

***In situ* nylon 6/graphite composites. Physico–mechanical properties**

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Nylon 6/graphite composites were obtained through reactive rotational moulding *via in situ* anionic ring–opening polymerization of ϵ -caprolactam monomer in the presence of various amounts of graphite microparticles. The content of graphite in the reaction mixture feed was varied from 0.0 to 15.0 wt %. The initial mould temperature (initial polymerization temperature) was 160 ± 2 °C. The degree of polymerization and the water absorption of nylon 6 matrix prepared in the presence of graphite are decreased as the amount of filler increases. The DSC results show that graphite content has a small influence on the melting temperatures of polyamide 6 in these composites. From melting enthalpy results it seems that graphite particles act as nucleating agents, giving rise to increased crystallinities of the polyamide. The increase of graphite content causes an increase of the degree of crystallinity of the nylon 6/graphite composites. The thermal stability of the nylon 6 graphite powder composites is better than that for of the pure nylon 6. Notched Izod impact strength decreases gradually with the increasing of graphite concentration, while flexural strength and flexural modulus improved.

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1. Introduction

The inclusion of inorganic particulates fillers into thermoplastics matrices is a well–known technique to obtain a promising class of hybrid materials by improving or modifying of some properties of neat polymers. The final properties of composites are controlled by composition, method of preparation, matrix characteristics, nature, size, shape, microstructure and state of agglomeration of the filler and interfacial interactions between polymer matrix and filler [1,2]. The new materials due to their interesting physico–chemical and mechanical properties are more suitable for the intended applications than the parent polymers and have motivated considerable multidisciplinary studies. Composite materials are widely used in various fields, such as transportation (automotive, aeronautics), construction, microelectronics, optics, communications, flame retardants, membranes, sporting goods and house hold [3–7].

Among various thermoplastic matrices, nylon 6 represents one of the best choices for preparation of various types of composites. It is well known that nylons are widely used as engineering plastics because of their desirable properties (high strength, stiffness, and resistance to nonpolar solvents), but at the same time some other characteristics (poor low–temperature toughness, moisture–sensitive) of this polymer limit its use in many applications [8,9]. Of the various methods, a new way to produce polyamide–based composite materials with remarkably improved performances is reactive polymerization–filling technique. By this method, polymer composite materials are produced by *in situ* polymerization involves the incorporation of filler

particulates before the polymerization process. One of the main targets of the polymerization–filling technique is homogeneity of the final composites and good physico–mechanical properties that can be achieved by this method. Anionic activated polymerization of ϵ -caprolactam has been shown to be particularly convenient for the preparation of nylon 6 (poly- ϵ -caprolactam, PCL) and its composites. This process is initiated with strong bases (Na, NaH, ethylmagnesium bromide) which cause the formation of free lactam anions and activated with N-acyllactam growth centers, e. g., isocyanates or their products with polyols [9–12]. Different types of fillers such as glass, graphite, carbon, calcium carbonate and silicates can be incorporated in polyamides as reinforcing agents [2,7,11,13].

This paper is concerned with the evaluation of the effects of addition of graphite as filler on the conversion, degree of polymerization, melting temperature T_m , crystallization temperature T_{cr} , crystallinity and morphology of the PCL matrix and mechanical properties of nylon 6/graphite composites. The preparation of the composites was performed by a polymerization–filling technique, namely rotational moulding *via* anionic polymerization of ϵ -caprolactam monomer in the presence of graphite microparticles

2. Experimental

2.1. Materials

ϵ -Caprolactam (technical grade, Fibrex–Savinesti, Romania) was purified according to the literature [7,9,11,14,15]. The synthetic graphite powder (carbon

content of >99.5%), as filler with a mean size of <20 μm , supplied by Aldrich Chemical Co., Inc. was preheated before the application at 110 $^{\circ}\text{C}$ in vacuum for 24 h to eliminate possibly absorbed water on the surface of the particles and then was kept in a desiccator before the use. Sodium dicaprolactamato-bis(2-methoxyethoxy)aluminumate as initiator (80% in toluene solution) supplied by Katchem Co.- Czech Republic was used without further purification.

Activator N,N' -[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam, of the formula:

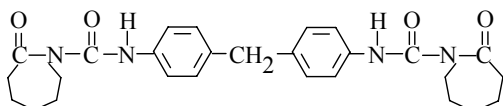


Fig. 1. Chemical structure of N,N' -[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam

was synthesized in our laboratories from 4,4'-diphenylmethane diisocyanate (MDI) and ϵ -caprolactam according to the procedure described in the literature [2,7,16,17]: m. p. (DSC), 177–178 $^{\circ}\text{C}$ (ref. [16]: 177–178 $^{\circ}\text{C}$).

The FT-IR spectrum of N,N' -[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam is given in Fig. 2.

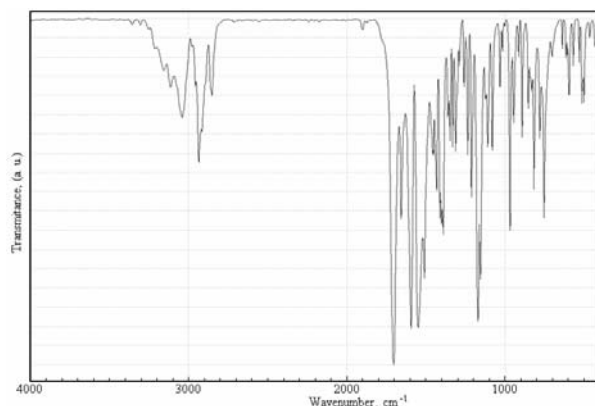


Fig. 2. FT IR spectrum of N,N' -[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam

The FT-IR analysis of N,N' -[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam showed characteristic absorption bands at about 1700 cm^{-1} and 1650 cm^{-1} , due to C=O stretching vibration from urethane groups and lactam ring, respectively. On the other hand, the spectrum did not exhibit NCO stretching vibration at 2270 cm^{-1} indicating the complete consumption of isocyanate groups in the reaction [18–20].

2.2. Preparation of nylon 6/graphite composites

The preparation of nylon 6/graphite composites was carried in a laboratory scale rotational moulding installation. The polymerization-moulding experiments were performed via a two step process: (1) preparation of the mixture of ϵ -caprolactam, initiator, activator and filler and (2) polymerization of ϵ -caprolactam in the presence of various amounts of graphite microparticles. For this purpose, to half of the total amount of ϵ -caprolactam in the melt state, the initiator and the total amount of graphite were added at 100 $^{\circ}\text{C}$, under stirring in the nitrogen atmosphere. The melt was mixed with the one obtained from the remaining amount of ϵ -caprolactam and the activator by heating under stirring in nitrogen atmosphere, at 100 $^{\circ}\text{C}$. The concentration of initiator (1.0 mol %) and activator (0.4 mol %), respectively were kept constant in all experimental processes. The content of graphite was varied between 0.0 and 15.0 wt % with respect to the total ϵ -caprolactam feed. The melt previously obtained was immediately transferred into a mould which was preheated at 160 $^{\circ}\text{C}$ in order to perform polymerization-moulding process. After 40 min, the polymerization-moulding was complete and products in the form of tubes with a circular section and uniform wall thickness have obtained. Before demoulding, the products were cooled at a rate of about 2 $^{\circ}\text{C min}^{-1}$ while the mould was still rotating.

2.3. Sample preparation

In order to obtain samples for the determination of polymer yield and viscosity measurements the 'as moulded' part was dried, cut, ground up and submitted to a Soxhlet extraction with methanol for 24 h. Subsequently the samples were dried at 95 $^{\circ}\text{C}$ for 48 h and stored in a desiccator over phosphoric oxide. The samples for the determination of mechanical properties were prepared by cutting and milling to dimensions required by the standards (see below) and then were dried at 60 $^{\circ}\text{C}$, to constant weight and stored in a desiccator over phosphoric oxide.

2.4. Methods of investigation

The degree of polymerization of the neat polyamide 6 and polymer matrix, respectively was carried out by viscosity measurements at $25 \pm 0.1^{\circ}\text{C}$ in *m*-cresol solutions with a polymer content of 0.5 wt % (determined after centrifugation of the filler). For the water absorption test, rectangular specimens with dimensions of 50 mm x 50 mm were cut from the tube. Three replicate specimens were tested and the results are presented as average. The samples were dried in an oven at 50 $^{\circ}\text{C}$ for 24 h, cooled in a desiccator and immediately weighed to the nearest 0.001 mg. In order to measure the water absorption of the nylon 6 and nylon 6/graphite composites, all samples were immersed in water, at room temperature as described in ASTM D 570 – 99 standard test method. Excess water on the surface of the samples was removed before weighing.

The percentage increase in weight during immersion was calculated to the nearest 0.01% as follows:

$$\text{Increase in weight\%} = \frac{\text{wet wt.} - \text{conditional wt.}}{\text{conditional wt.}} \times 100$$

A Vertex-70 spectrometer was used to acquire FT-IR data, over a range 400–4000 cm^{-1} , at a resolution of 4 cm^{-1} and co-addition of 100 scans. The non-isothermal crystallization and melting behaviour of the nylon 6 and nylon 6/graphite composites, respectively was studied by DSC using a METTLER DSC 112E that had been calibrated with a standard indium and under a N_2 flow rate of 20 mL/min. The cooling and heating rate of 10°C/min was used. All specimens were weighted in the range of 7 to 10 mg. The as-received sample were first heated to 250°C and then cooled to 25°C. The second heating curve was collected by heating the sample at the same rate to 250°C (see Fig. 3). The degree of crystallinity was determined using the enthalpy of fusion of nylon 6 with 100% crystallinity as 191.064 J/g. [7,9,11,14,15,21,22].

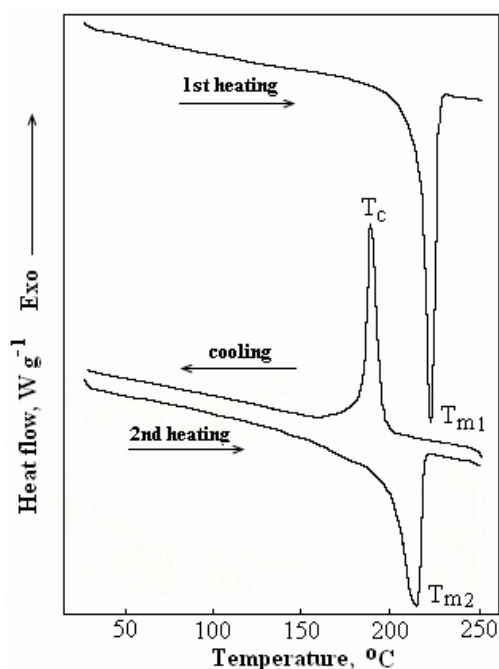


Fig. 3. DSC analysis of nylon 6 composites with 6 wt % of graphite content (PA6-06) consisting of three subsequent scans.

The crystal structures of the nylon 6 and nylon 6/graphite composite materials was followed by wide angle X-ray diffraction analysis (WAXD) as a function of wt % filler added, using a PW 1830 Philips diffractometer (Ni-filtered Cu K α radiation of wavelength 0.1542 nm) in the reflection mode over the range of diffraction angles (2θ) from 5 to 35°, at room temperature. The voltage and tube current were 40 kV and 30 mA, respectively.

Thermogravimetric analysis (TGA) of the extracted samples was carried out using a F. Paulik Derivatograph under air atmosphere with a flow rate of 40 mL/min. About 50 mg of the sample was heated from room temperature to 700°C at a linear heating rate of 10°C min^{-1} . The Izod impact strength of composites was evaluated as a function of filler content (0–15 wt %) and was performed at room temperature on notched samples in accordance with ISO-180-1982. Five specimens for each composition were used for measurement and average values were reported. The flexural properties (flexural strength and flexural modulus) were determined according to ASTM D790-86. All specimens were kept in a sealed desiccator under vacuum for 24 h before mechanical properties measurements. The values reported reflect an average from five measurements.

3. Results and discussion

The polyamide 6/graphite composites were obtained as constituent material of the parts in the form of tubes with a circular section made by activated anionic ring-opening polymerization of ϵ -caprolactam monomer in the presence of various amounts of graphite microparticles. The active caprolactam salts sodium dicaprolactamato-bis(2-methoxyethoxy)aluminate, as initiator and N,N'-[methylene-di(4,4'-phenylene)bis-carbamoyl]bis- ϵ -caprolactam, as activator were used. The content of the graphite powder was varied from 0.0 to 15.0 wt %. The initial polymerization temperature was kept constant at 160 ± 2 °C for all tests. All analyses were performed on the 'as-moulded' and extracted samples as is presented in Section 2.2.

The IR spectra of nylon 6 matrix display stretching and bending vibrations characteristic to amide group which allow their identification. The two strong bands at 1640 cm^{-1} and 1542 cm^{-1} are assigned to the amide I band and to the amide II band, which have main contributions of the C=O stretching and the NH deformation, respectively. The IR bands present at 1476 and 1417 cm^{-1} are attributed to $-\text{CH}_2-$ units adjacent to NH and C=O groups in the extended conformation of the chain in the α crystal modification of the obtained nylon 6 matrix. In the doublet band between 1202 and 1170 cm^{-1} the former band indicates that amide group is in *trans* structure, in α -form crystallinity and latter band corresponds to amorphous state [14,23,24]. The effect of variation in graphite concentration on the characteristics of nylon 6/graphite composites is given in Table 1. The data related to nylon 6 prepared in the same conditions as nylon 6/graphite composite are presented for comparison. As shown in Table 1 the results indicate that the yields and degree of polymerization of polymer matrices were high but somewhat lower than that of pure nylon 6 and decrease with increasing of graphite content in the mixture feed. Similar observations were reported in the literature for polyamide 6/graphite composite materials by Horsky et al. [25].

Table 1. Characteristics for polyamide 6 and polyamide 6/graphite composites.

Code	Graphite, wt %	Polymer yield ^{a)} , wt %	Polymerization degree ^{b)}	Water absorption, ^{c)} %
PA6-00	0.0	97.8	930	2.94
PA6-02	2.0	97.5	840	2.83
PA6-06	6.0	97.0	730	2.72
PA6-08	8.0	96.6	650	2.44
PA6-12	12.0	96.2	570	2.17
PA6-15	15.0	96.0	520	1.95

^{a)}Methanol-insoluble polymer (wt %) (the correction for the filler content was included)

^{b)}Degree of polymerization from viscosity measurements (0.5 gDL⁻¹, m-cresol, 25 °C)

^{c)}According to ASTM 570-81 (variant D)

The thermal properties of nylon 6 and nylon 6 composites with various graphite contents are determined by differential scanning calorimetry, DSC and

thermogravimetric analysis, TGA. Table 2 and Table 3, respectively provide summary of the results.

Table 2. Thermal properties and degree of crystallinity of the polyamide 6 and polyamide 6/graphite composites

Code	Graphite, wt %	First heating			Cooling		Second heating	
		T _{m1} (°C)	ΔH _{m1} (J g ⁻¹)	^{a)} α _{1DSC} (%)	T _c (°C)	ΔH _c (J g ⁻¹)	T _{m2} (°C)	ΔH _{m2} (J g ⁻¹)
PA6-00	0.0	225.0	95.08	54.0	175.6	75.38	220.0	78.14
PA6-02	2.0	222.1	87.14	54.5	179.1	77.59	217.7	81.29
PA6-06	6.0	226.0	95.57	55.5	188.3	83.76	218.6	79.83
PA6-08	8.0	227.2	97.02	57.0	187.9	79.32	219.0	79.89
PA6-12	12.0	227.0	94.53	58.0	188.2	84.69	220.0	80.19
PA6-15	15.0	227.0	95.89	60.5	184.3	81.81	218.6	78.55

Heating/cooling rate 10 °C min⁻¹ (1 and 2 mean first and second heating, c means cooling)

^{a)}Degree of crystallinity by DSC measurements

DSC thermograms of nylon 6 composites with various graphite content, recorded on the first and second run exhibit a single melting endotherm peak (noted T_{m1} and T_{m2}, respectively) associated with the α-form crystals of polyamide 6 [7,26-28], in the 222.1-227.2 and 217.7-220.0 °C temperature range, respectively (see Table 2). The melting temperatures values of polymer matrix slowly decrease from the value for pure nylon 6 to those of its composites containing 2 wt % graphite, after which the melting temperatures slightly increase with increasing graphite content. The initial decrease is probably the result of the weak interaction between nylon 6 and graphite. The DSC results show that graphite content has been a somewhat influence on the melting temperatures of polyamide 6 matrix in these composites. It is well-known that all of the fillers cause an increase in the crystallization temperature (T_c) relative to neat nylon 6 [29]. The crystallization temperature values of composites under study increased with increasing graphite content when the concentration of filler is less than 12 wt. %, and then they

have the tendency of decreasing with the increase of the content of the filler component. The graphite behaved as a nucleating agent for the nylon 6 [7]. After correcting the results for graphite content, the degree of crystallinity of the nylon 6 and nylon 6 composites was calculated from the experimental enthalpy of fusion (ΔH_m) and from the enthalpy of fusion ΔH_m^o of 100% crystalline nylon 6, by using the following equation:

$$\alpha_{\text{DSC}}(\%) = \frac{\Delta H_m}{(1 - \phi)\Delta H_m^o} \times 100$$

where: ΔH_m is the enthalpy of fusion of the sample, ΔH_m^o is the enthalpy of fusion of 100% crystalline sample of the same polymer and φ is the weight fraction of the filler in the composite. The enthalpy of fusion was calculated from the melting peak area, and the maximum of the endotherm and the minimum of exotherm were taken as melting temperature (T_m) and the crystallization temperature (T_c), respectively.

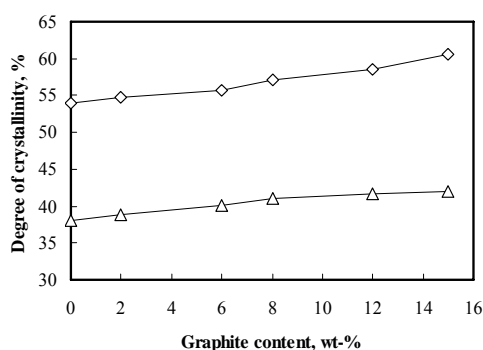


Fig. 4. Degree of crystallinity versus graphite content for Nylon 6 and Nylon 6/graphite composites (□) – first heating; (△) – second heating.

It can be seen from Table 2 and Fig. 4 that the degree of crystallinity of the nylon 6 composites increased with increasing graphite content (the first and second run). Also, degree of crystallinity values of nylon 6 composite in the first run (54.5–60.5%) are higher than that from the second run (38–42%), (see Fig. 2). These results are comparable to those presented in the literature [10,30,31]. Wide angle X-ray diffraction (WAXD) was used as an alternative method to characterize the crystalline nature of the polyamide matrix in these composites. X-ray diffraction patterns of nylon 6 and corresponding composites with different graphite weight contents are present in Fig. 5.

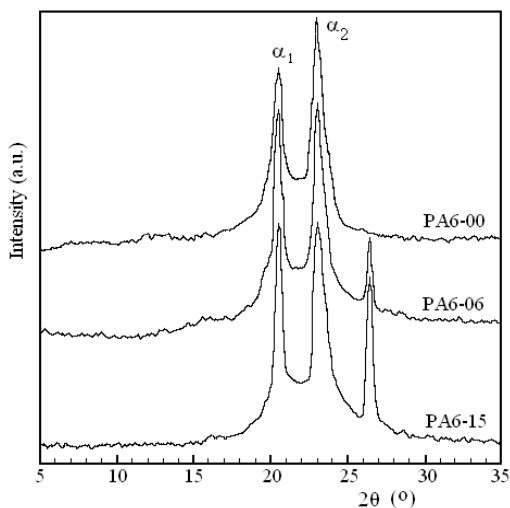


Fig. 5. X-ray diffraction patterns for nylon 6 and nylon 6/graphite composites.

It is seen from Fig. 5 that both the anionic PA 6–00 and the samples of nylon 6 composites show two peaks, near $2\theta = 20.5^\circ$ and 23° , corresponding to the reflections of the crystalline planes (200) and combined (002)/(202) (labelled α_1 and α_2), respectively, indicative of a

monoclinic α -phase morphology. X-ray spectra of the composites present an additional third peak at the Bragg's angle (2θ) of about 26.5° assigned to the (002) reflections in the graphite crystal. An increasing order of the intensity of this peak with increasing filler content was observed. As is expected the peak associated with the γ -phase of nylon 6 matrix is absent in the X-ray spectra of the composites because the graphite retards the formation of this crystalline form. Graphite is a layered material, characterized by strong intralayer covalent bonds and weak van der Waals interactions between successive carbon layers. In contrast with other filler (montmorillonite) graphite is not able to generate hydrogen bonding with $-\text{NH}-\text{CO}-$ units from nylon 6 chain structure [32].

Thermogravimetric analysis (TGA) of the extracted samples was performed using dry air as a carrier gas. The TGA experiments were carried out from room temperature to 700°C at a linear heating rate of $10^\circ\text{C min}^{-1}$. The temperature at which 10% degradation (T_{10}) occurs, representative of the onset temperatures of degradation and the temperature at which the maximum rate of degradation (T_{max}) occurs were taken as a measure of thermal stability. Data obtained by evaluation of the thermal behaviour of nylon 6 and nylon 6 composites related to the temperature corresponding to 10 wt% (T_{10}), the temperature taken for the maximum rate of decomposition (T_{max}) and the residues at 700°C are summarized in Table 3.

Table 3. TGA characteristic data of nylon 6 and nylon 6/graphite composite materials.

Code	Graphite, (wt %)	T_{10} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	Residue (wt-%)
PA6-00	0.0	384	428	4 ± 1
PA6-02	2.0	386	430	7 ± 1
PA6-06	6.0	392	438	11 ± 1
PA6-08	8.0	385	432	14 ± 1
PA6-12	12.0	387	440	17 ± 1
PA6-15	15.0	393	438	19 ± 2

It is seen from Table 3 that the addition of graphite slightly enhances the thermal stability of the nylon 6 composites with graphite loading up to 6% in comparison with pure nylon 6. The onset degradation temperatures for the PA6-06 composites increase by about 8°C compared with the pure nylon 6, whereas the maximum increase of T_{max} is about 10°C for the composite filled with 6.0 wt% graphite. The degradation onset temperature (T_{10}) of PA6 is around 384°C . All the nylon 6 composite materials retained 90% of their weight until around 385°C , in air. This thermal enhancement could be attributed to good thermal stability of filler and to interactions between the polymer matrix and graphite that restrict polymer chain mobility [33]. The major stage of weight loss occurs in the range $430\text{--}440^\circ\text{C}$, and should be associated to the break of amide groups. It is known from the literature data

related to the thermal degradation of the polyamides, that chain scission takes place at the -NH-CO- bonds in the neighbourhood of the carbonyl group [14,34,35]. The differences in the values of the maximum temperatures of degradation are not significant and the weight losses reached about 48 wt-%. A stable char residue was formed, the char yield being between 6.2 and 18.5 %, depending on the composite material composition. The amount of material which is non-volatile at 700 °C, in the case of composites is not significantly more than the amount of graphite that was added as is found in TGA experiments. The examination of the results evidenced that the thermal behaviour of the materials obtained is similar to that reported by Weng et al [36]. Fig. 6 display the thermogram of extracted nylon 6/graphite composite PA6-08 as illustrative example.

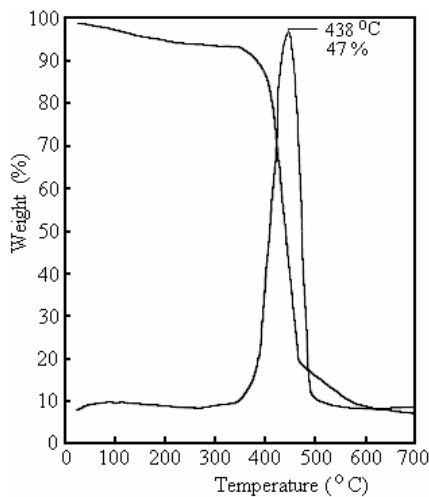


Fig. 6. Thermogravimetric analysis of the nylon 6/graphite composites (PA6-08)

It is well known that polyamide 6 being a semi-crystalline polymer can absorb up to 10 wt % of water from the ambient atmosphere. Water is distributed in to the amorphous phase. This behaviour is a consequence of the fact that -NH-CO- units from the polymer chain are able to generate hydrogen bonds with water molecules and can contribute significant to modifications of polymer characteristics [7,11,37,38]. The absorbed water has been shown to act as an effective plasticizer [7,39,40]. Water absorption is in direct proportion to the weight fraction of nylon matrix from the composite materials but it depends in reverse proportion to the degree of crystallinity of the matrix [39]. The amount of absorbed water was determined from the sample weight increase after dipping of sample in distilled water and the results obtained from the measurements are listed in Table 1. As can be seen from the Table 1, it is evident that the composites absorb less water than pure nylon 6 and water absorption behaviour of nylon 6 composites is determined by filler content.

It is generally known that the properties of the polymer composite materials are obviously determined by the properties of the individual components [41]. Data in the literature [42] indicate that the addition of rigid particles to a thermoplastic matrix results in an increase in modulus and dimensional stability but with sacrifice of toughness and impact strength. The mechanical properties of the nylon 6 and nylon 6/graphite composites were examined, and the effect of graphite content on flexural strength, flexural modulus and notched impact strength for the nylon 6 and nylon 6/graphite composites under study is graphically represented in Figs. 7 and 8.

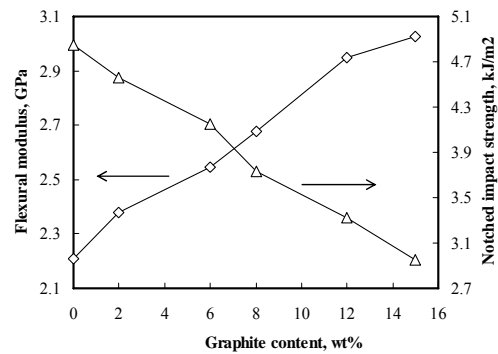


Fig. 7. Notched impact strength and flexural modulus versus graphite content for nylon 6/graphite composites.

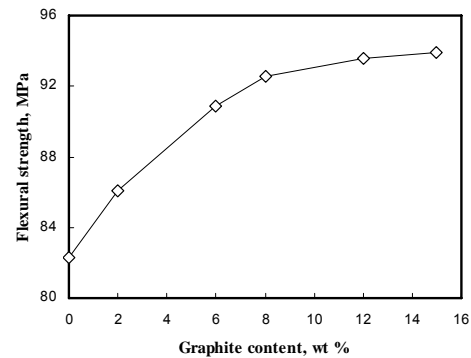


Fig. 8. Flexural strength versus graphite content for nylon 6/graphite composites

From the Figs 7 and 8, it can be seen that the flexural strength and flexural modulus of the nylon 6/graphite composites are increased remarkably with the rise of the graphite content. Figs. 7 and 8 evidence that the addition of the rigid graphite microparticles from 0.0 to 15 wt % increased the flexural modulus and flexural strength of polyamide 6 composites in the range 2.21–3.02 GPa and 82.3–93.9 MPa, respectively. By contrast with the flexural strength and flexural modulus the notched Izod impact strength of polyamide composites has a tendency of decrease. The reduction in impact strength with increasing filler content it is expected, because the graphite filler particles being rigid cannot be deformed by external stress

in the specimen but act only as stress concentrators or crack initiation sites during the deformation process [7,43–45]. Also, as the filler loading increases the tendency for agglomeration increases too and interfacial adhesion becomes weaker. This fact leads to weaker interfacial bonding between the polymer matrix and the filler, which induces microspaces between the filler and the matrix polymer, and that causes numerous microcracks when impact occurs and induces rapid crack propagation through the material. As shown in Fig. 7 the Izod impact strength for our samples decreased from 4.85 to 2.95 kJ/m² when filler loading increase from 0 to 15 wt %. The mechanical properties of the polyamide 6 composites under study are in general agreement with the behaviour expected of polymer composites with rigid fillers [46].

4. Conclusions

Composites with different concentrations of graphite were obtained by in situ anionic ring-opening polymerization of ϵ -caprolactam monomer in the presence of graphite microparticles using rotational molding process at a temperature well below the melting temperature of neat nylon 6. The investigations on the composite samples reveal that the melting temperatures values (T_{m1} , T_{m2}) of polymer matrix show a small decrease up to the content of graphite of 2.0 wt % as compared with that of the pure nylon 6 and then they increase as filler content increases. The crystallization temperatures of the nylon composite materials increase with addition of graphite powder. The degree of crystallinity of the composites increased with increasing graphite content for first and second heating cycles. An increase in flexural modulus and flexural strength as a function of filler percentage added (0–15 wt %), and a decrease in impact strength were obtained. The thermal stability of the nylon 6 graphite powder composites is better than that for of the pure nylon 6. The major stage of weight loss (48 wt %) occurs in the range 430–440 °C, and should be associated to the break of amide groups. A stable char residue was formed, the char yield being between 6.2 and 18.5wt %, depending on the composite material composition.

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