POLY(METHYL METHACRYLATE-CO-METHACRYLIC ACID) / N-HEXADECANE MICROCAPSULES TO IMPART THERMAL COMFORT IN TEXTILES

Ruhan Altun Anayurt[1], **Alev Arslan**[1], **Derya Kahraman Döğüşcü**[1], **Cemil Alkan**[1], **Sennur Alay Aksoy**[2]

[1]Gaziosmanpaşa University, Faculty of Arts and Science, Department of Chemistry, Tokat, Turkey;

[2]Süleyman Demirel University, Faculty of Engineering, Department of Textile Engineering, Isparta, Turkey

e-mail: [1]ruhanaltun@hotmail.com

Abstract

Thermal comfort using microencapsulated phase change materials (MPCMs) in innovative textile products and are widely investigated for their highly added value and processes related to microcapsule application to textiles are rapidly increasing to get the optimum performance. This study is focused on the preparation, characterization, and determination of thermal properties of microencapsulated n-hexadecane with poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-MA) to be used in textiles with heat storage property.

Introduction

In recent years, the use of phase change material (PCM) for thermal energy storage has gained extensive attention owing to increasing energy consumption and environment pollution problems [1]. Phase-change materials (PCMs) have been used as thermal storage and control materials because of the heat absorption and release that occur upon a change of phase [2-4]. In 1987, the microencapsulation technology of PCMs was developed and incorporated with textile materials [5]. Currently, for garments and home furnishing products, microencapsulated PCMs are incorporated into acrylic fibers or polyurethane foams, or are embedded into a coating compound and topically applied to a fabric or foam [6]. Some researchers have tried to apply PCM technology to protective garments worn in extreme environments, from cold water to hot deserts [7, 8].

Fabrics with thermal regulating property are intelligent textiles having the property responding to external temperature changes. The thermal comfort property depends on the heat fluctuations in the range of the human body and the environment. Many efforts have been devoted to induce a thermoregulatory effect into textiles, for example the presence of microcapsules containing phase change materials (PCM) are added to textiles [9, 10].

The microencapsulation of PCMs involves enclosing them in thin and resilient polymer shells so that the PCMs can be changed from solid to liquid and back again within the shells [9]. Applications of PCM containing microcapsules into textiles include apparel, blankets, medical field, insulation, protective clothing and many others [11].

This study focused on the preparation, characterization, and determination of thermal properties of microencapsulated n-hexadecane with poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-MA) to be used in textiles with heat storage property. n-Hexadecane core-poly(methylmethacrylate-co-methacrylic acid) (PMMA-co-MA) shell microcapsules were prepared with 1, 5, and 10% MA content to make the outer surface functional.

1 Materials and Methods

1.1 Materials

n-Hexadecane (Fluka) was of analytical grade and used as received. Methyl methacrylate and methacrylic acid monomers (Merck) were used to synthesize co-polymer shell of microcapsule. Methyl methacrylate monomer was washed by NaOH before use. Ethylene glycol dimethacrylate was used as a cross-linker. Triton X-100 (Merck) was used as received. Ferrous sulfate heptahydrate and ammonium persulfate were also of analytical grade and used without further purification.

1.2 Microcapsule Preparation

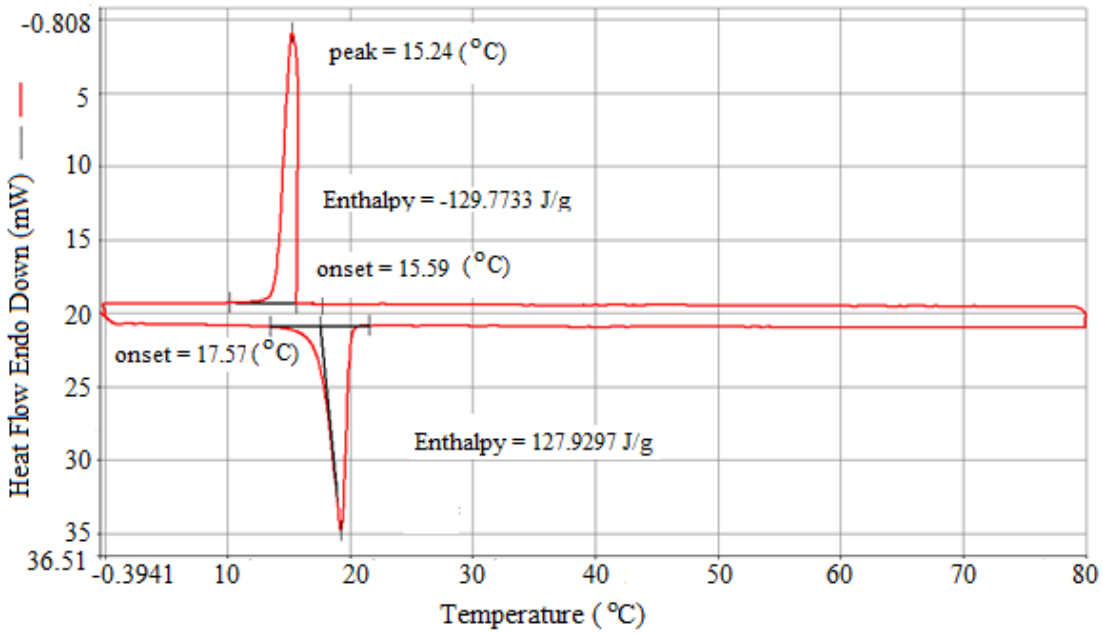
Methyl methacrylate (100 g), methacrylic acid (1, 5, and 10 g in each of 3 different products), ethylene glycol dimethacrylate (10 g or 20 g), and n- Hexadecane (100 g) were assembled as oil phase in emulsion system in a total of 400 mL deionized water. Oil phase was emulsified using 10 g of Triton X-100 (surfactant). Suitable mixing speed was determined as 10000 rpm. The reaction mixture was homogenized at 50 °C using a mechanical homogenizer. Reaction was initiated by the addition of 1 g of ammonium persulphate ($Na_2S_2O_7$) and 8 mL freshly prepared $FeSO_4 \bullet 7H_2O$ solution. Reaction medium was heated to 80 °C and maintained at that temperature for 30 minutes by stirring at 500 rpm. The reaction continued for five hours at the same temperature and stirring speed. The colloidal emulsion was concentrated by casting water and the precipitate was dried under vacuum at 40 °C.

1.3 Microcapsule Characterization

Thermal properties of microencapsulated PCMs were determined using a differential scanning calorimeter (DSC, Perkin-Elmer Jade) at the heating and cooling rate of 10 °Cmin^{-1} between – 5 °C and 80 °C under a constant stream of nitrogen at a flow rate of 60 mLmin^{-1}. The spectroscopic analyses of the microcapsules were performed on KBr disks using a FT-IR instrument (Jasco 430) between 4000-400 cm^{-1}. The particle sizes of microcapsules were measured using a particle sizer instrument (Malvern). Microcapsules were mixed in water at 10000 rpm to avoid clustering before testing. TGA was carried out on a thermal analyzer (PERKIN-ELMER TGA7). The TGA instrument was calibrated with calcium oxalate from 25 to 600 °C at a heating rate of 10 °Cmin^{-1} in a static air atmosphere. DTG was also obtained to determine maximum rate of weight loss.

2 Results and Discussion

DSC curves of poly(MMA-co-MA)/n-hexadecane-1 microcapsules were shown in Figure 1 and the data from the DSC analysis of poly(MMA-co-MA)/n-hexadecane microcapsules were given in Table 1. Thermal properties evaluated from the curves indicate that poly(MMA-co-MA)/n-hexadecane-1 microcapsules melted at temperature range of 16.4−17.5 °C, crystallized at temperature range of 14.5−15.5 °C when pure n-hexadecane had a melting point of 18.2 °C and a crystallization point of 16.2 °C. The latent heats of melting and freezing of microcapsules were measured to be between 127.9−67.9 J/g and between – 69.3−129.7 J/g, respectively.



Source: Own

Fig. 1: *DSC curves of poly(MMA-co-MA)/n-hexadecane-1 microcapsules*

Tab. 1: *DSC results of poly(MMA-co-MA)/n-hexadecane microcapsules*

Microcapsules	Monomer constitution	Melting Enthalpy (J/g)	Melting Point (°C)	Crystallization Enthalpy (J/g)	Crystallization Point (°C)
Poly(MMA-co-MA)/n-hexadecane-1	1 % MA	127.9	17.5	-129.7	15.5
Poly(MMA-co-MA)/n-hexadecane-2	5 % MA	76.9	16.9	-77.9	15.3
Poly(MMA-co-MA)/n-hexadecane-3	10 % MA	67.9	16.4	-69.3	14.5

Source: Own

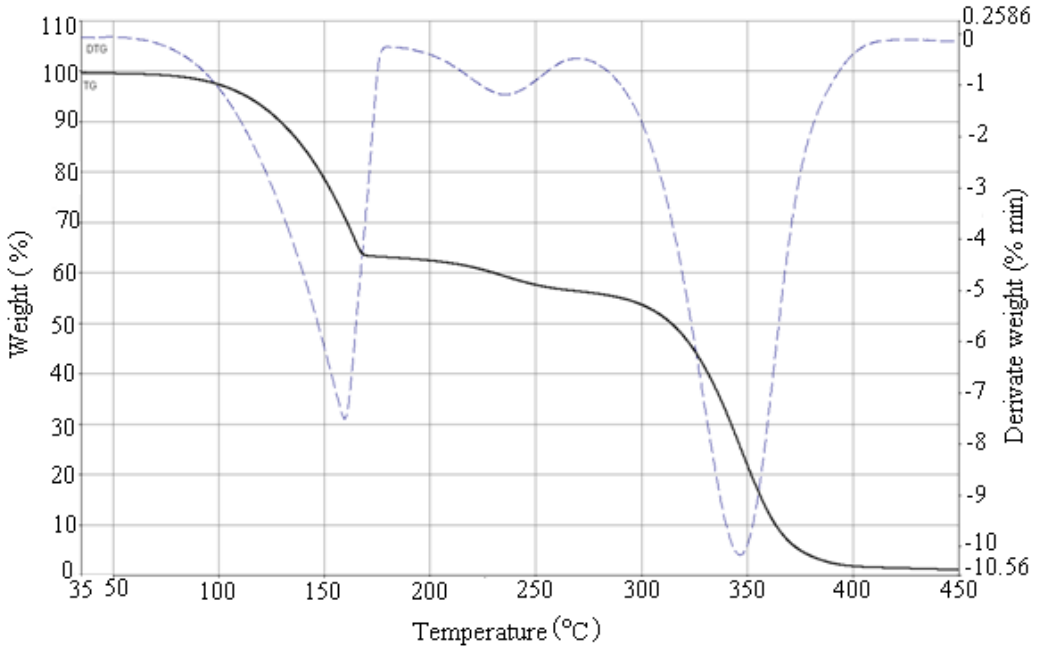
The thermal stability of the microencapsulated PCMs was investigated using TGA. Figure 2 shows the TGA curves of Poly(MMA-co-MA)/n-hexadecane microcapsules and the degradation temperatures of microcapsules were tabulated in Table 2.

Tab. 2: *TGA data for PMMA/n-hexadecane microcapsules*

Microcapsules	Degradation interval [°C]	Weight loss [%]
Poli(MMA-co-MA)/n- hexadecane -1	80-175 (1 step) 175-270 (2 step) 270-410 (3 step)	37 6 55
Poli(MMA-co-MA)/n- hexadecane -2	100-175 (1 step) 175-275 (2 step) 275-410 (3 step)	22 6 71

Source: Own

As it can be seen from the Figure 2 and Table 2 that poly(MMA-co-MA)/n-hexadecane-1 microcapsules degraded in three steps. The degradation of n-hexadecane started at 80 °C in Poly(MMA-co-MA) microcapsules while Poly(MMA-co-MA) shell degraded in two steps at 175 °C and 270 °C. Degradation processes were complete at around 410 °C in the microcapsules.

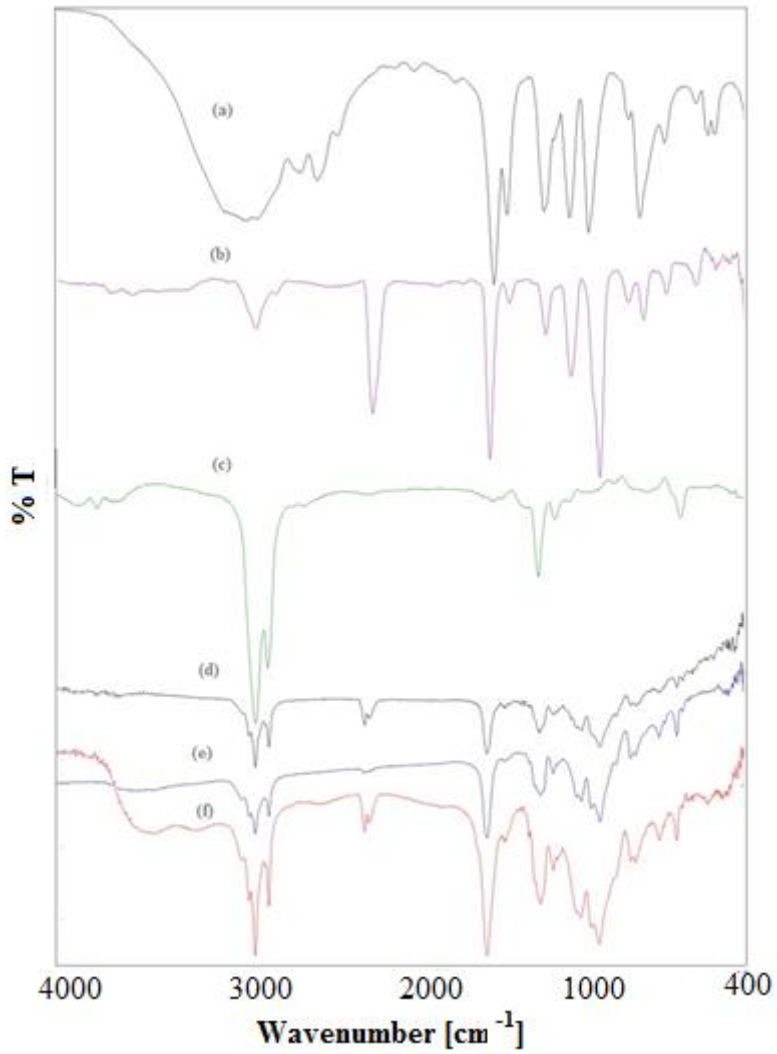


Source: Own

Fig. 2: *TG curves of poly(MMA-co-MA)/n-hexadecane-1 microcapsules*

FT-IR analysis were used to prove the synthesis of microcapsules. For this reason the spectra of the ingredients and the microcapsules were given in Figure 3 and tabulated in the Table 3. The following remarks are from the FT-IR spectroscopy analysis;

- The peaks of C = O at 1741 cm^{-1} and 1698 cm^{-1} in the IR spectra of MMA and MA, respectively were overlapped and emerged at 1731 cm^{-1} in the microcapsules.
- The peaks observed at 2923 cm^{-1}, 2854 cm^{-1}, and 1455-1388 cm^{-1} and 1241-1149 cm^{-1} ranges in IR spectra of microcapsules are characteristic peaks of paraffins. These peaks are proving the paraffin constitution in the microcapsules.
- The peaks at 1631 cm^{-1} and 1635 cm^{-1} in the spectra of MA and MMA are – C = C – stretching peaks and they are invisible in the spectra of microcapsules. This result proved the synthesis of poly(MMA-co-MA) microcapsules.
- According to the spectra of microcapsules, intensity of carbonly peaks at around 1440 cm^{-1} increases with the MA content and -OH stretching vibration band at 3400–3600 cm^{-1} becomes apparent.



Source: Own

Fig. 3: *FT-IR spectra of MA (a), MMA (b), n-hexadecane (c), poly(MMA-co-MA)/n hexadecane-1 microcapsules (d), poly(MMA-co-MA)/n hexadecane-1 microcapsules (e), poly(MMA-co-MA)/n hexadecane-1 microcapsules (f)*

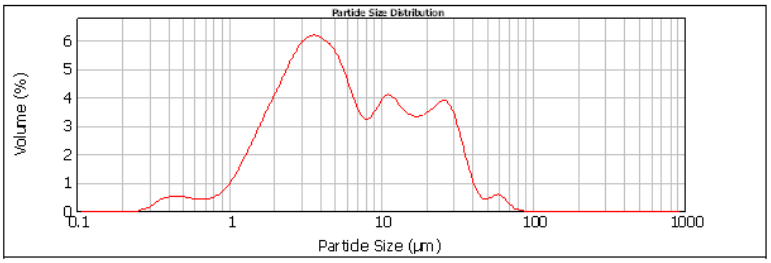
Tab. 3: *FT-IR data of poly(MMA-co-AA)/n-hexadecane microcapsules*

Materials	**Frequency (cm^{-1})**	**Bond**	**Functional groups**
Poly(MMA-co-MA)/n-hexadecane-1	2923 and 2854 1731 1455 and 1388 1241 and 1149	C-H stretch C=O stretch C-H bend C-O stretch	Paraffin Esters and Carboxylic acid Paraffin Esters
Poly(MMA-co-MA)/n-hexadecane-2	3400 and 3600 2923 and 2854 1729 1452 and 1388 1241, 1147	OH stretch C-H stretch C=O stretch C-H bend C-O stretch	Copolymer Paraffin Esters and Carboxylic acid Paraffin Esters

Materials	Frequency (cm^{-1})	Bond	Functional groups
Poly(MMA-co-MA)/n-hexadecane-3	3400 and 3600 2923 and 2854 1729 1454 and 1386 1267,1241 and 1147	OH stretch C-H C=O C-H bend C-O stretch	Copolymer Paraffin Esters and Carboxylic acid Paraffin Esters

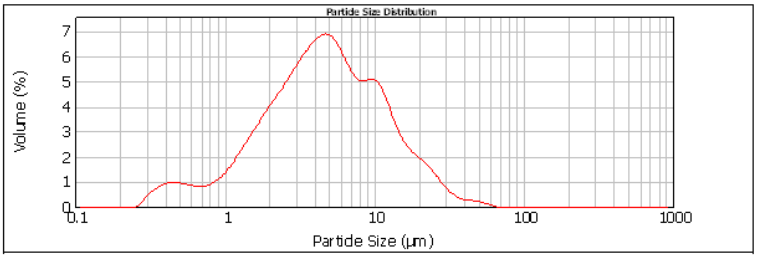
Source: Own

Figures 4, 5, and 6 present the particle diameter distributions of the prepared microcapsules. It is clear from the figures that the average particle sizes vary at different amounts of MA contents. The size of the poly(MMA-co-MA)/n-hexadecane-1 has a narrow distribution and the average particle size is 19.2 µm as shown in Figure 4 as it varies between 1–30 µm. When the amount of MA content is increased to 5% and then 10%, the average particle size of microcapsules goes to 14.77 and 24.51 µm, respectively. In the meantime, the particle size distributions are narrow as shown in Figures 5 and 6 as the particle size of Poly(MMA-co-MA)/n-hexadecane-5 and Poly(MMA-co-MA)/n-hexadecane-10 varies between 1–20 µm, and 2–20 µm, respectively.



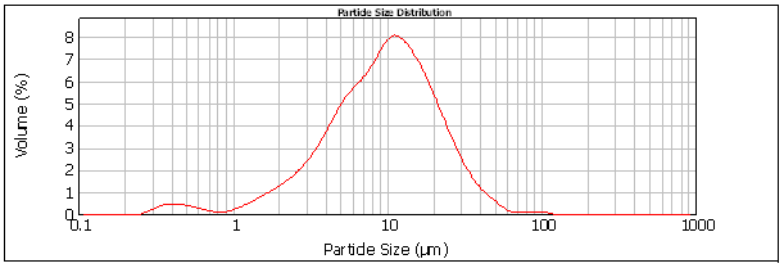
Source: Own

Fig. 4: *%1 Poly(MMA-co-MA)/n-hexadecane microcapsules*



Source: Own

Fig. 5: *%5 Poly(MMA-co-MA)/n-hexadecane microcapsules*



Source: Own

Fig. 6: *%10 Poly(MMA-co-MA)/n-hexadecane microcapsules*

Conclusion

Poly(MMA-co-MA) microcapsules containing n-hexadecane as a core material were produced for their functional surface to be exploited in textile applications. The microcapsules are capable of absorbing latent heats between 68 128 J/g during melting and releasing between – 69 and – 129 J/g during solidification. The data obtained from particle size analyzer instrument indicated that the mean particle sizes of microcapsules were ranged between 1 and 30 μm, which were suitably narrow for the applications. The synthesis, presence of n-hexadecane, and reactive groups in the microcapsules were proven by FT-IR spectroscopy analysis. The phase change temperatures of the poly(MMA-co-MA)/n-hexadecane microcapsules prepared were very close to that of n-hexadecane. Three types of PMMA/n-hexadecane microcapsules with suitable phase change temperatures and considerably high enthalpy were produced to be used as thermal comfort additives in textiles. The reactive surface of the microcapsules was bound to textiles easily due to electrolytic interactions, or reacted to textiles by chemical means.

Acknowledgements

The authors would like to acknowledge the financial support of the Scientific and Technical Research Council of Turkey (Project no.: 111M484).

Literature

[1] SARI, A.; ALKAN, C.; KARAIPEKLI, A.: *Applied Energy*, 87, 1529, 2010.

[2] SHIN, Y.; YOO, D.; SON, K.: *Journal of Applied Polymer Science*, 97, 3, 910, 5, 2005.

[3] MULLIGAN, J. C.; COLVIN, D. P.; BRYANT, Y. G.: *J Space Rockets*, 33, 278, 1996.

[4] COLVIN, D. P.; MULLIGAN, J. C.: US Patent, 4, 911, 232, 1990.

[5] BRYANT, Y. G.; COLVIN, D. P.: *Techtextil-Symposium*, 3, 1, 1992.

[6] PAUSE, B. H.: *J Ind Fabrics*, 33, 93, 2003.

[7] COLVIN, D. P.; BRYANT, Y. G.: HTD *Am Soc Mech Eng*, 362, 123, 1998.

[8] COLVIN, D. P.; HAYES, L. J.; BRYANT, Y. G.; MYERS, D. R.: Heat Transfer Division, *Am Soc Mech Eng*, 268, 73, 1993.

[9] SÁNCHEZ, P.; SÁNCHEZ-FERNANDEZ, M. V.; ROMERO, A.; JUAN RODRÍGUEZ, F.; LUZ SÁNCHEZ-SILVA: *Thermochimica Acta*, 498, 16, 2010.

[10] BRYANT, Y.G.; COLVIN, D.P.: Fiber with reversible enhanced thermal storage properties and fabrics made therefrom, US Patent, 4, 756, 958, 1988.

[11] SHIN, Y.; YOO, D.I.; SON K.: *J. Appl. Polym. Sci.* 96, 2005.

MIKROKAPSLE POLY(METHYLMETHAKRYLÁT – KOPOLYMER) / KYSELINY N-HEXADEKANOVÉ PRO TEPELNÝ KOMFORT TEXTILIÍ

Tepelný komfort získaný pomocí mikrokapsulovaných materiálů se změnou fází (MPCMs) u inovačních textilních výrobků je široce zkoumán pro svou vysokou přidanou hodnotou, a procesy spojené s aplikací mikrokapslí na textilie se rapidně zrychlují ve snaze dosáhnout optimálního výkonu. Tato studie se zaměřila na přípravu, charakterizaci a stanovení tepelných vlastností mikrokapslí kyseliny n-hexadekanové s poly (methyl -methakrylát-komethakrylovou kyselinou) (PMMA-co-MA), které mohou být využity u textilních výrobků s tepelně izolačními vlastnostmi.

POLYMETHYLMETHACRYLAT-MIKROKAPSELN ZUR GEWÄHRLEISTUNG VON WÄRMEKOMFORT IN TEXTILIEN

Der Wärmekomfort, wie er mit Hilfe von Mikrokapselmaterialien bei Änderung der Phasen (MPCMs) bei innovativen textilen Erzeugnissen gewonnen wird, wird wegen seines hohen Zugabewertes gründlich erforscht. Die Prozesse, die mit der Anwendung von Mikrokapseln an Textilien verbunden sind, beschleunigen sich rapide bei der Bemühung, optimale Leistung zu erreichen. Diese Studie konzentriert sich auf die Aufbereitung, Charakterisierung und die Festlegung von Wärmeeigenschaften der Mikrokapseln der Säure n-Hexadekan-Polymethylmethacrylat-Komethakryl-Säure (PMMA-co-MA), die bei Textilprodukten mit isolierenden Eigenschaften genutzt werden können.

MIKROKAPSUŁKI Z KWASU N-HEKSADEKANOWEGO Z POLIMETAKRYLANEM METYLU – KOPOLIMEREM DO KOMFORTU CIEPLNEGO TKANIN

Komfort cieplny uzyskany przy pomocy materiałów mikrokapsułowanych ze zmienioną fazą (MPCMs) w innowacyjnych produktach tekstylnych jest przedmiotem szeroko zakrojonych badań ze względu na wysoką wartość dodaną. Coraz bardziej do tkanin stosowana jest także technologia mikrokapsułowania, co ma na celu osiągnięcie optymalnej wydajności. Niniejsze opracowanie dotyczy przygotowania, scharakteryzowania i określenia właściwości cieplnych mikrokapsułek kwasu n-heksadekanowego z polimetakrylanem metylu-kopolimerem (PMMA-co-MA), które mogą być wykorzystane w produktach tekstylnych o właściwościach termoizolacyjnych.