

EFFECT OF CRYSTALLINE FORM (γ) OF POLYAMIDE 6 / GRAPHENE NANOPATELETS (PA6/GN) NANOCOMPOSITES ON ITS STRUCTURAL AND THERMAL PROPERTIES

Assist. Prof. Dr. F. Mindivan¹

Bozuyuk Vocational College, Bilecik S.E. University, Bilecik, Turkey¹
ferda.mindivan@bilecik.edu.tr

Abstract: In this article, graphene nanoplatelets (GN) were used as nanofiller and twin-screw extrusion process was applied to synthesis of Polyamide 6 / Graphene Nanoplatelets (PA6/GN) nanocomposites. Fourier-Transform Infrared spectroscopy (FTIR), X-Ray Diffractions (XRD), and Thermogravimetric analysis (TGA) were used to characterize the resultant structure. According to the results of FTIR and XRD measurement, α phase dominated in neat PA6, while the γ phase also could be observed at PA6/GN nanocomposites. Compared with the neat PA6, the PA6/GN nanocomposites exhibited better improvement in thermal analysis results due to the new and dominant crystal form.

Keywords: PA6, GN, TWIN SCREW EXTRUSION, CRYSTALLINE FORM, NANOCOMPOSITES.

1. Introduction

Graphene with attractive thermal properties, large specific surface area and low cost has attracted intense attention for various application areas [1 - 3]. All these positive features make it excellent candidate as filler for polymer nanocomposites [4]. But dispersion of graphene in the polymer matrix has always been extremely challenging, so new methods are tried out to obtain intercalated or exfoliated polymer nanocomposites [5]. Recently, a large number of papers have described the dispersion and exfoliation of graphene oxide (GO) and reduced graphene oxide (RGO) in the polymer matrix composites [6 - 8]. These researches had shown that PA6/GO or PA6/RGO polymer nanocomposites demonstrated remarkable physical, thermal and mechanical properties. However, very dangerous chemicals were used for synthesis of GO and RGO. Specially, hydrazine hydrate used to form RGO is highly toxic and unstable [9]. Thus in this paper, Graphene Nanoplatelets (GN), a candidate material for the application in thermal management [10-11], were used as nanofiller without using any chemical. Polyamide-6 (PA6) is an important group of the thermoplastic with several advantages such as good processability, solvent and chemical resistance. However, its thermal properties need to be improved [12- 14]. The improvement in thermal, mechanical and other properties of polymer composites with GN has been reported in many literatures [2, 3, 5, 15-18], but only a study on GN based PA6 nanocomposites is found [19]. The objective of this paper is to fabricate PA6/GN nanocomposites and investigate the effects of GN loading content on the structural and thermal properties of the PA6/GN nanocomposites without using any dangerous chemical.

2. Experimental Details

GN particles in this study were GRAFEN- IGP2 nanoplatelets (Grafen Chemical Industries, Turkey). These nanoparticles consist of short stacks of graphene layers having a lateral dimension of $\sim 5 \mu\text{m}$ and a thickness of $\sim 5\text{--}8 \text{ nm}$. Melt blending of PA6 and the GN was carried out in a co-rotating twin screw extruder (Thermoprism TSE 16 TC, L/D 24) at a screw speed of 100 rpm and barrel temperature profile of 230-230-230-230-230°C, followed by granulation (3-5 mm long and 3 mm in diameter) in a pelletiser and drying. Prior to extrusion, the PA6 polymer and GN were dehumidified in a vacuum oven at 90°C for a period of 24 h. The GN content in the PA6/GN nanocomposites was varied from 1 - 4 wt. % (Table 1). The nanocomposite mixture for structural characterization studies were molded using a laboratory scale plunger type injection-molding machine (Microinjector, Daca Instruments) at a barrel temperature of 200 °C and mold temperature of 30 °C. Figure 1 presents the neat PA6 and PA6/GN nanocomposite plates used in the present study.

Table 1: Ratios and codes of GN in the composites.

Samples	GN Content (in weight %)
PA6/GN1	1
PA6/GN2	2
PA6/GN4	4



Fig. 1 Digital image of neat PA6 and PA6/GN nanocomposite.

Fourier Transform Infrared spectroscopy (FTIR) analysis was performed by using IR-spectrometer (PerkinElmer 100). The spectra were analyzed from 4000 cm^{-1} to 400 cm^{-1} . The X-ray diffraction (XRD) patterns were obtained with a PAN analytical, Empyrean X-ray diffractometer using $\text{CuK}\alpha$ radiation. Samples were scanned from 10° to 50° with a scan speed of $2^\circ/\text{min}$. Thermogravimetric Analysis (TGA) curves were measured by using a STA 409, Netzsch analyzer from room temperature to 600°C with heating rate of $20^\circ\text{C}/\text{min}$. and a nitrogen flow rate of $100 \text{ mL}/\text{min}$.

3. Results and Discussions

FTIR spectra of the neat PA6 and PA6/GN nanocomposites were represented in Fig.2. The FTIR spectrum of the neat PA6 showed peaks at 3296 cm^{-1} , 2934 cm^{-1} and 2864 cm^{-1} which correspond to the N-H bending vibration in primary amine [20], C-H in phase and C-H out of phase stretching vibrations [12], respectively. The bands at 1635 cm^{-1} and 1538 cm^{-1} were assigned to C=O amide I [21] and N-H and C-N combination amide II stretch [20], respectively. The α form crystal exhibiting characteristic peaks at 1476 cm^{-1} and 1416 cm^{-1} could be attributed to CH_2 scissors vibration. The band corresponded to vibration of amide III and CH_2 wag was observed at 1373 cm^{-1} and the band at 1201 cm^{-1} corresponded to CH_2 twist-wag vibration [22]. The characteristic CO-NH in plane vibrations bands could be observed at 959 cm^{-1} and 929 cm^{-1} [23]. The γ form showing characteristic peaks at 1437 , $1372\text{--}1239$, 976 , 725 cm^{-1} in the PA6/GN nanocomposites was attributed to the CH_2 scissors vibration, CH_2 twist-wag vibrations, CO-NH in plane vibrations and amide V [22], respectively. The reflection shape of the neat PA6 was similar to PA6/GN nanocomposites and no new peak was formed. This

situation showed that there was no chemical interaction between PA6 matrix and GN nanoparticles because GN had not any functional groups.

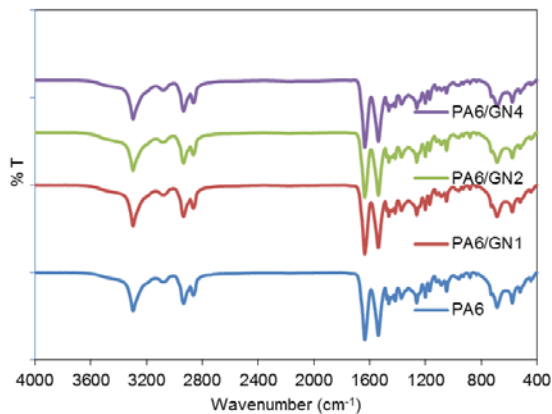


Fig. 2 FTIR spectra of neat PA6 and PA6/GN nanocomposites.

XRD experiments were conducted to examine whether the addition of GN caused a change of PA6 crystal structure. Fig. 3 showed XRD patterns of the neat PA6 and PA6/GN nanocomposites. PA6 exhibited polymorphic structures containing two types of crystal form: monoclinic (α) and pseudo-hexagonal (γ). The representative diffraction peaks observed at $2\theta=20.4^\circ$ and 21.8° corresponded to α and γ crystalline phases of the neat PA6 [24-25], respectively. As shown in Fig.3, α phase was the dominant crystalline phase for the neat PA6 [26]. Also, all nanocomposites showed two peaks at $2\theta=20.1^\circ$ and 22.1° , corresponding to α and γ crystalline phases. When compared to the neat PA6, the diffraction peak corresponding to α -form crystal phase was observed only as a less pronounced shoulder at all GN contents. However, the peak of γ form crystal phase in the PA6/GN nanocomposites grew more obvious. Especially, the PA6/GN1 nanocomposite had most intense crystalline γ phase peak. However, referring to Fig. 3, in addition to the two reflections as seen in the PA6/GN nanocomposites a other reflection was also detected at $2\theta=26^\circ$ which was related to the GN [10]. According to these results, GN did not dispersed homogeneously into PA6 matrix, but these nanoparticles changed crystal structure of all nanocomposites. Gong et al. [27] reported that the diffraction peaks of α -form crystals of modified graphene based Nylon-6 (PA6) composites become weaker with the increasing graphene content. O'Neill et al. [8] showed that functionalized graphene oxide (GO) and functionalized reduced graphene oxide (rGO) could promote the formation of γ phase crystals in the PA6 matrix.

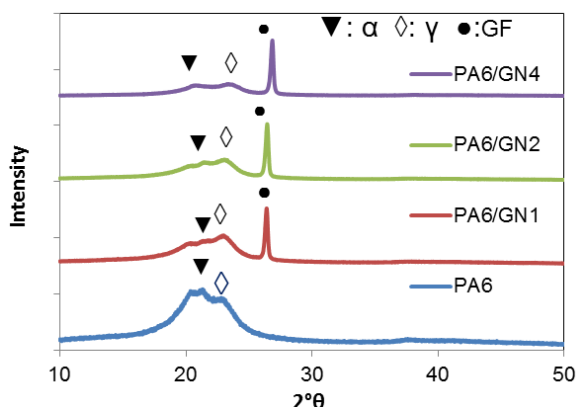


Fig. 3 XRD patterns of neat PA6 and PA6/GN nanocomposites.

The TGA and Derivative thermograms (DTG) curves of the neat PA6 and PA6/GN nanocomposites were shown in Fig. 4, and TGA data were listed in Table 2. From DTG curve, the initial weight loss for all samples in the temperature ranges of 207–217°C reflected loss of moisture from the nanocomposites because they had hydrophilic structure and hence some amount of water could be present in the PA6 matrix through hydrogen bonding [13]. The

second weight loss was observed at 465°C for the neat PA6, corresponding to the volatilization of monomer and chain fragments, as reviewed in the literature [28]. The major weight loss (T_2) was observed in between 450 and 500°C for all nanocomposites in Fig.4 b - d. Referring to Table 2, it was observed that the addition of GN caused an increase in the degradation temperatures (T_2) and residue mass i.e. char at 600°C of the nanocomposites compared to the neat PA6. These results showed that GN filled PA6 nanocomposites had much higher thermal stability than the neat PA6 [29].

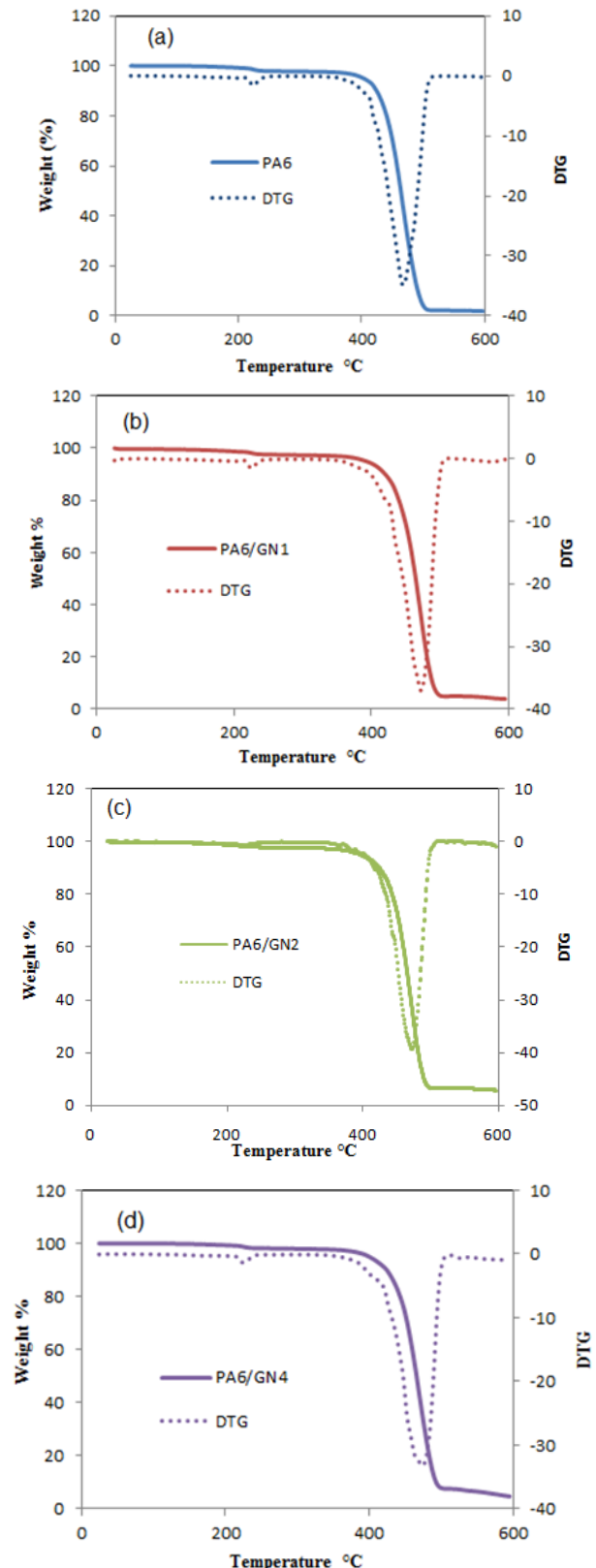


Fig.4 TGA and DTG curves for (a) neat PA6, (b) PA6/GN1, (c) PA6/GN2 and (d) PA6/GN4 nanocomposites.

Table 2: TG data of neat PA6 and PA6/GN nanocomposites.

Sample	DTG Peak (°C)		Residue at 600°C wt. (%)
	T ₁	T ₂	
PA6	217	465	1.95
PA6/GN1	215	469	3.99
PA6/GN2	207	469	5.78
PA6/GN4	216	467	5.09

4. Conclusion

PA6/GN nanocomposites were successfully prepared by twin-screw extrusion process. When compared to the neat PA6, the structural and thermal properties of the nanocomposites were improved by the addition of GN. The γ phase crystal structure in the PA6/GN nanocomposites was shown to be dominated by FTIR and XRD results. TGA analysis results showed that degradation temperatures (T₂) and residue mass i.e. char at 600°C of PA6/GN nanocomposites were higher than those of the neat PA6. These values indicated that the GN filled PA6 nanocomposites were more thermally stable than the neat PA6. Thus, twin-screw extrusion is a promising method to prepare PA6/GN nanocomposites without using more harmful chemicals.

Acknowledgements

The financial support of the research foundation (Project no.: 2014-01.BIL.07-01) of Bilecik S.E. University. The author would also like to thank the officials of the Central Research Laboratory of Bilecik S.E. University for their precious contribution.

5. Literature

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