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Nylon 6/Calcium Carbonate Nanocomposites: Characterization and Properties

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Summary: Two polymorphic modifications of calcium carbonate nanoparticles (calcite and aragonite) characterized by different shape and coated with fatty acids were used as reinforcement phases of Nylon 6. Nylon 6 based nanocomposites filled with 1% and 5% by weight of calcite and aragonite were prepared by melt mixing. Morphological analysis performed on the fractured surface of nanocomposites showed that the coating agent permits to obtain uniform and fine nanoparticles dispersion. DMTA analysis revealed that nanoparticles increase the glass transition temperature of Nylon 6 up to 12 °C in the case of calcite, while a less pronounced increase was recorded for aragonite. Finally, structural analyses (FT-IR and WAXS) underlined that calcite nanoparticles promote and stabilize the γ-crystalline form of Nylon 6, while in the case of aragonite nanofillers the α-crystalline form was still dominant.

Keywords: glass transition; infrared spectroscopy; nanocomposites; polymorphism wide-angle-X-ray scattering (WAXS)

Introduction

The use of inorganic nanoparticles as fillers of polymeric based composites can provide high performance materials that find application in several industrial fields. In fact they often exhibit properties that are completely different from those of polymeric systems in which an inorganic component is added to a polymeric matrix at micrometer level. These unique and unexpected behaviours are due to the enormous interfacial adhesion area of the nanoparticles.[1,2]

Nylon 6 is a semicrystalline polymer showing polymorphism. It is characterized by relatively low cost and high performances and it is mainly used in the field of fibers and engineering plastics. It has two major crystalline forms, the α form and the γ form. The α-form is characterized by a fully extended configuration of the polymer chains that show an anti-parallel orientation. Anti-parallel chains are situated such that the amide linkage and methylene units lie within the same plane and H-bonds occur between adjacent anti-parallel chains to form sheets of H-bonded chains. This structure repeats itself thereby creating stacks of H-bonded sheets in a monoclinic crystal. The γ crystalline form occurs when H-bonds form between parallel polyamide chains. In this case H-bond formation requires the amide linkages to twist approximately 60° out the plane of these molecular sheets. The chain packing of the γ-form resembles that of a hexagonal structure.

Every crystalline form has specific properties so that the whole material behaviour depends on the relative amount of α and γ-form.[3]

In literature, several studies[4–12] report the influence of clay on the crystal structure of Nylon 6 as well as the influence of the polymer crystal modification on final

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properties of polyamide based materials. In this paper results about the preparation and the structural characterization of Nylon 6 based nanocomposites filled with calcium carbonate nanoparticles are reported. In particular, two polymorphic modifications of calcium carbonate nanoparticles (calcite and aragonite) characterized by different shape (spherical and elongated) and coated with fatty acids were used as nanodispersed phases. The main objective of this research was focused on the study of the influence of the nanoparticles structural modification and dispersion on the Nylon 6 crystal structure.

Experimental

Materials

Nylon 6 (code F34L, $\eta = 3.4$ dL/g in concentrated H_2SO_4) was kindly supplied by SNIA-FIAT. Calcium carbonate nanoparticles were kindly supplied by Solvay Advanced Functional Minerals. The nanoparticles have different crystal modifications: calcite (trigonal-rhombohedral), aragonite (ortho-rhombic), which also result in different shape of the nanopowders, spherical and elongated, respectively. Both the $CaCO_3$ types were coated with fatty acids (FA).

Preparation of Nylon 6/$CaCO_3$ Nanocomposites

Nylon 6 based nanocomposites were prepared by mixing the components in a Brabender-like apparatus operating at 220 °C and 32 rpm for 10 min. The mixing ratios of Nylon 6/$CaCO_3$ (wt/wt) were 99/1 and 95/5. Neat Nylon 6 was processed in the same experimental conditions. Nylon 6 and Nylon 6 based nanocomposites were compression-moulded in a heated press at 220 °C for 5 min without any applied pressure. After this period, a pressure of 100 bar was applied for 3 min, then the plates were rapidly cooled to room temperature (cooling rate: about 15 °C/min) by cold water.

Techniques

Morphological Analysis

The morphological analysis was performed by using a Philips XL 20 series scanning electron microscope (SEM) on cryogenically fractured surfaces of the samples. Before the observation, the surfaces were coated with Au-Pd alloy with a SEM coating device (unit E5150, Polaron Equipment Ltd).

Dynamic-Mechanical Analysis (DMTA)

Dynamic-mechanical data were collected at 1 Hz at a heating rate of 3 °C/min from 0 to 150 °C under nitrogen with a Dynamic Mechanical Thermal Analyser MK III, Polymer Laboratories. Tests were performed in bending mode.

FT-IR Analysis

Infrared spectra were recorded at room temperature using 64 scans, 2 cm^{-1} resolution with a Perkin Elmer Paragon 2000 Fourier Transform Infrared spectrometer. The spectra were performed on films of the materials obtained by compression moulding.

Structural Analysis

Wide angle X-Ray Scattering (WAXS) measurements were carried out by using a Philips powder diffractometer (PW 1050 model) operated at the CuKα wavelength of 1.542 Å and equipped with a rotating sample-holder device. Measurements of the diffracted intensities were performed in the angular range of 2–60° (2θ), at room temperature and at a scanning rate 1°/min.

Results and Discussion

Nylon 6 based nanocomposites filled with calcium carbonate nanoparticles were prepared by melt mixing. In particular, two polymorphic modifications of calcium carbonate nanoparticles (calcite and aragonite) characterized by different shape and coated with fatty acids were used as nanofillers. Main properties of $CaCO_3$ are summarized in Table 1.

Table 1.
Main calcium carbonate nanoparticles properties.

Properties	Nanoparticles	
Shape	Spheres	Needle like
Crystal structure	Calcite (Trigonal-rhombohedral)	Aragonite (Ortho-rhombic)
Average particle size (nm)	50	250 (length) 50 (thickness)
Specific surface area (m^2/g)	75	10 ÷ 15
Coating agent	Fatty acids	Fatty acids

The morphology of the calcite and aragonite nanoparticles is reported in Figure 1A and 1B, respectively.

It is well known that nanoparticles exhibit a great tendency to agglomeration phenomena due to a very high surface energy and to a poor compatibility with the most of common polymeric matrices. On the other hand, one of the key factors in the preparation of enhanced performance nanomaterials is to obtain uniform distribution of discrete nanoparticles within polymer matrix and to promote a strong interfacial adhesion between matrix and nanofillers. The grafting of organic molecules onto the nanoparticle surface as well as on classical microparticles represents an effective strategy to overcome nanoparticle clustering. In fact, grafted chains increase the affinity of particle surface towards organic polymeric matrices improving the interfacial adhesion between the two nanocomposite components.

As a matter of fact, both calcite and aragonite nanoparticles were covered by fatty acids, which could act as nucleophile sites for the Nylon 6 functional groups, thus allowing polar interactions, such as hydrogen bonds, between the amide groups of the matrix and the carboxyl groups of the fatty acids.

To evaluate $CaCO_3$ nanoparticle dispersion into polymeric matrix, the fractured nanocomposite surfaces were observed by scanning electron microscope (SEM). SEM micrographs of nanocomposites containing the highest amount of calcite and aragonite nanoparticles (5% wt/wt) are shown in Figure 2A and 2B, respectively. As it is clearly evidenced by the figures, both the types of nanoparticles are covered and quite welded to the Nylon 6 matrix. Moreover, nanofillers appear homogeneously dispersed into polymer and no pull out phenomena are evidenced by the absence of voids. This morphology was also obtained at lower nanoparticles content. Therefore, SEM analyses permit to assess that the presence of fatty acids as coating agent provides a useful strategy to achieve uniform dispersion and strong Nylon 6/ nanoparticles interfacial adhesion.

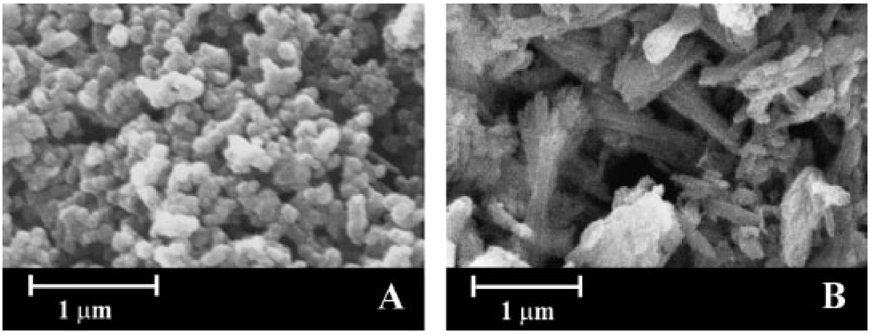

Figure 1.
SEM micrographs of $CaCO_3$ nanoparticles: A) calcite; B) aragonite.

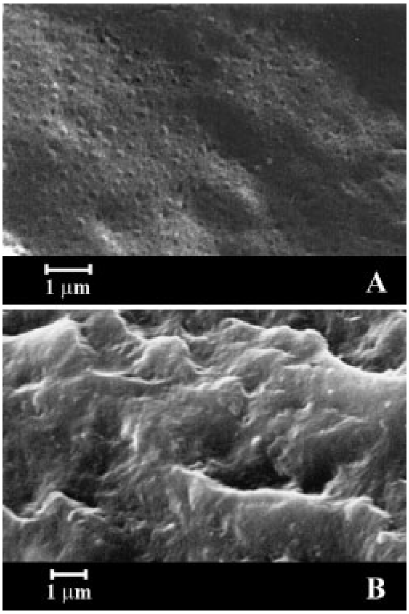

Figure 2.
SEM micrographs of Nylon 6/$CaCO_3$ nanocomposites containing 5% (wt/wt) of different nanoparticles: A) calcite; B) aragonite.

In Table 2, the glass transition temperatures (T_g), evaluated by DMTA analysis, are reported.

The presence of nanoparticles is responsible for an increase of T_g values as a function of nanofillers content and shape. In fact, calcite raises Nylon 6 T_g up to 12 °C while in the case of aragonite a less pronounced increase was recorded (5 °C).

Table 2.
Glass transition temperature (T_g) of neat Nylon 6 and Nylon 6 based nanocomposites.

Sample	Nanoparticles content (%, wt/wt)	T_g (°C)
Nylon 6	—	67
Nylon 6/Calcite	1.0	74
	5.0	79
Nylon 6/Aragonite	1.0	69
	5.0	72

These data are strictly correlated to the homogeneity of nanoparticles dispersion and to the good adhesion between the two phases (Figures 2A and 2B), responsible for a limited mobility of Nylon 6 chains. On the other hand, calcite nanoparticles are characterized by higher specific surface area with respect to that of aragonite, thus justifying the most significant effect on the glass transition temperature due to a large interfacial region.

Structural Analyses

Figure 3 shows FT-IR spectra of Nylon 6 and Nylon 6 containing calcite and aragonite nanoparticles. The spectrum of Nylon 6 sample (Figure 3A) is characterized by the typical absorption bands at 930 and 960 cm^{-1} attributable to CONH signals in a plane vibrational mode of the α-crystalline form.[13] The same absorption bands are also present in FT-IR spectra of Nylon 6 reinforced with aragonite nanoparticles (Figure 3B and 3C, respectively). Moreover, due to the presence of aragonite, a new absorption band at 855 cm^{-1} can be also evidenced whose intensity is clearly a function of the nanofillers content.

As concerning nanocomposites filled with calcite nanoparticles, FT-IR spectra (Figures 3D and 3E) show the raising of an absorption band at 975 cm^{-1}. This absorption band is more pronounced in the case of the sample containing the highest amount of calcite nanoparticles (Figure 3E), and it corresponds to a CONH signal in a plane

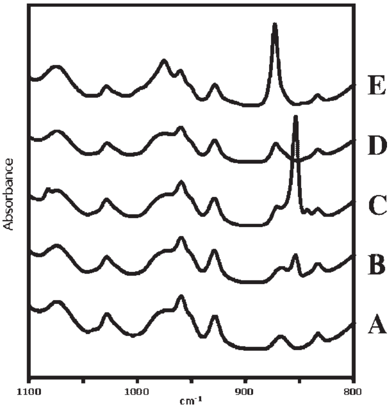

Figure 3.
FTIR spectra of: A) Nylon 6; B) Nylon 6/Aragonite 99/1 (wt/wt); C) Nylon 6/Aragonite 95/5 (wt/wt); D) Nylon 6/Calcite 99/1 (wt/wt); E) Nylon 6/Calcite 95/5 (wt/wt).

vibrational mode of the γ-crystalline form.[13] Moreover, FT-IR spectra reported in Figures 3D and 3E also evidence the typical band of calcite centered at 874 cm^{-1}.

These results reveal that Nylon 6 exhibits mainly the α-crystalline form. This form is still dominant in the case of nanocomposites containing aragonite as dispersed nanophase. On the contrary, the presence of calcite nanoparticles promotes the formation of the γ-crystalline form as a function of nanofillers content.

WAXS analysis was also performed on Nylon 6 and on nanocomposite films; whose intensity profiles are shown in Figure 4. As it is possible to observe Nylon 6 pattern (Figure 4A) shows two major diffraction peaks at $2\theta = 20.1^\circ$ and 23.7° that are assigned to the (200) reflection and (002)/(202) reflections respectively of the Nylon 6 α-crystalline form.

The same diffraction peaks can be evidenced from WAXS intensity profiles of nanocomposites filled with aragonite (Figures 4B and 4C). Moreover, aragonite induces an inversion of the relative intensity of the above mentioned diffraction peaks.

In the case of calcite nanoparticles a new diffraction peak centered at $2\theta = 21.6^\circ$ is to be remarked and it can be indexed as the $(200)/(001)/(\bar{2}01)$ reflections of Nylon 6 γ-crystalline form. The intensity of this signal is a function of the calcite amount.

The above described WAXS results, in agreement with the FT-IR analysis, underline that calcite nanoparticles induce and stabilize the formation of the Nylon 6 γ-crystalline form.

The formation of Nylon 6 α and γ-crystalline forms is strictly influenced by the process conditions.[14–16] In particular, rapid cooling and/or low crystallization temperatures induce the γ-crystalline form, whereas slow cooling and/or high crystallization temperatures stabilize the α-crystalline form.[17]

In order to verify the influence of the crystal modification and shape of nanoparticles on the Nylon 6 crystal structure, nanocomposites were crystallized from the melt at 190 °C that is the crystallization temperature normally leading only to the α-form.

As it can be observed in Figure 5, WAXS intensity profiles of Nylon 6 (Figure 5A) and Nylon 6 containing aragonite nanoparticles (Figure 5B), crystallized at 190 °C, confirm the formation of the α-crystalline form. On the contrary, in presence of calcite nanoparticles the γ-form can be still evidenced.

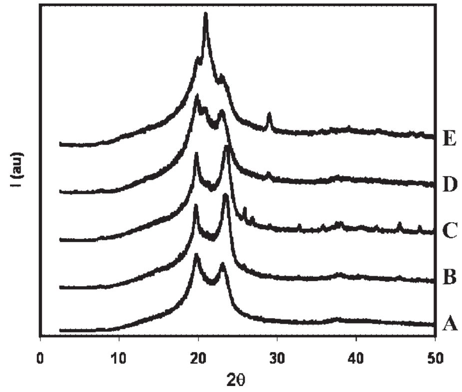

Figure 4.
WAXS profiles of: A) Nylon 6; B) Nylon 6/Aragonite 99/1 (wt/wt); C) Nylon 6/Aragonite 95/5 (wt/wt); D) Nylon 6/Calcite 99/1 (wt/wt); E) Nylon 6/Calcite 95/5 (wt/wt).

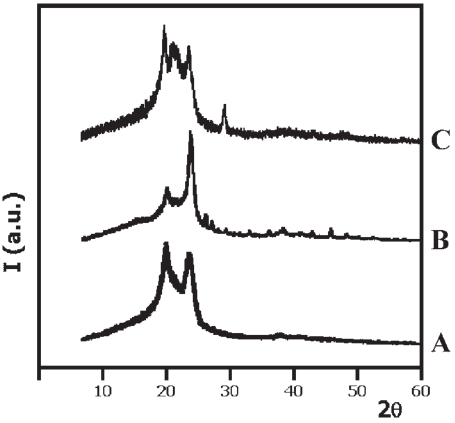

Figure 5.
WAXS profiles of Nylon 6 and Nylon 6 based nanocomposites crystallized from the melt at 190 °C: A) neat Nylon 6; B) Nylon 6/Aragonite 95/5 (wt/wt); C) Nylon 6/Calcite 95/5 (wt/wt).

These experimental findings allow assessing that calcite nanoparticles promote and stabilize the γ-crystalline form of Nylon 6. These results can be justified considering the high specific surface area of calcite nanoparticles and the strong matrix/nanofillers interfacial adhesion, both of them inducing a significant increase of the glass transition temperature, up to 12 °C, as a function of calcite content. The T_g increase is indicative of a restricted polymer chains mobility that is another condition favouring the Nylon 6 γ-crystalline form.[17]

Conclusions

Nylon 6 based nanocomposites filled with aragonite and calcite nanoparticles, coated with fatty acids, were prepared and characterized. The above discussed results can be summarized as follows:

- the fatty acids coating agents allow reaching uniform and fine nanoparticles distribution as well as strong matrix/nanofillers interfacial adhesion;
- a significant increase of the glass transition temperature was recorded as a function of calcite nanoparticles content, whereas a less pronounced variation was obtained in presence of aragonite nanoparticles;
- calcite nanoparticles promote and stabilize the γ-crystalline form of Nylon 6.

[1] B.M. Novak, *Adv. Mater.* **1993**, 5, 422.
[2] S.J. Ahmadi, Y.D. Huang, J.W. Li, *J. Materials Science* **2004**, 38, 1919.
[3] P. Bernado, C. Alema, J. Puiggalı, *Macromol. Theory Simul.* **1998**, 7, 659.
[4] P. Maiti, M. Okamoto, *Macromol. Mater. Eng.* **2003**, 288, 440.
[5] T.M. Wu, E.C. Chen, *Polym. Eng. Sci.* 2002, 42, 1141.
[6] T.M. Wu, C.S. Liao, *Macromol. Chem. Phys.* **2000**, 201, 2820.
[7] D.G. Martınez-Vazquez, F.J. Medellın-Rodrıguez, P.J. Phillips, S. Sanchez-Valdes, *J. Appl. Polym. Sci.* **2003**, 88, 360.
[8] G. Zhang, Y. Li, D. Yan, *Polym. Int.* **2003**, 52, 795.
[9] T. Kyu, Z.I. Zhou, G.C. Zhu, Y. Tajuddin, S. Qutubuddin, *J. Polym. Sci. B: Polym. Phys.* **1996**, 34, 1761.
[10] K.H. Yoon, M.B. Polk, B.G. Min, D.A. Schiraldi, *Polym. Int.* **2004**, 53, 2072.
[11] L. Liu, Z. Qi, X. Zhu, *J. Appl. Polym. Sci.* 1999, 71, 1133.
[12] Z. Zhao, W. Zheng, W. Yu, H. Tian, H. Li, *Macromol. Rapid Commun.* **2004**, 25, 1340.
[13] S. Murase, A. Inoue, Y. Miyashita, N. Kimura, Y. Nishio, *J. Polym. Sci. B: Polym. Phys.* **2002**, 40, 479.
[14] F. Auriemma, V. Petraccone, L. Parravicini, P. Corradini, *Macromolecules* **1997**, 30, 7554.
[15] M. Ito, K. Mizuochi, T. Kanamoto, *Polymer* **1998**, 39, 4593.
[16] J. Ho, K. Wie, *Macromolecules* **2000**, 33, 5181.
[17] T.D. Fornes, D.R. Paul, *Polymer* **2003**, 44, 3945.