POLYPROPYLENE/GRAPHITE COMPOSITES AND THEIR THERMAL STABILITY

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Abstract

Thinning fossil fuel deposits and increasing emphasis on ecological aspects of human activity call for new technology solutions. Energy industry and electronics industry search for novel materials and power sources. In electronics, the power source size is often a limiting parameter. In search of high density power sources carbon materials like nanotubes, graphene, graphite, etc. known for high electrical conductivity, thermal and chemical stability and good mechanical properties, are often utilized. These materials are ideal for use in composite electrodes. Polymers in such composites serve to improve mechanical properties and handling, e.g. moulding. Addition of photoactive semiconductors can help with disposal of the polymer after the use. This paper presents a study of compression molded samples of polypropylene (PP) / graphite composites and their thermal stability. The graphite served as a filler for the PP matrix and also as a substrate for MeOx particles, where Me stands for Ti and Zn. TiO_2 and ZnO functionalized graphite particles were further used as a filler of PP. The graphite and functionalized graphite content in the PP composites was 75 wt.%. The samples were characterized by X-ray diffraction (XRD), Raman spectroscopy and measurement of Martens hardness (HM). The highest HM value was exhibited by composite containing large grain graphite (denoted as PP/GRA1). The HM was affected by thermal treatment (170°C for 1 h). The HM of the composites containing graphite fillers increased, while in case of the composites containing functionalized graphite fillers the decrease in HM was observed.

Keywords: composite, polypropylene, graphite, thermal stability,

1. INTRODUCTION

Properties of the polymer composites are useful in wide range of applications for instance energy industry [1], as flame retardant [2], packaging [3], medicine [4]. The use of TiO_2 and ZnO nanoparticles as polymer fillers can lead to remarkable properties of the resulting composite (photodegradation of pollutants [5], antibacterial surfaces [6]). The polymers containing TiO_2 nanoparticles showed decrease in emissions during their disposal by incineration. The effect of photoactive nanoparticles on gradual decomposition of polymer composites is being studied. The use of graphite as polymer filler usually increases the conductivity of the composite. The aforementioned facts show positive effect of various metal oxide and graphite fillers on the properties of the composite material. The improved mechanical and other properties can be utilized in specific applications. The applications depend on the filler that was used. Present study is focused on polypropylene (PP) / graphite composites where graphite served as filler for the PP matrix either in pure state or functionalized by TiO_2 and ZnO nanoparticles. The prepared samples were characterized with X-ray diffraction and Raman spectroscopy methods and the Martens hardness of the material was determined. Special attention was paid to thermal changes in the material because thermal stability is important in many practical applications (car industry, machine parts).

2. EXPERIMENTAL PART

2.1. PREPARATION OF SAMPLES

Four fillers were used in experiment. Two of the fillers were pure graphite and the other two were nanoparticle/graphite composites. Grinded graphite (denoted as GRA1) and natural graphite (denoted as GRA2). According to the results of our previous research focused only on graphite-based fillers, different graphites were chosen for each nanoparticle. Therefore, GRA1 and GRA2 served as substrate for TiO_2 and ZnO, respectively. TiO_2 and ZnO on graphite substrates were prepared by hydrothermal method and after drying the resulting material containing 50 wt.% of TiO_2 or ZnO was calcined at 500 °C for 1 h. These fillers were denoted as GRA1Ti and GRA2Zn. For more information the reader is referred to the Czech Patent Application PV 2013-973 [7].

Granulated PP was mixed with MAH-g-PP (maleic anhydride grafted PP) and resulting mixture was dissolved in xylene under vigorous stirring at 130 °C. Then the filler was added (75 wt.%) and left to react in contact for 3 h. After 3 h the mixture was transferred to acetone in order to precipitate the polymer composite. Further, this product was rinsed with acetone, dried at 60 °C, and disintegrated in high speed disintegrator (29 000 rpm, for 5 min). Finally, prepared powder composite was compression molded at 180 °C under the pressure 8 MPa for 5 min. Composites were denoted as PP/filler, i.e. for example PP/GRA1 is composite containing grinded graphite GRA1.

Samples were thermally treated in Memmert laboratory oven at 170 °C for 1 h.

2.2. CHARACTERIZATION OF SAMPLES

The structure of the samples was determined using X-ray diffraction (XRD) analysis. Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with a fast position sensitive detector VÁNTEC 1 was used. XRD analysis was performed in reflection mode under $Co_{K\alpha}$ irradiation (λ = 1.7889 Å) and the phase compositions of samples were determined using database ICDD PDF-2 (2004 release).

For Raman spectroscopy analysis was used Raman microscope XploRA™ (HORIBA Jobin Yvon, France) equipped with 532 nm excitation laser source, 50×objective and using 1200 groove / mm grating.

Martens hardness (HM) of all samples was measured using hardened steel ball indentor with diameter ¼" (6.35 mm) under the load 100 N. ZWICK ZHU 2.5 hardness testing machine was used.

3. RESULTS AND DISCUSSION

Structural changes were examined by XRD and Raman spectroscopy. Measured Raman spectra of the samples PP, PP/GRA1, PP/GRA2, PP/GRA1Ti, and PP/GRA2Zn are compared in Fig. 1. Spectrum of the pure PP corresponds to the typical polypropylene spectrum with its characteristic bands. In the other prepared samples these bands are not clearly visible, probably due to the higher intensity of the graphite matrix. Presence of the PP is confirmed only by the broad structured band (2800-3000 cm^{-1}), which belongs to the symmetric and asymmetric C-H vibrations of CH_2- and CH_3- groups [8]. The band is most intensive in the PP spectrum, thus it is obvious that other less intensive bands are not observed.

In the spectrum PP/GRA1Ti presence of TiO_2 was proved. In measured points both forms of TiO_2 (anatase and rutile) were observed. Rutile was measured only in one of the measured points, thus is present in minority in the sample and only the spectrum with the anatase form is shown in the Fig. 1, as the typical spectrum of the sample. Presence of the anatase is proved by the band at 145 cm^{-1}, which is the main anatase band [9]. In the spectrum of PP/GRA2Zn bands typical for the ZnO presence were observed (e.g. 99 cm^{-1}) [10].

Bands belonging to the graphite structure are present at 1330, 1584 and 2714 cm^{-1}, these bands respectively correspond to the disorder band (D band), graphitic band (G band) and 2D (G') band [11,12]. D band specifies the level of disturbance in the sample and its increasing intensity is in good correlation with the increasing intensity of the structured band under 3000 cm^{-1} (main PP band).

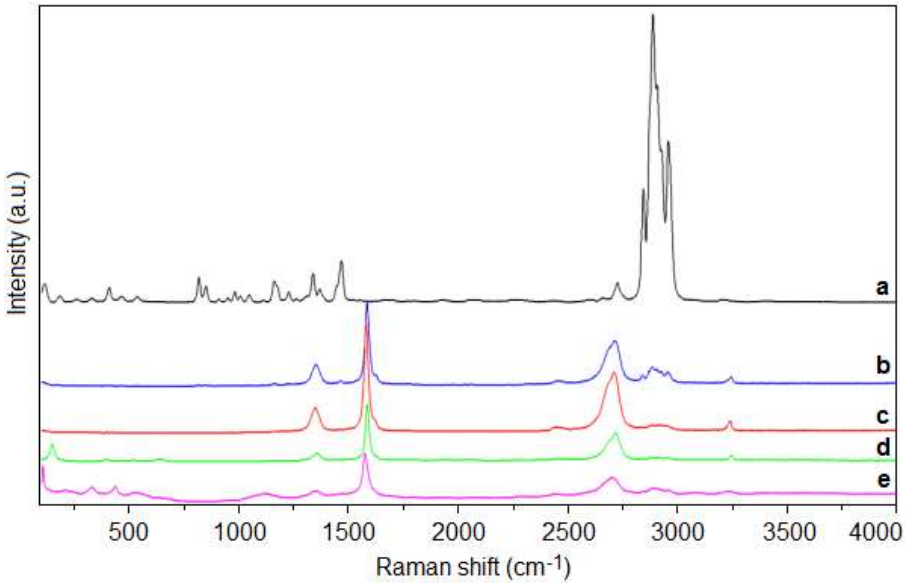

Fig. 1 Raman spectra of prepared samples PP (a), PP/GRA1 (b), PP/GRA2 (c), PP/GRA1Ti (d) and PP/GRA2Zn (e) before thermal treatment.

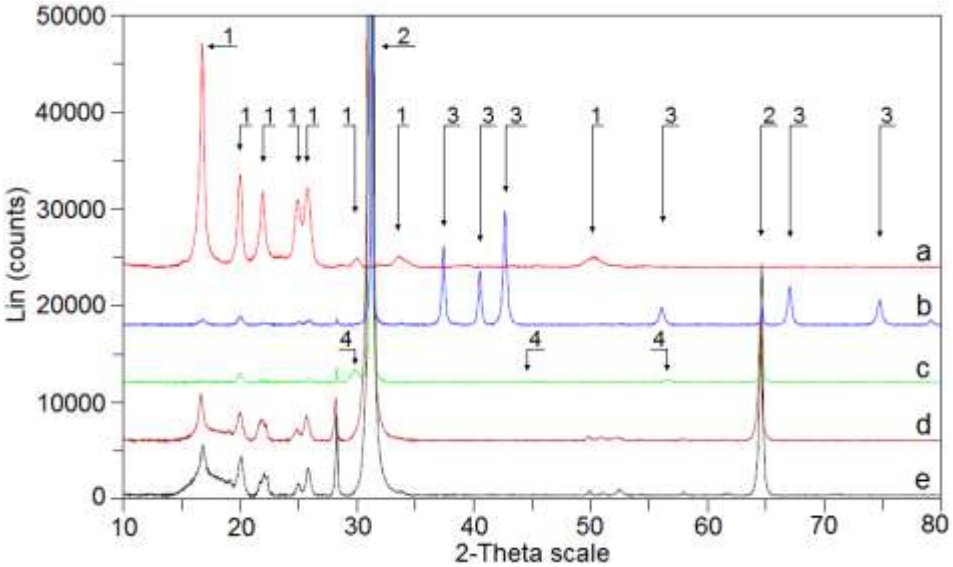

Fig. 2 XRD pattern of prepared samples PP (a), PP/GRA2Zn (b), PP/GRA1Ti (c), PP/GRA2 (d), and PP/GRA1 (e) before thermal treatment. 1 – α-polypropylene, 2 – graphite, 3 – ZnO, 4 – TiO_2.

In the XRD patterns (Fig. 2) presence of the main components of the fillers and also of the polymer matrix PP was identified. It was observed that the diffraction lines of PP are diminished in samples with photoactive fillers.

Results summarized in Table 1 revealed that pure PP and composites containing GRA1 and GRA2 fillers showed increase in Martens hardness (HM) after thermal treatment while in case of composites containing photoactive fillers the HM values decreased.

Table 1 Comparison of Martens hardness (HM) values for samples before and after thermal treatment at 170°C for 1 h.

Sample	HM	
	25 °C	170 °C (1h)
PP	31	490
PP/GRA1	548	653
PP/GRA2	378	405
PP/GRA1Ti	191	146
PP/GRA2Zn	269	224

Raman spectra of all prepared composites and pure PP after thermal treatment at 170 °C for 1 h are compared in Fig. 3. Spectrum of the pure PP is similar to the spectrum of PP before thermal treatment and no significant changes were observed. Only small increase of the background is visible. In the spectra of composite samples the broad structured band under 3000 cm^{-1} is not clearly visible in most measured points and the diminished intensity of this band is the only change in the spectra of PP/GRA1 and PP/GRA2 samples after thermal treatment.

Same as in previous case (see Fig. 2) the presence of anatase form of TiO_2 was confirmed in the sample PP/GRA1Ti. This spectrum exhibits high fluorescent background and therefore, even the bands of graphite structure have low intensity and the PP band was not clearly identified. Also in the sample of PP/GRA2Zn the background is high and the graphitic bands are less intensive. Moreover, no bands corresponding to the zinc presence were detected in the spectrum PP/GRA2Zn.

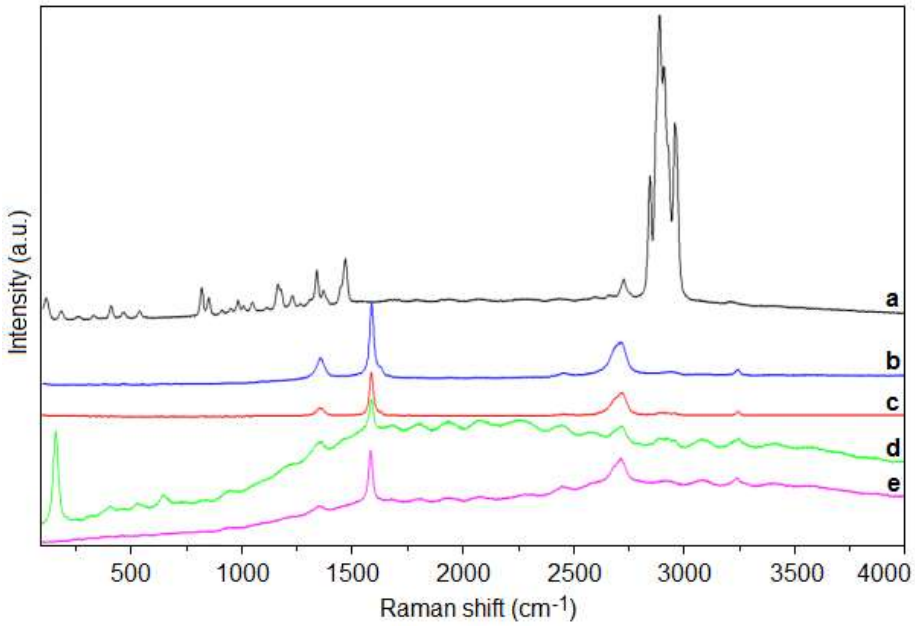

Fig. 3 Raman spectra of samples PP (a), PP/GRA1 (b), PP/GRA2 (c), PP/GRA1Ti (d), and PP/GRA2Zn (e) after thermal treatment at 170 °C for 1 h.

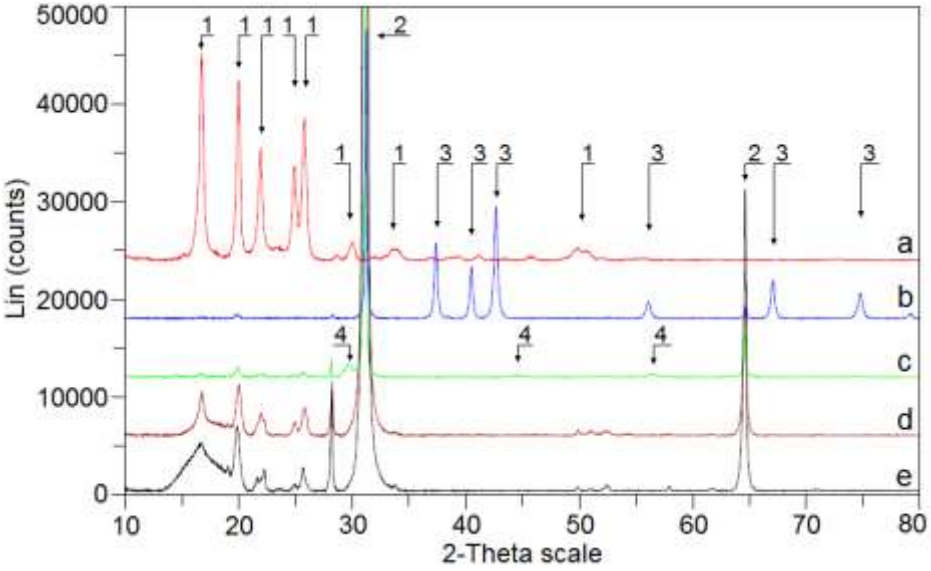

Fig. 4 XRD pattern of samples PP (a), PP/GRA2Zn (b), PP/GRA1Ti (c), PP/GRA2 (d), and PP/GRA1 (e) after thermal treatment at 170 °C for 1 h. 1 – α-polypropylene, 2 – graphite, 3 – ZnO, 4 – TiO_2.

Comparison of XRD patterns of samples before (Fig. 2) and after (Fig. 4) thermal treatment showed no significant structural changes. The most notable one is broadening of reflection at position ~ 17° 2θ for PP/GRA1 sample (Fig. 4e). Loss of sharpness of the reflection suggests partial loss of crystallinity of PP.

XRD analysis as well as Raman spectroscopy did not prove existence of significant structural changes after thermal treatment of the composites. Some of the samples showed increase of fluorescence background thanks to the high signal intensity of graphite over signal of PP and therefore it was not possible to observe any changes of PP structure.

4. CONCLUSIONS

Polypropylene-based composites containing grinded and natural graphite either in pure state or functionalized by TiO_2 and ZnO nanoparticles were successfully prepared and their thermal stability was tested by heating at 170 °C for 1 h. While in case of pure polypropylene and composites with grinded and natural graphite fillers the Martens hardness increased after thermal treatment, in case of composites containing graphite fillers functionalized by TiO_2 and ZnO nanoparticles the opposite trend was observed. X-ray diffraction analysis and Raman spectroscopy showed no significant structural changes after thermal treatment. Therefore, it can be concluded that temperature 170 °C applied for 1 h caused structural changes on the surface of samples but not in the whole volume. Taking this into consideration, the prepared composites can be recommended for applications where the working temperatures is lower than 170 °C or the exposition time to temperature 170 °C is shorter than 1 hour.

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