J Polym Environ (2009) 17:254–258
DOI 10.1007/s10924-009-0146-7

ORIGINAL PAPER

Preparation, Thermal Properties and Thermal Reliability of Form-Stable Paraffin/Polypropylene Composite for Thermal Energy Storage

Cemil Alkan · Kemal Kaya · Ahmet Sarı

Abstract This study is focused on the preparation, characterization, and determination of thermal properties and thermal reliability of paraffin/polypropylene (PP) composite as a novel form-stable phase change material (PCM) for thermal energy storage applications. In the composite, paraffin acts as a PCM when PP is operated as supporting material. The composites prepared at different mass fractions of paraffin (50, 60, 70, 80, and 90 w/w%) by solution casting method were subjected to leakage test by heating the composites over the melting temperature of the PCM. The paraffin/PP composite (70/30 w/w%) is found as the maximum paraffin containing composite and was characterized using Fourier transform infrared spectroscopy, optic microscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA) techniques. DSC analysis indicated that the form-stable paraffin/PP composite melts at 44.77–45.52 °C and crystallizes at 53.55–54.80 °C. It has latent heats of 136.16 and −136.59 J/g for melting and crystallization, respectively. These thermal properties make it potential PCM for latent heat thermal energy storage (LHTES) purposes such as solar space heating applications. Accelerated thermal cycling tests indicated that the form-stable PCM had good thermal reliability. TGA also showed that the form-stable PCM degrades in two distinguishable steps and had good chemical stability.

Keywords Polypropylene · Paraffin · Phase change material · Thermal energy storage

---

C. Alkan (✉) · K. Kaya · A. Sarı
Department of Chemistry, Gaziosmanpaşa University,
60240 Tokat, Turkey
e-mail: cemilalkan@gop.edu.tr

Introduction

Latent heat thermal energy storage (LHTES) is one of the most attractive methods of thermal energy storage due to allowing storage and release of energy in large quantities per unit weight of phase change material (PCM) at nearly constant temperature during the phase change [1, 2]. A great number of PCM materials have been investigated for heating and cooling applications [3–5]. Among the studied PCMs, paraffins have been used as a latent heat energy storage material with the advantages of high enthalpy of phase change, small segregation of components, and small changes in structure during repeated phase transitions, negligible super cooling, low vapor pressure, self-nucleating behavior and low cost [6–8].

Phase change materials require special LHTES devices in different shapes or elements such as shell and tube PCM heat exchanger or a lot of cans to encapsulate them since they changed from solid to liquid during the energy storage period. Although the use of materials solved the solid–liquid phase change problem, it increases not only the heat resistance but also the cost of the LHTES system. However, these problems can be overcome using a form-stable PCM prepared by encapsulation of PCM into a polymer matrix. The form stable PCMs have several advantages [9–11]. No leakage is observed in form stable PCMs during melting and an extra storage container is not needed. Also thermal resistance by capsule shell is eliminated. Interactions between PCM and environment are prohibited. In addition, they are easily prepared with the desired dimensions. Furthermore, being feasible for some heating applications in buildings such as under floor space heating and reducing electric peak load in heating in winter by using wallboard and plasterboard prepared by absorption of a PCM. These beneficial properties directed the researchers to develop new kinds of form-stable PCMs by melt blending and use them in practical LHTES applications [12–17].

On the other hand, some of the form stable PCMs have been prepared by solution casting method to increase energy storage intensity of form stable PCMs because solution blending method brings about a considerably high PCM/polymer encapsulation ratio and thermal reliability [18–20].

According to the literature survey, polyethylene seems to be the most frequently used polymer for blending with paraffin waxes to obtain form-stable PCM. It is mainly due to the availability, cheapness and easy process ability. However, it can not be used for solution blending due to solubility problem leading to restriction of encapsulation ratio. Atactic polypropylene is one of the most suitable alternative with the properties of cheapness, availability and processability in addition to the solubility in common solvents. Major markets for PP are filaments and fibers, automotive and appliance components, packaging materials, furniture, high tenacity yarns, tufted carpets and so on [21].

This study is focused on the preparation, characterization and determination of thermal properties and thermal reliability of form-stable paraffin/PP composite by optic microscopy (OM), Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA).

Experimental

Materials

Polypropylene (M_w 14000 g mol^{-1}) and paraffin were obtained from Fluka and Merck companies, respectively. *n*-Heptane was analytical grade and obtained from Petkim Petrokimya Company, Turkey.

Preparation and Characterization of the PP/Paraffin Composite

The Paraffin/PP composites were prepared by solution casting method. Solutions of Paraffin and PP in *n*-heptane were prepared in separate beakers and paraffin solution was added to PP solution dropwise. Then *n*-heptane was casted at room temperature in 15 days. The composites are prepared at 40, 50, 60, 70, 80 w/w% paraffin compositions to obtain the maximum encapsulation ratio without leakage of the paraffin from the composites when the temperature was over the melting point of the paraffin. The morphology of the form-stable composite was investigated using an OM (Laica model) as the spectroscopic analysis was performed on a KBr disk by using a Jasco 430 model FT-IR spectrophotometer.

Determination of Thermal Properties and Thermal Reliability of the PCM

Thermal properties of form-stable paraffin/PP composite such as melting and crystallizing points and latent heats were measured by DSC technique (SETARAM DSC 131). The analyses were carried out at 5 °C/min heating rate under a constant stream of argon at a flow rate of 60 mL/min. The melting and freezing points were taken as onset temperatures 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. The latent heat capacity was determined by numerical integration of the area of the phase transition peak. Reproducibility was tested by conducting three measurements. In order to determine thermal reliability of the form-stable PCM, accelerated thermal cycling test (3,000 melting/crystallizing processes) was conducted by using experimental procedure in literature [22]. The changes in thermal properties after thermal cycling were evaluated using DSC analysis. Moreover, the chemical stability of the PCM after thermal cycling test was also investigated by FT-IR analysis. For this reason, a Jasco 430 model FTIR spectrophotometer and SETARAM DSC 131 instrument were used.

Thermo-gravimetric analysis was carried out on a Perkin-Elmer TGA7 thermal analyzer which was calibrated with calcium oxalate from 25 to 600 °C at a heating rate of 10 °C min^{-1} in a static air atmosphere. Differential thermal gravimetry (DTG) was obtained to determine the maximum rate of weight loss.

Results and Discussion

Characterization of Form-Stable Paraffin/PP Composite

Paraffin containing composites in PP of 40, 50, 60, 70, 80, and 90 wt% were prepared starting with the minimum paraffin encapsulation ratio and continuing up to the finding of the ratio with leakage of paraffin (80% in this study). The maximum encapsulation ratio of paraffin without leakage is 70 wt% and therefore the composite is identified as form-stable PCM. Solution casting method was applied to prepare paraffin/PP composite in *n*-heptane. The solvent was casted at room temperature to prevent solvent residue in the composite and paraffin leakage from the composite system.

Polymer composites are commonly immiscible resulting in phase separation which can be observed by microscopy. As shown in the Fig. 1, there is only one phase on the

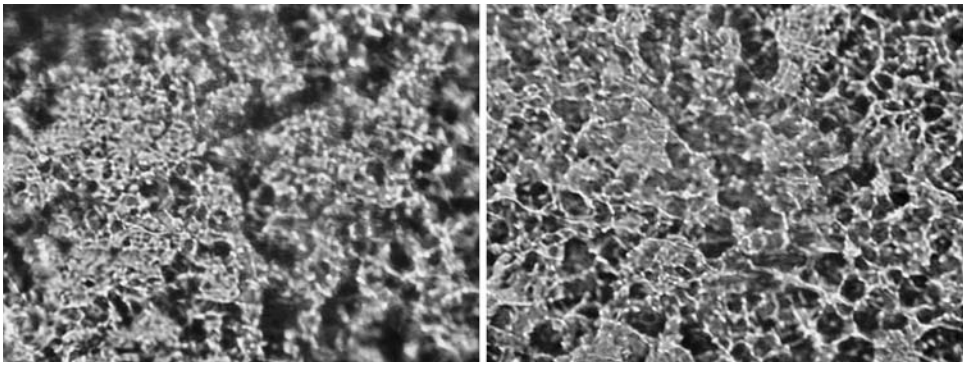

Fig. 1 Optical microscopy images of form-stable paraffin/PP composite

surface of the composites in ×1000 magnification. It does not mean that the components are miscible in microscopic scale. However, the PP is saturated by paraffin and paraffin is coated by PP upon coating. Increasing the amount of the paraffin in the composites did not cause a considerable change in the morphology of the composites.

Fourier transform infrared spectroscopy of the paraffin and form-stable paraffin/PP composite was used to investigate the possible interaction between the components of the composite (Fig. 2).

The CH stretching peaks was observed at the nearly same wave number and all of the other peaks maintain their positions in the form stable composite before and after thermal cycling. This shows that there is no considerable interaction between paraffin and polypropylene which is expected due to the similar chemical structures with non-interacting CH, CH_2, and CH_3 units. The consistency of the peaks in the FT-IR spectra after thermal cycling is the evidence of durability and therefore suitability of the composites to be used as form-stable PCM material.

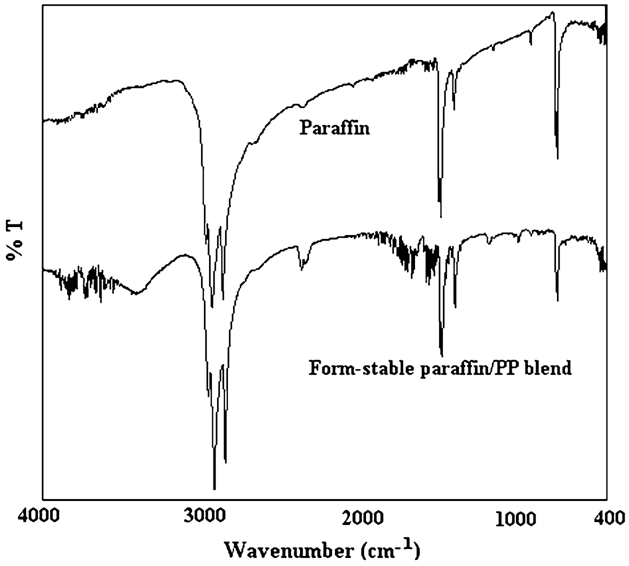

Fig. 2 Fourier transform infrared spectra of paraffin and form-stable paraffin/PP composite

Thermal Properties of Form-Stable Paraffin/PP Composite

Some thermal properties of isotactic polypropylene/soft and hard Fisher Tropsh wax composites were investigated by Krupa and Luyt [23] and Krupa et al. [24]. The DSC curve of pure paraffin displays two well-distinguished separated peaks at 41 and 57 °C. The first peak relates to the solid–solid transition of one crystalline structure into another as reported in the literature [25]. Crystalline paraffin waxes show a solid–solid transition from a soft (rotator, hexagonal) to a hard (non-rotator, orthorhombic) crystalline structure [26]. A detailed description of this can be found in a recent publication of Genovese et al. [25]. The second peak is associated with the melting point of the crystallites. It is clear that the PP and paraffin wax are not miscible due to the different morphologies. Atactic PP is amorphous as paraffin crystallizes. For this reason the melting regions of paraffin and PP are distinctly separated.

The result of DSC measurements of the form-stable PCM is shown in Fig. 3. The DSC cooling curves show that, in the case of the form-stable PCM, both exothermic peaks are related to the solid–solid transition and crystallization of paraffin within the form stable PCM. The latent heats of form-stable paraffin/PP composite were found to be 136.16 and −136.59 J/g for melting and crystallization, respectively. Based on the DSC results, the thermal properties of the form-stable PCM make it a potential PCM for LHTES purposes such as solar space heating applications.

Thermal Reliability of Form-Stable Paraffin/PP Composite

It is clear from Fig. 4 that the DSC curves of the form-stable PCM before and after 3,000 thermal cycles, both the endothermic and exothermic peaks belonging to the form-stable PCM looks like each other. The onset temperatures and phase change enthalpies are almost the same meaning that the form-stable PCM is thermally stable and reliable. The melting and crystallization latent heats of the form-stable

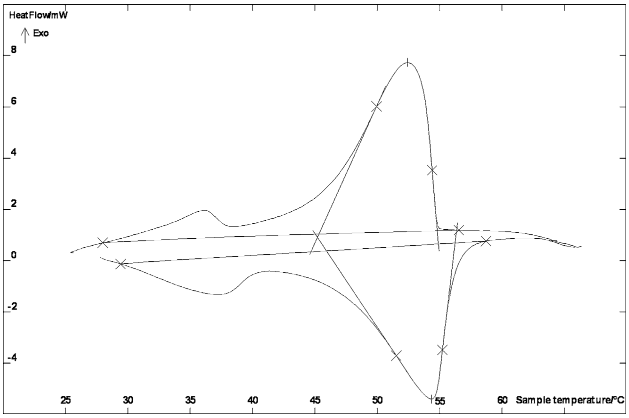

Fig. 3 Differential scanning calorimetry curves of form-stable paraffin/PP (70/30 wt%) composite

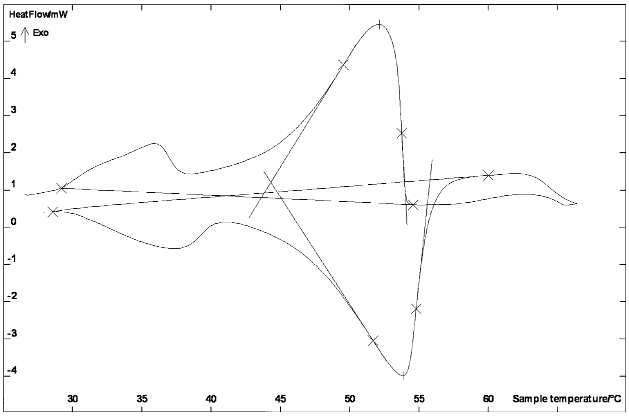

Fig. 4 Differential scanning calorimetry curves of form-stable paraffin/PP (70/30 wt%) composite after 3,000 thermal cycling

PCM after 3,000 thermal cycling were measured as 116.12 and −116.78 J/g, respectively. After thermal cycling, the deviations of the latent heat of melting of the paraffin within the composites are quite low. The averages and standard deviations were determined from the three measurements, where sampling was conducted in different places of the form-stable PCM. However, the peaks belonging to the paraffin within the form stable PCM are very broad, and it makes the evaluation of the latent heat of melting more complicated, which results in small differences upon integrating the latent heat during phase changes.

Chemical and Thermal Stability of the Form-Stable PCM

Figure 5 shows the FT-IR spectra of form-stable paraffin/PP composite before and after thermal cycling. The shape and frequency values of all peaks did not change after thermal cycling. This result indicates that the chemical structure of the composite was not affected by repeated melting/freezing cycling. Therefore, it is noteworthy to note that the form-stable paraffin/PP composite is stable chemically after 3,000 thermal cycling.

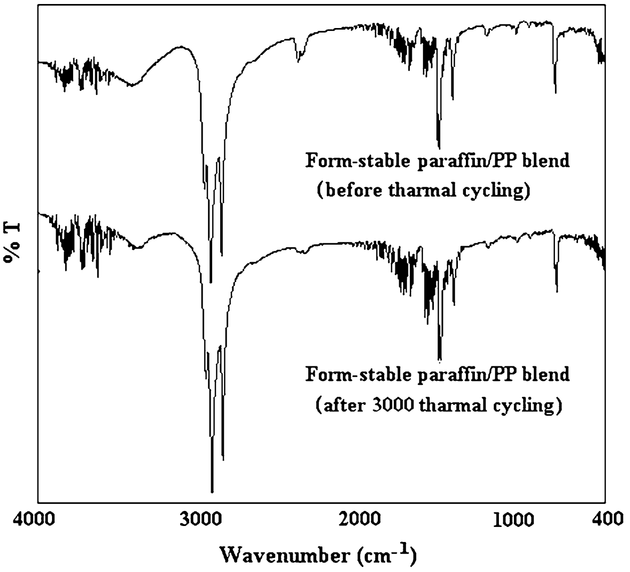

Fig. 5 Fourier transform infrared spectra of form-stable paraffin/PP composite before and after 3,000 thermal cycling

Composites consisting of paraffin and PP degraded in two clearly distinguishable steps as shown in Fig. 6. The results are also summarized in Table 1. DTG was obtained to determine maximum rate of weight loss. The measurements

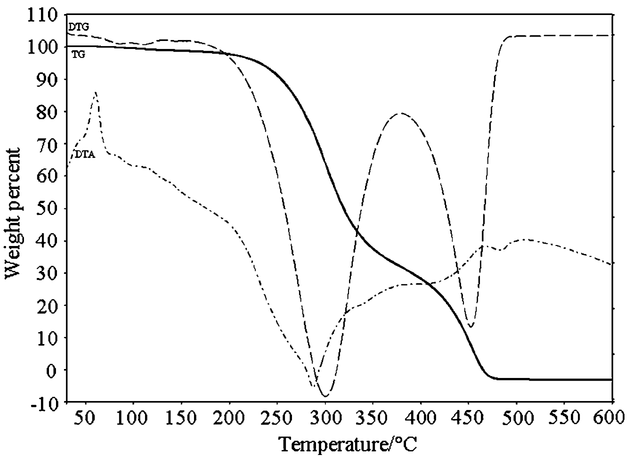

Fig. 6 Differential thermal gravimetry, TG, DTA curves of form-stable paraffin/PP composite

Table 1 Thermal gravimetric analysis data for paraffin/PP (70/30 wt%) composite as form-stable PCM

Stage	Temperature range (°C)	DTG_{max} (°C)	Mass loss Δm (%)
1	157–379	300	66.75
2	379–499	452	33.25

also showed no char yield at temperatures higher than 500 °C in both cases.

Degradation of polyolefin/paraffin composites in two well-distinguished steps found its application in the field of metal particle injection moulding, where these composites are utilized as processing binders during extrusion [27] in addition to the form-stable PCM.

Conclusions

Phase change materials, based on polypropylene composite with soft paraffin wax was prepared in n-heptane as a novel form-stable PCM for LHTES applications. In the composite, Paraffin is dispersed into the polymer matrix and serves as a latent heat storage material. The form-stable paraffin/PP composite (70/30 w/w%) keeps its shape even when the PCM undergoes phase change from solid to liquid. It was found that paraffin melt independently within the PP matrix (up to 70 wt% of wax), whereas material remains in the solid state. The composite was characterized by FT-IR and OM techniques. The FT-IR analysis showed that paraffin was hosted in PP without considerable interactions between the components as the composites without leakage of paraffin were in single phase morphology according to OM analysis. Paraffin is not miscible with PP due to different crystalline structures. It leads to a large scatter of specific melting enthalpies obtained from DSC analyses. The DSC analysis results also indicated that the prepared form-stable PCM has suitable phase change temperatures and latent heats, good thermal reliability for LHTES in solar space heating applications. FT-IR analysis results revealed that the form-stable PCM had good chemical stability after thermal cycling. In addition, thermo-gravimetric investigation showed that form-stable paraffin/PP composite degrades in two distinguishable steps.

Acknowledgements The author would like to acknowledge the financial support (Project No. 2003 K120510) by the Turkish State Planning Organization. Authors also thank Dr Ahmet Karadağ for TGA analysis and Dr Ibrahim Türkekul for OM analysis.

References

1. Abhat A (1983) Sol Energy 30(4):313–332
2. Dinçer I, Rosen MA (2002) Thermal energy storage. Systems and applications. Wiley, New York
3. Zalba B, Marín JM, Cabeza LF, Mehling H (2003) Appl Therm Eng 23:251–283
4. Alkan C, Kaya K, Sarı A (2008) Mater Lett 62:1122–1125
5. Kenisarin M, Mahkamov K (2007) Renew Sust Energ Rev 11(9):1913–1965
6. Hadjieva M, Kanev ST, Argirov J (1992) Sol Energy Storage Mater Sol Cells 27:181–187
7. Himran S, Suwono A, Mansoori GA (1994) Energy Sour 16:117–128
8. Alkan C (2006) Thermochim Acta 451(1–2):126–130
9. Ozonur Y, Mazman M, Paksoy HO, Evliya H (2005) Int J Energy Res 30(10):741–749
10. Alkan C, Sari A, Uzun O (2006) AIChE J 52(9):3310–3314
11. Pielichowski K, Flejtuch K (2005) Polym Adv Technol 16(2–3):127–132
12. Pielichowski K, Flejtuch K (2003) J Appl Polym Sci 90:861–870
13. Hong Y, Xin-Shi G (2000) Sol Energy Storage Mater Sol Cells 64:37–44
14. Inaba H, Tu P (1997) Heat Mass Transf 32:307–312
15. Sarı A (2004) Energy Convers Manage 45:2033–2042
16. Xiao M, Feng B, Gong K (2002) Energy Convers Manage 43:103–108
17. Liu X, Liu H, Wang S, Zhang L, Cheng H (2006) Energy Convers Manage 47:2515–2522
18. Alkan C, Sarı A (2008) Sol Energy 82:118–124
19. Sarı A, Alkan C, Uzun O, Kölemen U (2006) J Appl Polym Sci 101:1402–1406
20. Alkan C, Sarı A, Karaipekli A, Önal A (2008) Energy Convers Manage 49:373–380
21. Ulrich H (1993) Introduction to industrial polymers, 2nd edn. Hanser, Munich
22. Sarı A, Karaipekli A (2008) Mater Chem Phys 109:459–464
23. Krupa I, Luyt AS (2001) Thermochim Acta 372:137–141
24. Krupa I, Miková G, Luyt AS (2007) Eur Polym J 43:895–907
25. Genovese A, Amarasinghe G, Glewis M, Mainwaring D, Shanks RA (2006) Thermochim Acta 443(2):235–244
26. Tiwari GB, Sriwastava SP, Pandey SP, Purohit RC, Saxena AK, Goyal SK (1997) Petrol Sci Technol 15(3–4):335–346
27. Herranz G, Levenfeld B, Várez A, Torralba JM (2005) Powder Metall 48(2):134–138