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## NEW THERMOPLASTIC POLYAMIDE-CLAY HYBRID NANOCOMPOSITES FOR HI-TECH APPLICATIONS

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**Abstract:** *Three series of new polyamide-clay hybrid nanocomposites were prepared using a ternary copolyamide as thermoplastic matrix and various layered silicates. The copolyamide (coPA), having a lower melting point with respect to the initial homopolymers and competitive hot-melt adhesive properties, appears to be a promising matrix for new hybrid nanocomposites. Materials with three different smectite clays as filler (bentonite, montmorillonite K10 and Nanomer I.30P) were prepared by a solventless melt mixing process, in order to evaluate the specific influence of filler on the properties of new hybrid materials. Nanocomposites were preliminarily investigated by the means of FTIR spectroscopy and, subsequently, samples were submitted to thermal analysis by DSC and TG. The results have evidenced the inclusion of nanofillers in the coPA matrix, while the thermal study evidenced the decrease of the glass transition temperature ( $T_g$ ), along with an enhanced thermal stability of nanocomposites.*

**Keywords:** *polyamide, clay, hybrid materials, nanocomposites, thermal behaviour*

### 1. INTRODUCTION

Minerals have been added to thermoplastic polymers since the 1930s for various reasons, mainly to reduce the cost of the end products because many fillers have spectacular low-volume costs compared to thermoplastics. The term “*mineral fillers*” has been also used fairly broadly to include any particulate material, whether inorganic, natural or synthetic in origin (*i.e.*, short glass fibers) used as reinforcement [1]. It has been demonstrated that fillers play substantial roles in modifying the properties of various thermoplastics. The addition of these mineral fillers is an effective way to improve not only mechanical properties (elongation and stress at break, impact strength) of polymeric materials, but others characteristics as well, such as: thermal stability, gas barrier, flammability, ion

conductivity, anti-ablative properties, electro-rheological sensitivity [2]. In comparison with these benefits, costs reduction has become less important and the attention of researchers has been focused on the improvement of properties that could be achieved by using these fillers. Several factors that influence the processability and mechanical properties of polymer composites must be taken into account. These include the nature and amount of added filler, the average particle size, interactions between fillers and polymer matrix, as well as interactions between filler particles themselves, yielding in strong agglomerations [3-7].

The field of polymer-silicate hybrid nanocomposites has recently gained an increased attention. Use of clays to obtain polymer nanocomposites allowed new materials with tailored properties and

expanded the range of applications of the original polymers.

Two major findings pioneered the revival of these materials. First, the report on a new nylon 6-montmorillonite material from Toyota research department [8,9], where very moderate inorganic loadings was proven to yield in concurrent and remarkable enhancement of thermal and mechanical properties. Second, Giannelis found that it is possible to melt-mix polymers with clays without using organic solvents [10]. Since then, the high promise for hi-tech industrial applications (transportation and automotive industry, aeronautics, electronics & IT, construction) has motivated research, which revealed dramatic enhancement of many materials properties by the nanodispersion of inorganic layered silicates. Since all these improvements are due to the specific nanocomposite structure and interactions, it seems realistic to anticipate that the principle is generally applicable across a wide range of polymers. Still, further studies on polymer-clay pairs compatibility are of interest.

There is a real potential for this new class of polymeric hybrid materials to replace classic composite materials in the future. Consequently, it is important to understand the role of the clay composition, structure and interactions in enhancing the final material properties. Since the thickness of one clay platelet is on the order of 1 nm, it is decisive to elaborate experiments and models that can provide insight into the deformation process at the molecular level.

Various authors have also investigated the properties of this new class of nanocomposites as a function of processing conditions, degree of exfoliation of nanoclay and type of surfactant [11-15]. Studies on the effects of layered silicate nanoscale dispersion in melt compounded polyamide matrices are reported in literature [16-19]. However, there are still not so many articles concerning the copolyamide-silicate hybrid nanocomposites [20-25]. Actually, scarce literature reports upon the application of bentonite-type clays in thermoplastic nanocomposites, such as (co)polyamides [26-30].

Therefore, the purpose of this study is to investigate new polyamide-clay hybrid

nanocomposites obtained using a copolyamide (coPA) as matrix and a specific type of bentonite from Valea Chioarului (Maramures, Romania), prepared by the melt compounding technique. The use of the native bentonite as filler for nanocomposites was investigated as an alternate option to other commercial clays, because this bentonite is less expensive than pure montmorillonite.

For a better understanding of the processing-structure-properties relationship of the new nanocomposites, their structure and the thermal behaviour have been preliminarily investigated. The comparative study of properties of new composites with native and standard commercial silicate clays was performed in order to estimate the competitiveness of native bentonite based nanocomposites.

## 2. EXPERIMENTAL

### 2.1 Materials

*The matrix – the copolyamide (coPA)* was prepared in the “Petru Poni” Institute of Macromolecular Chemistry from Iasi (Romania) and was synthesized by direct melt polycondensation through a “one-pot” technique previously described [31]. Main characteristics of coPA are:  $M=2800-3000$  g/mol; melting temperature interval= $125-135^{\circ}\text{C}$ ; Vicat softening point= $118^{\circ}\text{C}$ ; melt flow index (MFI, 2.16 daN/ $190^{\circ}\text{C}$ ) =  $18-20^{\circ}\text{C}$ ; density (at  $23^{\circ}\text{C}$ )= $1.11$  g/ $\text{m}^3$ .

*Fillers - Na-bentonite (BTN)* was collected from Valea Chioarului (Maramures, Romania) and was supplied by S.C. Mateo S.R.L. BTN is a mixture of silicates, mainly montmorillonite (over 70%), with different size particles, and minor components such as quartz, mica, chlorite and feldspat [32-34]. Typical properties for the raw bentonite: powder presentation, light cream colored, specific surface area= $25-30$   $\text{m}^2/\text{g}$ ; specific gravity= $260-300$  g/L.

Data concerning the bulk chemical composition of BTN, presented in Table 1, indicate a very high content of silica and Na, and a low content of iron oxide, as compared with other Romanian bentonites [35].



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Table 1. Chemical composition of the native bentonite from Valea Chioarului (Maramures, Romania)

Com- ponent	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O + K <sub>2</sub> O	H <sub>2</sub> O
%	75.04	14.32	1.64	1.16	2.41	1.86	3.57

Other samples from related geological sites in Valea Chioarului were extracted and analysed prior to use. Results showed their composition vary within narrow limits, which is a solid indication on the composition homogeneity of the native bentonite deposit [32,36].

**Montmorillonit K10 (MMT)** was purchased from Sigma-Aldrich Company (USA). MMT was a high-purity grade and used as received (Table 2). Main characteristics: white powder; surface area 220–270 m<sup>2</sup>/g; bulk density=300-370g/L.

Table 2. Chemical composition of the Montmorillonite K 10 nanoclay [37]

Com- ponent	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	H <sub>2</sub> O*
%	43.77	18.57	1.02	1.03	35.61

\* amount of water lost through calcination at 150-1000°C

Table 3. Elemental composition of Nanomer I.30P by XRF [38]

Ele- ments	Si	Al	Mg	Na	Ca	Fe	O
%	39.03	13.46	2.59	0.18	0.23	2.19	41.83

**Nanomer I.30P** was purchased from Nanocor Inc., USA (Table 3). It represents a natural montmorillonite which was organically modified by octadecylamine (ODA) (70-75% montmorillonite and 25-30% ODA). Characteristics: white powder; density=1.7 g/cm<sup>3</sup>; mean dry particle diameter=10-25 μm, interlayer distance=2.10 nm.

## 2.2 Preparation of the coPA-clay hybrid nanocomposites

### Drying

Prior to processing, all materials were dried at 80°C in an oven for 24 hours, up to remanent moisture below 0.2 wt%, in order to prevent bubble formation and polymer hydrolytic degradation during processing.

### Melt compounding

After drying, the pre-calculated amounts of clay (5wt%) and polymer were premixed in a tumble mixer. A Haake Rheocord 9000 mixer was used for the preparation of the coPA-clay hybrid materials. The processing conditions were fixed to assure a good dispersion of clay on the matrix: temperature=160°C, rotating speed=100 rpm; mixing time = 7 min. For comparison, neat coPA was also melted in the mixer under the same processing conditions.

### 2.3 Characterization

The FTIR spectra (KBr pellets) were recorded in the range of 4000-400 cm<sup>-1</sup>, using a Bruker Vertex 70 spectrometer.

The DSC measurements were performed under nitrogen atmosphere by using a TA instrument from Perkin-Elmer (USA), Pyris Diamond model.

Thermal gravimetric (TG) analysis was performed on a Mettler Toledo TGA-SDTA 851 device, in air stream, with a heating speed of 10 K/min, in the temperature range of 25-700°C, using samples of 4-6 mg.

## 3. RESULTS AND DISCUSSION

**3.1 FTIR spectroscopy analysis.** Fourier transform infrared (FTIR) spectroscopy is most useful for identifying chemical bonds and their absorption spectra are almost like molecular fingerprints. In order to determine various functional bonds formed during the melt blending, FTIR was performed on the matrix, clays and hybrid composite samples.

Figure 1 presents the FTIR spectra of clays selected for our study, whilst Figure 2 shows FTIR spectra of coPA and its nanocomposites (all spectra have the same absorbance scale, but are vertically displaced for clarity).

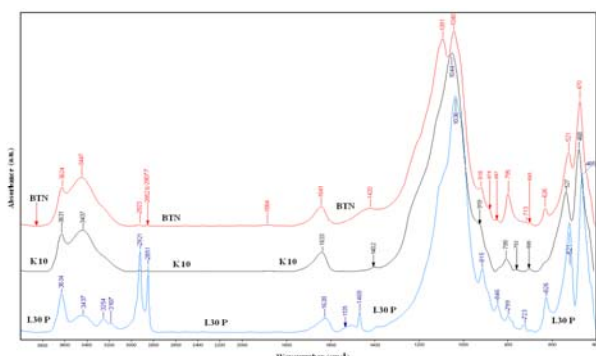


Figure 1. FTIR spectra of selected clays: BTN, K10 and I.30P

Silicates specific peaks due to Si-O bonds (bending and stretching vibration) can be easily identified for BTN, K10 and I.30P in the interval 400-600  $\text{cm}^{-1}$ . Other characteristic peaks were also observed: at 521-527  $\text{cm}^{-1}$  (Si-O bending) and at 915-919  $\text{cm}^{-1}$  (Si-O stretching, in-plane), at 527  $\text{cm}^{-1}$  due to Si-O-Al (octahedral) and 463  $\text{cm}^{-1}$  due to Si-O-Si bending vibration; signals at 1628-1641  $\text{cm}^{-1}$  were attributed to -OH bending due hydration; peaks at 1036-1091  $\text{cm}^{-1}$  are due to Si-O-Si stretching vibrations and those at 3624-3634  $\text{cm}^{-1}$  correspond to Al-Al-OH stretching. The strong signals at 795-799  $\text{cm}^{-1}$  are assigned to the presence of a quartz admixture in the sample (Si-O-Si vibrations) [39-41]. In the case of I.30P clay organically modified by ODA, specific bands were identified at 2851, 1469 and 1535  $\text{cm}^{-1}$  (attributed to symmetric stretching vibration of alkyl groups - $\text{CH}_3$ ), at 2921  $\text{cm}^{-1}$  (assigned to the asymmetric stretching vibration of - $\text{CH}_2$ - groups) [42,43].

The FTIR spectrum of neat coPA was discussed in previous papers [44,45]. Three basic polyamide bonds, *i.e.* amide N-H at 3280-3300  $\text{cm}^{-1}$ , hydroxyl O-H at 2850-2950  $\text{cm}^{-1}$ , and carbonyl C=O at 1630-1660  $\text{cm}^{-1}$ , are of primary interests. Peaks at 1018 and 1046  $\text{cm}^{-1}$  can be solely attributed to the Si-O vibrations in clays, since the only contribution from coPA in this region is the small peak at about 1030  $\text{cm}^{-1}$  which has a much lower intensity compared to clays peaks.

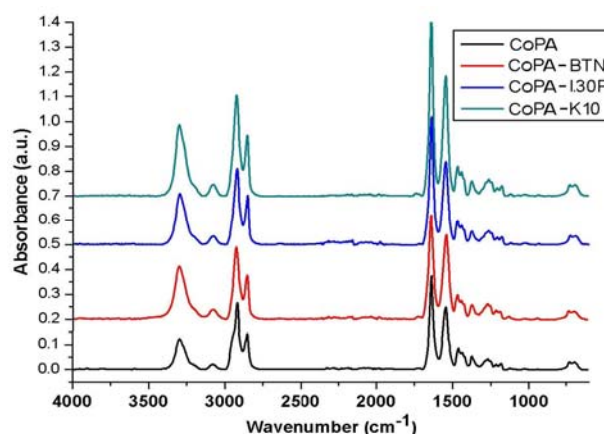


Figure 2. FTIR spectra of coPA (black), coPA-BTN (red), coPA-I.30P (blue) and coPA-K10 (green).

The common feature for these spectra is represented by peaks at 1000, 1100, 1112 and 1115  $\text{cm}^{-1}$ , respectively, that are absorption bands attributed to Si-O-, C-O-, Si-O-Si, C-O-C, Si-O-C stretching vibrations specific to coPA, clays and hybrid materials, as well, which is a clear indication of the inclusion of layered silicates in the coPA matrix. Unexpectedly, the differences between coPA and corresponding nanocomposites spectra are not remarkable. The FTIR analysis results indicated that silicate layers neither disturbed the coPA chains stacking, nor enhanced the order of this stacking [46].

**3.2 The differential scanning calorimetry (DSC).** The DSC allows the evaluation of the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_m$ ), crystallization temperature ( $T_c$ ) and heat of crystallization ( $\Delta H_c$ ) of coPA and its hybrid nanocomposites. Main data concerning thermal properties of coPA and its nanocomposites are presented in Table 4 and Figures 3 and 4, respectively.

As shown in Table 4, the addition of 5% nanoadditives generally lowered values of all parameters, except the heat of crystallization. The samples containing I.30P clay displayed a different behavior: all parameters values are higher as compared to the other hybrids, although still lower than those for the raw coPA. This might be explained considering the structure and properties of the modifier used



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Table 4. DSC data for coPA and its nanocomposites

Parameter Sample	$T_g$ (°C)	$\Delta C_p$ (J/g · °C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
coPA	18.10	0.629	122.21	21.61	85.67	22.19
coPA-BTN	15.09	0.543	117.56	20.61	78.65	28.77
coPA-K10	13.28	0.592	116.05	19.58	65.75	26.47
coPA-I.30P	16.55	0.604	116.38	19.49	66.97	26.15

$T_g$  – the glass transition temperature;  $\Delta C_p$  – heat capacity;  $T_m$  – the melting temperature;  $\Delta H_m$  – heat of fusion;  $T_c$  – crystallization temperature;  $\Delta H_c$  – heat of crystallization

for this silicate, namely ODA, whose conformation contributes to a higher order of the macromolecular chains.

**Glass transition temperature** offers a good indication on the effect of additives on the matrix polymer and enables the choice of processing conditions. The  $T_g$  of neat coPA is 18°C, lower than other aliphatic copolyamides [47-50], due to the copolymerisation that leads to flexible chains and lower  $T_g$ , respectively. At the same time, an increased aliphatic content in coPA enhances macromolecular flexibility. Addition of 5wt% clays determined a decrease of  $T_g$  for all hybrids, by disturbing the macromolecular backbones regularity. This can be attributed to the existence of a thin interface layer that tends to enhance the polymer segments dynamics during the melt processing, resulting in a plasticizing effect [51,52].  $T_g$  of coPA-I.30P nanocomposites is slightly higher as compared to the other hybrids due to the presence of ODA which weakens the polar interactions between adjacent clay layers, which is a prerequisite for polymer macromolecules to migrate and intercalate into the clay galleries.

Concerning the **heat capacity** values associated to the glass transition, it was proven that dynamics of coPA chains in the glass transition region is slightly reduced by the immobilization induced by clay particles.

**Crystallization and melting temperatures** of the hybrid materials are lower than those of neat coPA, except nanocomposite coPA-I.30P.

Thermograms (Figure 3) of the coPA-BTN and coPA-I.30P samples displayed peaks at lower temperatures, but of higher intensities probably as a result of increased degrees of crystallinity.

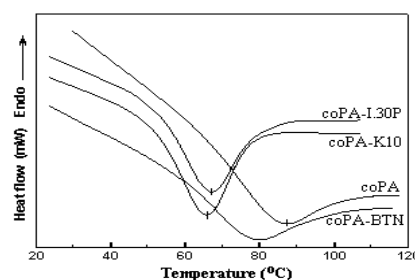


Figure 3. DSC scans on cooling of neat coPA and corresponding nanocomposites

The lower crystallisation temperatures might be explained by a feeble nucleating

effect and a lower diffusion rate of the polymer

chains. Thus, the polymer–clay interactions appear to hinder the mobility and diffusion of coPA chains and formation of crystalline segments in the space between silicate layers, which is in agreement with previous studies [53-57].

Another important feature concerns the **enthalpy of crystallization** ( $\Delta H_c$ ) of coPA-K10 and coPA-I.30P samples, which is the same ( $T_c$  is approx. 66-67°C), lower than  $\Delta H_c$  of coPA-BTN nanocomposites, but still



significantly higher than coPA's. It might be considered that K10 and I.30P nanoparticles delay crystallization process of these composites, due to the weak interactions at the coPA-clay interface.

**The melting temperature ( $T_m$ )** of coPA, a statistic copolyamide 6/6.6/6.10, is far lower than that of any corresponding homopolymer due to conformation changes of PA6 (approx. 70wt%). Incorporation of co-monomers and, subsequently, clays modifies the intermolecular phase angle along with progressive attenuation of the intermolecular interactions (hydrogen bonding) between nylon molecules, yielding in lower  $T_g$  and  $T_m$ . [48]. DSC signals (Figure 4) reveals the presence of other morphological segments developed in nanocomposites, which melt around of 97-98°C.

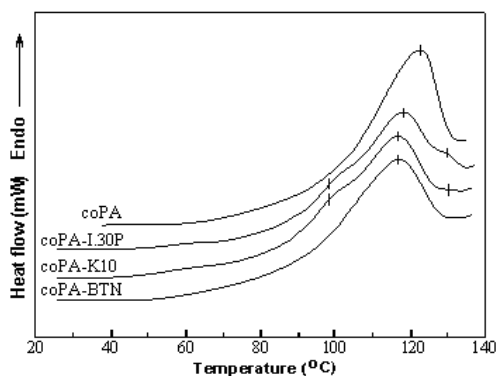


Figure 4. DSC scans on heating of neat coPA and corresponding nanocomposites

Even more, a weak melting process was recorded at 130°C, close to the main melting peaks. These weak melting processes are due to a small crystalline fraction that is more thermodynamically stable and melts at higher temperatures. The crystals of this fraction are bigger and better developed. Additionally, the decrease of the  $T_m$  for all nanocomposites compared with neat coPA is correlated with decrease of coPA crystallites dimension, when different clay types were added. This behaviour explains the development of a new morphology in nanocomposites due to the presence of clays, so, the thermal response is a consequence of the coPA polymorphism and the reduction in crystalline order [58]. Nevertheless, since the melting enthalpy values of all samples are very close, changes in terms of crystallinity are not as dramatic as expected.

### 3.3 Thermal Gravimetric (TG) Analysis

**Clays characterization.** For a better understanding of fillers effect on the properties of hybrid materials, the TG analysis was performed, first, on clay samples and themograms are presented in Figure 5.

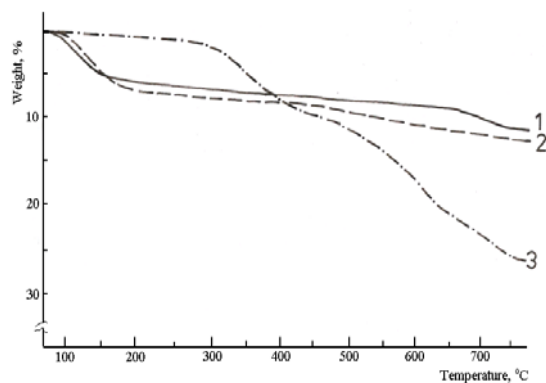


Figure 5. Thermograms of BTN (1), K10 (2) and I.30P (3)

The thermal curves of the BTN and K10 are very similar, but all decomposition processes occurred in three steps. The first degradation phase was in the temperature range of 20-200°C, where BTN and K10 displayed the maximum weight loss. It is known that clays contain three types of water molecules: free water molecules, hydrogen-bonded water molecules and water molecules strongly coordinated to the interlayer cations [43]. In the process of dehydration, an initial rapid weight loss, which occurs at temperatures up to 150°C due to the removal of the free water molecules from the interlayer space, is followed by slower losses until constant weight in the end of dehydration. The weight loss recorded in the temperature interval 150÷200°C may be due to the hydrogen-bonded and coordinated water molecules, finally yielding in the “collapsed” structure [43]. Interlayer water loss dominates the thermal behaviour below 350°C. However, the possibility to remove some of the hydrogen-bonded and coordinated water molecules in the lower temperature range cannot be ruled out.

The weight losses registered into the second phase (200-500°C) were obviously resulted from the decomposition reactions of the organic matter present in clays.

In the temperature range 500-750°C, the hydroxyl groups covalently bonded in the crystal lattice are dehydrated. In the interval



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600-750°C, the weight losses for BTN and K10 might be associated with the dehydroxylation reaction of Na-MMT [59].

In the case of the I.30P, the presence of organic cations increases the thermal stability in the range temperature 20-300°C and the weight loss that occurs between 300-500°C can be explained mainly by the decomposition of ODA and partly by the adsorbed water molecules [31,60]. The weight losses above 600°C are attributed to the removal of the interlayer and structural water present into the clays galleries. Total weight losses (%) for the considered clays, at 750°C, are: 12.70 - BTN, 11.69 - K10 and 26.20 - I.30P. The extent of loss for I.30P is due to the supplemental degradation of alkyl chains of ODA.

**TGA study of hybrid materials.** The thermal stability of the neat coPA and its corresponding nanocomposites was evaluated by TGA and Figure 6 displays TGA and DTG curves obtained for coPA and its hybrids.

The thermal stability of nanocomposites is definitely influenced by the dispersion of nanoclay platelets within the coPA matrix, which may act as thermal insulating layers,

thus reducing the diffusion of volatiles, as degradation products, out of the matrix. It has been found that the layered clays are excellent thermal and mass transport barriers, which slow down the rate of volatiles emission as the matrix decomposes [61].

TGA data for coPA and its corresponding nanocomposites are summarized in Table 5.

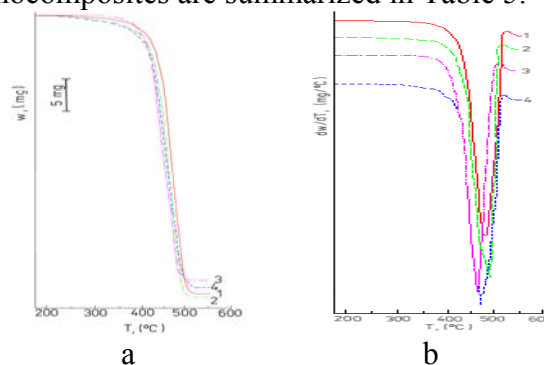


Figure 6. TG (a) and DTG (b) curves for neat coPA and its nanocomposites: coPA (red), coPA-BTN (green), coPA-K10 (violet) and coPA-I.30P (blue)

Table 5. TGA data of coPA and its hybrid composite materials

Sample	T <sub>i</sub> , °C	T <sub>max</sub> , °C	T <sub>f</sub> , °C	T <sub>5%</sub> , °C	T <sub>50%</sub> , °C	ΔW, %
coPA	205	480	524	385	430	86.28
coPA-BTN	225	483	520	225	426	86.40
coPA-K10	310	462	507	388	430	82.26
coPA-I.30P	215	470	517	320	430	84.28

where: T<sub>i</sub> – onset temperature of main decomposition stage; T<sub>max</sub> – temperature of maximum decomposition; T<sub>f</sub> – temperature at the end decomposition stage; T<sub>5%</sub>, T<sub>50%</sub> – temperature of decomposition for 5%, respectively 50% weight loss; ΔW – weight loss in the interval T<sub>f</sub>-T<sub>i</sub>

One possible explanation resides in the crystalline structure of coPA that disappears during melting (125-135°C) and is replaced by an irregular atomic arrangement. Literature data [62] indicate that covalent bonds (such as C=O, N-H and O-H) present in coPA and its

nanocomposites contribute to the thermal stability of the hybrid materials, because the strength of these bonds is enhanced by clay particles through interactions at the interface.

This increased thermal stability of nanocomposites may be also explained on the

basis of the stabilization due to transition metals (Fe, Mn, Ti, Cu) present in clays as impurities. It is well known [63] that metal ions have significant influence on the thermal stability of polyamides and are commonly used as antioxidants in products targeted for hi-tech applications. Even in low amounts (<50 ppm), the presence of transition metals (such as Fe) and their derivatives is partly responsible for the improved stability of the hybrid composites and are effective for the long-term stabilization of (co)polyamides, acting as radical scavengers.

Weight losses of coPA and its nanocomposites, measured up to 250°C, were found to be very small and may correspond to the loss of water and some volatiles.

The temperatures corresponding to 5% weight loss ( $T_{5\%}$ ) of coPA, coPA-BTN, coPA-K10 and coPA-I.30P were 385, 225, 388, and 320°C, respectively. The improved thermal stability of coPA-K10 nanocomposites might be explained by a better dispersion of clay particles that can prevent fast transmission of heat and limit the continuous decomposition [64]. For coPA-I.30P composites, limited improvement in thermal stability may be attributed to the decomposition of ODA used in the modified clay. The temperature values at the final stage of decomposition ( $T_f$ ) of nanocomposites are in a narrow range: 507-520°C.

### 3. CONCLUSIONS

Three series of new polyamide-clay hybrid nanocomposites were prepared by a solventless melt mixing process, using a ternary copolyamide as thermoplastic matrix and various layered silicates. Nanocomposites structure was investigated by the means of FTIR spectroscopy which have evidenced the inclusion of nanofillers in the coPA matrix.

Samples were also submitted to the thermal analysis and the study proved that the addition of 5% nanoadditives generally lowered values of all analyzed parameters, except the heat of crystallization. The main characteristic temperatures ( $T_g$ ,  $T_c$ ,  $T_m$ ) of the new hybrid materials are lower than those of the neat coPA. Clay particles act not only as nucleating agents, but they affect the movement of

macromolecular chains, yielding in a decreased crystallinity and  $T_g$ . Under these circumstances, the operational parameters for melt mixing processing need to be optimized for a better diffusion of polymer chains within the clay galleries.

Results obtained by TGA indicated that the presence of 5 wt% clay increased the thermal stability of coPA, proven by the temperature of the initial decomposition which increased by 10-95°C (thermal stability of samples: coPA-K10 > coPA-BTN > coPA-I.30P > coPA). This behaviour is explained on the basis of the stabilization due to transition metals present in the clays as impurities. The increased thermal stability of nanocomposites is a result of the thermal insulating properties of the layered silicates which act as barrier to the volatile products generated during decomposition.

Data presented in this article are only preliminary. Further study will correlate them with results from other measurements, in order to optimize the processing conditions, to better understand the effect of nanoclays on coPA and to establish the structure-properties-application relationship for the new hybrid materials.

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