

CHARACTERISTICS OF POLYMER COMPOSITES BASED ON NATURAL RUBBER

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ABSTRACT. This paper presents the obtaining and characterization of new types of polymeric composites based on natural rubber and plasticized starch, crosslinked using peroxide in the presence of a polyfunctional monomer - trimethylolpropane trimethacrylate. Composite variants containing 10 phr, 20 phr, 30 phr, 40 phr and 50 phr starch, respectively were made. Starch was plasticized and then incorporated in natural rubber in the roll mill, and then other ingredients were added; the resulting mixtures were cured in an electrical press. The physico-mechanical characteristics of resulting composites depends on the amount of plasticized starch added to the rubber mixture. The results of liquid action on composites show that it depends on the behaviour of mixture components in immersion media; thus, natural rubber is water resistant (variation of mass and volume in water has very low values) but not resistant to toluene (variation of mass and volume in toluene has high values); starch is hydrophilic – it absorbs water and, with the increased amount of starch in the mixtures, there is also an increase of mass and volume variation in water, but the values obtained are good, with mass and volume variation after 22 h of water immersion being below 8%. In toluene, there is an improvement in the behaviour of composites containing plasticized starch compared to control ones (without plasticized starch). The new polymer composites can be used in various fields such as in the food or pharmaceutical areas that require compositions free of toxic ingredients.

KEY WORDS: polymer composites, natural rubber, starch, characteristics

CARACTERISTICILE UNOR COMPOZITE POLIMERICE PE BAZĂ DE CAUCIUC NATURAL

REZUMAT. Această lucrare prezintă obținerea și caracterizarea unor noi tipuri de compozite polimerice pe bază de cauciuc natural și amidon plastifiat, reticulate utilizând peroxid în prezența unui monomer polifuncțional - trimetilolpropan trimetacrilat. Compozitele au fost realizate cu conținut de amidon 10 phr, 20 phr, 30 phr, 40 phr și respectiv 50 phr. Amidonul a fost plastifiat și apoi încorporat în cauciucul natural pe valț, după care s-au adăugat celelalte ingrediente; amestecurile obținute au fost vulcanizate în presa electrică. Caracteristicile fizico-mecanice ale compozitelor obținute depind de cantitatea de amidon plastifiat adăugat amestecului de cauciuc. Rezultatele acțiunii lichidelor asupra compozitelor arată că aceasta depinde de comportarea componentelor amestecului în mediul de imersie; astfel, cauciucul natural este rezistent la apă (variația masei și volumului în apă având valori foarte mici), dar nu este rezistent la toluen (variația masei și volumului în toluen are valori mari); amidonul este hidrofili – absoarbe apa și, odată cu creșterea cantității de amidon din amestecuri, are loc și o creștere a variației masei și volumului în apă, însă valorile obținute sunt bune, variația masei și volumului după 22 h de imersie în apă fiind sub 8%. În toluen se observă o îmbunătățire a comportării compozitelor care conțin amidon plastifiat față de cele martor (fără amidon plastifiat). Noile compozite polimerice pot fi utilizate în diferite domenii cum ar fi în domeniul alimentar sau farmaceutic, unde este cerută o compoziție lipsită de ingrediente toxice.

CUVINTE CHEIE: compozite polimerice, cauciuc natural, amidon, caracteristici

LES CARACTÉRISTIQUES DES COMPOSITIONS POLYMÉRIQUES EN CAOUTCHOUC NATUREL

RÉSUMÉ. Cet article présente la production et la caractérisation de nouveaux types de caoutchouc polymère à base de caoutchouc naturel et d'amidon plastifié, réticulés à l'aide de peroxyde en présence d'un monomère polyfonctionnel triméthacrylate de triméthylolpropane. Les composites ont été fabriqués contenant 10 phr, 20 phr, 30 phr, 40 phr et 50 phr d'amidon respectivement. L'amidon a été plastifié puis incorporé dans le caoutchouc naturel sur le rouleau, après quoi les autres ingrédients ont été ajoutés ; les mélanges obtenus ont été vulcanisés dans la presse électrique. Les caractéristiques physico-mécaniques des composites obtenues dépendent de la quantité d'amidon plastifié ajoutée au mélange de caoutchouc. Les résultats de l'action des liquides sur les composites montrent que cela dépend du comportement des composants du mélange dans le milieu d'immersion ; ainsi, le caoutchouc naturel est résistant à l'eau (variation de la masse et du volume dans l'eau a des valeurs très faibles) mais il n'est pas résistant au toluène (la variation de la masse et du volume dans le toluène est élevée) ; l'amidon a une nature hydrophile - il absorbe l'eau et avec l'augmentation de la quantité d'amidon dans les mélanges, il y a aussi une augmentation de la variation de la masse et du volume dans l'eau, mais les valeurs obtenues sont bonnes, la variation de la masse et du volume après 22 heures d'immersion dans l'eau est au-dessous de 8%. Dans le toluène a été observée une amélioration du comportement des composites contenant de l'amidon plastifié. Les nouveaux composites polymériques peuvent être utilisés dans divers domaines, comme dans le domaine alimentaire ou pharmaceutique, où une composition exempte d'ingrédients toxiques est nécessaire.

MOTS CLÉS: composites polymériques, caoutchouc naturel, amidon, caractéristiques

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INTRODUCTION

The oldest and most important elastomer that was the first model for attempts to synthesize rubber is natural rubber. This elastomer is obtained from a series of laticiferous plants, such as *Hevea brasiliensi*, *Ficus elastica* etc. Natural rubber is used mainly in the tire industry, and at least currently it cannot be fully replaced with any other type of synthetic rubber. Its long fatigue life and high strength makes it suitable for use up to approximately 100°C, and can maintain flexibility down to -60°C in combination with other substances. Other advantages include good creep and stress relaxation resistance and low cost. In terms of disadvantages, natural rubber has poor oil resistance and no resistance to oxygen and ozone, which can however be improved by compounding with specific chemicals [1].

Natural rubber (NR) as such has very limited applications. Basically all technical products made of rubber are compositions in which the elastomer matrix embeds: curing agents curing accelerators, ingredients for reinforcement and other components with the role of facilitating processability, increasing resistance to degradation, colouring the final product, etc. Reinforcing elastomers with certain ingredients called fillers is a process of high practical and technological importance. The most commonly used are active fillers such as silica and carbon black. Silica is known to have adverse effects on health: silicosis, cancer (Group 1 according to IARC—the International Agency for Research on Cancer), autoimmune diseases, tuberculosis, kidney disease, and so forth, and in 1995, the IARC rated carbon black as IARC classification 2B—possibly carcinogenic to humans and definitely carcinogenic to animals [2-4]. Carbon black is the most commonly used filler in NR compounds. For food applications, most furnace blacks are considered safe. According to existing food regulations, the type and the amount of carbon black is limited. According to FDA 177.2600, the amount of carbon black may not exceed 50% by weight of the rubber product. In rubber products intended for use in contact with milk or edible oils, the total carbon black amount may not exceed 10%. According to German BgVV

Recommendation XXI, the only carbon blacks that are allowed are those that fulfill the criteria for cleanliness according to German BGesundBL 15,268 (1972) [5]. For these reasons, efforts were made to replace them with other types of fillers. Currently the most viable way toward eco-friendly composites is the use of natural fibers as reinforcement. Natural fibers represent a traditional class of renewable materials which, nowadays, are experiencing a great revival [6, 7]. On the other hand, natural fibers exhibit many advantageous properties which promote the replacement of synthetic fibers in polymer composites. They are a low-density material yielding relatively lightweight composites with high specific properties and therefore natural fibers offer a high potential for an outstanding reinforcement in lightweight structures.

In this paper the active filler was replaced with starch in the form of plasticized starch. Starch is an organic substance found in the seeds, fruits and tubers of plants and is used in the food, chemical and other industries. Starch comes from renewable resources and has many advantages, such as: low price, availability, non-toxicity, and it is widely used in many areas (food, paper manufacturing, chemical industry, packaging material industry, etc.) [8]. Starch can be altered by plasticization to improve its processability and other properties required for certain applications. Plasticizers bind macromolecules to high molecular mass compounds, thus leading to better processability. In the case of mixtures based on starch, tensile strength and flow properties may significantly improve through their conversion to plasticized starch using compounds such as water, glycerine or formamide, as the latter lead to more stable properties [8-9]. In this paper, starch was plasticized using water and glycerine.

The most important step of the technological process for developing rubber products is curing. Out of the several possibilities to crosslink natural rubber, the best known method is vulcanization with sulphur and curing accelerators. This occurs by ionic mechanism and leads to the formation of sulphur bridges between (C–S_x–C) macromolecules or cyclic combination of sulphur. Physical–mechanical properties of samples containing C–S_x–C crosslinking bridges

exhibit better tensile strength values than those containing C–C bonds. Although vulcanization with sulphur and vulcanization accelerators leads to obtaining products with better characteristics, it also has disadvantages, such as the fact that during the process of vulcanization nitrosamines (carcinogen products) are formed and the obtained end products are toxic, contain heavy metals (Zn), have an unpleasant odor and exudate [10, 11]. For these reasons, efforts are made internationally to replace sulfur and curing accelerators vulcanization systems. In this paper, crosslinking is done using peroxide in the presence of vulcanization co-agent. The use of organic peroxides is the only vulcanization method that can compete with accelerated sulphur cure, with respect to vulcanization rate. Peroxide vulcanisation leads to a rubber network in which the polymer chains are linked to each other by very stable covalent carbon-carbon bonds. Peroxide cured vulcanisates have therefore good high temperature properties, like heat ageing and compression set, compared to sulphur cured articles [12-14].

This paper presents the process of obtaining and characterizing a new type of polymeric composite based on natural rubber and plasticized starch as filler, crosslinked using peroxide in the presence of a polyfunctional monomer - trimethylolpropane trimethacrylate. It also studies the influence of plasticized starch amount on the physical-mechanical properties and behaviour in aqueous and toluene environment.

EXPERIMENTAL

Materials

The following materials were used for rubber mixtures:

- 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%;
- 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%);
- Richon IPPD antioxidant (4010 NA) N-isopropyl - N-phenyl - phenylene diamine, 98% purity, molecular mass: 493.6374;

The following materials were used for crosslinking blends: Perkadox 40 benzoyl peroxide (density 160 g/cm³, 3.8% active oxygen content, 40% peroxide content, pH 7) and Luvomaxx TMPT DL 75 (TMPT) trimethylolpropane trimethacrylate polyfunctional monomer (22 % ash, pH 9.2, density 1.36 g/cm³, 75 ± 3 % active ingredient).

Plasticizing Starch

Starch (50%), water (20%) and then glycerine (30%) are mixed at 70°C for 15 min at 50-100 rpm until a homogenous mixture is obtained. It is left for 1 h at room temperature, then in the oven for 22h at 80°C and then for 2 h at 110°C. It is left for 16 h in a dry place.

Obtaining Polymer Composites

The process of obtaining composite materials based on natural rubber and plasticized starch comprises: operations of characterizing raw materials, dosing raw materials and obtaining the composite by roller mixing.

Polymer composites based on natural rubber and plasticized starch consist of a rubber mixture whose composition is shown in Table 1. Mixtures were crosslinked with peroxide in the presence of a curing co-agent/polyfunctional monomer. The roller mixer working method is presented in Table 2. Roller mixer working parameters are: working temperature is kept below 60°C, and friction is 1:1,1.

The products obtained as rubber mixtures in the form of sheets. These sheets were cured using molds and vulcanization press in order to obtain rubber plates with the sizes of 150 mm x 150 mm x 2 mm required for die punching test specimens for the characterization of polymer composites.

Table 1: Formulations

Mixture symbol	NR-0 (phr)	NR-10 (phr)	NR-20 (phr)	NR-30 (phr)	NR-40 (phr)	NR-50 (phr)
Natural rubber	100	100	100	100	100	100
Starch	-	10	20	30	40	50
Glycerine	-	6	12	18	24	30
Peroxide	8	8	8	8	8	8
TMPT	3	3	3	3	3	3
Antioxidant 4010	1	1	1	1	1	1

Table 2: Roller mixer working method

Order of adding ingredients	Time
(1) Rubber is mixed in the roller mixer	ca. 2'
+ (2) plasticized starch and glycerine	ca. 5'-30'
+ (5) antioxidant	ca. 1'
+ (3) + (4) peroxide and TMPT	ca. 1'
Homogenisation	ca. 2'
Removing the mixture from the roller	ca. 1'
TOTAL	12-37'

Preparation of Sample

Test specimen sheets of all compounds were produced using compression moulding. The temperature of the compression moulding machine was kept constant at 160°C, for 20' at a pressure of 300 kN. Cooling time 10' at 25°C and 300 kN.

Laboratory Tests

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, 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.

Determination of Liquid Action

Determinations were performed according to ISO 1817/2015 and the action of the following liquids was tested: water and toluene. The test pieces of known weight, m_0 , were immersed in various solvents in diffusion 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 (1):

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

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 (2):

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

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.

RESULTS AND DISCUSSIONS

Physical-Mechanical Characteristics

The influence of the plasticized starch amount on the physical-mechanical characteristics of mixtures is illustrated in Figures 1-5. Analyzing the physical-mechanical characteristics of mixtures based on natural rubber and plasticized starch, it can be noticed that when increasing the amount of starch in the mixtures: (a) hardness (Figure 1) increases indicating that starch leads to NR reinforcement, (b) elasticity (Figure 2) decreased as a result of lowering the amount of natural rubber in the mixtures and reinforcing the mixtures; (c) tear strength (Figure 3) decreased, and tensile strength (Figure 4) improved, however it shows a

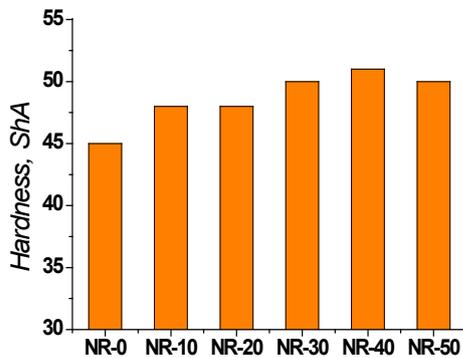


Figure 1. Hardness variation depending on the amount of plasticized starch introduced in the mixture

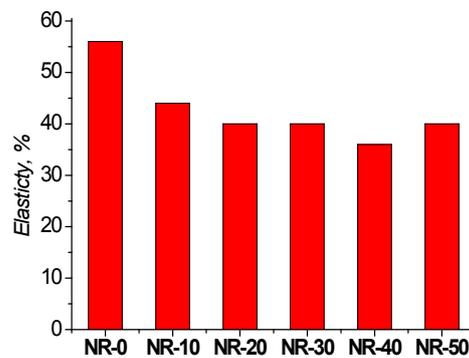


Figure 2. Elasticity variation depending on the amount of plasticized starch introduced in the mixture

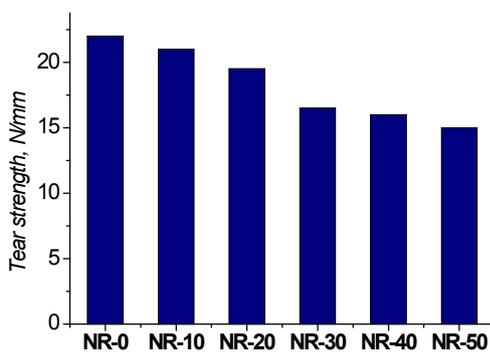


Figure 3. Tear strength variation depending on the amount of plasticized starch introduced in the mixture

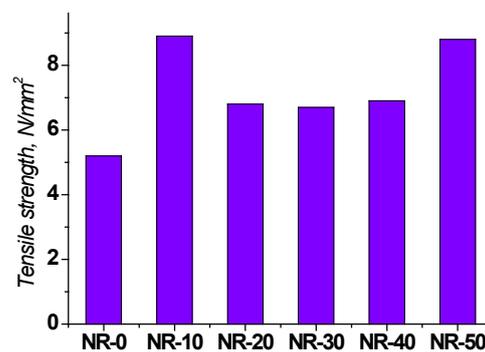


Figure 4. Tensile strength variation depending on the amount of plasticized starch introduced in the mixture

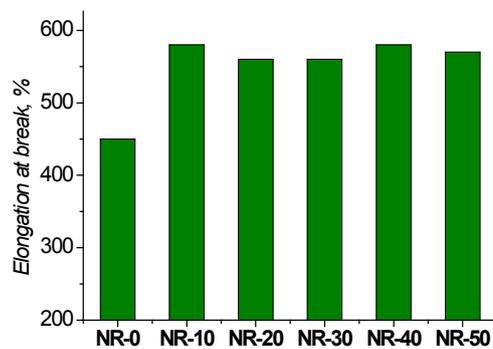


Figure 5. Elongation at break variation depending on the amount of plasticized starch introduced in the mixture

non-uniform variation to increasing the amount of starch; (d) elongation at break (Figure 5) shows a non-uniform increase with the increase of plasticized starch amount. The data shows that plasticized starch may replace active fillers such as carbon black or precipitated silica which are harmful and may cause occupational illnesses to employees in the rubber processing industry.

Action of Liquids on Composites

The results of liquid action on composites are presented in Figures 6-7. The data show

that it depends on the behaviour of mixture components in immersion media; thus, natural rubber is water resistant (variation of mass and volume in water has very low values) but not resistant to toluene (variation of mass and volume in toluene has high values); starch has a hydrophilic nature – it absorbs water and, with the increased amount of starch in the mixtures, there is also an increase of mass and volume variation in water.

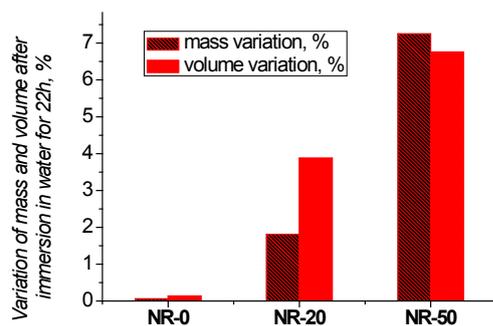


Figure 6. Variation of mass and volume after immersion in water for 22h

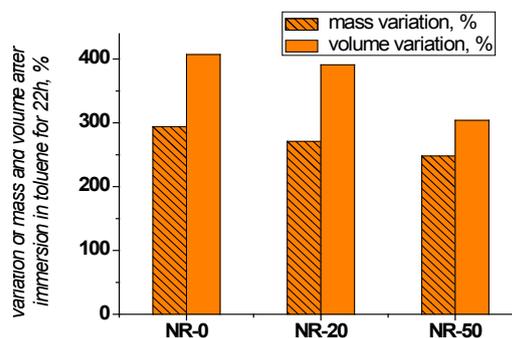


Figure 7. Variation of mass and volume after immersion in toluene for 22h

CONCLUSIONS

A new type of polymeric composites based on natural rubber and plasticized starch as filler was obtained and characterized, crosslinked using peroxide in the presence of

trimethylolpropane trimethacrylate. These composites have good physical-mechanical characteristics, indicating that plasticized starch may successfully replace inorganic fillers in rubber mixtures, which are harmful and may cause occupational illnesses to employees in the

rubber processing industry. The results of liquid action on composites show that it depends on the behaviour of mixture components in immersion media; thus, natural rubber is water resistant (variation of mass and volume in water has very low values) but not resistant to toluene (variation of mass and volume in toluene has high values); starch has a hydrophilic nature – it absorbs water and, with the increased amount of starch in the mixtures, there is also an increase of mass and volume variation in water, however the values obtained are good, mass and volume variation after 22 h of immersion being below 8%. In toluene, an improvement is seen in the behaviour of composites containing plasticized starch compared to control samples.

The new polymer composites may be used in various areas such as the food or pharmaceutical industry that requires compositions free of toxic ingredients.

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