POLYAMIDE/POLYETHYLENE/GRAPHITE NANOCOMPOSITES: DEVELOPMENT AND MORPHO-STRUCTURAL AND PHYSICAL-MECHANICAL CHARACTERISATION

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ABSTRACT. This paper presents the development of bipolymer nanopolymers - polyamide and polyethylene - compatibilised with polyethylene-graft-maleic anhydride and graphite nanoparticles. Polyamide/polyethylene (PA/PE) composites are studied because both components are relatively inexpensive, advantageous and are processed by injection. Compatibilisation of binary polymer compounds can be accomplished by adding a grafted copolymer, the segments of which have physical or chemical affinity with the two immiscible homopolymers. In this case, polyethylene-graft-maleic anhydride (PE-g-MA) was used. Graphite-containing polymer composites are considered a new generation of materials with predefined properties, in this case, resistance to impact. The combined effects of graphite and compatibilizing polymer (PE-g-MA) were studied on the structure and properties of the new materials. The tested nanocomposites were characterized morpho-structurally (SEM, FT-IR spectrometry) and physico-mechanically.

KEY WORDS: nanocomposites, compatibiliser, graphite, morpho-strucutral characterisation, bipolymer

NANOCOMPOZITE POLIAMIDĂ/POLIETILENĂ/GRAFIT: REALIZARE ȘI CARACTERIZARE MORFO-STRUCTURALĂ ȘI FIZICO-MECANICĂ

REZUMAT. În această lucrare se prezintă realizarea unor nanocompozite bipolimerice – poliamidă și polietilenă – compatibilizate cu polietilenă grefată cu anhidridă maleică și nanoparticule de grafit. Compozitele din poliamidă/polietilenă (PA/PE) sunt studiate deoarece ambele componente sunt relativ ieftine, cu proprietăți avantajoase și sunt prelucrate prin injecție. Compatibilizarea compușilor polimeri binari poate fi realizată prin adăugarea unui copolimer grefat, ale cărui segmente au afinitate fizică sau chimică cu cei doi homopolimeri imiscibili. În acest caz, s-a utilizat polietilenă grefată cu anhidridă maleică (PE-g-MA). Compozitele polimere conținând grafit sunt considerate o nouă generație de materiale cu proprietăți prestabilite, în acest caz de rezistență la impact. Au fost studiate efectele combinate ale grafitului și polimerul compatibilizator (PE-g-MA) asupra structurii și proprietăților materialelor noi experimentate. Nanocompozitele experimentate au fost caracterizate morfo-structural (SEM, spectrometrie FT-IR) și fizico-mecanic.

CUVINTE CHEIE: nanocompozite, compatibilizator, grafit, caracterizare morfo-structurală, bipolimer

NANOCOMPOSITES POLYAMIDE/POLYÉTHYLÈNE/GRAPHITE: RÉALISATION ET CARACTÉRISATION MORPHO-STRUCTURELLE ET PHYSICO-MECANIQUE

RÉSUMÉ. Dans cet article on présente la réalisation des nanopcomposites bipolymères - polyamide et polyéthylène - compatibilisés avec le polyéthylène greffé avec de l'anhydride maléique et des nanoparticules de graphite. Les composites polyamide/polyéthylène (PA/PE) sont étudiés car les deux composants sont relativement peu coûteux, avantageux et sont traités par injection. La compatibilité des composés polymères binaires peut être réalisée en ajoutant un copolymère greffé dont les segments ont une affinité physique ou chimique avec les deux homopolymères non miscibles. Dans ce cas, du polyéthylène greffé de l'anhydride maléique (PE-g-MA) a été utilisé. Les composites contenant des graphites contenant des polymères sont considérés comme une nouvelle génération de matériaux aux propriétés prédéfinies, dans ce cas la résistance aux chocs. Les effets combinés du graphite et du polymère compatibilisant (PE-g-MA) ont été étudiés sur la structure et les propriétés des nouveaux matériaux expérimentaux. Les nanocomposites expérimentaux ont été caractérisés du point de vue morpho-structurel (MEB, spectrométrie FT-IR) et physico-mécanique.

MOTS CLÉS : nanocomposites, compatibilisant, graphite, caractérisation morpho-structurelle, bipolymère

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INTRODUCTION

Compound polymers are widely used to prepare new materials. The disadvantage of this study is that polymers are not usually compatible, and preparation of compounds with suitable properties (mainly processing and physical-mechanical) is not high performance. During the last few decades, polymer-matrix composites have been of interest to industry and academia, especially in the areas of automotive, aerospace, electronic systems, medical products, civil construction, chemical industries and other consumer applications [1]. Polyamide/polyethylene (PA/PE) composites are interesting, because both components are relatively low cost, with advantageous properties and are processed by melt-injection [2]. Some researchers worked on blending PA6/HDPE (polyamide 6/high density polyethylene) with varying compositions. They reported that the composition PA6/HDPE (2%) had increased modulus, hardness and strength [3]. Zhou *et al*. [4] studied the PA6/PPS-CF (carbon fiber) composites and reported that increase in addition of carbon fiber (CF) content in PA6/PPS composite decreases the impact strength. Li *et al*. [5] investigated the mechanical properties of PA6-polyurethane (PU) block copolymer reinforced short glass fibers (SGF) and concluded that impact strength decreased with addition of SGF. Compatibilisation of binary polymer compounds can be accomplished by adding a grafted copolymer, the segments of which have physical or chemical affinity with the two immiscible homopolymers [3]. In this case, polyethylene-graft-maleic anhydride (PE-g-MA) was used. Polymer nanocomposites containing graphite were considered a new generation of composite materials due to their unique properties, attributed to the high aspect ratio of inorganic granules [4, 5]. Graphite nanoparticles are used as reinforcement in fabrication of polymer composites to enhance mechanical, electrical and thermal properties [6-10]. Some researchers tested the mechanical properties of high density polyethylene nanocomposites reinforced with graphite [11-14] or oxidized graphite [15]. The combined effects of graphite and compatibilising polymer (PE-g-MA) treatment on the structure and properties of graphite PA/PE/g-MA composites were studied. The optimal formulation was used to prepare a series of nanocomposites in various technological conditions. The correlation among their physical-mechanical and morpho-structural properties was also studied.

EXPERIMENTAL

Materials and Methods

Materials

Composites contain the same two polymer components in variable proportions: the polyamide (PA) elastomer PA6 (POLIMID B AV NATURALE – Poliblend Engineering Polymers, Italy), with the following characteristics: specific weight, 1.40g/cm^3; impact resistance, 1.4 KJ/m^2; melt flow index (230°C/2.16 kg), 14g/10 min; melt temperature, 215-230°C; and high density polyethylene (HDPE -TIPELIN 1108J - for impact and injection molding - MOL Petrochemicals Group) with the following characteristics: impact resistance, 3 KJ/m^2; flex module, 1.5 Mpa; M.F.I. (190°C/2.16 kg), 8g/10 min; specific weight, 0.96 g/cm^3; and melting point 170-180°C. Other components: compatibilizers - polyethylene grafted with maleic anhydride PE-g-MA from Sigma Aldrich and graphite nanoparticles (G), black pellets with dimensions 3-4 nm and 99,5% concentration from Skyspring Nanomaterials USA. As graphite is a material with high chemical inertia, to increase its reactivity, it was compounded with molybdenum bisulfite, in proportion of 0.2% compared to the polymer, purchased from Sigma Aldrich.

Preparation of Polymer Nanocomposites Polyamide/Polyethylene/Carbon Fibres

Polyamide (PA), polyethylene (HDPE), PE-g-MA, graphite nanoparticles (G) and molybdenum bisulfite were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 2 min. at 230°C to melt the plastomer, mixed for 3 min. at 240°C, and 2 min. at 200°C for homogenisation. The total time was 7 minutes. Table 1 shows tested formulations.

Table 1: Control and PA/PE-gMA/HDPE/G polymer nanocomposite formulations with varying G amounts (GPE1-0,1%; GPE2-0,5%; GPE3-1%; GPE4-2%; GPE5-3%)

Compound	GPE1	GPE2	GPE3	GPE4	GPE5
Polyamide - sebamid	270	270	270	270	270
Polyethylene	30	30	30	30	30
Graphite	0.3	1.5	3	6	9
PE-g-MA	9	9	9	9	9
Molybdenum bisulphite	0.6	0.6	0.6	0.6	0.6
Total	309.9	311.1	312.6	315.6	318.6

The Brabender mixing diagrams, figures 1 and 2, show that the temperature in the chamber drops from 220 to 213°C for higher percentages of graphite (starts at 213°C, decreases to about 140°C with a peak of 150°C at the end, in the case of the 0.1 g percentage, and a lower peak at 175°C in the case of 3% G percentage), and there are minor time variations in achieving maximum mixing forces. The maximum force is achieved at 90 s in the case of 0.1% G percentage and 80 s. in the case of maximum percentage of 3% and its value exceeds 400 Nm.

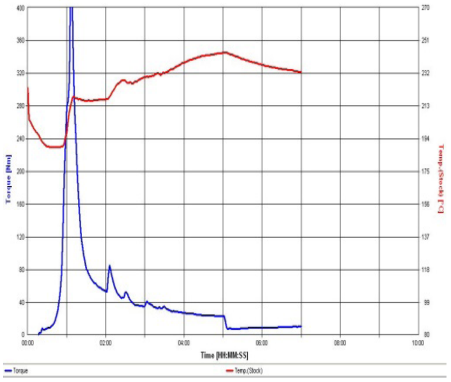

Figure 1. Brabender mixing diagram for PA

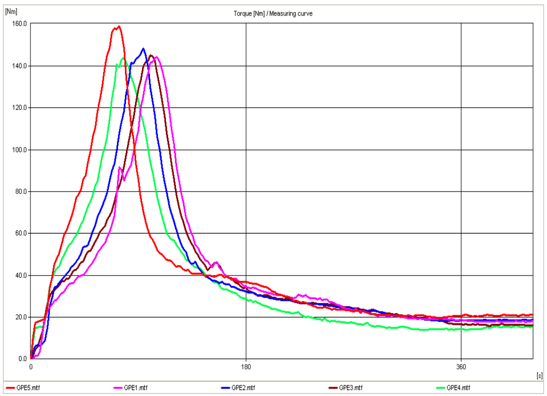

Figure 2. Brabender mixing diagram for composite GPE 1-5

The compounds were then compression-molded (using an electrically heated laboratory press) to achieve a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN.; temperature 230°C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore "D" Durometer according to SR ISO 7619-1:2011.

Melt flow index. Samples were tested using a Haake Melt Flow Index device that displays values for the melt volume rate (MVR – cm^3/10min) as well as melt flow rate (MFR – g/10min). Working temperature (chamber temperature up to 350°C), 2 heating areas, operating according to ISO 1133 standard.

Shock resistance tests were conducted using an INSTRON equipment with pendulum hammer, which can carry out Izod or Charpy tests with a wide range of testing capacity (0.7-27.847 J), according to STAS 7310-87.

SEM. Films obtained by evaporating the disperse medium at 105°C from the dispersions GPE1-GPE5 were cryogenically fractured and their cross sections were analyzed by SEM, using an ESEM QUANTA 200 instrument operating in low vacuum, equipped with LFD detector.

FT-IT spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm^{-1}.

RESULTS AND DISCUSSIONS

The polymer structures obtained, in initial state and after accelerated ageing were characterized in terms of their physical-mechanical properties, and results are presented in table 2. Analyzing the values of physical-mechanical tests reveals the following:

- Hardness of PA/PE-g-MA/G polymer nanocomposites increases by two percents, proportionally with the amount of oxidized graphite compared to that of polyamide (sample PA - 78°Sh). The higher value is given by the composite with 5% oxidized graphite – GPE5-80°Sh.

Table 2: Physical-mechanical characteristics of studied PA/GO polymer composites

Mixtures	PA	GPE1	GPE2	GPE3	GPE4	GPE5
NORMAL STATE						
Hardness °Sh D SR ISO 7619-1:2011	78	78	79	79	79	80
Tensile strength, N/mm^2 SR ISO 37:2012	30.5	21.0	24.4	25.5	26.5	36.4
Density, g/cmm^3 SR ISO 2781:2010	1.14	1.14	1.14	1.14	1.14	1.15
Izod shock resistance, [KJ/m^2] STAS 7310-87	2.5	6.12	7.23	7.81	7.26	6.84
Melt flow index - 230°C pressure of 5 Kg, g/10min	160	169	180	199	174	139
ACCELERATED AGEING 2000 X 168 h SR ISO 188 : 2007						
Hardness °Sh D SR ISO 7619-1:2011	77	77	77	77	78	79
Tensile strength, N/mm^2 SR ISO 37:2012	26.8	28.5	30	37.7	49.2	51.6

- Similar to hardness, the value of tensile strength of nanocomposites increases compared to the value specific to polyamide (sample PA – 30.5 N/mm^2), the higher value is that of sample GPE5-36.4 N/mm^2 (3% G).
- Density increases proportionally with the amount of graphite added to the mixture.
- In order to test resistance to high temperature, accelerated ageing tests were conducted on the samples conditioned at 200°C for 168h. The analysis of obtained values shows they have changed very little, the samples were not damaged and did not change their shape.
- In order to estimate the resistance of brittleness of polymer nanocomposites, they were tested by Izod shock resistance method (STAS 7310-87). This determination is the most important one due to the fact that one of the requirements of polymer nanocomposites is optimized shock resistance, for use in heavy blow conditions. PA value is 2.5 KJ/m^2. All tested nanocomposites have increased values compared to the control sample (PA), ranging between 6.12 and 7.81 KJ/m^2. Increased values were obtained for samples GPE3 (PA/PE-g-MA/PE/G-1% G) – 7.81 KJ/m^2 and GPE4 (PA/PE-gMA/PE/G-2% G) – 7.26. Graphene concentrations higher than 1% lead to decreases in shock resistance values similarly to tensile strength values. This leads to the conclusion that percentages in the 0.1-1% range lead to maximum values of Izod shock resistance

parameters, higher percentages result in lowering this parameter's values.

- In order to establish the technological parameters for processing GPE1-GPE5 polymeric architectures in finished products, tests were carried out to determine the melt flow index at a temperature of 230°C and a pressure of 5 kg. The analysis of the obtained values (Table 2) shows an increased flow compared to PA (160 g/10 min) for the samples: GPE1 (0.1% G) - 169 g/10 min, GPE2 (0.5% 180 g/10 min, GPE3 (1% G) 199 g/10 min, GPE4 (2% G) 174 g/10 min and GPE5 (3% G) 139 g/10 min. Graphite concentrations higher than 1% lead to lower melt flow index values, but higher than the sample PA.
- SEM image of the cross section of the fracture obtained from polyamide elastomer (PA), presented in Figure 3, emphasizes a lamellar structure. On the other hand, the SEM images of cross sections of the fracture obtained from the other three samples (PA, GPE1, GPE3 and GPE5), shown in the Figures 3-6, in which the nanocomposites with rates differ from G, have completely different aspects: they show a biphasic type morphology consisting in spheroid particles distributed within a matrix with less evident lamellar morphology. The number of particles increases directly with the amount of G of the nanocompound.

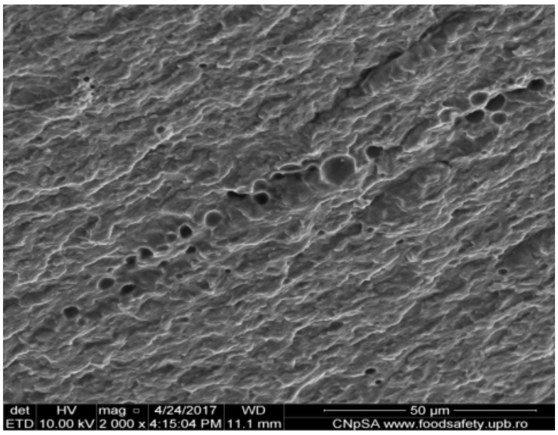

Figure 3. SEM image for PA sample

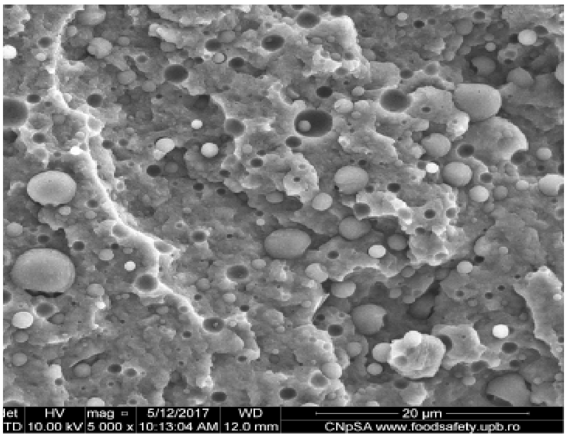

Figure 4. SEM image for GPE1 sample

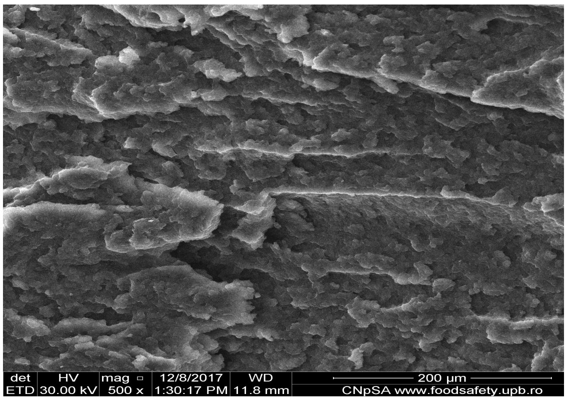

Figure 5. SEM image for GPE3 sample

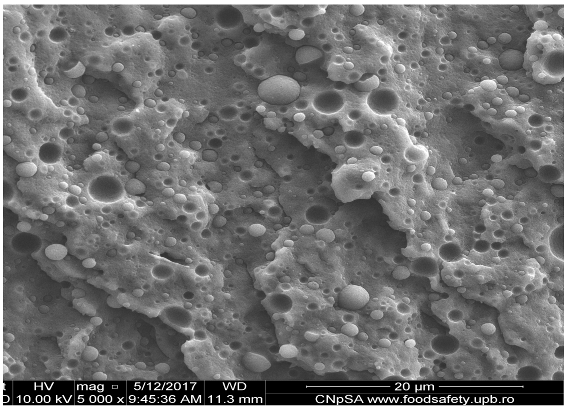

Figure 6. SEM image for GPE5 sample

- FT-IR spectroscopy. IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 µm. IR domain for usual organic chemistry is between 2.5 and 25 µm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm^{-1}, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the pure elastomer spectrum.

After the tests were carried out, the following were found:

1. The IR spectrum recorded for polyamide (figure 7) shows absorption at the following wavelengths: 1190 cm^{-1} specific to CO-CH$_2$ bonds, 1275 cm^{-1} absorption specific to C-O (carboxy), 1567 cm^{-1} absorption specific to the NH group, 1633 cm^{-1} absorption specific to the C=C bond, and the absorption band at 3300 cm^{-1} is specific to C-N bonds.
2. The overlapping spectra (figures 8, 9) show the presence of PA and very weakly G in compounds. The basic structural element of polyamide is the amide group (-CO-NH-), while graphite, C-O, C=C and C=O, and absorptions for the two materials overlap in the spectra. The major presence of PA is seen from the intensity of characteristic peaks.

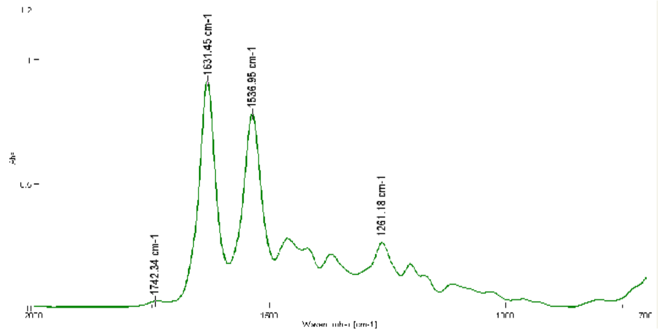

Figure 7. FT-IR spectra from PA

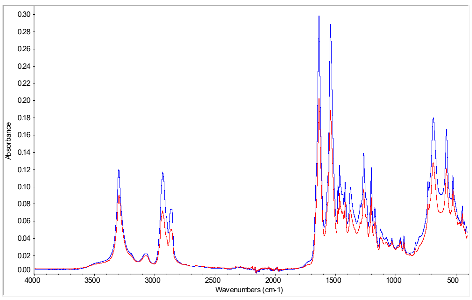

Figure 8. FT-IR spectra from PA/-GPE3

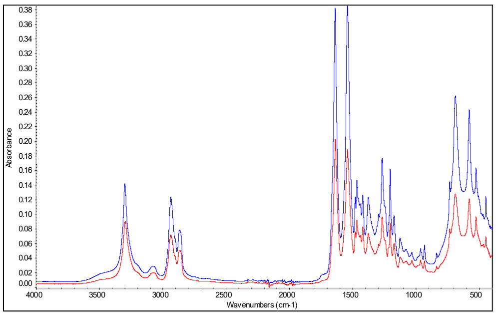

Figure 9. FT-IR spectra from PA/-GPE5

CONCLUSIONS

The paper presents the study of the new nanostructured polymer composites from polyamide/oxidized graphite nanoparticles-PA/G to manufacture, by injection, bearing seals, contact plates, and other components for the railway industry, with shock resistance higher than 5-8 kJ/m², wear resistance below 100 mm^3, resistance to temperatures of -40 - 240°C, resistance to impact and to outdoor applications, with temperatures ranging from -40 to +60°C, in rain, snow or sunshine.

Polyamide and oxidized graphite were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 2 min. at 230°C to melt the plastomer, mixed for 3 min. at 240°C and 2 min. at 200°C for homogenisation.

The polyamide/oxidized graphite nanocomposites were characterized by scanning electron microscopy (SEM) and Fourier transformation infrared spectroscopy (FT-IR) and physico-mechanically.

Graphene oxide concentrations higher than 1% lead to decreases in shock resistance values and tensile strength values. This leads to the conclusion that percentages in the 0.1-1% range lead to maximum values of physical-mechanical parameters.

Acknowledgements

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