Eudragit S (Methyl Methacrylate Methacrylic Acid Copolymer)/Fatty Acid Blends as Form-Stable Phase Change Material for Latent Heat Thermal Energy Storage

Ahmet Sari,[1] Cemil Alkan,[1] Ugur Kolemen,[2] Orhan Uzun[2]

[1]Department of Chemistry, Gaziosmanpaşa University, 60240 Tokat, Turkey
[2]Department of Physics, Gaziosmanpaşa University, 60240 Tokat, Turkey

ABSTRACT: By composing (Eudragit S) with fatty acids (stearic acid (SA), palmitic acid (PA), and myristic acid (MA)), form-stable phase change materials (PCMs), which can retain the same shape in a solid state even when the temperature of the PCMs is over the melting points of the fatty acids, are prepared. The compatibility of fatty acids with the Eudragit S is proved by microscopic investigation and infrared (FTIR) spectroscopy. The melting and crystallization temperatures and the latent heats of melting and crystallization of the form-stable PCMs are measured by Differential Scanning Calorimetry (DSC) method. The maximum mass percentage of all fatty acids in the form-stable PCMs is found as 70%, and no leakage of fatty acid is observed at the temperature range of 50–70°C for several heating cycles. Thermal properties obtained from the DSC analysis indicate that the Eudragit S/fatty acid blends as form-stable PCM have great potential for passive solar latent heat thermal energy storage (LHTES) applications in terms of their satisfactory thermal properties and utility advantage. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1402–1406, 2006

Key words: form-stable; Eudragit S; myristic; palmitic and stearic acids; LHTES; polymer-based PCM; DSC analysis; FTIR spectroscopy

INTRODUCTION

Thermal energy can be stored as a change in internal energy of a material as sensible heat, latent heat, and thermochemical heat, or as a combination of these. Latent heat thermal energy storage (LHTES) is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. Solid–liquid transition of phase change materials (PCMs) has proved to be economically attractive for use in thermal energy storage systems. PCMs themselves cannot serve as a heat transfer medium. Heat transfer mediums with a heat exchanger are required to transfer energy from the source to the PCM and from the PCM to the load. Therefore, designing of the heat exchanger is an important part for improving heat transfer in latent heat storage systems. PCMs also have positive volumetric expansion on melting, so, volume design of the containers is also necessary, which should be compatible with the PCM used.[1–3]

A great variety of PCMs such as salt hydrates, paraffins, nonparaffin organic compounds and their mixtures for latent heat thermal energy storage systems have been investigated.[1–5] The fatty acids in the class of nonparaffin organic compounds have superior properties over the other PCM groups, such as congruent melting and cooling, high latent heat of fusion, self-nucleating behavior, ready availability, nontoxicity, nonflammability, noncorrosive, small expansivity during solid–liquid phase change, and good thermal and chemical stability after a large number of accelerated thermal (melt/freeze) cycles.[4–8] However, the fatty acids cost more than the other PCMs on a bulk basis, but they are cheaper to package, so the final module costs are comparable.

In recent years, there has been growing interest in developing the polymer-based PCMs as new type of latent heat thermal energy storage materials for passive solar LHTES systems. Advantages the of polymer-based PCMs are as follows: (1) such a type of PCM can retain the similar shape in a solid state even when the temperature of the blend is over the melting point of the PCM; therefore, it is called as form-stable PCM; (2) they do not require any capsulation; thus, not only the encapsulation problem of PCM is solved, but also heat resistance caused by capsule shell of PCM is disappeared by using this kind of form-stable PCM; (3) because they contact with the heat transfer medium in a LHTES system directly, they are cost-effective; (4) they are easily prepared with desirable

dimensions. These superior properties over traditional PCMs have directed the researchers to develop novel form-stable polymer based PCMs.

The high density poly(ethylene) (HDPE)/paraffin composites as form-stable solid–liquid PCM were prepared and investigated in terms of thermal characteristics and thermophysical properties.[9–12] In these studies, it was reported that the HDPE/paraffin blends as form-stable composite PCMs could be used as direct contact heat exchangers in LHTES applications. Experiments and simulations have been conducted to evaluate the characteristics and performance of encapsulated paraffin in crosslinking agents in terms of encapsulation ratio and energy storage capacity.[13] It is found that a higher coating ratio led to a higher paraffin encapsulation and then lower product hydrophilicity. Thermal cyclic tests shows that the encapsulated paraffin keep up with its geometrical profile and energy storage capacity even after 1000 cycles of operation. A new material for low temperature LHTES is developed from acrylamide during its polymerization process by keeping water as a PCM within its three-dimensional network.[14] The shape of the resulting material is suitable for end use without any support or even coating. A thermoplastic-elastomer, poly(styrene–butadiene–styrene) (SBS)/paraffin(P) as form-stable composite PCM was developed to determine its thermal performance in another study.[15] The SBS/P blend as a form-stable PCM exhibits the same phase transition characteristics as paraffin and up to 80% of latent heat of paraffin. A stable heat storage tile module was investigated, and it is concluded that the proposed matrix type modules could be used as LHTES material with no outer container.[16] The poly-(ethylene glycol) (PEG)/fatty acid blends,[17] thermal energy storage systems based on poly(vinyl chloride) blends,[18] binary blends of polyethers with fatty acids,[19] and poly(ethylene oxide)/stearic acid blends[20] are investigated by calorimetric, spectroscopic, and optic methods. The encapsulations of low melt temperature phase change materials (PCM) such as paraffin waxes in bisphenol-A epoxy and styrene–ethylene–butylene–styrene (SEBS) polymers were studied.[21] In the study of Shuo et al., the results showed that, in the case of paraffin/epoxy, the interaction between these components is sufficient to provide adequate thermal and mechanical performance. The thermoplastic SEBS/paraffin system demonstrates excellent thermal and mechanical performance.

Eudragits belong to a group of commercially available acrylic resins and are fully polymerized copolymers of methacrylic acid and acrylic acid or methacrylic ester in varying ratios.[22]

Eudragits are used for coating crystals, rounded granules, microtablets, and pellets. It is also used for granulation as the first stage in building up matrix structures, particularly with freely soluble drugs. It acts as a film former or binding agent for the palletizing of drugs.[23]

The aim of this study is to prepare form-stable PCMs, Eudragit S (methacrylic acid methyl methacrylate copolymer)/fatty acid (myristic, palmitic, and stearic acids) blends. In this study, Eudragit S is especially chosen to retain high fatty acid content because of its encapsulation property. The blends are analyzed by microscopy and FTIR spectroscopy to reveal maximum encapsulation without leakage and secondary interactions between Eudragit S and fatty acids. The thermal properties of the developed PCMs, such as melting and crystallization temperatures and the latent heats of fusion and crystallization, are determined by using DSC technique.

EXPERIMENTAL

Materials

Eudragit S (molecular weight: 135,000 g/mol composed of a 1 : 2 copolymer of methacrylic acid and methyl methacrylate) is a commercial product from Röhm Pharma (Darmstadt, Germany), with a number average molecular weight of 135,000 g/mol is obtained from Röhm Pharma with a ratio of methacrylic acid groups of 1 : 2 (i.e., 33% methacrylic acid 66% methyl methacrylate copolymer). Fatty acids (purity >98%) used as PCMs in this work are myristic acid ($C_{13}H_{27}COOH$), palmitic acid (PA; $C_{15}H_{31}COOH$), and stearic acid (SA; $C_{17}H_{35}COOH$). These acids were obtained from Aldrich.

Preparation of blends

The blends of Eudragit S with fatty acids are prepared by solution casting method. Solutions of Eudragit S and one of the fatty acids in chloroform are prepared in separate beakers and fatty acid solution is added to Eudragit S solution dropwise. Then chloroform is casted at room temperature in 15 days. The blends are prepared at 40, 50, 60, 70, and 80% w/w fatty acid compositions to obtain the maximum encapsulation ratio without leakage of the fatty acid from the blends when the temperature is between the melting point of the Eudragit S and that of the MA, PA, and SA.

Thermal properties of the Eudragit S/fatty acid blends as form-stable PCMs such as the melting and crystallization, glass transition temperatures, and latent heats are measured by using a DSC (SETERAM DSC 131) instrument. Indium is used as a reference for temperature calibration. The analyses are performed in the temperature range of 20–100°C for the pure acids and 20–200°C for the blends at the same heating rate (5°C/min) and under a constant stream of argon at a flow rate of 60 mL/min. The temperature accuracy is ±0.01°C, and heat flow repeatability is 0.2 μW. A
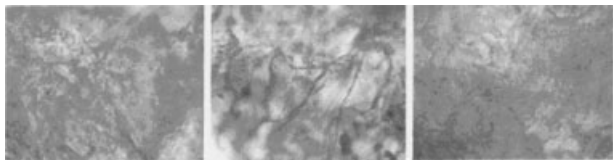
Figure 1 The micrographs of form-stable PCMs obtained by optical microscopy (a) 30% Eudragit S/70%SA; (b) 30% Eudragit S/70%PA; (c) 30%. Eudragit S/70%MA.

small quantity of sample (usually from 5 to 10 mg) is sealed in a small aluminum pan. The temperature of melting and crystallization are onset temperature obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating base line on the same side as the leading edge of the peak.

Infrared spectra of Eudragit S, fatty acids, and form-stable PCMs (the blends) are obtained on a KBr disk by using a Jasco 430 model FTIR spectrophotometer. Morphology of the blends is investigated by a Laica optical microscope.

RESULTS AND DISCUSSION

Characterization of Eudragit S/fatty acid blends

In the blends, the Eudragit S serves as a supporting material for the fatty acids, which melt and solidify in its matrix. So, the fatty acid seepage is not observed even when the blend is heated over the melting temperature of the PCM. This property makes them possible for use in solar LHTES systems without an outer container. On the other hand, it is naturally expected that the holding ability of the Eudragit S over the melting point of the PCM gets weak with increasing the amount of the fatty acid in the blend. In the experiments, the mixture mass percentage of all fatty acids in the blends is determined as 70 under the condition of no leakage of fatty acids after several heating cycles. It means that the confining possibility of fatty acid by Eudragit S is inversely proportional to the amount of fatty acid used in the blend and the leakage of the fatty acid begins when the ratio is over the 70 wt %.

The morphologic investigations on the Eudragit S/fatty acid blends are carried out to observe the dispersion of the fatty acid into Eudragit S by using an optical microscope. The micrographs of Eudragit S/PA and Eudragit S/SA blend as form-stable PCM are given as example in Figure 1.

Figure 1 shows that Eudragit S/MA, Eudragit S/PA, and Eudragit S/SA blends form single phase distribution with encapsulating property of Eudragit S in the blend. The particle sizes of the blends increase in the order of Eudragit S/SA, Eudragit S/MA, and
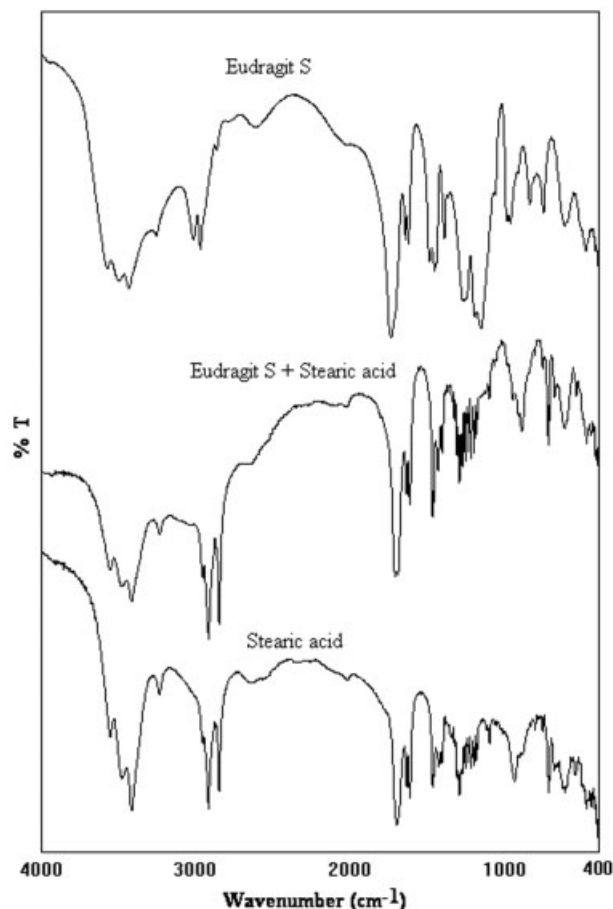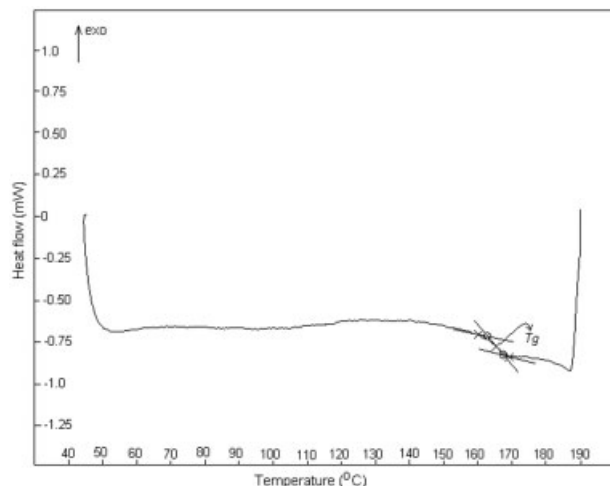

Figure 2 FTIR spectral peaks obtained for Eudragit S, SA and Eudragit S/SA blend.

Eudragit S/PA. It is due to particle size of the fatty acids in bulk.

On the other hand, the compatibility of fatty acids–Eudragit S system can be attributed to the interactions
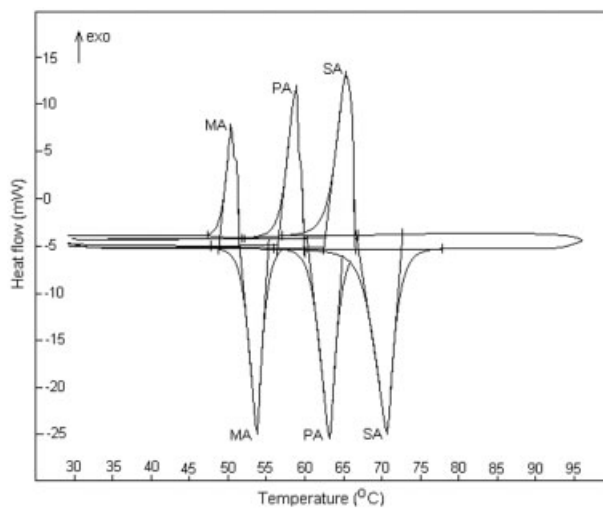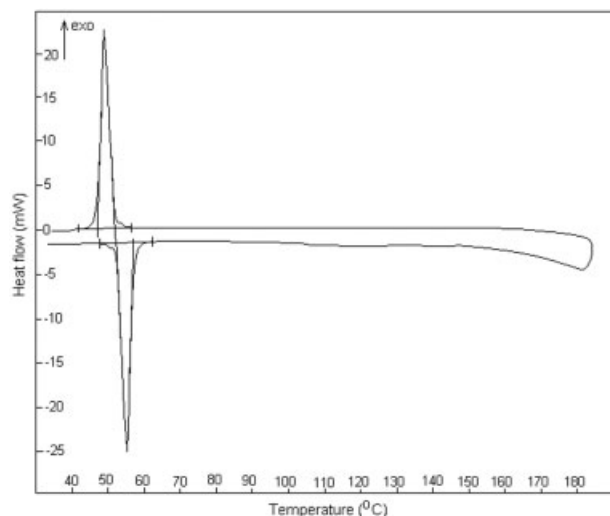

Figure 3 DSC curves of fatty acids.

Figure 4 DSC curve of Eudragit S.

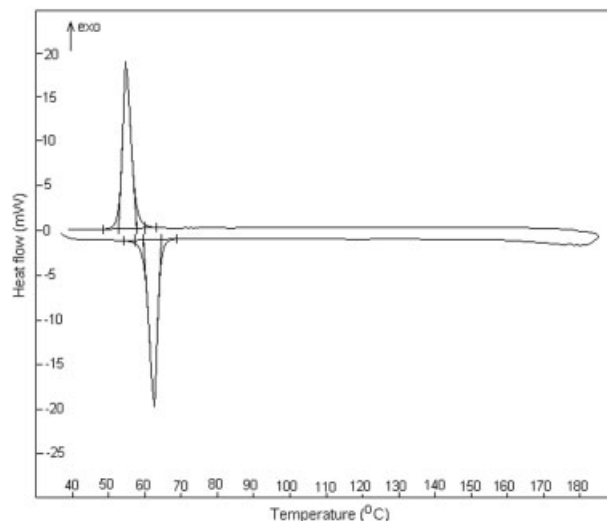**Figure 6** DSC curve of Eudragit S/PA blend as form-stable PCM.

between the blend components. Figure 2 shows the FTIR spectra of Eudragit S, Eudragit S/SA, and SA as an example. The C=O stretching peak is observed at 1714 cm^{-1} for the blend, as it is seen at 1731 and 1702 cm^{-1} for Eudragit S and SA, respectively. The self-association peaks (—OH stretching) are at 3550, 3478, and 3415 cm^{-1} for Eudragit S and at 3552, 3475, and 3413 cm^{-1} for SA. The peaks shift to 3556, 3478, and 3413 cm^{-1} for 30% Eudragit S/70% SA blend. The changes in the peaks of carbonyl and hydroxyl group stretching are due to the interactions of carbonyl and hydroxyl groups and hydrogen bonds between the blend components.

Thermal properties

The typical DSC curves for fatty acids, Eudragit S and Eudragit S/fatty acid blends are given in Figures 3–7,

respectively. Figures 3 and 4 are taken as a reference to evaluate the changes in thermal properties of the form-stable Eudragit S/fatty acid blends. Glass transition temperature of Eudragit S is not clearly observed in the blends because of the small percentage of Eudragit S in the blends. Thermal properties obtained from these curves are given in Table I. The changes in the melting temperatures of the fatty acids are in the range of 0.02–0.82°C, while the changes in the crystallization temperatures of the fatty acids are between 0.62 and 1.27°C in the blends. These changes are not significant for a LHTES application. Heat of melting and heat of crystallization values of the blends determined by DSC are slightly higher than expected from the theoretical values calculated by eq. (1)

Figure 5 DSC curve of Eudragit S/MA blend as form-stable PCM.
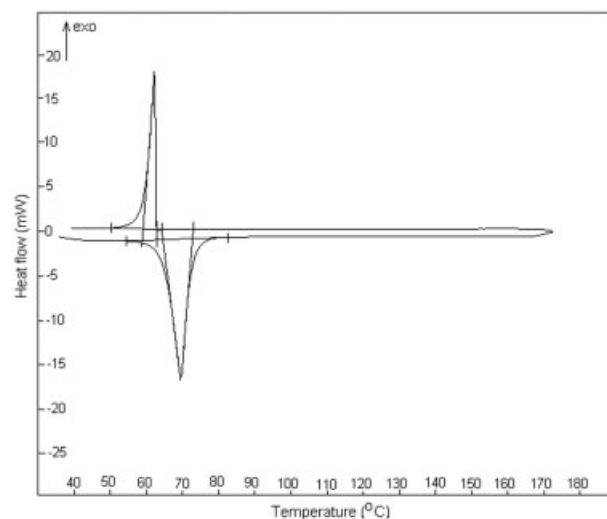
Figure 7 DSC curve of Eudragit S/SA blend as form-stable PCM.

	Melting point (°C)	Heat of melting (J/g)	Freezing point (°C)	Heat of crystallization (J/g)
Myristic acid (MA)	51.80	178.14	51.74	181.63
Palmitic acid (PA)	60.42	233.24	59.88	237.11
Stearic acid (SA)	66.82	258.98	66.36	263.32
Eudragit S/MA	51.82	132.47	50.47	133.01
Eudragit S/PA	59.60	170.64	59.26	170.92
Eudragit S/SA	66.70	184.22	65.43	184.88

Glass transition temperature of Eudragit S: 164.88°C.

$$\Delta H_{E/FA} = W_{FA}\% \Delta H_{FA} \qquad (1)$$

where $\Delta H_{E/FA}$, $W_{FA}\%$ and ΔH_{FA} are the calculated latent heat of fatty acid in form-stable Eudragit S/fatty acid blend, mass percentage of the fatty acid in the blend, latent heat of pure fatty acid, respectively. This is probably due to the facilitated formation of hydrogen bonding between the hydrogen atom from the carboxylic group in acid groups and the carbonyl oxygen from the Eudragit S chain, which, in turn, enhances the formation of crystalline structures. Results from FTIR spectra of the blends are in good agreement with this conclusion. The similar results are reported for polyethyleneoxide/fatty acid blends by Pielichowski and Flejtuch.[19]

By considering the melting and crystallization points of the form-stable Eudragit S/fatty acid blends, it is remarkably noted that they are suitable for passive solar space heating and solar building heating at an operating temperature range of 50–70°C. Furthermore, the heat of melting and crystallization of form-stable PCMs are as high as compared to some salt hydrates and paraffins used for low temperature LHTES system.[1–5]

CONCLUSIONS

It is possible to prepare form-stable Eudragit S/fatty acid blends as a novel LHTES material. In the blends, the fatty acid compound is dispersed into the matrix of solid polymer and it serves as a latent heat storage material when the polymer acts as a supporting material. Therefore, as long as the operating temperature is below the melting point of supporting material the blends can keep its shape even when the PCM undergoes phase change from solid to liquid. The maximum mass percentage of the investigated fatty acids in the blends under the condition of no seepage of the fatty acid in melted state is found as high as 70%. The satisfying thermal properties of the form-stable Eudragit S/MA, Eudragit S/PA, and Eudragit S/SA blends make them possible for LHTES applications at the temperature range of 50–70°C. By using this kind of form-stable PCM, the encapsulation problem of PCM is solved and also heat resistance caused by capsule shell is disappeared. The prepared form-stable PCMs are cost-effective materials because of their direct usage advantage without outer container in a LHTES system. Besides, Eudragit S/fatty acid blends have an additional advantage of easy preparation with desirable dimensions.

References

1. Abhat, A. Sol Energy 1983, 30, 313.
2. Zalba, B.; Marin, J. M.; Cabeza, L. F.; Mehling, H. Appl Therm Eng 2003, 23, 251.
3. Kaygusuz, K. Energy Sources 1999, 21, 745.
4. Rozanna, D.; Chuah, T. G.; Salmiah, A.; Thomas Choong, S. Y.; Sa'ari, M. Int J Green Energy 2004, 1, 495.
5. Sharma, S. D.; Sagara, K. Int J Green Energy 2005, 2, 1.
6. Sarı, A. Appl Therm Eng 2005, 25, 2100.
7. Hasan, A.; Sayigh, A. A. M. Renew Energy 1994, 4, 69.
8. Sarı, A.; Kaygusuz, K. Renew Energy 2003, 28, 939.
9. Inaba, H. P.; Tu, P. Heat Mass Tran 1997, 32, 307.
10. Lee, C. H.; Choi, H. K. Polym Compos 1998, 19, 704.
11. Sarı, A. Energy Convers Manage 2004, 45, 2033.
12. Hong, Y.; Xin-shi, G. Sol Energy Mater Sol Cells 2000, 64, 37.
13. Hawlader, M. N.; Uddin, M. S.; Zhu, H. J. Int J Energy Res 2002, 26, 159.
14. Royon, L.; Guiffant, G.; Flaud, P. Energy Convers Manage 1997, 38, 517.
15. Xiao, M.; Feng, B.; Gong, K. Energy Convers Manage 2002, 43, 103.
16. Feldman, D.; Shapiro, M.; Fazio, P. A. Polym Eng Sci 1985, 25, 406.
17. Pielichowski, K.; Flejtuch, K. Macromol Mater Eng 2003, 288, 259.
18. Pielichowski, K.; Flejtuch, K. Eur Polym J 1999, 35, 27.
19. Pielichowski, K.; Flejtuch, K. J Appl Polym Sci 2003, 90, 861.
20. Pielichowski, K.; Flejtuch, K. Polym Adv Technol 2005, 16, 127.
21. Shuo, P.; Fuchs, A.; Wirtz, R. A. J Appl Polym Sci 2004, 93, 1240.
22. Lin, S. Y.; Yu, H. L. J Polym Sci Part A: Polym Chem 1999, 37, 2061.
23. Ramrakhiani, M.; Parashar, P.; Datt, S. C. J Appl Polym Sci 2005, 96, 1835.