COMPOZITE POLIMERICE PE BAZĂ DE POLIOLEFINE, ARMATE CU ARGILĂ STRATIFICATĂ MODIFICATĂ CHIMIC
POLYOLEFIN POLYMER COMPOSITES REINFORCED WITH CHEMICALLY MODIFIED LAYERED CLAY

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The aim of this work was to obtain polyolefin polymer composites reinforced with chemically modified layered clay: polyolefin/rubber/compatibilizer /nanoparticles. The technology of making these polymer composites is extrusion-granulation, in strict compliance with the order of introduction of ingredients. Embedding montmorillonite nanopowders in the polymer composite mixture helps to increase the thermal resistance of the nanocomposite. The obtained polymer composites were tested in terms of physical-mechanical (hardness, elasticity, tensile strength normal state and accelerated aging for 168h at 70°C), resistance to solvents (immersion in iso-octane) and structural properties (FT-IR), according to standards in force.

Scopul acestei lucrări este obținerea de compozite polimerice pe bază de poliolefine armate cu agilă stratificată modificată chimic:
poliolefine/cauciuc/compatibilizatori/nanoparticule.
Tehnologia de realizare a acestor compozite polimerice este de extrudare-ganulare, cu respectarea strictă a ordinii de introducere a ingredientelor. Încorporarea nanopulberilor de montmorilonit în amestecul de compozit polimeric ajută la creşterea rezistenței termice a nanocompozitului. Compozitele polimerice obținute au fost testate din punct de vedere al parametrilor fizico-mecanici (duritate, elasticitate, rezistență la tracțiune stare normală şi îmbătrânire accelerată la 70°C timp de 168h), rezistență la solvenți (imersii în izo-octan) şi structurali (FT-IR) conform standardelor în vigoare.

***Keywords:** composites, EPDM- terpolymer rubber, hardness, reinforcing, montmorillonite*

1. Introduction

In the last years, nanocomposites and polymer nanocomposite have been proved to be of great interest for researchers as they exhibit preformance properties which have many applications in different industries like: footwear and consumer goods, automotive etc.[1] Polymer nanocomposites based on plastomer/elastomer with organically modified layered silicates are an area of substantial scientific interest and of emerging industrial practice.[2] The global trend of developing new advanced hybrid polymeric composites, made up of a mixture of polymers, rubber with thermoplastic polyolefins, reinforced with chemically modified layered clay, opens new possibilities of expanding their area of applications.[3] Due to the progress in science and production, it is necessary to develop new, innovative materials and techniques to eliminate waste, by reintroducing it in production, without adversely influencing quality of products [4], to protect human health, by improving the quality of elasto-plastic materials due to using new reinforcing agents with nano structure and, last but not least, to reduce the cost of products in the footwear and consumer goods industries.[5] In this context we set out to develop a dynamically vulcanized nanostructured material [3,6,7,8], based on polyolefins (PP) [3,9,10 - 13], rubber (EPDM) [3,5,14 - 16], compatibilizer (PP-g-MA) [3,5,17 - 19], reinforcing agents of nanometric size (MMT) [18,20,21], crosslinkers (PD) [3 - 5, 21] which provide qualitative performance, a greener processing technology, meeting the current quality and esthetic requirements, intended for the footwear and consumer goods industries, using extrusion-granulation technique and combining specific properties of each elastomer to develop products with pre-set characteristics.[3,4,20, 22] These composites were tested and characterized in terms of physical-mechanical, resistance to solvents and structural properties by adequate techniques.

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2. Materials properties and methods

The following materials was used: **PP**–polypropylene (copolymer Tipplen K 948, by Tiszai Vegyi Kombinat RT (TVK), HUNGARY), **EPDM**-ethylene-propylene-diene-terpolymer rubber (NORDEL IP 4760, specific gravity–0.872, Mooney viscosity–60 MU, ethylene content–67.5 wt%, ethylidene norbornene (EBN) contents–5.0 wt%, molecular weight distribution–medium, propylene content–27.5 wt%; DuPont Dow elastomer, LLC, USA), **PP-g-AM** - polypropylene-graft-maleic anhydride (average Mw~9.100 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt.%, Sigma Aldrich), **MMT**-montmorillonite (surface modified I.31.PS, contains 0.5-5wt% aminopropyltriethoxysilan, 15-35wt% octadecylamine, Sigma Aldrich); di(tert-butylperoxyisopropyl)benzen (powder 40% with calcium carbonate and silica (**PD**) - Perkadox 14-40B (1.65 g/cm^{3}density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%, Bayer).

Polymer nanocomposites based on EPDM rubber and polypropylene, compatibilized with polypropylene grafted with maleic anhydride were developed (Figure 1) using a twin screw extruder granulator, TSE 35 - China, in compliance with the recipe, Table 1. Polypropylene is added at 150°C and 150-200 rotations/min and is mixed until it becomes easy to process, then temperature is increased at 175°C, EPDM and PP-g-MA are added and mixed at 250-280 rotations/min, keeping parameters constant until the mixture is homogeneous, after that MMT is added and then PD (mixing time 3-5 min). The mixture is granulated through a die, as a string, cooled in a water bath fitted with a pull tape that directs the material entering the drying chamber with hot air and packed to be transported. The products obtained are shaped like granules the size of 3x3mm.

The obtained polymer nanocomposite granules are introduced in molds, according to samples used for physical-mechanical characterization, for finished products, using an Electrically heated press, TP 600 - Netherlands, by compression method, at the temperature of 165^{0}C and pressure of 150KN, pre-heating time 2 minutes, 10 minutes pressing and 10 minutes cooling (with water). The plates are conditioned for 24 h at room temperature and specimens are cut according to the physico-chemical and mechanical tests.

The obtained polymeric nanostructures have been tested in compliance with the physical-mechanical standards in effect: hardness ^{0}Sh D - SR ISO 7619-1:2011; tensile strength, N/mm^2 - SR ISO 37:2012; elasticity, %, ISO 4662:2003.

Table 1

Polymer nanocomposite compositions based on PP/EPDM/PP-g-MA/MMT/PD

Compozitiile nanocompozitelor polimerice pe baza de PP/EPDM/PP-g-MA/MMT/PD

		Sample code								
Material	**UM**	**$M_{115}M_1$**	**$M_{115}M_2$**	**$M_{115}M_3$**	**$M_{215}M_1$**	**$M_{215}M_2$**	**$M_{215}M_3$**	**$M_{315}M_1$**	**$M_{315}M_2$**	**$M_{315}M_3$**
PP	%	90	90	90	70	70	70	50	50	50
EPDM	%	10	10	10	30	30	30	50	50	50
PP-g-MA	%	5	5	5	5	5	5	5	5	5
MMT	%	1	3	7	1	3	7	1	3	7
PD	%	3	3	3	3	3	3	3	3	3

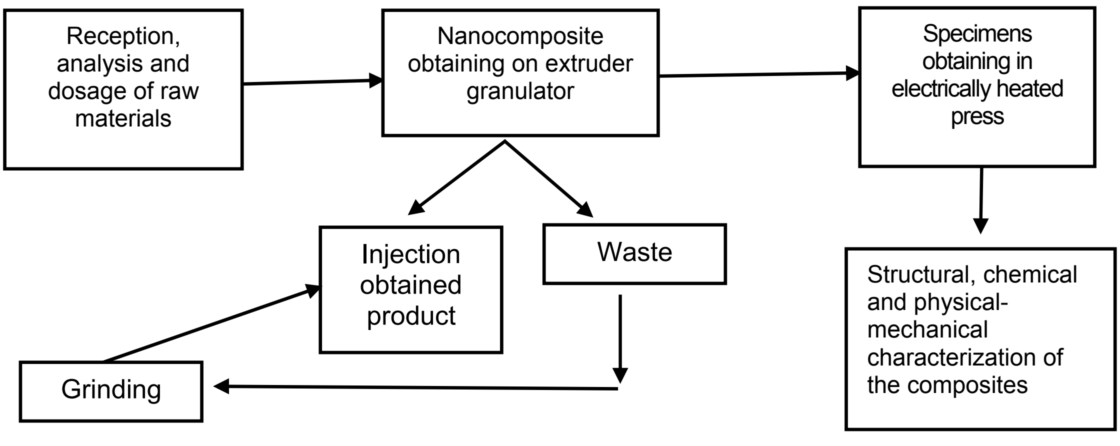

Fig. 1- Technological process for obtaining polymeric composites based on polyolefin reinforced with chemically modified layered clay

Procesul tehnologic de obținere a compozitelor polimerice pe bază de poliolefine armate cu argilă stratificată modificată chimic.

FT-IR determinations were performed on a double beam IR molecular absorption spectrometer, using the FT-IR 4200- Japan device equipped with ATR with diamond crystal and sapphire head for solid samples with high hardness. Solid specimens were placed in the ATR and the device recorded the transmittance spectrum of the sample, reported to the previously measured background spectrum, stored in the instrument's memory. The recorded spectra were compared with the spectra of raw plastomer, compatibilizing agent and elastomer control samples, with spectra found in the literature or with those available in the spectrum library of the device.

3. Results and Discussion

3.1. Physical-mechanical tests

The graphs sown in Figure 2 to Figure 7 present the results of physical-mechanical tests in natural state and after thermal processing (accelerated ageing) at 70^{0}C for 168h of polymeric composites based on EPDM rubber, polyolefins – PP, compatibilizer – PP-g-MA, reinforced with montmorillonite, PD – 40% - on silica and $CaCO_3$ substrate, with varying amounts of EPDM, PP, PP-g-MA, MMT, PD.

- *Tensile strength.* Adding the reinforcement agent in various amounts, of 1%, 3%, 7%, and dicumyl peroxide in a amount of 3%, yields a tensile strength of 5.6 N/mm^2 to 10.6 N/mm^2, and after accelerated ageing at 70^{0}C for 168 hours, a significant decrease in tensile strength is noticed in comparison with the control sample, due to the varying proportions of rubber –EPDM, reinforcement agent and dicumyl peroxide.
- *Elasticity*. By adding percadox, due to the process of EPDM rubber vulcanization, elasticity remains constant or slightly decreases. After accelerated ageing at 70^{0}C, for 168 h, it is noticed that by adding MMT in various amounts, elasticity decreases slightly by 2-4 percents, compared to polypropylene.

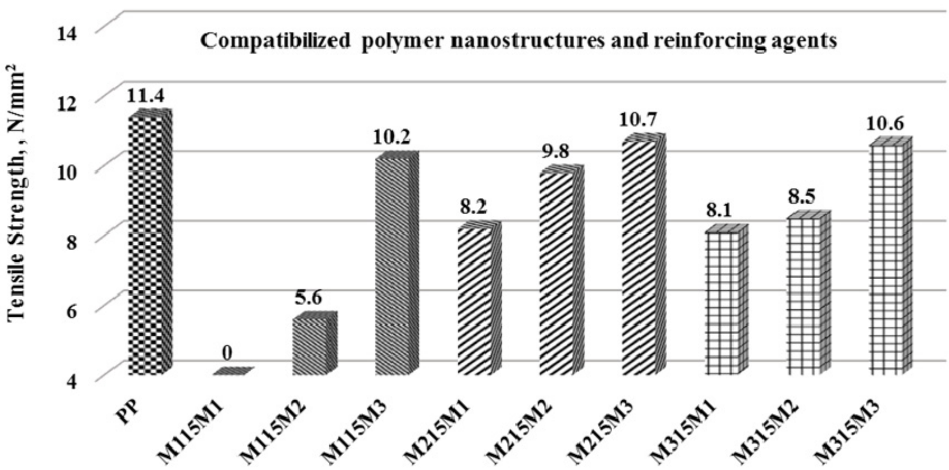

Fig. 2- Tensile strength depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, natural state
Rezistența la rupere în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea de cauciuc, stare normală.

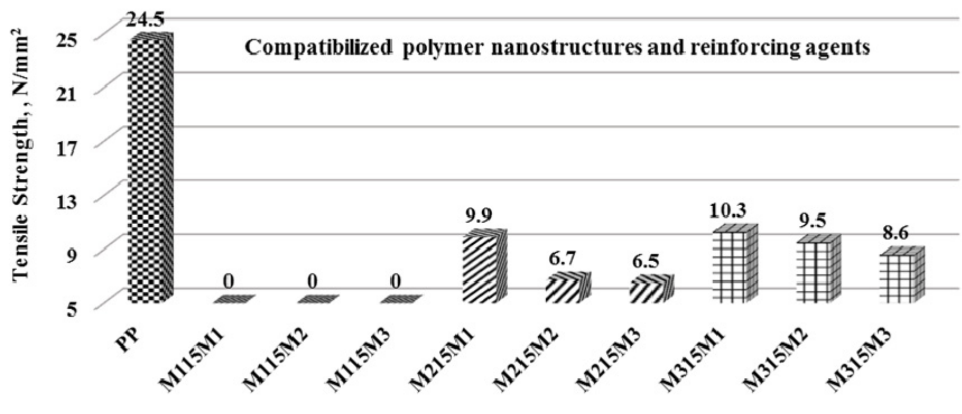

Fig. 3- Tensile strength depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, accelerated ageing 70° C x 168h / *Rezistența la rupere în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea de cauciuc, la îmbătrânire accelerată 70°C x 168h*

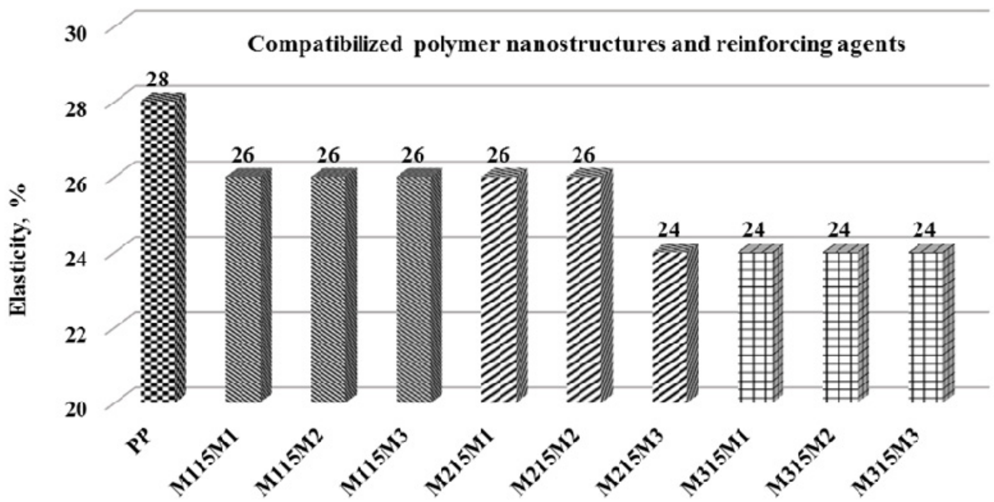

Fig. 4- Elasticity depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, natural state / *Elasticitate în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea cauciuc, stare normală.*

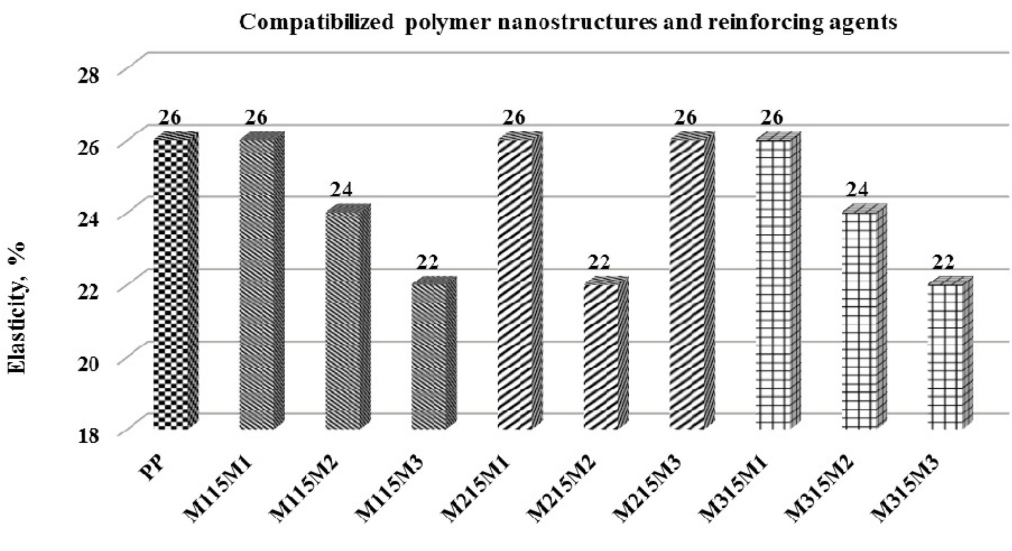

Fig. 5- Elasticity depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, accelerated ageing 70 ° C x 168h / *Elasticitate în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea de cauciuc, la îmbătrânire accelerată 70°C x 168h.*

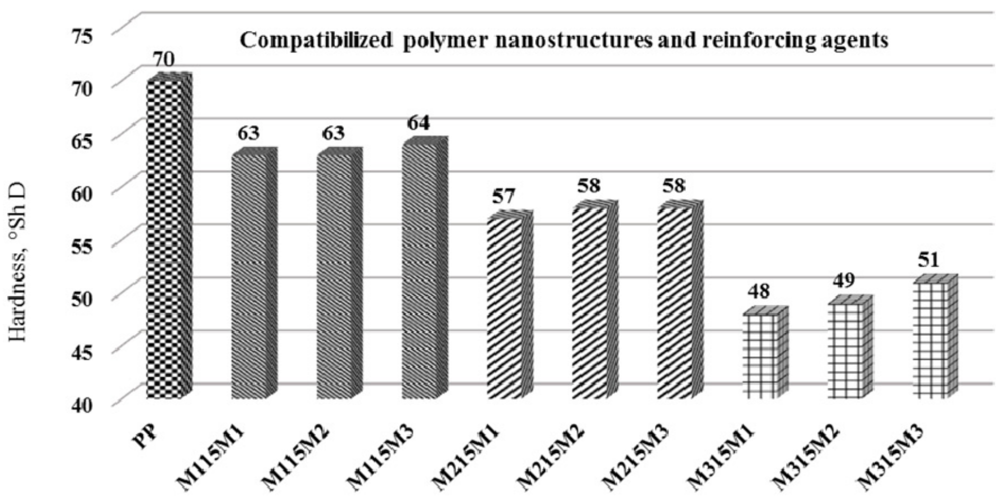

Fig. 6- Hardness depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, natural state / *Duritate în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea de cauciuc, stare normală.*

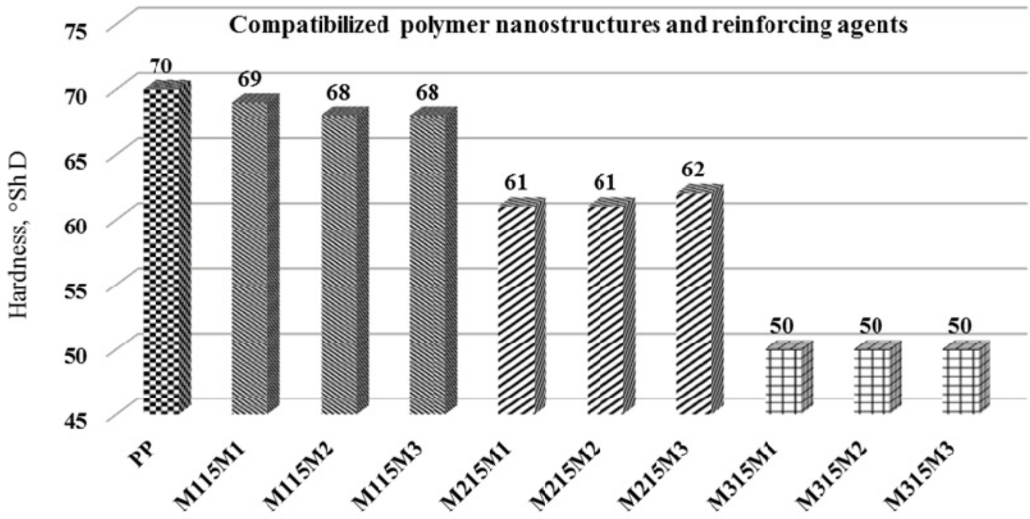

Fig. 7- Hardness depending on the content of montmorillonite and dicumyl peroxide, relative to the amount of rubber, accelerated ageing 70° C x 168h / *Duritate în funcție de conținutul de montmorilonit şi peroxid de dicumil, raportată la cantitatea de cauciuc, la îmbătrânire accelerată 70°C x 168h.*

Table 2

Immersions of mixtures based on PP/EPDM/PP-g-MA/MMT/PD
Imersii ale amestecurilor pe bază de PP/EPDM/PP-g-MA/MMT/PD

Mixture	**$M_{115}M_1$**		**$M_{115}M_2$**		**$M_{115}M_3$**	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
Iso-octane ISO 1817:2005	-0.41	63.9	0.3	4.3	4.3	-1.63
	$M_{21A}M_1$		**$M_{21A}M_2$**		**$M_{21A}M_3$**	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
	0.56	16.3	0.34	14.05	0.31	8.95
	$M_{315}M_1$		**$M_{315}M_2$**		**$M_{315}M_3$**	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
	1.71	52.7	1.27	37.85	1.59	35.45

- *Hardness* of test samples decreases compared to the control samples, depending on the montmorillonite and dicumyl peroxide amounts, reported to the rubber amount. After accelerated ageing at 70°C for 168h, a proportional decrease of hardness values is noticed in all tested nanocomposites, compared to the control sample - PP.

For mixing without dynamic vulcanization process EPDM's physical - mechanical values, showed above, fall below 50% compared to the control sample.

3.2. Resistance to solvents

Mixtures were analysed in terms of their behaviour after immersion in iso-octane and results are presented in table 2.

Immersions in iso-octane of compound based on PP/EPDM/PP-g-MA/MMT/PD, lead to the following:

- mass and volumetric variation, upon immersion in iso-octane depend on the concentration of elastomer - EPDM ranging between 0 and 50%;
- the concentration of MMT reinforcing agent influences the mass and volume variations, the latter decreasing proportionally with the amount of MMT added in the polymer structures, the percentage of MMT ranging between 1 and 7%;
- in the case of crosslinking the polymer nanocomposites using crosslinking agent (PD), the mass and volumetric variations are lower, with similar values.

3.3. Infrared spectroscopy

FT-IR spectra for nanocomposites based on polyolefins, reinforced and compatibilized, are presented in Figure 8.

The bands of PP-g-MA are difficult to identify because of its low amount of 5 % in the polymeric nanocomposites. The overlapping spectra show the presence of EPDM in variable percentages 10, 30, 50 % and it is noticed from the intensity of characteristic peaks.

The main of absorption bands of PP and EPDM’s as well as their assignments (Table 3) are: 1375 – (CH_2) (CH)O; 1455 – (CH_2) and (CH_3) and at 1166,83 - presence of isopropyl group. The absorption bands of EPDM are the following: 728 – CH_2 crystallinity, 1375 –symmetric CH_3 deformation, 1464 – CH_2 scissor vibration and CH_3 asymmetric.

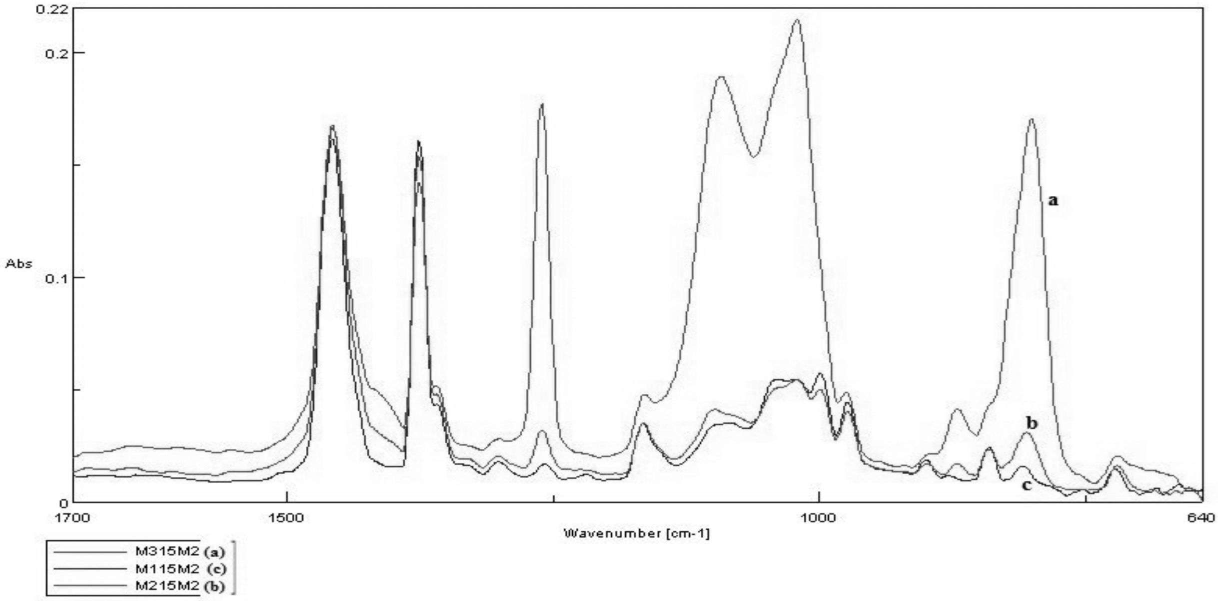

Fig. 8- FT-IR spectra for samples containing 10, 30, 50 % EPDM, 5% PP-g-MA, 3% MMT, 3% PD ($M_{115}M_2$ - **c**, $M_{215}M_2$ - **b**, $M_{315}M_2$ - **a**)
*Spectrul FT-IR pentru probe cu 10, 30, 50% EPDM, 5% PP-g-MA, 3% MMT, 3% PD ($M_{115}M_2$ - **c**, $M_{215}M_2$ - **b**, $M_{315}M_2$ - **a**)*

Table 3

IR frequencies (cm^{-1}) and vibration assignment for sample, PP, EPDM, $M_{115}M_1$, $M_{115}M_2$, $M_{115}M_3$, $M_{215}M_1$, $M_{215}M_2$, $M_{215}M_3$, $M_{315}M_1$, $M_{315}M_2$, $M_{315}M_3$ / *Frecvențele IR şi atribuiri de vibrații ale probelor PP, EPDM, $M_{115}M_1$, $M_{115}M_2$, $M_{115}M_3$, $M_{215}M_1$, $M_{215}M_2$, $M_{215}M_3$, $M_{315}M_1$, $M_{315}M_2$, $M_{315}M_3$*

Sample code	Frequency	Intensity	Vibration assignment
PP	1455.74	0.178386	(CH_2) and (CH_3)
	1375.83	0.248779	(CH_2) (CH)O
	1255.9	0.021153	(CH_2) (CH)
	1166.83	0.0409114	Presence of isopropyl group
EPDM	1463.71	0.1755108	(CH_2) CH_3 asymmetric
	1375. 96	0.0827913	CH_3 symmetric
	721.247	0.0512599	(CH_2) crystallinity
$M_{115}M_1$	1455.03	0.117944	(CH_2) and (CH_3)
	1375	0.117273	CH_3 symmetric
	1260.25	0.0405429	(CH_2) (CH)
	1165.76	0.037455	Presence of isopropyl group
	725.104	0.00961967	(CH_2) crystallinity
$M_{115}M_2$	1455.96	0.130375	(CH_2) and (CH_3)
	1375.96	0.161013	CH_3 symmetric
	1258.32	0.0170149	(CH_2) (CH)
	1165.76	0.035285	Presence of isopropyl group
	722.211	0.0150137	(CH_2) crystallinity
$M_{115}M_3$	1455.03	0.130376	(CH_2) and (CH_3)
	1375	0.122353	CH_3 symmetric
	1260.25	0.0561002	(CH_2) (CH)
	1165.75	0.0355282	Presence of isopropyl group
	723.175	0.0107241	(CH_2) crystallinity
$M_{215}M_1$	1475.92	0.276367	(CH_2) and (CH_3)
	1375.96	0.233558	CH_3 symmetric
	1164.76	0.0538778	Presence of isopropyl group
	721.247	0.0286599	(CH_2) crystallinity
$M_{215}M_2$	1456.92	0.167787	(CH_2) and (CH_3)
	1375.96	0.154169	CH_3 symmetric
	1260.25	0.0321375	(CH_2) (CH)
	1164.79	0.0353648	Presence of isopropyl group
	721	0.0163859	(CH_2) crystallinity
$M_{215}M_3$	1456.96	0.165903	(CH_2) and (CH_3)
	1375.96	0.141678	CH_3 symmetric
	1261.22	0.148603	(CH_2) (CH)
	1165.76	0.0461223	Presence of isopropyl group
	720.282	0.0257668	(CH_2) crystallinity

Table 3 continues on next page

Sample code	Frequency	Intensity	Vibration assignment
$M_{315}M_1$	1455.03 1375 1260.,25 720.282	0.07002199 0.0666941 0.0351063 0.00618272	(CH_2) and (CH_3) CH_3 symmetric (CH_2) (CH) (CH_2) crystallinity
$M_{315}M_2$	1455.99 1375 1163.83 720.282	0.166832 0.142305 0.0481621 0.020836	(CH_2) and (CH_3) CH_3 symmetric Presence of isopropyl group (CH_2) crystallinity
$M_{315}M_3$	1456.96 1375.96 1261.22 721.247	0.174604 0.136418 0.116693 0.0202893	(CH_2) and (CH_3) CH_3 symmetric $(C\text{-}CH_3)$ (CH_3) (CH_2) crystallinity

4. Conclusions

FT-IR spectroscopy confirms the presence of polypropylene and EPDM by the intensity of characteristic peaks and the spectrum show the presence of EPDM in variable percentages 10, 30, 50 %. The immersion in iso-octane (aggressive chemical solvent) of the specimens shows that polymer nanocomposites depend on the concentrations of elastomer, reinforcing agents and crosslinking agents. The values of physico-mechanical properties optimized highlights of polymer composites studied. The paper presented the optimal variants of polymer nanocomposites, a percentage higher than 50% does not improve their physical-mechanical and technological processing properties. Also, a MMT percentage higher than 7% does not lead to good values of physical-mechanical properties of nanocomposites. The obtained polymer nanocomposites PP/EPDM/PP-g-MA/MMT/PD have potential application in footwear industry, consumer goods etc.

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