Nylon Based Nanocomposites: Influence of Calcium Carbonate Nanoparticles on the Thermal Stability

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Summary: In this paper thermal and thermo-oxidative stability of nylon 6 based nanocomposites containing up to 5% by weight of fatty acid coated calcium carbonate ($CaCO_3$) nanoparticles is studied. Thermal stability of compression-moulded samples was evaluated by thermogravimetric analysis (TG) under air and nitrogen atmosphere. Kinetic analysis of TG data was performed by using the Flynn-Wall-Ozawa method. Results show that the presence of coated nanoparticles adversely affects the thermal and thermo-oxidative stability of nylon 6. Kinetic analysis shows that a complex, multi-step decomposition process occurs. Moreover, the presence of nanoparticles do not affect the rate limiting step of nylon 6 decomposition in air, while under nitrogen atmosphere the decomposition process occurs through a diffusion-driven regime in presence of high amounts of $CaCO_3$.

Keywords: activation energy; nanocomposites; nylon; thermal stability; thermogravimetric analysis (TG)

Introduction

The recent development of new materials based on nanometer sized filler particles in polymeric matrices represent a radical alternative to conventional-filled polymers or polymer blends thus resulting in a disruptive change in composite technology.[1,2]

Polymeric nanocomposites combine the excellent flexibility, low density and easy processability of polymers with high strength, rigidity, heat resistance of inorganic materials, and may become the most important and practical materials. Uniform dispersion of these nanoscopically sized filler particles produces ultra-large interfacial area per volume between nanophase and host polymer. This enormous interfacial region is responsible for the unexpected performances and represents the peculiar characteristic of the polymer based nanostructured materials, differentiating them from traditional composites and filled plastics.

The effects of filler on the final properties of nanocomposites depend strongly on filler size and shape, nature of nanoparticles and surface modifiers, polymer/nanoparticles interactions and degree of dispersion. The most commonly used nanofillers are calcium carbonate or clay, which are able to impart significant improvements of specific polymer properties, such as stiffness and tensile strength, permeability, flame and scratch resistance as well as thermal stability.[3–6]

In particular, the thermal stability of polymer-based materials is an important issue from both academic and industrial viewpoints. Controlling thermal degradation requires understanding of many different phenomena, including chemical mechanisms, influence of material morphology, complexity of oxidation chemistry, and effects of stabilizers, fillers and other additives.[7]

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In this study results about the influence of fatty acid coated calcium carbonate nanoparticles ($CaCO_3$) on the thermal and thermo-oxidative stability of nylon 6 are reported and discussed.

Experimental

Nylon 6 (SNIA-FIAT, code F 34 L, $\eta_{inh} = 3{,}4$ dL/g in concentrated H_2SO_4) based nanocomposites filled with 1, 3 and 5% wt/wt of $CaCO_3$(Solvay, code CPCC E23 050, particles average size 60 nm, specific surface area of 75 m^2/g) coated with partially unsaturated fatty acids (~10% wt/wt) were prepared by melt mixing using a Haake Rheocord 9000 batch mixer operating at 220 °C and 32 rpm for 10 min.

Thermal and the thermo-oxidative stability of fatty acid coated nanoparticles and compression-moulded nanocomposite films (average thickness 200 μm) were evaluated by thermogravimetry (TG). TG measurements were carried out on $10 \div 15$ mg sample at 2, 5, 10, and 20° C/min heating rates, from 25 to 650 °C both in nitrogen and air atmosphere (100 mL/min) by means of a Perkin Elmer Pyris Diamond TG-DTA. In order to calculate the activation energy, E_a, kinetic analysis of the TG data was performed by using the Flynn-Wall-Ozawa method.[8,9]

Results and Discussion

Thermal stability of nylon 6 and nylon 6 based nanocomposites was investigated by thermogravimetry under nitrogen flow. Multiple heating rates were used in order to study their influence on the degradation behaviour of neat polymer and nanocomposites.

In Figure 1 TG traces recorded at 2 and 20 °C/min for the investigated samples are reported, as an example. These TG curves show a single weight-loss step.

The presence of fatty acid coated nanoparticles strongly affects the thermal stability of nylon 6. In fact, a marked decrease of the nylon 6 degradation temperatures was observed for all the investigated nanocomposites. $CaCO_3$-induced thermal destabilization is a function of the nanopowder content at high heating rates (Figure 1b), while at lower heating rates the thermal stability of the samples seems to be influenced only by the presence and not by the amount of $CaCO_3$ (Figure 1a). In particular, at 2 °C/min and low conversion degrees (up to 20% weight loss) a noticeable decrease of thermal stability was observed for all the nanocomposites with respect to the polymeric matrix, irrespective of their $CaCO_3$ content.

Moreover, as it can be observed from the Figure 1b, by adding 5% by weight of nanoparticles the 20 °C/min curve shows a

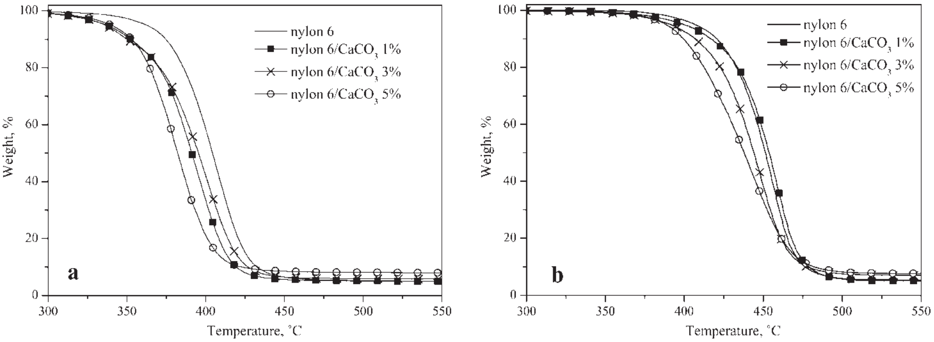

Figure 1.
TG traces under nitrogen for neat nylon 6 and nylon 6 based nanocomposites: a) 2 °C/min; b) 20 °C/min.

Table 1.

TG 5, 10 and 50 wt.% loss, char yield for nylon 6 and nylon 6 based nanocomposites with different $CaCO_3$ nanoparticles loadings (heating rates = 2 and 20 °C/min), in nitrogen.

$CaCO_3$ content	2 °C/min				20 °C/min			
	$T_{5wt.\%}$ (°C)	$T_{10wt.\%}$ (°C)	$T_{50wt.\%}$ (°C)	% Char yield @ 650 °C	$T_{5wt.\%}$ (°C)	$T_{10wt.\%}$ (°C)	$T_{50wt.\%}$ (°C)	% Char yield @ 650 °C
neat	362.6	374.8	404.2	3.6	393.0	408.0	446.3	4.8
1%	336.9	352.3	391.1	4.9	379.3	395.9	441.6	5.2
3%	336.1	350.1	395.5	5.4	370.0	386.0	437.2	6.7
5%	340.0	353.1	382.2	6.6	373.6	385.5	430.4	7.5

lower slope, suggesting that the degradation process occurs in a broader temperature range and the rate of this phenomenon is slowed down. The above-described results are summarized in Table 1, in which 5, 10, 50 wt.% loss temperatures and char yield, obtained at 2 and 20 °C/min, are compared. A similar behaviour was observed for all the heating rates adopted.

These results suggest that fatty acid coated nanoparticles increase the degradation rates and can lead to a change in the degradation mechanism.

As concerning the measurements carried out in air, an anticipated degradation is also observed, particularly for higher amounts of nanoparticles (3 and 5% wt/wt). The relative curves showed two decomposition steps, the latter due to an additional burning process (see Figure 2), as confirmed by the marked exothermal peak detected by DTA.

TG 5, 10, 50 wt.% loss temperatures and char yield for nylon 6 and nylon 6 based nanocomposites with different $CaCO_3$ loadings under air environment at 2 and 20 °C/min are summarized in Table 2. As it is possible to observe, the stability of nylon 6 decreases in presence of nanoparticles; however, the decrease in the decomposition temperature in air is smaller than that observed in nitrogen atmosphere, and it is slightly affected by the nanoparticles content. These results suggest that in air the oxidative process is the rate-limiting step of the degradation mechanism.

Therefore, fatty acid coated nanoparticles accelerate the thermal and thermo-oxidative degradation processes of nylon 6. In particular, $CaCO_3$ nanoparticles mainly decrease nylon 6 thermal stability under an inert atmosphere, while their destabilizing effect is reduced under an oxidizing environment.

As reported in recent studies, the presence of a low thermally stable nanoparticle surface modifier (less stable than polymer matrix) is responsible for a significant decrease of thermal stability of polymer based nanocomposites.[10] To get

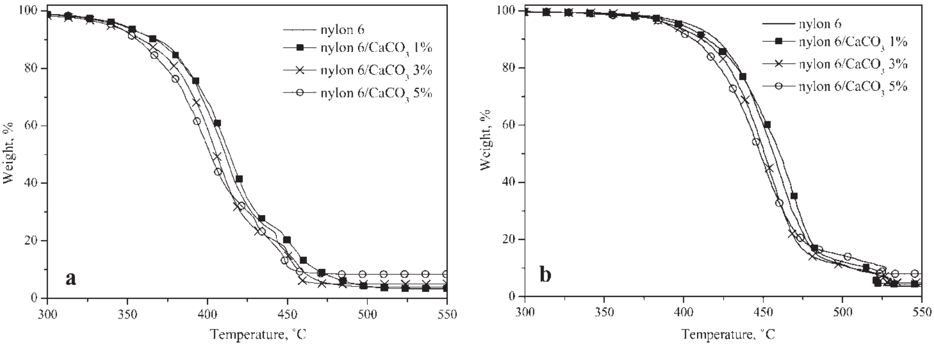

Figure 2.

TG traces under air atmosphere for neat nylon 6 and nylon 6 based nanocomposites: a) 2 °C/min; b) 20 °C/min.

Table 2.
TG 5, 10 and 50 wt.% loss, char yield for nylon 6 and nylon 6 based nanocomposites with different $CaCO_3$ nanoparticles loadings (heating rates = 2 and 20 °C/min), in air.

$CaCO_3$ content	2 °C/min				20 °C/min			
	$T_{5wt.\%}$ (°C)	$T_{10wt.\%}$ (°C)	$T_{50wt.\%}$ (°C)	% Char yield @ 650 °C	$T_{5wt.\%}$ (°C)	$T_{10wt.\%}$ (°C)	$T_{50wt.\%}$ (°C)	% Char yield @ 650 °C
neat	346.1	368.5	411.3	3.2	382.2	405.2	452.9	3.2
1%	347.5	367.2	414.0	3.5	383.5	401.6	454.3	3.6
3%	338.8	359.1	405.8	4.3	373.5	394.0	438.6	3.8
5%	341.6	356.1	401.9	5.4	372.5	387.6	438.9	6.5

further insight on the influence of coated nanoparticles on nylon 6 stability, TG-DTA measurements were also carried out on $CaCO_3$, revealing that both in air and nitrogen the decomposition of the coating agent occurs at temperatures lower than that of polyamide. Therefore, the presence of the fatty acid coating can induce a decrease in thermal stability of polymeric matrix. In Figure 3 the comparison between TG-DTA curves run in nitrogen, either on coated $CaCO_3$ or on neat fatty acid coating removed from $CaCO_3$ surface, is reported.

As it is possible to observe, the DTA signal of the removed, neat acid shows an endothermal peak corresponding to the volatilization of sample. On the contrary, an exothermal DTA peak was recorded during the degradation of the fatty acid grafted onto nanoparticles surface, suggesting a distinct change in the mechanism of fatty acid decomposition.

It can be hypothesized that an acid-base reaction between $CaCO_3$ and fatty acid occurs, thus leading to the formation of water. As a matter of fact, in nylon based nanocomposites the latter phenomenon causes hydrolysis of polyamide peptide linkages, resulting in a destabilization effect under nitrogen.

Moreover, strong interactions between polymer amide groups and electron-attracting metal cations, such as Ca^{2+} (which causes an electron displacement toward the metal center) can also reduce the stability of the chemical bonds adjacent to the amide groups within the polymer chains. This phenomenon increases the probability of radical formation, thus contributing to polymer thermal destabilization.[11]

On the other hand, the smaller catalytic effect observed under air is likely due to the fact that oxygen diffusion is typically slowed down in polymer-nanoparticle composites, so that thermo-oxidative stability increases.

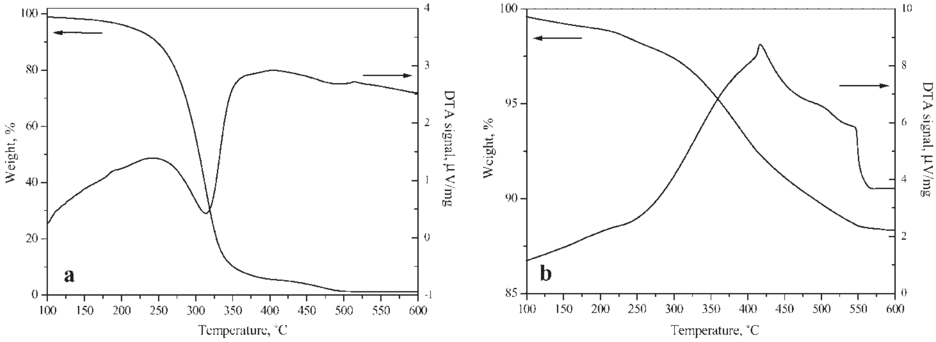

Figure 3.
TG-DTA traces under nitrogen atmosphere for: a) fatty acid coated $CaCO_3$ nanoparticles; b) neat fatty acid removed from coated $CaCO_3$ nanoparticles (heating rate 20 °C/min).

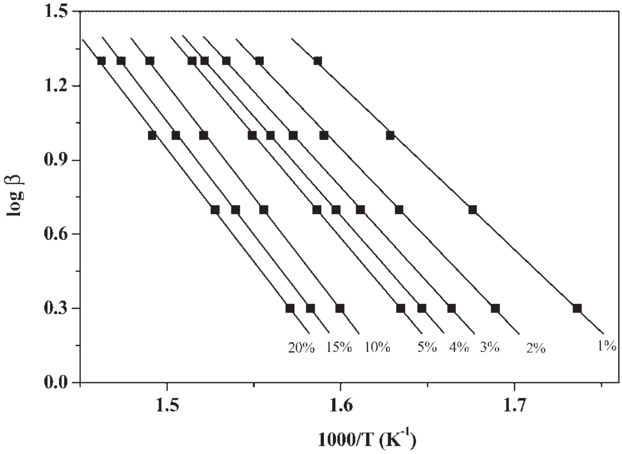

Figure 4.
Plot of log β vs. 1000/T in the conversion range 1–20% for the nanocomposite nylon 6/5% $CaCO_3$.

Nevertheless, even in this case an additional phenomenon should be taken into account, in order to explain higher stability of nanocomposites recorded in air with respect to nitrogen gas (cfr. Tables 1 and 2).

It is well known that nylon 6 degradation in air is mainly due to formation and decomposition of hydroperoxides. Thus, any process able to retard hydroperoxide formation can lead to a partial stabilizing effect. As already pointed out in the case of polyamides and poly(ethylene oxide)[11–12], several metal cations are able to retard hydroperoxidation in air atmosphere through complex formation with electron-donor heteroatoms present in the polymer backbone. This additional phenomenon, together with the slowed oxygen diffusion, can contribute to the observed stabilization under air.

Thermal Degradation Kinetics

In order to get further insight on the decomposition mechanism of nylon 6 based nanocomposites, kinetic analysis of the TG data recorded under air and nitrogen atmosphere was performed using the Flynn-Wall-Ozawa method. The activation energy E_a was obtained from a linear fitting of log β versus 1000/T at different conversions (α), where β is the experimental heating rate and T is the absolute temperature.

As an example, in Figure 4 the log β versus 1000/T for the nanocomposite containing 5% $CaCO_3$ in nitrogen, in a conversion range 1–20%, is reported.

As it is shown, the fitting straight lines are not parallel, suggesting that the degradation process occurs through a complex kinetic scheme that reveals a dependence of E_a on α. [13] This behaviour was observed for all the investigated compositions and for both the purging gases used.

In Table 3 the values of E_a as a function of α in the conversion range 1–80% are reported.

E_a increases with the conversion degree both for neat nylon 6 and nylon 6 based nanocomposites under nitrogen and air atmosphere.[14] The observed variation in E_a suggests that different processes govern the degradation phenomenon at the initial and final stages. The initial lower value of E_a is associated with the initiation step that occurs at the polymer weak links. In particular, in the case of nylon polymers the initiation step involves the methylene groups adjacent to the amide carbonyls. As the temperature increases, the limiting step of degradation shifts toward mechanism initiated by random scission characterized by higher activation energies.[15]

Table 3.
Activation energies determined from isoconversional plots according to the Flynn-Wall-Ozawa method.

α (%)	E_a(KJ/mol)							
	Nitrogen environment				Air environment			
	Nylon 6	1%	3%	5%	Nylon 6	1%	3%	5%
1	146.5 ± 7.7	111.2 ± 10.1	122.1 ± 3.2	121.1 ± 2.1	115.2 ± 16.5	107.7 ± 4.4	84.9 ± 10.4	124.1 ± 25.5
2	162.2 ± 9.1	113.0 ± 6.0	130.0 ± 4.6	133.1 ± 2.8	114.5 ± 8.4	115.0 ± 7.1	95.8 ± 12.3	147.8 ± 13.0
3	166.4 ± 13.1	116.2 ± 4.8	135.8 ± 6.9	140.3 ± 0.8	125.0 ± 9.9	120.1 ± 6.6	121.2 ± 10.0	135.3 ± 9.9
4	167.6 ± 16.0	119.2 ± 4.2	137.4 ± 7.3	145.5 ± 0.3	135.0 ± 13.7	126.8 ± 7.4	131.4 ± 10.9	143.2 ± 7.4
5	168.8 ± 18.2	119.3 ± 3.3	137.2 ± 8.0	151.0 ± 1.2	140.3 ± 14.6	130.5 ± 8.3	138.6 ± 12.5	150.1 ± 6.3
10	169.8 ± 16.8	122.5 ± 0.9	138.1 ± 7.5	165.5 ± 2.5	154.2 ± 20.8	152.7 ± 5.2	148.3 ± 18.5	155.4 ± 5.3
15	171.0 ± 14.5	126.0 ± 2.8	151.7 ± 8.4	166.4 ± 1.8	164.7 ± 20.9	170.8 ± 7.0	162.4 ± 8.4	161.6 ± 6.5
20	172.8 ± 14.1	128.8 ± 5.1	159.3 ± 10.7	165.7 ± 4.2	171.0 ± 17.2	172.5 ± 8.3	172.7 ± 7.3	169.8 ± 9.7
25	174.4 ± 15.0	130.6 ± 6.3	166.7 ± 12.7	163.3 ± 4.4	176.7 ± 17.5	180.5 ± 10.1	181.0 ± 4.5	176.3 ± 5.1
30	177.0 ± 13.2	132.6 ± 5.1	170.2 ± 13.8	159.9 ± 4.4	181.4 ± 16.9	181.1 ± 11.3	184.0 ± 4.1	180.6 ± 4.0
35	177.1 ± 14.1	134.4 ± 6.0	174.3 ± 14.2	157.8 ± 4.7	188.6 ± 13.4	185.7 ± 12.9	187.7 ± 5.8	182.7 ± 4.2
40	180.0 ± 13.9	135.0 ± 5.7	177.2 ± 14.0	156.0 ± 5.2	191.7 ± 11.4	189.3 ± 12.3	191.3 ± 6.5	186.0 ± 2.6
45	181.5 ± 13.4	136.9 ± 6.1	179.7 ± 14.3	153.2 ± 5.8	192.9 ± 8.9	192.6 ± 12.9	193.4 ± 6.6	186.9 ± 4.0
50	183.3 ± 13.4	138.6 ± 5.6	183.8 ± 15.5	151.3 ± 5.2	193.7 ± 9.5	196.2 ± 12.6	193.6 ± 8.1	190.3 ± 2.1
55	186.3 ± 14.3	139.5 ± 5.7	185.7 ± 15.6	150.9 ± 5.9	194.4 ± 7.8	196.6 ± 12.7	197.5 ± 7.2	192.7 ± 0.8
60	186.7 ± 13.6	140.7 ± 5.8	187.6 ± 15.1	150.1 ± 5.7	199.5 ± 8.5	199.2 ± 12.5	201.3 ± 6.6	198.7 ± 2.8
65	191.2 ± 14.2	143.6 ± 6.1	193.0 ± 19.5	149.3 ± 5.9	205.6 ± 7.6	207.3 ± 12.5	203.7 ± 7.5	206.2 ± 6.8
70	194.3 ± 14.7	146.0 ± 5.7	194.7 ± 18.7	147.7 ± 6.2	217.8 ± 6.0	218.9 ± 11.2	211.4 ± 8.5	221.5 ± 17.3
75	196.2 ± 14.2	148.8 ± 6.2	197.2 ± 19.1	149.4 ± 5.4	250.0 ± 6.4	240.0 ± 6.0	226.1 ± 8.6	249.9 ± 34.4
80	202.0 ± 16.2	151.4 ± 6.2	200.8 ± 20.5	150.4 ± 5.1	324.1 ± 23.2	289.6 ± 30.8	267.9 ± 12.7	272.8 ± 37.6

As far as the measurements performed in nitrogen are concerned, the presence of nanoparticles leads to a decrease in the activation energy. This can be related to the above-mentioned effect of the coated nanofillers, which catalyse the thermal decomposition resulting in an accelerated degradation.

On the contrary, in air atmosphere, slight variations of E_a are recorded with respect to the nanoparticles content, since the thermal oxidation is the main degradative process.

In order to investigate how the amount of $CaCO_3$ affects the mechanism of the degradation process, E_a values were plotted *vs.* α for all the prepared materials. In Figure 5 the above-mentioned curves related to measurements carried out under nitrogen and air for neat polymer and nanocomposites containing 1 and 5%

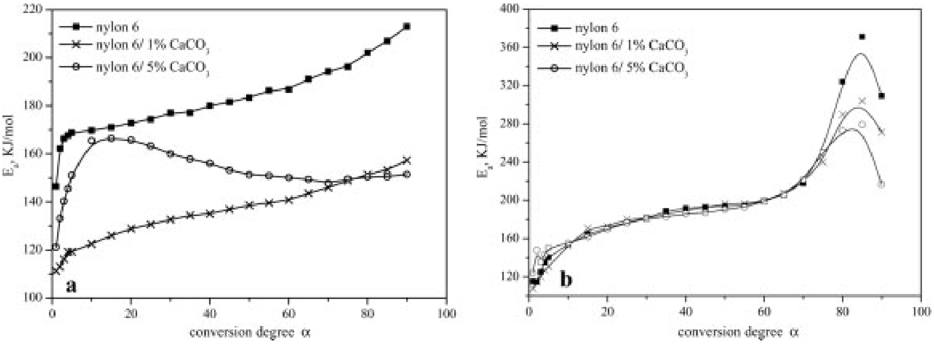

Figure 5.
Activation energy (E_a) as a function of the conversion degree for the decomposition processes of neat nylon 6, nylon 6/1% $CaCO_3$ and nylon 6/5% $CaCO_3$ nanocomposites in: a) nitrogen, and b) air atmosphere.

$CaCO_3$ are reported as an example. The shapes of the dependence of E_a on α were identified from model data for competing, independent, consecutive as well as reactions complicated by diffusion.[16,17] The experiments carried out under nitrogen flow show that the addition of 1% by weight of $CaCO_3$ does not change the dependence of the activation energy on the conversion degree, however the curve is lowered by about 50 kJ/mol through all the conversion range.

This behaviour indicates that at a low content of nanoparticles the degradation rate of nylon 6 increases, while the overall degradation mechanism seems not to be affected.

In the case of 5% by weight of nanoparticles E_a decreases only at higher conversion degrees, the initial build-up of E_a being followed by a steady decrease up to $\alpha \approx 0.6$. This result can be justified taking into account the diffusion process of the gases escaping from the polymer matrix during decomposition. Actually, high loadings of nanoparticles are responsible for a change from a kinetic to a diffusion regime. It was pointed out that such processes are widely met in solids decomposed in the following way: solid → solid + gas. As a surface layer of the solid product grows, diffusion of a gas through it gradually becomes the rate limiting step of the decomposition.[13] As for measurements performed in air, E_a increases with α, Figure 3b. Moreover, three different zones are evident in the curves. The first increase (up to $\alpha \approx 0.4$) and the subsequent plateau ($\alpha = 0.4$ to 0.6) can be explained by competition between pyrolysis and oxidation taking place in presence of oxygen. The last kinetic stage is due to the burning process of the char, as also observed by the marked exothermal peak in the DTA traces. However, it should be underlined that at these conversion degrees the mechanism can be hardly described with a first order approximation, thus compromising the applicability of the Flynn-Wall-Ozawa method.

Conclusions

The above discussed results can be summarized as follows:

- the presence of coated nanoparticles negatively affects the thermal and thermo-oxidative stability of nylon 6;
- kinetic analysis showed a dependence of E_a on α, thus indicating that a multi-step decomposition process occurs;
- measurements performed under nitrogen demonstrated that higher amounts of nanoparticles are responsible for a diffusion-driven regime of the decomposition process under an inert atmosphere;
- measurements carried out in air showed that $CaCO_3$ nanoparticles do not affect the rate limiting step of the decomposition process.

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