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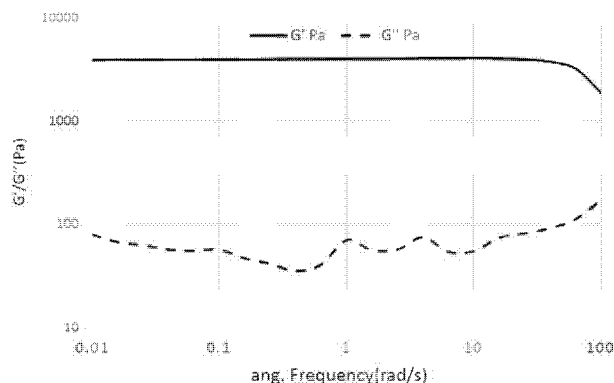


Fig. 1a

(57) Abstract: Provided is a gel obtained from: obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) a phase change material selected from the group consisting of urea, neopentyl glycol, KCl, and tertiary butanol, and iii) water.



## GEL COMPRISING PHASE CHANGE MATERIALS

### FIELD OF THE INVENTION

The present invention relates to a gel comprising phase change materials, in particular  
5 to a gel comprising phase change materials for low temperature control.

### INTRODUCTION

An external packaging system is often needed to provide a temperature range suitable  
for the storage and/or transport of temperature-sensitive materials, such as pharmaceuticals,  
biological samples, food, beverages and electronic products. One means to achieve the  
10 desirable temperature range is to incorporate phase change materials (PCMs), which have a  
phase change temperature within the desired temperature range, into the packaging systems.  
PCMs are generally in liquid state.

For some applications, the temperature needs to be controlled in the range of  $-20^{\circ}\text{C}$  to  
 $0^{\circ}\text{C}$ . For transportation of frozen food (such as fruits, vegetables, meats and dairy products),  
15 the temperature is required to be below  $-12^{\circ}\text{C}$ . For electronic products transported by  
railway in extremely cold areas, the temperature is required to be higher than  $-20^{\circ}\text{C}$ .  
However, commercially available PCMs for these applications often are in liquid state at  
room temperature, and solid-liquid phase change occurs with the temperature change. Such  
PCMs must be encased within closed containers, such as rigid bottles and polyethylene  
20 tubes, in which the package accounts for approximately 20-40% weight of the whole  
product. Even so, leakage would still happen if the package is damaged during storage or  
transportation.

There is a need to provide a novel article comprising PCM which can avoid the  
above-mentioned problems.

25

### SUMMARY OF THE INVENTION

The present disclosure provides a novel article comprising PCMs, which can avoid  
the above-mentioned problems. In particular, the article according to this present disclosure  
is light weight, a gel rather than liquid at room temperature, and can be used for low  
temperature control, for example in the range of  $-12$  to  $-20^{\circ}\text{C}$ .

In a first aspect, the present disclosure provides a gel obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) a phase change material selected from the group consisting of urea, neopentyl glycol, KCl, and tertiary butanol, and iii) water.

In a second aspect, the present disclosure provides a method for preparing a gel,  
5 comprising the steps: mixing a phase change material and water to form a solution; mixing the resultant solution with at least one hydrophilic polyurethane prepolymer to form a gel.

In a third aspect, the present disclosure provides a packaging article comprising a gel according to the present disclosure.

## 10 Drawings

Fig. 1a showed storage module and loss module versus angle frequency of Inventive example 3.

Fig. 1b showed storage module versus angle frequency of Inventive example 3 and Inventive example 1.

15 Fig. 2 showed temperature profile versus time at constant ambient temperature of -40°C in environmental chamber.

Fig. 3 showed temperature profiles versus time.

## DETAILED DESCRIPTION OF THE INVENTION

20 In a first aspect, the present disclosure provides a gel obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) a phase change material selected from the group consisting of urea, neopentyl glycol, KCl, and tertiary butanol, and iii) water.

In one embodiment of the present disclosure, the hydrophilic polyurethane prepolymer is an isocyanate-terminated prepolymer, and is the reaction product of (a) a  
25 polyether polyol having at least 30 wt% of oxyethylene groups, and (b) a di-functional isocyanate composition selected from the group consisting of a composition of a pure diisocyanate, a composition of diisocyanates, or a composition of a diisocyanate and a polyisocyanate.

The term “pure diisocyanate” refers to only one kind of di-functional isocyanate  
30 without considering how many isomers this kind of di-functional isocyanate may comprise.

The term “composition of diisocyanate” refers to at least two kinds of different di-functional isocyanate without considering how many isomers each kind of di-functional isocyanate may comprise.

The term “poly-functional isocyanate” refers to isocyanates with at least three  
5 functionalities, such as tri-isocyanate.

In another embodiment of the present disclosure, the polyether polyol has a nominal hydroxyl functionality of from 1.6 to 8, and a number average molecular weight of from 1,000 to 12,000.

In yet another embodiment of the present disclosure, the hydrophilic polyurethane  
10 prepolymer has a free NCO content of from 1 to 5 wt%, or from 1.5 to 3 wt%, based on the total weight of the hydrophilic polyurethane prepolymer.

Suitable polyols and isocyanates are commercially available or can be prepared using standard processes known to those skilled in the art.

Examples of suitable di-functional isocyanates include but are not limited to  
15 isophorone diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, mixtures of toluene-2,4- and 2,6-diisocyanate, ethylene diisocyanate, ethylidene diisocyanate, propylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, m-phenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate,  
20 1,6-hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,10-decamethylene diisocyanate, cumene-2,4-diisocyanate, 1,5-naphthalene diisocyanate, methylene dicyclohexyl diisocyanate, 1,4-cyclohexylene diisocyanate, p-tetramethyl xylylene diisocyanate, p-phenylene diisocyanate, 4-methoxy-1,3-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4-bromo-1,3 -phenylene diisocyanate, 4-ethoxy-1,3-phenylene  
25 diisocyanate, 2,4-dimethylene-1,3-phenylene diisocyanate, 5,6-dimethyl-1,3-phenylene diisocyanate, 2,4-diisocyanatodiphenylether, 4,4'-diisocyanatodiphenylether, benzidine diisocyanate, 4,6-dimethyl-1,3-phenylene diisocyanate, 9,10-anthracene diisocyanate, 4,4'-diisocyanatodibenzyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, 2,6-dimethyl-4,4'-diisocyanatodiphenyl, 2,4-diisocyanatostilbene, dimethoxy-4,4'-diisocyanatodiphenyl, 1,4-  
30 anthracenediisocyanate, 2,5-fluorenediisocyanate, 1,8-naphthalene diisocyanate, 2,6-diisocyanatobenzofuran, and mixtures thereof.

Examples of suitable poly-functional isocyanates include but are not limited to 2,4,6-toluene triisocyanate, p,p',p''-triphenylmethane triisocyanate, trifunctional trimer of isophorone diisocyanate, trifunctional biuret of hexamethylene diisocyanate, trifunctional trimer of hexamethylene diisocyanate and polymeric 4,4'-diphenylmethane diisocyanate, and mixtures thereof.

In one embodiment of the present disclosure, the polyether polyol and the diisocyanate are admixed at from 20 to 100°C, optionally in the presence of a urethane-forming catalyst such as a tin compound or a tertiary amine, for a time sufficient to form the hydrophilic polyurethane prepolymer. The ratio of the reactive functional groups of the polyol to the reactive functional groups of the isocyanate is sufficient to obtain the desired free NCO content, e.g. from 1 to 5 wt%, in the prepolymer, and can be readily calculated by one skilled in the art in order to determine how much polyol and isocyanate to employ in the preparation of the prepolymer.

Conventional additives, such as additives known in the art for use in forming prepolymers and polyurethanes, may be used in the preparation of the hydrophilic polyurethane prepolymer. For example, the composition for forming the hydrophilic polyurethane prepolymer may include at least one catalyst, at least one crosslinker, and/or at least one chain extender. Further information on the preparation of the hydrophilic polyurethane prepolymer may be found in US 2006/0142529 and US 2015/0087737.

Suitable common catalysts are substances generally known in the art for promoting the reaction of isocyanate with a polyol and includes basic substances such as sodium bicarbonate or the tertiary amines and organometallic compounds. Illustrative examples of suitable catalysts include n-methyl morpholine, n-ethyl morpholine, trimethylamine, tetramethyl butane diamine, triethylenediamine, dimethylaminoethanolamine, bezylidimethylamine, dibutyl tin dilaurate and stannous octoate.

Suitable examples of the cross-linker may include low molecular weight polyols typically having an average hydroxyl functionality of from 3 to 4, or low molecular weight amines having typically 3 or 4 amine moieties. Illustrative and preferred examples are glycerin, trimethylolpropane and low molecular weight alkoxyated derivatives thereof. Ethylene diamine is also commonly used although it is a less preferred amine crosslinking agent for use with the present invention. Such cross-linking agent may be present in an

amount of from 0.1 to 5, preferably from 0.5 to 3 and more preferably from 1 to 3 percent of the total amount by weight of polyether polyol.

Suitable examples of the chain extender may include low molecular weight hydroxyl and amine terminated compounds with functionality of 2. Illustrative and preferred examples  
5 are diethylene glycol, 1,4-butanediol, 1,6-hexanediol, ethanolamine, diethanolamine, methyl diethanolamine, etc.

The polyether polyol advantageously is a polyoxypropylene-polyoxyethylene polyol having a number average molecular weight of from 3,000 g/mole to 9,000 g/mole and a polyoxyethylene content of at least 30 wt.%, based on a total weight of the polyoxyethylene-  
10 polyoxypropylene polyol. The polyoxypropylene-polyoxyethylene polyol may have a nominal hydroxyl functionality from 1.6 to 8.0, e.g., from 1.6 to 4.0. In one embodiment of the invention, the remainder of the weight content of the polyoxyethylene-polyoxypropylene polyol based on a total of 100 wt.% is accounted for with polyoxypropylene, e.g., the polyoxypropylene content is at least 5 wt.% in the polyol. For example, the polyoxyethylene  
15 content advantageously is from 55 wt.% to 85 wt.%, from 60 wt.% to 80 wt.%, from 65 wt.% to 80 wt.%, from 70 wt.% to 80 wt.%, and/or from 74 wt.% to 76 wt.%, with the remainder being polyoxypropylene.

The polyether polyol may include at least one other polyether polyol other than the polyoxypropylene-polyoxyethylene polyol. The at least one other polyether polyol may have  
20 an average nominal hydroxyl functionality from 1.6 to 8, e.g., from 1.6 to 4.0, and a number average molecular weight from 1000 to 12,000, e.g., from 1,000 to 8,000, from 1,200 to 6,000, from 2,000 to 5,500, etc. Further, combinations of optional amines, and other polyether polyols including monohydroxyl substances and low molecular weight diol and triol substances, of varying functionality and polyoxyethylene content may be used in the  
25 composition for preparing the hydrophilic polyurethane prepolymer.

The polyether polyol may also include polyethylene glycol (also known as PEG and polyoxyethylene glycol). The polyethylene glycol may have a weight average molecular weight from 500 g/mol to 2000 g/mol, e.g., from 500 g/mol to 1500 g/mol, from 750 g/mol to 1250 g/mol, from 900 g/mol to 1100 g/mol, etc.

30 Advantageously, a hydrophilic polyurethane prepolymer having a positive amount of less than 5 wt.%, or less than 3 wt.%, isocyanate groups are employed to prepare the coolant

gel. In various embodiments of the invention, the hydrophilic polyurethane prepolymer has from 1 to 3 wt.%, from 1 to 5 wt.%, from 1.5 to 5 wt.%, or from 1.5 to 3 wt.%, free isocyanate groups. Advantageously, the hydrophilic polyurethane prepolymer is contacted with a stoichiometric excess of water to form the coolant gel. Mixtures of hydrophilic polyurethane prepolymers can be employed.

Various hydrophilic polyurethane prepolymers are known in the art. Useful prepolymers are available from The Dow Chemical Company under the HYPOL™ brand including, HYPOL JT6005 prepolymer and HYPOL 2060GS prepolymer. HYPOL JT6005 prepolymer is a TDI-based polyurethane prepolymer having an NCO content of 3.0% as determined by ASTM D 5155 and a viscosity at 23°C of 12,000 mPa·s as determined by ASTM D 4889. HYPOL 2060GS prepolymer is a TDI-based polyurethane prepolymer having an NCO content of 3.0% as determined by ASTM D 5155 and a viscosity at 23°C of 10,000 mPa·s as determined by ASTM D 4889.

In the present disclosure, the at least one hydrophilic polyurethane prepolymer may have a content of 1-15wt%, preferably 2-10wt%, more preferably 2-8wt%, most preferably 2-6wt%, based on the weight of the gel.

In the present disclosure, the phase change material may be selected from the group consisting of urea, neopentyl glycol, KCl, and tertiary butanol. Said urea, neopentyl glycol, KCl, or tertiary butanol may be commercially available.

In the present disclosure, the phase change material may have a content of 0.1-60wt%, preferably 0.5-50wt%, more preferably 1-40wt%, based on the weight of the gel.

In the present disclosure, said water may have a content of 40-95wt%, preferably 50-95wt%, more preferably 60-95wt%, based on the weight of the gel.

In one embodiment of the present disclosure, the ratio by weight between water to the at least one hydrophilic polyurethane prepolymer may be 5:1 to 28:1, preferably 10:1 to 20:1.

In the present disclosure, the gel may also be obtained by further adding additives. The examples of suitable additives include, but not limited to, water soluble polymers, fillers, defoamers and biocides. Examples of water soluble polymers include, but not limited to, polysaccharide, cellulose, polyacrylic acid or its salt, polyacryamide, and mixture thereof. Examples of defoamers include, but not limited to, silicone-based defoamers, mineral oil-based defoamers, ethylene oxide/propylene oxide-based defoamers, or mixtures thereof.

In the present disclosure, the additives may have a total content of 0.01-10wt%, preferably 0.05-5wt%, more preferably 0.1-1wt%, based on the weight of the gel.

In one embodiment of the present disclosure, the gel is free of thermally conductive filler. Examples of thermally conductive fillers are selected from the group consisting of  
5 oxide powders, flakes and fibers composed of aluminum oxide (alumina), zinc oxide, magnesium oxide and silicon dioxide; nitride powders, flakes and fibers composed of boron nitride, aluminum nitride and silicon nitride; metal and metal alloy powders, flakes and fibers composed of gold, silver, aluminum, iron, copper, tin, tin base alloy used as lead-free solder; carbon fiber, graphite flakes or fibers; silicon carbide powder; and calcium fluoride powder;  
10 and the like.

In a second aspect, the present disclosure provides a method for preparing a gel, comprising the steps: mixing a phase change material and water to form a solution; mixing the resultant solution with at least one hydrophilic polyurethane prepolymer to form a gel.

In the present disclosure, the above step of mixing a phase change material and water  
15 to form a solution may be carried out at 10 rpm to 5000 rpm, preferably 30 rpm to 2000rpm, more preferably 50 rpm to 500 rpm.

In the present disclosure, the above step of mixing a phase change material and water to form a solution may be carried out for 0.5 min to 60 min, preferably 1 min to 40 min, more preferably 5 min to 20 min.

20 In the present disclosure, the above step of mixing the resultant solution with at least one hydrophilic polyurethane prepolymer to form a gel may be carried out at 100 rpm to 5000 rpm, preferably 500 rpm to 3000rpm, more preferably 800 rpm to 2000 rpm.

In the present disclosure, the above step of mixing the resultant solution with at least one hydrophilic polyurethane prepolymer to form a gel may be carried out for 0.1 min to 30  
25 min, preferably 0.5 min to 10 min, more preferably 1 min to 5 min.

In one embodiment of the present disclosure, the above method may comprise the step of mixing a water soluble polymer with water to form a solution. This step of mixing a water soluble polymer with water may be carried out before or after the step of mixing a phase change material and water to form a solution. The solution obtained by mixing a water  
30 soluble polymer with water may be mixed with at least one hydrophilic polyurethane

prepolymer, separately or together with the solution obtained by mixing a phase change material and water.

In one embodiment of the present disclosure, the above method may comprise:

- (a) mixing a phase change material and water to form a solution;
- 5 (b) mixing a water soluble polymer with water;
- (c) combining the solution obtained in step (a) and the solution obtained in step (b) to obtain a solution; and
- (d) mixing the solution obtained in step (c) with at least one hydrophilic polyurethane prepolymer to form a gel.

10 In a third aspect, the present disclosure provides a packaging article comprising a gel according to the present disclosure.

In the present disclosure, the packaging article may be flexible. In one embodiment, the gel according to the present disclosure may be coupled with a barrier film to form the flexible wrapping material. In another embodiment, the packaging article may be rigid, for  
15 example, it may be a rigid box having the gel according to the present disclosure.

### EXAMPLES

Raw materials:

| Ingredients                                       | Suppliers                              |
|---------------------------------------------------|----------------------------------------|
| HYPOLJT6005 (hydrophilic polyurethane prepolymer) | The Dow Chemical Company               |
| Urea                                              | Sino Pharm Chemical                    |
| Neopentyl glycol (NPG)                            | Sino Pharm Chemical                    |
| Tertiary butanol (TBA)                            | Sino Pharm Chemical                    |
| Propylene glycol (PG)                             | Sino Pharm Chemical                    |
| KCl                                               | Sino Pharm Chemical                    |
| Tiguar 415 Guar 2-hydroxypropyl ether (HPG)       | Shree Ram Industries, Rajasthan, India |

### Example 1: Gel Preparation

#### 1. Water phase preparation

Polymer solution preparation: HPG powder was added into water during stirring at  
5 about 500 rpm. Then the stirring continued for 1 hour until the polymer was dissolved completely.

Solution preparation: the phase change material was added into water with stirring at 100 rpm for 8 min to for a clear solution.

Water phase preparation: water phase was prepared by mixing the polymer solution  
10 and the solution together under stirring at 500 rpm for about 10min.

If the HPG powder was not used, the solution was used directly as the water phase.

#### b) Gel preparation

HYPOL JT6005 was mixed with the prepared water phase under stirring at 1000 rpm  
for 2 min to form a gel.

15

### Example 2: Mechanical properties

The gels were prepared according to the method as described in the above example 1. The components and their amounts were listed in Table 1 below. The gels can be obtained using HYPOL as gelling agent, and the liquid was well trapped within the gel matrix without  
20 leakage. The gels were flexible and bendable at room temperature.

Rheological measurements were conducted on a TA instrument (AR 2000ex) equipped with a 20mm steel plate geometry. Frequency sweep was from 0.1 to 100 Hz at 0.2% strain. The modulus changed with time and temperature was decreased from 30°C to -15°C, the heating rate was 3 °C/min, while the strain was 0.2% and angular frequency was 6.28  
25 rad/s.

Fig. 1a showed storage module and loss module versus angle frequency of Inventive example 3, and Fig. 1b showed storage module versus angle frequency of Inventive example 3, (1), and Inventive example 1, (2). As shown in Fig. 1a and Fig.1b, the behavior of the gels was solid-like rather than liquid-like, proving that cross-linked network was formed within  
30 the gels.

**Table 1**

| Examples              | Formulation |      |       |        |              | Gel formation? |
|-----------------------|-------------|------|-------|--------|--------------|----------------|
|                       | Solute      | HPG  | Water | JT6005 | Total weight |                |
| Inventive Example 1   | NPG 25g     | 0.6g | 69.5g | 4.9g   | 100.0g       | Yes            |
| Inventive Example 2   | TBA 25g     | 0.6g | 69.6g | 4.8g   | 100.0g       | Yes            |
| Inventive Example 3   | Urea 30g    | 0.5g | 64.5g | 5.0g   | 100.0g       | Yes            |
| Inventive Example 4   | Urea 32.4g  | /    | 60.7g | 6.9g   | 100.0g       | Yes            |
| Inventive Example 5   | KCl 1.7g    | 0.6g | 92.7g | 5.0g   | 100.0g       | Yes            |
| Comparative Example 1 | /           | /    | 94.0g | 6.0g   | 100.0g       | Yes            |
| Comparative Example 2 | PG 86.0g    | /    | 10.0g | 4.0g   | 100.0g       | No             |
| Comparative Example 3 | Urea 32.4g  | 0.6g | 67.0g | 2.3g   | 102.3g       | No             |
| Comparative Example 4 | NaCl 20g    | 0.6g | 74.3g | 5.1g   | 100.0g       | No             |

Example 3: Performance as gel of PCM

5            1000g of the gel or a commercial liquid PCM (comprising 1000g of a phase change material) (Shenzhen Fresh Cold Chain Co., Ltd; Product x005) was evaluated for the temperature control performance in an ESPEC environmental chamber (ESPEC CORP. Japan, Model PL-2J).

10           Firstly, the temperature control performance of the gel or the commercial liquid PCM was evaluated at constant low temperature of -40°C. The gel or the commercial liquid PCM was put in an incubator at room temperature, and a Bluetooth temperature sensor was put on the surface of the gel or the commercial liquid PCM to monitor and record the temperature change against time. The incubator was sealed and put in the environmental chamber immediately. The temperature of the environmental chamber was firstly decreased from  
15           room temperature to -40°C within around 1 hour, and was then kept for more than 24 hours.

Then the temperature profiles of the chamber and the PCM gel were monitored and recorded in Fig.2.

Fig. 2 showed temperature profile versus time at constant ambient temperature of  $-40^{\circ}\text{C}$  in environmental chamber, in which the curve (a) represented environmental chamber temperature, the curve (b) represented the temperature of the commercial liquid PCM, the curve (c) presented the temperature of Inventive example 1, and the curve (d) represented the temperature of Inventive example 3.

As shown in Fig. 2, as the environmental temperature dropped quickly from  $20^{\circ}\text{C}$  to  $-40^{\circ}\text{C}$  within one hour, the temperatures of commercial liquid PCM and the gels decreased gradually due to heat exchange, but with much lower cooling rate (as shown in Figure 3 area “A”). In the second to sixth hour (as shown in Figure 2, area “B”), the temperature of the commercial liquid PCM or the gel continued to drop down at similar cooling rate as in area “A”. After that, a temperature plateau was achieved, which showed the phase change, and released a large amount of latent heat. The PCM’s phase change temperature was maintained in the environment of  $-40^{\circ}\text{C}$  (as shown in Figure 2, area “C”). The phase change temperature and duration time above  $-20^{\circ}\text{C}$  were listed in Table 2 below.

**Table 2**

| Examples              | Phase change temperature ( $^{\circ}\text{C}$ ) | Latent heat(J/g) | Duration time above $-20^{\circ}\text{C}$ (hour) |
|-----------------------|-------------------------------------------------|------------------|--------------------------------------------------|
| Inventive Example 1   | -12.2                                           | 248              | 19.9                                             |
| Inventive Example 3   | -16.4                                           | 280              | 25.2                                             |
| Comparative Example 5 | -15.0                                           | 288              | 24.9                                             |

Example 4: Performance as gel of PCM

Example 3 was repeated, except that the temperature was controlled as follows: the temperature of the environmental chamber was decreased from room temperature to 0°C, and then to -11°C within 24 hours; the temperature was further decreased from -11°C to -15°C in 24 hours; then the temperature was decreased from -15°C to -33°C in 24 hours; and then the temperature was decreased from -33°C to -35°C in 24 hours.

Figure 3 showed temperature profiles versus time, in which the curve (a) represented the temperature of the environmental chamber, the curve (b) represented the temperature of the commercial liquid PCM, and the curve (c) represented the temperature of Inventive example 3.

As shown in Figure 3, as the temperature of the environmental chamber reached -20°C (point “A” in Figure 3), and further decreased to -35°C (point “B” in Figure 4) at various cooling rates, the temperature of the gel or the commercial liquid PCM still maintained well above -20°C, with a duration time above -20°C of ~30 hours. See Table 3 below.

**Table 3**

| Examples                 | Duration time above -20°C (hour) as environmental temperature dropped below -20°C |
|--------------------------|-----------------------------------------------------------------------------------|
| Inventive Example3       | ~30                                                                               |
| Comparative Example<br>5 | ~30                                                                               |

#### 20 Example 5: Freeze-thaw stability

The gels of Inventive Examples 1-5 and Comparative Example 1 in Ziploc bags were first frozen at -20°C, and then kept at room temperature to thaw. After thaw, it was observed whether there was liquid leakage from the gel. Then the above freeze-thaw process was repeated for 10 cycles. The results were listed in Table 4 below.

**Table 4**

| Examples              | Freeze-thaw stability (liquid leakage upon thaw?) |
|-----------------------|---------------------------------------------------|
| Inventive Example1    | Stable as gel, no leakage                         |
| Inventive Example2    | Stable as gel, no leakage                         |
| Inventive Example3    | Stable as gel, no leakage                         |
| Inventive Example4    | Stable as gel, no leakage                         |
| Inventive Example5    | Stable as gel, no leakage                         |
| Comparative Example 1 | Liquid, leakage                                   |

According to the above examples, the PCMs according to the present disclosure were  
5 combined together with HYPOL hydrophilic polyurethane prepolymer to form a gel. On the one hand, the gel according to the present disclosure can be used in a low temperature condition, such as -12°C to -20°C. On the other hand, the resultant gel could be leak-proof and avoid the risk of contamination to the temperature sensitive materials.

What is claimed is:

1. A gel obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) a phase change material selected from the group consisting of urea, neopentyl glycol, KCl, and tertiary butanol, and iii) water.

2. The gel according to claim 1, wherein the at least one hydrophilic polyurethane prepolymer is an isocyanate-terminated prepolymer which is the reaction product of at least (a) a polyether polyol having at least 30 wt.% of oxyethylene groups, and (b) a diisocyanate composition selected from the group consisting of a composition of a pure diisocyanate, a composition of diisocyanates, or a composition of a diisocyanate and a polyisocyanate.

3. The gel according to claim 1, wherein the at least one hydrophilic polyurethane prepolymer has a content of 1-15wt%, based on the weight of the gel.

4. The gel according to claim 1, wherein the phase change material has a content of 0.1-60wt%, based on the weight of the gel.

5. The gel according to claim 1, wherein said water has a content of 40-95wt%, based on the weight of the gel.

6. The gel according to claim 1, wherein the gel further comprises additives selected from the group consisting of water soluble polymers, fillers, defoamers and biocides.

7. A method for preparing a gel, comprising the steps: (a) mixing a phase change material and water to form a solution; and (b) mixing the resultant solution with at least one hydrophilic polyurethane prepolymer to form a gel.

8. The method according to claim 7, further comprising a step (c) of mixing a water soluble polymer with water to form a solution.

9. A packaging article comprising a gel according to any one of claims 1-6.

10. Usage of a gel according to any one of claims 1-6 in a low temperature control in the temperature range of -12°C to -20°C.

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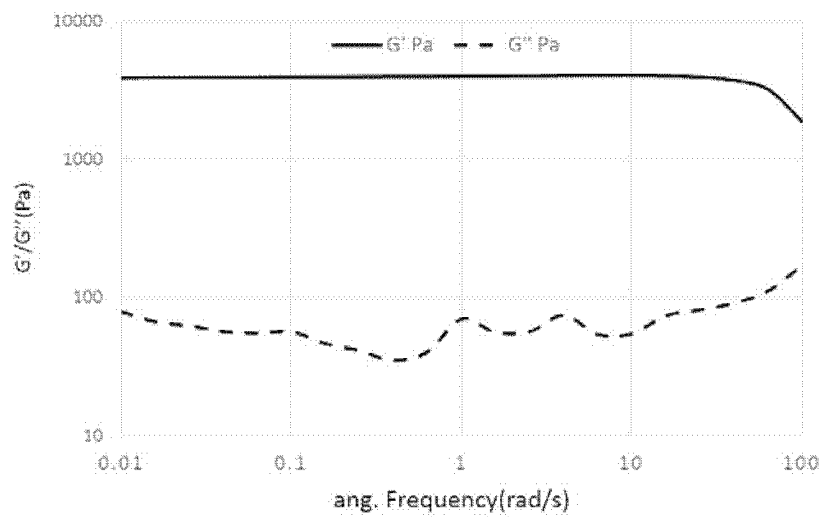


Fig. 1a

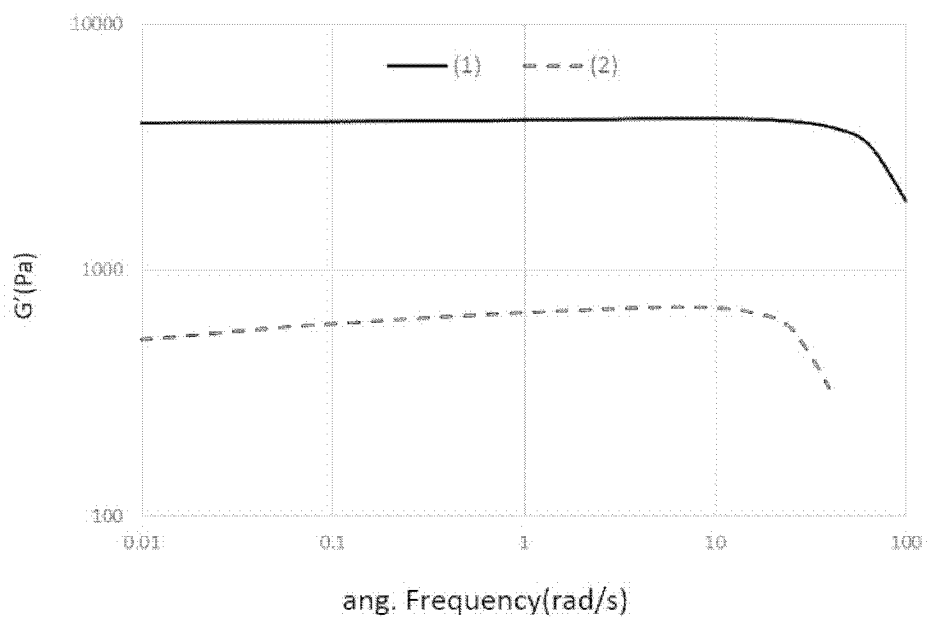


Fig. 1b

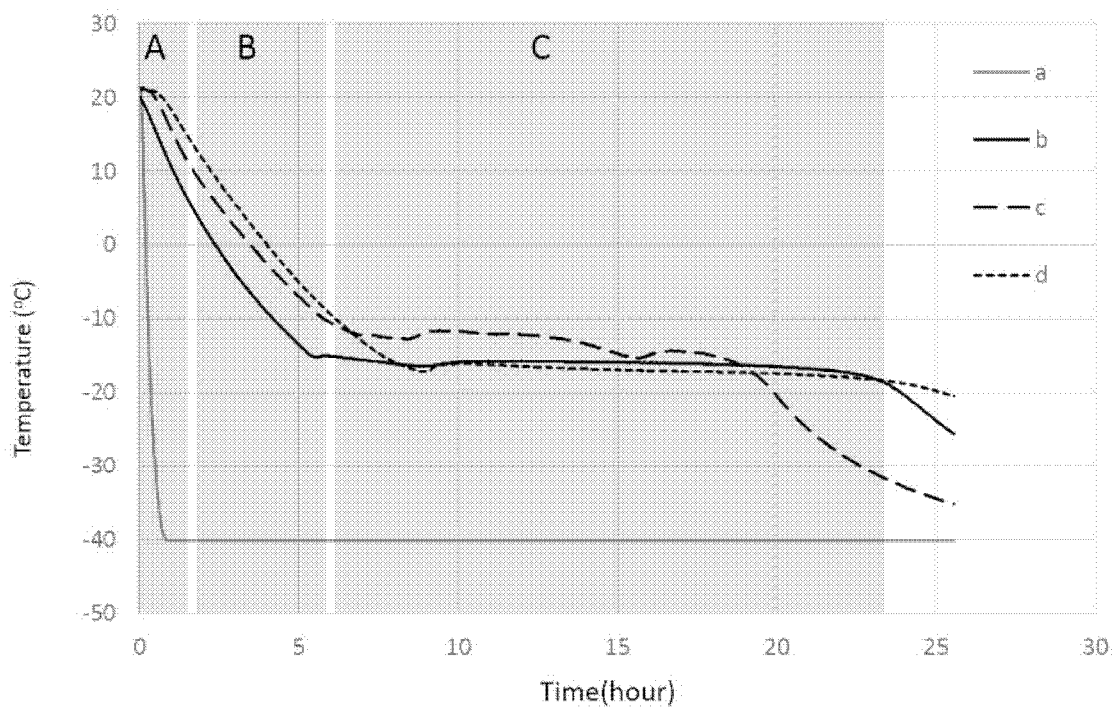


Fig. 2

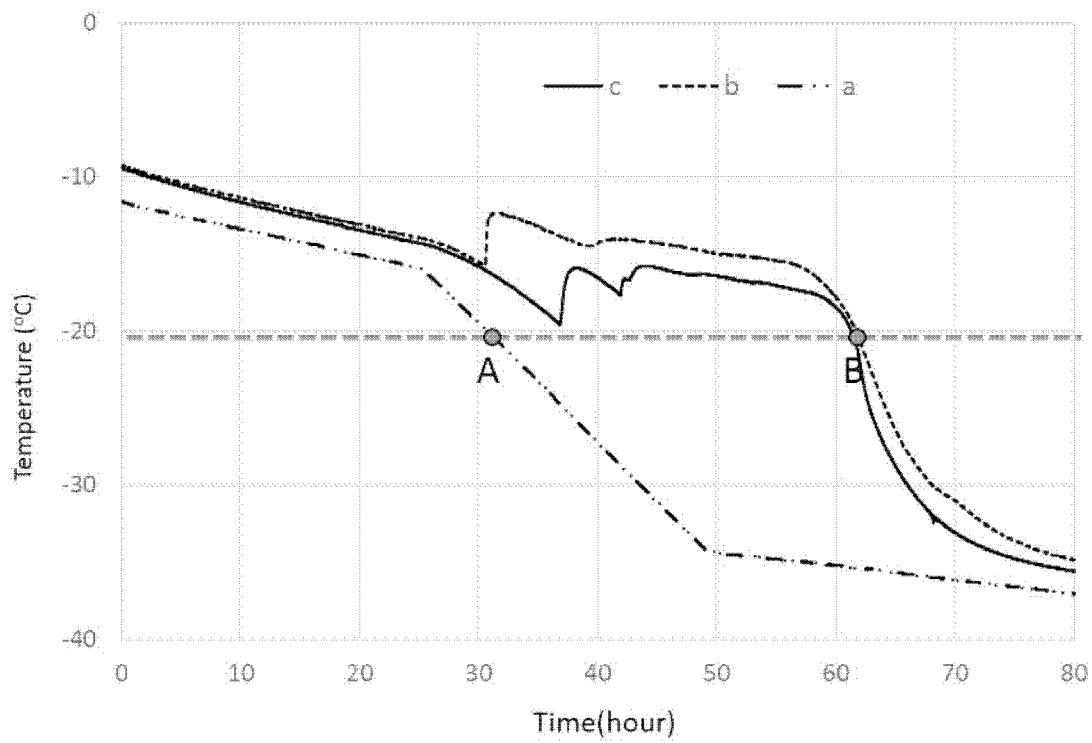


Fig. 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/110589

**A. CLASSIFICATION OF SUBJECT MATTER**

C08L 75/00(2006.01)i; C08L 75/04(2006.01)i; C08L 75/08(2006.01)i; C08L 101/14(2006.01)i; C08L 101/12(2006.01)i;  
C08K 3/10(2018.01)i; C08K 3/16(2006.01)i; C08K 5/05(2006.01)i; C08K 5/053(2006.01)i; C08K 5/205(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C08L 75/-; C08L 101/-; C08K 3/-; C08K 5/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI, SIPOABS, CNABS, CNKI, CNTXT, gel, phase, change, PCM, hydrophilic, polyurethane, aqueous, water, solution, urea, carbamide, KCL, potassium, chloride, neopentyl, glycol, dimethyl, propanediol, dimethylpropane, diol, tertiary, butanol, methyl, propanol, butyl, alcohol, package

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                            | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------|-----------------------|
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance  
“E” earlier application or patent but published on or after the international filing date  
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
“O” document referring to an oral disclosure, use, exhibition or other means  
“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
“&” document member of the same patent family

Date of the actual completion of the international search

**11 February 2019**

Date of mailing of the international search report

**22 February 2019**

Name and mailing address of the ISA/CN

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## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CN2018/110589****C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2018/110589**

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