

A Composition And A Composite Material

References to Related Application

- 5 This application claims priority to Singapore application number 10202201482V filed with the Intellectual Property Office of Singapore on 16 February 2022, the contents of which are hereby incorporated by reference.

Technical Field

- 10 The present invention generally relates to a composition comprising at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte, wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule. The present invention further relates to a composite material, a method of forming the same and a capacitor comprising the same.

Background Art

- 15 Super-capacitor are capacitors with much higher capacitance than electrolytic capacitors. Electro-chemical super-capacitor typically consist of two electrodes separated by an ion-permeable membrane and an electrolyte ionically linking both electrodes.

- 20 Conventional super-capacitors employ either a polar organic solvent or water as an electrolyte and metal hydroxide as mobile ionic species dispersed within the electrolyte. However, the polar organic solvents in the conventional super-capacitors are highly flammable, while water possesses a narrow electro-chemical window (ECW), which makes it vulnerable to electrolysis.

- 25 Another convention super-capacitor includes an ionic liquid (IL) bounded and integrated within a polymeric thermo-plastic matrix, which is utilized as a freestanding, semisolid electrolyte film. Under an electrical potential, the negative ions of the IL would migrate to the positive electrode, while the positive ions would migrate to the negative electrode. These polymer-IL based super-capacitor electrolytes are typically prepared by dispersing a polar thermoplastic polymer precursor (e.g., polyvinyl alcohol, polyvinyl pyrrolidone and polyacrylamide) into a polar solvent that is irritant, toxic and/or carcinogenic (e.g. DMF, NMP), together with an ionic liquid (e.g., 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). However, this conventional super-capacitor possesses very low ion conductivity and poor mechanical properties (e.g., leaky and tacky). When IL is integrated within the thermoplastic matrix, they take up position
35 in between the polymer chains. As these chains are held together via weak Van der Waals intermolecular forces, which could be easily overcome, IL may leach out of

the super-capacitor when stressed either mechanically or thermally. The ion conductivities of these thermoplastic-IL are anisotropic (e.g., higher conductivity measured lateral to the polymer chains). The leaching of IL out of the electrolyte film causes the electrolyte ion conductivity to degrade overtime. Furthermore, due to similar polar nature of the ionic liquid and the polar polymer matrix, the mobility of the ionic liquid molecules would be hindered. This is due to attractive transient ion-dipole interaction between IL and polar groups of the polymer matrix resulting in a poor electrical conductivity when a potential is applied. Thus, the development of a super-capacitor system with both superior ion conductivity and mechanical property is an area of opportunity worthy of detailed investigation.

Accordingly, there is a need for a composite material for super-capacitor that ameliorates one or more disadvantages mentioned above.

Summary

There is provided a composition comprising at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte, wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule.

In one aspect, there is provided a composition comprising at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte, wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule, wherein the at least one cross-linker is selected from triethylenetetramine or tetraethylenepentamine, and wherein the at least one chain extender comprises at least three ethoxy groups, propyloxy groups, or a combination thereof.

There is provided a method of forming a composite material, comprising the steps of:

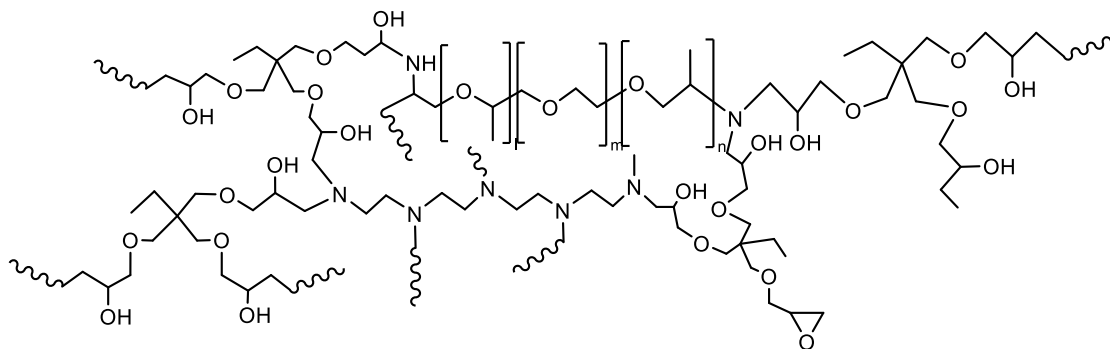
- (a) mixing at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte to form a composition; and
- (b) curing the composition of step (a) in a silicone to form the composite material.

In another aspect, there is provided a method of forming a composite material, comprising the steps of:

- (a) mixing at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte to form a composition; and
- (b) curing the composition of step (a) to form the composite material,

wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule, wherein the at least one cross-linker is selected from triethylenetetramine or tetraethylenepentamine, and wherein the at least one chain extender comprises at least three ethoxy groups, propyloxy groups, or a combination thereof.

- 5 In another aspect, there is provided a composite material having a polymeric network comprising a plurality of moieties, each moiety independently having a formula of:



wherein:

each wavy bond represents a site of cross linking to another moiety;

- 10 l is an integer in the range of 2 to 4;
m is an integer in the range of 6 to 39; and

n is an integer in the range of 2 to 4.

In another aspect, there is provided a capacitor comprising the composite material as described herein.

Definitions

- 5 The following words and terms used herein shall have the meaning indicated:

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

- 10 Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

- 15 The term "about" as used herein typically means +/- 5 % of the stated value, more typically +/- 4 % of the stated value, more typically +/- 3 % of the stated value, more typically, +/- 2 % of the stated value, even more typically +/- 1 % of the stated value, and even more typically +/- 0.5 % of the stated value.

- 20 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

- 30 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a composition will now be disclosed.

- 35 The composition comprises at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte, wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule.

Advantageously, the chain extender may help to improve ion conductivities and mechanical rigidity of a composite material formed from the composition. This is because the chain extender may link globules of the electrolyte within the composite material, instead of forming isolated and confined electrolyte globules.

Further advantageously, the at least one cross-linker may increase the mechanical strength of a film formed from the composition, and may possess a repulsive effect on the electrolyte. Thus, at a microstructural level, the at least one cross-linker may segregate the film into 2 distinct regions. One region may be dominated by the cross-linker that is devoid of the electrolyte and the other region may consist of the chain extender as well as the electrolyte, which becomes larger in size due to the presence of the electrolyte. This may cause distinct and pronounced ion percolation channels to form within the film, resulting in a higher ion conductivity compared to a film formed from a generic thermoplastic system, in which the electrolyte resides in between matrix layers of the polymer chains and cannot form pronounced percolation channels.

Still further advantageously, as the at least one epoxy precursor comprises at least three glycidyl groups per molecule, the composition would have a higher ion conductivity. This is because the glycidyl groups may form aliphatic bonds with the at least one cross-linker, which are lyophobic in nature. The aliphatic bonds may have a repulsive impact on the electrolyte, thus forcing the electrolyte to come closer together and form more distinct percolation channels.

In the composition, the at least one epoxy precursor may be a small-molecule compound or an oligomer. The at least one epoxy precursor may further comprise at least one epoxy group. The at least one epoxy precursor may be selected from pentaerythritol tetraglycidyl ether or trimethylolpropane triglycidyl ether.

The at least one cross-linker may be a small-molecule compound or an oligomer. The at least one cross-linker may comprise at least one epoxy group and/or at least one glycidyl group. The at least one cross-linker may comprise straight or branched molecules comprising at least two functional groups independently selected from the group consisting of amino, carboxylic acid, imidazolyl and hydroxy. The at least one cross-linker may comprise at least two amino functional groups. The at least one cross-linker may comprise a sufficient number of amino functional groups that allows the composition to form a solid gel upon curing.

The at least one cross-linker may be selected from triethylenetetramine or tetraethylenepentamine. The at least one cross-linker may be tetraethylenepentamine. Advantageously, tetraethylenepentamine has 7 N-H bonds within each molecule, which may increase non-polar alkyl functionality regions within the composition, thus improving ion conductivities of the composite material formed from the composition. This is because a cross-linker with more N-H bonds may result in a composite with a higher storage modulus (e.g., being stiffer). A cross-linker with a higher number of primary amine functionalities would also result in a higher measured ion conductivity. Due to a high reactivity of primary amine to epoxy, a cross-linker having a higher amount of primary amine may result in a more rapid formation of segregated zones (e.g., zones engorged with ionic liquid) within the composite material, allowing more defined ion percolation channels to be established within the composite material.

The at least one chain extender may be a small-molecule compound or an oligomer. The at least one chain extender may comprise at least one epoxy group and/or at least one glycidyl group. The at least one chain extender may comprise at least three ethoxy groups, propyloxy groups, or a combination thereof. The at least one chain extender may alternatively or additionally comprise at least three groups that have lone pair (e.g., not bonded) electrons, such as fluorine, nitrogen, chlorine, oxygen and benzyl. As the electrolyte comprises cations, the lone pair electrons of the at least one chain extender may strongly coordinate with the cations of the electrolyte. Where the at least one chain extender comprises at least three ethoxy groups, the ethoxy groups may form coordination bonds with the electrolyte via an ion-dipole interaction during curing of the composition. The ion-dipole interaction may be regarded as an “clinging” effect, which allows more distinct ion percolation channels to form within a composite material formed by curing of the composition, giving rise to a higher ion conductivity. Moreover, the ethoxy groups comprise oxygen atoms that are electron-withdrawing. The oxygen atoms would reduce a reactivity of other functional groups (such as terminal amines) on the at least one chain extender, as compared to the at least one cross-linker. This helps to segregate the electrolyte into more defined ion conductivity channels. The at least one chain extender may further comprise at least two functional groups independently selected from the group consisting of amino, carboxylic acid, imidazolyl and hydroxy. The at least one cross-linker may comprise at least two amino functional groups.

The at least one chain extender may be selected from O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol, poly(propylene glycol) bis(2-aminopropyl ether), poly(propylene glycol) bis(2-aminopropyl ether) or 4,7,10-trioxatridecane-1,13-diamine.

The composition may further comprise a catalyst. The catalyst may advantageously speed up a reaction between the remaining components in the composition. For example, the catalyst may increase a reaction rate between amino groups (e.g., in the at least one cross-linker and the at least one chain extender) and glycidyl groups (e.g., in the at least one epoxy precursor), which ensures reaction completeness, especially for secondary amine bonds in tetraethylenepentamine. The catalyst may ensure that the at least one cross-linker react with the at least one epoxy precursor more rapidly than the at least one chain extender, thus forcing the at least one chain extender to be coupled with the electrolyte and become more tightly packed. This promotes formation of more defined ion percolation channels and a higher ion conductivity of a composite material formed from the composition. The catalyst may comprise a tertiary amine group. The catalyst may be selected from 2,4,6-tris(dimethylaminomethyl)phenol or a BF₃-amine complex.

The electrolyte may be in a liquid state at 25 °C. The electrolyte may be able to dissolve lithium salts. Where the electrolyte is able to dissolve lithium salts, the composition may be used in a Li-ion battery. The electrolyte may be non-aqueous. The electrolyte may comprise at least one ionic liquid. Where the electrolyte comprises at least one ionic liquid, the composite material formed from the composition may be regarded as an ionogel.

The at least one ionic liquid may be selected from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium

trifluoromethanesulfonate, 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate.

Where the electrolyte consists of one ionic liquid, the electrolyte may advantageously have a higher storage modulus as the ionic liquid has a low plasticizing effect.

- 5 Where the electrolyte comprises at least two ionic liquids, the electrolyte may advantageously have a higher ion conductivity due to a difference in sizes of ions of the at least two ionic liquids. The difference facilitates greater ease for the ions to move past each other when a potential is applied.

10 The at least one epoxy precursor may have a weight percentage in the range of about 15 weight% to about 35 weight%, about 20 weight% to about 35 weight%, about 25 weight% to about 35 weight%, about 30 weight% to about 35 weight%, about 15 weight% to about 30 weight%, about 15 weight% to about 25 weight% or about 15 weight% to about 20 weight%, based on the total weight of the composition.

15 The at least one cross-linker may have a weight percentage in the range of about 5 weight% to about 20 weight%, about 10 weight% to about 20 weight%, about 15 weight% to about 20 weight%, about 5 weight% to about 15 weight% or about 5 weight% to about 10 weight%, based on the total weight of the composition.

20 The at least one chain extender may have a weight percentage in the range of about 10 weight% to about 35 weight%, about 20 weight% to about 35 weight%, about 30 weight% to about 30 weight%, about 10 weight% to about 30 weight% or about 10 weight% to about 20 weight%, based on the total weight of the composition.

25 Where present, the catalyst may have a weight percentage in the range of about 0.1 weight% to about 4 weight%, about 1 weight% to about 4 weight%, about 2 weight% to about 4 weight%, about 3 weight% to about 4 weight%, about 0.1 weight% to about 3 weight%, about 0.1 weight% to about 2 weight% or about 0.1 weight% to about 1 weight%, based on the total weight of the composition.

30 The electrolyte may have a weight percentage in the range of about 20 weight% to about 50 weight%, about 30 weight% to about 50 weight%, about 40 weight% to about 50 weight%, about 20 weight% to about 40 weight% or about 20 weight% to about 30 weight%, based on the total weight of the composition.

35 The electrolyte may have a weight percentage in the range of about 30 weight% to about 50 weight%, about 40 weight% to about 50 weight% or about 30 weight% to about 40 weight%, based on the total weight of the composition. The electrolyte may have a weight percentage of about 40 weight% based on the total weight of the composition.

Advantageously, where the electrolyte has a weight percentage as described above, the composite material formed from the composition may have an optimal balance between ion conductivity and storage modulus.

40 The composition may comprise epoxy functional groups and amino functional groups at a total molar ratio in the range of about 1 to about 3.8, about 2 to about 3.8, about 3 to about 3.8, about 1 to about 3 or about 1 to about 2. Advantageously, where the total molar ratio is at least 1, the composition becomes less corrosive to metals (such as metallic electrodes).

The at least one cross-linker and the at least one chain extender may have a molar ratio in the range of 0.5 to 3.2, about 1 to about 3.2, about 2 to about 3.2, about 3 to about 3.2, about 0.5 to about 3, about 0.5 to about 2 or about 0.5 to about 1.

In one example,

- 5 (a) the at least one epoxy precursor may be trimethylolpropane triglycidyl ether;
 - (b) the at least one cross-linker may be tetraethylenepentamine;
 - (c) the at least one chain extender may be O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol; and
 - (d) the catalyst may be 2,4,6-tris(dimethylaminomethyl)phenol.
- 10 Exemplary, non-limiting embodiments of a method of forming a composite material will now be disclosed.

The method comprises the steps of:

- (a) mixing at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte to form a composition; and
- 15 (b) curing the composition of step (a) to form the composite material.

In the method, the mixing step (a) may be undertaken in a one-pot system. The mixing step (a) may be undertaken in a single reaction vessel.

The mixing step (a) may be undertaken by stirring the composition.

- 20 The stirring may be undertaken at a stirring rate in the range of about 250 rpm to about 350 rpm, about 300 rpm to about 350 rpm or about 250 rpm to about 300 rpm. The stirring may be undertaken at a stirring rate of about 250 rpm.

The stirring may be undertaken for a duration in the range of about 1 minute to about 10 minutes, about 5 minutes to about 10 minutes or about 1 minute to about 5 minutes. The stirring may be undertaken for about 10 minutes.

- 25 The method may further comprise a step (a1) of adding a catalyst to the composition of step (a) after step (a) but before step (b).

Where the composition of step (a) or (a1) is not in a liquid state, the method may further comprise a step (a2) of heating the composition of step (a) or (a1).

- 30 The heating step (a2) may be undertaken at a temperature in the range of about 50 °C to about 70 °C, about 60 °C to about 70 °C or about 50 °C to about 60 °C. The heating step (a2) may be undertaken at a temperature of about 60 °C.

The heating step (a2) may be undertaken for a duration in the range of about 2 minutes to about 5 minutes, about 3 minutes to about 5 minutes, about 4 minutes to about 5 minutes, about 2 minutes to about 4 minutes or about 2 minutes to about 3 minutes.

- 35 The heating step (a2) may be undertaken for about 5 minutes.

The heating step (a2) may be undertaken until the composition is completely in a liquid state, where all solid components are dissolved or melt.

The curing step (b) may be undertaken in a silicone dish, tray or container. The silicone dish, tray or container may serve as a non-stick vessel for the composition during the curing step (b). The reaction vessel may be a silicone container.

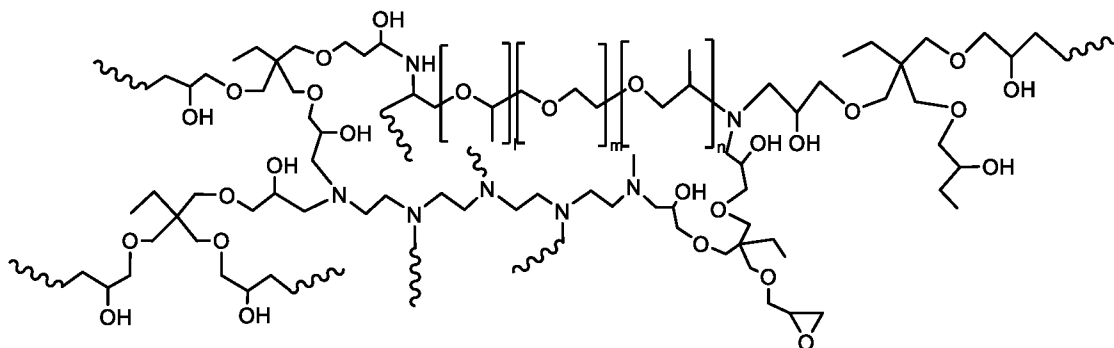
The curing step (b) may be undertaken at a temperature in the range of about 60 °C to about 80 °C, about 70 °C to about 80 °C or about 60 °C to about 70 °C. As the temperature for the curing step (b) is kept below 80 °C, the composite material may be advantageously prevented from heat-induced warping.

The curing step (b) may be undertaken for a duration in the range of about 2 hours to about 8 hours, about 4 hours to about 8 hours, about 6 hours to about 8 hours, about 2 hours to about 6 hours or about 2 hours to about 4 hours.

During the curing step (b), the at least one cross-linker may react very rapidly with the at least one epoxy precursor as compared to the at least one chain extender. As the electrolyte may comprise ions that form an ion-dipole interaction with ethoxy groups (e.g., from the at least one chain extender) and temporarily bind with the ethoxy groups. Therefore, where the at least one chain extender comprises a higher number of ethoxy groups per molecule, it may advantageously bind with the electrolyte more strongly during the curing step (b).

Exemplary, non-limiting embodiments of a composite material will now be disclosed.

The composite material may have a polymeric network comprising a plurality of moieties, each moiety independently having a formula of:



wherein:

each wavy bond represents a site of cross linking to another moiety;

l is an integer in the range of 2 to 4;

m is an integer in the range of 6 to 39; and

n is an integer in the range of 2 to 4.

For the sake of clarity, the range of integers for l, m and n includes the end values. Therefore, l may be an integer selected from 2, 3, or 4; m may be an integer selected from 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38 or 39; and n may be an integer selected from 2, 3, or 4.

In the polymeric network, the moieties as described above may be cross-linked to each other via the sites of cross linking.

In one example, l may be 3.

In another example, n may be 3.

The composite material may be formed by the method as described herein.

Advantageously, the composite material may have improved ion conductivities and mechanical rigidity due to the chain extender used in the present method.

- 5 The composite material may have an ion conductivity of more than 10^{-4} S/cm. The ion conductivity may be measured using a potentiostat after thermally drying the composite material at 90 °C for 3 hours in vacuum in a Swagelok Cell Assembly.

The composite material may have a storage modulus of more than 7 MPa.

The composite material may be in the form of a free-standing film.

- 10 Exemplary, non-limiting embodiments of a capacitor will now be disclosed.

The capacitor may comprise the composite material as described herein. As the composite material has improved ion conductivities and mechanical rigidity, the capacitor may be regarded as a super-capacitor.

Brief Description of Drawings

- 15 The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

FIG. 1

- 20 [Fig. 1] shows schematic illustrations of microstructures of exemplary composite materials according to the present application, that have varying ratios of cross-linkers and chain extenders.

FIG. 2

- 25 [FIG. 2] shows a schematic illustration of microstructures of an exemplary composite material according to the present application compared with a composite material in the art.

Examples

- Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting
30 the scope of the invention.

Example 1 – Preparation of A Composite Material

- Generally, at least one epoxy precursor, at least one cross-linker, at least one chain extender, a catalyst and an electrolyte were mixed vigorously in a one-pot system with/without heat to form a composition. The composition was subsequently poured
35 into a silicone, followed by curing at 60 °C to 90 °C for 2 to 8 hours to form the composite material. Particularly, an exact amount of reagents (as provided in tables

below) for each type of chemical was measured using a mass balance/micro-pipette, and subsequently mixed in a glass bottle using a Teflon stir bar to form a mixture. Where all reagents were already in a liquid state at room temperature, the mixture was stirred at 250 rpm for 10 minutes and subsequently poured into a silicone dish for curing at 70 °C for 2 hours. Where not all reagents were in a liquid state, the mixture was additionally heated at 60 °C for 5 minutes before pouring into the silicone dish for curing at 70 °C for 2 hours.

A list of the compounds used is provided below:

Epoxy precursor - pentaerythritol tetraglycidyl ether (purchased from LeapChem, Hong Kong) and trimethylolpropane triglycidyl ether (TMP, purchased from Sigma Aldrich, Singapore).

Cross-linker - triethylenetetramine (TETA, purchased from Sigma Aldrich, Singapore) and tetraethylenepentamine (TEPA, purchased from Sigma Aldrich, Singapore).

Chain extender - O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (APG, purchased from Sigma Aldrich/Huntsman, Singapore under product label XTJ-501; ED-2003, purchased from Sigma Aldrich/Huntsman, Singapore under product label XTJ-502) and poly(propylene glycol) bis(2-aminopropyl ether) (PPG, purchased from Sigma Aldrich, Singapore), 1,5-diamino-2-methylpentane (DAMP, purchased from Sigma Aldrich, Singapore), 4,7,10-trioxatridecane-1,13-diamine (TTD, purchased from Sigma Aldrich, Singapore).

Catalyst - 2,4,6-tris(dimethylaminomethyl)phenol (DMP, purchased from Sigma Aldrich, Singapore) and BF₃-amine complex (purchased from Sigma Aldrich, Singapore).

Electrolyte - 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI, purchased from Solvionic, France), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMFM, purchased from Sigma Aldrich, Singapore), 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF, purchased from Sigma Aldrich, Singapore) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMTF, purchased from Sigma Aldrich, Singapore).

To investigate the impact of the cross-linkers, chain extenders, electrolytes and epoxy precursors on the mechanical properties and ion conductivities of the composite material formed, a series of different experiments are conducted to elucidate their influences as set forth below. The electrolyte is exemplified using ionic liquids (IL) in the experiments.

Example 2 – Impact of Weight Percentage of Electrolyte Loaded on Ion Conductivity of Composite Material

Table 1A. Formulation of composite materials with different weight percentage of EMI-TFSI loaded

	Mol				Mass (g)
	TMP	TEPA	APG	DMP	EMI-TFSI
P-20 (20 weight% loading)	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	0.442
P-30 (30 weight% loading)	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	0.7577
P-40 (40 weight% loading)	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.768
P-50 (50 weight% loading)	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	2.652
P-60 (60 weight% loading)	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	3.978

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Table 1B. Impact of weight percentage of EMI-TFSI loaded on ion conductivity of composite material

	P-20	P-30	P-40	P-50	P-60
Ion Conductivity (S/cm)	1.6883×10^{-5}	0.00013373	0.00022962	0.00073476	0.00106675
Storage Modulus (MPa)	9.3593	8.5726	7.81	6.5853	5.6756
Loss Modulus (MPa)	0.2153	0.8633	1.322	2.04	2.941

The loading of EMI-TFSI within the composite material varied between 20 weight% (P-20) and 60 weight% (P-60) as shown in Table 1A.

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To measure ion conductivity, the as-prepared material was thermally dried at 90 °C for 3 hours in vacuum, and subsequently measured using a potentiostat within a Swagelok Cell Assembly in vacuum. Storage modulus and loss modulus were measured according to the dynamic mechanical analysis (DMA) measurement procedures as follows. Three individual samples with a thickness of less than 2 mm, a width of 5 to 7 mm and a length 9 to 11 mm were prepared. The dynamic mechanical analysis was conducted on the samples under “strain mode”, with an amplitude 10 μm (micron) and a frequency of 1 Hz, under isothermal at room temperature conditions for 15 minutes. The storage modulus/loss modulus of each sample were obtained when curves plotted from the analysis stabilized and reached a plateau, and the storage modulus/loss modulus values were read straight off the y-axis of the plots (Storage Modulus vs Time) or (Loss Modulus vs Time). The values were averaged for the triplicate samples.

It can be deduced from Table 1B that an increase in IL loading resulted in an increase in ion conductivities and loss modulus, as well as a decrease in storage modulus. The increase in ion conductivity can be explained by the increase in IL loading resulting in the formation of more percolation channels, allowing for greater ion mobility. The increase in IL content would also cause the IL to serve as plasticizers for the polymer matrix, resulting in decrease in storage modulus and increase in loss modulus of the composite. P-40 was used as a basis upon which further investigations were conducted, as the 40 weight% loading of EMI-TFSI delivered a composite material with the best balance of ion conductivity and storage modulus.

Example 3 – Impact of Molar Ratio between Cross-linker and Chain Extender on Ion Conductivity of Composite Materials Having 40 Weight% of EMI-TFSI

Table 2A. Formulation of composite materials having 40 weight% of EMI-TFSI, with different molar ratios between TEPA and APG

	Mol				Molar Ratio	
	TMP	TEPA	APG	DMP	Epoxy/Amino	TEPA/APG
T1	0.005291705	5.2826×10^{-4}	0.001	1.959×10^{-4}	3.832	0.52826
T2	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.4496	1.1887
T3	0.005291705	0.00158478	7.777×10^{-4}	1.959×10^{-4}	1.117	2.0375
T4	0.005291705	0.00211304	6.666×10^{-4}	1.959×10^{-4}	0.9093	3.1698
T5	0.005291705	0.00528262	-	1.959×10^{-4}	-	-

Table 2B. Impact of molar ratio between TEPA and APG on ion conductivity of composite material having 40 weight% of EMI-TFSI

	T1	T2	T3	T4	T5
Ion Conductivity (S/cm)	7.0276×10^{-5}	0.00022962	0.00032328	0.00059158	1.8643×10^{-8}
Storage Modulus (MPa)	4.624	7.81	8.148	2.199	379.53
Loss Modulus (MPa)	0.0385	1.322	1.648	0.413	110.27

To determine the impact of the molar ratio between cross-linker and chain extender on the mechanical and ion conductivity properties of the composite material (which were measured as described in Example 2), composite materials with different molar ratios between TEPA and APG were prepared as shown in Table 2A. It could be deduced from Table 2B that an increase in TEPA/APG molar ratio increased the storage modulus and ion conductivity of the composite material. The increase in TEPA content in the composite material resulted in a greater extent of cross-linking within the polymeric matrix, as well as an increase in non-polar alkyl groups within the composite material. This led to greater repulsion and confinement of the ions of IL to form more defined percolation channels, thus leading to higher ion conductivity.

Sample T1 with the lowest TEPA/APG molar ratio experienced leaching of IL out of the composite material when the sample was left standing for a few weeks. This phenomenon could be attributed to an insufficient cross-linking within the composite material; thus, the IL could not be held firmly within the composite, which led to the leaching of IL. Sample T4 had the highest ion conductivity but also the lowest storage modulus. This was due to the composite material containing a higher number of moles of amino groups compared with a number of moles of epoxy groups. The excess, un-reacted amino functionalities served as plasticizers, increasing the chain mobility of the composite material, resulting in the reduction in storage modulus. Sample T5 was prepared without any chain extenders and possessed the lowest ion conductivity. This proved that some form of chain extender was required to afford bridging of individual IL globules to form coherent, interconnected percolating channels to allow ion mobility when a potential is applied. The very high storage modulus measured in sample T5 was further evidence that the IL in composite material was “locked” into individual, isolated globules, which did not have a plasticizing effect on composite material.

Example 4 – Impact of Varying Cross-linkers and Chain Extenders on Ion Conductivity of Composite Materials Having 40 Weight% of EMI-TFSI

Table 3A. Formulation of composite materials having 40 weight% of EMI-TFSI, with varying cross-linkers and chain extenders

	Mol			
	TMP	Cross-linker	Chain extender	DMP
T2	0.005291705	0.00105652 (TEPA)	0.0008888 (APG)	1.959×10^{-4}
TTG	0.005291705	0.00105652 (TETA)	0.0008888 (APG)	1.925×10^{-4}
TTD	0.005291705	0.00105652 (TEPA)	0.0008888 (TTD)	1.504×10^{-4}
TED	0.005291705	0.00105652 (TEPA)	0.0008888 (ED-2003)	2.695×10^{-4}
TPG	0.005291705	0.00105652 (TEPA)	0.0008888 (PPG-2000)	2.695×10^{-4}
TPP	0.005291705	0.00105652 (TEPA)	0.0008888 (DAMP)	1.434×10^{-4}

Table 3B. Impact of varying cross-linkers and chain extenders on ion conductivity of composite material having 40 weight% of EMI-TFSI

	TTG	T2	TTD	TED	TPG	TPP
Ion Conductivity (S/cm)	0.000163005	0.00022962	3.3567×10^{-7}	0.0003414	0.000479717	3.0464×10^{-7}
Storage Modulus (MPa)	7.125	7.81	136.53	3.185	1.564	225.1
Loss Modulus (MPa)	1.279	1.322	110.27	0.2498	0.4005	140.36

- 10 To elucidate the impact of the chain extender and cross-linker species on the mechanical and ion conductivity properties of the composite material (which were measured as described in Example 2), diamine terminated polyether of different chain lengths and cross-linkers with different number of N-H bonds within the molecules were used to composite material (based upon the formulation of P-40). By comparing
- 15 TTG and T2, T2 possessed higher ion conductivity and storage modulus. T2 was prepared using tetraethylpentamine (TEPA) as the cross-linker while TTG was made using triethylenetetramine (TETA) as the cross-linker. The difference in ion conductivity between T2 and TTG could be accounted by the fact that TEPA contained 7 N-H bonds while TETA possessed 6 N-H bonds. Accordingly, the higher
- 20 N-H bond content of TEPA led to an increase in non-polar alkyl functionality regions within the composite material. The presence of a greater amount of alkyl groups

within the polymeric matrix led to greater repulsion and confinement of IL to form more defined percolation channels, thus leading to higher ion conductivity. The higher extent of cross-linking also led to higher storage modulus.

To investigate the role of chain extender species in ion conductivity of the composite material, chain extenders with different degrees of ethoxy contents were used to prepare ionogel electrolytes T2, TED, TPP, TPG and TTD. The number of ethoxy groups within each type of chain extender molecule were as follows; 12 in T2, 3 in TTD, 39 in TED and 0 in TPP (based on the commercial brochures of these compounds). The chain extender species utilized in the composite materials were as follows, O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol MW~900 (APG) & MW~2000 (ED-2003) in T2 and TED respectively, 4,7,10-trioxatridecane-1,13-diamine in TTD and 1,5-diamino-2-methylpentane in TPP.

From Table 3B, samples TPP and TTD possessed significantly lower ion conductivities as compared to T2 and TED, but their storage modulus was higher. By comparing samples TTD, T2 and TED, it could be observed that the utilization of polyether-amine (PEA) with higher ethoxy content as chain extender led to a higher measured ion conductivity. However, the storage modulus decreased with the increase in ethoxy contents of polyether-amine. These differences in ion conductivities could be because of the increase in ethoxy groups of higher molecular weight of PEA, result in a longer and more flexible chain extender molecule. This increase in chain flexibility within the polymeric matrix would enable greater linking up of IL globules created by cross-linker confinement, thus allowing larger extents of continuous percolation channels to be achieved and leading to higher ion conductivity.

The ethoxy content of PEA within sample TTD was low, thus the chain was short and rigid. Accordingly, the islands of IL globules were isolated and not interconnected to form conduction channels, which led to very low ion conductivity. This low conductivity was also observed in sample TPP, as the absence of ethoxy groups in 1,5-diamino-2-methylpentane (DAMP) resulted in isolated, non-connected IL islands, which resulted in deficiency of conducting channels. The storage modulus of samples TTD, T2, TED further proved this hypothesis of the role of chain extenders.

Sample TED contained longer, more flexible PEA portions, leading to greater extents of linking up of IL globules to form channels. This caused the IL to have a greater "plasticizing" effect on the electrolyte composite, leading to lowering of storage modulus. Sample TTD had a very short PEA portion, which instead of linking up the IL globules to form channels, reinforced the cross-linkers to "lock-up" the IL globules as isolated, individual IL islands, thus leading to a very high storage modulus.

Sample TPG used polypropylene glycol (Mw=2000) diamine as the chain extender. The cured sample experienced some IL leaching issue. This could be explained by the methyl functional group (-CH₃) of the PPG chain extender being lyophobic to the IL, thus not being able to interact cohesively with the IL. This resulted in the matrix not being able to hold onto the IL and caused the IL leaching issue. This was unlike APG or ED-2003 where ion dipole interaction between the oxygen atoms and the cation of IL would discourage IL from leaching out of the composite material and

encourage IL retention. However, sample TPG had higher ion conductivity than TED despite both chain extender having the same molecular weight. The methyl groups of PPG had a more confining effect of the IL within more defined IL channels in the composite material, thus leading to higher ion conductivity.

- 5 Schematic illustrations of microstructures of samples TED and T5 are shown in FIG. 1. With reference to FIG. 1, sample TED (102) had ionic liquid globules (106) that formed coherent, inter-connected percolating channels across unreacted dangling chains (108) of tetraethylenepentamine and O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol. A distinct, interconnected Li-ion percolation channels was formed with well-established interpenetrating network within the solid gel battery electrolyte, resulting in higher measured ion conductivity. In Sample T5 (104), ionic liquid (106) was "locked" into individual, isolated globules by a polymeric matrix (110) in the absence of any chain extender, resulting in a very poor conductivity.

15 Example 5 – Impact of Ionic Liquid Species on Ion Conductivity of Composite Materials

Table 4A. Formulation of composite materials having 40 weight% of varying ionic liquid species / mixtures

	Mol				Mass (g)
	TMP	TEPA	APG	DMP	Ionic Liquid
BMTF	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.768 (BMTF)
EMFM	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.768 (EMFM)
FMSI-40/60	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.0608/0.7072 (EMI-TFSI / EMFM)
FMSI-60/40	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.0608/0.7072 (EMFM / EMI-TFSI)
BMSI-40/60	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.0608/0.7072 (EMI-TFSI / BMTF)
BMSI-60/40	0.005291705	0.00105652	0.0008888	1.959×10^{-4}	1.0608/0.7072 (BMTF / EMI-TFSI)

Table 4B. Impact of varying ionic liquid species / mixtures on ion conductivity of composite material

	Ion Conductivity (S/cm)	Storage Modulus (MPa)	Loss Modulus (MPa)
EMI-TFSI	0.00022962	7.81	1.322
BMTF	0.000294592	3.014	0.265
EMFM	0.000324226	5.083	0.1
FMSI-40/60	0.000709054	2.36	0.05927
FMSI-60/40	0.000642921	1.4	0.12288
BMSI-40/60	0.000602972	7.144	0.6805
BMSI-60/40	0.000650812	2.359	0.1182

To investigate the impact of different IL species on the mechanical properties and ion conductivity of the composite material (which were measured as described in Example 2), EMFM and BMTF were used either directly as a replacement for EMI-TFSI or mixed with EMI-TFSI as a partial replacement. Partial substitution of EMI-TFSI within the composite material was achieved by either adding 40wt% or 60wt% of the total IL loading for a sample composite material.

Based upon Table 4B, Samples BMTF and EMFM possessed higher ion conductivities as compared to EMI-TFSI. Higher ion conductivity for sample BMTF was measured as compared to EMI-TFSI (T2) despite the pure form of BMTF possessing lower ion conductivity. This could be due to the longer butyl group attached to azole positive ion exerting steric hindrance on the oxygen atoms of the polymeric matrix as compared to ethyl of EMI-TFSI. The steric hindrance resulted in the transient interaction between the oxygen and the positive ion, allowing the positive ion to move more easily within the composite.

Samples BMSI and FMSI were prepared with IL combinations of BMTF/EMI-TFSI and EMFM/EMI-TFSI respectively. The IL mixtures had higher ion conductivity as compared to their pure form (e.g. samples EMFM, BMTF), which could be due to the difference in sizes of the cations and anions of the ILs, facilitating greater ease for the ions to move past each other when a potential is applied. This difference in ion sizes also greatly increased the IL's plasticizing effect on the composite matrix as it can be observed from Table 4B that the composite materials having mixed ILs had a poorer storage modulus than the composite materials having pure EMI-TFSI as the electrolyte.

Comparative Example 1 – Comparison between Epoxy-based Composite Material and Thermo-plastic Matrix-based Composite Material

As shown in Table 5, the ion conductivities and mechanical properties of epoxy and thermo-plastic matrix based composite materials with 40wt% EMI-TFSI loading

were further compared (which were measured as described in Example 2). The thermo-plastic matrix (PVA-40) was a polyvinyl alcohol ($M_w=40000$) and was a typical generic polymeric matrix frequently cited in scientific literatures.

Table 5. Comparison on ion conductivities and mechanical properties between the present composite material and the PVA-based composite material

	Ion Conductivity (S/cm)	Storage Modulus (MPa)	Loss Modulus (MPa)
TA2	0.00022962	7.81	1.322
PVA-40	2.211×10^{-6}	31.43	3.158

It could be deduced from Table 5 that the present composite material possessed 100-fold higher ion conductivity than the PVA-based composite material. However, the corresponding mechanical properties of the present composite material are significantly poorer than that of PVA-IL. The poorer ion conductivity of the PVA-based composite material could be due to the IL globules taking up position between the PVA polymer chains when IL is integrated within the polymeric matrix. These globules were aligned to allow for ion mobility under an applied potential, but this conductivity was directional as the mobility of the ions could only happen laterally to the polymer chains. This could also explain why the IL leached out of the PVA-based composite material after it had been left standing for a few months, as the intermolecular Van der Waals forces were not strong enough to retain the IL within the gaps of the polymer chains.

Conversely, the storage modulus of the PVA-based composite material was much higher than that of TA2. This could be due to the measured storage modulus of the PVA-based composite material was primarily the mechanical properties of the pure PVA chains and not the composite with IL incorporated. This postulation was validated as strips of the PVA-based composite material cut-outs for dynamic mechanical analyzer measurements were very wet in nature, which was a sign that most of the IL had already leached out the film before measurement.

Schematic illustrations of the microstructures of the present composite material and the PVA-based composite material are shown in FIG. 2. With reference to FIG. 2, Sample TA2 (202, labelled as EMI-TFSI in Table 4B) had ionic liquid globules (206) forming coherent, inter-connected percolating channels across long and flexible polymer chains (208), together making a fully cured polymeric network. In a typical composite material based on polyvinyl alcohol (PVA) matrix (204), ionic liquid globules (212) were sandwiched between (or resided in) PVA polymer chains (210) when the ionic liquid was integrated within the composite material.

Industrial Applicability

The composition and composite material of the disclosure may be used in a variety of applications such as regenerative braking, short-term energy storage, burst-mode power delivery, or batteries (where a lithium salt is dissolved in the electrolyte).

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure

without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A composition comprising at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte, wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule, wherein the at least one cross-linker is selected from triethylenetetramine or tetraethylenepentamine, and wherein the at least one chain extender comprises at least three ethoxy groups, propyloxy groups, or a combination thereof.
2. The composition of claim 1, wherein the at least one epoxy precursor is selected from pentaerythritol tetraglycidyl ether or trimethylolpropane triglycidyl ether.
3. The composition of claim 1 or 2, wherein the at least one chain extender is selected from O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol, poly(propylene glycol) bis(2-aminopropyl ether), poly(propylene glycol) bis(2-aminopropyl ether) or 4,7,10-trioxatridecane-1,13-diamine.
4. The composition of any one of claims 1 to 3, which further comprises a catalyst selected from 2,4,6-tris(dimethylaminomethyl)phenol or a BF₃-amine complex.
5. The composition of any one of claims 1 to 4, wherein the electrolyte is non-aqueous, and comprises at least one ionic liquid.
6. The composition of claim 5, wherein the at least one ionic liquid is selected from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium tetrafluoroborate.
7. The composition of claim 5 or 6, wherein the at least one ionic liquid has a weight percentage of 30 weight% to 50 weight% based on the total weight of the composition.
8. The composition of any one of claims 1 to 7, which comprises epoxy functional groups and amino functional groups at a total molar ratio in the range of 1 to 3.8.
9. The composition of any one of claims 1 to 8, wherein the at least one cross-linker and the at least one chain extender have a molar ratio in the range of 0.5 to 3.2.
10. The composition of any one of claims 4 to 9, wherein:
 - (a) the at least one epoxy precursor is trimethylolpropane triglycidyl ether;
 - (b) the at least one cross-linker is tetraethylenepentamine;
 - (c) the at least one chain extender is O,O'-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol; and
 - (d) the catalyst is 2,4,6-tris(dimethylaminomethyl)phenol.
11. A method of forming a composite material, comprising the steps of:
 - (a) mixing at least one epoxy precursor, at least one cross-linker, at least one chain extender, and an electrolyte to form a composition; and
 - (b) curing the composition of step (a) to form the composite material,

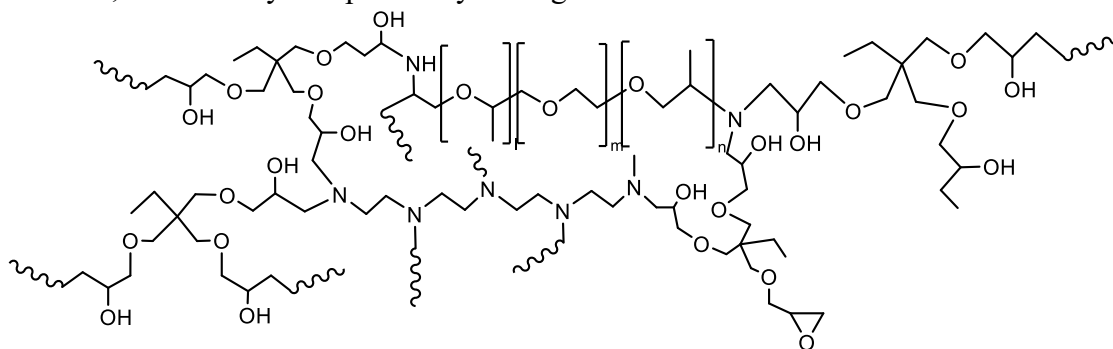
wherein the at least one epoxy precursor comprises at least three glycidyl groups per molecule, wherein the at least one cross-linker is selected from triethylenetetramine or tetraethylenepentamine, and wherein the at least one chain extender comprises at least three ethoxy groups, propyloxy groups, or a combination thereof.

12. The method of claim 11, wherein the mixing step (a) is undertaken in a one-pot system.

13. The method of claim 11 or 12, wherein the curing step (b) is undertaken at a temperature in the range of 60 °C to 90 °C.

14. The method of any one of claims 11 to 13, wherein the curing step (b) is undertaken for a duration in the range of 2 hours to 8 hours.

15. A composite material having a polymeric network comprising a plurality of moieties, each moiety independently having a formula of:



wherein: each wavy bond represents a site of cross linking to another moiety;

l is an integer in the range of 2 to 4;

m is an integer in the range of 6 to 39; and

n is an integer in the range of 2 to 4.

16. The composite material of claim 15, which is in the form of a free-standing film.

17. The composite material of claim 15 or 16, which has an ion conductivity of more than 10^{-4} S/cm.

18. The composite material of any one of claims 15 to 17, which has a storage modulus of more than 7 MPa.

19. A capacitor comprising the composite material of any one of claims 15 to 18.