POLYAMIDE/POLYPROPYLENE/GRAPHITE NANOCOMPOSITES WITH FUNCTIONAL COMPATIBILIZERS

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Bipolymeric composites are widely used to make new materials with predefined properties. Polyamide / Polypropylene (PA/PP) based compounds are often subjects of research because both components are relatively cheap, have useful and good properties, and can be processed by melt blending and extrusion-injection technologies, which are time-saving and environment-friendly technologies due to the possibility of reusing the material. Compatibility of binary polymeric 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 paper, maleic anhydride grafted polypropylene (PP-g-MA) was used. Composites having nanofiller are considered as a new generation of composite materials due to their unique properties. To increase the impact resistance of polymer composites (PA / PP-g-MA / PP) dispersion of graphite nanoparticles (nanoG) in polymeric mass was achieved. In addition to the PA / PP-g-MA / PP / nanoG bipolymer nanocomposite obtaining methodology, the combined effects of graphite treatment and compatibiliser polymer (PP-g-MA) on the structure and properties of the composites were studied. A number of optimal receptions have been developed in different technological conditions. Experimental composites have been physico-mechanically characterized by standardized methods specific to plastics and microscopic analysis -SEM.

Keywords: nanocomposites; polyamide; graphite.

INTRODUCTION

Bipolymeric composites are widely used to make new materials with predefined properties. Polyamide / Polypropylene (PA/PP) based compounds are often subjects of research because both components are relatively cheap, have useful and good properties, and can be processed by melt blending and extrusion-injection technologies, which are time-saving and environment-friendly technologies due to the possibility of reusing the material. Compatibility of binary polymeric compounds can be accomplished by adding a grafted copolymer, the segments of which have physical or chemical affinity with the two immiscible homopolymers. Various types of PA based nano blend composite have been studied by numerous researchers. PA nanocomposites obtained by thermoplastic-thermoplastic blending (both functionalized and simple): PA6/PP (Chen *et al.*, 2006; Suter *et al.*, 2007; Brune and Bicerano, 2002; Balandin, 2008), PA6/polyimide/organoclay (Ward and Sweeney, 2004); PA6/thermotropic liquid crystalline polymer/organoclay (Das *et al.*, 2013); Nylon 66/Nylon 6/organoclay (Paul and Robertson, 2008); PA6/acrylonitrile- butadiene-styrene (ABS) (Lonjon *et al.*, 2013); PA6/low density polyethylene (LDPE)/nanoclay (Biswas and Ray, 2001); PA6/polymethyl methacrylate (PMMA) (Lonjon *et al.*, 2013); PA6/polystyrene (PS) (Hyunwoo *et al.*, 2010) PA6/PS/nanosilica (Biswas and Ray, 2001). Nanocomposites have been considered a stimulating way for creating a new type of high performance material that combines the advantages of polymers and nanoparticles. Polymer nanocomposites are multiphase

materials, which consist of a polymer or copolymer having nanoparticles or nanofillers (with dimension of 1–50 nm) dispersed in the polymer matrix, significantly affecting different physical properties. Recently, graphite has emerged as the most promising nanofiller, due to its extraordinary physical properties, which has opened a new class of polymeric nanomaterials (Sandeep *et al.*, 2017).

In this paper graphite nanoparticles were selected for PA/PP composites reinforcement. A big challenge in developing polymer/graphite composites with high efficiency is achieving the individual graphene sheets within a polymer matrix in order to have a better dispersion and strong interfacial interactions, in order to decrease percolation threshold in graphite sheets loading and enhancing the graphite-polymer matrix interface (Bhattacharya, 2016) Graphite is a material with high chemical inertia, which leads to low compatibility with many organic or inorganic matrices. To eliminate this disadvantage, graphite nanoparticles are subjected to superficial oxidation, in which case adhesion improves by increasing surface polarity, or treated with an acid, thus improving the mechanical anchoring effect due to increased surface roughness (Alexandrescu *et al.*, 2017).

EXPERIMENTAL

Materials

All composites contain the same two polymer components: the polyamide elastomer PA6 (POLIMID B AV NATURALE – Poliblend Engineering Polymers Italy), with the following characteristics: specific weight, 1.40g/cm³; impact resistance, 1.4 KJ/m²; Mt = 215-230°C, and polypropylene PP (Triplen 949- MOL Petrochemicals Group), with the following characteristics: impact resistance 4 KJ/m², flex module-1.2 Mpa, specific weight 0.89-0.91 g/cm³, Mp 160-1850°C. Other components: compatibilizer: maleic anhydride grafted polypropylene PP-g-MA, viscosity of 330000 cps and an acidity index of 43.1 mg KOH/g, manufactured by Sigma Aldrich, and the graphite powders (C) 0520BX- Skyspring Nanomaterials USA with average particle size 3-4 nm.

Method

Polyamide, polypropylene, PP-g-MA, and graphite were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 3 min. at 230°C to melt the plastomer, mixed for 5 min. at 240°C, and 2 min. at 210°C for homogenisation. The total processing time was 10 minutes. Table 1 shows tested formulations.

Table 1. Control – PA, and PA/PP-gMA/PP/G polymer nanocomposite formulations with varying G amounts (GPP1-0,1%; GPP2-0,5%; GPP3-1%; GPP4-2%; GPP5-3%)

Compound	GPP0	GPP1	GPP2	GPP3	GPP4	GPP5
Polyamide	270	270	270	270	270	270
Polypropylene	30	30	30	30	30	30
Polypropylene graft methylmetacrylate	9	9	9	9	9	9
Graphite nanoparticles	-	0,3	1,5	3	6	9
Molybdenum bisulphite	0,6	0,6	0,6	0,6	0,6	0,6
Total	309,6	310,1	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 at higher percentages of graphite (starts at 260°C, decreases to about 220°C with a peak of 216°C at the end in the case of the 0.15 G percentage and a lower one at 240°C in the case of 3% G percentage), and there are minor time changes in mixing forces, the maximum force is 0,8 min. in the case of 0.1% G percentage and 1.5 min. in the case of maximum percentage of 5% and its value exceeds 105 Nm for GPP01 and decreases of 85 Nm with a larger mixing area between 70-175s.

Figure 1. Brabender mixing diagram for composite GPP01

Figure 2. Brabender mixing diagram for composites GPP1(-), GPP3(-) and GPP5(-)

Testing Methods

1. **Tensile strength 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.
2. **Hardness** of the samples was measured by Shore “D” Durometer according to SR ISO 7619-1:2011.
3. **Melt flow index.** Samples were tested using a Melt Flow Index device – Haake that displays values for the melt volume rate (MVR – $\text{cm}^3/10\text{min}$) as well as melt flow rate (MFR- $\text{g}/10\text{min}$). Working temperature (chamber temperature up to 350°C), 2 heating areas, operating according to ISO 1133 standard,
4. **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.
5. **SEM.** Films obtained from fracture of specimens used for physico-mechanical testing of nanocomposites GPP01, GPP1-GPP5 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.

RESULTS AND DISCUSSION

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/PP-g-MA/PP/G polymer nanocomposites increases proportionally with the amount of graphite compared to that of polyamide (PA - 80°Sh) and PA/PP-g-

MA/PP composite -blank (GPP01-79°Sh). The higher value is given by the composite with 3% oxidized graphite (GPP5-80°Sh).

Table 2. Physical-mechanical characteristics of polymeric PA/PP-g-MA/PP/G composites

Formulations	GPP01	GPP1	GPP2	GPP3	GPP4	GPP5
<i>NORMAL STATE</i>						
Hardness 0Sh D	79	78	78	78	79	80
SR ISO 7619-1:2011						
Tensile strength, N /mm ²	44,5	28,5	33,9	46,6	37,2	37,5
SR ISO 37:2012						
Density, g /cm ³	1,13	1,14	1,14	1,14	1,15	1,15
SR ISO 2781:2010						
Izod shock resistance, [KJ/m ²]	4,11	4,22	5,19	5,81	6,42	5,93
STAS 7310-87						
Melt flow index - 230°C	41,9	38,6	41,5	42,4	41,8	40,9
pressure of 5 Kg, g/10min						
<i>ACCELERATED AGEING 2000 X 168 h SR ISO 188 : 2007</i>						
Hardness 0Sh D	80	77	77	77	78	79
SR ISO 7619-1:2011						
Tensile strength, N /mm ²	43,8	16,8	20,1	32,6	34,2	35,7
SR ISO 37:2012						

- Similar to hardness, the value of tensile strength of nanocomposites increases compared to the value specific to polyamide (PA – 30.5 N /mm²) and PA/PP-g-MA/PP composite -blank (GPP01-44.5 N /mm²), the higher value is that of sample GPP3-46,6 N /mm² (1% G). The percentages of 2 and 3% graphene oxide added to the composite leads to an increase in tensile strength values, but lower than values obtained for samples with G below 1%.
- Density increases proportionally with 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 very small changes, the samples were not damaged and did not modify 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 shock resistance optimization, for use in heavy impact conditions. PA value is 2.5 KJ/m² and GPP01-4,11 (compound PA/PP-g-MA/PP). All nanocomposites tested have increased values compared to the control sample PA and GPP01, ranging between 4.22 and 6.42 KJ/m². Increased values were obtained for samples GPP3 (PA/PP-g-MA/PP/G-1% G) – 5.19 KJ/m² and GPP5 (PA/PP-g-MA/PP/G-1,5% G) – 6.42 KJ/m². Graphite concentrations higher than 1,5% lead to decreases in shock resistance values. This leads to the conclusion that percentages in the 0.1-1,5% range lead to maximum values of physical-mechanical parameters.
- In order to establish the technological parameters for processing GPP1-GPP5 polymeric architectures in finished products, tests were carried out to determine the melt flow index at temperatures of 230°C and a pressure force of 10 kg. The analysis

of the obtained values (Table 2) show an increased flow compared to GPP01 (41,9 g / 10min) for the samples: GPP1 (0.1% G) -38,6; g/10min, GPP2 (0.5% G) 41,5 g/10 min and GPP3 (1% G) 42,4 g / 10 min. The other samples, with concentrations above 1% G in the composite, GPP4-2% G and G5-3% G have flow values below the control sample value, which demonstrates that higher graphite concentrations in the nanocomposite have a positive influence on the flow of the material in the injection process, the value is GPP4 41,8 g/10 min and GPP5 40,9 g/10 min.

- SEM image of the cross section of the fracture obtained from GPP01 compound, presented in Figure 3, emphasize a lamellar structure. On the other hand, the SEM images of cross sections of the fracture obtained from the other tree samples (GPP1, GPP3 and GPP5), shown in the Figures 4-6, 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 sample GPP01

Figure 4. SEM image for sample GPP1

Figure 5. SEM image for sample GPP3

Figure 6. SEM image for sample GPP5

CONCLUSION

- 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 mm³, resistance to temperatures from -40 to +240°C, resistance to impact and to outdoor applications, with temperatures ranging from -40 to +60°C, in rain, snow or sunshine.

- Polyamide and graphite were mechanically mixed in a Brabender Plasti-Corder

PLE-360 at 10-120 rotations/min for 2 min. at 230°C, melt the plastomer for 3 min. at 240°C, and 2 min. at 200°C for homogenisation.

- The nanocomposites polyamide/oxidized graphite were characterized by scanning electron microscopy (SEM) and physico-mechanical.

- Graphene 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 best values of physical-mechanical parameters.

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