

Solution Miscibility and Phase-Change Behavior of a Polyethylene Glycol–Diacetate Cellulose Composite

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ABSTRACT: Polyethylene glycol (PEG) and diacetate cellulose (CDA) exhibit good miscibility in acetone solution. The miscibility is related to the molecular weight of PEG, which increases as miscibility decreases. The phase-change behavior of PEG in composite with CDA prepared from the miscible solution was found to be completely different from that of pure PEG. When the PEG fraction in the composites was less than 85%, PEG within the composite did not melt into liquid; even when the temperature was 40°C higher than the melting point of PEG, the PEG–CDA composite

exhibited solid–solid phase-change behavior. Thermal analysis indicated that the PEG–CDA composite had greater enthalpy and exhibited good thermal stability. The PEG–CDA composite that exhibited solid–solid phase-change behavior can be used as a new kind of phase-change material for thermal energy storage and temperature control. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 652–658, 2003

Key words: blending; miscibility; polyethylene glycol; phase-change behavior

INTRODUCTION

The research and development of phase-change thermal storage for solar applications have proceeded rapidly over the last decade.^{1,2} Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$, has been considered a promising phase-change material for thermal energy storage and temperature control because of its relatively large heat of fusion, congruent melting behavior, noncorrosiveness, and wide melting point range.³ However, only low-molecular-weight PEG has been used as a phase-change heat storage medium. This type of PEG belongs to the category of classical solid–solid phase-change substances, and so it cannot be stored in conventional storage tanks but must be packaged in special sealed containers to prevent its leakage in the melting state. Thereby, the high cost of properly packaging PEG restricts its anticipated broad application in thermal energy storage in industrial fields. Chemically crosslinking PEG with high-density polyethylene or encapsulating PEG to make a form-stable particle could retard the flowability of phase-change material in its molten state.^{4,5} This would simultaneously re-

duce its heat of fusion and thermal conductivity, with a consequent decrease in the thermal storage and temperature control capabilities of the phase-change material.

In our previous article,^{6,7} we reported a special phase-change behavior of PEG when in a blend with cellulose (CELL). When the CELL fraction was larger than 5%, PEG within the blend did not melt into a liquid state, even at a temperature greater than 50°C above its melting point. Instead of fusion, the blend exhibited crystalline–amorphous solid–solid phase behavior, which completely overcame the flowability of PEG in its melting state. The PEG–CELL composite with this special phase-change behavior had enthalpy as large as 109 J/g. It can be used as a solid–solid phase-change material for thermal energy storage and temperature control.⁸ However, the complicated procedure and poisonous solutions system of preparing the PEG–CELL composite restricts its industrial application. The structural study of PEG–CELL showed that intermolecular interaction based on hydrogen bonds between PEG and CELL and the semirigidity of CELL played important roles in the special solid–solid phase-change behavior of PEG–CELL.⁷ To further investigate the essence of this special phase-change behavior of PEG and to prepare new PEG composite with solid–solid phase-change behavior and other excellent thermal properties, a series of experiments blending PEG with CDA, chitin, chitosan, ethyl cellulose, and starch were carried out in our laboratory. The results show that PEG–chitosan and PEG–CDA exhibit special solid–solid phase-change behavior, and

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hydrogen bonds between PEG, chitosan, and CDA have a great impact on the thermodynamic properties of PEG–chitosan and PEG–CDA composites. This article reports on our investigation of the miscibility of mixed solution and the phase-change behavior of PEG–CDA composite. An article about the thermal properties and structural characteristics of PEG–CDA composite is in preparation.

EXPERIMENTAL

Materials

Diacetate cellulose (CDA), composed 55.4% of acetyl with an average molecular weight (\bar{M}_w) of 98,300 was purchased from Cellanese Company (USA). Polyethylene glycol (PEG) with \bar{M}_w of 400, 1000, 2000, 4000, 6000, 10,000, and 20,000 and reagent-grade acetone were purchased from Guangzhou Chemical Agent Company (Guangzhou, China).

Preparation of CDA–PEG sample

Acetone and CDA were treated in advance. CDA was washed successively in distilled water and alcohol and then dried under reduced pressure at 90°C. Acetone was redistilled after having been dehydrated by CaCl_2 for 72 h. CDA and PEG solutions (10 wt %) were prepared by dissolving CDA and PEG in acetone with vigorous continuous stirring for 24 h. The separately prepared PEG and CDA solutions were mixed at room temperature in the desired ratios so that the relative composition of the two polymers in mixed solution ranged from 95:5 to 5:95 (throughout this article the first number in content ratios refers to PEG). After stirring vigorously for 12 h, the mixed solutions were held for 12 h while observing the miscibility. The miscibility was determined by the transparency of solution. If the mixed solution was optically clear to the naked eye, without the precipitation of CDA or the crystallization of PEG, it was regarded as miscible; otherwise, it was deemed immiscible. The solid composite was obtained by casting miscibly mixed solution into a glass pan forming a thin layer. The evaporation of the solvent was first performed in atmosphere at room temperature for 12 h and then under a reduced pressure at 40°C for 24 h.

Measurements

Measurement of the phase-transition temperature and enthalpy of the solid composite was performed on a sample of about 10 mg with a Perkin-Elmer differential scanning calorimeter (DSC-2C) calibrated with an indium standard, with heating at a rate of 5°C/min in the range from 0°C to 100°C. The phase-change behavior of the composite was detected by a Shimadzu-1

TABLE I
Miscibility State of Mixed Solution of PEG and CDA

Mp/Mc	Molecular weight						
	400	1000	2000	4000	6000	10000	20000
95/05	T	T	C	C	C	C	C
90/10	T	T	T	C	C	C	C
85/15	T	T	T	T	T	T	T
80/20	T	T	T	T	T	T	T
70/30	T	T	T	T	T	T	T
60/40	T	T	T	T	T	T	T
50/50	T	T	T	T	T	T	T
40/60	T	T	T	T	T	T	T
30/70	T	T	T	T	T	T	T
20/80	T	T	T	T	T	T	T
10/90	T	T	T	T	T	T	T
05/95	T	T	T	T	T	T	T

T = transparent; C = crystallization of PEG; Mp/Mc, blend ratio of PEG and CDA; 10 wt % PEG, 10 wt % CDA.

thermomechanical analyzer (TMA). A small weight of 10 g was put on the upper surface of the sample, and the displacement of the weight was recorded to an accuracy of 0.001 mm. The sample was heated at a rate of 5°C/min from 15°C to 100°C, more than 40°C than the melting point of PEG. If the solid–liquid transition occurs, it will be detected by a rapid shift of the displacement of this weight. The phase-change behavior of sample was also directly observed by visual examination. The sample observed was put on a stainless-steel plate and heated slowly with an infrared lamp. Any change in the state of the sample was clearly noticeable. The thermal stability of the PEG–CDA composite was investigated with a Shimadzu-DT-30 combined thermogravimetric-differential thermal analyzer.

RESULTS AND DISCUSSION

Miscibility of PEG and CDA in blending solution

The miscibility of the blending solution has a great impact on the corresponding properties of the obtained solid composite and affects the application of the composite as a material.⁹ In our previous article we reported that the miscibility of a PEG and CELL blending solution affected the thermodynamic properties of solid PEG–CELL composite obtained.¹⁰ So it is imperative to investigate the miscibility of the PEG–CDA blending solution. Solutions of 10 wt % PEG of various molecular weights were mixed with a 10 wt % CDA solution at different ratios from 95:5 to 5:95. Having been vigorously stirred for 12 h, the blending solutions were held for 12 h for the observation of miscibility. The observation results were collected and are shown in Table I. It can be seen that CDA and PEG exhibited high miscibility in the acetone solution. Miscibility was related to the molecular weight (MW) of the PEG. At a low MW, such as 400 or 1000, all mixed

solutions at the whole blending ratios ranging from 95:5 to 5:95 were clear and transparent; PEG and CDA coexisted stably in the mixed solution, neither precipitation of CDA nor crystallization of PEG took place, and PEG and CDA were miscible. With an increase in the molecular weight of the PEG, the stability of the mixed solution decreased, and the PEG crystallized easily from mixed solutions at the high PEG composition ratio. For the PEG whose MW was 2000, only when the blend ratio of PEG–CDA was lower than 95:5 was the PEG compatible with the CDA. PEG with molecular weights of 4000, 6000, 10,000, and 20,000 coexisted with the CDA if the blend ratios were less than 90:10. These results show that the MW of PEG affects the miscibility of the blending solution. Because there are many oxygen atoms and OH groups in the PEG and CDA molecular chains, respectively, so it is easy for PEG and CDA to form intermolecular bonds, making PEG and CDA exhibit high miscibility in blending solutions. However, it has been reported that intermolecular hydrogen bonds that are too strong allow polymers to form hydrogen-bonding complexes and to decrease the miscibility of blending solutions.¹¹ For the PEG and CDA blending solution, it is also possible that the hydrogen bonds also make PEG and CDA form hydrogen-bonding complexes that easily aggregate from the blending solution and decrease the miscibility or stability of the blending solutions. With an increase in the MW of PEG, the probability of forming hydrogen-bonding complexes between CDA and PEG increased. A detailed investigation of the intermolecular interaction is being carried out and will be reported in a future article.

Phase-change behavior of PEG in blends with CDA

First, PEG with the same molecular weight ($M_r = 4000$) as that used in the PEG–CELL blending sys-

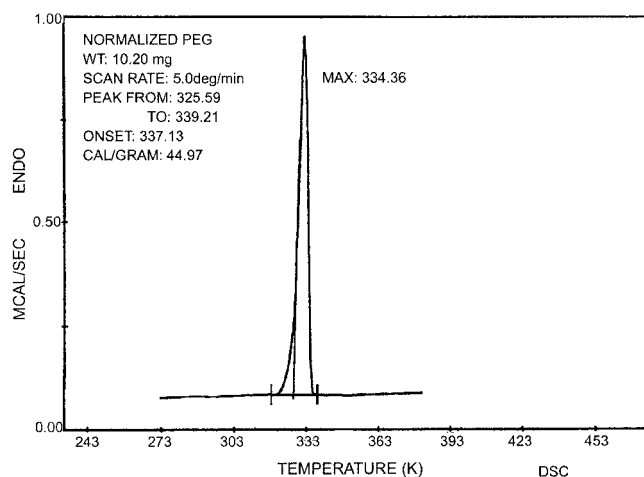


Figure 1 DSC curve (heating cycle) of PEG 4000.

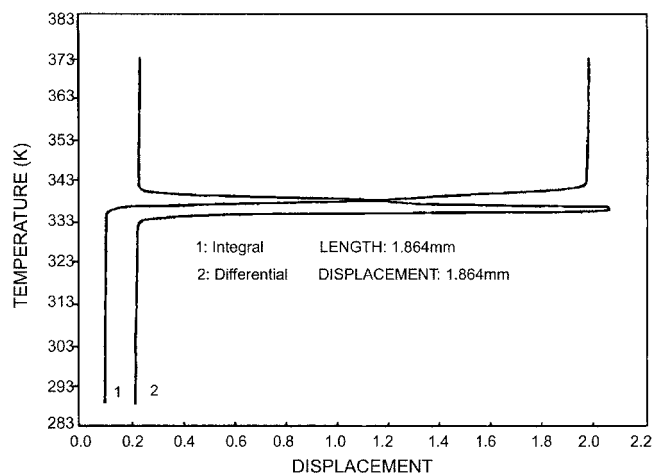


Figure 2 Thermomechanical analysis of PEG with MW 4000: (a) differential displacement curve; (b) integral displacement curve.

tem⁷ was selected as the sample blending with CDA for the investigation of its phase-change behavior within the composite. Figures 1 and 2 are DSC and TMA measurements, respectively, of the sample PEG with a MW of 4000. Figure 1 shows a large heat absorption with an enthalpy of 44.97 cal/g (188 J/g) at about 58°C in the heating cycle, indicating that a phase transition has taken place. A sharp peak of the differential and the rapid shift of the integral curve of TMA (Fig. 2) demonstrate that this transition should be a solid–liquid phase change. An additional direct heating experiment, in which the white crystal solid PEG melting into a liquid with low viscosity was observed, indicated that this solid–liquid transition is the fusion of PEG; the transition enthalpy is the fusion heat of PEG.

However, in contrast with pure PEG, PEG in composite with CDA did not exhibit solid–liquid phase-change behavior, even at a temperature 40°C higher than the fusion point of PEG. Figures 3 and 4 show the results of, respectively, the DSC and TMA investigations of composite C_1 with a blending ratio of 85:15 (PEG–CDA). From the DSC measurement (Fig. 3), it is indicated that a phase change with an enthalpy of 33 cal/g (155 J/g) happens at 52°C. The TMA measurement (Fig. 4) shows that at a temperature rise to 100°C, 40°C higher than the melting point of PEG, no rapid shift occurs in the integral curve, but little shrinkage of volume happens, indicating that C_1 remains in the solid state during the phase transition and exhibits solid–solid phase-change behavior. The little shift (only 3% of the full thickness of the sample) of the integral possibly can be attributed to the volume shrinkage of the sample caused by the plasticity of the composite. This special solid–solid phase-change behavior of C_1 was further confirmed by visual observation. Heating the sample C_1 slowly directly to 100°C

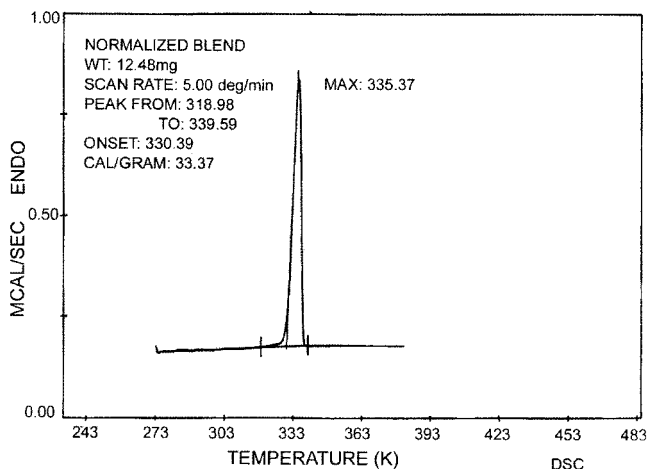


Figure 3 DSC curve (heating cycle) of CDA-PEG ($M_r = 4000$) composite C_1 with a blend ratio of 85:15 (PEG-CDA).

on the stainless-steel plate, it was still observable in the solid state. No liquid leaked from the sample, even when the sample was pressed with a glass rod in the high-temperature state (higher than the phase transition point of sample C_1). We also observed that C_1 exhibited plasticity during the direct heating experiment, which corresponded to the volume shrinkage of the sample mentioned above.

These results show that the phase-change behavior of PEG was completely changed through mixing with CDA; PEG within the composite with CDA exhibited solid-solid phase-change behavior.

Phase-change behavior and composite content

PEG is the effective phase-change substance in PEG-polymer phase-change composites, and the capacity for heat storage and temperature control of PEG-poly-

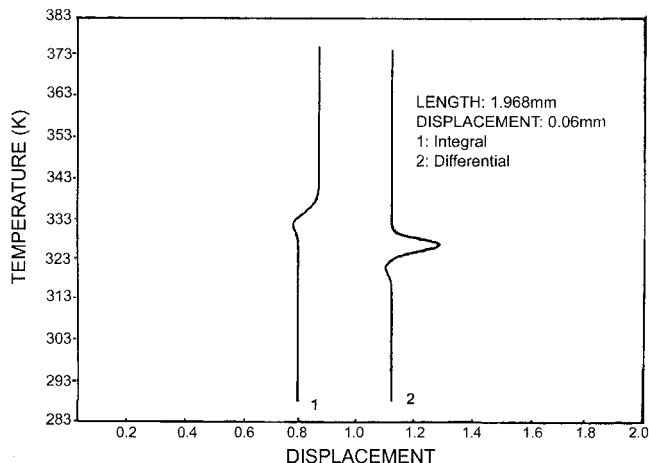


Figure 4 Thermomechanical analysis of CDA-PEG ($M_r = 4000$) composite C_1 with a blend ratio of 85:15 (PEG-CDA).

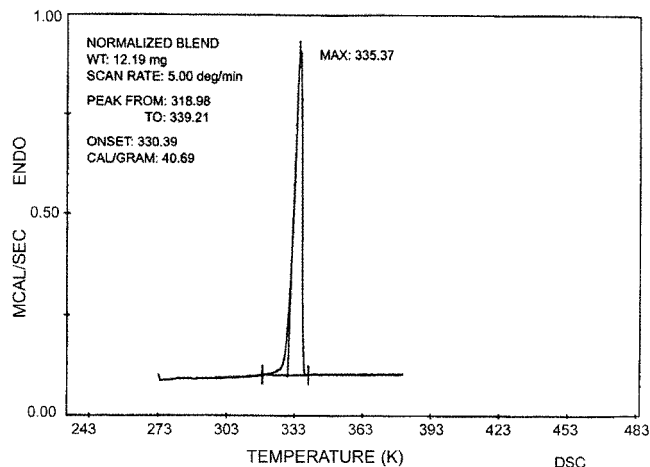


Figure 5 DSC curve (heating cycle) of CDA-PEG ($M_r = 4000$) composite C_2 with a blend ratio of 95:5 (PEG-CDA).

mer composites is decided by the PEG content of the composite.¹² So an efficient way to prepare PEG-CDA composite with the largest possible enthalpy is to increase the composite's PEG content as much as possible. Meanwhile, the composite should hold solid-solid phase-change behavior. Therefore, it is necessary to investigate the phase-change behavior of the composite and its PEG content. C_2 is a sample of a PEG-CDA composite obtained from blending PEG ($M_r = 4000$) with CDA at a blending ratio of 95:5 (PEG-CDA). The DSC measurement of C_2 , shown in Figure 5, indicates that, as with C_1 , a phase transition absorbing a large quantity of thermal energy (167 J/g) takes place in the heating cycle. Nevertheless, the TMA measurement result for C_2 (Fig. 6) is completely different from that of C_1 . A sharp peak of the differential curve and a rapid shift of the integral curve of TMA indicate that C_2 does not exhibit a solid-solid phase-change behavior like that of C_1 , but a solid-liquid one like that of

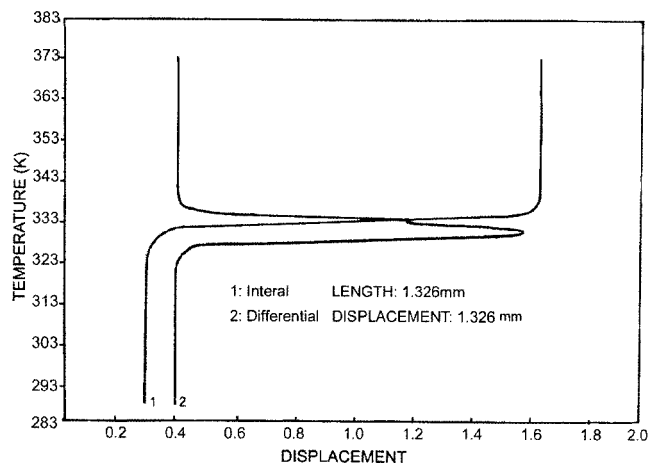


Figure 6 Thermomechanical analysis of CDA-PEG ($M_r = 4000$) composite C_2 with a blend ratio of 85:15 (PEG-CDA).

TABLE II
Phase Change Properties of M_w 4000 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/05	167	S-L
90/10	151	S-L
85/15	139	S-S
80/20	132	S-S
70/30	100	S-S
50/50	40	S-S

S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

PEG. The pulverized sample of C_2 was heated directly by the infrared lamp; as temperature increased to the melting point of PEG, the pulverized sample first shrank and then melted into a transparent liquid, which exhibited higher viscosity and lower flowability than those of the melting pure PEG liquid. For further investigation of the relationship between the phase-change behavior and the components of CDA-PEG composites, several other samples with different blending ratios were measured by these same means, and the results were shown in Table II. It is clear from Table II that the phase-change behavior of PEG-CDA composite was found to be affected by its composition. Only if the PEG fraction in the composite was less than 85% did the composite exhibit solid-solid phase-change behavior.

Phase-change behavior and molecular weight of PEG

As thermal energy storage and temperature control media, phase-change material should have a wide temperature range to meet application requirements.¹³ For PEG composite various phase-transition temperatures can be realized by adjusting the molecular weight of PEG within the composite.¹² To obtain PEG-CDA composites with different phase-transition temperatures, in addition to that of the PEG sample of MW 4000, several others PEG samples, with molecular weights of 400, 1000, 6000, 10,000, and 20,000, were selected for mixing with CDA at different blending

TABLE III
Phase Change Properties of M_w 400 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/05	83	S-L
90/10	72	S-L
85/15	65	S-S
70/30	38	S-S
50/50	12	S-S

S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

TABLE IV
Phase Change Properties of M_w 1000 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/5	109	S-L
90/10	101	S-L
85/15	92	S-S
70/30	51	S-S
50/50	33	S-S

S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

ratios to investigate their phase-change behaviors. It can be seen from the results, shown in Tables III-VII, that the PEG samples of all these varied molecular weights were able to form a composite exhibiting solid-solid phase-change behavior with CDA. Nevertheless, a direct heating experiment indicated that a composite with different molecular weights took on a different morphology despite the similarity of the phase-change behavior. If PEG was low molecular weight, for instance, 400 or 1000, the composites exhibited elasticity, but, as the MW of PEG increased to 4000, 6000, 10,000, and 20,000, respectively, the composites exhibited plasticity when the temperature was higher than the melting point of the corresponding PEG.

The above investigations indicate that the PEG-CDA composite exhibits a solid-solid phase-change behavior similar to that of the PEG-CELL blend.⁷ The obvious difference between the two composites is that, to maintain the composites with solid-solid phase-change behavior, the largest PEG fraction in the PEG-CDA composite was less than that of the PEG-CELL composite, with the former 85% and the latter 95%. For the PEG-CELL composite it was suggested that the strong intermolecular interaction based on the hydrogen bonds between the end OH groups of PEG and the OH groups of the CELL-fixed PEG molecule to the semirigid CELL chain, making PEG lose transitional motion freedom and exhibit solid-solid phase-change behavior in the composite.⁷ Intermolecular hydrogen bonding also plays an important role in affecting the miscibility and morphology of the solid PEG-CELL

TABLE V
Phase Change Properties of M_w 6000 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/5	161	S-L
90/10	153	S-L
85/15	142	S-S
70/30	104	S-S
50/50	63	S-S

*S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

TABLE VI
Phase Change Properties of M_w 10,000 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/5	159	S-L
90/10	151	S-L
85/15	138	S-S
70/30	105	S-S
50/50	66	S-S

S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

composite.¹⁴ CDA is a derivative of CELL, having the same chemical structure as CELL, so in theory a hydrogen bond also can be formed between CDA and PEG, which is a possible reason why PEG-CDA exhibits a solid-solid phase-change behavior similar to that of the PEG-CELL composite. But, in comparison with CELL, which has three OH groups in each glucose unit, CDA has only one OH group and two COCH₃ groups, so in the CDA-PEG composites the intermolecular interaction should be weaker than that of the PEG-CELL composites. The intermolecular interaction difference between PEG-CELL and PEG-CDA shows that the largest PEG fraction within each composite had to differ to maintain the solid-solid phase-change behavior.

Thermal stability of PEG-CDA composite

Thermal stability is an important factor of concern in phase-change material research and applications for its impact on the capacity of thermal storage.¹² A Shimadzu-DT-30 combined thermogravimetric-differential thermal analyzer (TG-DTA) was used to measure the stability of PEG-CDA composites. The measurement was performed in the atmosphere; Figure 7 shows an example. Composite C₁ was heated at a rate of 5°C/min up to 100°C. A solid-solid phase-change of the sample, which had been indicated by the DSC and TMA investigations above, was also observed in the DTA curve. However, no weight loss was observed in the TG-DTA recorder, even at temperatures up to 100°C, almost 50°C above the melting point of

TABLE VII
Phase change properties of M_w 20,000 PEG/CDA

Blend ratio Mp/Mc	Enthalpy (J/g)	Phase change behavior
95/5	154	S-L
90/10	147	S-L
85/15	136	S-S
70/30	103	S-S
50/50	67	S-S

S-S, solid-solid; S-L, solid-liquid; Mp/Mc, blend ratio of PEG and CDA.

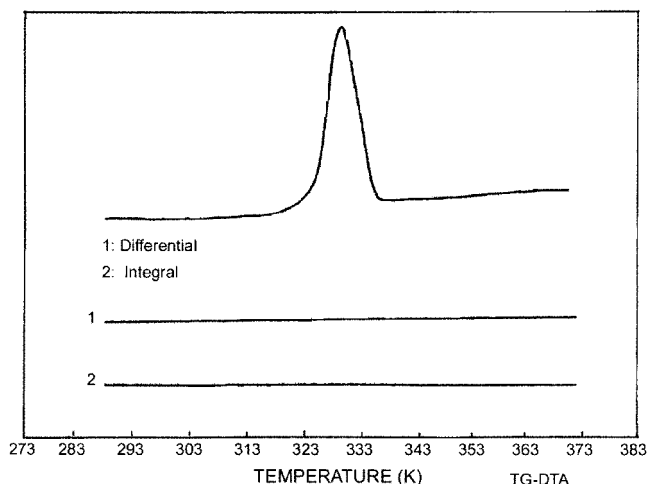


Figure 7 Combined thermogravimetric-differential thermal analysis of CDA-PEG ($M_r = 4000$) composite C₁ with a blend ratio of 85:15 (PEG-CDA).

PEG. This means neither volatilization nor decomposition had occurred. This provides an excellent advantage when used for energy storage, compared with the normal solid-state phase-change materials containing polyols, paraffin, or fatty acids, whose practical use has been limited by their thermal decomposition, degradation, evaporation and sublimation.¹⁵ For investigating the influence of the heating cycle on the phase-change behavior of the composite, the sample was repeatedly heated from room temperature to 160°C and then cooled to room temperature, and then its phase-change behavior and other thermal properties were measured. Table VIII shows the thermal properties of C₁ after undergoing the heating-cooling cycle 200 times. Being subjected to this heating and cooling cycle 200 times did not change the phase-change behavior, enthalpy, and phase-change temperature of sample C₁, further confirming the thermal stability of the composite.

CONCLUSION

PEG and CDA exhibited high miscibility in acetone solution, which is related to the MW of PEG; with an increase in MW, miscibility decreased. Through mixing with CDA in acetone, the phase-change behavior

TABLE VIII
Properties of Composite C1 with 200 Heating-Cooling Thermal Cycles

	ΔH_{TR} (J/g)	$T_{TR}/^{\circ}\text{C}$	Phase change behavior
Uncycled	139	56	S-S
Cycled	138	56	S-S

ΔH_{TR} , enthalpy; T_{TR} , phase change temperature; S-S, solid-solid.

of PEG in the solid composite obtained could be completely changed from a solid–liquid phase transition to a solid–solid one. The PEG fraction within the composite affected the phase-change behavior of composite; only when it was less than 85% did the composite exhibit solid–solid phase-change behavior; otherwise, it exhibited a solid–liquid one. The PEG–CDA composite with this special phase-change behavior showed good thermal stability and could be used as a new sort of phase-change material for thermal energy storage and temperature control.

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