Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Development of thermo-regulating fabric using microcapsules of phase change material

Dounia Benmoussa, Kolos Molnar, Hassan Hannache & Omar Cherkaoui

To cite this article: Dounia Benmoussa, Kolos Molnar, Hassan Hannache & Omar Cherkaoui (2016) Development of thermo-regulating fabric using microcapsules of phase change material, Molecular Crystals and Liquid Crystals, 627:1, 163-169, DOI: 10.1080/15421406.2015.1137385

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1137385

Published online: 13 May 2016.

MOL. CRYST. LIQ. CRYST.
2016, VOL. 627, 163–169
http://dx.doi.org/10.1080/15421406.2015.1137385

Taylor & Francis
Taylor & Francis Group

Development of thermo-regulating fabric using microcapsules of phase change material

Dounia Benmoussa[a,b], Kolos Molnar[c], Hassan Hannache[b,d], and Omar Cherkaoui[a]

[a]Higher School of Textile and Clothing Industries, Laboratory REMTEX, Casablanca, Morocco; [b]University Hassan II, F. S. Ben M'Sik, Department of Chemistry Materials Team Thermostructural, Casablanca, Morocco; [c]Budapest University of Technology and Economics, Faculty of Mechanical Engineering, Department of Polymer Engineering; [d]Mohammed VI Polytechnic University Ben Guerir Morocco

ABSTRACT

In textiles, the major interest in microencapsulation is currently in the application of durable fragrances, skin softeners, phase-change materials, antimicrobial agents and drug delivery systems onto textile materials. In our research "Polyethylene Glycol" was applied as phase change material and it was encapsulated in polymethacrylic acid (PMA) by radical polymerization in suspension of methacrylic acid in presence of N,N'-methylenebisacrylamide (MBAM) as crosslinking agent. Thereafter the obtained microcapsules were modified by amidation with ethylenediamine as a spacer molecule. At the end of this spacer trichlorotriazine reactive group was fixed. Microcapsules were grafted onto a cotton textile substrate. The surface morphologies of the microencapsulated phase change materials (micro PCMs) were studied by scanning electron microscopy (SEM). Thermal properties, thermal reliabilities and thermal stabilities of the as-prepared micro PCMs were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The obtained results reveal that the produced microcapsules had a mean diameter of 10 μm and the resistance of the microcapsules was demonstrated by thermal analysis.

KEYWORDS

Microencapsulation; phase-change materials; energy storage

1. Introduction

Fundamental principles of science are now increasingly employed for the manufacturing of innovative textile products. One such principle is "phase change" [2] the process of going from one physical state to another, i.e. from a solid to a liquid and vice versa. Fiber and textile products having automatic acclimatizing properties are recently attracting more and more attention. Phase change materials (PCMs) have been applied to the textiles in a variety of processes to improve thermal comfort of end-use products due to their high heat storage capacities [8]. This technology was introduced at textiles by microencapsulation [3].

The microencapsulation [1] may be defined as a process to entrap one substance within another substance, thereby producing particles with diameters of a few micrometers. The substance that is encapsulated is called core material, active agent, fill, internal phase or payload phase.

CONTACT Dounia Benmoussa douniabenmoussa1@gmail.com Higher School of Textile and Clothing Industries, Laboratory REMTEX, Casablanca, Morocco

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

The substance that is encapsulating is called the coating, membrane, shell, carrier material, wall material, external phase. Microencapsulation techniques are normally used to enhance material stability, reduce adverse or toxic effects, or extend material release for different applications in various fields of manufacturing. The properties of microcapsules, size, shape, wall material, active substance release mechanism have to be adapted to the requirements of textile processing methods and to the use of final products [6, 9].

In this study, polyethylene glycol 600 was used as PCM [10] for developing a fabric with thermo-regulating properties. Its melting point is 22°C and it allows the PCM to be stabilized in a Slurry state below the comfortable skin temperature. In addition, thermal properties, air permeability, moisture vapor permeability and moisture regain of materials also influence the heat balance of the body and consequently, affect clothing comfort [4]. The incorporation of PCM microcapsules to textiles can affect other comfort-related properties and hand of the materials adversely, especially when the topical application of microcapsules results in drastic changes in the surface characteristics of materials. The extent of change in these properties depends on the filling weight of PCM microcapsule [5, 7].

Polyethylene glycol 600 was encapsulated in polymethacrylic acid (PMAA) by free radical polymerization in a suspension of acrylic acid in the presence of N,N′-methylene bisacrylamide (MBAM) that is a crosslinking agent. Thereafter the obtained microcapsules were modified by amidation with ethylene diamine as a spacer molecule. At the end of this spacer a reactive group of trichlorotriazine was fixed. Microcapsules were then grafted onto a cotton textile substrate. The surface morphologies of the microencapsulated phase change materials (microPCMs) were studied by scanning electron microscopy (SEM). Thermal properties, thermal reliabilities and thermal stabilities of the as-prepared micro PCMs were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The fabrics containing microPCMs have a special effect that can be used in a wide variety of applications including apparel, home- and technical textiles.

2. Experimental

2.1. *Microcapsules synthesis*

Microcapsules were prepared from water-in-oil emulsions using an interfacial polymerization technique. The aqueous phase of this emulsion containing methacrylic acid monomers, MBAM crosslinker and APS initiator and the organic phase, which was a mixture of paraffin oil and Tween 20 emulsifier obtanined from Sigma Aldrich. The polymerization was carried out in a 100 ml volume round bottom reactor equipped with a stirrer, reflux condenser, sampling port and inlet for nitrogen supply. The stirrer blade was kept at a constant distance of 5 mm from the bottom of the reactor. The reactor was maintained at 25°C in a water bath throughout the whole procedure of 3 hours. A microcapsule shell which was insoluble in both water and oil was formed at the interface.

After the completion of the synthesis, microcapsules were separated from the oil phase by multiple washing in a mixture of acetone and water (1:1) and finally with pure water.

To confer a resistance of microcapsules we decided to optimize the synthesis parameters to control the morphology and the physicochemical characteristics of hollow microcapsules. On the other hand their resistance to dissolution is provided by the crosslinks between the polymer network chains. The presence of chemical or physical crosslinks provides a network structure and a physical integrity to the system. For this reason the influence of crosslinking agent on the stability of hollow microcapsules were studied.

2.2. *Functionalization of the membrane by ethylenediamine*

The microcapsules were taken up in 100 ml mixture of cyclohexane and Span 83 emulsifier at 10 g/l. This was placed in a reactor set to 25°C, previously. Then 35 ml mixture of cyclohexane, Span 83 at 10 g/l and a 0.5 mol/l ethylenediamine solution were admixed. Stirring was maintained at 200 rpm for 1 hour then the reaction was stopped. After that the reaction medium was centrifuged. The capsules were then washed according to the method described in microcapsules synthesis part (2.1).

2.3. *Activation of microcapsules functionalized by grafting trichlorotriazine*

The previously obtained functionalized microcapsules were taken up in 100 ml mixture of cyclohexane and Span 83 at 10 g/l. the whole mixture was placed in a reactor set to 25°C and 35 ml mixture of cyclohexane, Span 83 at 10 g/l and 0.5 mol/l 2,4,5-trichlorotriazine solution were added. Stirring was implented at 200 rpm for 45 minutes. After the reaction had stopped the reaction medium were centrifuged and the microcapsules were washed according to the method described above at microcapsule synthesis (2.1).

2.4. *Grafting the microcapsules onto the cotton sample*

At the first step the microcapsules conserved in a cyclohexane/Span 83 at 10 g/l were centrifuged at 2000 rpm for 5 minutes in order to separate them from the organic medium.

The pellet of the microcapsules was recovered then dispersed in 100 ml water at pH 5. The obtained dispersion was stirred for 15 min at 200 rpm. The dispersion was centrifuged at 2000 rpm for 5 minutes. These three operations were repeated three times to eliminate any trace of cyclohexane. Finally, the microcapsules were recovered in 100 ml water at pH 5.

In the second step, a programmable autoclave fitted with 6 bottles fixed onto a drum was used. The ratio of grafting bath of this example was fixed at 1:15. In order to favor adsorption of the microcapsules on the cotton fabric, 30 g/l Na_2CO_3 was added. The heating rate of the autoclawe was set to 3°C/min. The final temperature for grafting microcapsules onto the cotton fabrics was fixed at 50°C. The bath was kept under stirring for 15 min at that temperature. At the end of this adsorption step, the bottle was removed from the machine. Sodium hydroxide (NaOH) was added to increase the pH and to enable the chemical reaction between the reactive groups at the surface of the capsules (2,4,6-trichlorotriazine chlorine atoms) and the hydroxyl groups of the cotton fibers. The bottle was put back into the machine, the temperature of the bath was brought to 50°C and the pH was approximately reached 11. The reaction was carried out for 90 min. At the end of the reaction the fabric was recovered then rinsed with water until neutralized, that is to say the surface of the adjacent fabric had a pH of 7. This last step also makes possible to eliminate particles which had not been fixed on the fabric appropriately.

3. Characterization

3.1. *ATR-IR spectroscopy*

The structure of the monomer microcapsules was analyzed by FT-IR spectroscopy (Model-Nicolet iS10). The wavelength was between 900 – 4000 cm^{-1}.

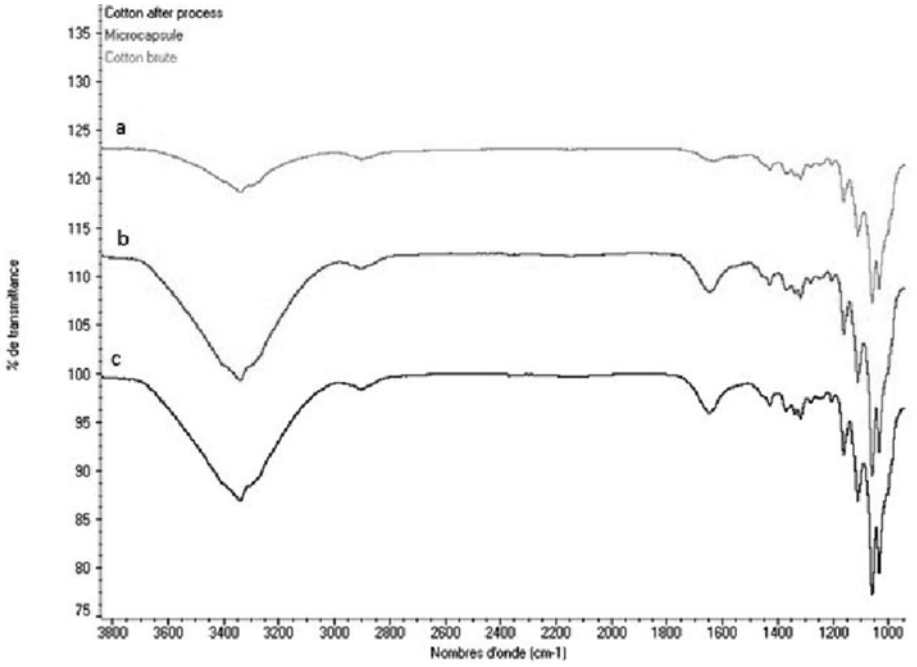

Figure 1. ATR-IR spectra of cellulosic substrate (a), polymethacrylic acid microcapsules shell (b) and cellulosic substrate (c) after process application.

3.2. *Scanning electron microscopy (SEM)*

The SEM micrographs of the microcapsules surfaces were taken by using a FE-SEM MIRA/LMU, Tescan microscope.

3.3. *Thermogravimetric analysis*

Thermogravimetric analysis (TGA, VersaTherm) of microcapsules were carried out to evaluate their moisture uptake capacity and to determine their thermal stability. Experiments were done from 50 to 800°C in nitrogen atmosphere with a heating rate of 10°C/min. In each case, the mass of the samples was fixed at 5 mg.

4. Results and discussion

4.1. *ATR-IR spectroscopy*

The recorded ATR-IR spectra can be seen in Figure 1.

The spectrum of the cellulosic sample (curve a) is characterized by an intense and broad band in the 3600–3100 cm^{-1} wave number range associated with inter- and intra-chain –OH-O groups of the hydrogen bonding interacting chains. The peak at 3276 cm^{-1} can be assigned to the O–H stretching vibration of adsorbed water. Furthermore, the peak around 1650 cm^{-1} shows the presence of interstitial or adsorbed water. The absorption in the 3000–2800 cm^{-1} range is due to the stretching vibration of methylene $–CH_2–$, and the bending vibration of this group appears between 1450 and 1350 cm^{-1}. The stretching vibration of the bond (–C–O–C–) is found at 1155 cm^{-1}. In the second spectrum (b) the peaks at 2906 cm^{-1} and 3402 cm^{-1} were caused by $–CH_3$ and $–CH_2$ asymmetrical stretching vibration, respectively. However,

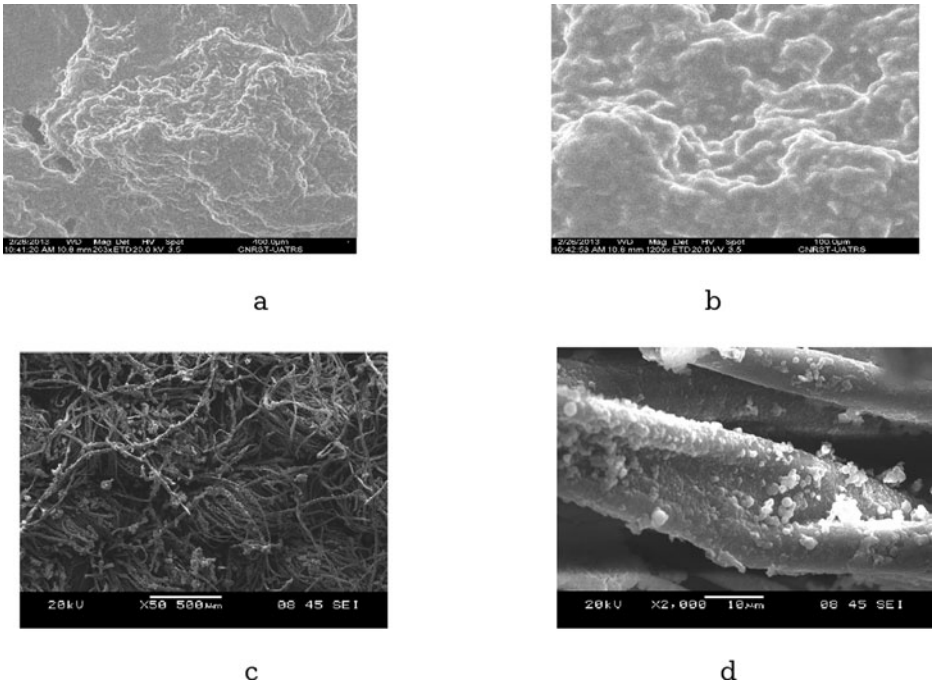

Figure 2. SEM graphs of hollow microcapsules (a, b) and SEM graphs of grafted cotton (c, d).

no peak appeared at 1770 cm^{-1}, which is assigned to unsaturated esters, also suggesting that methacrylic acid had reacted completely. The peaks at 1179 cm^{-1} were ascribed to the C–O–C asymmetrical and symmetrical stretching vibration of polymethacrylic acid. The third spectrum (c) presents characteristic bands of cellulose, namely C–O and C–O–C stretching vibrations between 1200 and 900 cm^{-1}, and also the C=O stretching vibration at 1650 cm^{-1}. All these bands clearly indicate that the grafting of microcapsules was successfully realized.

4.2. *Scanning electron microscopy (SEM)*

The SEM images of the microcapsules can be seen in Figure 2. It can be seen that the microcapsules are spherical, and it cannot be told whether the particles are hollow or multi-porous. In Figure 2 (c, d) the images show that the surface of the fabric is not uniformly coated with spherical microcapsules, and thus some cracks at the surface can be observed. Furthermore, the formation of agglomerated microcapsules can be seen inside the core of the fabric, which implies that during the microencapsulation process. The close examination of the fabric reveals the presence of microcapsules having a mean diameter of about 0.5–5 µm

4.3. *Thermogravimetric analysis*

Thermal stabilities oft he microcapsules were evaluated using TGA analysis. Samples showed two-step decomposition profiles (Figure 3).

The thermogram of P (MAA-MBA) is shown in Fig. 3. The polymeric adsorbent shows fair thermal stability until about 180°C; then in the temperature range of 180–260°C a weight loss corresponding to a first degradation process is observed. Above 260°C no relevant thermal event occurs until 300°C, when a second weight loss, corresponding to the decomposition

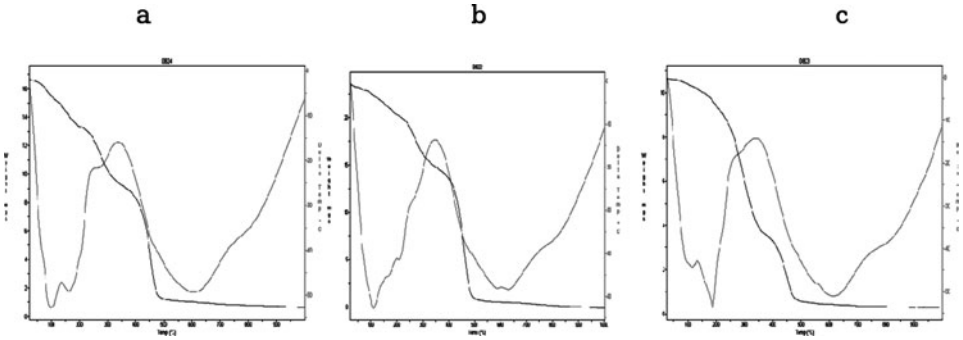

Figure 3. TG curves of microcapsules hollow with different concentration of crosslink agent a: 1/5, b: 1/15, c: 1/25.

of the polymer starts. As reported by McNeill [11], the first degradation process is related to the loss of water molecules through the formation of intra- and inter-molecular anhydride linkages and also to the decarboxylation of a fraction of the –COOH groups by which CO_2 is produced. In the second degradation stage, the polymer decomposes with the elimination of CO and CO_2 by way of abundant backbone scission and formation of a small concentration of unsaturation. Similar results have also been reported elsewhere (Polacco [12]). Above 500°C, the microcapsules were decomposed completely.

The Decomposition process in Fig. 3 shows that the polymer's thermal stability increases with the amount of crosslinking agent due to the development of greater fraction of masses of cross-linked polymeric chains that stabilizes the whole polymer. According to this, the developed microcapsules are resistant to high temperatures.

5. Conclusions

Micro-PCMs possessing polyethylene glycol as phase change temperature core materials and P(MA-co-MBA) as copolymer shell were successfully prepared by the radical polymerization in suspension method. The SEM micrographs indicated that the microcapsules had smooth, compact surface and spherical profiles. The average particle size of these micro-PCMs was about 0.5–5 μm.

The thermogravimetric analysis demonstrated that the microcapsules had high decomposition temperature which can ensure their stability below 500°C. Furthermore, increasing certain amount of MBA can optimize the properties of micro-PCMs. The results of this study showed that the P(MA-co-MBA) containing polyethylene glycol microcapsules are potential micro-PCMs for thermal energy storage.

Acknowledgments

This work was supported by the Hungarian Science and Technology Foundation through the international TÉT_12_MA_1-2013-0008 cooperation between Morocco and Hungary, and also by the National Research, Development and Innovation Office (OTKA K100949 and PD116122).

References

[1] Zuidam, N. J., & Nedović, V. A. (2010). *Encapsulation Technologies for Active Food Ingredients and Food Processing*, Springer, Dordrecht.

[2] Agafonov, I. A., Garkushin, I. K., & Miftakhov, T. T. (1999). *Journal of Physical Chemistry*, *73*:681–685.
[3] Aggarwal, A. K., Dayal, A., & Kumar, N. (1998). *Colourage*, 15–24.
[4] Ren, Y. J., & Rickman, J. E. (2004). *Int. J. Clothing Sci. Tech.*, *16*, 335.
[5] Shin, Y., Yoo, D. I., & Son, K. (2005). *Journal of Applied Polymer Science*, *6*, 96.
[6] Anitha, R., Ramachandran, T., Rajendran, R., & Mahalakshmi, M. (2011). *Elixir Bio. Phys.*, *40*, 5196–5200.
[7] Sharma, R.K., Ganesan, P., Tyagi, V.V., Metselaar, H.S.C., & Sandaran, S.C. (2015). *Energy Conversion and Management*, *95*, 193–228.
[8] Jacob, R., & Bruno, F. (2015). *Renewable and Sustainable Energy Reviews*, *48*, 79–87.
[9] Alkan, C., Sari, A., Karaipekli, A., & Uzun, O. (2009). *Solar Energy Materials & Solar Cells*, *93*, 143–147.
[10] Alkan, C., Sarı, A., & Uzun, O. (2006). *AIChE J.*, *529*, 3310–3314.
[11] McNeill, I. C., Ahmed, S. & Memetea, L. (1995). *Polym. Degrad. Stabil.*, *47* (3), 423–433.
[12] Polacco, G., Cascone, M. G., Peterca, L. & Peretti, A. (2000). *Eur. Polym. J.*, *36*, 2541–254.