POLYAMIDE/POLYETHYLENE/CARBON FIBRE POLYMER NANOCOMPOSITES

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Polyamide and polyethylene are well known as engineering thermoplastic materials that are widely used in industrial applications for their good mechanical and thermal properties. The paper presents the study of the new nanostructured polymer composites based on polyamide/ compatibilizers/polyethylene/carbon fibres nanoparticles-PA/PE-g-MA/PE/CF in order to obtain, by injection, centre pivot liner, centre plates, and other components for the railway industry, with impact resistance higher than 5-8 kJ/m², abrasion 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. The influence of carbon fibres nanoparticles (CF) on the rheological and physico-mechanical properties of the polyamide was studied. The nanocomposites based on polyamide/ compatibilizers/ polyethylene/carbon fibres nanoparticles were characterized by scanning electron microscopy (SEM) and Fourier transformation infrared spectrum (FT-IR) and in terms of physico-mechanical properties. The studied nanocomposites have higher values compared to the blank samples, and the requirements of the railway of impact strength of 5 KJ/m^2. Carbon fiber concentrations greater than 1.5% result in decreases in impact strength values, similar to traction resistance values, but not lower than standard values. This leads to the conclusion that the percentages of carbon fibers in the range of 0.1-1.5% achieve maximum values of physical-mechanical parameters.

Keywords: nanocomposites, polyamide, carbon fibres, impact resistance

INTRODUCTION

The disadvantage is that the polymers are usually not compatible and the preparation of compounds with suitable (mainly processing and physico-mechanical) properties is not performant. Polyamide (PA) is a thermoplastic material, widely used in the industry, with varied applications (e.g. fibres, films, textiles, and various casting products) due to its mechanical and thermal properties. However, it has some limitations, such as: humidity absorption, sensitivity to shock, relatively low impact resistance and a weak dimensional stability. As a result, it is necessary to modify PA to improve physical-mechanical properties favourable for the industrial environment (Bhattacharya, 2016). Polyamide-based polymer composites are currently used to obtain components in the field of transport equipment. This equipment is used in working environments with varying temperatures (-40–200°C), subject to shocks and are equipped with elastomeric components, which deteriorate due to the environment, are purchased from abroad and are made of expensive materials and through lengthy technical processes (Dintcheva *et al*., 2017). Polyethylene is a thermoplastic polymer obtained by polymerizing ethylene at low, medium or high pressures, with the use of oxygen as initiator. It is presented in translucent solid form (granules or powders) for molding or viscous liquid for lubrication. High-density polyethylene (HDPE) is obtained at low pressure 8-10 at and has the following applications: - various foils and packaging; - rigid packaging such as bottles, cans, crates, barrels and auxiliaries such as caps; - printed foils in the form of

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rolls for processing on packaging machines; - synthetic foam materials in the form of foils used as shock absorbers; - as coating material for other supports (e.g. glass). The compatibilisation of binary polymer compounds can be achieved by the addition of graft copolymer, segments of which have physical or chemical affinity with two immiscible homopolymers. In this case, polyethylene grafted with maleic anhydride (PE-g-MA) was used (Mistretta *et al*., 2015; Périé *et al*, 2012). Nano reinforcement materials are therefore components of composite materials designed to improve their mechanical properties. They are presented in different forms and orientations, according to which, the following aspects are pursued: 1. Increasing mechanical features; 2. Improving thermal resistance; 3. Compatibility with the composite matrix; 4. Good adaptation to processing; 5. lightness; 6. low price (Bose *et al*., 2011). Carbon fibers have remarkable properties, resulting from the preferential orientation of the crystals parallel to the fiber axis, and refer to very high stiffness and strength in the longitudinal direction, associated with a very low coefficient of linear dilatation in the same direction. The electrical and thermal conductivity of the carbon fiber composite depends on the degree of graphitization and the degree of anisotropy. Carbon fibers are obtained by pyrolysis of organic fibers. Two groups of fibers are distinguished: high tenacity fibers (Rm = 2500 ... 3100 MPa, and E = 200000Mpa); high modulus fibers (Rm = 2000 ... 2500 Mpa, and E = 400000Mpa). The thermal decomposition of an organic matter in a non-oxidizing atmosphere produces a carbon residue, which has a structure consisting of hexagonal carbon atoms arranged on parallel planes, offset so that a carbon atom projects into the center of a hexagon from the adjacent plan (Xu *et al*., 2016; Alexandrescu *et al*., 2018).

The paper presents the study of the new nanostructured polymer composites from PA/PE-g-MA/PE/CF nanoparticles to manufacture, by injection, bearing seals, contact plates, and other components for the railway industry, with impact resistance higher than 5-8 kJ/m², resistance to temperatures of -40 - 240°C and to outdoor applications, with temperatures ranging from -40 to +60°C, in rain, snow or sunshine.

EXPERIMENTAL SECTION

Materials

All composites contain the same two 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 and carbon nanofibres (CF), black pellets with dimensions DxL-10x20-50 nm, all two products from Sigma Aldrich.

Preparation of Polyamide/Polyethylene/Carbon Fibre Polymer Nanocomposites

Polyamide (PA), polyethylene (HDPE), PE-g-MA and oxidized carbon fibres were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for

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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. 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 carbon fiber (starts at 213°C, decreases to about 200°C with a peak of 220°C at the end, in the case of the 0.15 CF percentage, and a lower at 213°C in the case of 5% CF percentage), and there are minor time variations in achieving maximum mixing forces. The maximum force is achieved at 30s in the case of 0.1% CFO percentage and 1.5 min. in the case of maximum percentage of 5% and its value exceeds 400Nm.

Table 1. Control and PA/HDPE/CFO polymer nanocomposite formulations with varying CF amounts (CFPE1-0.1%; CFPE2-0.3%; CFPE3-1%; CFPE4-2.5%; CFPE5-5%)

Compound	CFPE1	CFPE2	CFPE3	CFPE4	CFPE5
Polyamide – sebamid	270	270	270	270	270
Polyethylene	30	30	30	30	30
Carbon fibres	0.3	1.5	3	6	9
PE-g-MA	9	9	9	9	9
Total	309.3	310.5	312	315	318

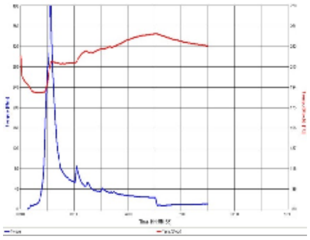

Figure 1. Brabender mixing diagram for PA

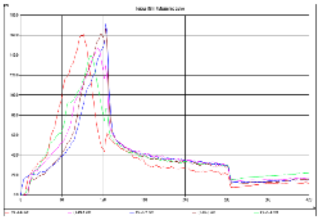

Figure 2. Brabender mixing diagram for composite CFPE 1-5

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.

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/PE-g-MA/HDPE/CF polymer nanocomposites reinforced with carbon fibers varies within the range of 78-83 °Sh D, proportional to the amount of carbon fibers in the composites (0.1-3% mass percentages compared to the mass of polymers).

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Table 2. Physico-mechanical characteristics for PA / HDPE composites - Oxidized carbon fibers

Mixtures	PA	CFPE1	CFPE2	CFPE3	CFPE4	CFPE5
Normal state						
Hardness °Sh D SR ISO 7619-1:2011	78	80	81	81	82	83
Tensile strength, N /mm^2 SR ISO 37:2012	30.5	65.3	68.5	73.8	69.4	55.9
Density, g /cm^3 SR ISO 2781:2010	1.14	1.14	1.14	1.14	1.15	1.16
Izod test, [KJ/m^2] STAS 7310-87	2.5	3.58	5.01	6.40	4.60	3.99
Melt flow index - 230°C force of 5 Kg, g/10min	160	169	180	159	139	126
Accelerated ageing 200°C 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	30.0	37.7	49.2	51.6

The value of the ***tensile strength*** of the nanocomposites increases compared to the concentration of carbon fibers (PA sample – 30.5 N/mm^2), the highest value is that of the CFPE3 sample – 73.8 N/mm^2 (1% CF). The percentage of carbon fibers of 2 and 3% added to the composite leads to an increase in the tensile strength values, compared to the control sample (69.4 and 55.9 N/mm^2, respectively).

The ***density*** values increase by two units, compared to the control sample (1.14 g/cm^3, proportionally with amount of carbon fibers added to the composites.

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 the resulting values shows that they have changed within normal limits; samples are not deteriorated.

In order to estimate the resistance of brittleness of polymer nanocomposites, they were tested by ***Izod test*** method. This determination is the most important one due to the fact that one of the requirements of polymer nanocomposites is optimized impact resistance, for use in heavy impact conditions. PA value is 2.5 KJ/m^2. All nanocomposites tested have increased values compared to the control sample (PA), ranging between 3.58 to 6.40 KJ/m^2. Increased values were obtained for samples CFPE3 (PA/PE/1% CF) – 6.40 KJ/m^2 and CFPE2 (PA/PE/-0.5% CF) – 5.01 KJ/m^2. CF concentrations higher than 1% led to decreases in impact resistance values similarly to tensile strength values, but not lower than the reference value of 2.5 KJ/m^2.

In order to establish the technological parameters for processing CFPE1-CFPE5 polymeric structures in finished products, tests were carried out to determine the ***melt flow index*** at temperatures of 230°C and a pressure of 5 kg. The analysis of the obtained values (Table 2) shows an increased flow compared to PA (160g/10min) for the samples: CFPE1 (0.1% CF) – 169 g/10min, CFPE2 (0.5% CF) 180 g/10 min, CFPE3 (1% CF) 159 g/10 min, CFPE4 (2% CF) 139 g/10 min. and CFPE5 (3% CF) 126 g/10 min. The presented data indicate that carbon fibers decrease flow, which leads to modified technological parameters compared to the reference material, PA. Thus, product processing parameters are the following: temperature of 230-235°C, injection machine equipped with piston screw, pressure of 150-200 atm.

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SEM image of the cross section of the fracture obtained from polyamide elastomer (PA), presented in Figure 3, emphasize a lamellar structure. The SEM images of cross sections of the fracture obtained from the other three samples (CFPE1, CFPE3 and CFPE5), shown in the Figures 4-6, in which the nanocomposites with rates differ from CF, have completely different aspects: they show a biphasic type morphology consisting in spheroid particles of PE distributed within a matrix of PA with evident lamellar morphology. The number of particles increases directly with the amount of CF of the nanocompound.

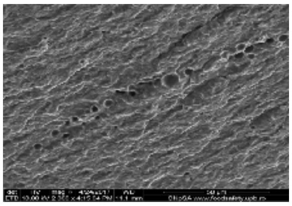

Figure 3. SEM Images from sample PA

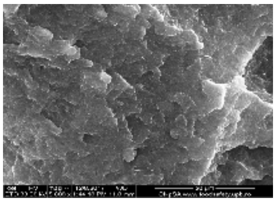

Figure 4. SEM Images from sample CFPE1-10

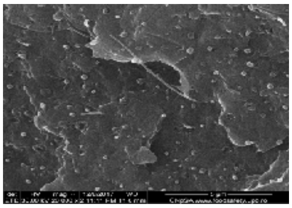

Figure 5. SEM Images from sample CFPE3

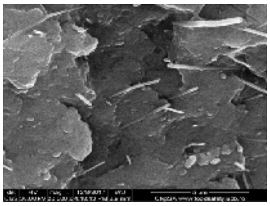

Figure 6. SEM Images from sample CFPE5

TG/DSC – To highlight thermal changes of the studied composites, the samples CFPE0-control sample (polymeric composite based on PA, PE and compatibilizer) and CFPE4 (polymeric composite based on PA, PE, compatibilizer and 1.5% carbon fibers) were compared.

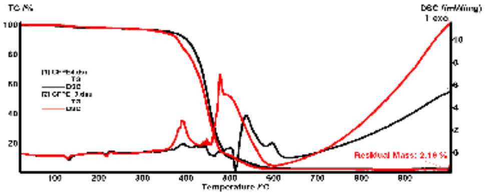

Figure 7. TG/DSG Images from sample CFPE0 and CFPE4

Between 335 and 500°C, the main degradation process of the sample takes place, which is accompanied by a multitude of slightly exothermic effects. The jagged appearance of the DSC curve indicates the multitude of overlapping and chained processes taking place. Between 335 and 480°C, the main stage of degradation takes place, with a mass loss of 81.44%. The process is a complex one, consisting of several overlapping and chained reactions, as can be seen from the shape of the DSC curve.

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Between 480-600°C, the burning of the carbon mass left after the degradation of the polymer takes place, the process being accompanied by a strong exothermic effect, with a maximum at 497°C. The residual mass is 2.19%. Because the residual mass at 1000°C is higher in the case of the CFPE4 sample compared to the control sample CFPE0, it also indicates the fact that the carbon material additionally stabilizes the composite.

CONCLUSIONS

The paper presents the study of the new nanostructured polymer composites based on polyamide/polyethylene/PE-G-MA/carbon fibres in order to obtain, by injection, centre pivot liners, centre plates, and other components for the railway industry, with impact resistance higher than 5-8 kJ/m², abrasion resistance below 100 mm^3, resistance to impact and to outdoor applications, with temperatures ranging from -40 to +60°C, in rain, snow or sunshine. Polyamide, polyethylene, PE-g-MA and carbon fibres 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 nanocomposites polyamide/polyethylene/PE-g-MA/carbon fibres were characterized by scanning electron microscopy (SEM), TG/DSC and physico-mechanical tests. Carbon fibres concentrations higher than 1% lead to decreases in impact 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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