INFLUENCE OF GRAPHENE OXIDE ON THE PROPERTIES OF POLYPROPYLENE NANOCOMPOSITES

Petranka Naydenova-Marinova, Vasil Samichkov

University of Chemical Technology and Metallurgy
8 Kliment Ohridski Blvd.
Sofia 1797, Bulgaria, pnaydenova@utm.edu (P.N-M.); samichkov@uctm.edu (V.S.).

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ABSTRACT

In this work, the influence of small concentrations of graphene oxide on the physicomechanical properties of nanocomposites based on polypropylene and polyester oil was studied. A nano dispersed filler was added to the polypropylene matrix in amounts of 0.01 %, 0.05 % and 0.1 %. A rotary mixer with adjustable speed was used to homogenize the mixtures. To determine the characteristics of the new nanocomposite, test specimens were manufactured in accordance with EN 527 - 2 using the injection molding method. From the studies conducted, it was found that the introduction of graphene oxide nanoparticles into the polyolefin matrix in amounts of 0.01 %, 0.05 % and 0.1 % did not significantly affect the temperature-phase transitions. The addition of 0.1 % filler increased the hydrophobicity of polypropylene by 8 %, the tensile strength at break increased by 14 %. There is a tendency towards an increase in the fluidity of the composite materials, but in general it can be concluded that the filler in these quantities does not significantly change the rheology of the polymer material. The filler has an impact on the thermal conductivity properties of the compound, since the graphene particles serve as nuclei for crystal formation.

Keywords: graphene oxide, polypropylene, nanocomposite, injection molding, masterbatch.

INTRODUCTION

As a representative of polyolefins, polypropylene is a polymer of essential strategic importance for industry. It is characterized by several useful properties such as heat and cold resistance, chemical stability and easy processability. A significant modification of its properties is obtained by introducing nano - sized fillers into its matrix, which in many cases impart properties uncharacteristic of polypropylene. In recent years, significant interest has been shown by polypropylene nanocomposites with carbon nanofillers, such as nanotubes and fullerenes, aimed at imparting increased thermal and electrically conductive properties. To produce polymer nanocomposites, dispersion of the fillers to the nanoscale level is essential. One of the significant problems in the production of nanocomposites is the tendency to strong aggregation of nano-sized fillers due to the large cohesive forces resulting from the extremely small sizes. As a result, in many cases, aggregation structures are formed in the polymer matrix, and the filler phase is discrete, not continuous. As a result, local internal stresses can be observed, leading to a decrease in the entire complex of properties of the composite. Therefore, the development of dispersions and masterbatches in which the fillers are dispersed to the nanoscale level is essential for obtaining high - quality nanocomposites. Along with these developments, the development of polypropylene nanocomposites containing graphene (Gr) and its homologues, such as graphene oxide and modified or reduced graphene oxide, is of particular interest. Graphene as a material is a monolayer of carbon atoms arranged in a hexagonal (hexagonal) lattice resembling a honeycomb, located in sp^2 hybridization. The preparation of dispersions of graphene and its

derivatives in polymer matrices is important to produce graphene-polymer nanocomposites. It is well known that most polymers and graphene have poor compatibility, and therefore the polymer chains may not adsorb tightly to the graphene nanosheets. Graphene nanofillers allow to obtain nanocomposites, the properties of which are fundamentally different from those of the polymer matrices or to combine some properties according to specific applications [1 - 8]. The inclusion of additives such as antioxidants, light and thermal stabilizers in polyolefins is usually a prerequisite for extending their performance properties and expanding their applications. In addition, the presence of nanoparticles can affect the kinetics of photooxidation of polymers. It is known that carbonaceous substances are good photo stabilizers and this behaviour has already been reported for composites and nanocomposites based on polyolefins, including carbon nanotubes, including those based on polypropylene [9 - 12]. There are data in the literature on the physicochemical properties of polypropylene containing graphene. Emphasis has been placed on how the size of graphene fillers affects certain properties of polypropylene [13]. There is no data in the literature on the influence of graphene oxide on the physical and mechanical properties of polypropylene nanocomposites with polyester oil. The aim of the study is to obtain a nano dispersed oligomeric masterbatch of graphene oxide and polyester oil, which increases the tensile strength, elastic modulus and thermal stability of products produced by extrusion or injection molding.

EXPERIMENTAL

Materials and testing methods

Materials

To study the influence of nanoscale graphene oxide on the physicomechanical properties of polypropylene (PP), the following was selected:

PP homopolymer, brand ECOLEN HZ40S, manufactured by HELLENIC PETROLEUM.

Graphene oxide (GrO), synthesized and provided by "Grafen Inovations" LTD, Bulgaria.

Mixture

From the pre-measured amounts of polymer and 17 % masterbatch based on BYK® -300 (a solution of polyether-modified polydimethylsiloxane), mixtures were prepared in which the graphene oxide was in an amount of 0.01 %, 0.05 % and 0.1 % relative to the polyolefin. A rotary mixer with adjustable speed was used to homogenize the mixtures.

To produce test specimens type "A" according to EN 527 - 2 and determination of strength indicators, the injection molding method was used, using a Spritzguss machine, brand "Trusioma Kuasi". The drive of the screw and the closing press is hydraulic. The heating of the material cylinder is electrically resistive, and the temperature is regulated by means of thermoregulators. The products are manufactured at a temperature regime that complies with the recommended processing temperature given in the accompanying material certificate.

Test methods

EN ISO 527 - 2:2025 Plastics - Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics; EN ISO 1133 - 1 : 2022 Plastics - Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics - Part 1: Standard method; A wetting angle; X - ray diffraction analysis (XRD); IR spectroscopy; Dynamic Mechanical Thermal Analysis (DMTA).

RESULTS AND DISCUSSION

The physicomechanical tests were carried out on a Zwick/ Roell dynamometer, according to BDS EN ISO 527 - 1, 2:2025. The results obtained are presented in Table 1.

According to the technical specification of PP homopolymer, brand ECOLEN HZ40S, the tensile strength is 36 MPa [14]. From the measurement data presented in the table, when adding different percentages of graphene oxide, the tensile strength varies from 39 MPa to 41 MPa, which is an increase of about 14 % compared to the pure polymer.

The melt index of the prepared nanocomposite materials was determined. The measurement was carried out at 230°C and 2.16 kg. The results obtained are presented in Table 2.

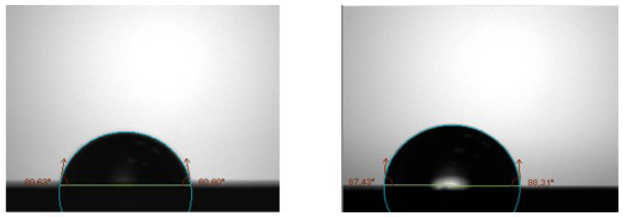
The obtained results show a tendency towards an increase in the fluidity of the composite materials, which is more pronounced at 0.1 % graphene oxide content, but in general it can be concluded that the filler in these

Table 1. Physicomechanical properties of polypropylene containing different amounts of graphene oxide.

GrO content in PP composite, %	Elongation at break, %	Tensile Strength, MPa
0.00	320	41
0.01	327	40
0.05	733	39
0.1	647	39

Table 2. Melt Flow Index of polypropylene nanocomposite with different amounts of GrO.

GrO content in PP composite, %	Melt Flow Index, g 10 min^{-1}
0.00	22
0.01	22.2
0.05	22.8
0.1	23.6



a) b)

Fig. 1. Wetting angle of raw PP and PP with 0.1 % GrO.

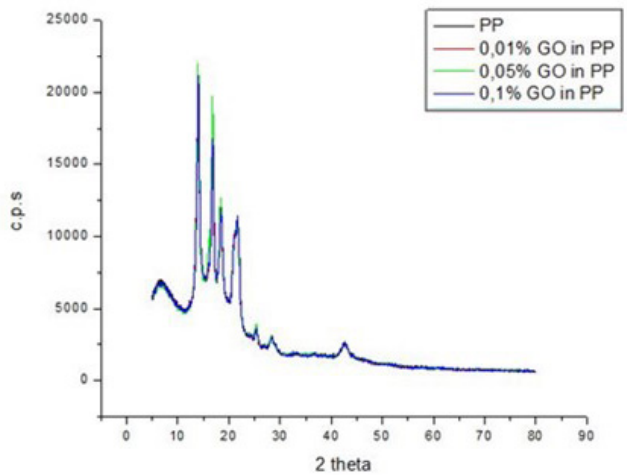


Fig. 2. X - ray diffraction pattern of a polypropylene - based composition with different graphene oxide contents.

quantities does not change the rheology of the polymer material.

Fig. 1 presents the results of determining the water contact angle for PP without filling and the composite with a filling of 0.1 % GrO.

As can be seen from Fig. 1, the contact angle of polypropylene has an average value of 80.72°, and for PP with a content of 0.1 % GrO the value is 87.87°. Although polyolefins are hydrophobic, the addition of 0.1 % filler increases the hydrophobicity of polypropylene by 8 %.

A polypropylene - based composition with different graphene oxide contents was studied using XRD.

Fig. 2 presents an X-ray structural analysis of a polypropylene - based composition with different graphene oxide contents.

From the obtained X - ray diffraction patterns, the degree of crystallinity was determined, which is shown in Table 3.

From the obtained results it can be concluded that graphene particles have an influence on the degree of crystallinity. In general, it increases. The reason for this is that nanoparticles serve as nuclei for crystal formation [15]. A finer crystalline structure can be expected. The change in the degree of crystallinity, depending on the concentration of nanoparticles, shows that their action is bidirectional. The course of the curves and the maximum points indicate that it is possible that the filler influences the cooling rate of the test samples in the injection mold, which would have a direct impact on the crystallinity of the polymers. For this reason, the influence of the filler on the thermal conductivity of test samples was also studied. Polypropylene and polypropylene filled with 0.1 % graphene oxide were used for the measurement. Plates with dimensions of 250 mm × 250 mm and a thickness of 3.0 mm were prepared from both materials. A thermocouple was attached to both sides of the plates,

Table 3 Degree of crystallinity of PP compositions with different amounts of GrO.

GrO content in PP composite, %	Degree of crystallinity, %
0	46
0.01	48
0.05	56
0.1	50.1

centrally, and each of the plates was placed in a hand press, the top plate of which was heated and tempered to 60°C. The heat transfer rate was determined by recording the thermocouple temperature every minute until equilibrium was reached. It was found that for PP the rate was 0.24°C min^{-1}, and for PP + 0.1 % GrO it was 0.35°C min^{-1}. The results prove that the filler influences the thermal conductivity properties of the composite, which in turn is directly related to the crystallization processes [16, 17].

The starting polymers and the composites with the maximum filling degree were characterized using IR spectroscopy.

Fig. 3 presents the results of IR spectroscopy of the starting polymers and the composites.

The presented IR spectra clearly show the characteristic vibrational oscillations for polypropylene. When introducing graphene oxide nanoparticles, a significant change in the spectral bands is observed with the disappearance of the absorption band for the carbonyl group in the filled polyolefin chain (1726 cm^{-1}). The observed effect can most likely be explained by the chemisorption of graphene with the polyolefin chain, in which the hydroxyl groups of graphene interact with the carbonyl groups of polyolefins. The fact that it disappears in the filled nanocomposites allows us to assume that the filler will have an impact on the aging rate.

Fig. 4 presents the results of a study using DMTA of the influence of graphene nanoparticles on the thermophysical properties of the polypropylene composite.

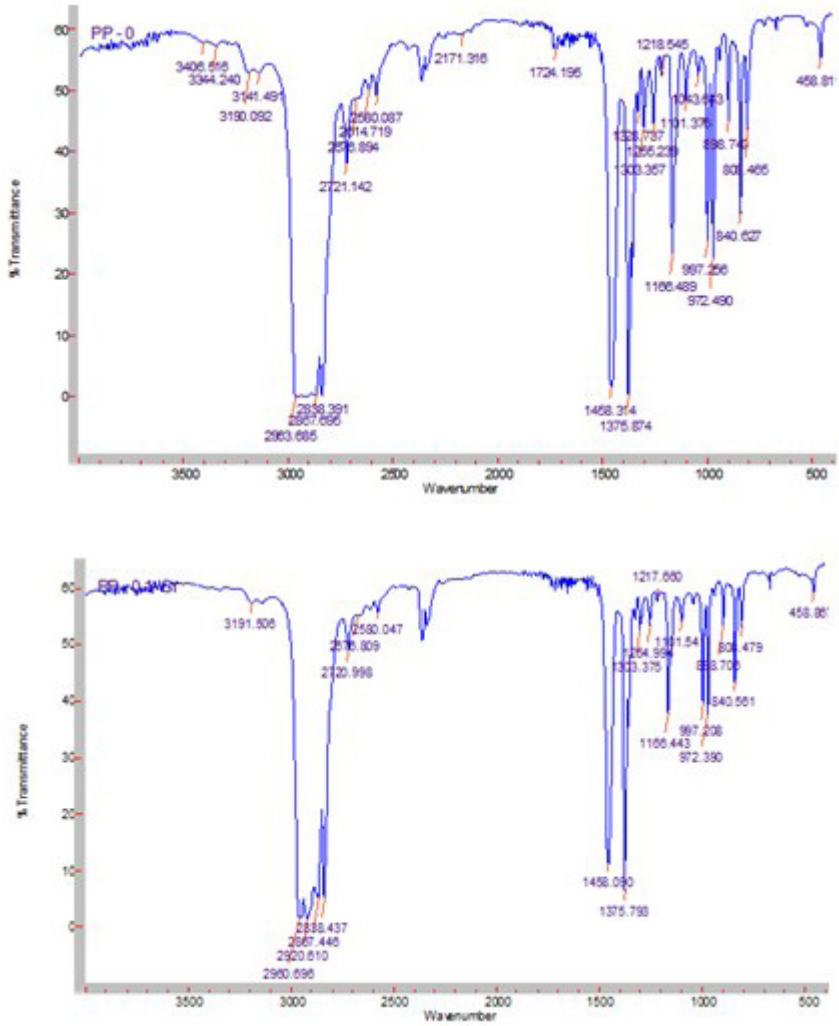


Fig. 3. IR spectroscopy of the starting polymers and the composites with 0.1 % filling level.

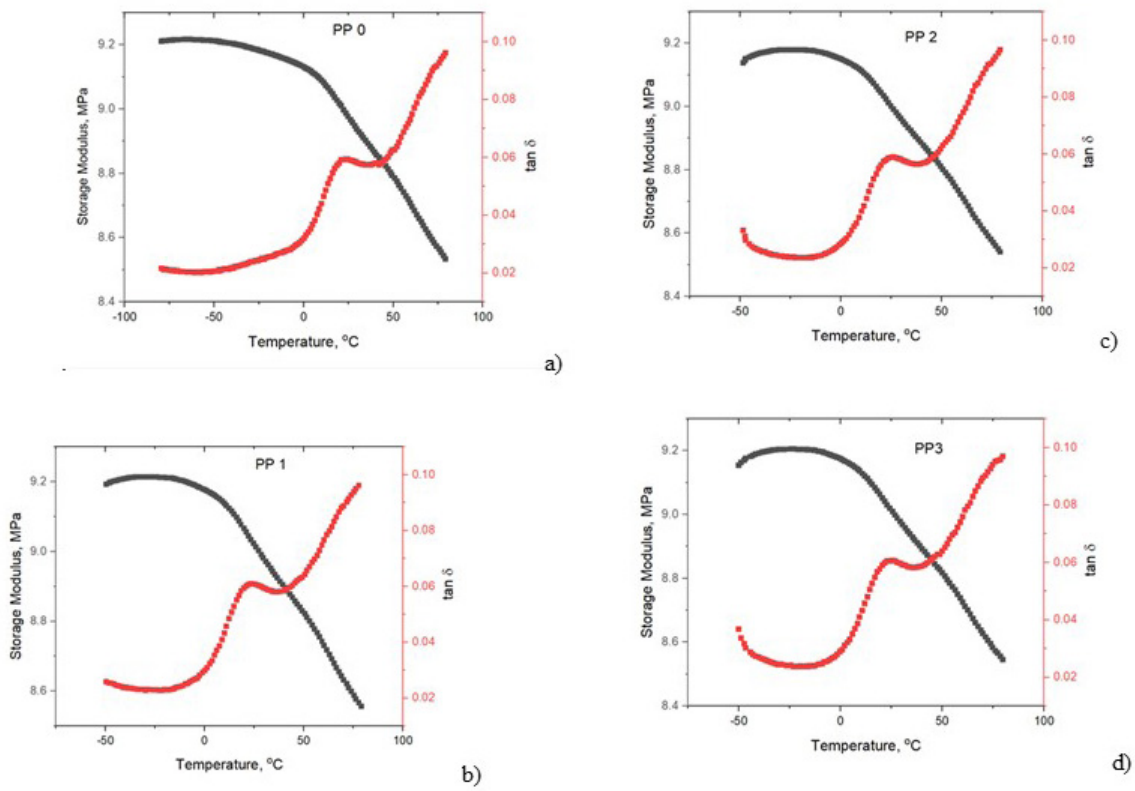


Fig. 4. Influence of graphene nanoparticles on the thermophysical properties of the polypropylene composite.

As can be seen from the results presented in Fig. 4, the introduction of graphene oxide nanoparticles into the polyolefin matrix does not significantly effect the temperature-phase transitions. The glass transition temperature is around minus 50°C, while that of primary crystallization is around 20°C, and the melting temperature of the amorphous phase is at around 75°C.

CONCLUSIONS

From previously measured amounts of polymer and 17 % masterbatch based on BYK - 300 (a solution of polyether - modified polydimethylsiloxane), mixtures were prepared in which graphene oxide was added in an amount of 0.01 %, 0.05 % and 0.1 % relative to the polyolefin. A rotary mixer with adjustable speeds was used to homogenize the mixtures.

"Blade" type test bodies were manufactured, and the strength indicators of the products were determined. The work was carried out using the injection molding method, with the temperature regime of the technological equipment being consistent with the recommended processing temperature given in the accompanying material certificate. It was found that when 0.1 % graphene oxide was added, the tensile strength increased by about 14 % compared to the pure polymer. A tendency towards an increase in the fluidity of the composite materials is observed, which is more pronounced at 0.1 % graphene oxide content, but in general it can be concluded that the filler in these quantities does not change the rheology of the polymer material. The addition of 0.1 % filler increases the hydrophobicity of polypropylene by 8 %. Graphene particles affect the degree of crystallinity. In general, it increases, since the nanoparticles serve as nuclei for crystal formation. The filler does not significantly affect the temperature-phase transitions. The starting polymers and composites with the maximum degree of filling were characterized using IR spectroscopy.

A significant change in the spectral bands is observed with the disappearance of the absorption band for the carbonyl group in the chain of the filled polyolefin. The

fact that it disappears in the filled nanocomposites allows us to assume that the filler will affect the aging rate.

Authors' contributions

P. N-M: Literature research, original draft preparation, review, editing, V. S.: Experiments, data processing and analysis.

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