	5.73	3.96
- Δ volume, %	8.93	6.67

Sunflower oil		
- Δ mass, %	21.3	15.8
- Δ volume, %	33.7	27.6

Table 4. Variation of mass and volume in liquids

3.4. Other properties of obtained nanocomposites

For the nanocomposites, other properties have been determined in order to fit into the product standard for the O-rings for different areas of use. These are presented in **Table 5**. As a result of these determinations, the following were observed: (a) the permanent deformation values at 70°C for 24h are very good (13.3% and 25.8% respectively) indicating a very good return after compression, (b) analyzing the flexion behavior - both at first crack appearance and crack propagation, the behavior was very good, (c) the variance in hardness after accelerated aging was less than 5°ShA; (d) after the sugar solution test, it is noteworthy in both cases that the solution has no taste or odor, and has not changed color, (e) mixture densities are small, of 1.1 g/cm³, (f) exhibit good abrasion resistance values below 300 mm³.

4. CONCLUSIONS

It was observed that by introducing small quantities (3 and 6 phr - parts per 100 parts of rubber) of organically modified montmorillonite nanofiller, Nanomer I44P, in composites based on natural rubber, plasticized starch and precipitated silica, the following occurs: (1) a decrease of the optimal curing time, which indicates a more rapid curing due to OMMT filler, which leads to increased crosslinking degree, (2) increase of hardness by 5-6°ShA and an improvement in 100% elongation modulus, tear strength, and tensile strength - these changes may be due to both the nanofiller reinforcement effect and the changes in the morphology of the mixture, (3) better behavior to the action of liquids. In order to determine the areas of use of the new nanocomposites, other determinations were carried out such as: permanent deformation at 70°C for 24 hours, flexion behavior and accelerated aging, sugar solution test, density determination and abrasion resistance.

Properties	Mixture symbol	
	C3	C6
a. Permanent deformation values at 70°C for 24h	13.3	25.81
b. Flexion resistance, no. Cycles	Resists, no crack appearance after 100000 flexions	Resists, no crack appearance after 100000 flexions
	Resists, crack <6 mm after 100000 flexions	Resists, crack <6 mm after 100000 flexions
c. Accelerated ageing – Hardness variation, °Sh A	+4	+3
d. Behavior in sugar solution	After the sugar solution test, the solution has no taste or odor, and has not changed color	After the sugar solution test, the solution has no taste or odor, and has not changed color
e. Density, g/cm ³	1.1	1.1
f. Abrasion resistance, mm ³	218	300

Table 5. Other properties of nanocomposites

Following these determinations, it has been established that the new nanocomposites can be used to make: (a) O-rings (**Figure 1**) - Rubber gaskets for sugar industry, hardness class 60, according to STAS 4149-74, used in purification plants with industrial and drinking water, in carbon dioxide washers, etc., (b) pressed mechanical products (O-rings) type A rubber, Class 50-60, Component 100 for motor vehicles, according to STAS 9606-77, (c) soles and heels type A and type C, hardness class 60, (d) Compact rubber sheets which can be used for the manufacture of sealing gaskets in industrial installations (STAS 11419-80) - Type 1, general purpose, for temperatures between -35 ... + 70°C or type 7, for the food industry, non-resistant to grease, for temperatures between -30 ... +150°C.



Fig. 1. O-rings from nanocomposites based on natural rubber, plasticized starch, precipitated silica and layered clay

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