Study on Polyurethane Solid-Solid Phase Change Materials

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Abstract: Polyethylene glycol (PEG) was used as the host material and the inorganic nano-material opal was introduced as nucleating agent to synthesize a novel organic-inorganic polyurethane/opal solid-solid phase change energy storage material. The composition, phase transition properties and the thermal properties of the materials were tested by infrared spectroscopy (IR), proton nuclear magnetic resonance spectroscopy (1HNMR), differential scanning calorimetry (DSC), polarized microphotograph (POM), and thermogravimetric (TG), respectively. The results show that a novel polyurethane/opal solid-solid phase change material (PUPCM) was synthesized which had great transition enthalpy, good thermal stabilities, controllable transition temperature and no liquids leakage during transition. Meanwhile, due to the presence of the opal, not only the transition enthalpy increased but the crystallization rate also increased so that the crystallization properties were improved and the spherulites were regular and integrated.

Key words: polyethylene glycol (PEG); opal; polyurethane (PU); solid-solid phase change
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Polyethylene glycol (PEG), due to its enthalpy change regularly with its molecular weight and exhibits excellent energy storage properties, is worthwhile for broad investigation. In this paper, PEG of high molecular weight was used as the soft segment, 2, 4-tolylene diisocyanate (TDI) and glycerin were used as hard segment to synthesize a novel PUPCM. The composition, phase transition properties and the thermal properties of the materials were tested by means of IR, 1HNMR, DSC, POM and TG, respectively[1-2].

1 Experimental

1.1 Materials and Equipments

PEG (CP, $n = 2.0 \times 10^4$), TDI, Glycerine and Acetone was purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. Opal powder was supplied by opal science development Co., Ltd of Nenjiang. Magnetic Stirrer (DF—101S Heat-focused Temperature-consistant Stirrer), FTIR-Raman Spectrometer (NEXUS—670), Nuclear Magnetic Resonance Spectrometer (Bruker Avance—400), Modulated DSC 2910.

1.2 Preparation of Polyurethane/Opal Solid-Solid Phase Change Material

The preparation of PUPCM includes two steps:

(1) Preparation of prepolymer. TDI (0.005 ~ 0.05 mol) was dissolved in solvent (10 ~ 30 mL), then poured in the three-necked flask and the right amount catalyst was dripped in. After being stirred for a moment, few opal fine powders was added. With the protection of N_2, 20 ~ 50 mL PEG of certain molecular weight solution which contained 0.002 ~ 0.02 mol solvent.

After being stirred for 5 ~ 30 min, the solution was heated up to backflow. After being reacted for 2 ~ 3 hours, the activation sample was namely obtained.

(2) Preparation of PU/Opal Solid-Solid PCMs: Glycerine (0.005 ~ 0.05 mol) was dissolved in solvent (10 ~ 30 m), then poured in the three-necked flask and the right amount catalyst was dripped in. After being tirred for a moment, the solution was heated up to backflow with the protection of N_2. After being reacted

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for 2 ~ 3 hours, the products were moved to the vacuum oven in order to volatilize the solvent.

2 Results and discussion

2.1 FTIR Analysis of the prepolymer and PU/Opal Solid-Solid PCMs

The FT-IR spectra of PU/Opal Solid-Solid PCMs shows the characteristic vibration peak of -NH is at 3 567 cm^{-1}. The stretching vibration peak of —C=O and —CH_2 are at 1 723 cm^{-1} and 2 873 cm^{-1}, respectivily. The absorption peaks of —C—O are at 1106 cm^{-1} which is consistent with the composition of PE. It is observed that methylene turn to be narrow due to the strong stretching vibration peak of —CH_2 that cover the peaks belong to —CH_3 of TDI. The absorption peaks of 1 601, 1 539, 1 472 and 1 454 cm^{-1} correspond to the characteristic vibration peaks of benzene ring which prove the existence of TDI. Another prove is the peaks at 3 264 and 2 873 cm^{-1} which correspond to the vibration peaks of —OH and —CH_2 of glycerin. The characteristic vibration peaks of —C=O and -NH indicate the product prepared is the prospective sample as well[3]. We can get the same conclution from the ^{1}HNMR spectra of the PU/Opal Solid-Solid PCMs.

2.2 Phase Transition Behavipors and Mechanism of the novel PCMs

2.2.1 Phase transition Behaviors

The thermal analysis data of PU/Opal solid-solid PCMS is shown in Table 1, the transition enthalpy of the material increased remarkably with the presence of the opal nano nucleating agent.

Table 1　DSC Analysis Data of PUPCM and PUPCM/Opal

Sample	Phase transition	△H/ (J·g^{-1})		t_t/℃	
		Heating cycle	Cooling cycle	Heating cycle	Cooling cycle
PUPCM	solid-solid	57.24	36.81	27.33	—11.33
PUPCM/Opal	solid-solid	64.25	45.93	28.2	—12.30

t_t— Peak transition temperature; △H — Phase transition enthalpy; PUPCM— PEG-TDI-glycerol

2.2.2 Phase Transition Behaviors

Fig 1 is the POM Photographs of the PU/Opal PCMs. As it is shown, the PCMs exhibit a good crystalinity. During the crystallization process, many small regular spherulites formed. The addition of the opal super fine powder has a big contribution to increase the enthalpy value and the crystalinity of the polymer.

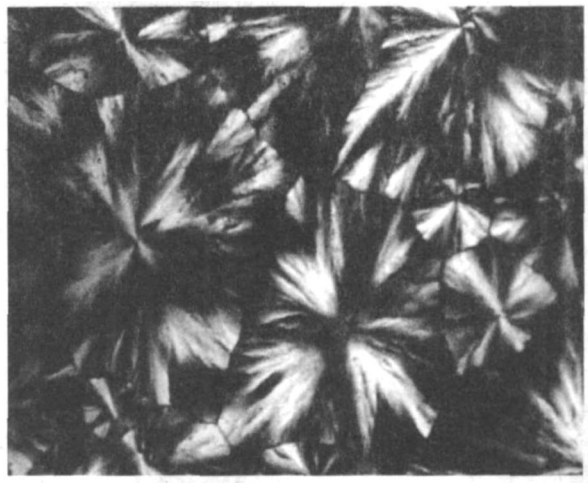

Fig 1　POM Photographs of the PU/Opal PCM (T= 35℃)

2.3 Thermal Stability of PUPCM

The maximum decomposition speed of PU/Opal solid-solid PCMs corresponds to temperature of 410 ℃, terminate temperature is at 427.3℃. Thus it may be known the thermal decomposition temperature of the materials prepared is high, also the stability is very good in the transformation temperature range and not easy to volatilize or decompose[5].

3 Conclusion

In this paper, a novel organic-inorganic Polyurethane (PU) /opal solid-solid phase change energy storage material was prepared successfully which also has an optimum transition temperature and high phase transition enthalpy. The addition of the inorganic nano-material opal improved the polymer crystallization and enhanced the enthalpy value as well. The novel material also has a good thermostability.

References

[1] LIU Y F, HUA H, ZHOU Z F, et al. Study evolve of Opal Shale Exploitation and Application[J]. Chemical Industry Times, 2005, 19(4): 36—41.

[2] GU X H, XI P, LI Q S, et al. Study on the Composite of ABS resin/Nano-Opal[J]. China Plastics, 2006, (6): 27—31.

[3] GU X H, XI P, JIA Y T, et al. Preparation and Characterization of P(AN/VAC) /Clay Based Nanocomposites[J]. Applied Polymer Science, 2006, (102): 703—706.

[4] ZHANG M, NA Y, JIANG Z H. Preparation and Properties of Polymeric Solid-solid Phase change Materials of Polyethylene Glycol (PEG) /poly (vinyl alcohol) (PVA) copolymers by Graft Copolymerization[J]. Chem J Chinese Universities, 2005, 26(1): 170—174.

[5] WANG J F. Review of Latent Thermal Energy Storage (6) LTES with Multiple PCNS and Potential Applications [J]. New Energy Sources, 2000, 4 (22): 22—23.

聚氨酯固—固相变储能材料的研究

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摘 要：利用聚乙二醇（PEG）为主体，加入无机纳米材料蛋白石（Opal），制备出的新型的有机—无机体系的聚氨酯/Opal固—固相变储能材料，利用了IR、^{1}HNMR、DSC、POM、TG等测试手段，对其结构和性能进行了表征分析。结果表明，该聚氨酯型相变材料具有较高的相变焓值、适宜的相变温度、热性能稳定和相变过程中不产生液体等特点。同时，加入天然纳米无机材料蛋白石后，不仅提高了材料的相变焓值，而且提高了其结晶性能，促使其结晶速率加快，结晶呈现出很规整的球晶状态。

关键词：聚乙二醇；蛋白石；聚氨酯；固固相变

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