Functional Textiles Based on Polymer Composites

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Summary: Functional textiles provide ample evidence of the potential wealth of opportunities still to be realised in the textile industry. In this paper, intelligent-wear garments with thermoregulating properties are prepared using phase change materials (PCMs) microcapsules and tested. At the same time, a series of nylon 6 nanocomposites with different filler/Jojoba Oil contents have been prepared with the purpose of obtain active fibers providing care, comfort and protection for the skin. Jojoba Oil delivery through polyamide matrix in conditions simulating current applications was studied by FT-IR.

Keywords: microcapsules; nanocomposite; textiles; thermoregulation

Introduction

The textile and clothing industry, normally considered as a "traditional industry" represents an important part of the European manufacturing industry; significant restructuring has taken place over the last decade, however, there is a general recognition that producing traditional apparel may no longer be sufficient to sustain a viable business, and the EU textile industries may have to move towards more innovative, high quality products in order to differentiate themselves and compete.^[1]

Health and well being is the new demand for innovative textiles that are increasingly oriented to match material innovation, new technologies and fashion. The new products are not only different for their lines, patterns and volumes, they are characterized by what they can do. As an example, since the level of thermal wellbeing depends on the heat exchange between the human body and environment that surrounds it, many efforts have been devoted to induce a

thermoregulating effect into textiles. It is well known that the human body works by mean of the energy it obtains from food. To ensure life, the heat produced through metabolism is dispersed during physical activity. The most efficient way to dissipate energy occurs through perspiration and evaporation. It is possible to microencapsulate phase change materials (PCMs) and then additivate them into yarns in order to use the melting/crystallization heat as a buffer to get more comfortable cloths. In many technical applications, workers handle hot or cold subjects. The use of phase change materials in technical clothing can reduce the thickness and hence the weight of the garment. The buffer effect is significant if the exposition to cold/hot conditions is repetitive and cyclic, in such a way to allow phase change materials to return to their initial state in the ambient environment.[2-4] In this paper the thermoregulating effect of Kevlar fabrics charged with microcapsules containing paraffines is described.

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 fiber-forming material

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increasing the tensile strength, the elastic modulus, heat resistance as well as gas and water barrier properties.

As an example of the 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 nanofiller acts as a carrier which absorbs and promotes the dispersion of the cosmetic substance through the polymer matrix also protecting it by degradation.

A series of nylon 6 nanocomposites with different nanofiller/Jojoba Oil contents have been prepared by direct melt compounding. To check Jojoba Oil concentration and its desorption through the polyamide FTIR microscope analyses have been carried out, since esteric characteristic group of Jojoba Oil at 1740 cm⁻¹ does not appear in polyamide 6 spectrum.^[8] Blends nanoscale morphology and mechanical properties of fibers have been studied as well.

Experimental

Materials

Materials used in this study were:

- for termoregulation tests, Kevlar[®] commercial sheets, PCM microcapsules (phase transition at 32,5 °C supplied by Frisby).
- for cosmetic fibers, 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.); nanosized CaCO₃ (supplied by Solvay); natural jojoba oil (MCY products).

Preparation of Kevlar[®] Multilayer Samples

Three layers of Kevlar® were assembled using a vinylic adhesive on which PCM microcapsules were dispersed. The amount

of PCM was 0.75 g per layer of Kevlar[®]; the dimension of each layer was $40 \times 40 \times 1$ mm, the final specimen had dimension of $40 \times 40 \times 4$ mm. The composite was pressed under a weight of 500 g/cm² at 150 °C for 60 minutes.

MEV Tests

To test the thermoregulation effect due to the presence of microcapsules locked between Kevlar[®] layers, a special equipment (MEV) was projected and made in our laboratory.^[9] The instrument is based on a Peltier cell activated by an external voltage; on one side of the cell heat is absorbed and on the other side heat is released. The efficiency of the cell is related to temperature differences between the two surfaces.

Preparation of Blends and Fibers of Polyamide 6/Nanofiller-Jojoba Oil

Nanocomposites were melt blended using a Haake Rheocord Rheomix 600 co-rotating twin mixer with a screw speed of 30 rpm at $240\,^{\circ}\mathrm{C}$ for 2 minutes to avoid Oil degradation.

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

Nanocomposite blends were reduced to pellets, 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.

Mechanical Tests

Tensile properties of 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 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 pressed at 100 atm to further reduce thickness and then observed by FT-IR Perkin Elmer System 2000 equipped with optic microscope IR Autoimage.

TEM Observations

Ultrathin sections (with thickness of ca.50 nm) for transmission electron microscopy (TEM) were cut from as-extruded nanocomposite pellets under cryogenic conditions using a Leica EM FCS ultramicrotome with a diamond knife.

The TEM microghraps were taken using ZEISS EM 900 transmission electron microscope under an accelerated voltage of 50 kV.

Results and Discussion

MEV Analysis

During sports and jobs people alternate activity and inactivity. As the activity increases, the heat produced by human body need to be disrupted. With the use of PCM it can be demonstrated^[7] the improvement of the level of comfort, since PCM garments will absorb some of the heat produced during

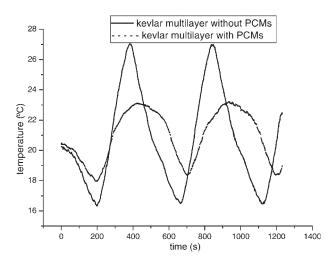
exercise or work, changing to the liquid state and producing a temporary cooling effect. During inactivity, PCMs solidify back and release heat. The comfort is much higher the lower is the amplitude of oscillation of temperature. With the use of PCM into Kevlar layers[®], this amplitude is reduced, therefore providing thermal well being.

When the Kevlar[®] multilayer sample is interposed between the surfaces of the Peltier cell, it is able to delay and smooth the thermal response because of the presence of microcapsules which absorb heat during the melting process of paraffin waxes. In Figure 1 the thermoregulation effect of a Kevlar[®] multilayer sample with PCM microcapsules is reported: the thermal wave is time delayed (about 100 s) and less intense (about 3–4 °C) if compared with the Kevlar[®] multilayer sample without microcapsules.

Nanostructure and Morphology of Active Fibers

In a previous work^[8] we have discussed WAXS results for nanocomposite blends containing montmorillonite clays.

TEM studies (Figures 2–5) were carried out to probe the exact dispersion of the clay layers within the polyamide nanocomposite blends. The dark lines are intersections of



 $\begin{tabular}{ll} \textbf{Figure 1.} \\ \textbf{Thermoregulation effect of a Kevlar}^{\circledR} \ multilayer sample with and without PCM microcapsules. \\ \end{tabular}$

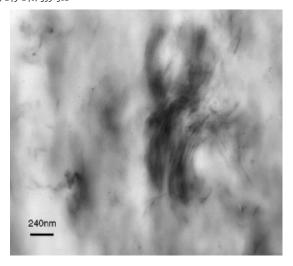


Figure 2.
TEM photo of polyamide 6/1.5 wt% nanjoj.

clay layers (1 nm thick) and white or light gray regions are polymer. [10] It is worth noting that all the photos show bright holes probably formed by sublimation of oil drops trapped into the matrix as a consequence of high local temperatures generated by incident electron beam. Higher is Jojoba Oil content, morel are voids.

Photos show individual dispersion of delaminated clay sheets in the matrix, as well as regions where the regular stacking arrangement is maintained with a layer of polymer between the sheets. Although a face to face layer morphology is retained, the layers are irregularly separated by the polymer; some stacks appear parallel to the plane of observation (large dark regions). For all the samples a portion of nanoclay is well dispersed in polyamide matrix and some of it is aggregated.

Mechanical Tests and FTIR Analysis

In order to use nanocomposite fibers with cosmetic effects in the ordinary range of

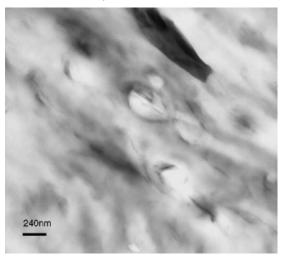


Figure 3.
TEM photo of polyamide 6/3.5 wt% nanjoj.

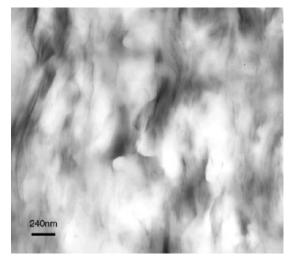


Figure 4.
TEM photo of polyamide 6/7 wt% nanjoj.

application of nylon collant, they should show mechanical properties values similar to that of pure polyamide 6. In a previous work^[8] we have discussed mechanical properties of nanoclay fibers; in Table 1 mechanical properties of 1.5, 3.5 and 8.5 wt% nanofiller-Jojoba Oil are reported.

It is worth noting that Young Modulus does not change too much increasing CaCO₃ loading and values of yield strength

and strain at yield point are nearly similar to that of pure polyamide 6. One might think that this nanosized filler could be better compared to the organoclay since it doesn't vary significantly nylon 6 mechanical properties, especially for high level of filler.

On the other hand, FTIR analysis showed that the characteristic esteric Jojoba Oil peak had not equal intensity in CaCO₃ and



Figure 5.
TEM photo of polyamide 6/8.5 wt% nanjoj.

Table 1.Mechanical properties of polyamide 6/nanofiller-Jojoba Oil fibers.

Sample	Young Modulus (GPa)	Yield strength (MPa)	Strain at yield point (%)
PA 6	0.953 ± 0.100	0.041 ± 0.003	0.0943 ± 0.00231
PA 6/1.5%CaCO ₃ -Joj	0.813 \pm 0.150	$\textbf{0.036} \pm \textbf{0.003}$	0.0858 \pm 0.00871
PA 6/3.5%CaCO ₃ -Joj	$\textbf{0.566} \pm \textbf{0.063}$	$\textbf{0.029} \pm \textbf{0.002}$	0.0927 \pm 0.00798
PA 6/8.5%CaCO ₃ -Joj	0.792 \pm 0.064	0.030 ± 0.004	0.0751 ± 0.00820
PA6/1.5%nanjoj	0.846 \pm 0.097	$\textbf{0.045} \pm \textbf{0.002}$	0.0832 ± 0.0037
PA6/3.5%nanjoj	0.909 \pm 0.097	$\textbf{0.050} \pm \textbf{0.003}$	0.0666 ± 0.0058
PA6/8.5%nanjoj	$\textbf{2.14} \pm \textbf{0.402}$	0.072 ± 0.007	0.0433 ± 0.0036

organoclay systems at the same experimental content (Figure 6 and Figure 7).

This means that degradation occurs since the CaCO₃ structure does not exert oil and polymer protection. For this reason, any desorption experiment in isopropanol was carried out as for polyamide 6/nanjoj nanocomposites.^[8]

Fibers Washing and Skin Contact Simulation

The last step on nanoclay fibers study has been to test their behavior in conditions simulating daily applications.

For this purpose a 8.5 wt% nanjoj fiber was pressed under 150 atm and observed by FTIR microscope after 2 hours contact with water and soap (2 g of DASH-commercial laundry detergent-in 100 ml water) at 50 °C.

As it can be seen in Figure 8, CO signal at 1740 cm⁻¹ does not change its intensity.

To simulate human skin surface, sebum formulation was prepared according approximately to literature.^[11] Human sebum is a mixture of triglycerides, fatty acids, wax esters, squalene, cholesterol, and cholesterol esters.

The following percentage quantity of components (supplied by Aldrich) was used:

At normal skin temperature (skin surface temperature is 32 °C), sebum contains both a solid and a liquid phase; the 8.5 wt% organoclay/Jojoba fiber was pressed and dipped into sebum formulation for 48 h at 37 °C.

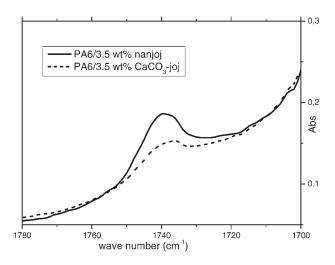


Figure 6.
Polyamide 6/organoclay-Jojoba and polyamide 6/CaCO₃-Jojoba sections at the same filler content.

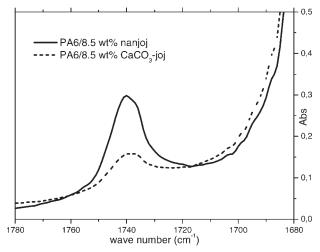


Figure 7.
Polyamide 6/organoclay-Jojoba and polyamide 6/CaCO₃-Jojoba sections at the same filler content.

To be sure that any solid sebum residue was on the sample fiber, before FTIR observation the fiber was kept in isopropanol for 5 minutes. Recorded spectra showed that CO signal of Jojoba Oil changed in shape and position: two shoulders are present at 1737 cm⁻¹ and 1730 cm⁻¹, probably due to different rates of release of Jojoba components in contact with long alkyl chains of sebum formulation (Figure 9).

Conclusions

Microcapsules incorporation between layers of Kevlar[®] give thermoregulating capacity to technical textile, allowing their use also in extreme temperature conditions.

To compare the effect of nanofiller type on the effective release properties of active cosmetic fibers, polyamide 6/Jojoba Oil blends were prepared using both commercial organoclay and nanosized CaCO₃.

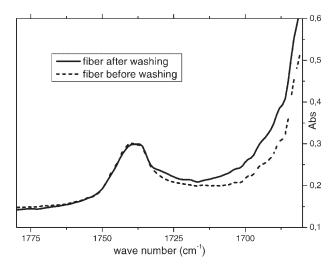


Figure 8. Simulation of washing laundry at 50 °C for 2 hours.

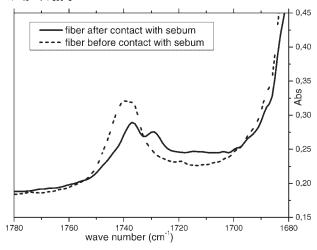


Figure 9. Simulation of skin contact at 37 $^{\circ}$ C for 48 hours.

TEM analyses show that organoclay nanocomposites have exfoliated and partially intercalated morphologies. FTIR observations allow to check Jojoba Oil presence in every polymer blend: cosmetic agent degradation is prevented by layers structure of the organoclay and time desorption in solvent of Jojoba Oil was studied by variation of peak intensity at 1740 cm⁻¹.

Concerning systems containing CaCO₃, mechanical tests confirmed that these nanoparticles did not vary significantly tensile properties of nylon fibers, even at high nanofiller loading. Nevertheless FTIR analysis show that Jojoba Oil is not protected by degradation during extrusion processes.

Simulations of application conditions were carried out and qualitative considerations are as follows:

- 1. the cosmetic oil content did not vary after nylon fibers washing, allowing regular textile laundry treatments,
- when nanofibers are in contact with sebum at body temperature, Jojoba Oil characteristic peak is split in two signals indicative of different rates of components release

Future developments of innovative technologies in textiles will further upgrade existing functions and performances of textile materials and develop smart and intelligent textiles with unprecedented functions.

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