Structure and properties of polypropylene containing organo-clay and carbon nanotubes as fillers

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The present work is focus on polymer composites containing multiwall carbon nanotubes (MWCNT) and organically modified clay (OC) in different proportions as nanofiller in isotactic polypropylene (iPP). The composites were prepared by extrusion method in a twin-screw co-rotating extruder and were subjected to a number of studies as X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA). Establishing a connection between the structure and properties are expected to provide opportunities for controlling the processes of the resulting materials. An XRD result shows changes in the position of the diffraction peaks towards right side of the clay basal reflection peak, which can be explained by collapsing of the clay layers after compounding. XRD results are consistent with TEM images confirming that the layered silicate particles are dispersed in thin stacks consisting only of few layers. TEM and SEM structure analysis on the state of organo-clay and carbon nanotubes dispersed in PP matrix proves homogeneous, but non-uniform filler dispersion due to formation of regions with well dispersed fillers and on the other hand, the presence of regions with nanofiller aggregates. The thermal stability and thermal degradation of the matrix as well two- and three-component materials was analyzed in nitrogen atmosphere. It was found a significant improvement on thermal stability of PP with nanotubes loading in the investigated concentration range (0.5–5 wt.%). The conducted studies concerning those composites showed that the structural changes or changes in the properties was not the result of the synergistic effects or in other words fillers exhibit self-influence on the host matrix and its properties.

Key words: polypropylene, multiwall carbon nanotubes, organo-clay, XRD, TGA, SEM, TEM

INTRODUCTION

Although, the interest in polymer/layered silicate nanocomposites is still at high level in the last few years began to appear a new area on polymer nanocomposites which refers to nanocomposites with more than one filler. The most common reason for investigating hybrid composite blends containing two fillers is synergy effects which could occur when using two different types of nanofiller and the resulted properties of nanocomposites are substantially different or better than those of the matrix [1]. In our studies on polymer composites we have chosen to use polypropylene (PP) because it is the second most commercial polymer with wide use in many areas such as packaging, automotive industry, consumer goods, fibers and textiles [2]. Furthermore, PP offers good chemical and fatigue resistance and have stress cracking resistance, good hardness and ease of machining, together with good processability by injection molding and extrusion [3]. Great part of modern applications of plastics is associated with specific requirements in terms of performance, processing and good price make the introduction of fillers in polymer matrices [1]. Usually layered silicates offers good opportunities to overcome the disadvantages, but organo-clay (OC) truly affects the structure and properties of polypropylene [4]. Many results have been reported in the literature relating to the study of polymer reinforced with layered silicates [5] and is described the use of compatibiliser in nanocomposites to improve dispersion of the silicate layers in the volume of the surrounding polymer. Secondly point of view in this study refers to multiwall carbon nanotubes (MWCNTs) which are recently used to reinforce the polymer and to add novel physical properties to the composite, due to their remarkable electrical, mechanical, optical, thermal and chemical properties [6–9] this making them a perfect for many engineering applications.

Literature reveals limited information [10–12] on hybrid composites combining two types of nanofiller in a common matrix. This provokes our interest to find joint effect between the two additives (MWCNTs and OC), and to study the influence of fillers on the structure and subsequent properties.

MATERIALS AND METHODS

Isotactic polypropylene, PP6231 (Buplen 6231 Lukoil Neftochim Bourgas AD, having MFI 16–25 g/10 min at 230°C) is the matrix polymer. Organi-

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Table 1. Two-component and three-component blends containing MWCNT and OC in isotactic polypropylene.

Short name	Composites	PP	MA-g-PP (wt.%)	MWCNT (wt.%)	Clay (wt.%)
PP	PP6231	100	—	—	—
PP0.5CNT	PP+0.5%MWCNT	99.5	—	0.5	—
PP1CNT	PP+1%MWCNT	99	—	1	—
PP3CNT	PP+3%MWCNT	97	—	3	—
PP5CNT	PP+5%MWCNT	95	—	5	—
PPMA	PP+12%MA-g-PP	88	12	—	—
PPMA3OC	PP+3%Clay	85	12	—	3
PPMA0.5CNT3OC	PP+0.5%MWCNT+3%Clay	84.5	12	0.5	3
PPMA1CNT3OC	PP+1%MWCNT+3%Clay	84	12	1	3
PPMA3CNT3OC	PP+3%MWCNT+3%Clay	82	12	3	3
PPMA5CNT3OC	PP+5%MWCNT+3%Clay	80	12	5	3

cally modified clay, Cloisite 30B (Southern Clay Products, Inc) and PLASTICYLTMPP2001 – commercial masterbach of 20 wt.% MWCNT in PP, with real density 872 G/L are used as fillers. For the preparation of nanocomposites 20 wt.% clay is dispersed by extrusion mixing in PP adding 12 wt.% MA-g-PP (Fusabond 613, Maleic anhydride content 0.5 wt.%, Mw = 95000; MFI = 120 g/10 min, Du Pont data), as a compatibiliser. Then, the appropriate amount of both masterbatches – 20 wt.% MWCNT/PP and 20 wt.% OC/PP are diluted with the polypropylene by melt mixing with a 25-mm twin-screw co-rotating extruder Collin Teach-line Compounder (L/D=24) and Collin Teach-line Strand Pelletizer. The temperature setting of the extruder from the hopper to the die was 180/200/200/190/180°C and the screw speed was 45 rpm. In order to improve the carbon nanotube dispersion, the compositions were extruded in three runs. Variety of compositions was prepared containing 3 wt.% OC and 0.5–3 wt.% MWCNT in PP, summarized in Table 1.

X-ray analysis

The X-ray characteristics of tested composites were obtained using Bruker D8 Advance diffractometer. Powder X-ray diffraction patterns were collected within the range from 5.3 to 80 deg 2θ with a constant step 0.02 deg 2θ. Measurements were performed using a nickel-filtered Cu Kα radiation and LynxEye detector with wavelength $\lambda = 1.5418$ nm at 40 kV and 30 mA. To obtain diffraction patterns at small angles it was used plug-in device attached to the diffractometer which provides 2–10 deg 2θ diffraction range. The results are superimposed on a com-

mon graphics and the typical clay peak is analyzed. The peak is indicative of the platelet separation or d-spacing in clay structure. Any changes in this peak (width or height) provide information about delamination of clay stacks in the matrix volume which in turn depends on the dispersion. The interlayer distance of clay in the hybrids was calculated using Bragg's law (Eq. (1)).

$$d_{001} = \frac{n\lambda}{2\sin\theta},\qquad(1)$$

where n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

From the results, it was possible to calculate the number of clay platelets per average stack [13, 14] with the interlayer distance d_{001} using Eq. (2)

$$N = 1 + t/d_{001},\qquad(2)$$

where t is given by the Scherrer Eq. (3)

$$t = 0.9\lambda/(B_{1/2}\cos\theta_b),\qquad(3)$$

where λ is the wavelength, $B_{1/2} = \theta_1 - \theta_2$ (in radians) at half peak height $(I_{max}/2)$, $\theta_b = (\theta_1 + \theta_2)/2$.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a well-known method used to study polymer degradation mechanisms and kinetic to predict the thermal stability of the polymers. The effect of nano-fillers presence on thermal stability of the composites was observed by TGA Diamond Perkin-Elmer Instrument

(TG/DTA) at the following conditions 30°C to 800°C at 20°C/min under nitrogen atmosphere. Charts allow defining features as temperature corresponding to initial 10% of weight loss (T_{10}) and peak temperature (T_p).

Electron microscopy

Microstructure and morphology of the fresh-cut nanocomposite samples was studied by scanning electron microscopy (SEM), using an FEI Quanta 600 SEM equipped with a field emission gun. All samples were cut in liquid nitrogen and coated with chromium prior to examination. Transmission electron microscopy (TEM) was carried out with a Philips CM20 instrument with an accelerating voltage from 60 kV to 200 kV and is equipped with a 4 megapixel AMT camera, enabling digital recording of images.

RESULTS AND DISCUSSION

The XRD diffraction pattern of composite materials, neat PP and Cloisite 30B using in this study are shown in Fig. 1. The diffraction peaks of PP/CNT/OC composite and neat PP show a number of characteristic peaks in the range $2\theta = 14° \div 22°$ due to the semi-crystalline structure of polypropylene. The addition of carbon nanotubes and clay is not influenced significantly the characteristic peaks within this range

of 2θ. However, a strong effect of the clay is found in the small angle region of $2\theta = 3° \div 7°$ due to the clay dispersion.

The basal reflection peak of Cloisite 30B, as well as the clay containing composites (PPMA3OC, PP1CNT3OC) and masterbatch of 20%Cloisite30B/PPgMA are shown on Fig. 2. The interlayer distances are calculated from the basal peak by Bragg's equation Eq. (1). Pure Cloisite 30B indicates a (d_{001}) peak around $2\theta = 4.9°$ corresponding to an interlayer spacing of 1.8 nm. The 20%Cloisite30B/PPgMA masterbatch shows (d_{001}) peak between the values of Cloisite 30B and the PPMA3OC composite indicating that the dilution with pure PP led to a decrease in the d-spacing in comparison – 1.44 nm. It is seen from Fig. 2. that nanocomposite peaks is appear to the right side of the main peak of Cloisite 30 B, which indicates collapsing of the silicate layers after compounding with no evidence of exfoliation. Brief review of the literature [15–17] related to the use of Cloisite 30B as filler in different polymers shows that there are many reports of collapsing of the silicate layers after compounding in nanocomposite. At the same time, this behavior is not typical for other clays, as for example Cloisite 15A [13, 16] or Cloisite 20B [18, 19]. Results can be explained otherwise, the Cloisite 30B peak
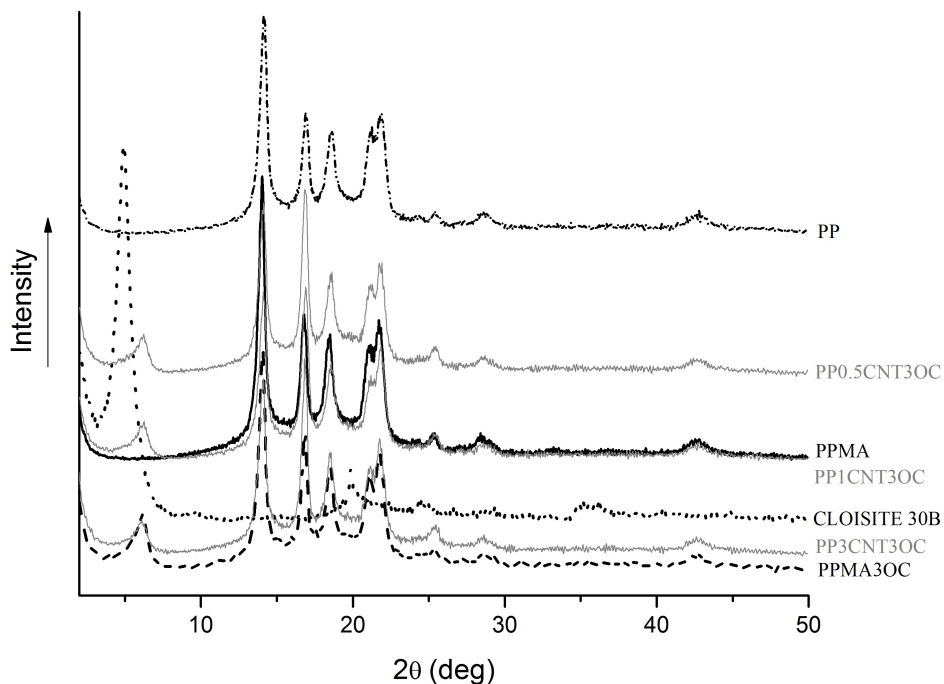

Fig. 1. X-ray diffraction patterns of Cloisite 30B, neat PP, PPMA, PPMA3OC and selected three-component systems.
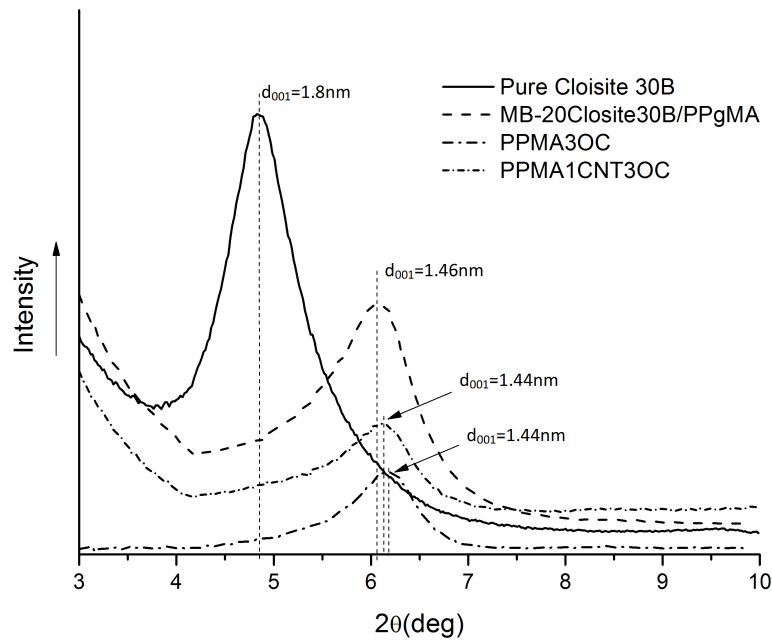
Fig. 2. X-ray diffraction patterns covering small angles region where 2θ values are between 2-10 deg.

in the composites is masked by the angular shoulder slope and appears at $2\theta = 6.1°$, which assume the hypothesis that the layered silicate particles are dispersed in thin stacks consisting only of few layers, as shown in Fig. 3. These fine stacks are fastened each other at their end parts forming edge-to-edge structure and the distance between the plates (stack) at these points of contact decreases causing a reduction in peak height.

The XRD parameters calculated for the Cloisite 30B, as well as MB-20Closite30B/PPgMA and two composites (PPMA3OC, PPMA1CNT3OC) are summarized in Table 2 below. By using Eq. (2) and Eq. (3), the number of clay platelets per average stack was calculated. The interlayer distance of the clay does not increases in the nanocomposite or masterbatch, but XRD peak profiles shown that some reorganization occurs.

Table 2. XRD results obtained for Cloisite30B, MB-20Closite30B/PPgMA and two composite blends, where 2θ indicate main peak location, d_{001} is interlayer distance, and N is the number of clay platelets per average stack.

Sample name	2θ (deg)	d_{001} (deg)	N
Cloisite30 B	4.9	1.8	5.55
MB-20Closite30B/PPgMA	6.05	1.46	5.42
PPMA3OC	6.1	1.44	6.97
PPMA1CNT3OC	6.3	1.44	6.55

TEM analysis allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization Fig. 3. TEM morphology images show clay tiles divided into finer stacks, with confirming the result suggested by the XRD. Fig. 3(a) shows a TEM micrograph with focus on single tubes of ternary blend at a low CNTs concentration (0.5 wt.%). It is difficult to determine the distribution of the clay in the first micrograph, but Fig. 3(b) clear shows several individual flakes clay scattered in the volume, as well as a stack of parallel plates in the middle of the image. The last TEM image (Fig. 3(c)) at highest concentration of nanotubes – PP/3CNT/3OC composite shows nanotube aggregation section.

In Fig. 4(a, b), SEM images are shown in different magnifications in order to observe the details. The fractured surfaces of neat PP extruded three times are shown in magnification $\times 5000$ (a) and $\times 30000$ (b). SEM micrographs show that the fracture surface of neat PP is smooth with linear propagation lines. Fig. 4(c, d) shows the micrographs of PP1CNT3OC system at magnifications of $\times 5000$ and $\times 50000$, respectively. It is observed by PP1CNT3OC image at magnification $\times 50000$ the presence of nanotubes and clay stacks leads to significantly different structure related to pure PP morphology. Fig. 4(e, f) micrograph of PP3CNT3OC nanocomposite is similar
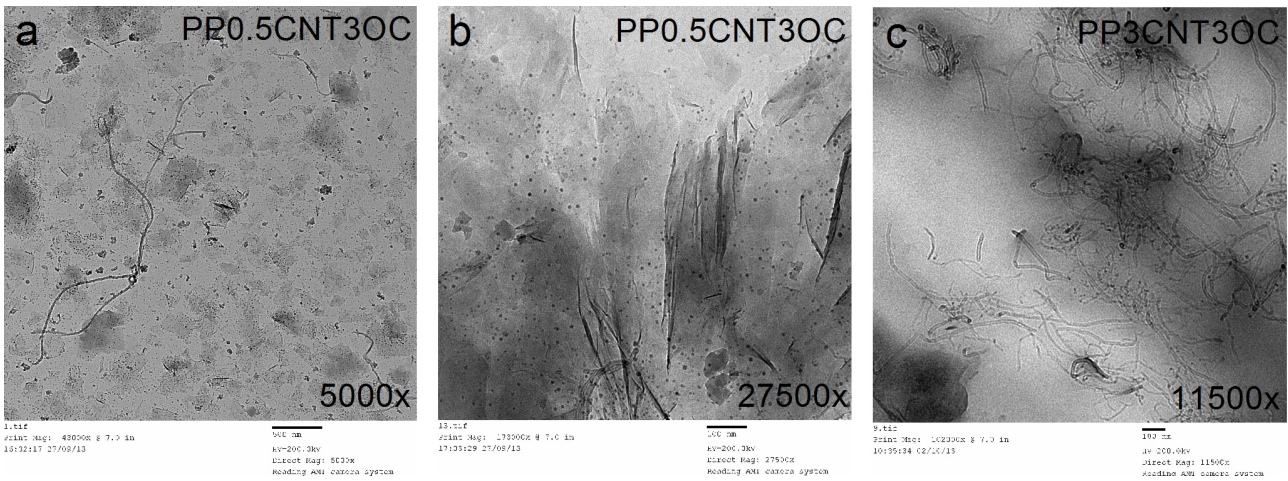
Fig. 3. TEM micrographs of PP0.5CNT3OC nanocomposites on (a) and (b); and PP3CNT3OC on (c).

to PP1CNT3OC, but surface fracture looks much rougher with small cracks indicating a more rigid structure. The surface in Fig. 4(d) reveals group of relatively closely located MWCNTs in this area and adjacent to this part of image is visible surrounding matrix structure. The structure image analysis on state of organo-clay and carbon nanotubes dispersed in PP matrix investigated by TEM and SEM proves homogeneous, but non-uniform filler dispersion due to formation of areas with presence of better nanotubes distributions, but also areas with poor dispersion.
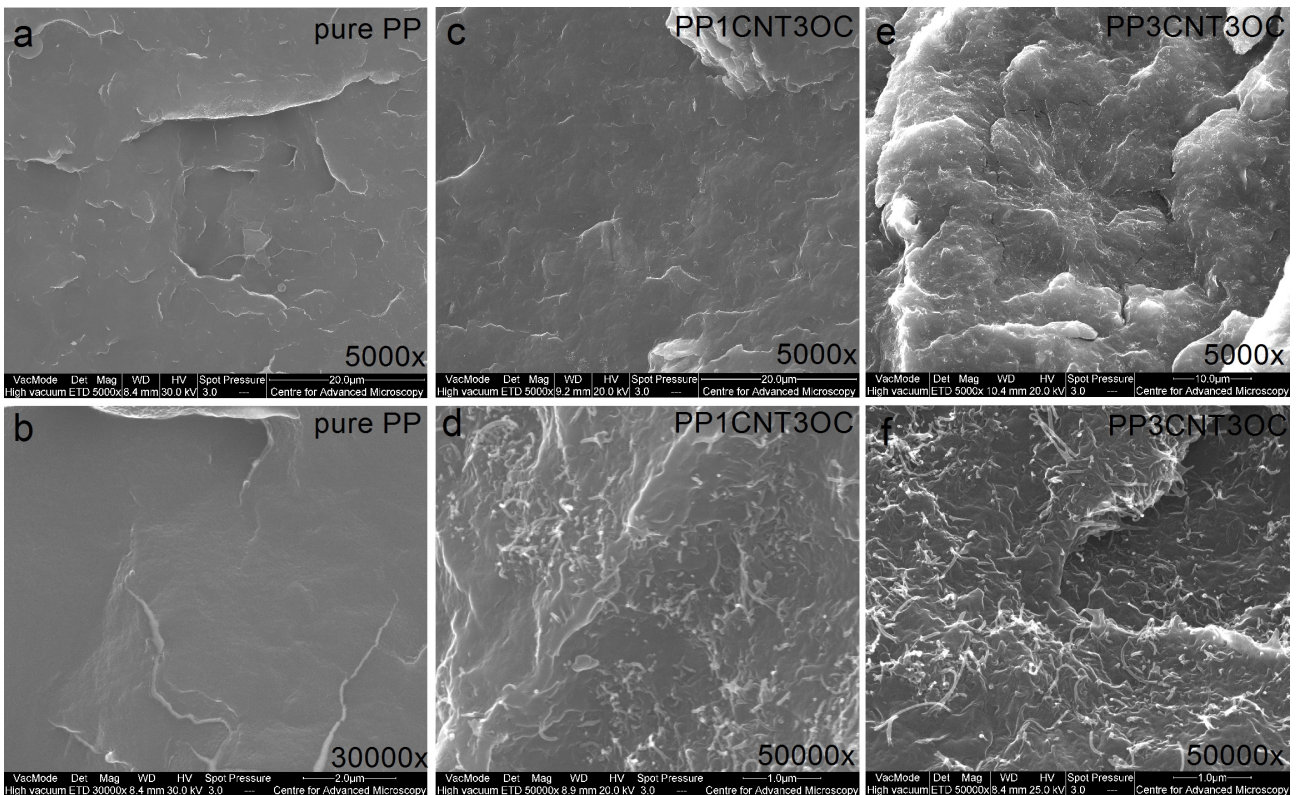

Fig. 4. SEM micrographs of pure PP (a, b); PP1CNT3OC on (c, d); and PP3CNT3OC nanocomposites on (e, f) at low and high magnification.
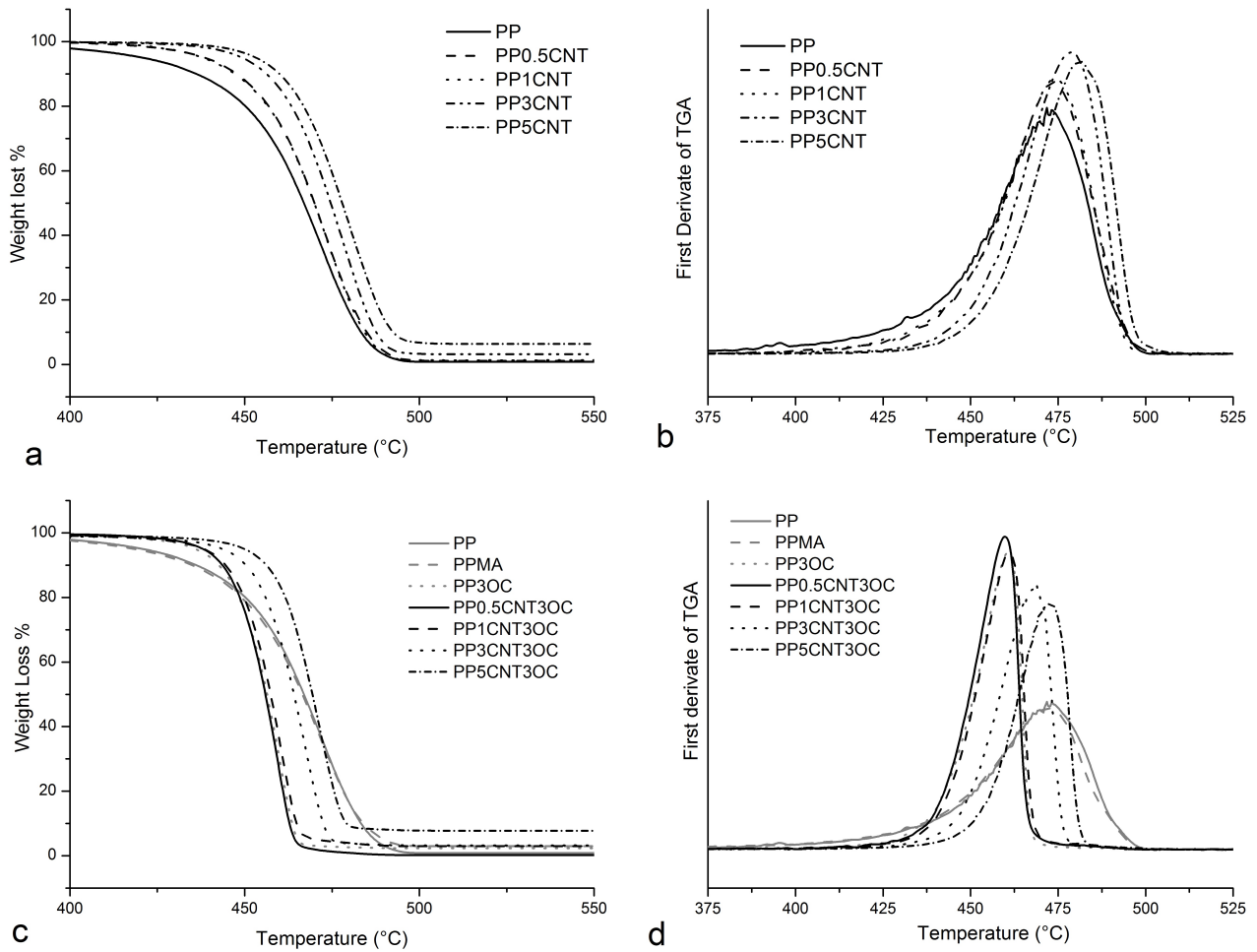
Fig. 5. TGA and DTG curves in nitrogen atmosphere for binary PP/CNT (a, b) and ternary PP/CNT/OC(c, d) systems

TGA and DTG curves for neat PP and PP/CNT nanocomposites at a heating rate of 20°C/min under nitrogen atmosphere are presented in Fig. 5(a, b). Temperature values at 10% weight loss ($T_{10\%}$) and peak temperature (T_P) for pure PP, PPMA, PPMA3OC, binary PP/CNT and ternary PP/CNT/OC composites are presented in Table 3. The addition of the nanotubes in the investigated concentration range (0.5–5 wt.%) improves the thermal stability of PP in nitrogen atmosphere. The addition of carbon nanotubes causes a weak displacement of the curves in the direction on the high temperatures from 2 to 7°C. Further increase on amount of nanotubes in two-phase compositions up to 5 wt.% shifts the curves 10°C toward higher temperature values. The thermal stability of the binary composites is improved by approximately 25°C and around 20°C of ternary composites. Regarding the three-phase composites there

is a slight shift of the curves at low temperatures from 4 to 12°C by adding organoclay Fig. 5(c, d).

Table 3. Temperature values at 10% weight loss ($T_{10\%}$) and peak temperature (T_P) in nitrogen atmosphere determined from corresponding TGA and DTG diagrams

Sample name	$T_{10\%}$ (°C)	T_P (°C)
PP	436.19	471.88
PP0.5CNT	447.79	473.48
PP1CNT	447.15	474.21
PP3CNT	456.23	478.84
PP5CNT	460.01	481.45
PPMA	434.89	472.16
PPMA3OC	442.66	460.53
PPMA0.5CNT3OC	443.70	459.79
PPMA1CNT3OC	444.63	460.99
PPMA3CNT3OC	450.39	468.01
PPMA5CNT3OC	456.08	472.88

Thermal degradation of binary and ternary composites under nitrogen decreases with 7°C and 10°C, respectively.

CONCLUSIONS

In this work, the effect of the addition of two different types of nanofillers (MWCNT and OC) upon the structure and properties of PP was investigated through XDR, Electron microscopy and TGA. According to the XRD results the diffraction peaks of composites are shifted to right side of the main clay peak, which indicates collapsing of the silicate layers after compounding. These results are explained with the dispersion of clay in fine stacks, which form edge-to-edge structure and the distance between the edges at the points of contact decreases causing a reduction in peak height.

This is consistent with the analysis of the microscopic images. TEM and SEM observations proved relatively homogeneous, but non-uniform filler dispersion due to formation of areas with presence of better nanotubes distributions, but also areas with poor dispersion. Thermal stability increases with 30% at 10% mass loss, but this effect is mostly due to the addition of MWCNTs and there is no difference between the thermal stability in a two-phase and three-phase composites. Finally, it is important to note that despite the changes in the structure and properties of the composites studied, these changes dependent on either one (OC) or the other (MWCNT) filler, but a synergistic effect is not confirmed.

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СТРУКТУРА И СВОЙСТВА НА ПОЛИПРОПИЛЕН, СЪДЪРЖАЩ ОРГАНИЧНА ГЛИНА И ВЪГЛЕРОДНИ НАНОТРЪБИЧКИ КАТО ПЪЛНИТЕЛИ

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(Резюме)

Нанонауката и технологията дават уникални възможности за създаване на революционно нови комбинации от материали със специфични свойства и със значителни предимства по отношение на качество и нови свойства пред класическите материали. По тази причина напоследък се отделя все повече внимание на напълнените инженерни полимери с наноразмерни пълнители.

В настоящата работа се разглеждат хибридни композити съдържащи многостенни въглеродни нанотръбички (MWCNT) и органично модифицирана глина (OC) в различно съотношение като нанопълнители в изотактен полипропилен (iPP). Композитите са получени чрез екструзия в двушнеков екструдер и са подложени на редица изследвания за пълното им характеризиране и изучаване [1,3]. Установяването на връзка между структурата и свойствата се очаква да предостави възможности за управляване на процесите на получените материали [2]. Ефективен метод за получаване на информация за кристалографската структура и структурни промени на полимерите е рентгеноструктурен анализ (XRD). Органичната глина показва характерен пик, дължащ се на нейната регулярна структура, който е показателен за разслояването на силикатните стековете или така нареченото d-разстояние в композитната структура, което се изчислява по закона на Браг. Термичната стабилност и термичната деградация на матрицата и дву- и трикомпонентни състави в азотна и въздушна среда се анализира посредством термогравиметричен анализ (TGA). Значително подобряване на термичните свойства се появява при ниско съдържание на пълнител от 0.5 об.%, където TGA-кривите на iPP/MWCNT композитите са изместени към по-висока температура в сравнение с чистия полипропилен. Сканиращата електронна микроскопия (SEM) осигурява възможност за директна визуализация на степента на диспергиране на пълнителите в матрицата, формата и структурното разпределение на частиците, междуфазовата повърхност в композитите. Основната цел на тези експериментални изследвания е намирането на съвместен ефект на двата вида нанопълнители върху свойствата и структурата на получените композитните материали.

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