Nanocomposite Fibers for Cosmetotextile Applications

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Summary: In this work, a series of nylon 6 nanocomposites with different nanoclay/jojoba oil contents have been prepared by direct melt compounding. Nanocomposite morphologies were characterized by means of WAXS analysis. Thermal and mechanical fibers properties were studied as well. The kinetic desorption of the cosmetic oil through the polymer matrix was evaluated by FT-IR microscopy. It was found that the state of the clay particles affected the thermal behaviour and the tensile mechanical properties of each polymer/clay hybrid. On the other hand, the release of the cosmetic oil, tested by FT-IR microscopy, is a good perspective for the application of polyamide 6 nanocomposite fibers as textiles in cosmetic field.

Keywords: cosmetotextile; fibers; nanocomposite; polyamide

Introduction

Polymer/clay nanocomposites- a new class of reinforced plastics formed by dispersing nano-sized clay particles throughout a polymer matrix- have received much attention in both scientific and industrial areas due to their enhanced mechanical and barrier properties as well as flame resistance.[1–5]

Although the high aspect ratio of silicate nanolayers is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophobic engineering plastics. The replacement of the inorganic exchange cations in the galleries of the native clay by alkylammonium surfactants can favour the compatibility between the surface chemistry of the clay and the hydrophobic polymer matrix. Moreover the replacement expands the clay galleries, this facilitates the penetration of the gallery space (intercalation) by either the polymer precursor or preformed polymer.[2]

The direct melt intercalation into clay layers is, for example, a preferred process for the formation of hybrid materials not only with respect to environmental issues (solvent free) but also due to the ease of fabrication for its promising commercial applications.[6]

Polyamides are widely used materials due to their several properties and variety of end-uses such as in automotive, food packaging, textiles. The use of nanotechnology in textile engineering leads to opportunities for increasing the performance of fibers and for creating unprecedented functions. The incorporation of laminar aluminosilicate allows the formation of nanocomposite fibers characterized by the dispersion of intercalated/exfoliated montmorillonite in the fibre-forming material increasing the tensile strength, the elastic modulus, heat resistance as well as gas and water barrier properties.[7]

To the best of our knowledge, no study on nylon 6/clay nanocomposites in the field of textiles for cosmetics application has been reported yet.

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New materials and technologies promote development of high-tech textiles, characterized by unprecedented functions and effects.

An example of the new way to combine tradition and innovation is represented by fibers having skin care activity, which are able to release on the wearer cosmetics and perfumes agents: the active agent embedded into the fabric can be transferred thanks to humidity exchange between skin and fibers surface.

For this application, the nanoclay acts as carrier which adsorbs and promotes the dispersion of the cosmetic substance throughout the polymer matrix also protecting it by degradation.

In this work, a series of nylon 6 nanocomposites with different organo-modified nanoclay/jojoba oil contents have been prepared by direct melt compounding. To check jojoba oil concentration and its time desorption through the polyamide matrix FT-IR microscope analyses have been carried out. Blends nanoscale morphology, thermal and mechanical fibers properties have been characterized as well.

Experimental

Materials

The materials used in this study were nylon 6 (polyamide 6) pellets (supplied by NYLSTAR-Italy); organically modified clay Nanomer®I.28 (montmorillonite containing 25 wt% trimethyl stearyl ammonium groups supplied by NANOCOR Inc.); cosmetic natural jojoba oil (MCY products); isopropanol (Aldrich).

Preparation of Polyamide 6/Nanoclay-jojoba Oil Hybrid Nanocomposites

Melt blended nanocomposites were formed using a Haake Rheocord Rheomix 600 co-rotating twin mixer with a screw speed of 30 rpm at 240 °C for 2 minutes to avoid cosmetic oil degradation.

The organo- modified nanoclay and jojoba oil were mixed in weight ratio 1:1 and a wide range of polyamide 6/nanoclay-jojoba oil nanocomposites (polyamide 6/nanjojo) containing 1.5, 3.5, 5, 7 and 8.5 wt% nanoclay-jojoba oil paste were prepared.

Preparation of Polyamide 6/Nanoclay-jojoba Oil Nanocomposites Fibers

Nanocomposite blends were reduced in pellets and were dried at 100 °C for 24 h and then extruded through the die of a Bohlin Instruments Inc mod.RH7 capillary rheometer at 240 °C to form fibers.

Standard die diameter was 1 mm, velocity of extrusion was 5 mm/min, the take up speed was manual so it was not possible to calculate the DR.

TGA Measurements

Thermal properties of polyamide 6/nanomer-jojoba oil nanocomposites were analysed by TGA performed at a heating rate of 10 °C/min from room temperature up to 550 °C under N_2 flow by using a Hi-Res TGA 2950 from TA Instruments. The inorganic content of each composite was calculated from the residue left at 500 °C. The actual percentage of organo-modified nanoclay, closely related to the amount of jojoba oil, was determined by 25% correction of organic content in Nanomer®I.28.

X-ray Diffraction

Wide-angle X-ray Scattering (WAXS) measurements of the as-mixed samples were performed at room temperature using a PW 1830/00 Philips diffractometer (Cu Kα Ni-filtered radiation) equipped with Philips (PW 3020model) powder goniometer and a sample holder for sample spinner. The high voltage was 40 kV and the tube current was 30 mA. A standard sample was employed to determine the instrumental broadening.

The scanning rate was conducted over a range of $2\theta = 1$–$10°$.

Mechanical Tests

The tensile properties of the fibers were determined using an Instron mechanical tester (Model 4204) at a crosshead speed of 8.4 mm/min at room temperature. Property values reported here represent an average of the results for tests run on at least 20 specimens.

FT-IR Analysis

Thin sections of c.a. 20 micron were cut using a Reichert-Jung 1150/Autocat microtome at room temperature. Sections were compressed at 100 atm to further reduce thickness and then observed by FT-IR Perkin Elmer System 2000 equipped with optic microscope IR Autoimage.

FT-IR spectra were recorded before starting sections extraction using isopropanol and after solvent contact time of 2, 4, 6, and 26 hours.

Results and Discussion

Nanostructure and Morphology

The clay dispersion within polyamide 6 matrix has been characterised by WAXS.

The WAXS results for neat polyamide 6 and its nanoclay-jojoba oil nanocomposites with different clay concentrations are shown in Figure 1.

The first reflection for the surface-modified clay, Nanomer®I.28, was found at $2\theta = 3.39^\circ$ which corresponds to an interlayer distance of 26 Å.

The WAXS first peak for nanoclay-Jojoba Oil mixture was found at $2\theta = 2.14^\circ$ that can be related to an interlayer distance of 41 Å, probably jojoba oil alkyl chains have great physical affinity with the organo-modifier in Nanomer®I.28, such a resulted increasing of the interlayer spacing causes a big shift of the diffraction peak toward lower values of 2θ.

In general, one might expect that larger spacing may allow to easier exfoliation since platelet-platelet attraction is reduced. It is implied that diffusion of polymer chains inside clay galleries is less hindered due to increased spacing and ultimately leads to improved exfoliation[8] resulting in hybrids with better dispersion of clay and jojoba oil.

Actually, after melt compounding with polyamide 6, the basal plane of organo-modified nanoclay disappears in the WAXS patterns for the obtained nanocomposites with different clay-jojoba oil loading levels up to 8.5 wt%.

The absence of basal plane peaks indicates the delamination and dispersion of the clay nanolayers within the polyamide 6 matrix, i. e., the formation of an exfoliated nanostructure.

It is worth noting that in spite of the absence of the basal plane, a broad shoulder in the small angle region is usually observed in WAXS patterns for the obtained nanocomposites with high clay loading (e.g. 8.5 wt%), probably indicating the formation of partially exfoliated/partially intercalated nanostructures.[8]

There is a quite small peak in the 3.5 wt% scan occurring around $2\theta = 5.5^\circ$ corresponding to a basal spacing of 16 Å. This spacing is less than that of repeat spacing of the organo-modified nanoclay, this may be due to the collapse of a small fraction of the nanoclay galleries caused by ammonium ion degradation.[9]

It is well accepted that the state of the clay particles affected the thermal behaviour and the tensile mechanical properties of each polymer/clay hybrid.

Thermal Properties

The thermal stability of pure polyamide 6 and its nanocomposites has been investigated (Figure 2).

The improved thermal stability for polymer/clay nanocomposites is mainly due to the formation of char which hinders the out-diffusion of the volatile decomposition products, as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposites.[10]

In this case, despite exfoliation occurs (as evidenced by WAXS), the decomposition temperature is not improved by the presence of nanoclay, excepted at nanofiller concentration of 1.5 wt%.

Since Jojoba Oil degradation temperature under N_2 flow is 393 °C at 50% weight loss and for pure polyamide 6 is 441 °C, Jojoba Oil decomposition process is faster than that of polyamide and its

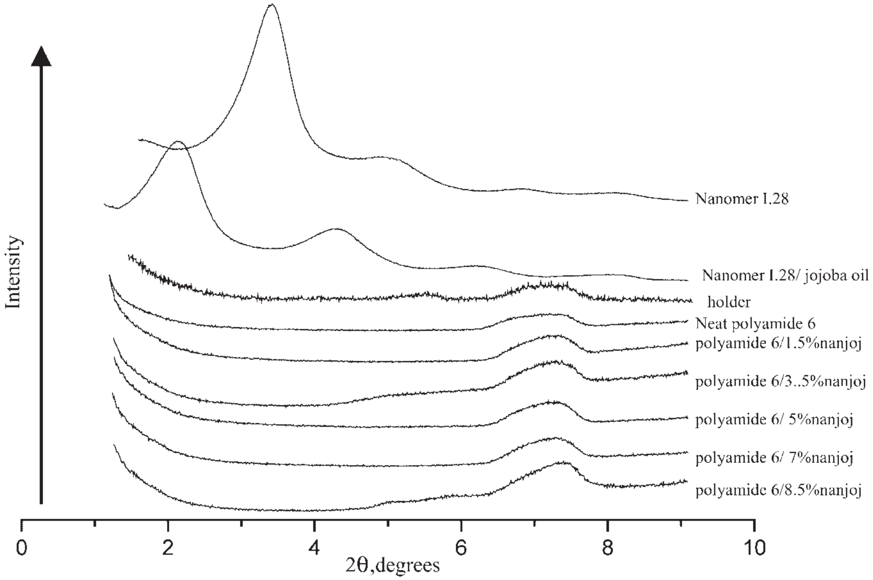

Figure 1.
WAXS results for neat polyamide 6 and its nanoclay-jojoba oil nanocomposites with different clay concentrations.

dispersion through polymer matrix promotes in advance the degradation mechanism. This feature is valid for every sample loading.

Thus, increasing nanoclay/jojoba oil concentration, the nanocomposites degrade at the same temperature or even inferior to that of unfilled polyamide 6 matrix; decomposition temperatures at 5% and 50% weight loss are listed in Table 1.

The weight of the final residue at 500 °C was found to increase by between 0.9 and

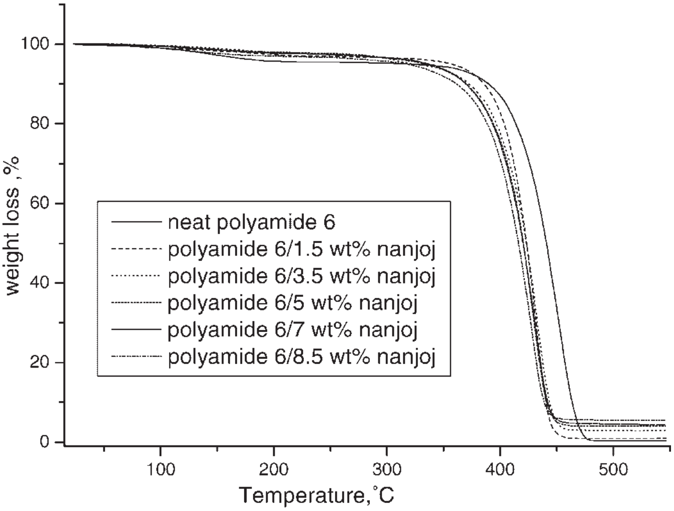

Figure 2.
Weight loss of neat polyamide 6 and its nanocomposites as function of temperature.

Table 1.
Degradation temperatures by TGA at 5% and 50% weight loss.

Samples	Degradation temperature (5% weight loss)	Degradation temperature (50% weight loss)
pure polyamide 6	322 °C	441 °C
polyamide 6/1.5 wt% nanjoj	357 °C	424 °C
polyamide 6/3.5 wt% nanjoj	322 °C	423 °C
polyamide 6/5 wt% nanjoj	335 °C	420 °C
polyamide 6/7 wt% nanjoj	335 °C	420 °C
polyamide 6/8.5 wt% nanjoj	316 °C	416 °C

5.3 wt% in accordance with the increase in nanoclay loadings (from 1.5 up to 8.5 wt%).

The actual percentage of jojoba oil in the final nanocomposite was calculated from

$$\% \text{ jojoba} = \% \text{ nanoclay}$$

$$= \% \text{ MMT}_{\text{ash}}/100 - \text{OC}$$

where % MMT_{ash} is the mass after incineration relative to the original nanocomposite mass; OC is the % organic content in the nanoclay as reported by suppler.

The experimental nanofiller contents and the relative corrections are listed in Table 2.

Mechanical Properties

The effect of clay content on the tensile properties of polyamide 6 nanocomposites compared to neat polyamide 6 has been investigated. Table 3 summarizes the modulus and the other mechanical properties of the hybrid fibers. Figure 3 shows the effect of montmorillonite concentration on the modulus of nanocomposites.

The tensile modulus of the hybrid fibre containing theoretical 5 wt% of organo-modified nanoclay (experimental 4.1 wt%) was 1.7 times greater than that for pure polyamide 6. When the organo-modified nanoclay content in PA6 reached 8.5 wt% (experimental 7.1 wt%), the modulus increased about 2.2 fold over that of pure polyamide 6. This was consistent with the general observation that the introduction of an nanoclay into a polymer matrix is found to improve its mechanical modulus.

It is worth noting that for hybrid fibers containing 1.5 wt% and 3.5 wt% of organo-modified nanoclay the tensile modulus was nearly identical to that of pure polyamide 6. This seems to be the result of debonding between nanoclay and PA6; debonding could be also the explanation of tensile modulus declination when the theoretical amount of nanoclay in polyamide was 7 wt%.[11]

Figure 4 shows the dependence of yield strength and strain at yield point on montmorillonite content: as expected yield strength slightly increased with the concentration of montmorillonite, on the contrary the strain at yield point decreased with clay loading.

In general virgin polyamides are very ductile at low test rates. Increasing the clay content leads to a sacrifice in ductility compared to pure polyamide 6, in this case elongation at break values are quite similar

Table 2.
Experimental nanofiller contents by TGA and relative corrections.

Sample	Experimental filler content (wt%)	Actual nanoclay content (wt%)
PA6	0	0
polyamide 6/1.5 wt%nanjoj	0.90	1.20
polyamide 6/3.5 wt%nanjoj	2.48	3.31
polyamide 6/5 wt%nanjoj	3.06	4.08
polyamide 6/7 wt%nanjoj	4.14	5.52
polyamide 6/8.5 wt%nanjoj	5.34	7.12

Table 3.
Mechanical properties of nanocomposite fibers.

Samples	Actual filler content (wt%)	Young's modulus (GPa)	Yield strength (MPa)	Strain at yield point (%)	Elongation at break (%)	Ultimate strength (MPa)
PA 6	0	0.953 ± 0.100	0.041 ± 0.003	0.0943 ± 0.0023	#	#
PA6/1.5%nanjoj	1.20	0.846 ± 0.097	0.045 ± 0.002	0.0832 ± 0.0037	#	#
PA6/3.5%nanjoj	3.31	0.909 ± 0.097	0.050 ± 0.003	0.0666 ± 0.0058	2.34 ± 0.19	50 ± 3
PA6/5%nanjoj	4.08	1.66 ± 0.095	0.062 ± 0.002	0.0465 ± 0.0027	2.37 ± 0.25	54 ± 4
PA6/7%nanjoj	5.51	1.60 ± 0.102	0.060 ± 0.002	0.0460 ± 0.0033	2.23 ± 0.31	53 ± 5
PA6/8.5%nanjoj	7.12	2.14 ± 0.402.	0.072 ± 0.007	0.0433 ± 0.0036	2.36 ± 0.09	66 ± 8

breaking does not occur.

up to 3.5 wt% montmorillonite concentration, such a behaviour is consistent with results found by Fornes et al.[12] for low molecular weight polymer matrix.

FT-IR Analysis

It was possible to check jojoba oil content in nanocomposite blends observing the characteristic peak signal of jojoba oil at 1740 cm^{-1}, which appears in spectra of polyamide 6 nanocomposites containing jojoba oil and does not appear in polyamide 6 nanocomposite without it (Figure 5). Polymer blend thin sections were dipped in isopropanol for increasing time (2 to 26 h) to study jojoba oil desorption through the polymer matrix: the decrease of the peak intensity at 1740 cm^{-1} corresponded to a jojoba oil release from the polyamide. For every sample a progressive content reduction of the cosmetic agent was observed (Figure 6 and Figure 7).

It is interesting to note that jojoba oil is released slowly at low organo-modified nanoclay concentration (1.5 wt%, 3.5 wt%, 5 wt%) and faster when nanoclay concentration is higher (7 wt%, 8.5 wt%).

It seems that the polyamide 6 has a maximum capacity, related to the hydrophobic nature of the matrix, to hold back the lypoid agent; going beyond this physicochemical limit the release mechanism cannot be controlled.

Conclusions

A series of polyamide 6/nanoclay-jojoba oil nanocomposites with different nanoclay-jojoba oil contents has been prepared by

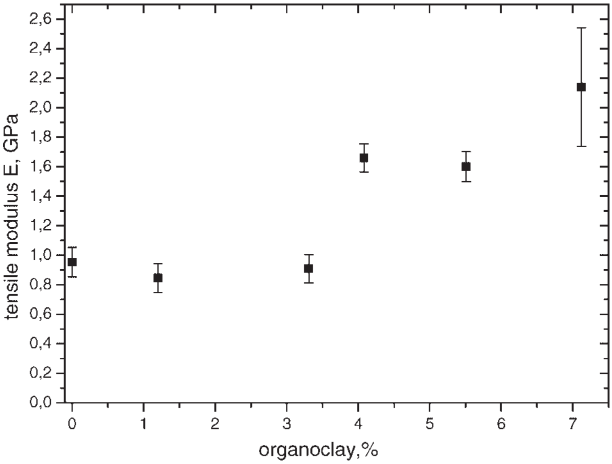

Figure 3.
Effect of nanoclay content on tensile modulus of nanocomposite fibers.

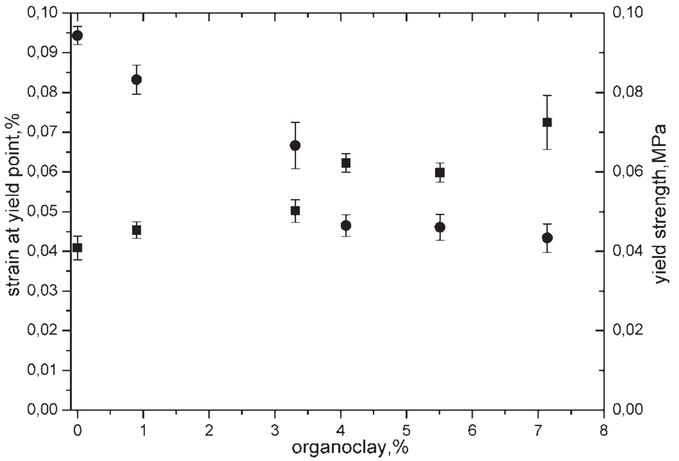

Figure 4.
Effect of organo-modified nanoclay content on yield strength (■) and strain at yield point (●) of nanocomposite fibers.

melt compounding and then extruded through the die of a capillary rheometer to obtain fibers for skin care applications.

WAXS analyses show the exfoliated nanocomposites are formed at low concentrations (less than 7 wt%) and a mixture of exfoliated and intercalated nanocomposites is obtained at higher clay content.

TGA shows that thermal stability of the nanocomposites is improved by about 30 °C when clay loading is 1.5 wt%; higher concentrations lead to a less significant improvement, probably due to the presence of jojoba oil which is characterized by a faster degradation mechanism.

Tensile tests indicate that the elastic modulus of polyamide 6/nanoclay-jojoba oil nanocomposites at high clay loadings is enhanced compared with neat polyamide 6, when clay concentration is low (less than 5 wt%) the behaviour of nanofibers is overall similar to that of polyamide 6 neat

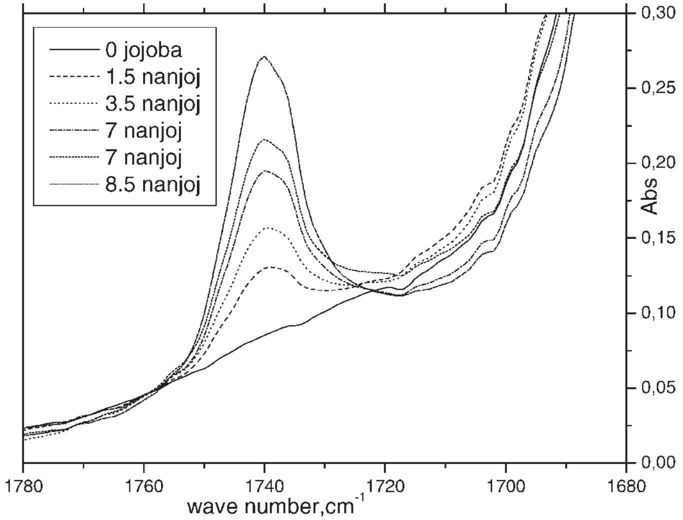

Figure 5.
FT-IR spectra before contact with solvent of polyamide 6 nanocomposite sections.

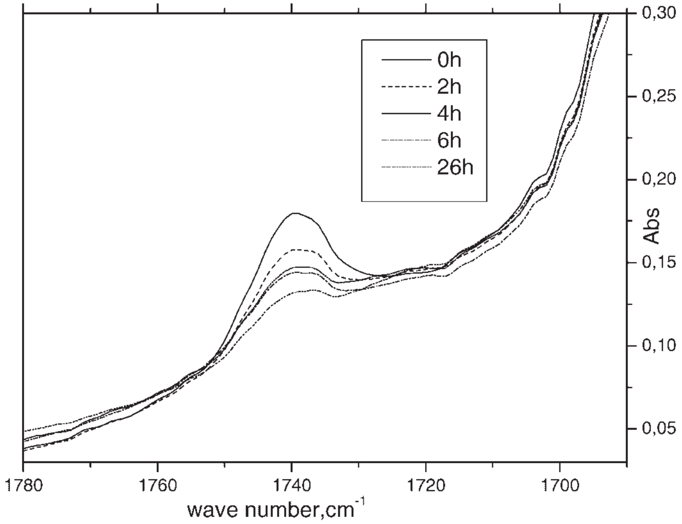

Figure 6.
Release of jojoba oil through polyamide matrix for polyamide 6/3.5 wt% nanjoj.

fibers. Such a result seems to be promising for our purpose, since these new nanofibers designed to applications in cosmetic field should have the same range of utilization of traditional nylons.

FT-IR observations allow to check jojoba oil presence in every polymer blend: cosmetic agent degradation is prevented by layers structure of the nanoclay and time desorption in solvent of jojoba oil was studied by variation of peak intensity at 1740 cm^{-1}. It was found that time release of the cosmetic agent of polyamide 6/clay-jojoba nanocomposites (containing less than 7 wt% clay concentration) is slow and controlled due to the finer dispersion of nanoclay within polymer matrix.

These results encourage further investigation on release mechanism of the cosmetic agent through the polymer matrix,

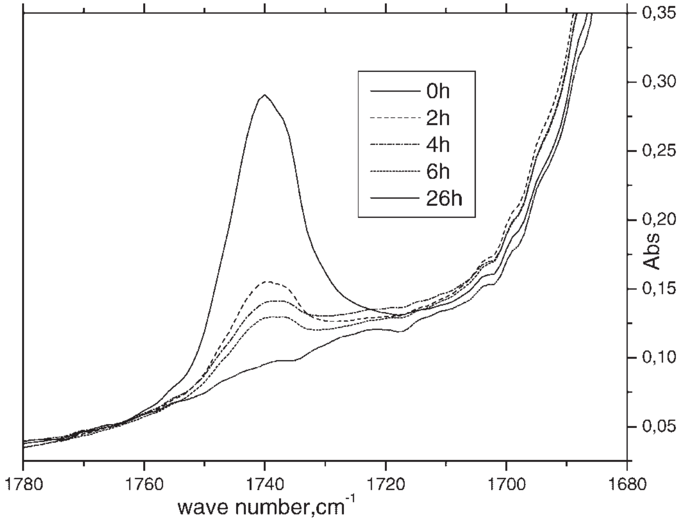

Figure 7.
Release of jojoba oil through polyamide matrix for polyamide 6/8.5 wt% nanjoj.

promoting the interest on potential applications of such nanofibers for textiles in cosmetic field.

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