Nylon 6/copper composites by *in situ* polymerization

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Composite materials based on nylon 6 (PA6) and unmodified copper particles, were prepared by *in situ* anionic polymerization of ϵ–caprolactam (CL) in the presence of the metallic fillers using rotational moulding technique. The above materials were characterized by some experimental techniques, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X–ray diffraction (WAXD). The electrical conductivity and mechanical properties of the composites under study were also evaluated. Both molecular weight and crystallinity of the nylon 6 matrix were found to be strongly influenced by the presence of the copper powders. WAXD analysis has evidenced a close relationship between metallic filler used and nylon 6 crystal structure. The presence of copper particles into nylon 6 favours the formation of γ–phase crystal and reduces the fraction of the α–form crystal. For the copper particles incorporated in the nylon 6 matrix only one main peak at $2\theta =43.4°$ was observed. Analysis of the results obtained on nylon 6/copper composite materials with DSC show that the incorporation of copper particles lowers the melting temperatures but rises the crystallization temperatures of the matrix of the composites while its crystallinity degree decreases. The addition of metal particles to nylon 6 played the role of nucleating agent and enhanced the crystallization rate. An improved thermal stability of the nylon 6/copper composite materials with respect to the neat nylon 6 can be noticed. The investigations on the nylon 6/copper composite materials show also that their mechanical properties are superior to those of neat nylon 6 in terms of the flexural strength and flexural modulus, but with sacrificing their impact strength.

1. Introduction

The fields of the engineering plastic, fibers and composites would have been less interesting if it hadn't been discovered aliphatic polyamides. Nylons are one of the most widely used engineering thermoplastics such as in automobile, electrical, electronic, packaging, textiles and consumer applications because of their excellent mechanical properties [1–4]. Often these polymers, especially nylon 6 are preferred as matrices in composite materials which have generated a growing interest for researchers from academic and industrial laboratories. The properties of polymer composites can be tailored by properly choosing the components and their relative concentration. Moreover, other physical properties and processing methods are typical for polymer materials. Polymer materials are often used as insulators because of their low thermal and electrical conductivity. Recently, metallic particles have attracted considerable attention in polymer composites community as fillers for the composite materials with increased mechanical, thermal and electrical properties. All these make composites attractive from point of view of applications and competitivity to other alternative materials. They are useful in many fields of engineering such as antistatic media, thermal fuses, shielding for electromagnetic or radio–frequency interference of electronic devices [5–10]. The preparation of composites can be carried out by various routes such as solvent processing, melt–compounding or *in situ* polymerization [11–17]. The

polyamide 6, currently used as matrix in different composites is obtained by hydrolytically polymerization of caprolactam, especially at industrial scale. The process is performed at about 270 °C for 10–20 h. An alternative way to obtain nylon 6 is through anionic polymerization of the ϵ–caprolactam. This process is performed at 140–170 °C well below the polymer melting temperature at a significantly faster rate. Final conversions can be obtained in 5 to 40 minutes, depending on the type and amount of activator and initiator added. Polymers with high molecular weight and highly crystalline (40–50%) can be obtained. The polyamides thus obtained can be further processed into composites through a variety of melt or solvent blending processes with various fillers. Polymerization–filling technique, new way to produce polyamide–based composites facilitates their preparation in a single step. The monomer is polymerized in presence of the filler. Among the routes that lead to nylon composites, described in the literature *in situ* ϵ–caprolactam anionic polymerization in the presence of various fillers represents one of the best choices for preparation of nylon 6 composites [16,18–24]. The advantages of the anionic polymerization of ϵ–caprolactam have been put to use in reactive polymerization–filling technique for preparation of composites based polyamide 6.

The present article deals with the preparation of the composite materials based on nylon 6 (PA6) and unmodified copper particles, The process was performed by *in situ* anionic polymerization of ϵ–caprolactam (CL)

in the presence of various weight content of copper particles on a laboratory scale rotational moulding installation. The effects of addition of copper as filler on the degree of conversion, molecular weight, melting temperature T_m, thermal stability, crystallization temperature T_c, degree of crystallinity, water absorption of the nylon 6 composites were evaluated. The electrical conductivity and mechanical tests were also performed and the results are discussed herein.

2. Experimental

2.1. Materials

ϵ–Caprolactam (CL) (technical grade, Sigma–Aldrich Chem. Gmbh) was purified according to the literature [16, 25–29]. The copper powder (copper content of >99%), as filler with a mean particles size ranged from 1 to 5μm was supplied by Aldrich Chemical Co., Inc. The filler was preheated at 110 °C in vacuum for 24 h to eliminate possibly absorbed water on the surface of the particles and then it was kept in a desiccator before the use. ϵ–Caprolactam magnesium bromide (1.6 mol/kg concentration in caprolactam) with a melting point of about 70 °C, as initiator, was obtained in our laboratories from ethyl magnesium bromide (3.0 mol L^{-1} in diethyl ether solution) and ϵ–caprolactam under nitrogen atmospheric conditions, according to the procedure described in the literature [26,29,30]. Activator, N,N′–isophthaloyl–bis–ϵ–caprolactam was synthesized in our laboratories by adding 1 mole of isophthaloyl dichloride to 2 moles of ϵ–caprolactam. The HCl formed was neutralized with an amine and the product was recovered. [26,31]; m. p. (DSC), 141 °C (Ref. [32]:139.2 °C). Sulfuric acid (97%) supplied by Riedel–de Haen–Germany and other chemicals were of reagent grade and used without further purification.

2.2. Preparation of nylon 6/copper composite materials

Nylon 6 and nylon 6/copper composites materials were prepared by reactive rotational moulding process via anionic ring opening polymerization of caprolactam in the presence of various weight content of copper particles. The process was performed in a laboratory scale rotational moulding installation. With respect to caprolactam: 1.0 mol% difunctional N,N′–isophthaloyl–bis–ϵ–caprolactam was added as activator, together with 0.4 mol% initiator, ϵ–caprolactam magnesium bromide, while the content of copper particles was varied between 0.0 and 25.0 wt %. Pure nylon 6 was also pepared under similar conditions for the purpose of comparison. The initial polymerization temperature (initial mould temperature) (160 ± 2 °C) were kept constant in all experimental processes. The details related to the obtained nylon 6 and nylon 6 composite materials was presented in previously published articles [16,20–23,29]

2.3. Sample preparation

In order to obtain samples for the determination of the degree of conversion (DC) and viscosity measurements the 'as moulded' part was dried, cut and ground up. The removing of unreacted caprolactam monomer was carried out by extraction with methanol in a Soxhlet apparatus. The samples for the determination of mechanical properties were prepared by cutting and milling to dimensions required by the standards (see below). The samples were dried in vacuo at 60 °C until constant weight was reached and stored in a desiccator over phosphoric oxide.

2.4. Methods of investigation

The degree of conversion (DC) was estimated using samples of polymer and composite materials parts that were dried and weighed before and after Soxhlet extraction with methanol for 16 h. Whereas the monomer caprolactam dissolves easily in methanol, the polyamide 6 does not.

The degree of conversion was determined according to Eq. (1).

$$DC = \frac{W_{pol}}{W_{tot}} \times 100 \qquad (1)$$

where (w_{pol}) is weight of the sample before extraction with methanol and (w_{tot}) is weight of the sample after extraction with methanol.

The weight–average molecular weight ($\overline{M}_w$) of both neat nylon 6 and nylon 6 composite materials was determined from viscosity measurements. The solutions were obtained from samples prepared as is presented in section 2.3. Solution viscosity was measured in a suspended level Ubbelohde viscometer (capillary II) at 25±0.1 °C in 97% H_2SO_4 after centrifugation of the metal filler. A single–point measurement at a concentration of 0.2 g dL^{-1} was used to obtain an approximation of the molecular weight for each sample according to the method discussed in [26,33].

Water absorption values of both neat nylon 6 and nylon 6 composite materials were calculated from the weight differences between the sample (rectangular specimens with dimensions of 50.4mm x 50.2 mm x 4 mm) dried and soaked in distilled water at room temperature as described in ASTM 570–81 (variant D). Test samples were conditioned for 24 h, at 50 °C before immersing them in distilled water. Excess water on the surface of the samples was removed before weighing. The percentage increase in weight during immersion was calculated according to Eq. (2).

$$\text{Increase in weight } \% = \frac{\text{Wet wt. - Reconditioned Wt.}}{\text{Reconditioned Wt.}} \times 100 \quad (2)$$

Three replicate specimens were tested and the results are presented as average.

The crystal structures of nylon 6 and nylon 6/copper composite samples were followed by X–ray diffraction analysis (WAXD) as a function of metal particle fillers content, using a PW 1830 Philips diffractometer (Ni–filtered Cu–K$_\alpha$ radiation of wavelength 0.1542 nm) in the reflection mode over the range of diffraction angles (2θ) from 5 to 45°, at room temperature. The voltage and tube current were 40 kV and 30 mA, respectively. Mettler DSC 112E differential scanning calorimeter calibrated with indium was used for the evaluation of the thermal characteristics of the nylon 6 and nylon 6/copper composite materials. The measurements were carried out under dry, oxygen free nitrogen flowing at a rate of 40 mL/min to protect the materials from degradation. The weight of samples was in the range of 7–10 mg. The samples were not dried before measurements. All samples were first heated from 25 to 250 ^{o}C, and then cooled to 25°C and finally heated a second time from 25 to 250 ^{o}C at a rate of 10 ^{o}C/min (see figure 1).

After correcting the results for filler content, the degree of crystallinity of both nylon 6 and nylon 6 matrix was calculated by assuming the enthalpy of fusion (ΔH_m^o) for 100% crystalline nylon 6, to be 191,064 J/g [20,25,26,29,34].

The thermal stability of nylon 6/Cu composite materials and neat nylon 6 was investigated by TGA using a F. Paulik Derivatograph Q–1500D thermal analyser under air flow from 50 to 700 ^{o}C at the heating rate of 10 ^{o}C min^{-1}.

The mechanical measurements on materials under study were performed just after the drying procedure to avoid water absorption prior to testing.

The notched Izod impact strength and flexural properties (flexural strength and flexural modulus) were determined according to ISO–180–1982 and ASTM D790–86, respectively.
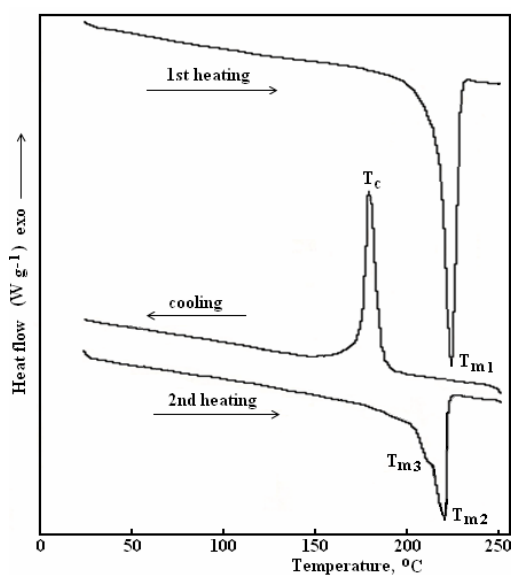
The values reported reflect an average from five measurements. The volume electrical conductivity in the polyamide 6 composite materials was measured according to ASTM D257. In order to achieve good electrical contact between the sample surface and the electrode of the conduction tester an electro–conductive solution was used.

3. Results and discussion

Composite materials based on nylon 6 and copper commercial fillers were prepared by using *in situ* anionic polymerization of ∊–caprolactam in the presence of various weight content of copper particles as a fillers on a laboratory rotational moulding installation. The nylon 6 and nylon 6/copper composite materials were obtained as constituent material of the parts in the form of tubes with a circular section. The content of the copper particles was varied from 0.0 to 25.0 wt %.

The active caprolactam salt, ∊–caprolactam magnesium bromide, as initiator and N,N'–isophthaloyl–bis–∊–caprolactam, as activator were used. The initial polymerization temperature was kept constant at 160 ± 2 ^{o}C for all tests. The determinations were performed on the samples prepared as is presented in Section 2.2.

The influence of the initial copper particles concentration on the degree of conversion (DC), the intrinsic viscosity [η], weight–average molecular weight ($\overline{M}_w$) and water absoption of neat nylon 6 and nylon 6/copper composite materials is presented in Table1. Incorporating of metal particles into the polymerization–moulding mixture the degree of conversion shows a small decrease of approximately 0.4–2.7 wt.% when copper as the initial filler content increases from 2.0 to 25.0 wt.%. As can be observed in Table 1, the degree of conversion of caprolactam monomer in neat nylon 6 was 97.8 wt %. In the case of nylon 6 composite materials the degree of conversion in the nylon 6 matrix was between 95.1–97.4 wt %. These results evidenced that the copper additions have no obvious effect on monomer conversion.

Fig. 1. DSC curves of nylon 6/copper composite materials (Pa6/8% Cu)

Table 1. Characteristics of both composite materials and neat nylon 6.

Sample	Copper, (wt–%)	Degree of conversion [a], wt %	[η] [b] (dl g^{-1})	$\overline{M}_w \times 10^3$ [c]	Water absorption, [d] wt %
PA6/0%Cu	0.0	97.8	2.54	99.4	2.94
PA6/2%Cu	2.0	97.4	2.35	84.8	2.81
PA6/6%Cu	6.0	97.1	2.13	79.5	2.73
PA6/8%Cu	8.0	96.5	1. 98	74.0	2.48
PA6/12%Cu	12.0	96.2	–	–	2.30
PA6/15%Cu	15.0	96.0	1.89	70.6	2.21
PA6/20%Cu	20.0	95.3	–	–	2.01
PA6/25%Cu	25.0	95.1	1.81	67.0	1.98

[a] Methanol–insoluble polymer (wt %) (correction for the filler content was included).
[b] 0.2 g dl^{-1}, 97 % H$_2$SO$_4$, 25 ^{o}C (intensity method) [26,33]
[c] M$_w$ was calculated by equation $\overline{M}_w = 2.81 \times 10^4 [\eta]^{1.35}$ [35,36]
[d] According to ASTM 570–81 (variant D).

The weight–average molecular weight ($\overline{M}_w$) of neat PA6 and hybrid samples was estimated by intrinsic viscosity measurement (intensity method) [33] using Eq. (3)]:

$$\overline{M}_w = 2.81 \times 10^4\, [\eta]^{1.35} \qquad (3)$$

Molecular weights values of all samples determined by viscosity measurement are shown in Table 1. As shown by the data of Table 1, the addition of the metallic filler affects the intrinsic viscosity [η] and weight–average molecular weight ($\overline{M}_w$) of nylon 6 matrix prepared in the presence of the copper which decreased as the amount of the filler increased. The values of the $\overline{M}_w$ of the nylon 6 matrix prepared in presence of copper powder were between 84800 and 67000 g/mol, while the value corresponding to the pure nylon 6 was 99400 g/mol. The values of the intrinsic viscosity [η] of the nylon 6 composite materials were between 2.35 and 1.81 and the value corresponding to the pure nylon 6 was 2.54. Indeed, [η] and $\overline{M}_w$ of the composite materials were found to be lower, as compared to that of neat nylon 6. It is well known that filler particles has an inhibiting role on anionic polymerization [16,37]. Consequently, we can draw the conclusion that copper particle fillers act as inhibitor on anionic ring opening polymerization of the caprolactam.

The amide groups in the aliphatic polyamides are able to generate strong electrostatic forces between the –NH– and the –CO– units (hydrogen bonds), resulting in high melting points, exceptional strength, high barrier properties and excellent chemical resistance. In addition, the amide units also form strong interactions with water, causing the polyamides to absorb water in a range between 2 and 10%. Amorphous phases are more vulnerable to water penetration than crystalline phases, which are considered as impermeable to water. The water molecules are inserted into the hydrogen bonds, loosening the intermolecular attracting forces and acting as an effective plasticizer. This effect drastically increases the elastic properties of polyamide such as: flexibility, elongation at break and impact strength, but with sacrifices in flexural properties and glass transition temperature [16,26,27,38,39]. Water absorption behaviour of the polymer composite materials is determined by factors such as processing techniques, matrix and filler characteristics, polymer/filler ratio, and duration of immersion in water. From Table 1 it can be seen that the water absorption of the nylon 6/copper composite materials decreased as the copper filler content in the polymerization–moulding mixture increased, because the weight fraction of the remaining nylon, responsible for water absorption decreases with increasing of the filler weight fraction. A similar observation was made by Gh. Rusu et. al [29] in the case of polyamide 6/graphite composites.

In order to obtain more information about the effect of metallic filler on melting and crystallization behaviours of nylon 6/copper composite materials, non–isothermal thermal analyses are applied to the samples. The non–

isothermal crystallization conditions are much more closer to the real processing conditions in comparison with isothermal crystallization conditions ones.

It is well known that semicrystalline polyamide 6 can exhibit, two main crystalline forms, the stable monoclinic α–form and unstable monoclinic γ–form [16,40,41]. The γ–forms can reorganize into the α–form during the DSC scan. The melting temperatures (the first and the second heating), crystallization temperature T_c and degree of crystallinity of pure nylon 6 and nylon 6/copper composite materials were evaluated by differential scanning calorimetry (DSC). DSC thermograms of nylon 6 and nylon composite materials with copper particles recorded on the first run displayed a single endothermic peak (noted as T_{m1}), referred to the melting of α–crystalline phase of their polyamide 6 sequences [16,42–44]. On the second heating scan appear two endothermic melting peaks (T_{m2}) and (T_{m3}). The second heating process, after the first cooling, reveals the existence of two main crystalline phases (α and γ) of polyamide in each samples studied (see Fig 1).

The variation of the melting temperature and degree of crystallinity (first run) (measured by DSC) for neat nylon 6 and its composite with the addition of copper filler is shown in Fig. 2.
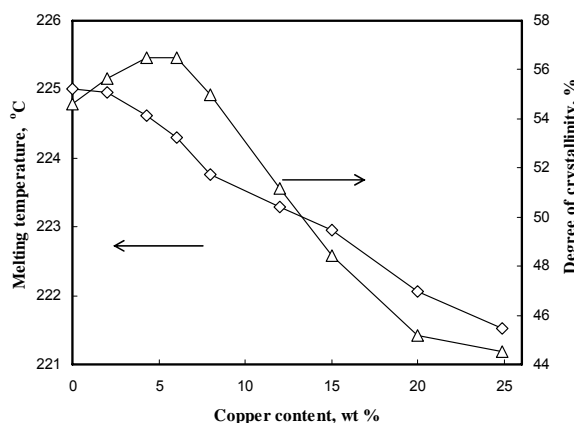
Fig. 2. Variation of the melting temperature and degree of crystallinity (DSC, first heating, 10 °C min⁻¹) of nylon 6 and its composites versus copper particles filler content (◇) – melting temperature; (△) – degree of crystallinity

It can be seen from Fig. 2 that the melting temperature values T_{m1} (first run) of nylon 6 composite materials decrease with the addition of the copper particles, while the degree of crystallinity values increases initially, through a maximum at 6.0 wt% of filler and thereafter diminished progressively with the filler content. The melting temperature T_{m1} (firt run) of the polyamide copper composite materials decreases from 225 to 221.5°C for filler contents ranging within 0–25 wt %. This phenomenon may be related with the reduction in crystallite size due to the incorporation of the copper in the crystalline regions of the polyamide 6 [24,45]. The

decrease of the crystallinity degree of the composite materials (for copper content higher than 6%) can be explained by using the copper particles, which can hinder the motion of the polymer chains segments and, thus, retard crystal growth [16].

The degree of crystallization α_{DSC} (first and second run), of the nylon 6 component was calculated according to Eq. (3):

$$\alpha_{DSC}(\%) = \frac{\Delta H_m}{(1 - \varphi)\Delta H_m^o} \times 100 \qquad (3)$$

where α_{DSC} – degree of crystallization of nylon 6 component, ΔH_m^o – enthalpy of fusion for 100% crystalline nylon 6, ΔH_m – enthalpy of fusion for the nylon 6 and nylon6/copper composite materials and φ – weight fraction of the copper filler in the composite materials.

The results presented in the fig. 3 show that the crystallization temperature increases with the incorporation of the copper particles.
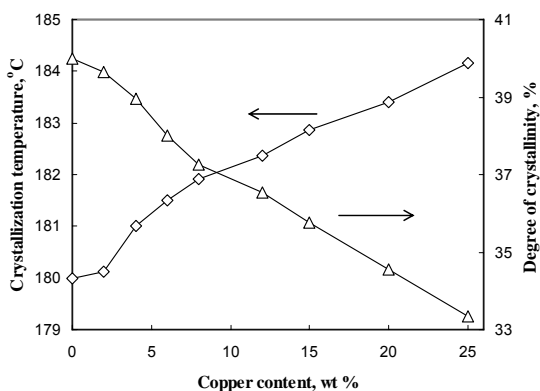

Fig. 3. Variation of the crystallization temperature and degree of crystallinity (DSC, cooling, 10 °C min⁻¹) of nylon 6 and its composites versus copper particles content (◇) – crystallization temperature; (△) – degree of crystallinity.

This behaviour can be explained by using the presence of copper particles, which can act as nucleating agent and increase the nucleation ratio [46,]. The results are in agreement with the literature data [47,48].

In Fig. 4, the variation of the melting temperature and degree of crystallinity (the second heating process, after the cooling) measured by DSC with the filler content is shown.

It can be seen from figure 4 that in the second heating process, after the cooling, the melting temperature, T_{m2} of the nylon 6 composite materials showed initially a tendency to increase with the increase of the content of the filler component, possessed a maximum value at 6.0 wt.%. Further increasing the filler content leads to a decrease in T_{m2} values of nylon 6 composite materials.
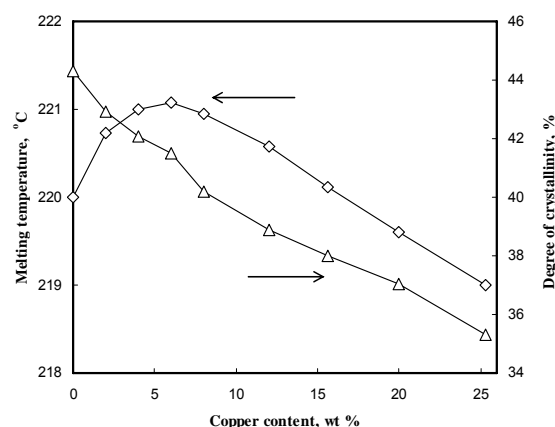

Fig. 4. Variation of the melting temperature and degree of crystallinity (DSC, second heating, 10 °C min⁻¹) of nylon 6 and its composites versus copper particles content (◇) – melting temperature; (△) – degree of crystallinity

The degree of crystallinity, α_{DSC} (the second heating) of nylon 6 composite materials diminished continously from 42.2 to 33.2% for filler contents ranging within 0–25 wt % (see Fig. 5). From Figs. 3 and 5 it can be observed that the degree of crystallinity values of nylon 6 composite in the first run (47,3–56,5%) are higher than that from the second run (36,5–44,3%), (see Fig. 3 and 5). These results are comparable to those presented in the literature [49–51]. The lower degree of crystallinity ascertained in the second heating indicate (Figs. 3 and 5) that the conditions for crystallization during cooling are much less favourable than those in the course of the polymerization–moulding [49]. The lower melting temperature observed in the second heating reflects imperfections of the crystalline phase formed during the cooling (crystallization of all specimens under identical conditions).

Fig. 5 illustrates the X–ray diffraction patterns of neat nylon 6 and nylon 6/copper composite materials with different proportions of copper filler. The sharp diffraction peaks that are observed at $2\theta = 20.5°$ and $23.0°$ correspond to α_1– and α_2–form crystal, respectively of the nylon 6. The α_1 orginates from the distance between hydrogen–bonded chains, whereas α_2 comes from the distance between hydrogen–bonded sheets. Thus is evidenced that α–form crystal is the dominant crystalline phase for nylon 6. In the case of the nylon 6/copper composite materials in addition to the two reflections peaks, another reflection is also observed at $2\theta=21.6°$, which is related to γ crystal planes of nylon 6. The presence of copper particles into nylon 6 favours the formation of γ–phase crystal and reduces the fraction of the α–form crystal. Moreover, for the copper particles incorporated in the nylon 6 matrix as mentioned above, only one main peak at $2\theta = 43.4°$ was observed. The reflections associated with γ–phase crystal and copper particles become prominent with the increasing of the cooper concentration.
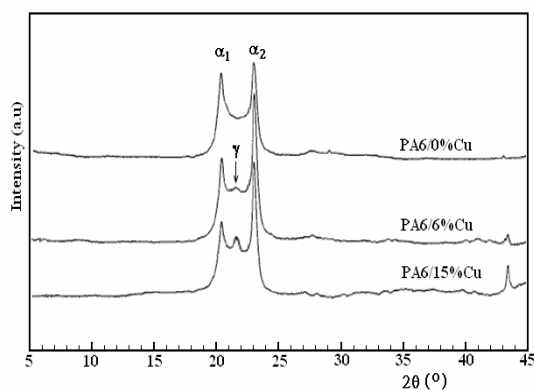
Fig. 5. X–ray diffraction patterns of pure PA6 and PA6/Cu composite materials from 5° to 45° of 2θ.

The evaluation of the thermal behaviour of the nylon 6 and its composites was carried out using the data obtained from measurements by thermogravimetry analysis (TGA). Table 2 shows the effect of copper particles content on thermal stability of composites under study. The TGA experiments were performed in air in the temperature range from 25 to 700 ºC at a linear heating rate of 10 ºC min^{-1}. The temperature representative for the onset temperatures of degradation, T_{10} and T_{max}, the temperature corresponding to the maximum rate of degradation were taken as measure of thermal stability.

The data gained in table 2 reveals a slight increase in the thermal stability of nylon 6–Cu composite materials, as function of the amounts of added copper with respect to the neat nylon 6 was observed. Compared with the control neat nylon 6, which had a thermal decomposition temperature T_d of 428.0 ºC, the nylon 6/copper samples have higher T_{ds}, with values in the range 433.0–450.0 ºC (see table 2), when the copper content increases from 2.0 to 25.0%. This behaviour is justified by the fact that metallic components of composites themselves had good thermal stability.

Table 2. The thermogravimetric analysis (TGA) data of nylon 6 and nylon 6/copper composites.

Sample	Copper (wt–%)	T_{10} (ºC)[a]	T_d (ºC)[b]	Residue (%)
PA6/0%Cu	0.0	384.0	428.0	4.8
PA6/2%Cu	2.0	388.2	433.4	6.5
PA6/4%Cu	4.0	391.5	437.6	8.6
PA6/6%Cu	6.0	394.2	441.3	10.2
PA6/8%Cu	8.0	397.3	445.3	12.5
PA6/12%Cu	12.0	398.2	446.2	16.7
PA6/15%Cu	15.0	399.3	447.5	20.6
PA6/20%Cu	20.0	401.3	449.1	24.7
PA6/25%Cu	25.0	402.2	450.5	29.5

[a]Polymer decomposition temperature at which 10% weight loss was recorded on TG curve at a heating rate in air of 10 ºC/min.
[b]Polymer decomposition temperature determined by the position of the maximum on the differential TGA curve.

On the other hand by the introduction of metallic filler into nylon 6 matrix the macromolecular chains mobility are restricted due to the interactions between polymer the and copper particles [52]. It is known that the thermal degradation of the aliphatic polyamides occurs by chain scission takes place at the –NH–CO– bonds in the neighbourhood of the carbonyl group [24,28,53,54].

Fig. 6 shows the thermogravimetric analysis (TGA) curves for the pure nylon 6 (PA6/0%Cu) and nylon 6/copper composites with 6.0 (PA6/0%Cu), 15.0 (PA6/15%Cu) and 25.0 wt % of copper, respectively (PA6/25.0%Cu) pyrolysed under dry air flow. A stable char residue was formed, the char yield being between 6.5 and 29.5 % (see table 2), depending on the composite material composition.
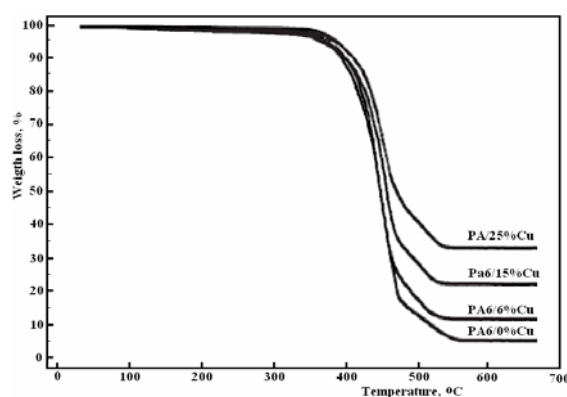

Fig. 6. The thermograms of the neat nylon 6 and the nylon 6/copper composites with 6.0, 15.0 and 25.0 wt % copper.

The amount of material which is non–volatile at 700 ºC, in the case of composites is not significantly more than the amount of copper that was added as is found by TGA analysis.

A general analysis of the mechanical properties of nylon 6/copper particles composite materials indicates that the presence of the metallic filler into the polymer causes the modiffication of these properties. The results related to the variations in flexural strength, flexural modulus and notched impact strength with copper filler by weight procentage for the composites preparate in this study are given in Table 3. For comparison, the properties of neat nylon 6 are also shown in this table. These results show that the addition of copper filler leads to a substantial increase in flexural modulus for all composite materials. Nearly similar trends were observed for flexural strength, as shown in Table 3. Flexural strength of the polyamide 6/copper composite materials has direct dependency to the copper content. Take the mechanical properties of pure nylon 6 as a reference, the flexural strength and flexural modulus increased in the range 2.57–3.42 GPa and 85.4–95.7 MPa, respectively, for the nylon composites when the copper content increases from 2.0 to 25.0%. By contrast with the flexural strength and flexural modulus, the Izod impact strength of nylon 6/copper composite materials has a tendency of decrease, when the copper content increases

from 0.0 to 25.0%. This decreasing in impact strength of nylon composites can be attributed to: (i) immobilization of the polyamide chains by the metallic fillers, which limits their ability to deform freely and so makes the material more brittle [20,22–24,] and (ii) each particle behaves as a site of stress concentration and can act as a microcrack initiator [16].

Table 3. Mechanical properties of the nylon 6 and nylon 6/copper composites.

Code	Copper (wt%)	Notched impact strength (kJ/m^2)	Flexural modulus (GPa)	Flexural strength (MPa)
PA6/0%Cu	0.0	4.97	2.21	82.3
PA6/2%Cu	2.0	4.90	2.57	85.4
PA6/4%Cu	4.0	4.73	2.82	87.7
PA6/6%Cu	6.0	4.26	2.98	89.9
PA6/8%Cu	8.0	3.91	3.10	90.4
PA6/12%Cu	12.0	3.53	3.16	92.2
PA6/15%Cu	15.0	3.35	3.31	93.4
PA6/20%Cu	20.0	3.15	3.35	95.1
PA6/25%Cu	25.0	3.05	3.42	95.7

The mechanical properties of the polyamide 6 composites under study are in general agreement with the behaviour expected of polymer composites with rigid fillers [23,24].
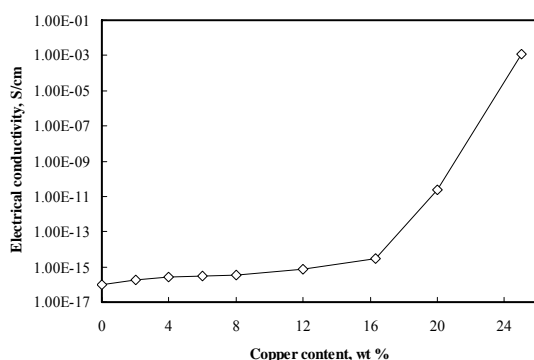

Fig. 7. The variation of the volume electrical conductivity of nylon 6 and nylon 6/copper composites as a function of the metallic filler content.

The electrical conductivity of a polymer composite materials is generally characterized by its dependence on the filler volume fraction. In the case of composite materials with low filler content their conductivity is still very close to that of the pure polymer. When filler content exceeds some critical value, called the percolation threshold, the conductivity of composite materials drastic increases. Thus enough filler has been added so that it begins to form a continuous conductive network through the composite. The conductivity of composites can reach values close to that of the filler material.

Fig. 7 shows the variation of the volume electrical conductivity of nylon 6 and nylon 6/copper composite materials as a function of the metallic filler content. Like most polymers, nylon 6 is not electrically conductive and its room temperature, its volume conductivity in a dry state is as low as about 10^{-15} S/cm [55]. Electrical conductivity value of copper filler is 5.96×10^5 S cm^{-1} [56]. The addition of copper significantly improved the conductivity of nylon 6 with a sharp transition from an electrical insulator to an electrical semiconductor. The nylon 6/copper composite materials exhibited a percolation threshold of about 20.0 wt % (3.11 vol %.) copper particles. At 20.0 wt % of copper content, conductivity for the nylon 6/copper composite materials is about 5 orders of magnitude higher than that of the neat nylon 6.. The increasing in electrical conductivity at higher filler concentration is attributed to the enhanced number of conductive paths in the composites.

4. Conclusions

A series of the nylon 6/copper composite materials with various content of the copper particles were prepared. The reactive rotational moulding technique *via* anionic polymerization of the ε–caprolactam in presence of the metallic fillers was used in this aim. The polymerization–moulding process was performed at 160°C, well below the melting temperature of the nylon 6 (T$_m$ ~225°C). The intrinsic viscosity and molecular weight of the nylon 6 matrix were found to be strongly influenced by the presence of the copper powders. The influence of cooper content on monomer conversion is insignificant. The results evidenced a decrease in water absorption of the nylon 6/copper composite materials as the copper filler content in the polymerization–moulding mixture increased. As is expected the peak associated with the γ–phase of nylon 6 matrix appear in the X–ray spectra of the composites. The TGA measurements show that the thermal stability of the polyamide 6/copper composites is better than that of the pure polyamide 6. The incorporation of copper particles leads to decrease of the melting temperatures, but it increase the crystallization temperatures. The investigation on nylon 6/copper composites materials show that their mechanical properties are better in comparison with those corresponding to neat nylon 6 in terms of the flexural strength and flexural modulus, but with sacrificing their impact strength. The presence of copper particles leads to increase of the

electrical conductivity of the resulting composites, which exhibited a percolation threshold of about 20.0 wt % (3.11 vol %.) copper particles content.

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