

## Preparation of PNHMPA/PEG Interpenetrating Polymer Networks Gel and Its Application for Phase Change Fibers

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**ABSTRACT:** In this study, poly(*N*-hydroxymethyl acrylamide)/polyethylene glycol (PNHMPA/PEG) interpenetrating polymer networks gel was prepared as a novel form-stable composite phase change materials (PCMs) successfully. And PP/IPN (PNHMPA/PEG, herein-after referred to as IPN) phase change fibers were also prepared by melt spinning. The composite PCMs and PP/IPN phase change fibers were characterized using scanning electron microscope (SEM) and mechanical analysis. The SEM results show that the PNHMPA/PEG interpenetrating polymer networks has porous structure but has no phase separation among multicomponent. In addition, the form-stable composite PCMs distribute evenly in PP. The breaking strength of PP/IPN phase change fibers is slightly smaller than that of pure PP fiber. Thermal properties and thermal stabilities of the composite PCMs and fibers were determined by using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC results show that the melting temperature and the latent heat of the prepared composite PCMs are 54.79°C and 82.08 J g<sup>-1</sup>, respectively. The melting temperatures of PEG in composite PCMs and PP/IPN phase change fibers has a little fluctuation, and the relevant data indicate that the latent heat enthalpy of the composite PCMs and fibers are slightly smaller than the theoretical value. TGA indicated that the composite PCMs have good thermal stability. Furthermore, damping performance of phase change fibers has been improved due to IPN. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1563–1568, 2013

**KEYWORDS:** composites; synthesis and processing; fibers; properties; characterization

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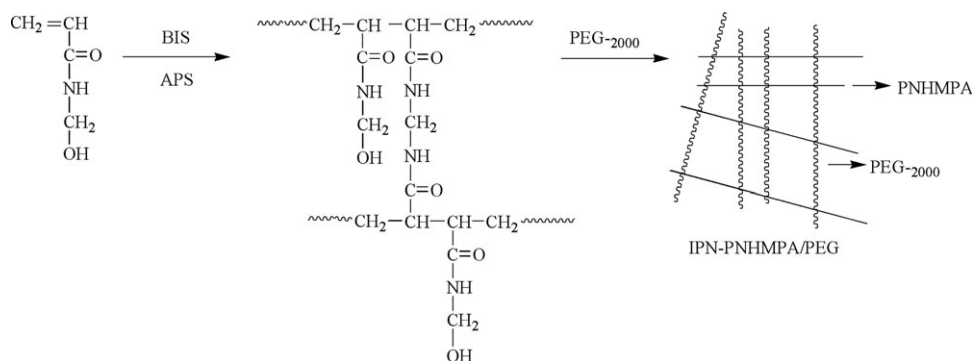
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### INTRODUCTION

Phase change materials (PCMs), also called latent thermal energy storage (LTES), which absorb or release thermal energy during melting and solidification processes are believed to have outstanding capability to store a mass of heat efficiently during phase change processes. Moreover, PCMs have attracted a great interest due to its low cost, high heat efficiency, small volume equipment, high energy storage density, as well as isothermal characteristics.<sup>1–12</sup> The production of phase change fibers is an important theme in developing PCMs in recent years.<sup>13</sup> According to the ambient temperature changes, phase change fiber could freely adjust the internal temperature of textiles. It can store energy when the outside ambient temperature rises and release when the environmental temperature decreases. Therefore, it can make internal temperature of textiles vary in small range, thus making the human body feel comfortable.<sup>14</sup> However, PCMs used for phase change fiber are not enough, they should satisfy some conditions such as large thermal capacity, reversible phase transformation, nontoxicity, manufactureability, etc. Most of PCMs used for fibers are solid–liquid PCMs pres-

ently, but solid–liquid PCMs will make spinnability of polymers decline if used for spinning directly. In addition, they are easy to wash away during processing, which makes the production difficult to go smoothly and fibers cannot be used normally. Thus before preparation of fiber, solid–liquid PCMs should be packaged, carry grafting copolymerization with capsule, inorganic porous materials in order to form form-stable phase change materials (FSPCM) without liquidity. Therefore, many of the researches have studied the modification of the PCMs,<sup>15</sup> which have invented a variety of shape-stabilized PCMs and various preparation technologies.<sup>16,17</sup>

FSPCM is a composite material composed of working substances and carrier. When working substances carry on a phase transformation, it keeps solid shape, which makes it have wide applications. Now there are many technologies of preparing FSPCM, but most of them have limitations. Physical adsorption method is to use a porous medium as a matrix liquid adsorption work material, although the process is simple and easy to transform existing building materials, compatibility of PCMs and substrate materials is difficult to obtain effectively and the



**Scheme 1.** Sketch of synthesis course of PNHMPA/PEG interpenetrating polymer networks gel.

working substances exude easily in use.<sup>18</sup> Molten blending method is suitable for the preparation of industry and construction with FSPCM of lower temperature, however, its thermal conductivity is low.<sup>19</sup> Suppress sintering method can not only play the role of saving energy, but also reduce the volume of the regenerator. But the method is mainly used for high temperature FSPCM, which limits the variety of our products.<sup>20</sup> Microcapsules method for preparing FSPCM is not easy to leak, but this method has complex production process, high cost, low heat resistance, and is only applicable to spinning solution method, thus resulting in high cost of products.<sup>21,22</sup>

On this basis, this research proposed a solution polymerization method, using *N*-hydroxymethyl acrylamide (NHMPA) as a monomer, *N,N*-methylene double acrylamide (BIS) as a crosslinking agent, to synthesize ploy(*N*-hydroxymethyl acrylamide) (PNHMPA) crosslinking networks gel as a carrier matrix. Using PCMs polyethylene glycol (PEG) as the working substance, ploy(*N*-hydroxymethyl acrylamide)/polyethylene glycol (PNHMPA/PEG) interpenetrating polymer networks gel was prepared, which is a new type of form-stable composite PCMs. The process is simple, with low cost and the substrate material has a good compatibility with PCMs, and the working substance is not easy to leak in high temperature and high shear function. Therefore, it has great advantage in the preparation of melt-spinning tempering fibers. In addition, PP/IPN melt spun fiber was prepared by PNHMPA/PEG and PP, and the performance was subsequently studied.

## EXPERIMENTAL

### Materials

*N*-hydroxymethyl acrylamide (NHMPA, AR), obtained from Shandong Zibo Chemical Reagent Co., Ltd. *N,N*-methylene double acrylamide (BIS, AR) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Ammonium persulfate (APS, AR) was supplied by Tianjin No.3 Chemical Reagent Factory. Polyethylene glycol (PEG, AR) with average molecular weights of 2000 was purchased from Sinopharm Chemical Reagent Co. Ltd. Polypropylene (PP, 71735) was gained from China Petroleum Liaoyang Petrochemical Company. Poly(ethylene glycol) acrylates (PEGA) used as compatibilizer was prepared by our laboratory. All materials were used without further purification except for PEGA.

### Preparation of PNHMPA/PEG Interpenetrating Polymer Networks Gel and PP/IPN Phase Change Fibers

The process of synthesis of PNHMPA/PEG interpenetrating polymer networks gel is depicted in Scheme 1. The synthesis procedure were carried out as follows: (a) the quantified amount of NHMPA and BIS (molar ratio BIS:NHMPA = 1 : 8) were dissolved in deionized water in a flask, and the PNHMPA crosslinking networks gel by solution polymerization using APS (accounted for 3.5% of NHMPA mass) as initiator; (b) the PEG weighed accurately was slowly poured into the flask and totally dissolved before putting BIS into the flask; (c) the mixture was dispersed with ultrasound for 5 min and then polymerized at 75°C in water bath for 3 h. Thus the new type of FSPCM—PNHMPA/PEG interpenetrating polymer networks gel was obtained. Then the gel obtained was soaked in deionized water, and removed unreacted material after such repeated several times. The PP/IPN phase change fibers were prepared by blends of PNHMPA/PEG interpenetrating polymer networks gel dried and PP using PEGA as compatibilizer by melt spinning.

### Characterization

The morphology and microstructure of the prepared PNHMPA/PEG interpenetrating polymer networks gel and PP/IPN phase change fibers sputtered with gold were observed using scanning electron microscope (SEM) (JSM-6460LV, Japan) at acceleration voltage of 20 kV under low vacuum.

Thermal gravimetric analysis (TGA) was carried out using a TA thermal analysis system (TGAQ50, USA). About 5 mg of samples were weighed into an alumina crucible and the analysis was carried out at temperature range from 0°C to 700°C at a heating rate of 20°C min<sup>-1</sup> under a constant stream of nitrogen at a flow rate of 80 ml min<sup>-1</sup>.

Mechanics analysis was performed with Single Fiber Tensile Strength Tester (LLY-06B, Lanzhou). The analysis was carried out at a speed of 20 mm min<sup>-1</sup> under 5 mm of the distance between the fixture.

Thermal analysis was determined (each used about 3.0–5.0 mg) by differential scanning calorimetry (DSC) (DSC-60A, Japan). Both the heating rate and the cooling rate were 10°C min<sup>-1</sup>, ranging from 25°C to 70°C, in a nitrogen atmosphere.

Dynamic mechanical analysis was performed by DMA (DMAQ80-0, USA). The samples were measured during heating

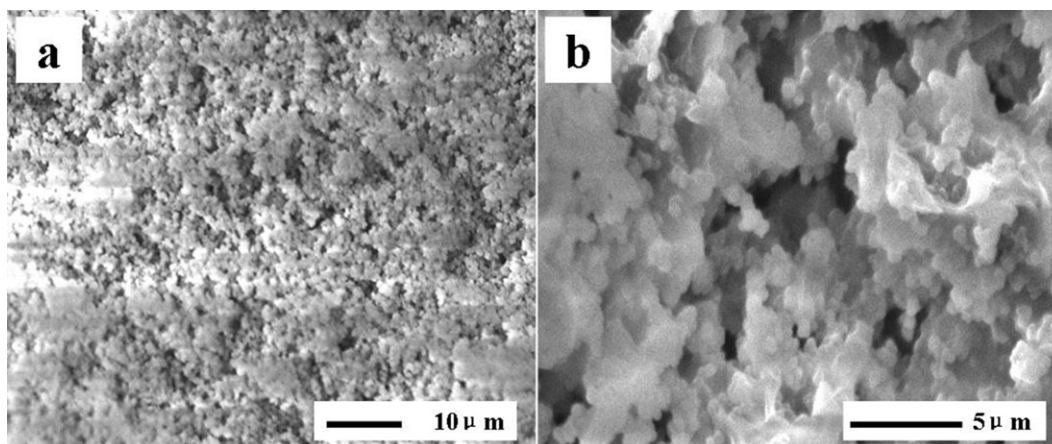


Figure 1. SEM images of PNHMPA/PEG interpenetrating polymer networks gel.

with a rate of  $3^{\circ}\text{C min}^{-1}$ , ranging from  $20^{\circ}\text{C}$  to  $160^{\circ}\text{C}$ . Measurements were performed at one frequency: 1 Hz. By means of this technique the authors can obtain three parameters which characterize a polymer: the storage modulus ( $G'$ ), the loss modulus ( $G''$ ), and the loss factor (usually known as  $\tan \delta$ ). The loss factor can be calculated as the ratio of the loss versus the storage modulus:

$$\tan \delta = G''/G'$$

## RESULTS AND DISCUSSION

### Microstructures of PNHMPA/PEG Interpenetrating Polymer Networks Gel

Figure 1 shows the morphology of the fractured surfaces of PNHMPA/PEG interpenetrating polymer networks gel by SEM. Figure 1(a) and (b) were images of 1000 times and 4000 times magnification, respectively. According to SEM observations of PNHMPA/PEG composites, the PEG is uniformly encapsulated and embedded inside the 3D PNHMPA network. This dispersion provides a mechanical strength to the composite. It still can be seen that PNHMPA/PEG interpenetrating polymer networks gel has no phase separation among multicomponent and the network structure has obvious porous structure. This kind of unique porous network structure of IPN networks gel not only can enhance physical tangles ability of PEG, but also provide space for segment motion and crystallization of PEG. Consequently, on the condition that the PCMs could be encapsulated in the 3D PNHMPA network without any leakage.

### Thermal Stability of PNHMPA/PEG Interpenetrating Polymer Networks Gel

The TGA curve of the form-stable composite PCMs is illustrated in Figure 2. During thermal degradation between  $0^{\circ}\text{C}$  and  $700^{\circ}\text{C}$ , the TGA curve of the composites display two-stage degradation process. The first step ( $50\text{--}350^{\circ}\text{C}$ ) is decomposition steps corresponding to the evaporation of water from the gel and volatilization of unreacted monomers and initiator. The second step ( $400\text{--}465^{\circ}\text{C}$ ) is assigned to the thermal degradation of the form-stable composite PCMs. As can be seen from the curve, it appears a sharp weightlessness peak and the decomposition temperature is  $438^{\circ}\text{C}$ .

In addition, as can be seen from TGA curve, the form-stable composite PCMs do not degrade at the temperature lower than  $350^{\circ}\text{C}$  and almost no weight loss can be observed. It means that the form-stable composites are very stable in the working temperature region, or in their temperature range of phase transition. Based on the TGA results, it can be concluded that the prepared composite PCMs have good thermal stability, and can be used repeatedly in thermal energy storage applications. And it also shows that PNHMPA/PEG interpenetrating polymer networks gel meet the requirements of experiment that it is suitable for process temperature of molten spinning of this experiment.

### Microstructures of PP/IPN Phase Change Fibers

Figure 3 shows the morphology of the surface and section of PP/IPN phase change fibers by SEM. Figure 3(a) and (b) were surface morphology images of w (IPN) 10% and w (IPN) 20%, respectively. And Figure 3(c) and (d) were section morphology

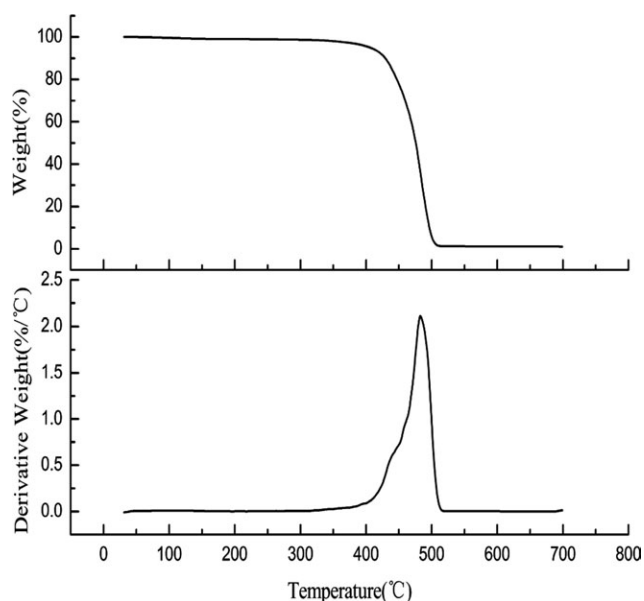


Figure 2. TGA curve of PNHMPA/PEG interpenetrating polymer networks gel.

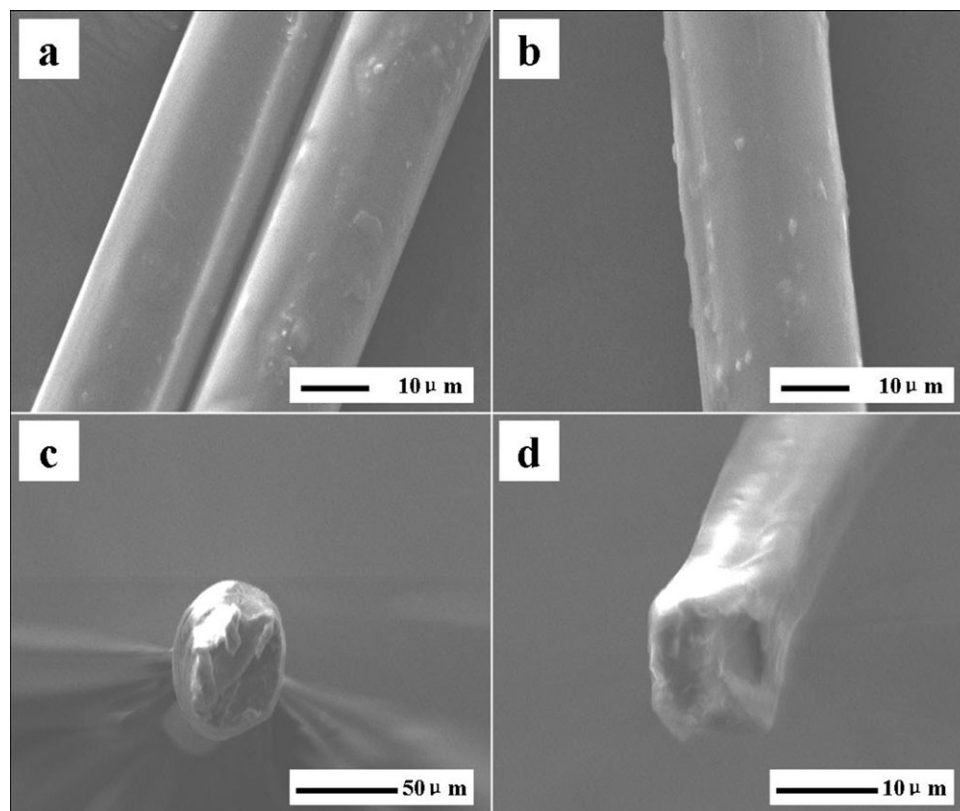


Figure 3. SEM images of PP/IPN phase change fibers.

images of w (IPN) 10% and w (IPN) 20% after brittle fracture with liquid nitrogen, respectively. As seen from Figure 3(a) and (b), when the IPN content are 10% and 20%, respectively, the surface of the phase change fibers smooth mainly and individual protuberant place should be the form-stable composite PCMs embedded in the fibers. And it also shows that composite PCMs particles not only increase but also distribute evenly with content of the form-stable composite PCMs increasing. The section morphology images in Figure 3(c) and (d) show clear interior of fibers has no obvious phase separation, which indicates composite PCMs particles and PP have good compatibility after using compatibilizer.

#### Mechanical Properties of PP/IPN Phase Change Fibers

Figure 4 shows analytical diagram of the breaking strength and breaking elongation of pure PP and PP/IPN phase change fibers with different mass fractions of IPN (w (IPN) is 5%, 10%, 15%, and 20%). The breaking strength of PP/IPN phase change fibers is slightly smaller than that of pure PP fiber. This is partly due to the out-of-phase IPN particles scattered in matrix material PP, which cause stress concentration. On the other hand, it is due to the polar IPN particles that is scattered in nonpolar PP, which would block the orientation crystallization of the PP macromolecular chain. It still can be seen that phase change fibers of different formula have different mechanical properties. The reasons are as follows: the well-defined structures of PP macromolecular chain is destroyed to some extent because of the existence of the IPN, and also increases the distance between molecules PP, and reduces the intermolecular forces. Besides, it

affects the formation of orientation and crystallization aggregated structure. On the other hand, because the existence of PEGA with the active of terminal double bond, it not only plays a role in compatibility between PP and IPN, but also reduces the reunion phenomenon. Therefore, the spinnability is improved and breaking strength and breaking elongation have

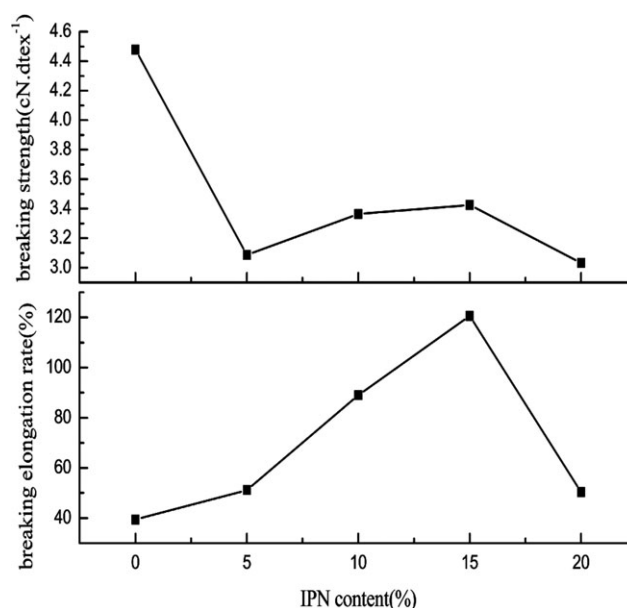


Figure 4. The influence of IPN content on fiber mechanical properties.

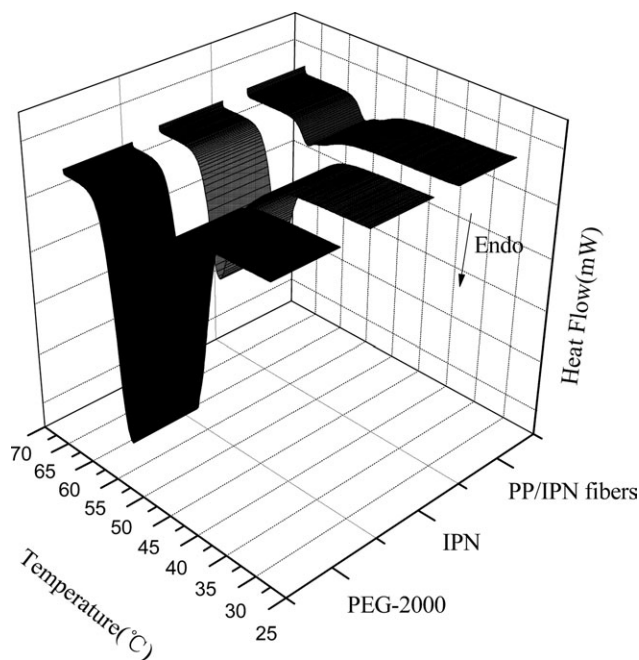


Figure 5. DSC curves of PEG<sub>2000</sub>, IPN, and PP/IPN phase change fibers.

increased. The result is that the breaking strength of blending fiber remains above 3cN/dtex when  $w$  (IPN) is 20%.

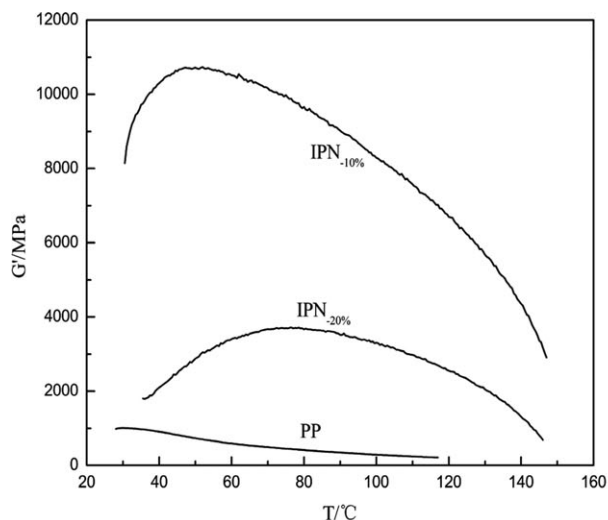
#### Thermal Properties of PNHMPA/PEG Interpenetrating Polymer Networks Gel and PP/IPN Phase Change Fibers

The DSC thermograms of PEG<sub>2000</sub>, IPN and PP/IPN phase change fibers ( $w$  (IPN) is 20%) during the melting process are shown in Figure 5 and the relevant data of which are given in Table I. The relevant data received from the DSC curves include  $T_m$ ,  $\Delta H_m$ , theoretical latent enthalpy in melting process ( $\Delta H_{Tm}$ , calculated by multiplying the value of pure PEG according to the theory of mixtures) and loading level of PEG (i.e., percentage of accounted for percentage of  $\Delta H_m$  compared to the  $\Delta H_{Tm}$ ).

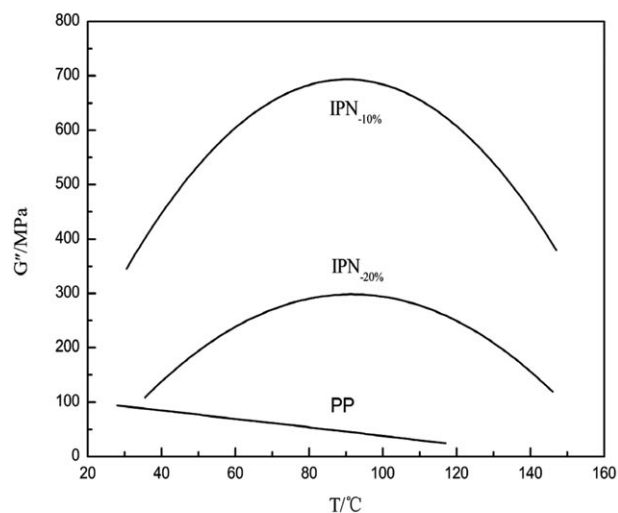
As can be seen from Table I, the  $T_m$  of PEG in composite PCMs and PP/IPN phase change fibers has a little fluctuation. These little changes in the phase change temperatures of PEG in case of composite are probably due to the physical interactions. The  $\Delta H_m$  of IPN is  $82.08 \text{ J g}^{-1}$  accounted for 70% of  $\Delta H_{Tm}$  ( $117.88 \text{ J g}^{-1}$ ) and the  $\Delta H_m$  of PP/IPN phase change fibers ( $w$  (IPN) is 20%) is  $17.06 \text{ J g}^{-1}$  accounted for 72% of  $\Delta H_{Tm}$  ( $23.58 \text{ J g}^{-1}$ ), which indicates that the latent heat enthalpy of the composite PCMs and fibers are slightly smaller than the theoretical value. It is thought that the phenomenon is possibly correlated with

Table I. The Thermal Transition Temperature and Phase Change Enthalpy of PEG<sub>2000</sub>, IPN, and PP/IPN Phase Change Fibers

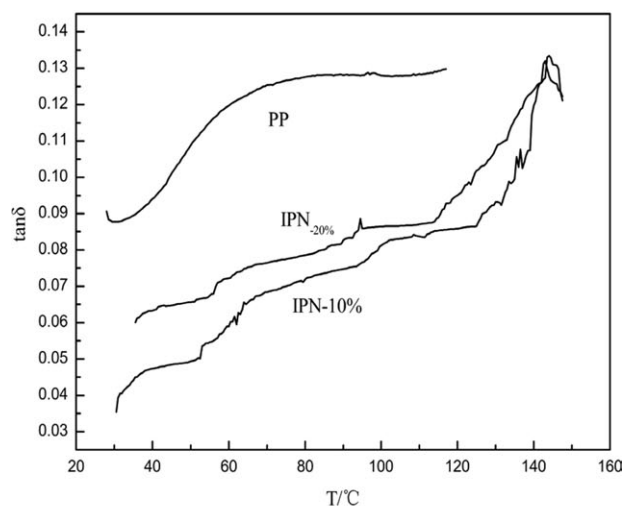
Samples	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$\Delta H_{Tm}$ (J g <sup>-1</sup> )	Loading level (%)
PEG-2000	54.39	168.40	168.40	100.00
IPN(70%PEG)	54.79	82.08	117.88	70.00
PP/IPN fibers	54.63	17.06	23.58	72.00



(a)The relationship between temperature and storage modulus  $G'$



(b)The relationship between temperature and loss modulus  $G''$



(c)The relationship between temperature and  $\tan\delta$

Figure 6. The dynamic mechanics figures of PP/IPN phase change fibers and pure PP.

the restricted thermal molecular movements of PEG during the phase transformation, which is caused by the 3D netted structure formed by NHMPA and BIS. Although the latent heat enthalpy has a little loss, the prepared FSPCMs could still provide available latent heat capacity.

### Dynamic Mechanical Analysis of PP/IPN Phase Change Fibers

Figure 6 shows dynamic mechanical analysis of PP/IPN phase change fibers. As can be seen from Figure 6 (a) and (b), the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of PP/IPN phase change fibers are higher than those of pure PP, and those of phase change fibers ( $w$  (IPN) is 10%) are higher than phase change fibers ( $w$  (IPN) is 20%), which indicate that mixing of IPN could enhance  $G'$  and  $G''$ . From Figure 6(a) and (b) we can see that the descender of curve of the phase change fiber is drastically decreased than pure PP, which show that the strength of PP/IPN blending systems in relaxation process is greater than pure PP. Moreover, the toughness of the system is better than the pure PP. As the temperature increases,  $G'$  and  $G''$  reduce in certain temperature range. The phenomena is possibly correlated with higher temperature, which strengthens sports ability of motion unit, reduces macromolecules inter-atomic forces and bound node of macromolecular chain. Therefore, the modulus descended.

Figure 6(c) shows the relationship between temperature and the loss factor ( $\tan \delta$ ). With the increase of temperature,  $\tan \delta$  goes up accordingly. It can also be seen that  $\tan \delta$ -T curves fluctuate smoothly before phase change fibers have obvious peaks. The peak is at about 0.07–0.09, and the area between the peak and the coordinate of temperature is more than pure PP, which show that damping performance of phase change fibers has been improved compared with pure PP.<sup>23</sup>

### CONCLUSIONS

In this study, PNHMPA/PEG interpenetrating polymer networks gel was prepared as novel form-stable composite PCMs successfully. And PP/IPN phase change fibers were also prepared by melt spinning. The evaluation of PNHMPA/PEG interpenetrating polymer networks gel and PP/IPN phase change fibers by SEM, TGA, DSC, DMA, and Single Fiber Tensile Strength Tester.

PNHMPA/PEG interpenetrating polymer networks gel has obvious porous structure but has no phase separation among multicomponent. In addition, the form-stable composite PCMs distribute evenly in PP. Although the breaking strength of PP/IPN phase change fibers are slightly smaller than that pure PP fiber, the breaking strength of blending fibers remain in 3cN/dtex above when  $w$  (IPN) is 20%. The novel form-stable composite PCMs, i.e., IPN we have prepared, has good thermal stability. The melting temperatures of PEG in composite PCMs and PP/IPN phase change fibers has a little fluctuation, and the relevant data indicate that the latent heat enthalpy of the composite PCMs and fibers are slightly smaller than the theoretical value. Furthermore, damping performance of phase change fibers has been improved pure PP due to addition of IPN.

The PNHMPA/PEG interpenetrating polymer networks gel that prepared by our group could be encapsulated in the 3D PNHMPA network without any leakage, and could be suitable for processing at high temperature and high shear function.

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