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Study on transition characteristics of PEG/CDA solid–solid phase change materials

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Abstract

New kinds of solid–solid phase change materials (PCMs) with netted structure have been prepared. In these new materials, the rigid polymer cellulose diacetate (CDA) serves as skeleton, and the flexible polymer polyethylene glycol (PEG) serves as functional branch chain. The transition mechanism of these functional polymers is the transfer between the amorphous and crystal states of the PEG. During the transition, PEG gives or takes in latent heat, and at the same time, the whole composite always remains in the solid state. The series experiments show that the PCMs' latent heats, phase transition temperatures and mechanical strengths depend on the molecular weights and weight percentages of PEG. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Solid–solid phase change material; Polyethylene glycol; Cellulose diacetate

1. Introduction

Phase change materials (PCMs) can be used for energy storage and temperature control [1–3]. Recently, as energy crisis is becoming more and more serious, PCMs are increasingly receiving more and more attention. They can be applied conveniently in many fields such as solar energy utilization [4], waste heat recovery, intelligent air-conditioned buildings [5], temperature-control greenhouses, electric appliances with thermostatic regulator, energy-storage kitchen utensil, insulation clothing [6] and so on [7]. And new fields of application are expanding rapidly nowadays.

Most traditional PCMs store or deliver energy by means of solid–liquid phase transitions. But the solid–solid PCMs (SSPCMs) carry on this course by solid–solid phase transitions. During the solid–solid phase transitions, there is no liquid or gas generated, so accordingly no recipient is needed to seal them in. Furthermore these kinds of PCMs can be processed into arbitrary shapes directly. Therefore SSPCMs become very fashionable for their unique solid–solid phase change properties [7].

Some inorganic salts and polyhydric alcohol are two main kinds of SSPCMs. But there exist some deadly defects, respectively, in these kinds of materials. Firstly, polyhydric alcohol can sublimate easily, so in order to use them, the appropriate receptacle must be provided to seal them in [8,9], which results in the high cost and few applications. Secondly, although some inorganic salts, layer perovskite, Li_2SO_4, KHF_2, etc. are SSPCMs, their latent heats are too small to satisfy our general demands, so they are seldom used practically.

Moreover, some polymeric SSPCMs have been synthesized with chemical methods. In these polymer materials, some polymer components serve as solid frameworks, and other polymers serve as the working substances that are fixed on the frameworks by chemical bonding. The transition mechanism of these functional polymers is the transfer between the amorphous and crystal states of the working substances. During the transition, the working substances give or take in latent heat, and at the same time, the whole system always remains in the solid state. These new SSPCMs are very hopeful for future use [10–13].

Another kind of polymer PCM is worthy to be mentioned here. They are prepared by physical methods (blending, adsorbing, soaking, etc.), that are generally called form-stable PCMs or shape-stabilized PCMs [14,15]. The transition mechanism of these materials is the solid–liquid phase change of the working substances.

In our laboratory, both chemical grafting methods and physical blending methods have been used and some new functional cellulosic materials with phase change properties were firstly prepared [16,17]. The contrast study results for

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the two types of materials reveal that the composites prepared by chemical grafting methods are SSPCMs, but those prepared by physical blending methods are solid–liquid PCMs [18].

In this article, we use polyethylene glycol (PEG), a typical solid–liquid PCM, to graft onto the skeleton that was made by cellulose diacetate (CDA). They have typical solid–solid phase transition property, quite good energy storage effect and have better thermal stability [19]. We will use differential scanning calorimetry (DSC) to study the relationships between the thermal properties of the composite materials and the weight percentage or molecular weight of PEG. This will supply some theoretical foundations for the improvement and the application of these materials.

2. Experimental

2.1. Material preparation

PEG, a white crystalline solid, and chemically pure reagent with average molecular weight from 2000 to 20,000, was imported from Japan and was subpackaged by Guangzhou Wholesale Department of Chemical Reagent and Glass Apparatus. If the molecular weight of PEG is less than 2000, the latent heats of obtained PCMs are too small to satisfy our general demands, so they cannot be used practically. If the molecular weight of PEG is larger than 20,000, the latent heats of obtained PCMs become small and their mechanical strengths become very weak. For the same reason, they are also not suitable for practical usage. During the appropriate range of the molecular weight of PEG from 2000 to 20,000, only the specimens with molecular weight 2000, 4000, 6000, 10,000 and 20,000 can be purchased, so the experimental data in this paper is not many.

CDA, a white loose granules, was produced by Qunli Plastomer Factory, and was subpackaged by Shanghai Purchase and Sale Branch of Chemical Reagent of china.

Toluene-2, 4-diisocyanate (TDI-80), a chemically pure reagent, was imported from Mitsui Chemicals, Inc., Japan.

Acetone, an analytically pure reagent, was produced by Chemical Reagent Factory of Guangzhou.

Firstly, we reacted TDI, a cross-linker, with the hydroxyl end groups of the PEG in order to modify PEG chemically. Thus, the hydroxyl end groups were changed into isocyanic acid functional groups. Then, we grafted the PEG onto the side hydroxyl groups of the CDA chain to form a comb-like or cross-linked structure [17,18]. Thus a side-chain PCM was prepared. The preparation course is as follows:

PEG was desiccated with a silica-gel drier and CDA was dried in an oven at 383 K for at least 4 h. The solvent acetone was purified by adding sufficient solid $KMnO_4$ such that the red color of the $KMnO_4$ did not fade in 4 h. It was then desiccated with anhydrous calcium sulfate or anhydrous magnesium sulfate for 10 h and then distilled.

The dried PEG and CDA were dissolved individually in the purified acetone in the ratio of 1/3 and 1/10 by weight, respectively. Next, TDI of certain stoichiometric proportions was added to the PEG solution with a microcontent catalyst, di-*n*-butyltin dilaurate. The mass of TDI was that which would keep the ratio of the –NCO groups in TDI 1.1 times that of the –OH groups in the PEG and CDA. The TDI/PEG mixture was firstly pre-reacted partially for 30 min under the conditions of reflux. Then the mixture was added to the CDA solution. The whole mixture was placed in an oven at 313 K for 4 h so that the reactants would react together completely. After the reaction, the mixture turned into gel. Finally, the acetone was volatilized, so the sample was desiccated completely and became a hard solid.

2.2. Performance analysis

DSC: Transition temperatures and the enthalpies of these new materials were obtained by means of a DSC-2C made by Perkin–Elmer Corporation, USA. The transition temperature and the latent heat were calibrated using high-pure indium (purity: 99.999%) as a standard. The heating rate was 5 K/min with the temperature range from 273 to 373 K. The material was about 10 mg and was protected by high purity nitrogen with a discharge rate of 40 ml/min. Because the measurement on energy storage characteristics of the PCMs was contrasted at the same condition, the results of their transition temperatures and the enthalpies were comparable.

In the DSC experiments, at first, with the heating rate 40 K/min, the sample was heated from room temperature to 373 K and kept for 10 min at 373 K, thus the thermal history of the sample can be eliminated. After the elimination of sample's thermal history, the sample was cooled from 373 to 273 K at the cooling rate 40 K/min and kept at 273 K for 10 min, then the sample was heated from 273 to 373 K at the heating rate 5 K/min. In this final heating process, the transition temperature and the enthalpy of the sample was measured.

3. Results and discussion

3.1. Relationships between the energy storage properties and the weight percentage of PEG

The relational curves between the enthalpies and the weight percentage of PEG were obtained, as shown in Fig. 1. The curves (a)–(d) in Fig. 1 show the relationship curves of different molecular weight of PEG, respectively. From Fig. 1, it can be found that the regular change is basically the same in spite of the sample prepared with the PEG of different molecular weight. The enthalpy decreased as the diminution of the weight percentage of PEG and the enthalpy change into zero after the weight percentage of PEG drop to a certain value.

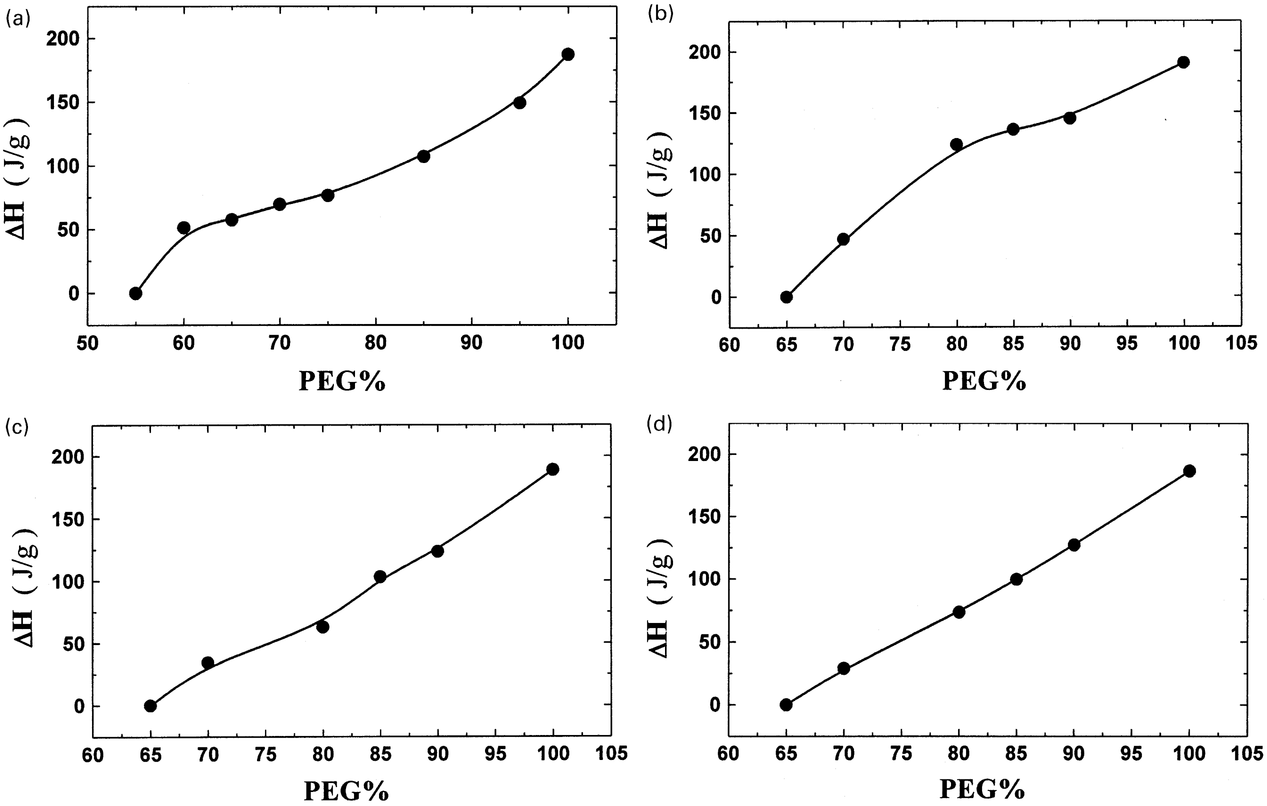

Fig. 1. Relational curves between the enthalpy and the weight percentage of PEG.

PEG is a linear polymer chain made up of (CH_2–CH_2–$O)_n$ and has hydroxyl groups on two ends. It can easily crystallize and has quite large enthalpy because of its simple structure. The transition temperature of PEG is in the range of room temperature. CDA is a stable material with good mechanical strength. Furthermore, on its long chain, CDA has many side hydroxyl groups, which is active for the grafting.

In these PCMs modified by chemical methods, PEG is regarded as the functional group for energy storage, while CDA is regarded as skeleton for structure support which can restrict the free movement of PEG and ensure the PEG loses the macro-fluidity even though PEG is in the amorphous state. Furthermore, because PEG is linked onto CDA by chemical bond, the strength of the bonds is strong enough to ensure no PEG detached even at or above the melting temperature of PEG. Therefore these kinds of materials are real SSPCMs.

The reasons why the addition of CDA causes the enthalpy decline are many. Firstly, the addition of CDA can lead to the weight percentage of PEG fall down as the result of which the enthalpy declines. But it is only one of the causes, from the deep analysis we could find that CDA is quite stable in the phase transition of PEG and contribute nothing to the enthalpy. Thus CDA is the impurity for PEG and will affect the perfection of the crystallization course. At the same time the end hydroxyl group of PEG has been grafted on the CDA by the chemical reacting, so the segments nearby were confined and cannot arrange freely to form the crystalline. Accordingly, the number of the segments that can crystallize reduced, which cause the decline of the enthalpy too.

The movement of the whole PEG chain was limited because of the fixation of the PEG end groups. The crystal aggregation of the whole chain was impeded as the result of steric effect. The influence on the crystallization becomes bigger with the decrease of the weight percentage of PEG. Therefore if the weight percentage of PEG falls down to certain degree, it cannot aggregate to form crystals regions. Thus, in this situation the enthalpy of the composite is zero.

At the same time we got the relational curves between the transition temperatures and the weight percentage of PEG, as shown in Fig. 2. In Fig. 2, T_{onset} is the onset temperature which corresponds to the point of intersection of the tangent (drawn at the point of maximum slope of the leading edge of the peak of DSC curve, and the extrapolated baseline. Good agreement has been reported between literature and experimental melting point temperatures, the latter being determined by the extrapolated onset technique [20]. In Fig. 2, $T_{\max}$ is the temperature which correspond to the peak point of DSC curve. From the Fig. 2, we could find that the changes of transition temperatures have the similar rules as the enthalpies. The transition temperatures fall down as

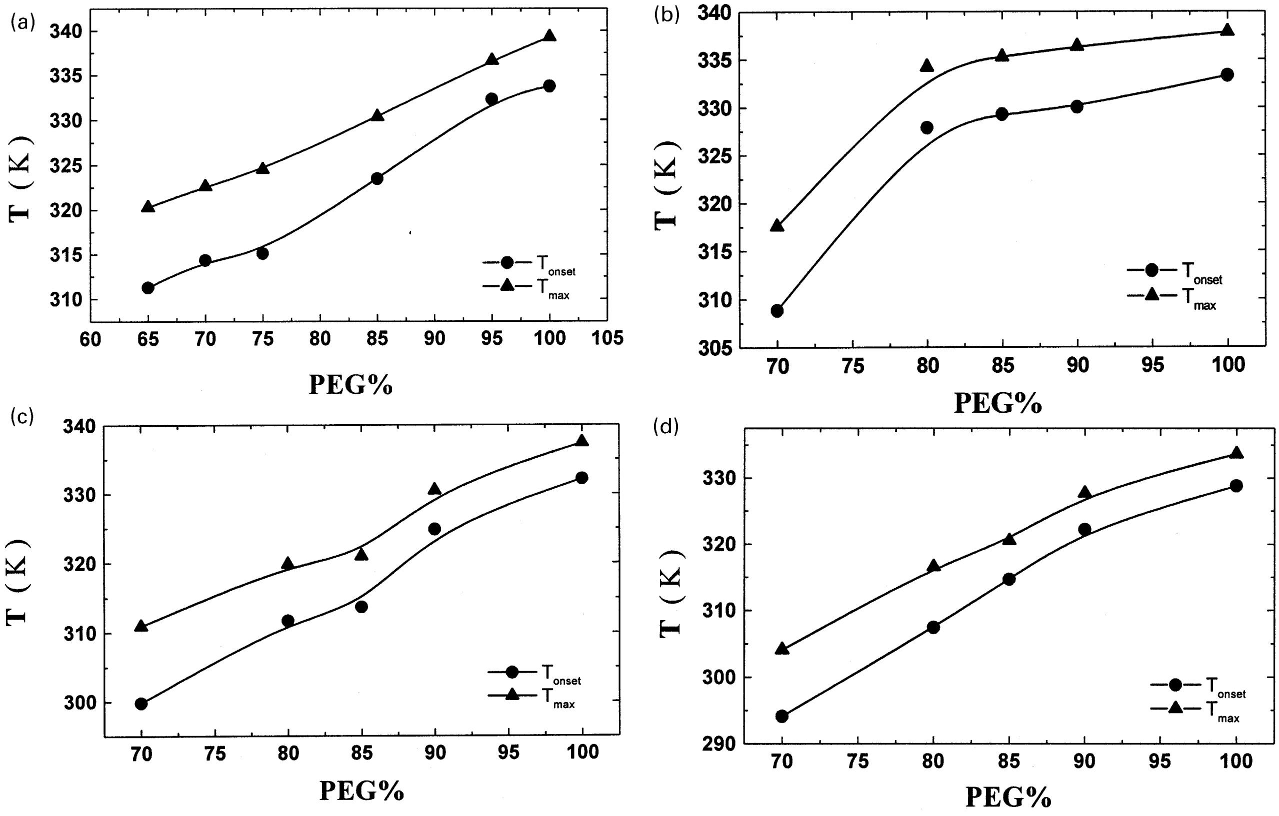

Fig. 2. Relational curves between the transition temperature and the weight percentage of PEG.

the weight percentages of PEG decline. But an important phenomenon is that the transition temperatures of the composites are much lower than that of pure PEG with the maximum beyond 30 K.

The reason for this phenomenon is discussed as follows. CDA is the impurity to PEG and can destroy the perfection of the crystallization. So the defects of crystal lattices increased with the increase of the CDA, which cause the crystals can be damaged at lower temperature. Thus the transition temperatures of PCM decline sharply with the increase of CDA. Moreover, the end groups of PEG chain were fixed by chemical bonding as discussed above. So the segments nearby cannot crystallize well because of the steric effect and drag effect, which leads to the number of segments that can really crystallize decreases. This is similar to the decline of the molecular weight. So the crystalline regions turn smaller, which also lead to the fall down of the transition temperature in certain degree. For all the reasons above, the transition temperatures of the composites decrease in the great degree.

3.2. Relationship between the energy storage properties and the molecular weight of PEG

Then the relationship between the thermal characteristics and the molecular weight of PEG was studied and the relational curves between the enthalpy and molecular weight of PEG were obtained as shown in Fig. 3. From Fig. 3, it can be seen that the enthalpy is correlative to the molecular weight of PEG apparently with the same weight percentage of PEG.

Fig. 3(a) is the relationship between the enthalpy and pure PEG with different molecular weight. We can find that the enthalpy reaches the maximum when the molecular weight of PEG is 10,000 and the enthalpy decline when the molecular weight becomes greater or less than this value. One of the causes is that the crystallinity reaches the maximum when the molecular weight is 10,000, i.e. the number of segments (CH_2–CH_2–O) is about 227. If the number of segments becomes less, the ratio of the segments near end groups that cannot crystallize increase. If the number of segments is greater than about 227, then the chain becomes too long and will tangle each other, which also impede to form well-defined crystal. Therefore, above two factors work together and lead to the crystallinity and the enthalpy reach the maximum when the molecular weight is 10,000. The crystal structure of the PEG with high molecular weight (larger than 10^4) is different from that with lower molecular weight (less than 10^4), that may be another possible cause [21]. But just as in the polyethylene (PE), if its molecular weight is very high, its enthalpy also declines. So among all the causes, steric hindrance may be the most important. Curves (b)–(d) in Fig. 3 explore the relationship that the weight percentage of PEG is 90, 80 and 70% respectively.

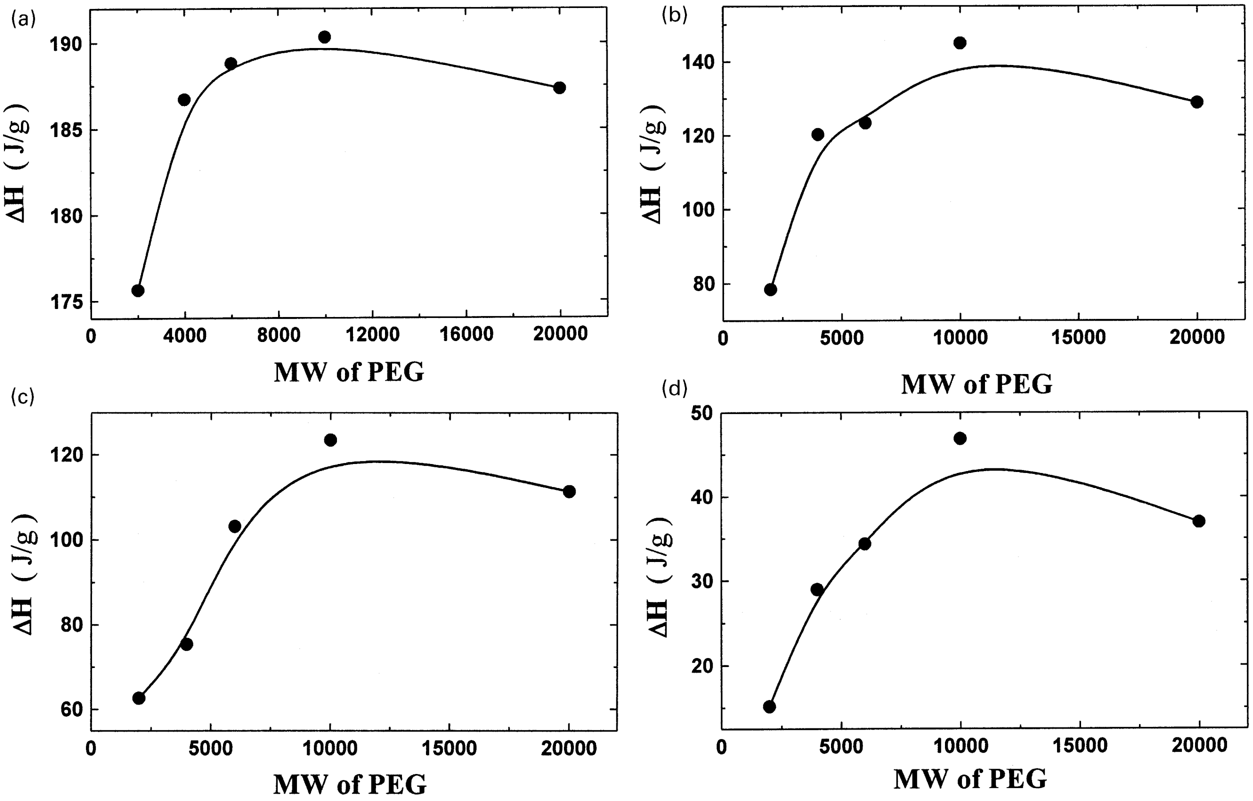

Fig. 3. Relational curves between the enthalpy and the molecular weight of PEG.

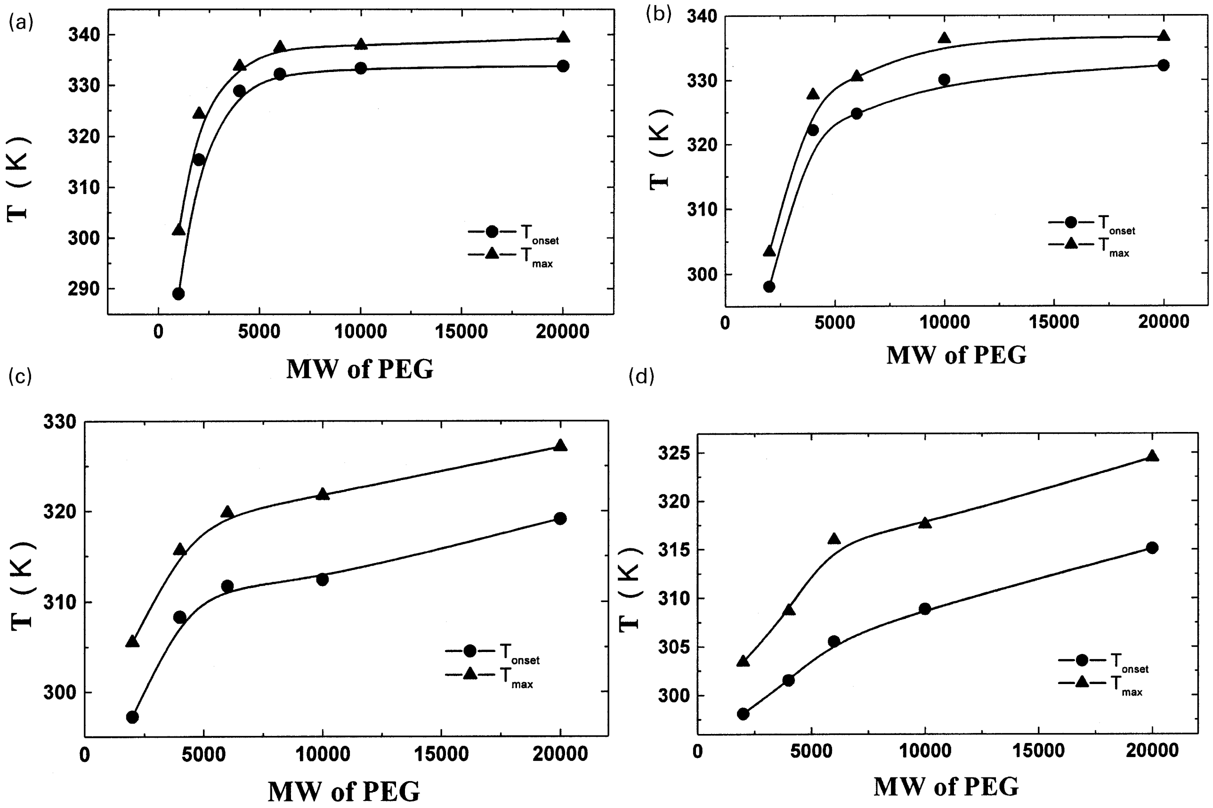

Fig. 4. Relational curves between the transition temperature and the molecular weight of PEG.

These curves show that the PCMs with different PEG contents have the same variation rules as that of pure PEG.

From the above analysis, we find that in order to change the enthalpy of the composites, we also can adjust the molecular weight of PEG besides changing the weight percentage of PEG in PCM.

Fig. 4 shows the relationship between the transition temperatures and molecular weight of PEG. Curve (a) in Fig. 4 is the curve of pure PEG. When the molecular weight of PEG is less than 6000, the transition temperatures of PEG become high rapidly with the increase of its molecular weight. But when the molecular weight of PEG is greater than 6000, the transition temperatures tend to a stable value, and at last it reach the maximum 333 K. Curve (b) describes the variation rules of the transition temperatures of PCMs in which contain 90% of PEG with different molecular weight of PEG. It has the similar regularity as curve (a), but to the low molecular weight (molecular weight of PEG < 6000), the variation becomes a little milder and to high molecular weight of PEG (molecular weight of PEG > 6000), the variation turns to be more obviously. When the weight percentage of PEG drops down to 80 or 70%, this variation becomes more apparent and the curve trends to be line shape, which can be seen in curves (c) and (d) in Fig. 4.

4. Conclusions

The CDA modified with PEG by chemical grafting method is a new kind of SSPCMs. The solid–solid transition characteristics of these composites are sensitive to the proportion of components. By changing the weight percentage and the molecular weight of PEG, the composites will have different enthalpies and different transition temperatures.

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