

Crystalline-amorphous phase transition of hyperbranched polyurethane phase change materials for energy storage

Qi Cao · Pengsheng Liu

Received: 1 July 2006 / Accepted: 24 August 2006 / Published online: 28 March 2007
© Springer Science+Business Media, LLC 2007

Abstract Hyperbranched polyurethane solid–solid phase change material (HB-PUPCM) has been prepared via a two-step process. The phase transition behaviors and morphologies of these HB-PUPCM films were investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM). PEG soft segment in the polyurethane was found to be crystalline at room temperature. However, when the temperature was raised to PEG's melting point, polyurethane did not melt into the liquid state as in the case of pure PEG but changed to an amorphous solid state. In HB-PUPCM, PEG's molecules probably are tied to the hard segment chain so strongly by the chemical bonds that they cannot change to a liquid state but change to the amorphous state in the transition processing.

Introduction

Polymer-based phase changed materials for thermal energy storage applications are currently a subject of growing interest since they exhibit good chemical stability, small volume changes during the phase transition, and low vapor pressure at room temperature, and are non-corrosive materials [1–3].

Poly (ethylene glycol) (PEG) is a crystalline solid at room temperature and its average molecular weight exceeds 800. The crystalline solid of PEG changes to the liquid state without going through a glass state when the temperature increases to the melting point. However, recent research [3–7] demonstrates that the phase change behavior of PEG in polymer-based solid–solid phase changed materials is completely different. Instead of the solid–liquid phase transition of pure PEG, PEG polymer-based solid–solid phase changed materials exhibits a solid–solid phase transition at a temperature slightly below the melting point of pure PEG.

In this paper, the structural features of this HB-PUPCM and the mechanism of its solid–solid phase change were studied. These HB-PUPCMs were investigated with differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), wide-angle X-ray diffraction (WAXD), polarizing optical microscopy (POM) and tapping-mode atomic force microscopy (AFM). The results were discussed in the context of the crystalline-amorphous transition of PEG.

Experimental

Materials

Boltorn[®]H30, Hyperbranched polyester end-capped with hydroxyl groups (Third generation, $\overline{M}_w = 3,500$ g/mol, hydroxyl number equals 470–500 mg KOH/g, Sweden) was purchased from Perstorp Specialty Chemicals, dried at 60 °C under vacuum for overnight prior to use; Polyethylene glycol (PEG, $\overline{M}_n = 6,000$, from Shantou Guanghua Chemical Reagent Co. Inc., China) was degassed and dried in a round flask under high vacuum (20 Pa) at 100–120 °C

Q. Cao · P. Liu (✉)
College of Chemistry, Xiangtan University, Xiangtan 411105
Hunan Province, P.R. China
e-mail: lpsh@xtu.edu.cn

Q. Cao
e-mail: wjcaoqi@163.com

for 3–4 h; Toluene-2,4-diisocyanate (2,4-TDI), a chemically pure reagent, was purchased from Tianjin Chemical Reagent Co. Inc., China; N, N-dimethylformamide (DMF, from Shantou Guanghua Chemical Reagent Co. Inc., China) was dried by 5 Å molecular sieve for 24 h followed by distillation before use.

Synthesis of HB-PUPCM

The preparation course is as follows: The dehydrated PEG and excess of 2,4-TDI in freshly distilled DMF were mixed with stirring in a thermostatic oil-bath at 80 °C under vacuum for 3 h. The mass of TDI was that which would keep the ratio of the –NCO groups in TDI 1.0 times that of the –OH groups in the PEG and H30. A predetermined of Boltorn® H30 was dissolved in dried DMF and added to the mixture. After stirring for another 2 h, the reaction mixture was cast in glass pan. Curing was conducted at 80 °C for 24 h, after which the polymer films with a thickness of 0.2–1.0 mm were obtained. The samples were kept in vacuum at room temperature for 2 weeks before testing.

Characterization

Differential scanning calorimetry (DSC) of the resulting TPU was carried out using a 2920 TA Instrument. Samples (ca. 10 mg) were sealed in aluminum pans and measurements were performed in nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of –50–150 °C. In the first scanning, the sample was heated to 150 °C, kept at this temperature for 5 min, and cooled to –50 °C. In the second scanning, the sample was heated again to 200 °C, and the second scan was recorded.

Wide-angle X-ray diffraction (WAXD) curves ranging from ca. 10° to 40° were collected at selected temperatures with a Rigaku D/Max-1200 X-ray diffract meter. The incident X-ray was CuK α with a power of 40 kV, 25 mA, passed through a nickel.

An observation of polarizing optical microscopy (POM) was performed on a Leitz Laborlux 12POL microscope equipped with a video camera. The sample was placed between a microscope glass and a coverslip and heat with a Leitz 350 hot stage.

Tapping-mode atomic force microscopy (AFM) was used to visualize the images of HB-PUPCM on a DI Nanoscope IIIa AFM, Micro-fabricated cantilevers or silicon probes (Nanoprobes, Digital Instruments) with 125 μ m long cantilevers were used at their fundamental resonance frequencies, which typically varied from 270 kHz to 350 kHz depending on the cantilever. Cantilevers had a very small tip radius of 5–10 nm. The AFM was operated at ambient with a double-vibration isolation system. Extender electronics were used to

obtain height and phase information simultaneously. The lateral scan frequency was about 1.5 Hz.

Results and discussions

Visual observation

Solid HB-PUPCM is hard and slightly yellow in color at room temperature. When the temperature rises to 60 °C, the polyurethane becomes more and more transparent. It becomes quite transparent at about 70 °C and higher temperatures. Even up to 100 °C, the HB-PUPCM remains solid, as observed visually. In contrast with pure PEG, PEG in HB-PUPCM does not change to the liquid state even at a temperature much higher than PEG's melting point. The visual observation indicates that PEG in the HB-PUPCM remains in the solid state even when the temperature rises to 100 °C, over 33 °C above the melting point of pure PEG. Since the hard segment domain, serving as skeleton, restricts the free movement of PEG, when it is heated to the temperature 30–40 °C above PEG's melting point, PEG in HB-PUPCM still does not move freely and keep its solid state.

Thermal properties investigations

Figure 1 shows the DSC traces of pure PEG6000 and HB-PUPCM. A summary of the thermal property of PEG6000 and HB-PUPCM measured by DSC analysis is given in Table 1. The DSC measurement of HB-PUPCM with 90% SSC shows heat absorption at about 66.6 °C, in the heating cycle, indicating that there is a phase transition having taken

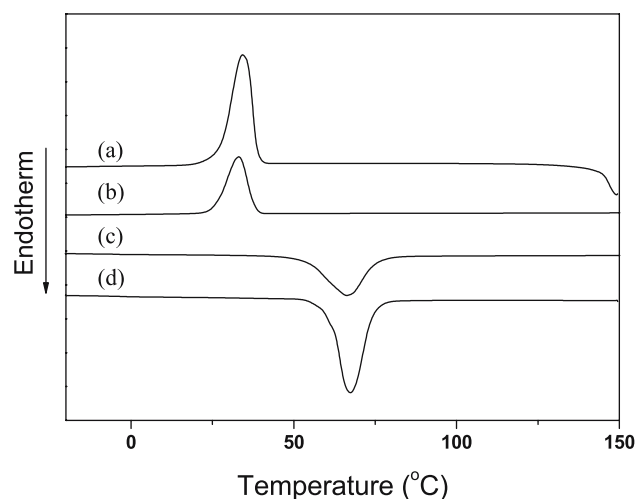


Fig. 1 DSC curves of samples: (a) Cooling cycle of PEG6000; (b) Cooling cycle of HB-PUPCM; (c) Heating cycle of HB-PUPCM; (d) Heating cycle of PEG6000

Table 1 Thermal property of PEG6000 and HB-PUPCM measured by DSC analysis

Sample	Phase transition	Temperature of peak transition T_r (°C)		Enthalpy of phase transition ΔH (J/g)	
		Heating cycle	Cooling cycle	Heating cycle	Cooling cycle
PEG	Solid–liquid	67.2	34.6	155.1	152.0
HB-PUPCM	Solid–solid	66.6	33.1	124.8	121.4

place. This should be a solid–solid phase transition, since the sample has not melted to a liquid at that time. Both pure PEG and HB-PUPCM undergo phase transition with high transition enthalpy, but their phase transition states are quite different. Pure PEG’s phase transition is a process from solid to liquid. Viewing from the micro-level, in the process of phase transition of HB-PUPCM, with the temperature increasing, the molecular thermal movement of PEG soft segment is quickening. It breaks away from the intermolecular force and hydrogen bonds. The crystalline perfection of PEG has been destroyed. So it turns into amorphous state. But the amorphous PEG is connected with the hard segment. It can only vibrate and rotate, but can’t translate freely. It shows a special solid–solid phase change behavior. So we can come to a conclusion that solid–solid phase change of HB-PUPCM is the soft segment PEG’s transition from a crystalline solid state to an amorphous solid state essentially. The energy is mainly obtained from the heat caused by entropy change between the low entropy crystal state and high entropy amorphous state.

Thermal stability is an important factor of concern in phase change material research and applications for its impact on the capacity of thermal storage [8]. For investigating the influence of the heating cycle on the phase change behavior of the HB-PUPCM, the sample was repeatedly heated from 0 °C to 200 °C, and then cooled to 0 °C. Figure 2 shows the thermal properties of HB-PUPCM with 90 SSC% after undergoing the heating–cooling cycle 1, 50, 100 times. Being subjected to this heating and cooling 100 times did not change the phase change behavior, enthalpy, and phase change temperature of the sample, confirming the thermal stability of the HB-PUPCM as a solid–solid phase transition material.

Crystalline morphology investigations

Figure 3 shows the WAXD patterns of two samples, PEG with a MW of 6,000 and HB-PUPCM, respectively. Table 2 collects the WAXD data of the highest three peaks of these two samples. It is obvious that both pure PEG and PEG in the polyurethane are crystalline at room temperature. Furthermore, they have the same unit cell, as demonstrated by their exactly identical X-ray diffraction spacing, as shown in Table 2. In other words, the crystal

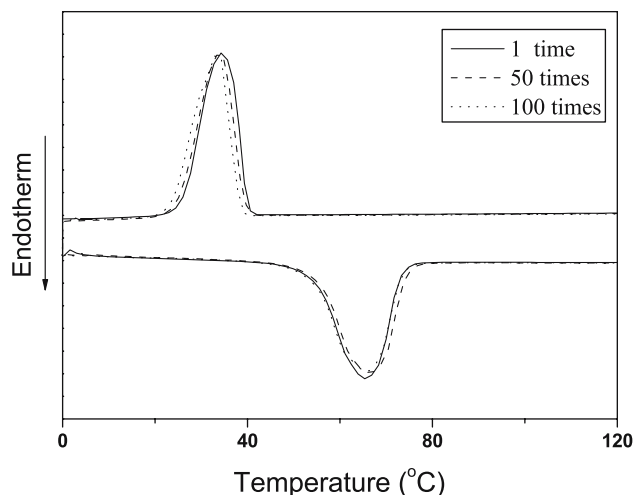


Fig. 2 DSC curves of HB-PUPCM with 1, 50 and 100 times heating–cooling thermal cycles

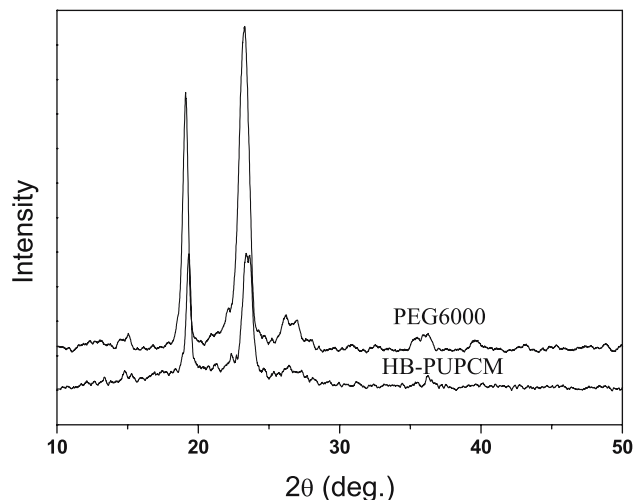


Fig. 3 WAXD profiles of the pure PEG6000 and HB-PUPCM with 90% soft segment contents

structure of PEG has not been changed by the procedure of polymerization. The only difference between these two samples shown by Table 2 is that the half-widths of the X-ray peaks of PEG in the HB-PUPCM are greater than those of pure PEG, indicating that the crystallite size of PEG becomes smaller after polymerization.

Table 2 Highest three peaks of WAXD of PEG and HB-PUPCM with 90% soft segment contents

Sample	Peaks	2 θ (deg)	d (nm)	Half-width	Rel intens
PEG	1	23.22	0.383	0.84	100
	2	19.07	0.465	0.44	86
	3	26.18	0.340	0.59	11
HB-PUPCM	1	23.55	0.378	0.88	100
	2	19.53	0.454	0.44	123
	3	26.59	0.335	0.65	7

Figure 4 shows the WAXD patterns of HB-PUPCM at several different temperatures. PEG in the HB-PUPCM maintains its quite perfect crystalline state when the temperature is not higher than 50 °C, as indicated by its high and sharp X-ray peaks. However, when the temperature rises to 60 °C, the crystalline perfection of PEG in the HB-PUPCM begins to be destroyed. When the temperature rises to 70 °C, all the X-ray peaks disappear, and PEG in the HB-PUPCM becomes completely amorphous, it does not change to liquid, so it should be an amorphous solid. In other words, there is a crystalline-amorphous transition-taking place at a temperature between 60 °C and 70 °C. As mentioned above, HB-PUPCM presents a solid–solid phase change at a temperature of 66.62 °C, indicated by DSC investigation. So we can come to the conclusion that the solid-solid phase change of the HB-PUPCM in fact is a crystalline-amorphous transition of PEG in the polymer. This is in agreement with the visual observations. As mentioned above, HB-PUPCM sample becomes more transparent at temperatures of 70 °C or higher.

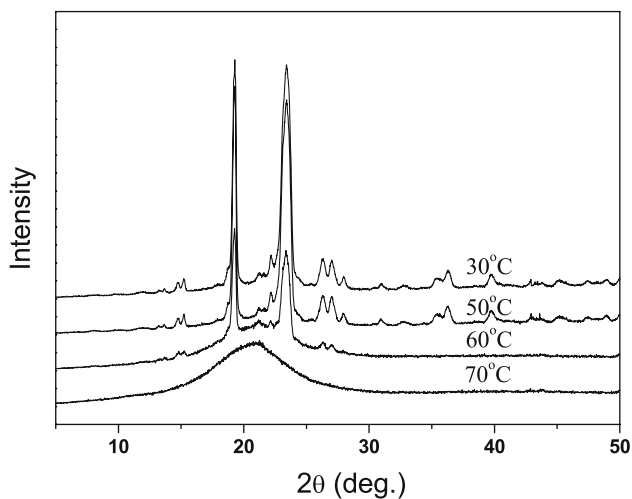
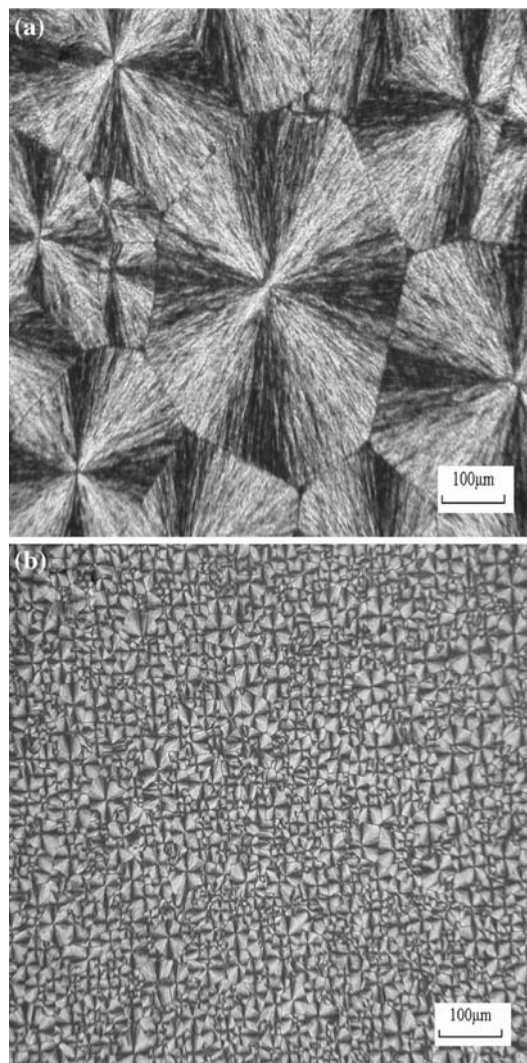
**Fig. 4** WAXD profiles of the HB-PUPCM at different temperature

Figure 5 displays the typical room temperature POM images of pristine PEG with Mn of 6,000 and HB-PUPCM at 200 magnifications. For pristine PEG (Fig. 5a), only few spherulites with the size of 80–100 μm can be observed. PEG spherulites exhibit a typical compact spherulitic morphology and the cross-extinction pattern can be observed clearly. It is interesting to note that, crystal structure of PEG has not changed by the procedure of polymerization. But the amount of PEG spherulites in the HB-PUPCM increases and the average radius of spherulites decrease to only about 20–40 μm (Fig. 5b).

The dark area in HB-PUPCM is larger than that in PEG, suggesting that the ratio of amorphous PEG in HB-PUPCM is higher than that in pristine PEG. The POM images agree well with DSC results. Part of hard segment in HB-PUPCM particles may act as the nucleus of PEG spherulites and thus increase the amount of PEG spherulites. On the other

**Fig. 5** Polarized optical microscopy (POM) images at 25 °C for: (a) PEG and (b) PEG in HB-PUPCM

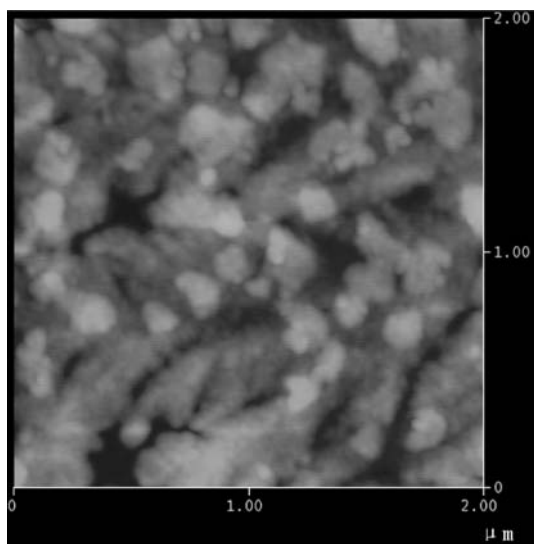


Fig. 6 AFM height images of HB-PUPCM film

hand, hard segment can restrain the recrystallize tendency of PEG chains through chemical bond interactions and hence decrease the growth speed of PEG spherulites. The increasing amount of PEG spherulites, decreasing size of PEO spherulites, and the incomplete crystallization are all unbeneficial for creating more continuous crystalline phase of PEG, which is very important for the thermal storage.

To investigate the morphology in the transition process, micro-morphology is recorded by POM in a heating process. Under the transition temperature, the spherulite has no change with the temperature increasing. The spherulite starts to be destroyed when the temperature reaches transition temperature. At last, the spherulite structure is destroyed completely, and the visual field of POM is dark, but no liquid is observed at the heating process. The transition is also proved to be a solid–solid phase change.

For a moderate force image, the high height corresponded to low modulus; therefore, the lighter height image was richer in polyurethane, while the darker height image corresponded to the hard segment. We used a conventional interpretation of modulus-sensitive height images

at light tapping where the lighter color portions were assigned to the crystallites of PEG soft segments. The AFM image (see Fig. 6) reveals the connected PEG soft segment domains. Importantly, the AFM image of HB-PUPCM showed the existence of crystallites. This was in general agreement with the DSC, WAXD and POM results.

Conclusions

From the above analysis, PEG soft segment in the polyurethane was found to be crystalline at room temperature. However, when the temperature was raised to PEG's melting point, polyurethane did not melt into the liquid state as in the case of pure PEG but changed to an amorphous solid state. In HB-PUPCM, PEG's molecules probably are tied to the hard segment chain so strongly by the chemical bonds that they cannot change to a liquid state but change to the amorphous state in the transition processing. Also, we can conclude that the HB-PUPCM with special solid–solid phase change behaviors, high thermal energy storage capability, suitable phase transition temperature, reversible latent heat transition and good thermal stability could be used as a new kind of solid–solid phase change materials for thermal energy storage and temperature control. It has a great potential for thermal energy storage applications.

References

1. Feldman D, Banu D (1996) *Thermochim Acta* 272:243
2. Zalba B, Marin JM, Cabeza LF, Mehling H (2003) *Appl Therm Eng* 23:251
3. Pielichowski K, Flejtuch K (2005) *Polym Adv Technol* 16:127
4. Liang XH, Guo YQ, Guo LZ, Ding EY (1995) *Macromolecules* 28:6551
5. Jing Y, Ding EY, Li GK (2002) *Polymer* 43:117
6. Zhang M, Na Y, Jiang ZH (2005) *Chem J Chinese Univ* 26:170
7. Guo YQ, Tong Z, Chen MC, Liang XH (2003) *J Appl Polym Sci* 88:652
8. He TB, Hu HJ (2001) *Functional polymer and new technology*. Chemical Industrial Press, Beijing, China