

형태안정성 PCM: 잠열저장을 위한 Polypropylene과 n-Eicosane으로 구성된 고화젤의 제조 및 특성

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Shape-Stabilized Phase Change Materials: Preparation and Properties of Frozen Gels from Polypropylene and n-Eicosane for Latent Heat Storage

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초록: 본 연구에서는 상전이 온도가 36 °C인 n-eicosane을 열가소성 폴리올레핀 고분자인 폴리프로필렌과 블렌드 하였으며, 또한 최근의 형태안정성 PCM(SSPCM)의 연구검토를 통하여 폴리프로필렌과 n-eicosane의 특성과 잠열저장체로서의 적용 가능성을 확인하였다. 상전이 온도가 36 °C인 n-eicosane과 폴리프로필렌을 멜팅방법과 흡수 방법을 이용하여 시료를 제조하였다. 제조된 형태안정성 PCM(SSPCM)을 DSC, WAXD, FTIR spectroscopy, ARES로 분석결과 형태안정성, 열용량의 향상을 확인하였다.

Abstract: Phase change materials based on polypropylene blended with n-eicosane were studied in this paper. In addition, this paper reviews recent studies on the preparation of shape stabilized phase change materials (SSPCM), such as SSPCM from polypropylenes and n-eicosane, their basic properties and possible applications to latent heat storage. The preparation methods used were the melting method and absorption methods. Shape stabilized PCM(SSPCM) prepared for DSC, WAXD, FTIR spectroscopy, ARES, results of the analysis of shape stability heat capacity to improve were identified.

Keywords: phase change material(PCM), polypropylene, n-eicosanes, frozen gel, latent heat, SSPCM, melt index(melt flow index).

Introduction

Heat is absorbed or released during a phase change, while the temperature is relatively constant. This heat is known as latent heat. The word “latent heat”, means hidden heat, and it has also been referred to as hidden energy. During a phase change, the amount of heat is proportion to the mass and latent heat of the material. The latent heat depends of the substance and the nature of the phase change. A positive and negative sign is used if energy is added to the system or released from the system, respectively.

Significant research on the preparation of shape-stabilized frozen gels from a phase change material (PCM) and polymers has been performed over the last few years.¹ PCMs of an alkane allow for the storage and transport of large quantities of thermal energy using simple techniques because the absorbed latent heat cannot be lost by conduction, convection or radiation. Alkane hydrocarbon waxes are mainly mixtures of linear chain alkanes ($\text{CH}_3(\text{CH}_2)_n\text{CH}_3$). The methylene segments of the linear alkanes are capable of crystallization due to their high symmetry and weak van der Waals interactions. In general, the melting temperature and latent heat increase with increasing chain length. Alkanes display little or no degree of supercooling with crystallization and melting

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Table 1. Physical Properties of PCMs

Properties	T_m (°C)	T_c (°C)	Thermal conductivity		Density		Specific heat		Latent heat (J/g)
			/W/(m · K)		(g/m ³)		capacity/J (kg.K)		
PCM			Solid	Liquid	Solid	Liquid	Solid	Liquid	
Na ₂ SO ₄ · 10H ₂ O	32.4				1.46	1.33	1460	2130	190
n-octadecane	28.2	25.4	0.31	0.18	0.85	0.78	2200		244
n-nonadecane	32.1	26.4	0.23	0.14	0.784		2090		222
n-eicosane	36.6	30.6		0.15	0.956	0.778	2210		247
n-heneicosane	40.5	35.9			0.792				213
Paraffin wax	59.1		0.24		0.897		1850		200
MicroPCMS(C ₁₈)	28		0.310	0.144	1.00	0.936			167

occurring over narrow temperature ranges. Alkanes have relatively high latent heat as well as other characteristics suitable for applications as PCM, i.e. chemically non-aggressive, non-toxic, non-corrosive and possessing long-term stability.^{2,3} Eicosane (also known by the IUPAC name icosane or as didecyl) is an alkane with the chemical formula, CH₃(CH₂)₁₈CH₃(C₂₀H₄₂). Eicosane has little use in the petrochemical industry, as its high flash point makes it an inefficient fuel. The gel compounds of a polymer and PCM are believed to have low density and high thermal storage capacity.^{4,5} They can be used in consumer products in the form of fibers, fabrics and clothing or formed as food or beverage containers. So, such a frozen gel can be used in building materials for the generation of thermal insulating and waste energy recycling.⁶ Table 1 lists the physical properties of some organic and inorganic materials. In this experiment, n-eicosane was used as the phase change material. As shown in the table, the specific heat capacity of latent heat of n-eicosane is 2210 J/(kg · K) when it is in the solid state. The latent heat of n-eicosane is 247 J/g. These values for n-eicosane make it suitable as a phase change material for capturing or releasing heat.⁷⁻¹⁴

In order to make PCMs adhere to fibers, previous studies have attempted to disperse PCMs directly into the solvent.¹¹ However, the direct dispersion method has problems with washing durability.⁷ Another favorable method is encapsulation, which places PCMs into a micro capsule that prevents this material from melting at environmental temperatures and detaching from the fibers to maintain the thermal performance.¹⁵ Despite keeping PCMs inside effectively, micro-encapsulation also has difficulties because the thermal physical durability decreases due to the knife overall method. These theoretical and academic studies highlight the necessity of a methodology to minimize the deterioration of the thermal and physical properties of PCM-applied composites. Paraffin is a preferred material for producing a problem-solving

composite because it is an innocuous substance with outstanding capacity of heat storage/release, and can be classified into a range of composites according to the number of carbon atoms in the molecular structure.⁹

In this study, several composites (shape stabilized phase change materials polymer, SSPCM) were produced from n-eicosane (PCMs) and PP, and their thermal, physical and rheological properties were examined according to the compounding condition. The optimum composition is proposed from these results. The composite condition control factors were the content, types (chip/powder) of n-eicosane and compounding method (melting/absorption).

Experimental

Materials. Moplen HP653P (melt index 17, chemical pure; PolyMirae, Korea), Moplen HP563S (melt index 38, chemical pure; PolyMirae, Korea), PP5014 (melt index 4.8, chemical pure; PolyMirae, Korea), PP3045 (melt index 0.5, chemical pure; PolyMirae, Korea), n-eicosane (98.0%; Tokyo Kasei Kogyo, Japan)

Preparation of Shape Stabilized Pphase Change Materials.

Preparation of SSPCM Composite by Melting: The mixture in the reaction container was heated to 200 °C for 2 hrs. The mixing time of the laboratory scale preparation is quite long compared to the short working time in a compounder vessel. The melting point of the phase change materials in this experiment was 37 °C. The melting temperature of polypropylene is approximately 154 °C. The polypropylenes used in the melting method were chip type polypropylene with a melt index 0.5, 17, 37 and 4.8, respectively. Therefore, the mixture was heated to 200 °C to ensure complete melting of the mixture. A melting method of a frozen gel with a 50/50 weight ratio of polypropylene and n-eicosane was prepared by adding polypropylene chips and n-eicosane.

Figure 1 shows the prepared SSPCM using the melting

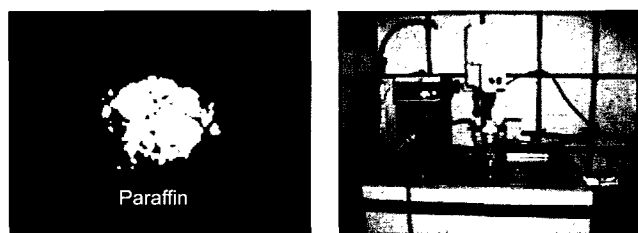


Figure 1. Photographs of the melting method (at oil bath).

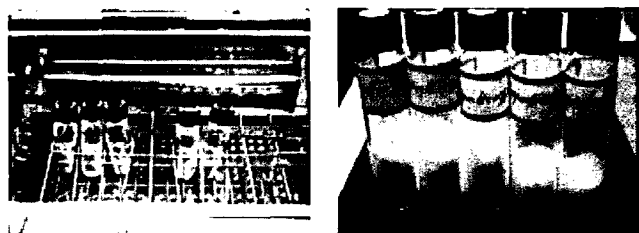


Figure 2. Photographs of the absorption method (at thermostat).

method and the experiment system for manufacturing the SSPCM. The remaining mixture was used directly for thermal analysis, chemical composition analysis, and mechanical properties analysis by differential scanning calorimetry (DSC, Instrument Model : TA Instrument 2010).

Preparation of SSPCM Composite by Absorption: The SSPCM mixture in the reaction container was heating to approximately 60~80 °C for 2 hrs. Powder shaped polypropylene with a melt index of 4.8 was used. Polypropylene powder and n-eicosane were mixed. An absorption method of a frozen gel with a 50/50 weight ratio of polypropylene/4.8-n-eicosane was prepared by adding polypropylene powder and n-eicosane. Figure 2 shows photographs of the absorption method.

Results and Discussion

Properties of SSPCM. The miscibility and thermal properties of the SSPCM composite were determined by mixing n-eicosane with 3 types of polypropylene with different MI(melt index). The results showed that the polypropylene SSPCM composite containing n-eicosane had excellent miscibility and phase change properties.

Figure 3, 4 shows the DSC results of the endo-exo heat of SSPCM(n-eicosane) and n-eicosane, polypropylene. The heat flow graph of the endothermic and exothermic reaction reached its peak at 36~37 °C and 28~33 °C, respectively. These results were attributed to the phase change properties of PCM, which absorbs heat by melting if the environmental temperature increases, while it releases heat by crystallizing in the opposite case. Moreover, PCM(n-eicosane)

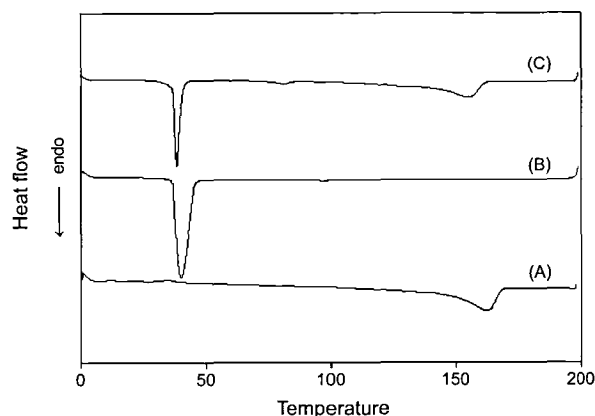


Figure 3. DSC heating curves for (A) Polypropylene(melt index 17); (B) n-eicosane; (C) SSPCM3-30%.

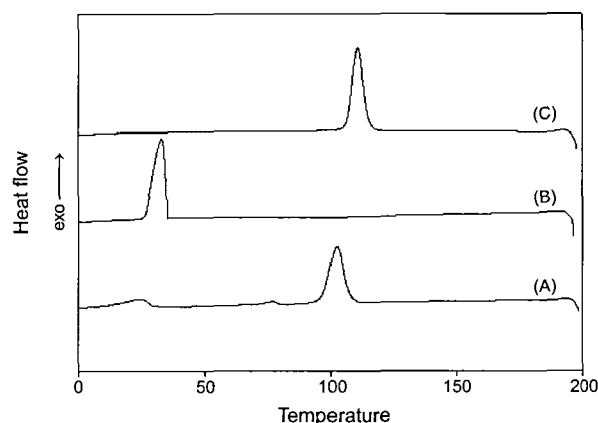


Figure 4. DSC cooling curves for (A) SSPCM3-30%; (B) n-eicosane; (C) Polypropylene(melt index 17).

can maintain shape stability as a solid even when the environmental temperature increases to more than the melting point(37 °C) by blending with the polypropylene and storing latent heat. This composite material is known as a “frozen gel”, which contains liquid PCM and solid polypropylene, producing a solid substance that is adaptable to a range of areas. The results suggest that this material can be adapted to energy storage units.

DSC Thermograms of Frozen Gels SSPCM Composites. The thermal properties of the frozen gels using the melting and absorption method were measured using a differential scanning calorimeter with a ramping rate of 5.0 K/min.

Tables 3~7 and Figures 5~9 show the heat capacity of the 5 types of SSPCMs(SSPCM 1-5) with 4 different n-eicosane contents of 10, 20, 30, 40 until 50 wt%. Table 2 lists the compounding method of the SSPCMs. From the graphs, the heat flows of SSPCMs reached a peak at approximately 37 °C, which is the same as the melting point of n-eicosane, irrespective of the n-eicosane content. Figure 10 shows the

Table 2. Description of the SSPCM Compositions

SSPCM	PP MI (melt index)	PCM	PCM ratio	Method
SSPCM1 (10, 20, 30, 40, 50 wt%)	0.5 (chip)	n-eicosane	10-50%	Melting
SSPCM2 (10, 20, 30, 40, 50 wt%)	4.8 (chip)	n-eicosane	10-50%	Melting
SSPCM3 (10, 20, 30, 40, 50 wt%)	17 (chip)	n-eicosane	10-50%	Melting
SSPCM4 (10, 20, 30, 40, 50 wt%)	37 (chip)	n-eicosane	10-50%	Melting
SSPCM5 (10, 20, 30, 40, 50 wt%)	4.8 (powder)	n-eicosane	10-50%	Absorption

Table 3. Thermal Properties of SSPCM1 (melting)

Composition	Melting point (°C)	Heat capacity (J/g)
SSPCM1 (10%)	36.41	2.75
SSPCM1 (20%)	37.24	13.52
SSPCM1 (30%)	38.52	30.46
SSPCM1 (40%)	38.67	91.40
SSPCM1 (50%)	39.30	84.31

Table 4. Thermal Properties of SSPCM2 (melting)

Composition	Melting point (°C)	Heat capacity (J/g)
SSPCM2 (10%)	36.41	0.48
SSPCM2 (20%)	36.68	0.34
SSPCM2 (30%)	37.36	30.56
SSPCM2 (40%)	37.90	48.93
SSPCM2 (50%)	37.65	74.01

Table 5. Thermal Properties of SSPCM3 (melting)

Composition	Melting point (°C)	Heat capacity (J/g)
SSPCM3 (10%)	37.29	1.59
SSPCM3 (20%)	36.95	11.61
SSPCM3 (30%)	36.98	23.33
SSPCM3 (40%)	37.41	55.13
SSPCM3 (50%)	38.05	76.78

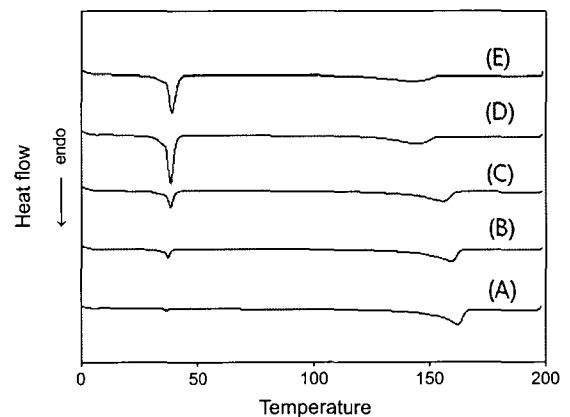
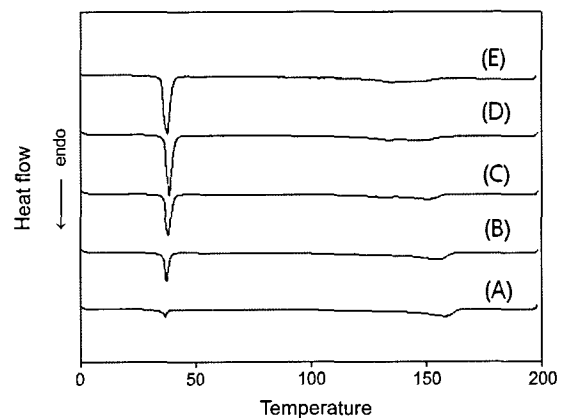
Table 6. Thermal Properties of SSPCM4 (melting)

Composition	Melting point (°C)	Heat capacity (J/g)
SSPCM4 (10%)	37.28	2.85
SSPCM4 (20%)	37.26	7.29
SSPCM4 (30%)	37.91	35.46
SSPCM4 (40%)	37.68	48.39
SSPCM4 (50%)	37.77	80.18

endothermic amount increased with increasing amount of n-eicosane from 10 to 50 wt%. Figure 11 shows the tendency of the melting point of PP according to the PCM content in SSPCM. The peak point moved to a lower temperature with increasing PCM content. For example, peak moved from 162 °C (10 wt% content) to 142 °C (50 wt% content). In the mixture, the melting point of polypropylene decrease with an increase in n-eicosane content, which indicates the formation of

Table 7. Thermal Properties of SSPCM5 (absorption)

Composition	Melting point (°C)	Heat capacity (J/g)
SSPCM5 (10%)	36.72	10.18
SSPCM5 (20%)	37.37	31.48
SSPCM5 (30%)	38.24	61.02
SSPCM5 (40%)	38.50	89.24
SSPCM5 (50%)	37.69	99.04

**Figure 5.** DSC Thermo-diagrams of SSPCM1: (A) n-eicosane 10%; (B) n-eicosane 20%; (C) n-eicosane 30%; (D) n-eicosane 40%; (E) n-eicosane 50%.**Figure 6.** DSC Thermo-diagrams of SSPCM2: (A) n-eicosane 10%; (B) n-eicosane 20%; (C) n-eicosane 30%; (D) n-eicosane 40%; (E) n-eicosane 50%.

smaller crystallites due to the miscibility of the components in the molten state.¹⁶

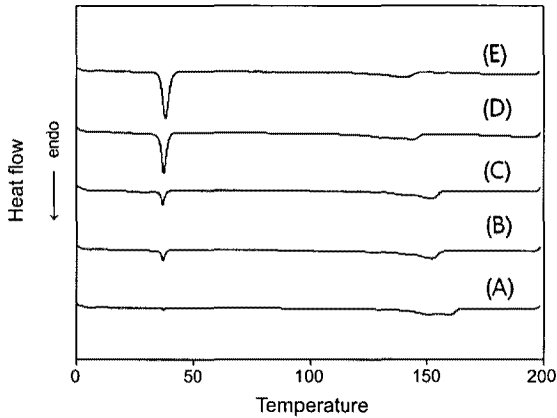


Figure 7. DSC Thermo-diagrams of SSPCM3: (A) n-eicosane 10%; (B) n-eicosane 20%; (C) n-eicosane 30%; (D) n-eicosane 40%; (E) n-eicosane 50%.

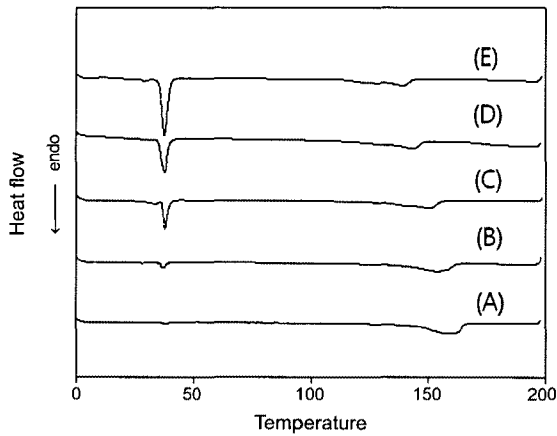


Figure 8. DSC Thermo-diagrams of SSPCM4: (A) n-eicosane 10%; (B) n-eicosane 20%; (C) n-eicosane 30%; (D) n-eicosane 40%; (E) n-eicosane 50%.

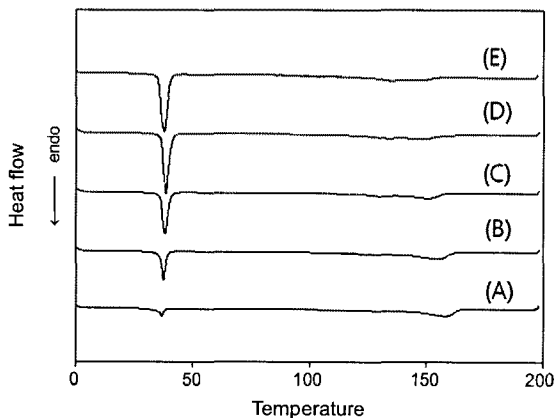


Figure 9. Thermo-diagrams of SSPCM5: (A) n-eicosane 10%; (B) n-eicosane 20%; (C) n-eicosane 30%; (D) n-eicosane 40%; (E) n-eicosane 50%.

XRD Prepared Frozen Gels SSPCM Composites. The incorporation of phase change materials into a binding polymer by

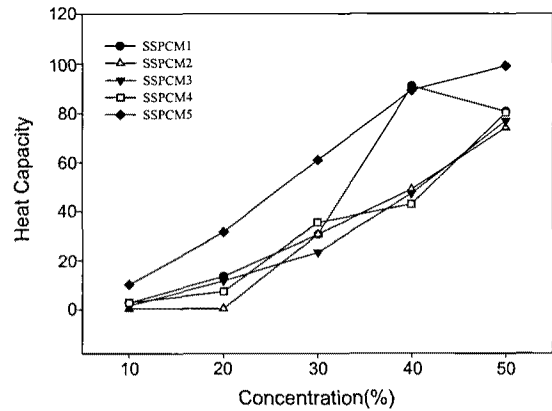


Figure 10. Endothermic reaction of SSPCM1-5. This shows the endothermic amount increased with increasing amount of n-eicosane from 10 to 50 wt%.

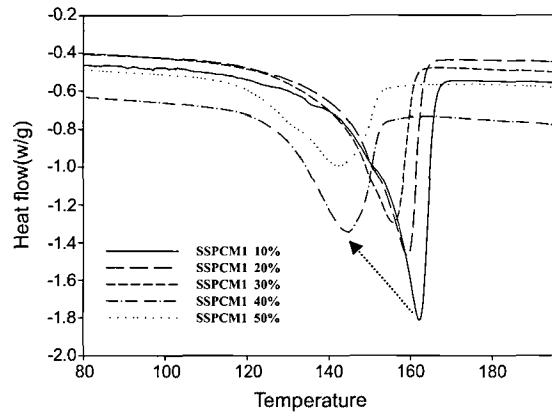


Figure 11. Thermo-diagrams of SSPCM5-10, 20, 30, 40, 50 according to the n-eicosane content.

the melting method was confirmed by the wide-angle X-ray diffraction (Model : D/MAX-2200H, Rigaku Co., Japan) patterns of polypropylenes, phase change materials, and prepared frozen gels. The operation conditions were 15 kV and 10 nA, and natural and synthetic standards were used. The X-ray diffraction (XRD) data was obtained using reflection mode with Ni-filtered Cu K α radiation at 40 kV and 100 mA.

Figure 12 shows the XRD patterns of SSPCM5-30 wt%, n-eicosane and frozen gel obtained with 10~50 wt% n-eicosane in a polypropylene powder with a melting index of 4.8. The n-eicosane and polypropylene X-ray diffraction patterns are characterized by 4-major reflections: (110), (040), (130), (111) at 14, 17, 18.5 and 21.5° 2 θ , respectively. The observed XRD patterns are consistent with those reported by other research groups examining polypropylene powder. The polypropylene (melt index 4.8) line, n-icosane XRD patterns were characterized by major reflections at low 2 θ below 10° and at approximately 23° and 40°. The XRD patterns of n-eicosane are consistent with those reported in the

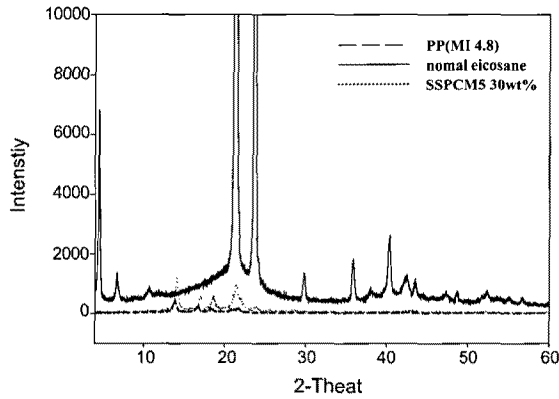


Figure 12. Equatorial scanning wide angle XRD patterns of *n*-eicosane, PP(melt index 4.8) and SSPCM5-30 wt%.

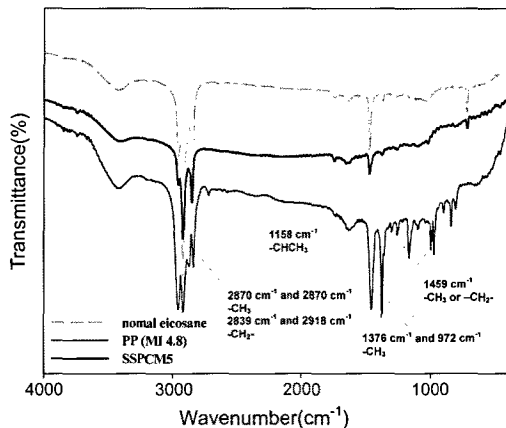


Figure 13. FTIR spectra of SSPCM5.

literature. The XRD patterns of the prepared frozen gel with more than 30 weight % *n*-eicosane incorporated into the polypropylene binder polymer (SSPCM5-30 wt%) were obtained (Figure 12). Some peaks were observed at 21.5° and 23°. These diffraction patterns were characteristic of *n*-eicosane. The 4 characteristic peaks from polypropylene could also be seen. From these results, it was confirmed that the phase change materials had been incorporated successfully into the binder polymer.

FTIR Spectra Prepared Frozen Gels SSPCM Composite. The incorporation of phase change materials into the binding polymer was confirmed by Fourier transform infrared (FTIR, spectrometer Instrument Model : Bruker IFS-66v/s) spectroscopy of polypropylenes, phase change materials, and prepared frozen gels (Figure 13).

Figure 13 shows the FTIR spectra of the polypropylene powder and *n*-eicosane and PP 4.8/*n*-eicosane frozen gel. Both characteristic peaks of polypropylene and *n*-eicosane were observed in the spectrum of the frozen gel. Therefore, the prepared SSPCM5 frozen gel contained *n*-eicosane as a phase change material. *n*-Eicosane is an ordinary hydro-

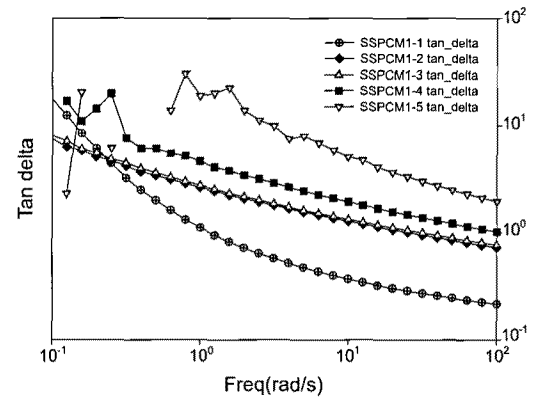


Figure 14. Tan δ properties of SSPCM1-10, 20, 30, 40, 50 wt% (Temp: 220 °C, Frequency sweep).

carbon. The representative infrared transmittance spectra showed multiple peaks at 2900, 1466 and 717 cm^{-1} . The multiple peaks at 2916~2848 cm^{-1} are associated with the aliphatic C-H stretching vibration. The absorbance at 1446 cm^{-1} is associated with the C-H deformation vibration. The transmittance peak at 717 cm^{-1} was assigned to the in-plane rocking of the CH_2 group. The infrared spectrum of polypropylene is indicated as PP(melt index 4.8). The bands at 2870 and 2954 cm^{-1} were assigned to $-\text{CH}_3$, the bands at 2839 and 2918 cm^{-1} were attributed to $-\text{CH}_2-$, and the bands at 972 and 1376 cm^{-1} were due to $-\text{CH}_3$. The band at 1459 cm^{-1} was assigned to either CH_3 or CH_2 , and the band at 1158 cm^{-1} was assigned to $-\text{CHCH}_3$. Hence, the spectrum is a typical polypropylene IR spectrum. The SSPCM5 line in the figure is the infrared spectrum of the obtained SSPCM5 frozen gel. Both characteristic peaks for polypropylene and *n*-eicosane were observed in the frozen gel infrared spectra. These infrared spectra confirm that the prepared SSPCM5 frozen gel contained *n*-eicosane as a phase change material. Therefore, a phase change material had been incorporated successfully into the binder polymer.

Tan Delta and ARES Properties of Frozen Gels PP/PCM Composite. Dynamic measurements were carried out on an advanced rheometric expansion system (ARES) to measure the physical properties. ARES is synonymous with high performance rheological measurements. The storage modulus and loss modulus as well as the tan δ were obtained from the ARES data.

Figure 14 shows the tan δ value of the melts of the obtained frozen gels with different concentrations of phase change material at 220 °C as a function of frequency. Tan δ was obtained as the loss modulus divided by the storage modulus value. The triangle and circles represents the storage modulus and loss modulus from the ARES results, respectively. The frequency dependence was similar regardless of the concentration of phase change material, but the frequency

dependence covers a large frequency range. This result was attributed to an elasticity-dominant response on a short time scale. The physical properties of the prepared frozen gels can be estimated from the $\tan \delta$ value. The melt of a frozen gel shows viscous liquid properties if $\tan \delta > 1$ but near solid properties if $\tan \delta < 1$. The storage modulus value increased sharply with increasing frequency.

Figure 15 shows a temperature sweep of the melt of the frozen gel from polypropylene with a melt index of 17 and n-eicosane using melting method. These results are due to the constant strain during the ARES measurements. In this case, 1.0% was applied. As shown in this figure, the values for each physical property, such as stress, storage modulus,

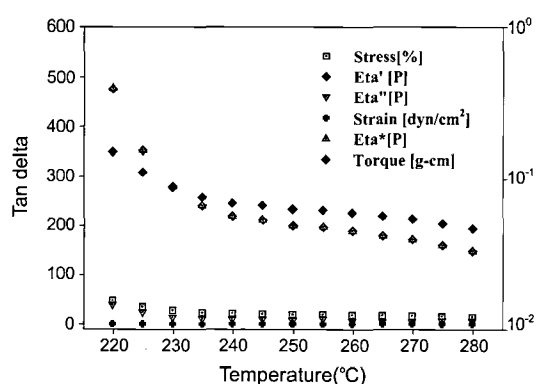


Figure 15. Rheological properties of SSPCM3-30 wt% gel (Temp: 250 °C, Temperature sweep).

and η^* (viscosity), decreased considerably with increasing temperature. However, these values became saturated when the temperature was 250 °C. However, the loss modulus and stress values showed small changes with temperature. Therefore, the spinning temperature is an important parameter. The aim of these experiments was to produce a shape stabilized phase frozen gel. The spinning temperature is important for applying these frozen gels as heat storage materials or other applications. From 250 °C, all physical properties were relatively constant. Therefore, the proper spinning temperature for frozen SSPCM3-30 wt% is 250 °C.

Morphology of SSPCM Composites by Melting Method. The morphology of prepared frozen gels from melting method was examined by scanning electron microscopy (SEM, Model: Hitachi S-4200, Hitachi Co., Japan). Figure 16 shows SEM images of the frozen gel by mixing n-eicosane as a phase change material with polypropylene chips with a melting index of 17 using the melting method. The surface of the polypropylene was quite smooth before treatment. However, after treatment using the melting method, the surface of the prepared frozen gel was quite rough. This was observed in all samples prepared by the melting method. This is evidence of the incorporation of a phase change material into the binder polymer from the melting method. The results show that the melting method is effective way of preparing frozen gels for latent heat storage.

Morphology of PP/PCM Composites by Absorption Method. The

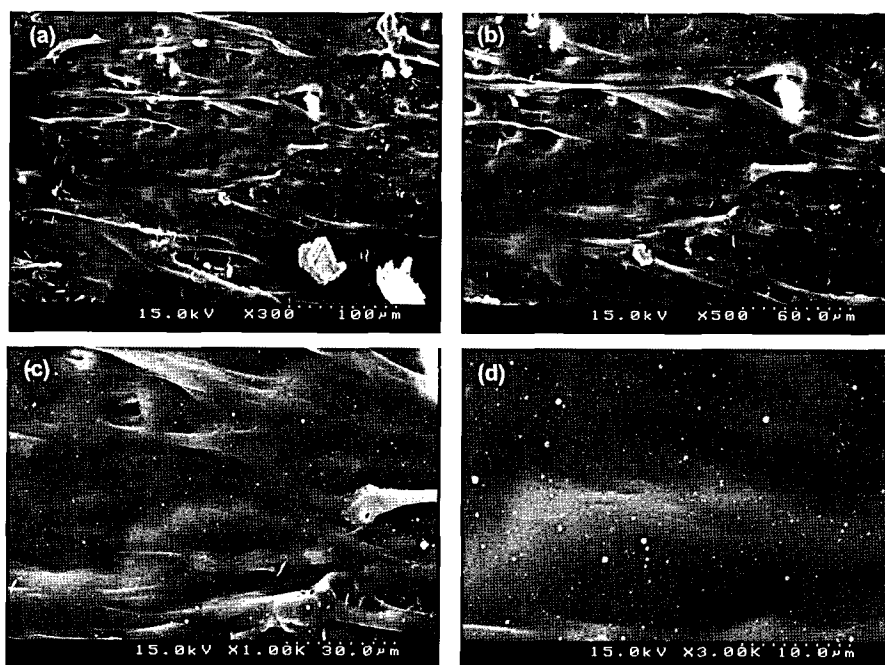


Figure 16. SEM images of cross-section of SSPCM2-30 wt% : (a) SSPCM composite ($\times 300$); (b) SSPCM composite ($\times 500$); (c) SSPCM composite ($\times 1000$); (d) PP/PCM composite ($\times 3000$).

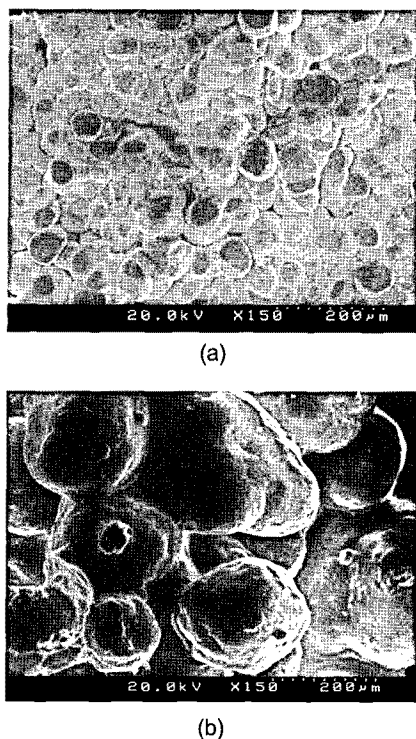


Figure 17. SEM images of surface of SSPCM5: (a) PP (melt index 4.8) powder ($\times 150$); (b) SSPCM5-30 wt% composite ($\times 150$).

morphology of the prepared frozen gels was examined by SEM. Figure 17 shows SEM images of the frozen gel before and after the absorption of *n*-eicosane as a phase change material. The left figure shows an image of the polypropylene powder before treatment. The polypropylene powder has a smooth surface. However, the surface of the prepared frozen gel showed a very rough surface after treatment using the absorption method. This was observed in all samples prepared in this manner. This is evidence of the incorporation of a phase change material into the binder polymer from the absorption method. Therefore, the absorption method is an effective way of preparing frozen gels for latent heat storage.

Conclusions

This study examined the optimum compounding conditions to minimize the deterioration of the physical property and maintain the thermal capacity. Shape stabilized phase change materials were produced from a thermal plastic polymer, PP with various MI, and paraffin (*n*-eicosane), a representative PCM. The thermal, physical and rheological properties were examined under each experimental condition by DSC, FT-

IR spectroscopy, XRD, SEM, and ARES. The aim of this study was to determine the most reasonable manufacturing process and conditions for the SSPCM gel, such as the content and viscosity of *n*-eicosane as well as the compounding method. The composite material containing 20 and 30 wt% *n*-eicosane showed less deterioration of the physical properties and more effective thermal properties than the other samples. With decreasing MI, PP showed an improvement in the thermal properties due to its high viscosity. Both the absorption and melting methods produced strong bonding between *n*-eicosane and PP. However, the absorption method produced a composite with more outstanding heat capacity than that prepared by the melting method. These frozen gels can be used as latent heat storage materials in several applications, such as packing materials for semi-conductors and transistors, etc.

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