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DYNAMICALLY CURED HYBRID POLYMER NANOCOMPOSITE BASED ON POLYPROPYLENE AND EPDM RUBBER

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This paper presents the development and characterisation of a dynamically cured hybrid polymer nanocomposite based on polypropylene (PP) and EPDM (ethylene-propylene-diene-terpolymer) rubber, made compatible with polypropylene grafted with maleic anhydride (PP-g-MA) and reinforced with montmorillonite (MMT) nanopowders, in the presence of curing agents. Hybrid nanocomposite materials were developed using the extrusion-granulation technique, tested to determine physico-mechanical properties, resistance to solvents and structural properties by FT-IR spectroscopy.

Keywords: polypropylene, EPDM, nanoparticles, polymer nanocomposite

1. Introduction

Dynamic curing of rubber dispersed in thermoplastic elastomer (TPV) was used for the first time by Fisher [1] and then developed by Coran *et al.* [2] Ismaeil Ghasemi optimized this process and made possible properties such as resistance to high temperatures, resistance to oils, tensile strength etc. [3]

Throughout the years of study, it was found that, by dynamic curing and compatibility, EPDM particles are dispersed more efficiently in the mixture. Due to the advances in science and production, it is necessary to develop new and innovative materials, as well as techniques able to eliminate waste and recycle it in the production process. The waste recycling process is important; it does not adversely influence the quality of products [4], but optimizes them by using new nano-sized reinforcing agents. These lead to a reduction in the price of products in the footwear and consumer goods industries.[5] Polymeric structures based on

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plastomer/elastomer (PP/EPDM) were selected, as a single polymer cannot meet all requirements regarding the set of mechanical, physical and thermal properties necessary in a series of specific applications. By compounding a plastomer with elastomer, the characteristics of the two will combine: chemical resistance, low water permeability, resistance to extreme temperatures, ozone and UV, flexibility at low temperatures, resistance to petroleum oils, alkalis and acids, low vapour permeability, etc. [5]

Developing and testing dynamically cured composites [1,2,6] based on plastomers – PP [7,8,9,10,11], rubber – EPDM [5,11,12,13], compatibilizer – PP-g-MA [14,15,16], reinforcing agent of nanometric sizes – MMT [17,18] and vulcanization agents (S – sulfur, TH – tetramethylthiuram disulfide and D – diphenylguanidine) [19] leads to quality performance, greening of their development technology, and thus meeting current quality and aesthetics requirements for the footwear industry. [20]

This paper aims at developing a novel dynamically cured hybrid polymer nanocomposite based on polypropylene and EPDM rubber using extrusion-granulation technique. This composite was tested and characterized to determine physical - mechanical properties, resistance to solvents and structural properties by adequate techniques.

2. Material properties and Methods

The following materials were used: **polypropylene** – PP, impact copolymer Tipplen K 948; **ethylene-propylene-diene-**terpolymer – *EPDM* 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%); **polypropylene-graft-maleic anhydride** - PP-g-MA (average Mw~9.100 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt%); **montmorillonite** – MMT (Nanoclay, surface modified I.31.PS, contains 0.5-5wt% aminopropyltriethoxysilan, 15-35wt% octadecylamine); **technical grade sulfur** (S), as curing agent, TH - **tetramethylthiuram disulfide** and D – **diphenylguanidine**, the last two substances having the role of curing accelerators.

The steps of the technological process used to develop the hybrid nanocomposite polymer reinforced with nanoparticles based on polypropylene and EPDM, made compatible with polypropylene grafted with maleic anhydride, in the presence of curing agents is shown schematically in Fig. 1.

Polymer nanocomposites based on EPDM rubber and polypropylene, made compatible with polypropylene grafted with maleic anhydride were developed using a twin screw extruder granulator, TSE 35, in strict compliance with the order of introduction of ingredients (PP, EPDM, PP-g-MA, MMT, S, TH, D). The temperature profile in the 9 areas is 155-160-170-175-175-175-160-150-170°C, the rotational speed of the screws varies between 250-280 rpm and the parameters were kept constant.

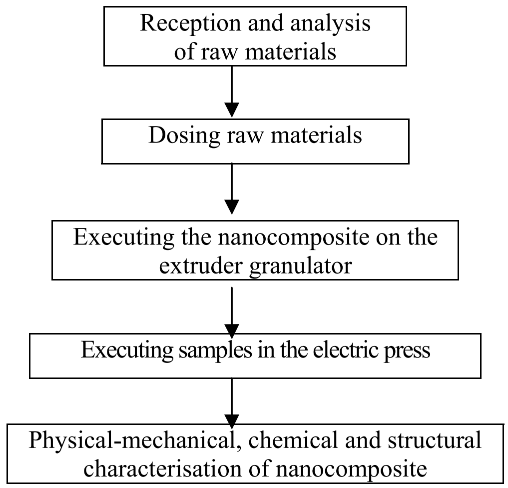

Fig. 1. Steps of the technologic process for developing hybrid polymer nanocomposites based on EPDM rubber and PP

The mixture is extruded through the die in the form of a string, cooled in a water bath, which is provided with a pulling belt with the purpose of directing the introduction of the material in the drying chamber, hot air-dried, granulated and packed for transport. The products are in the form of granules of 3x3 mm size.

From the resulting granules, plates with the size of 150x150x2 mm are developed by pressing in a mold by compression method, in the electrical press, TP 600. Test plates are obtained using the above-mentioned size and method, with the following optimum parameters: disk temperature – 165^0C; pre-heating time – 2 minutes; pressing time – 10 minutes; cooling time – 10 minutes (water cooling); pressure – 150 kN.

Plates are stabilized for 24 h at room temperature, dumbbell-shaped test pieces are punched out, and then physical-mechanical tests, immersions in isooctane and structural measurement (FT-IR spectroscopy) were performed.

FT-IR measurements were carried out on a molecular IR absorption spectrometer with a double beam, using the FT-IR 4200 device equipped with ATR with diamond crystal and sapphire head. Solid test samples were positioned in ATR devise and the transmittance spectrum of the sample related to the background spectrum measured previously, stored in the instrument's memory was recorded. Then the spectra were compared with spectra of standard raw elastomer and plastomer, with the spectra indicated in the literature or with those available in the device's library of spectra.

3. Results and Discussion

3.1. Physical-Mechanical Tests

Table 1 presents formulations of polymer nanocomposites. Polymer nanocomposites were tested in terms of their physical-mechanical parameters according to standards in force, and results are presented in table 2.

Table 1

Formulations for hybrid polymer nanocomposites based on PP/EPDM/PP-g-MA/MMT/curing agent

		Sample code					
Material	UM	$M_{11A}M_1$	$M_{11A}M_2$	$M_{11A}M_3$	$M_{21A}M_1$	$M_{21A}M_2$	$M_{21A}M_3$
PP	%	90	90	90	70	70	70
EPDM	%	10	10	10	30	30	30
PP-g-MA	%	5	5	5	5	5	5
MMT	%	1	3	7	1	3	7
S	%	1.5	1.5	1.5	1.5	1.5	1.5
TH	%	1	1	1	1	1	1
D	%	0.5	0.5	0.5	0.5	0.5	0.5

Table 1 continued

		Sample code		
Material	UM	$M_{31A}M_1$	$M_{31A}M_2$	$M_{31A}M_3$
PP	%	50	50	50
EPDM	%	50	50	50
PP-g-MA	%	5	5	5
MMT	%	1	3	7
S	%	1.5	1.5	1.5
TH	%	1	1	1
D	%	0.5	0.5	0.5

Table 2

Physical-mechanical characteristics of hybrid polymer nanocomposites based on PP/EPDM/PP-g-MA/MMT/curing agent in normal state and after accelerated ageing

Sample code	PP	$M_{11A}M_1$	$M_{11A}M_2$	$M_{11A}M_3$	$M_{21A}M_1$	$M_{21A}M_2$	$M_{21A}M_3$
Physical-mechanical characterisation - normal state							
Hardness ^{0}Sh D SR ISO 7619-1:2011	70	66	66	67	60	60	59
Tensile strength, N/mm^2, SR ISO 37:2012	28	30	28	28	26	26	28
Elasticity, %, ISO 4662:2003	11.4	17.5	160.	13.46	15.4	12.6	11.46

Accelerated ageing 70^0 x 168 h							
Hardness ^{0}Sh D SR ISO 7619-1:2011	70	69	68	67	61	62	62
Tensile strength, N/mm^2, SR ISO 37:2012	26	30	32	30	29	30	28
Elasticity, %, ISO 4662:2003	24.5	13.25	19.1	15.7	12.3	12.1	11.33

Table 2 continued

Sample code	$M_{31A}M_1$	$M_{31A}M_2$	$M_{31A}M_3$
Physical-mechanical characterisation - normal state			
Hardness ^{0}Sh D SR ISO 7619-1:2011	50	48	47
Tensile strength, N /mm^2, SR ISO 37:2012	32	30	30
Elasticity, %, ISO 4662:2003	8.63	7.3	7.23
Accelerated ageing 70^0 x 168 h			
Hardness ^{0}Sh D SR ISO 7619-1:2011	49	50	51
Tensile strength, N /mm^2, SR ISO 37:2012	30	30	30
Elasticity, %, ISO 4662:2003	9.6	8.9	8.2

The obtained results for samples of mixtures based on rubber - EPDM, plastomer – polypropylene, compatibilizer – PP-g-MA, reinforced with montmorillonite, in the presence of curing agents (S – sulfur, TH – tetramethylthiuram disulfide, D – diphenylguanidine) lead to the following conclusions:

(1) Hardness of samples decreases compared to the control sample, depending on the montmorillonite and curing agent content, related to the amount of rubber. After accelerated ageing at 70°C for 168h, a proportional decrease of hardness values is noticed in all tested nanoalloys, values corresponding to the range of standardized values, due to the fact that as a result of ageing, the degree of plasticity is reduced,

(2) Elasticity. By adding montmorillonite and curing agents, elasticity increases or is approximately equal to that of polypropylene. After accelerated ageing at 70°C, for 168 h, it is noticed that, by adding MMT in various percentages, elasticity increases slightly by 2-6 percents compared to polypropylene.

(3) *Tensile strength.* The presence of the reinforcing agent in various proportions (1%, 3% and 7%), as well as curing agents (1.5% technical grade sulfur as curing agent, 1% TH- tetramethylthiuram disulfide and 0.5% D- diphenylguanidine) in the mixtures leads to tensile strength values of 7.23 N/mm^2 to 17.1 N/mm^2. After

accelerated ageing at 70°C for 168 hours, a decrease of approximately 20% of tensile strength is noticed compared to the control sample, due to the different proportions of EPDM rubber, reinforcing agents and curing agents.

3.2. Resistance to solvents

Mixtures were analysed in terms of their behaviour after immersion in iso-octane and results are presented in table 3.

Table 3

Immersions of mixtures based on PP/EPDM/PP-g-MA/MMT/curing agents

Sample code	$M_{11A}M_1$		$M_{11A}M_2$		$M_{11A}M_3$	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
Iso-octane ISO 1817:2005	0.27	14.55	0.29	14.3	0.27	7.6
	$M_{21A}M_1$		$M_{21A}M_2$		$M_{21A}M_3$	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
	1.23	25.5	1.18	28.75	1.14	28.85
	$M_{31A}M_1$		$M_{31A}M_2$		$M_{31A}M_3$	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
	2.35	59.15	2.5	54	2.2	54

Immersions in iso-octane of mixtures based on PP and EPDM rubber (in proportions of 0-50%), reinforced with montmorillonite, compatibilized with PP-g-MA, in the presence of curing agents, 1.5% technical grade sulfur as curing agent, 1% TH- tetramethylthiuram disulfide and 0,5 % D – diphenylguanidine, the last two substances having the role of curing accelerators, lead to the following conclusions:

1. mass and volumetric variation, upon immersion in iso-octane depend on the concentration of elastomer (EPDM ranging between 0 and 50%) in the PP/EPDM/PP-g-MA/MMT/curing agent nanocomposites,
2. 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 based on PP/EPDM/PP-g-MA/MMT/curing agent, the percentage of MMT ranging between 1 and 7%,
3. in the case of crosslinking the polymer nanocomposites using curing agents, the mass and volumetric variations are lower, with similar values, resulting in a homogenous crosslinking with more stable sulfur bridges.

3.3. Infrared Spectroscopy

Infrared spectroscopy is a tool of composite material characterization, because it can give information even for non-crystalline phases of the composite material.

The spectrum recorded for the PP sample shows IR frequencies (cm^{-1}) for isotactic PP presented in the table 4. Table 5 shows IR frequencies (cm^{-1}) obtained for EPDM.

Table 4

IR frequencies (cm^{-1}) for isotactic PP

Frequency		Vibration assignment
Observed	Calculated	
1742	υ_{12}^{E} 1744	(CH_2) (CH)35
1454,99	υ_{12}^{A} 1452	(CH_2) and (CH)
1374	υ_{13}^{A} 1364	(CH_2) (CH)O
1255,33	υ_{13}^{E} 1288	(CH_2) (CH)

Table 5

IR frequencies (cm^{-1}) for EPDM

Frequency	Vibration assignment
1450	(CH_2) CH_3 asymmetric
1379	CH_3 symmetric
1155	$(C\text{-}CH_3)$ (CH_3)
995	(CH_3) $(C\text{-}CH_3)$
729	(CH_2) crystallinity

The overlapping spectra show the presence of PP and EPDM in the compounds. The presence of EPDM in variable percentages is noticed from the intensity of characteristic bands while PP is in excess compared to the other ingredients, due to the fact that it represents the disperse phase and is the main material. PP-g-MA cannot be distinguished due to low amount (PP-g-MA: 5%).

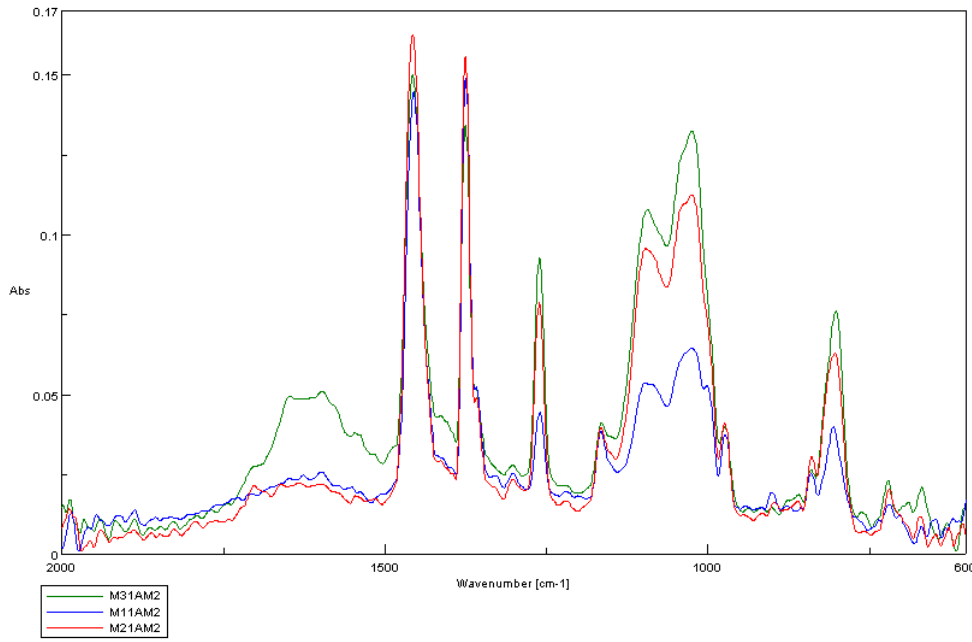

Fig. 2. FT-IR spectrum for samples containing 10; 30; 50 % EPDM, 5% PP-g-MA, 3% MMT ($M_{11A}M_2$, $M_{21A}M_2$, $M_{31A}M_2$)

4. Conclusions

This paper presents the technology for developing dynamically cured hybrid polymer nanocomposites based on EPDM rubber and PP, made compatible and reinforced with montmorillonite in the presence of curing agents using a twin-screw extruder granulator. Physical-mechanical, chemical and FT-IR spectroscopy tests were conducted.

FT-IR spectroscopy confirms the presence of polypropylene and EPDM by the intensity of characteristic bands. Polypropylene is found to be in a higher proportion compared to the other ingredients.

Resistance of nanocomposites to aggressive chemical solvents was tested by immersion in iso-octane and it was found to be influenced by the concentration of EPDM elastomer.

The obtained dynamically vulcanized hybrid polymer nanocomposites PP/EPDM/PP-g-MA/MMT/ curing agent (S, TH, D) have potential application in footwear industry, automotive industry and consumer goods.

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