

# Elasto-Plastic Materials Based on EPDM Rubber, LDPE, Plasticized Starch and OMMT

MARIA DANIELA STELESCU<sup>1</sup>, ADRIANA STEFAN<sup>2</sup>, MARIA SONMEZ<sup>1</sup>,  
MIHAELA NITUICA<sup>1\*</sup>, MIHAI GEORGESCU<sup>1</sup>

<sup>1</sup> National Research and Development Institute for Textile and Leather, Division Leather and Footwear Research Institute, 93 Ion Minulescu Str., 031215, Bucharest, Romania

<sup>2</sup> National Institute of Aerospace Research “Elie Carafoli”, 220 Iuliu Maniu Blvd., 061126, Bucharest, Romania

**Abstract:** *This paper describes the development of new types of dynamically cross-linked thermoplastic elastomers based on ethylene-propylene-terpolymer rubber and low-density polyethylene, reinforced with plasticized starch and montmorillonite with a chemically modified surface. An octylphenol-formaldehyde resin in the presence of stannous chloride dihydrate was used as a vulcanizing agent. The samples were obtained on a Brabender Plasti-Corder mixer, at appropriate temperatures and rotation speeds, using the dynamic vulcanization method and the melt intercalation technique. The mixtures obtained were modeled in the form of plates with standard dimensions using specific molds and a laboratory-scale electrical press. The obtained samples were analyzed from the point of view of the physical-mechanical properties, the melt flow index, as well as from the structural and morphological point of view. It was observed that the characteristics of the samples are influenced by both the composition and the methods of obtaining used. According to the obtained characteristics, the new elasto-plastic materials can be used in fields such as the footwear industry (for the production of: soles, heels, protective boots), in the rubber and plastics industry, the automobile industry, agriculture or construction (when making gaskets, technical items, hoses, etc.). They can be easily processed into different finished products by methods specific to plastics.*

**Keywords:** TPV, EPDM, LDPE, OMMT, plasticized starch

## 1. Introduction

The 21<sup>st</sup> century is considered by specialists in the field to be the century of advanced polymers [1]. The polymer production and processing branch is considered one of the largest industrial sectors. In today's society, with a wide spectrum of lifestyles, obtaining new advanced materials based on polyolefins, elastomers, compatibilizing and reinforcing agents in the form of nano-sized particles with chemically activated surfaces, with high-performance physical and mechanical properties and ecological processing technology into finished products with short processing time is essential for various fields of research [2-4]. Among these, elasto-plastic nanomaterials are currently considered materials with high industrial performance applications. Therefore, their development has recently proven to be of great interest for industries such as footwear, consumer goods, technical rubber products, etc. [5]. Among these, a special place is occupied by nanocomposites based on chemically modified layered clay of the montmorillonite type (OMMT). These are generally obtained by the intercalation melt method, which is an ecological method of obtaining elasto-plastic nanocomposites that leads to the improvement of physical-mechanical characteristics and more [6, 7].

In order to obtain new sustainable polymer materials, several studies have been carried out regarding the replacement of a part of the polymers obtained by synthesis with organic, biodegradable polymers obtained from renewable resources, such as starch [8-9]. Starch cannot be processed in the melt as such, because it degrades before melting. In order to reduce the melting temperature of starch, plasticizers such as glycerin, water, etc. are generally used. At high temperatures (55°C-120°C), they form a viscous suspension with the starch following a gelatinization process, which leads to the decomposition of the

\*email: [mihaelavilsan@yahoo.com](mailto:mihaelavilsan@yahoo.com); [mihaela.nituica@icpi.ro](mailto:mihaela.nituica@icpi.ro)

granular tissue of the starch and to the decrease of its melting temperature [10-11]. Currently, there are studies on obtaining mixtures based on plasticized starch and synthetic polymers that present properties suitable for a large number of applications [8-9].

An advanced method that allows improving the morphology and properties of materials based on elastomers and plastomers is called dynamic vulcanization, and the products obtained are called dynamically vulcanized thermoplastic elastomers (TPV) [12-14]. This method consists in dynamic cross-linking of the elastomer in the melt of thermoplastic material, using reduced amounts of cross-linking agents, when micron-sized particles of finely cross-linked elastomer distributed in the plastomeric matrix are obtained. These types of materials are generally obtained in the form of granules and can be processed on equipment specific to both plastics and vulcanized materials, through kneading, extrusion, injection, and thermoforming processes. The waste resulting in the technological flow can be easily re-circulated without affecting the quality of the finished products, and the technological process corresponding to obtaining finished products can be fully automated, etc. [12-14].

This paper presents the production of new types of elasto-plastic materials based on EPDM elastomer (ethylene-propylene-diene-terpolymer) and LDPE (low density polyethylene) reinforced with starch which was plasticized and chemically modified surface OMMT (organic montmorillonite-type nanofiller). The samples were obtained by the methods and techniques presented above and then were characterized from the point of view of physical-mechanical properties, flow indices, as well as from a structural and morphological point of view.

## 2. Materials and methods

### 2.1. Materials

The following materials were used: (1) ethylene-propylene-diene-terpolymer rubber Nordel rubber 3745P (ethylene content 70%, density 0.88 g/cm<sup>3</sup>), from Dow Chemical Company; (2) low density polyethylene (LDPE) Tipolen MF 243-51 (melt flow index - MFI 22.4 g/10 min. at 190°C with a pressure of 2.16 kg, density 0.922 g/cm<sup>3</sup>) produced by Mol Petrochemicals Co Ltd, Hungary; (3) Compatibilizer: polyethylene graft maleic anhydride (PE-g-AM) Bonyram TL 4109-E from Polyram, Israel (density 0.905 g/cm<sup>3</sup>, MFI 2g/10 min. at 190°C with a 2.16 kg force, density of 0.905 g/cm<sup>3</sup>); (4) soluble starch obtained from potatoes produced by Lach; (5) starch plasticizer - glycerin (free acidity 0.02%, specific gravity - 1.26 g/cm<sup>3</sup>), produced by S.C. Chimreactiv S.R.L.; (6) organic modified montmorillonite (OMMT) - Nanoclay I 31.PS (chemically modified montmorillonite layered clay with 0.5 - 5% propyl-amino-trietoxysilane and 15-35% octadecylamine, particle size below 20 microns), produced by Nanocor.; (7) antioxidant Irganox 1010 (98% active ingredient), (8) vulcanize agent - heat-reactive resin SP-1055 - based on octylphenol-formaldehyde containing methylol groups (bromine content 4%, methylol content 11%, density 1.05 g/cm<sup>3</sup>) produced by Akrochem Corporation, Ohio, (9) Catalyst for the crosslinking reaction - stannous chloride dihydrate SnCl<sub>2</sub>xH<sub>2</sub>O produced by Merk KGaA, Darmstadt, Germania; (10) zinc oxide I grade quality (99% purity) and (11) stearic acid (0.02% ash).

(1) ethylene-propylene-diene-terpolymer rubber Nordel rubber 3745P (ethylene content 70%, density 0.88 g/cm<sup>3</sup>), from Dow Chemical Company; (2) low density polyethylene (LDPE) Tipolen MF 243-51 (melt flow index - MFI 22.4 g/10 min. at 190°C with a pressure of 2.16 kg, density 0.922 g/cm<sup>3</sup>) produced by Mol Petrochemicals Co Ltd, Hungary; (3) Compatibilizer: polyethylene graft maleic anhydride (PE-g-AM) Bonyram TL 4109-E from Polyram, Israel (density 0.905 g/cm<sup>3</sup>, MFI 2g/10 min. at 190°C with a 2.16 kg force, density of 0.905 g/cm<sup>3</sup>); (4) soluble starch obtained from potatoes produced by Lach; (5) starch plasticizer - glycerin (free acidity 0.02%, specific gravity - 1.26 g/cm<sup>3</sup>), produced by S.C. Chimreactiv S.R.L.; (6) organic modified montmorillonite (OMMT) - Nanoclay I 31.PS (chemically modified montmorillonite layered clay with 0.5 - 5% propyl-amino-trietoxysilane and 15-35% octadecylamine, particle size below 20 microns), produced by Nanocor.; (7) antioxidant Irganox 1010 (98% active ingredient), (8) vulcanize agent - heat-reactive resin SP-1055 - based on octylphenol-formaldehyde containing methylol groups (bromine content 4%, methylol content 11%, density 1.05

g/cm<sup>3</sup>) produced by Akrochem Corporation, Ohio, (9) Catalyst for the crosslinking reaction - stannous chloride dihydrate SnCl<sub>2</sub>xH<sub>2</sub>O produced by Merk KGaA, Darmstadt, Germania; (10) zinc oxide I grade quality (99% purity) and (11) stearic acid (0.02% ash).

## 2.2. Sample preparation

The composition of the mixtures made is presented in Table 1. To obtain the mixtures, in the first stage, the starch was plasticized as follows: the starch was dried at 80°C for 8 h and then plasticized with glycerin in a 2:1 mass ratio with continuous stirring at 70°C until a homogeneous mixture was obtained. In the second stage, nanocomposites are obtained using a Brabender Plasticorder 828703 V230 internal mixer (Duisburg, Germany) at high temperatures, and the working method is indicated in Table 2.

**Table 1.** Blend formulations

Ingredients	Sample symbol								
	A	B	C	D	E	F	G	H	I
EPDM, g	60	60	60	60	60	60	50	50	30
LDPE g	40	40	40	40	40	40	50	50	70
PE-g-AM, g	5	5	5	5	5	5	5	5	5
Zinc oxide, g	3	3	3	3	3	3	2.5	2.5	1.5
Stearic acid, g	0.75	0.75	0.75	0.75	0.75	0.75	0.63	0.63	0.4
Antioxidant, g	1	1	1	1	1	1	1	1	1
OMMT, g	-	-	3	3	3	3	3	3	3
Plasticized starch, g	50	50	50	50	80	80	50	22.5	12
Resin SP 1055, g	-	3	3	4	-	3	6	6	3
SnCl <sub>2</sub> x2H <sub>2</sub> O, g	-	1	1	2	-	1	1.67	1.67	1

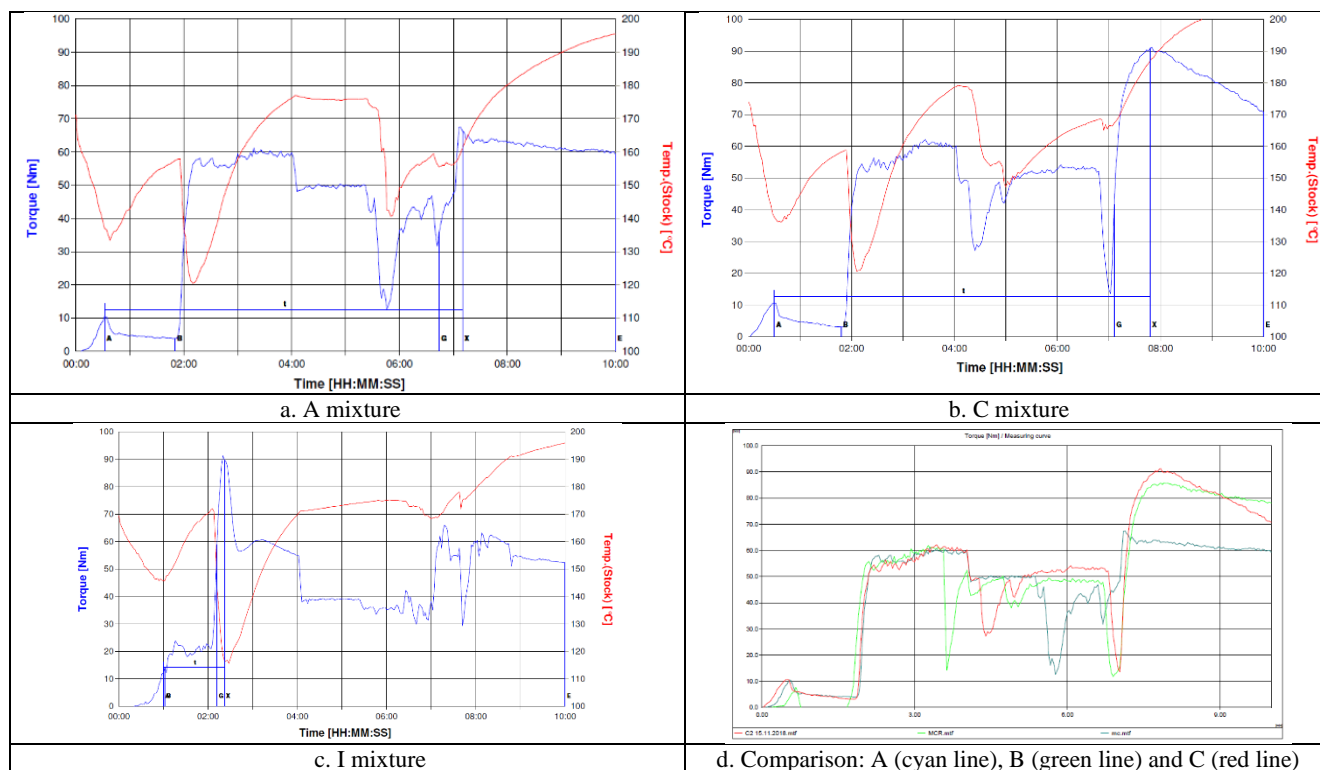
**Table 2.** Procedure for obtaining mixtures using the Brabender Plasticorder mixer

Order of introducing ingredients	Time
LDPE +EPDM + PE-g-AM +OMMT + plasticized starch + ZnO + stearic acid + heat-reactive resin SP-1055 + SnCl <sub>2</sub> xH <sub>2</sub> O Homogenisation	2 min. at 60 rotations/minute (rpm) 2 min. at 60 rpm 2 min. at 30 rpm 3 min. at 30 rpm 3 min. at 80 rpm
Total time	12'

The diagram of the torque variation versus time and temperature recorded using the Brabender Plasticorder mixer during the production of mixtures A-C is presented in Figure 1. According to the diagrams presented, in the first part that corresponds to the introduction of LDPE into the mixer (approx. 2 min. at 60 rpm, Table 2), the torque increases initially and then as the LDPE melts, the torque decreases. A significant increase in the torque is then observed, which corresponds to the introduction of the EPDM elastomer and the PE-g-AM compatibilizing agent. Due to shear forces, the temperature rises as the torque increases. As the melting point is achieved, the torque starts to decrease slightly, and the homogenization and plasticization of the EPDM elastomer begins. The following ingredients are introduced for mixing in the Brabender mixer: plasticized starch, OMMT nanofiller, ZnO and stearic acid, mixing them at a speed of 30 rpm (Table 2 and Figure 1).

The torque starts to increase as the inclusion of the fillers and stearic acid takes place. After incorporating them, the crosslinking resin and stannous chloride dihydrate are added, followed by closing the mixer and increasing the rotation speed to 80 rpm. The torque increases to a maximum point, after which it decreases. It is observed that the values of the torque in this part are higher in the mixture containing the OMMT nanofiller due to its high strengthening effect. For the sample containing the vulcanization resin, due to the dynamic crosslinking of the elastomer in the LDPE melt, an even greater increase in the torque can be observed, which may indicate an increase in the viscosity of the mixtures due to the crosslinking reactions [15]. In this stage corresponding to the homogenization of the mixtures (Figure 1c), due to the shear forces, the temperature increases exponentially until minimum torque is reached. Comparing the torque variation of mixture C with that of mixture I (Figures 1b and 1c), it is

observed that when the amount of LDPE increases and the amount of EPDM decreases, the torque changes accordingly.



**Figure 1.** Changes in the time-dependent torque recorded by the Brabender Plasti-Corder for: (a) A mixture, (b) C mixture, (c) I mixture, (d) comparison: A, B and C

The mixtures obtained were processed on a laboratory-scale roller with a heating-cooling system of the rollers. Sheets with a thickness of about 2 mm were obtained. These were shaped into plates to determine the characteristics using specific molds and a laboratory-scale Fortune Presses model no. TP 600 electrical press manufactured by Fontijne Grotnes, Vlaardingen, The Netherlands. The working method and processing parameters for the press were selected according to the flow index and the melting temperature of the components, as follows: preheating time 2 min. at a temperature of 170°C, molding time 5 min at 170°C and 300 kN pressing force, followed by cooling time 8 min. until reaching 45°C and 300 kN pressing force. Plates with dimensions 150x150x2 mm<sup>3</sup> and 50x50x6 mm<sup>3</sup> were made from which samples were punched.

### 2.3. Specimen characterization

Tensile strength, modulus 100% (tensile stress required to yield an elongation of 100%), elongation at break and residual elongation tests were carried out according to ISO 37 and tearing strength tests were carried out according to EN 12771. Samples were tested on a Schopper 1445 strength tester with testing speed 460 mm/min.

Hardness was measured both in °Sh A (scale specific to elastomeric materials with low hardness), and in °ShD (scale specific to plastics or elastomeric materials with high hardness) by according to ISO 48-4, using 6 mm thick specimens. Resilience was determined according to ISO 4662 with a Schob test machine.

Melt flow index (MFI) was measured with a capillary rheometer - Melt Flow Index – Haake, at 190°C and a 10 kg force.

Abrasion resistance was determined using the cylinder method, at a 10 N force, according to ISO 4649 and samples with a diameter of 16 mm and a height of 6 mm were used. The samples were punched with the help of a rotary die with a cylindrical shape.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of all the samples were obtained using Nicolet iS50 FT-IR spectrophotometer in the wave number ranging from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ .

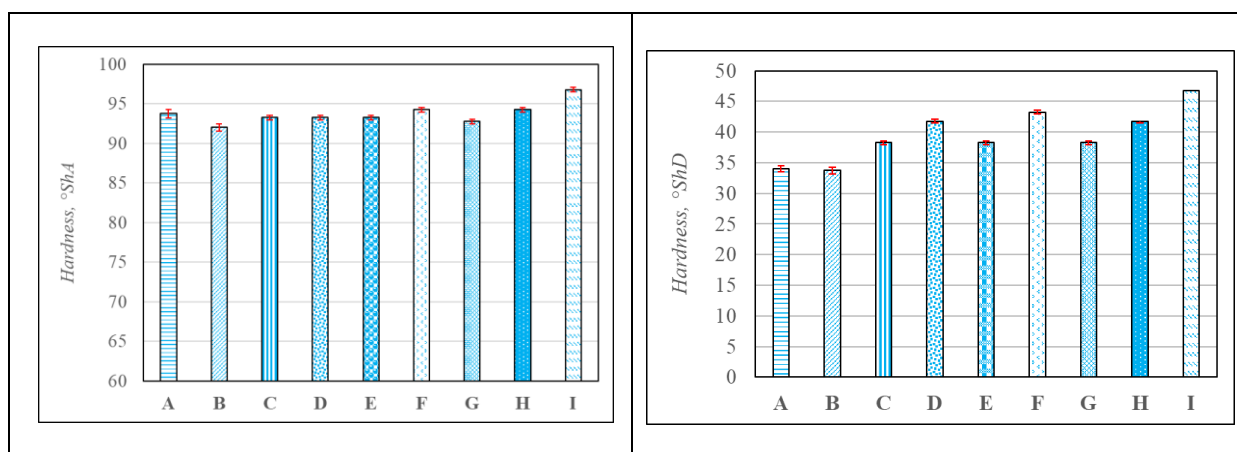
Scanning electron microscopy (SEM) was performed using QUANTA 250 FEI scanning electron microscope equipped with an EDS module, in low vacuum conditions. The samples preparation included the deposition of a conductive layer on the sample surface for morphostructural analysis.

### 3. Results and discussions

#### 3.1. Mechanical characteristics

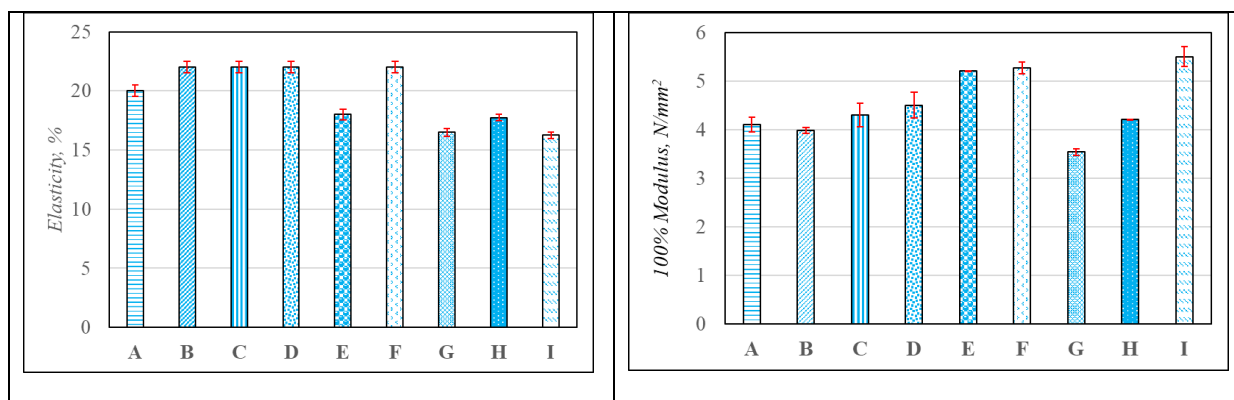
The physical-mechanical characteristics of the samples are presented in Figures 2-10.

*Hardness* is higher in the mixture with a higher content of LDPE (mixture I) and varies between  $92\text{--}94^\circ\text{ShA}$ , and  $33\text{--}42^\circ\text{ShD}$ , respectively (Figure 2). An increase in hardness can be observed due to the reinforcing effect of the nanofiller - the hardness value increases from  $33^\circ\text{ShD}$  (mixture B) to  $38^\circ\text{ShD}$  (mixture C) by adding 3 parts per 100 parts of rubber (phr) of OMMT nanofiller. Comparing the hardness values of mixtures A, B, C, and D, an increase in hardness can be seen with the increase in the amount of phenolic crosslinking resin, indicating that the crosslinking of the EPDM elastomer in the LDPE melt was achieved with the formation of a three-dimensional network that led to an additional reinforcement of the samples [15].



**Figure 2.** Hardness expressed in  $^\circ\text{ShA}$  (left) and in  $^\circ\text{ShD}$  (right)

Values of *elasticity* or resilience (Schob) are of  $16\text{--}22\%$  and their decrease (of about  $10\text{--}27\%$ ) is observed when the percentage of elastomer in the mixture decreases, as well as an improvement by dynamic crosslinking (of about  $17\%$ ) of the elastomer (Figure 3).



**Figure 3.** Elasticity

**Figure 4.** 100% Modulus

Figures 4-6 show the values of the *100% modulus*, *tensile strength* and *tear strength*. The values of



these characteristics are improved by increasing the amount of crosslinking agent as a result of increasing the degree of crosslinking of the elastomer [15], as well as by adding OMMT which leads to the formation of a nanocomposite by intercalating the polymer melt between the layers of OMMT [16]. When increasing the amount of plasticized starch (samples E-F compared to samples A-C), a slight improvement of the 100% modulus is observed, but also a slight decrease in the elongation at break due to the strengthening effect of the organic filler. At the same time, the mixtures with a greater amount of plastic mass - LDPE, present higher values of the tensile strength and the tear strength, indicating that these properties are additive and depend on the characteristics of the polymers included in the composition of the mixture [17].

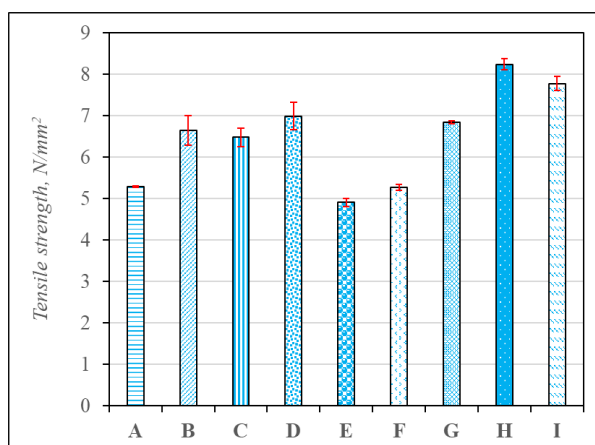


Figure 5. Tensile strength

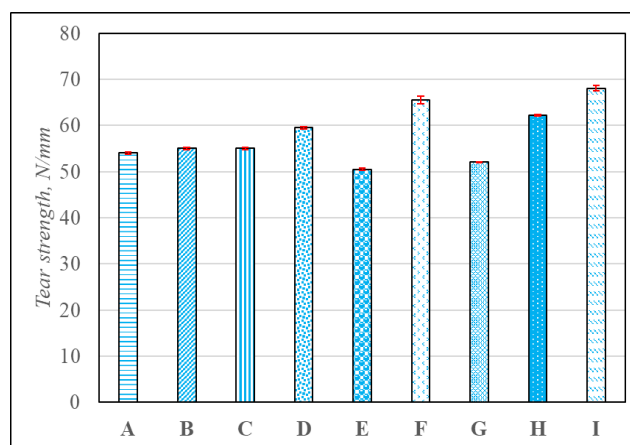


Figure 6. Tear strength

The values of *elongation at break and residual elongation* (Figures 7-8) are high, of 520-820%, and 420-540%, respectively. These are specific to plastic and elasto-plastic materials, which form a neck when a force is applied. These values are an indication of the ductility of a polymer [16].

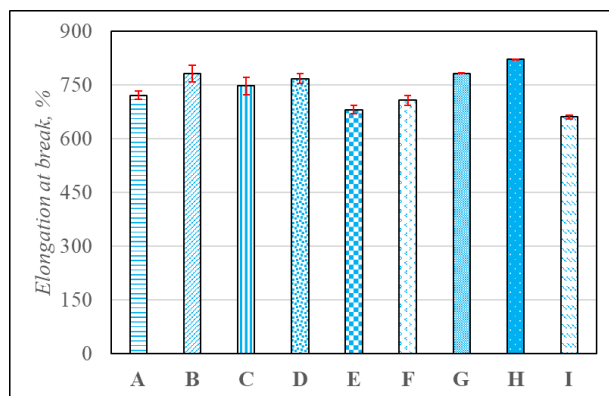


Figure 7. Elongation at break

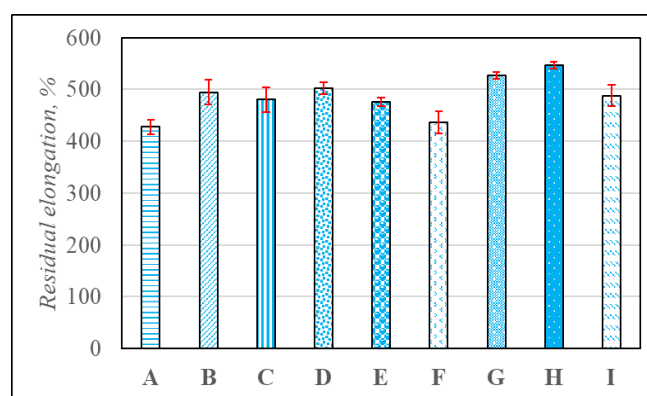


Figure 8. Residual elongation

*Melt Flow Index (MFI)* for all samples has values above 14.7 g/10 min. at 190°C for a force of 10 kg (Figure 9), indicating that the new materials can be processed by methods specific to plastics, such as injection processing. Compared to the control sample (sample A and E), the MFI value decreases by introducing the brominated octylphenol-formaldehyde resin (sample B and sample F), as a result of the crosslinking of the elastomer in the plastomer melt, and the change in the morphology of the samples with the formation of micron-sized elastomer particles, located in a matrix of plastic material (LDPE) [1, 5]. The MFI value improves for samples H and I compared to samples E-F, because they contain a smaller amount of plasticized starch [18].

*Abrasion resistance* has high performance values, between 41.17-86.68 mm<sup>3</sup> for all samples due to the very good wear values of LDPE – the polymer matrix of these (nano) composites (Figure 10).

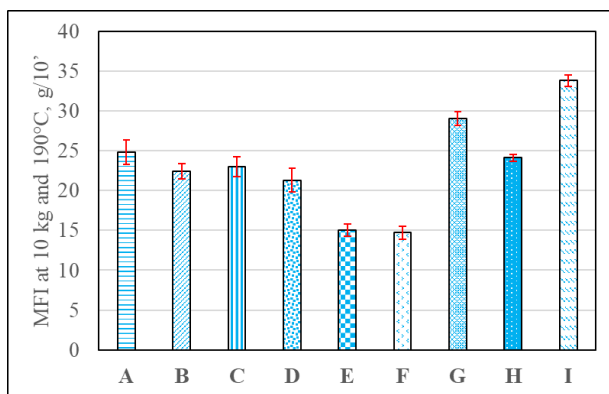


Figure 9. Melt Flow Index (MFI)

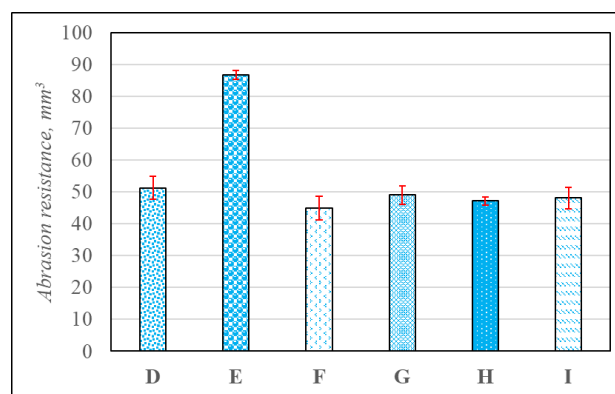
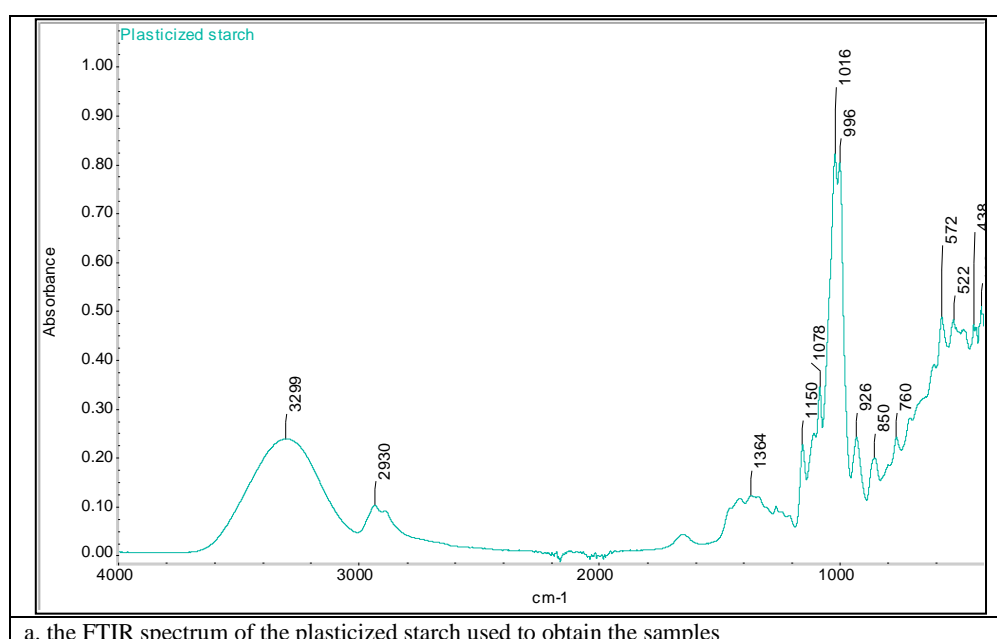
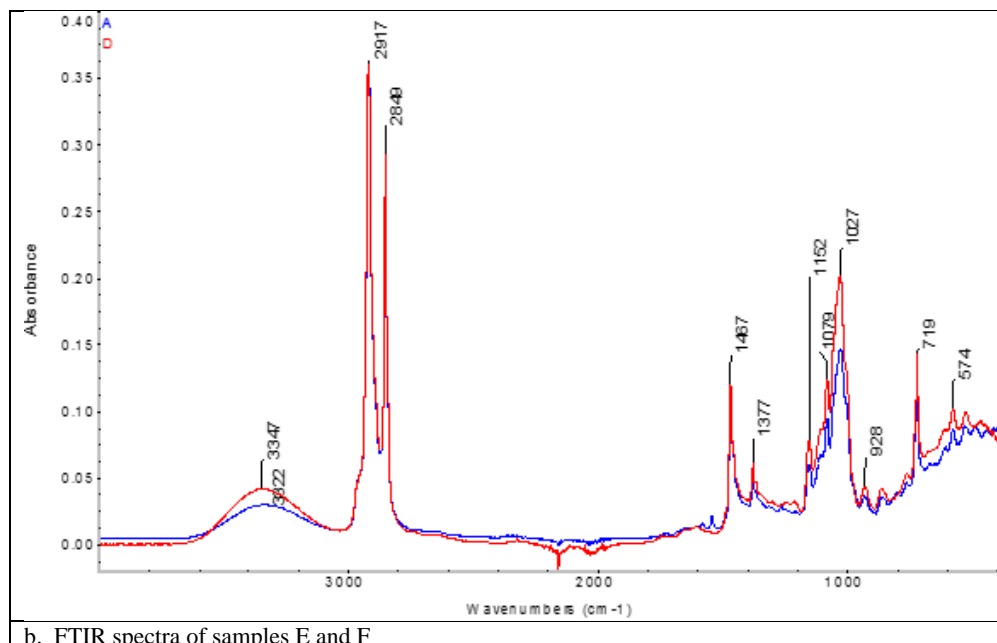


Figure 10. Abrasion resistance

### 3.2. FTIR analysis

In order to evaluate the structural modification, analysis of the FT-IR spectral of the samples was carried out (Figure 11). The FTIR spectrum of the plasticized starch presented in Figure 11a indicates both starch-specific bands such as: bands at  $2885\text{--}2930\text{ cm}^{-1}$  (C-H stretching vibrations of aliphatic groups),  $1150\text{ cm}^{-1}$  (C-O, C-C and C-O-H stretching),  $1100\text{--}900\text{ cm}^{-1}$  (C-O-H bending, C-O-C stretching), and  $926\text{ cm}^{-1}$  ( $\alpha$ -(1-4) glycosidic-bonding associated with starch), as well as the plasticizer-glycerin specific bands, such as the absorption bands from  $3299\text{ cm}^{-1}$  specific for hydrogen bonds, the absorption bands from the region  $1200\text{--}1000\text{ cm}^{-1}$ ,  $570\text{--}720\text{ cm}^{-1}$  due to C-O, C-C, C-OH stretching and C-OH bending [19-22]. Figure 11b shows the FTIR spectrum of sample A (without resin) and that of sample D, which has the same composition as sample A, but contains phenolic resin and OMMT. Comparing the two FTIR spectra, it is observed that due to the stretching vibration of -OH from the phenolic resin and the hydrogen bonds formed by dynamic crosslinking at  $3300\text{--}3380\text{ cm}^{-1}$ , there is a shift of the band from  $3322\text{ cm}^{-1}$  to  $3347\text{ cm}^{-1}$ , as well as an increase in the intensity of this band [23]. At the same time, the bands specific to EPDM and LDPE rubber can be easily distinguished, which is in agreement with the existing data in the literature [23]. Thus, the bands originating from the symmetric and asymmetric stretching vibrations of the methyl and methylene groups ( $\nu_{\text{as}}$ ,  $\nu_{\text{s}}$ ,  $(-\text{CH}_3)_2=\text{CH}_2$ ) are, respectively, centered at  $2917\text{--}2970\text{ cm}^{-1}$  and  $2849\text{ cm}^{-1}$ . The symmetric and asymmetric bending vibrations ( $\delta(\text{C-H})$ ) of the methyne, methyl and methylene groups can be observed at  $1300\text{--}700\text{ cm}^{-1}$ ,  $1377\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$ , the specific groups of polyethylene of the  $(-\text{CH}_2)_n$ -rocking type, which appear at  $719\text{ cm}^{-1}$  [20-23].



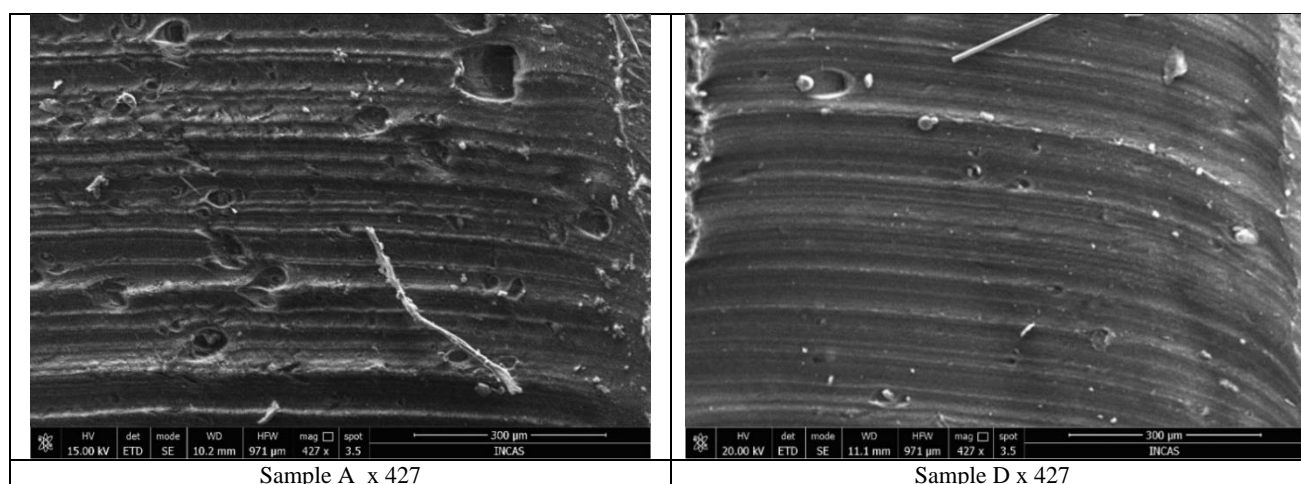


b. FTIR spectra of samples E and F

**Figure 11.** Infrared spectra in a range of 4000-500  $\text{cm}^{-1}$

### 3.3. SEM

The SEM images of samples A and D, Figure 12, show the change in morphology as a result of the dynamic vulcanization techniques, and the melt intercalation method, resulting in a nanocomposite that led to the improvement of the mechanical properties by increasing strength. The analyzed composites have a rough fractured surface with clearly marked lines, indicating an optimal melt intercalation of the component phases. At the same time, a limited area with microvoids is observed in the morphology of the sample, these microvoids having a smaller size in sample D which, compared to sample A, also contains OMMT and phenolic resin. Particles are observed in the melt, but these are small in size and could be due to impurities or ZnO particles. No starch granules are observed, indicating that they have been properly gelatinized and do not affect the properties of the new materials [24-25].



**Figure 12.** SEM images of the fracture surfaces of the A and D composites

## 4. Conclusions

The work presents the obtaining of new types of sustainable elasto-plastic materials based on EPDM, LDPE, OMMT and plasticized starch with improved properties as a result of the use of advanced processing methods such as the dynamic vulcanization or melt intercalation method. It was observed that the samples containing heat-reactive resin vulcanizing agent based on octylphenol-formaldehyde in





the presence of  $\text{SnCl}_2 \cdot x\text{H}_2\text{O}$ , obtained by the dynamic vulcanization technique, show an increase in hardness, elasticity, 100% modulus and a decrease in the melt flow index. In the samples containing OMMT, obtained by the melt intercalation method, an increase in hardness and 100% modulus was observed. In the samples containing plasticized starch it is observed that the starch had a strengthening effect and led to an increase in the 100% modulus and a decrease in the elongation at break and the flow index. The values of abrasion resistance, hardness, 100% modulus, tear resistance, elasticity and melt flow rate for the samples show good, high-performance values, due to the specific characteristics of the LDPE polymer matrix. The FTIR and SEM analyses highlight both the cross-linking reactions and the obtaining of homogeneous mixtures. The materials obtained can be processed by methods specific to plastic materials, the waste obtained in the technological flow (or when the finished products are taken out of use) can be reused without affecting the quality of the finished products. They can be used in fields such as: the footwear industry, the rubber and plastics industry, the automobile industry, agriculture or construction.

**Acknowledgments:** This research was funded by the Romanian Ministry of Education and Research through Contract No. 184CI/2018 and 712PED/2022, Aeroexpert-PN 23 17 04 02 and 4 PFE/2022

## References

1. NIȚUICĂ (VÎLSAN), M., MEGHEA, A., GURĂU, D., STELESCU, M. D., PP/EPDM polymeric compounds dynamically cured compatibilized and reinforced with nanoclay, *Mater. Plast.*, **53**(3), 2018, 335-339.
2. CARVALHO, A.J.F., JOB, A.E., ALVES, N., CURVELO, A.A.S., GANDINI, A., Thermoplastic starch/natural rubber blends, *Carbohydrate Polymers*, 53(1), 2003, 95, [DOI:10.1016/S0144-8617\(03\)00005-5](https://doi.org/10.1016/S0144-8617(03)00005-5).
3. CRACIUN, G., MANAILA, E., IGHIGEANU, D., STELESCU, M.D., A Method to Improve the Characteristics of EPDM Rubber Based Eco-Composites with Electron Beam, *Polymers*, 12(1), 2020, 215; [DOI:10.3390/polym12010215](https://doi.org/10.3390/polym12010215).
4. SATHEES KUMAR S., ARUNA G., SRIDHAR BABU B., ABDUL RAHEEM M., Experimental study and simulation of Natural Fibers Reinforced Polyester, Matrix composit, *Materials Today: Proceedings*, 46(1), 2021, 862-867, [doi.org/10.1016/j.matpr.2020.12.970](https://doi.org/10.1016/j.matpr.2020.12.970).
5. NIȚUICĂ (VÎLSAN), M., TRUSCA, R., GURĂU, D., Polymer structure based on dynamically cured plastomer/elastomer, *Mater. Plast.*, **53**(3), 2016, 424-427.
6. LÜ W., ZHAO G., XUE Z., Preparation and characterization of wood/montmorillonite nanocomposites, *Forestry Studies in China*, 8(1), 2006, 35-40, [DOI 10.1007/s11632-006-0007-6](https://doi.org/10.1007/s11632-006-0007-6).
7. ANANDHAN S., BANDYOPADHYA S., Polymer Nanocomposites: From Synthesis to Applications, from the edited volume: *Nanocomposites and Polymers with Analytical Method*, Edited by Cuppoletti J., 2011, ISBN: 978-953-307-352-1., [DOI: 10.5772/17039](https://doi.org/10.5772/17039).
8. CAICEDO C, PULGARIN HLC. Study of the Physical and Mechanical Properties of Thermoplastic Starch/Poly(Lactic Acid) Blends Modified with Acid Agents. *Processes.*; 9(4), 2021, 578. <https://doi.org/10.3390/pr9040578>.
9. KUCIC GRGIC, D., MILOLOŽA, M., OCELIC BULATOVIĆ, V., UKIC, Š., SLOUF, M., GAJDOSOVA, V. Screening the Efficacy of a Microbial Consortium of Bacteria and Fungi Isolated from Different Environmental Samples for the Degradation of LDPE/TPS Films. *Separations* 10, 2023, 79. <https://doi.org/10.3390/separations10020079>.
10. ULINIUC A., Modificări chimice ale polizaharidelor și ale hidrogelurilor lor prin procedeuul "click chemistry". Other. Université Claude Bernard-LyonI; Universitatea tehnică "Gheorghe Asachi" (Iași, Roumanie), 2011, Romanian, NNT:2011LYO10220, HAL Id:tel-00834679 <https://theses.hal.science/tel-00834679>.
11. LE CORRE D., BRAS J., DUFRESNE A., Starch Nanoparticles: A Review, *Biomacromolecules* 11(5), 2010, 1139–1153, <https://doi.org/10.1021/bm901428y>.



- 12.NASKAR K., “Dynamically vulcanized PP/EPDM thermoplastic elastomers”, ph. D Thesis, University of Twente, 2004, Enschede, Olanda.
- 13.CORAN A.Y., CHUNG O., The Morphology of Rubber/Plastic Blends, *Rubber Chemistry and Technology*, 70(5), 1998, 781.
- 14.UTRACKI L. A., *Comercial Polymer Blends*, ed. Chapman & Hall London, Publisher Springer New York, NY, 1998, DOI:<https://doi.org/10.1007/978-1-4615-5789-0>.
- 15.GHELLER J., JACOBI M. M., Influence of different components in a TPV PP/EPDM based with low hardness, *AIP Conf. Proc.* 1593, (2014) 526–529, <https://doi.org/10.1063/1.4873836>.
- 16.THONGPIN C., KUTTANATE N., KAMPUANG K., SUWANWANIT N., Study of dynamic vulcanized PLA/ENR TPV filled with various organic modified MMT (OMMT), *Journal of Metals, Materials and Minerals*, 22(2), 2012, 105-117.
- 17.NIȚUICĂ VÎLSAN M., MEGHEA A., SONMEZ M., GEORGESCU M., Dynamically cured hybrid polymer nanocomposite based on polypropylene and EPDM rubber, *U.P.B. Sci. Bull., Series B*, 77(30), 2015, 165-174.
- 18.DEWIR., ZULNAZRI N., S., RIZA M., Melt flow Index (MFI) analysis of sago based thermoplastic starch blend with polypropylene and polyethylene, *Materials Today: Proceedings*, 87, 2023, 396–400, <https://doi.org/10.1016/j.matpr.2023.04.173>.
- 19.PALUCH M., OSTROWSKA J., TYŃSKI P., SADURSKI W., KONKOL M., Structural and Thermal Properties of Starch Plasticized with Glycerol/Urea Mixture, *Journal of Polymers and the Environment*, 30, 2022, 728–740, <https://doi.org/10.1007/s10924-021-02235-x>.
- 20.WARREN F., GIDLEY M., FLANAGAN B., Infrared spectroscopy as a tool to characterise starch ordered structure - a joint FTIR–ATR, NMR, XRD and DSC study, *Carbohydrate Polymers*, 139(30), 2016, 35-42, DOI: 10.1016/j.carbpol.2015.11.066.
- 21.NAFCHI A. M., MORADPOUR M., SAEIDI M., ALIAS A. K., Thermoplastic starches: Properties, challenges, and prospects, *Starch/Starke*, 65, 2013, 61–72, DOI: 10.1002/star.201200201
- 22.CARVALHO, A.J.F., JOB, A.E., ALVES, N., CURVELO, A.A.S., GANDINI, A., Thermoplastic starch/natural rubber blends, *Carbohydrate Polymers*, 53(1), 2003, 95-99, DOI:10.1016/S0144-8617(03)00005-5.
- 23.VAN DUIN M., SOUPHANTHONG A., The Chemistry of Phenol-Formaldehyde Resin Vulcanization of EPDM: Part I. Evidence for Methylene Crosslinks, *Rubber Chemistry and Technology*, 68(5), 1995, 717-727, DOI:10.5254/1.3538768.
- 24.NING, W., JIUGAO, Y., XIAOFEI, M., YING, W., The Influence of acid citric on the properties of thermoplastic starch/linear low-density polyethylene blends, *Carbohydrate Polymers*, 67(3), 2007, 446-453, DOI:10.1016/j.carbpol.2006.06.014.
- 25.CARVALHO, A. J. F., ZAMBON, M. D., CURVELO, A. A., GANDINI, A., Thermoplastic starch modification during melt processing: Hydrolysis catalyzed by carboxylic acids, *Carbohydrate Polymers* 62(4), 2005, 387-390, <https://doi.org/10.1016/j.carbpol.2005.08.025>.

Manuscript received: 31.10.2023