MORPHOLOGICAL AND STRUCTURAL CHARACTERISATION OF A DYNAMICALLY CURED MMT-REINFORCED ANTIMICROBIAL POLYMER COMPOSITE

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Compounding elastomers and plastics by reactive melt processing in the presence of correct curing systems has led to elastic-plastic alloys with advanced properties. At global scale, however, the new polymeric architectures obtained by dynamic curing, made compatible and reinforced with nanometric particles expand their area of application. Dynamic curing yields elastic-plastic alloys that combine features of both components (elastomer and plastomer) such as chemical resistance, low permeability to water, resistance to extreme temperatures, ozone and UV, low temperature flexibility, resistance to aggressive chemical environments, etc. Through dynamic curing, elastomer particles (EPDM rubber) are more easily dispersed in the polymer matrix (plastomer - PP). This paper aims to morpho-structurally characterize (DSC, SEM, FT-IR) a dynamically cured polymer composite based on polypropylene and ethylene propylene diene terpolymer rubber, made compatible with polypropylene-graft-maleic anhydride reinforced with nanometric particles with antimicrobial properties (MMT), and addition of crosslinking agents. The dynamically cured polymer-based composite based on PP/EPDM/PP-g-MA/MMT/curing agents was obtained using technologies specific to elastomers and plastics and characterized according to current standards.

Keywords: polymeric composite, dynamic vulcanization, morphostructural characterization

INTRODUCTION

In recent years, renowned companies worldwide have changed their production by focusing on special polymers with particular properties. The trend of developing new advanced hybrid polymeric composites, from mixtures of polymers, mixtures of elastomers with olefin plastomers and nanometric reinforcing agents, leads to the development of a new field of application (Stelescu *et al.*, 2011; Vîlsan *et al.*, 2009).

Compounding elastomers and plastics by reactive melt processing in the presence of correct curing systems has led to elastic-plastic alloys with superior properties and special qualities that continue to broaden their area of use in the footwear industry and other branches of economy (Anandhan and Bandyopadhya, 2011; Coran and Patel, 1980; Fisher, 1975; Ionescu *et al.*, 2008). Their vulcanization is a milestone, with a major impact on the properties of the final product (Stelescu *et al.*, 2013; Stelescu *et al.*, 2011). The amount and type of curing agent, time, curing temperature and pressure are important factors that control the degree of crosslinking and the properties of the final product (Volintiru and Ivan, 1974). The resulting advanced materials can be used as thermoplastic elastomers because they have rubber-like properties, but are processed as thermoplastics and do not require vulcanization to manufacture the finished product (Sönmez *et al*., 2014a; Sönmez *et al*., 2014b; Alexandrescu *et al*., 2014).

The new materials and advanced technologies improve the quality of products, environmental protection through recycling, protection of human health by removing pollutants during production, increase turnover of businesses and provide technological competitiveness worldwide. (Vîlsan *et al*., 2009).

The performance of polymer alloys, based on plastomer - PP, elastomer - EPDM, made compatible with PP-g-MA and reinforced with MMT nanoparticles, depends on their concentration and morphology, the processing parameters, the type of auxiliary materials used in compounding, and the equipment used to obtain polymer alloys, etc. (Niţuică *et al*., 2014).

EXPERIMENTAL PROCEDURE

Materials

The following materials were used: (1) polypropylene (PP), impact copolymer Tipplen K 948; (2) ethylene-propylene-diene (EPDM) 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% (3) polypropylene-graft-maleic anhydride (PP-g-AM), average Mw~9.100 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt.%, manufactured; (4) montmorillonite (MMT), Nanoclay, surface modified I.31.PS, contains 0.5-5wt% aminopropyltriethoxysilane, 15-35wt% octadecylamine; (5) di(tert-butylperoxyisopropyl) benzene, 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%).

Procedure

Polymer composites based on PP/EPDM, compatibilized with PP-g-MA, reinforced with MMT and crosslinked with dicumyl peroxide were obtained in a Plasti-Corder Brabender Mixer and then plates were moulded for morpho-structural characterization and other purposes by molding method using an electrically heated press, considering the optimal technological processing parameters. The basic materials were added to the mixture in different proportions, as follows: PP - 90 and 50%, EPDM rubber - 10 and 50% PP-g-MA - 5%, PD - 3%, and the percentage of MMT nanoparticles varied from 1 to 3 and 7%. Formulas for $M_{115}M_1$, $M_{115}M_2$, $M_{115}M_3$ samples contained: PP - 90%; EPDM - 10%; PP-g-MA - 5%; PD - 3% and MMT - 1/3/7% and for $M_{315}M_1$, $M_{315}M_2$, $M_{315}M_3$ samples: PP - 50%; EPDM - 50%; PP-g-MA - 5%; PD - 3%; MMT - 1/3/7%.

Polymer composites based on plastomer - PP, elastomer - EPDM, compatibilized with PP-g-MA, reinforced with nanometric particles (MMT) and crosslinked with dicumyl peroxide (Perkadox, PD) were obtained by mixing at the speed of 280 rpm, the temperatures in the three zones are 165/175/175°C, air cooled, stirring for 3-5 minutes after adding the crosslinking and reinforcing agent.

For the characterization, the obtained polymer composite is added in the molds, using the electrically heated press, TP 600, by means of compression method, between its platters at temperature of 165°C and 150 KN pressure for 2 minutes preheating, 10 minutes actual forming in the press and 10 minutes cooling with water.

Characterization of Composites

Composites were characterized in terms of morphological and structural properties using adequate techniques. The specific methods for morphological and structural characterization of dynamically cured polymer nanocomposites are as follows: in terms of morphology, measurements were made using scanning electron microscopy - SEM

and thermal behaviour was determined by differential scanning calorimetry - DSC, while FT-IR spectroscopy was carried out to determine the structure.

SEM analysis was performed with scanning electron microscope QUANTA INSPECT F - Netherlands, provided with field emission gun (FEG) with a resolution of 1.2 nm and energy dispersive X-ray spectrometer (EDS) with MnK resolution of 133 eV.

The thermal behavior of the sample was monitored by TG-DSC using a Netzsch 449C STA Jupiter device, in a closed aluminum crucible and heated with 10 K min^{-1} from room temperature to 200°C at the rate of 20 mL min^{-1} dry air. Spectral FT-IR measurements were carried out using a molecular absorption FT-IR ATR spectrometer, Able Jasco 4200, with a double beam in the 4000-600 cm^{-1} range, equipped with ATR diamond crystal and sapphire head.

RESULTS AND DISCUSSIONS

FT-IR Spectrometry

For polymer composites based on PP/EPDM, reinforced compatibilized and cured with PD, IR sequences and vibration assignments of samples $M_{115}M_1$, $M_{115}M_2$, $M_{115}M_3$, $M_{315}M_1$, $M_{315}M_2$, $M_{315}M_3$, are shown in Figures 2 and 3. Vibration assignments are similar to those obtained for polypropylene and EPDM elastomer, Table 1.

Table 1. Vibration assignments and IR frequencies of samples based on PP/EPDM/PPg-MA/MMT/PD

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

It is noticed that the amount of PP is higher than that of the other ingredients, due to the fact that it represents the disperse phase and is the main material. The main absorption bands of PP and EPDM as well as their assignments are: 1375 – (CH_2) (CH)O, 1455 – (CH_2) and (CH_3) and at 1166,83 - presence of isopropyl group. The overlapping spectra show the presence of EPDM in variable percentages, and 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.

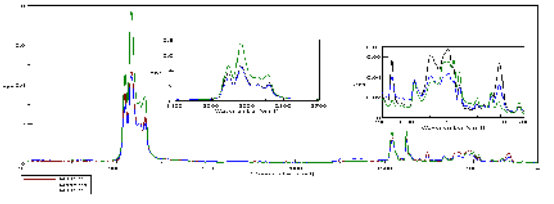


Figure 2. FT-IR spectrum for samples with 90% PP, 10% EPDM, 5% PP-g-MA, 1/3/7% MMT, 3% PD ($M_{115}M_1$ – 1%MMT, $M_{115}M_2$ – 3%MMT, $M_{115}M_3$ – 7%MMT)

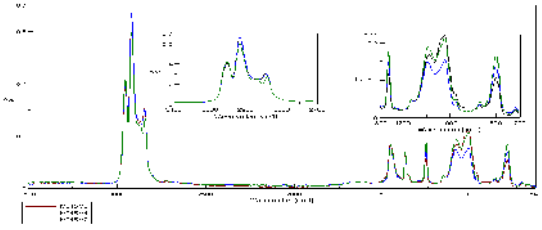
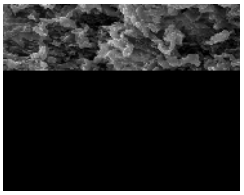


Figure 3. FT-IR spectrum for samples with 50% PP, 50% EPDM, 5% PP-g-MA, 1/3/7% MMT, 3% PD ($M_{315}M_1$ – 1%MMT, $M_{315}M_2$ – 3%MMT, $M_{315}M_3$ – 7%MMT)

Scanning Electron Microscopy (SEM)

SEM micrographs (Figures 4 and 5) of samples based on PP/EPDM/PP-g-MA/MMT/crosslinkers - PD show a homogeneous dispersion of the elastomer (EPDM) and MMT nanoparticles, as well as crosslinking agents (PD) in the mass of dynamically cured polymer composites, which proves that dynamically vulcanized polymeric nanoalloys are properly obtained at effective temperatures and mixing times depending on the characteristics of plastomers, elastomers, nanopowders and crosslinking agents used in the compounds.



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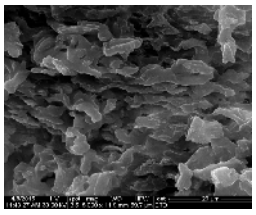

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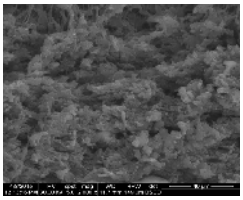
Figure 4. SEM images, sample $M_{315}M_1$



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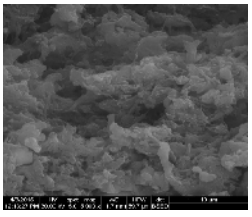

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Figure 5. SEM images, sample $M_{315}M_3$

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was carried out in a temperature range from 120°C-190°C, and the area was measured between 130°C-180°C, Figures 6-8.

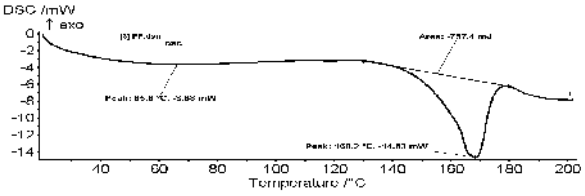

Figure 6. DSC analysis of PP sample (as such)

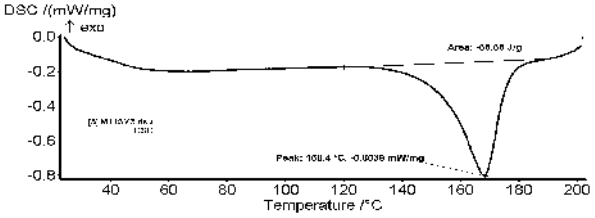

Figure 7. DSC analysis of $M_{115}M_3$ sample (90% PP; 10% EPDM; 5% PP-g-MA; 3% D; 7% MMT

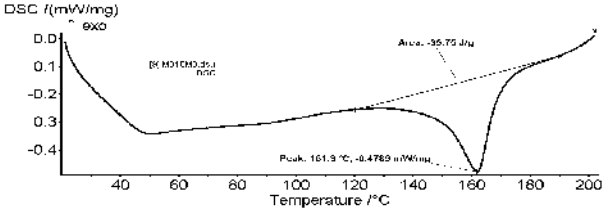

Figure 8. DSC analysis of $M_{315}M_3$ sample (50% PP; 50% EPDM; 5% PP-g-MA; 3% PD; 7% MMT)

The thermograms recorded for the samples M115M3 (90% PP, 10% EPDM, 7% MMT) and M315M3 (50% PP, 50% EPDM, 7% MMT), with PP as the basic material in which the other components disperse, show that the amount of EPDM is in greater proportion in the M315M3 sample. A decrease in temperature, is also noticed, due to changes in viscosity of samples by adding different proportions of EPDM and MMT.

CONCLUSIONS

Scanning electron microscopy was performed in the region of the fracture on the gold film coated samples. SEM analysis of the fracture was conducted in order to highlight the dispersion of the EPDM elastomer in the plastomer matrix, of montmorillonite nanoparticles, and also the homogeneity of the compounded after the dynamic vulcanization and pressing. SEM micrographs of dynamically vulcanized polymer composite and nanocomposite samples indicate a homogenous dispersion of EPDM rubber in the plastomeric matrix, MMT nanoparticles and curing agents used in compounding vulcanized polymer nanoalloys. DSC measurements in a temperature

range from 120°C to 190°C and area measurement of samples subjected to the determination were carried out in a temperature range of 130°C-180°C. The values of the melting temperature of the thermograms reflect small changes in the samples, compared to the thermogram recorded for polypropylene, which is the basic material in which the other components are distributed.

The FT-IR spectra show the main absorption bands of polypropylene and EPDM, and their vibration assignments: 1375 - (CH_2) (CH)O, 1455 - (CH_2) and (CH_3), at 1167 - the presence of isopropyl group, and for EPDM absorption bands are the same as the dynamically vulcanized polymer composites (728 - CH_2 crystallinity, 1375 - CH_3 symmetric deformation, 1465 - CH_2 and CH_3 asymmetric shear vibration).

The experimental data of dynamically vulcanized polymer nanocomposites based on PP/EPDM/PP-g-MA/MMT/PD demonstrate the possibility of their application in the footwear industry and for consumer goods.

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