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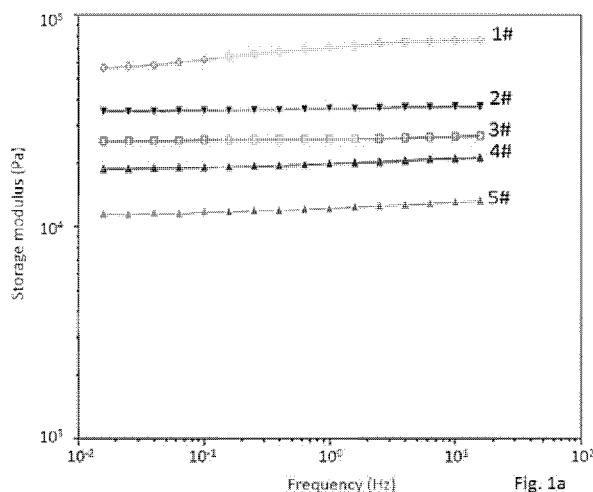
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(54) Title: GEL COMPRISING HYBRID PHASE CHANGE MATERIALS



(57) Abstract: Provided is a gel obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) an organic phase change material comprising one or more alkanes, iii) an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt, and iv) a surfactant.

GEL COMPRISING HYBRID PHASE CHANGE MATERIALS

FIELD OF THE INVENTION

The present invention relates to a gel comprising hybrid phase change materials, in particular to a gel comprising a dispersion of hybrid phase change materials.

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 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.

A known PCM is water with a phase change temperature of 0°C. For a desired temperature range of 0°C or below, an aqueous solution of an inorganic salt, with a eutectic composition, is typically used. For a desired temperature range of 0°C or greater, a hydrate of an inorganic salt, and an organic PCM, such as paraffins, fatty acids and alcohols, are generally used.

Although a solution of an inorganic salt or a hydrate of an inorganic salt has relatively low cost, and shows good thermal conductivity and latent heat, it causes a lot of problems, such as phase separation, poor cycling stability, sub-cooling, considerable volume change (e.g., up to 10 vol%), and corrosion to external packages (e.g., metals). On the other hand, although organic PCMs have some problems such as lower latent heat, lower thermal conductivity and considerable volume change, they show good compatibility with metals, little or no sub-cooling, no phase separation and good cycling stability. Generally, the inorganic and organic PCMs are not compatible, so they are used singly.

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

SUMMARY OF THE INVENTION

The present disclosure provides a novel article comprising PCMs, which can avoid the above-mentioned problems.

In a first aspect, the present disclosure provides a gel obtained from: i) at least one hydrophilic polyurethane prepolymer, ii) an organic phase change material comprising one or more alkanes, iii) an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt, and iv) a surfactant.

5 In a second aspect, the present disclosure provides a method for preparing a gel, comprising the steps: mixing an organic phase change material, an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt and a surfactant to form a dispersion; mixing the resultant dispersion 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.

Drawings

Fig. 1a showed storage module versus angle frequency curves of the gels of Inventive Examples 1#-5# at room temperature.

Fig. 1b showed storage module-angle versus temperature curves of the gels of Inventive Examples 6# and 7#.

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) an organic phase change material comprising one or more alkanes, iii) an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt, and iv) a surfactant.

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

30 The term “pure diisocyanate” refers to only one kind of di-functional isocyanate 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, methyldiethanolamine, 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-polyoxypropylene polyol. The polyoxypropylene-polyoxyethylene polyol may have a
10 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 organic phase change material comprising one or more alkanes may be a conventional one in the art. In one embodiment, the alkane comprises 4 to 50 carbon atoms, preferably 5 to 40 carbon atoms, more preferably 8 to 35 carbon atoms, most preferably 10 to 30 carbon atoms. In another embodiment, the alkane comprises, but not limited to, tetradecane, hexadecane, heptadecane, dodecane and octadecane, eicosane, triacontane, or mixtures thereof. In another embodiment, the alkane comprises, but not limited to, n-tetradecane, n-hexadecane, n-heptadecane, n-dodecane and n-octadecane, n-eicosane, n-triacontane, or mixtures thereof.

In the present disclosure, the organic phase change material comprising one or more alkanes may have a content of 10-80wt%, preferably 15-70wt%, more preferably 20-60wt%, based on the weight of the gel.

In the present disclosure, the organic phase change material may further comprise an additional phase change material selected from the group consisting of a fatty acid, a fatty acid ester and an alcohol. In one embodiment, said fatty acid comprises 4 to 30 carbon atoms, preferably 6 to 25 carbon atoms, more preferably 10 to 20 carbon atoms. Suitable examples

of fatty acids include, but not limited to, hexylic acid, palmitic acid, stearic acid and the like. In one embodiment, said fatty acid ester comprises a fatty acid moiety having 4 to 30 carbon atoms, preferably 6 to 25 carbon atoms, more preferably 10 to 20 carbon atoms. Suitable examples of fatty acid esters include, but not limited to, glycerin ester of palmitic acid, stearic acid and the like. In one embodiment, said alcohol includes, but not limited to, ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol, glycerin, water soluble polyol like polyethylene glycol, and any combination thereof.

In the present disclosure, the additional phase change material selected from the group consisting of a fatty acid, a fatty acid ester and an alcohol has a content of 0-40wt%, preferably 1-30wt%, more preferably 10-30wt%, based on the weight of the gel.

In one embodiment, the inorganic phase change material according to the present disclosure may be water. In another embodiment, the inorganic phase change material may be an aqueous solution of an inorganic salt.

The inorganic salt according to the present disclosure may be the conventional phase change materials in the art. Suitable examples of the inorganic salt include, but not limited to, chlorides (such as NaCl and KCl), carbonates, sulfates and the like.

In the present disclosure, the inorganic phase change material may have a content of 5-70wt%, preferably 10-60wt%, more preferably 20-50wt%, based on the weight of the gel.

In the present disclosure, the surfactant may be conventional in the art. Generally, the surfactant comprises a cation surfactant, an anion surfactant and a non-ionic surfactant. In one embodiment, the surfactant is preferably a non-ion surfactant, including, but not limited to, poly(ethylene oxide)-based non-ionic surfactant and glycol-based non-ionic surfactant. Examples of non-ionic surfactants include, but not limit to, ECOSUR™ available from The Dow Chemical Company.

In the present disclosure, the surfactant may have a content of 0.1-10wt%, preferably 0.5-8wt%, more preferably 1-5wt%, based on the weight of the gel.

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.

5 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 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
10 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; and the like.

 In a second aspect, the present disclosure provides a method for preparing a gel, comprising the steps: mixing an organic phase change material, an inorganic phase change
15 material selected from the group consisting of water and an aqueous solution of an inorganic salt and a surfactant to form a dispersion; mixing the resultant dispersion with at least one hydrophilic polyurethane prepolymer to form a gel.

 In the present disclosure, the above step of mixing an organic phase change material, an inorganic phase change and a surfactant may be carried out under stirring at 100-5000 rpm,
20 preferably 200-3000 rpm, more preferably 300-2000 rpm.

 In the present disclosure, the above step of mixing an organic phase change material, an inorganic phase change and a surfactant may be carried out under stirring for 1-120 min, preferably 5-60 min, more preferably 10-30 min.

 In the present disclosure, the above step of mixing the resultant dispersion with at
25 least one hydrophilic polyurethane prepolymer may be carried out under stirring at 100-5000 rpm, preferably 200-3000 rpm, more preferably 300-2000 rpm.

 In the present disclosure, the above step of mixing the resultant dispersion with at least one hydrophilic polyurethane prepolymer may be carried out under stirring for 0.1-60 min, preferably 0.5-30 min, more preferably 0.5-10 min.

30 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 example, it may be a rigid box having the gel according to the present disclosure.

5

EXAMPLES

Raw materials:

Category	Ingredients	Suppliers
Gelling agent	HYPOL JT6005 (hydrophilic polyurethane prepolymer)	The Dow Chemical Company
	Sodium polyacrylate (A190)	mitsui Co., Ltd
	LAPONITE RD clay (RD)	Rockwood Additives Ltd.
Phase change material	n-tetradecane	Sino Pharm Chemical Reagent Co., Ltd. Shanghai, China.
	Propylene glycol	The Dow Chemical Company
Surfactant	ECOSURF™ SA-9	The Dow Chemical Company
Water soluble polymer	Tiguar 415 Guar 2-hydroxypropyl ether (HPG)	Shree Ram Industries, Rajasthan, India

Example 1: Gel Preparation

10

1. Preparation of PCM dispersion

The PCM dispersion was first prepared by mixing water, a surfactant and phase change material(s) under stirring at 800 rpm for about 20 min.

2. Preparation of gel

HYPOL JT6005 was mixed with the prepared PCM dispersion under stirring at
15 1000rpm for 2 min to form a gel.

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.

As a comparative example, the formulation in Table 2 was tried to form a gel, but it failed.

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 rad/s.

Fig. 1a showed storage module versus angle frequency curves of the gels of Inventive Example 1#-5# at room temperature, and Fig. 1b showed storage module-angle versus temperature curves of the gels of Inventive Example 6# and 7#. As shown in Fig. 1a and 1b, the behavior of the gels was solid-like rather than liquid-like, proving that cross-linked network was formed within the gels. Moreover, the storage modulus of the gels was also measured during temperature change from 30 to -15°C. As shown in Fig. 1b, the storage modulus of the gels was almost independent on temperature change before the phase change, while it increased significantly after phase change.

Table 1 Formulations and modulus of gels at room temperature

Examples	Formulation					Storage modulus
	Tetradecane	Water	PG	SA-9 20% solution	HYPOL JT 6005	
Inventive Example 1#	59.1g	19.2g	12.8g	3.7g	5.4g	56 kPa
Inventive Example 2#	42.2g	29.7g	19.8g	3.7g	4.7g	35 kPa
Inventive Example 3#	59.5g	19.3g	12.9g	3.7g	4.7g	25 kPa
Inventive Example 4#	23.8g	41.1g	27.4g	3.7g	4.0g	19 kPa
Inventive Example 5#	43.1g	30.4g	20.2g	3.7g	2.7g	12 kPa
Inventive Example 6#	42.0g	49.0g	0g	3.7g	5.3g	65 kPa
Inventive Example 7#	42.1g	30.4g	20.0g	3.7g	3.8g	2 kPa

Table 2 Formulation of comparative example

Examples	Formulation					Storage modulus
	Tetradecane	Water	PG	SA-9 20 wt% solution	Gelling agent	
Comparative Example 1#	42.1g	32.7g	20.0g	3.7g	1.2g Clay, 0.3g A190	Could not form gel

5 Example 3: Thermal conductivity

The gel was prepared according to the method as described in the above example 1.

The components and their amounts were listed in Table 3 below.

Thermal conductivity was measured by Hot Disk® Thermal constants analyzer (Model 2700 Multimeter/Data Acquisition System).

10 Thermal conductivity of n-tetradecane was only 0.15 W/m·K. While n-tetradecane was added into the gel with water, the thermal conductivity was significantly increased to 0.42 W/m·K (Inventive Example 6# in Table 3).

Table 3 Thermal conductivity

Formulation	Thermal conductivity (W/m·K)
Comparative Example 2# (n-tetradecane)	0.15
Inventive Example 6#	0.42

15

Example 4: Cold release profile

The gels of Inventive Examples 8# and 9# were prepared according to the method as described in the above example 1. The components and their amounts were listed in Table 4 below.

20 The gels of Inventive Examples 8# and 9# as well as commercial products of Comparative Examples 3# (the main ingredient of the PCM is n-tetradecane, available from

Hangzhou RUHR New Material Technology Co. Ltd as product OP5E) and 4# (the PCM is water absorbed in the super water absorption resin grains, available from Shenzhen Fresh Cold Chain Co., Ltd in the form of ice pack) were first kept in a refrigerator at -20°C for a certain period of time to allow the temperature of the gel drop from room temperature to -20°C, upon which cooling phase change was happened. The PCMs changed from liquid to solid state, with the cold stored simultaneously.

Then the frozen gels and commercial products were put in incubators at room temperature, and Bluetooth temperature sensors were put on the surfaces of the gels and the commercial products to monitor and record the temperature change along with time. Then, the incubators were sealed immediately.

The duration time of temperature below 8°C was recorded and listed in Table 5 below. As shown in Table 5, when the cold storage time at -20°C was 6 hours, the duration time below 8°C of the gel of Inventive Example 8# was 29.1 hours, significantly longer than those of commercial products, which were 21.8 hours for Comparative Example 3# and 15.9 hours for Comparative Example 4#. As cold storage time at -20°C was increased to 8, 10 or 12 hours, respectively, the duration time below 8°C of the gels of Inventive Example 8# or 9# was still longer than commercial products, as shown in Table 5.

In addition, as shown in Table 5, even with lighter weight, the gel of Inventive Example 9# (518g) still showed longer duration time below 8°C than those of Comparative Examples 3# and 4#.

Table 4 cold release measurement

Examples	Formulation					Total weight	Latent heat
	Tetradecane	Water	SA-9 20% solution	HPG	JT 6005		
Inventive Example 8#	183.2g	662.3g	22.9g	4.6g	43.1g	916g	265 J/g
Inventive Example 9#	103.6g	374.5g	13.0g	2.6g	24.4g	518g	265 J/g

Comparative Example 3#	Commercial oil PCM bottle	903g	220 J/g
Comparative Example 4#	Commercial ice bag	925g	291 J/g

Table 5 Duration time below 8°C

Cold storage time at -20°C Duration time ≤ 8°C	6 hours	8 hours	10 hours	12 hours
Inventive Example 8#	29.1 hours	37.7 hours	37.2 hours	37.8 hours
Inventive Example 9#	/	24.5 hours	/	/
Comparative Example 3#	21.8 hours	21.1 hours	21.7 hours	21.2 hours
Comparative Example 4#	15.9 hours	20.6 hours	26.7 hours	33.2 hours

5 Example 5: Freeze-thaw stability

The gels of Inventive Examples 2# and 8# in ziplock bags were first frozen at -20°C, and then kept at room temperature to thaw. Then the above freeze-thaw process was repeated for 10 cycles. The commercial product of Comparative Example 3# was also subjected to freeze-thaw cycling following the same procedure. The results were listed in Table 6 below.

10

Table 6 Stability upon 10 freeze-thaw cycles

	Liquid PCM release upon package broken?
Inventive Example 2#	No
Inventive Example 8#	No
Comparative Example 3#	Yes

15 According to the above examples, inorganic and organic PCMs according to the present disclosure were combined together with HYPOL hydrophilic polyurethane prepolymer to form a gel. On one hand, the hybrid PCMs achieved synergistic effects such

as longer temperature control, longer cold/heat release and higher efficiency with less weight. 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) an organic phase change material comprising one or more alkanes, iii) an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt, and iv) a surfactant.

2. The gel according to claim 1, wherein the 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 one or more alkanes comprise 4 to 50 carbon atoms.

4. The gel according to claim 1, wherein the organic phase change material further comprises an additional phase change material selected from the group consisting of a fatty acid, a fatty acid ester and an alcohol.

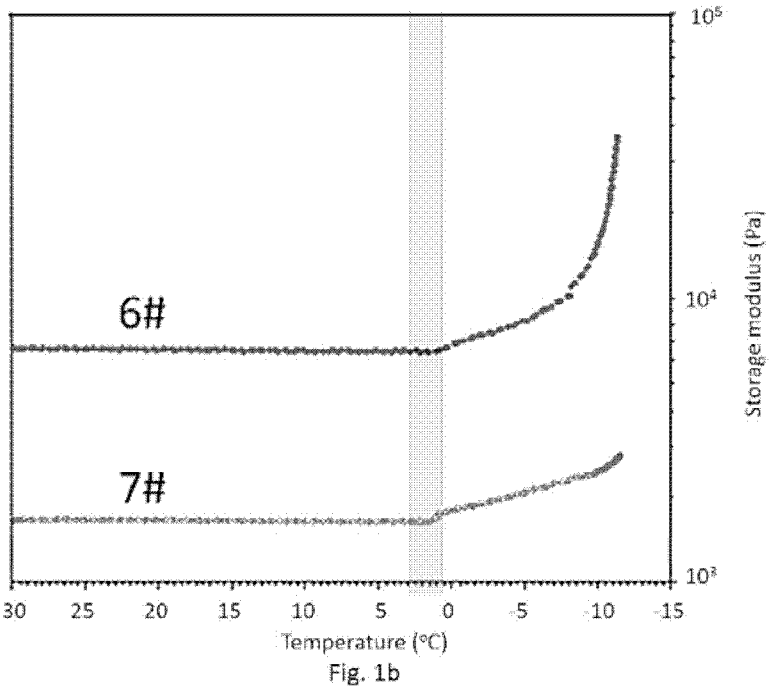
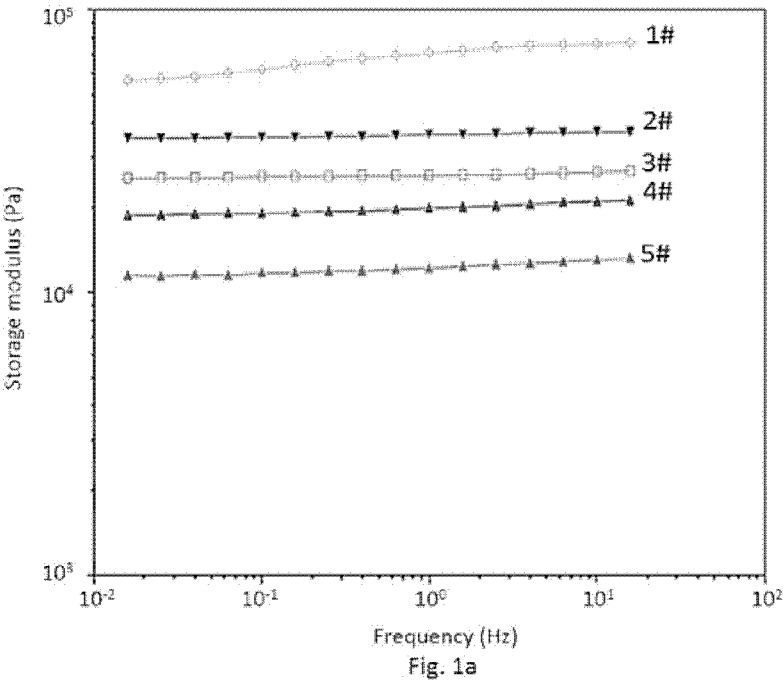
5. The gel according to claim 1, wherein the inorganic phase change material is water.

6. The gel according to claim 1, wherein the inorganic salt is selected from the group consisting of chlorides, carbonates and sulfates.

7. The gel according to claim 1, wherein the surfactant comprises a non-ionic surfactant.

8. A method for preparing a gel, comprising the steps: mixing an organic phase change material, an inorganic phase change material selected from the group consisting of water and an aqueous solution of an inorganic salt and a surfactant to form a dispersion; and mixing the resultant dispersion with at least one hydrophilic polyurethane prepolymer to form a gel.

9. A packaging article comprising a gel according to any one of claims 1-7.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/110590

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 5/01(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, organic, alkane, inorganic, salt, surfactant, package

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 101503617 A (UNIV CHINA SCI & TECHNOLOGY) 12 August 2009 (2009-08-12) see the whole document	1-9
A	CN 101555401 A (CHINESE ACAD SCI CHEM INST) 14 October 2009 (2009-10-14) see the whole document	1-9
A	CN 107090075 A (TECHNOGEL ITAL SRL) 25 August 2017 (2017-08-25) see the whole document	1-9
A	CN 101455856 A (UNIV SHENZHEN TSINGHUA ACAD) 17 June 2009 (2009-06-17) see the whole document	1-9
A	CN 102321452 A (UNIV XINJIANG) 18 January 2012 (2012-01-18) see the whole document	1-9
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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

12 February 2019

Date of mailing of the international search report

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/110590**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/110590

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