

METHOD OF UPCYCLING CONDENSATION POLYMERS IN PLASTIC WASTE VIA CO-CATALYTIC PARTIAL DEPOLYMERIZATION

Field of Invention

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The current invention relates to a method of recycling condensation polymers through a catalytic degradation of the polymers back to oligomers, and the further application of said oligomers to new uses.

10 Background

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

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The urgent need for efficient depolymerisation techniques to manage the vast and increasing amount of waste plastics cannot be further emphasized, with predicted total cumulative global plastic production reaching 34 billion ton by 2050 (R. Geyer, J. R. Jambeck & K. L. Law, *Sci. Adv.* **2017**, 3, e1700782). The plastic material with the highest recycling potential has been identified by the industry to be poly(ethylene terephthalate), more commonly known as PET. Global PET demand of 26 million ton in 2018 is projected to further increase 60% to 42 million ton by 2030, yet less than 20% of such PET products are recycled (Source: Indorama Ventures). Waste PET products recovered from the community that are clean and relatively uncontaminated, such as beverage bottles, can be directly reincorporated as feed material for PET manufacturing without significant detrimental effects (K. Choudhary, K. S. Sangwan & D. Goyal, *Procedia CIRP* **2019**, 80, 422-427). However, heavily contaminated products or composite materials based on PET either in the form of multilayer laminates with other polymers or with the inclusion of fillers such as dye pigments and nano-additives would require a chemical depolymerisation approach instead.

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Chemical depolymerisation of PET involves the addition of small molecules such as alcohols, glycol or water to cleave the ester linkage within PET; typically under the influence of catalyst and high temperature/high pressure conditions (K. Choudhary, K. S. Sangwan & D. Goyal, *Procedia CIRP* **2019**, 80, 422-427). As such, chemical depolymerisation is an energy intensive process that greatly increase the cost of recycled materials, but there are several technology start-ups working on developing novel catalyst and processes to reduce the energy intensity and increase the scope of treatable PET waste products (A. H. Tullo, *Chem. Eng. News*

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October 6, 2019). Separation of depolymerised chemical products such as bis(2-hydroxyethyl) terephthalate (BHET) from glycolysis or dimethyl terephthalate (DMT) from methanolysis from the depolymerisation mixture is difficult due to their low volatility, resulting in product often contaminated with oligomers and residual catalysts. Highly purified BHET or DMT is required to reintroduce the recycled material back into the PET supply chain, thus costly purification procedures must be implemented which further increase the cost of the chemical recycling process.

The most widely promoted approach utilizes ethylene glycol (EG) as both solvent and cleaving agent in a catalyzed transesterification procedure to depolymerize PET into BHET, which is a precursor suitable for re-polymerisation back into PET (A. M. Al-Sabagh *et al.*, *Ind. Eng. Chem. Res.* **2014**, 53, 18443-18451; D. Paszun & T. Szychaj, *Ind. Eng. Chem. Res.* **1997**, 36, 1373-1383; V. Sinha, M. R. Patel & J. V. Patel, *J. Polym. Environ.* **2010**, 18, 8-25; T. T. L. Bui *et al.*, *J. Appl. Polym. Sci.* **2016**, 133, 43920; H. Wang *et al.*, *Eur. Polym. J.* **2009**, 45, 1535-1544; Y.-H. Chen *et al.*, *ACS Sustain. Chem. Eng.* **2021**, 9, 3518-3528; Q. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2015**, 3, 340-348; and L. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2020**, 8, 13362-13368). EG is typically employed in off-stoichiometry molar ratios exceeding 10:1 in relation to the amount of available repeating units in PET to facilitate its solubilizing role in breaking apart the crystalline PET matrix to make available the ester moieties for subsequent catalytic transesterification, while also shifting the chemical equilibrium towards the BHET product. Although the use of excess EG increases BHET yield, the cost of BHET separation also increases. Typically, BHET is separated from the EG product solution by precipitation through the addition of water; thus, higher EG content would inevitably require more water to decrease solubility of BHET to effect precipitation. Considering that solvent recovery systems are typically an integral part of the chemical recycling process flow, the subsequent distillation effort to separate water from the EG solution waste stream would thus require more energy per unit of waste PET converted. Furthermore, due to the tendency of oligomeric by-products to co-crystallize with BHET during the precipitation step, a subsequent purification by recrystallization step in hot water is required to obtain BHET of sufficient purity for repolymerisation into PET. Coupled with the need for a certain degree of prior plastic waste sorting, the BHET approach to recycle PET is a labor, energy and water intensive process. The overall economic cost of this waste-to-resource process in its current scale simply cannot compete with the cost of virgin PET from fossil fuel sources.

When reassessing the economic feasibility of the BHET process, the beneficial potential for direct repolymerisation of oligomers became apparent. Every available literature on chemical recycling of PET reported 100% conversion or depolymerisation of initial PET feedstock,

regardless of the type of catalyst used or the subsequent BHET yield (A. M. Al-Sabagh *et al.*, *Ind. Eng. Chem. Res.* **2014**, 53, 18443-18451; D. Paszun & T. Szychaj, *Ind. Eng. Chem. Res.* **1997**, 36, 1373-1383; T. T. L. Bui *et al.*, *J. Appl. Polym. Sci.* **2016**, 133, 43920; H. Wang *et al.*, *Eur. Polym. J.* **2009**, 45, 1535-1544; Y.-H. Chen *et al.*, *ACS Sustain. Chem. Eng.* **2021**, 9, 3518-3528; Q. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2015**, 3, 340-348; L. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2020**, 8, 13362-13368; M. Liu *et al.*, *ACS Sustain. Chem. Eng.* **2018**, 6, 15127-15134; and D. R. Merkel *et al.*, *ACS Sustain. Chem. Eng.* **2020**, 8, 5615-5625). This is in part due to the solubilization of PET in hot EG and chain scission into lower molecular weight products. The depolymerisation of PET by transesterification in the presence of cleaving agents is an entropy-driven equilibrium reaction, which favors an increase in monomer population and the formation of oligomers with wide molecular weight distribution. Thus, it is impossible to avoid the presence of oligomers under realistic reaction conditions and duration. While the chemical structure of oligomers is the same as PET, it does not form well-defined crystals due to significant chain-end mobility, which likewise increases solubility of oligomers in solvent. However, oligomers still possess the similar end-group moieties that enable repolymerisation with addition of fresh monomer. Higher molecular weight oligomers may even be directly reintroduced into PET value chain in combination with chain extender additives to meet molecular weight requirements (Z. Zhao *et al.*, *ACS Omega* **2020**, 5, 19247-19254). While the well-defined chemistry of BHET monomers allow for precise polymerisation, one must not discount the economic benefits of repolymerizing PET oligomeric mixtures since costly separation and purification processes can be eliminated. The partial depolymerisation of PET into the oligomeric state before subsequent repolymerisation have been demonstrated and successfully commercialized by both CuRE and PerPETual, but they are relatively closed-loop solutions requiring clean, uncontaminated feedstocks (I. Vollmer *et al.*, *Angew. Chem. Int. Ed.* **2020**, 59, 15402-15423). Another issue plaguing the oligomerisation approach is the mediocre control over molecular weight and large polydispersity, since depolymerisation is performed in excess EG which limits the extent of molecular weight control only to time and temperature.

Ionic liquid (IL) have been shown to be excellent transesterification catalysts for PET depolymerisation (Q. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2015**, 3, 340-348; and L. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2020**, 8, 13362-13368). Imidazolinium-based ILs have been shown to be capable of interacting with Lewis-bases to form N-heterocyclic carbenes with significantly enhanced reactivity to drive transesterification (L. Wang *et al.*, *ACS Sustain. Chem. Eng.* **2020**, 8, 13362-13368). Such IL-based catalysts hold great promise for the metal-free catalytic depolymerisation of PET, although concerns remain over the safety and energy efficiency of the subsequent separation of IL from the depolymerised product stream

especially when the recycle may be reintroduced back into consumer products including food contact packaging (T. H. Begley & C. H. Hollifield, *ACS Symp. Ser.* **1995**, 609, 445-457).

Alternatively, to circumvent the necessity for costly purification, waste PET can be directly upcycled into high-value additives for various polymer-based applications. In one example (US 9,840,584), PET is depolymerised in glycol and then subsequently esterified with dimer fatty acids in a one-pot process to give an oligomeric polyol product. No tedious purification process is required and the one-pot depolymerisation technique is relatively straightforward, yielding a viscous liquid polyol product that can be readily incorporated for polyurethane (PU) coating applications. PET depolymerisation into polyols has also been demonstrated using various alkyl glycols (US 10,273,332) and then further esterified with fatty acids to obtain high-value chemical products such as lubricant base oil (US 10,336,958), drilling fluids additives (US 10,662,364) and as sustainable plasticizers for polyvinylchloride-based plastics (US 9,890,243).

However, barely any recycling solution exists for other plastics such as polyamides, PUs and polyesters other than PET. The real problem lies in the fact that with the exception of certain well-established mono-material plastic products such as single-use beverage bottles based on PET, most plastic wastes are not well sorted and comprise mixtures of various polymer types. For example, a seemingly simple food wrapper comprises of multilayer laminate that includes PET as a substrate layer, PU-based adhesive layer, aluminium foil layer, polymer-based inks and polyolefin layers. Such a composite plastic waste cannot be recycled using existing PET-based recycling process without further separation process to extract the PET. Another prominent source of mixed plastic waste with high PET content is textile waste, including both factory trimmings and disposed clothing. Such textile wastes compose of fibres from PET, polyamides, polyurethanes and cellulose, and separation is next to impossible.

In the absence of economically viable recycling alternatives, the current state of the art process for extracting the maximum value from such mixed plastic waste is energy recovery by incineration. While the energy recovery approach is better than landfilling such mixed plastic waste, it is not a sustainable solution in light of resource depletion. Therefore, there is an urgent need for a sustainable, urban mining approach that treat such mixed plastic waste as a secondary resource capable of being upcycled into valuable products.

Summary of Invention

Aspects and embodiments of the invention are discussed in the following numbered clauses.

1. A method of partially depolymerising a depolymerisable condensation polymer, the method comprising the steps of:

(a) forming a mixture comprising a depolymerisable condensation polymer, a polar aprotic solvent, a catalyst and a cleaving agent;

(b) heating the mixture to a temperature from greater than 150 °C to less than 200 °C and allowing the depolymerisation reaction to take place for a period of time to provide oligomers derived from the depolymerisable condensation polymer, wherein the cleaving agent is a polyol compound.

2. The method according to Clause 1, wherein the process involves quenching the mixture into water with stirring after the period of time to precipitate out the oligomers derived from the depolymerisable condensation polymer to provide a branched oligomeric resin after collection of the precipitated oligomers derived from the depolymerisable condensation polymer.

3. The method according to any one of the preceding clauses, wherein the polyol compound is selected from one or more of the group selected from glycerol, ethylene glycol, propylene glycol, tris(hydroxymethyl)aminomethane, tris(hydroxymethyl)methane, pentaerythritol, and sugar alcohols (e.g. one or more of the group consisting of erythritol, threitol, arabitol, xylitol, ribitol, mannitol, galactitol, fucitol, iditol, inositol, volemmitol, isomalt, maltitol, lactitol, maltotriitol, maltotetraitol, polyglycitol, and sorbitol).

4. The method according to Clause 3, wherein the catalyst is selected from one or more of the group consisting of an ionic liquid, a secondary amine, a tertiary amine, a heterocyclic amine, an organometallic compound, and a metal salt.

5. The method according to Clause 4, wherein the catalyst is selected from one or more of the group consisting of an ionic liquid, a tertiary amine and a metal salt, optionally wherein the catalyst is an ionic liquid.

6. The method according to Clause 5, wherein the catalyst is selected from one or more of the group consisting of hexamethylenetetramine, ZnCl_2 and 1-ethyl-3-methylimidazolium chloride, optionally wherein the catalyst is 1-ethyl-3-methylimidazolium chloride.

7. The method according to any one of Clauses 1 and 3 to 6, wherein, when the catalyst is an ionic liquid, the process involves a subsequent step of cooling the mixture after the period of time to provide an ionogel, suitable for use as a solid-state electrolyte.
- 5 8. The method according to any one of the preceding clauses, wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of a thermoplastic polyamide, a thermoplastic polyester, and a thermoplastic and/or crosslinked polyurethane.
- 10 9. The method according to Clause 8, wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of a polyurethane, nylon 6,6, nylon 6, polyethylene terephthalate, polylactic acid, and elastane, optionally wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of nylon 6,6, nylon 6, polyethylene terephthalate, and polylactic acid.
- 15 10. The method according to any one of the preceding clauses, wherein the period of time is from 3 hours to 48 hours, such as from 4 hours to 24 hours, such as from 5 hours to 18 hours.
- 20 11. The method according to any one of the preceding clauses, wherein the temperature is from 155 °C to 195 °C, such as from 170 °C to 190 °C, such as about 180 °C.
- 25 12. The method according to any one of the preceding clauses, wherein the stoichiometric ratio of the depolymerisable condensation polymer to the cleaving agent is from 1.25:1 to 10:1, such as from 5:3 to 5:1, such as about 5:2.
13. The method according to any one of Clauses 7 to 12 as dependent upon Clause 7, wherein the ionogel is used in further processing steps to provide a reinforced composite material, which additional steps include:
- 30 (ai) providing a plurality of glass fiber meshes coated in the ionogel; and
(a ii) stacking the plurality of glass fiber meshes coated in an ionogel and subjecting the resulting stack to heat and pressure to provide a reinforced composite material.
- 35 14. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Clause 2, wherein the branched oligomeric resin is used in further processing steps to provide a transparent film coating, which additional steps include:

- (bi) melting the branched oligomeric resin; and
- (bii) applying the melted brached oligomeric resin onto a surface to provide a transparent film coating upon cooling.

5 15. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Clause 2, wherein the branched oligomeric resin is used in further processing steps to provide a blended material suitable for use in coating, which additional steps include:

- (ci) forming a mixture comprising the branched oligomeric resin, an isocyanate resin and a solvent; and
- 10 (cii) removing the solvent to provide a blended material suitable for coating.

16. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a crosslinked material suitable for use in coating, which additional steps include:

- 15 (ci) forming a reaction mixture comprising the branched oligomeric resin, an triglycidyl isocyanurate epoxy crosslinker and a solvent, which is allowed to react for a period of time; and
- (cii) removing the solvent to provide a crosslinked material suitable for use in coating.

20 17. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Clause 2, wherein the branched oligomeric resin is used in further processing steps to provide a vitrimer material, which additional steps include:

- (di) providing a melted mixture of the branched oligomeric resin, an anhydride material (e.g. maleic anhydride) and a metal salt (e.g. zinc acetate);
- 25 (dii) subjecting the melted mixture to extrusion to provide a vitrimer material.

18. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Clause 2, wherein the branched oligomeric resin is used in further processing steps to provide a vitrimeric resin, which additional steps include:

- 30 (ei) forming a reaction mixture comprising the branched oligomeric resin, a dicarboxylic acid (e.g. succinic acid), a metal salt (e.g. zinc acetate) and a solvent;
- (eii) quenching the reaction mixture by using a water and/or an alkyl alcohol (e.g. isopropyl alcohol) and then collecting a precipitated material, which is the vitrimeric resin.

35 19. The method according to Clause 18, wherein the vitrimeric resin is further melted and subjected to extrusion to provide an extruded vitrimeric material.

20. The method according to any one of Clauses 2 to 6 and 8 to 12 as dependent upon Clause 2, wherein the branched oligomeric resin is used in further processing steps to provide a solid-state electrolyte, which additional steps include:

- (fi) providing an ionogel slurry comprising the branched oligomeric resin, an ionic liquid (e.g. 1-ethyl-3-methylimidazolium chloride), a first solvent (e.g. propylene carbonate) and a second solvent (e.g. ethyl acetate); and
- (fii) film casting the ionogel slurry onto a substrate and drying the slurry to provide a solid electrolyte.

21. The method according to any one of Clauses 7 to 12 as dependent upon Clause 7, wherein the ionogel is used in further processing steps to provide a composite product, which additional steps include:

- (ai) applying the ionogel to a first substrate to form a coated surface and pressing a second substrate against the coated surface to form a pre-adhered composite material; and
- (aia) heating the pre-adhered composite material to an elevated temperature for a period of time to substantially remove the solvent in the ionogel and provide the composite material.

Drawings

FIG. 1 depicts (A) reaction scheme showing the transesterification of PET with multifunctional alcohol including EG, glycerol (GLY) or pentaerythritol (PEN); and (B) description of the catalytic partial depolymerisation (CPD) process leading to the formation of branched oligomers.

FIG. 2 depicts (A) viscosity change during the CPD process. Upon heating, PET swells in the presence of N-methyl pyrrolidone (NMP) solvent, leading to the increase in viscosity. With addition of IL, PET dissolves and depolymerises leading to minimal viscosity changes; (B) Fourier-transform infrared (FTIR) analysis of both neat PET and GLY-reacted branched oligomers shows minimal changes to the molecular structure; (C) Optimization studies showing the effect of reaction time and GLY content on the subsequent mechanical properties of the branch oligomer gel; (D) Gelation of the IL/solvent containing branched oligomer mixture upon cooling; and (E) The gel can be formed by casting in a mould.

FIG. 3 depicts that control over molecular weight and architecture was demonstrated using different stoichiometric ratios of PET repeating unit to cleaving agent hydroxyl molar concentration. (A) Increasing hydroxyl ratios correlate with lower molecular weight and narrower polydispersity; (B) Increasing hydroxyl ratios correlate with lower gel modulus of the

IL/solvent containing branched oligomer gel product; (C) Ionic conductivity of the IL/solvent containing branched oligomer gel product was observed to be optimised at 5:1 PET/Hydroxyl ratio, as that ratio have the largest intramolecular volume available for unhindered diffusion of ionic species. Control over molecular weight and architecture was also demonstrated by
5 varying depolymerisation reaction time at 5:1 PET/Hydroxyl ratio; (D) Increasing reaction time correlate with lower molecular weight and narrower polydispersity; (E) Increasing reaction time correlate with lower gel modulus of the IL/solvent containing branched oligomer gel product. G' and G'' represent the elastic shear modulus and viscous shear modulus respectively, which correlates to how hard or soft the ionogel appears to be; and (F) Ionic conductivity of the
10 IL/solvent containing branched oligomer gel product was observed to be optimised after 2-3 hours.

FIG. 4 depicts the schematic showing the effect of depolymerisation reaction time on the molecular weight and architecture of PET polymer chains.

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FIG. 5 depicts (A) schematic describing the mechanism giving rise to ionic conductivity; (B) proof of conductivity using a simple series circuit connecting the IL containing branched oligomer gel with LED bulb and battery; (C) schematic layout of electrochemical double layer capacitor incorporating ionogel from waste PET oligomer; and (D) its nominal supercapacitor
20 performance with wide potential range.

FIG. 6 depicts (A) demonstration showcasing ability of process to rapidly depolymerise PU foam from waste cushions; and (B) demonstration showcasing ability of process to rapidly depolymerise mixed plastic waste containing polyester and PU from waste textile.

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FIG. 7 depicts the simplicity of the CPD process (inner cycle) compared to the PET complete depolymerisation into BHET process (outer cycle).

FIG. 8 depicts photographs of (A)(i) a close up of an ionogel film specimen sandwiched
30 between two aluminium plates. The aluminium plates are themselves sandwiched between two glass plates and the entire assembly is clamped together by a bulldog clip. This arrangement was then subjected to curing of the ionogel to enable adhesion between the aluminium plates and the ionogel film specimen, after which the bulldog clip and glass plates are removed; (A)(ii) the same arrangement as (A)(i) but showing the relative length of the
35 aluminium plates; and (B) an adhesion experiment after curing of the ionogel film specimen, where a bulldog clip with a weight attached to it is applied to one of the distal ends of the aluminium plates (the proximal end of each plate being that attached to the ionogel film

specimen) and the other distal end of the aluminium plate is used to suspend the resulting assembly in the air to show the adhesion between the plates and the ionogel film specimen.

FIG. 9 depicts (A) a single ply of ionogel-coated glass mesh and (B) a densified fibre reinforced composite formed by hot-pressing 10 of the single ply ionogel-coated glass meshes together.

FIG. 10 depicts (A) FTIR analysis showing negligible changes in the fingerprint region of PET, indicating that the PET chemistry and ester linkages are maintained after depolymerisation with GLY, EG and PEN, respectively; (B) dynamic scanning calorimetry (DSC) melt exotherms showing distinctive PET crystallite melting peak at 240 °C compared to the broad exotherm of the oligomeric products indicative of low crystallinity due to the branched and amorphous molecular architecture; (C) the branched oligomers can be redissolved in hexafluoroisopropanol/chloroform (2/98wt%) solvent mixture, and the polymer colloid size obtained from dynamic light scattering (DLS) is indicative of the molecular weight and architecture; (D) ionic conductivity of the IL/solvent containing branched oligomer gel product was measured using the parallel plate method, demonstrating its excellent ionic conductivity; and (E) photographs of the dispersion of PET oligomers after depolymerisation with EG, GLY and PEN in hexafluoroisopropanol/chloroform (2/98wt%) solvent mixture.

20 Description

Surprisingly it has been found that it is possible to depolymerise a condensation polymer using a simple chemical treatment that allows one to obtain oligomeric materials that can be used in multiple applications.

Disclosed herein is a facile method to enable control of molecular weight and molecular architecture of oligomers including branched and hyperbranched structure obtained via a facile depolymerization of condensation polymers using a co-catalytic ionic liquid/aprotic solvent mixture performed at ambient pressure and reaction temperature typically below 200°C, or any other suitable catalytic depolymerization systems.

The technical means of control is multifold: firstly, referring to the intelligent selection of cleaving agents including polyols on the basis of their molecular structure and functionality, secondly, by managing the stoichiometric ratio between the cleaving agent and number of repeating units within the condensation polymer. Besides, reaction conditions including temperature and time could also render effects over the ensuing molecular weight, degree of branching and polydispersity.

The same principle applies for controlled depolymerization using polyamine-based cleaving agents. The depolymerisable condensation polymers includes but not limited to thermoplastic polyamides such as nylon 6,6 and nylon 6, thermoplastic polyesters such as polyethylene terephthalate, polylactic acid, thermoplastic/crosslinked polyurethane and/or mixtures of such polyesters, polyamides and polyurethanes.

The catalytic depolymerization system includes but not exclusively to systems based on either transesterification, transamidation, transurethanisation or transcarbonation, as catalysed by either ionic liquids, secondary amines, tertiary amines, heterocyclic amines, organometallic compounds, or metal salts.

Thus, in a first aspect of the invention, there is disclosed a method of partially depolymerising a depolymerisable condensation polymer, the method comprising the steps of:

- (a) forming a mixture comprising a depolymerisable condensation polymer, a polar aprotic solvent, a catalyst and a cleaving agent;
- (b) heating the mixture to a temperature from greater than 150 °C to less than 200 °C and allowing the depolymerisation reaction to take place for a period of time to provide oligomers derived from the depolymerisable condensation polymer,

wherein the cleaving agent is a polyol compound.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

The polymers of interest that are present in the mixed plastic waste targeting condensation/stepwise polymers such as polyesters, polyamides and polyurethanes, can readily dissolve into the co-catalytic catalyst (e.g. ionic liquid)/aprotic solvent mixture. Impurities such as polyolefins, metal, glass and other inorganic residues are unable to dissolve and can be readily separated from the reaction mixture. Furthermore, the transesterification process is tolerant of chemical impurities such as salt, oil and surfactants residues that are present in the mixed plastic waste. By eliminating the sorting and purification steps, the reaction process can be simplified while improving the cost efficiency of recycling.

10 The depolymerisation reaction disclosed herein between polymer and cleaving agent may lead to the formation of branched oligomers. Depending on the type and content of cleaving agent added, the degree of branching and molecular weight of the depolymerized oligomer may be controlled, as discussed in more detail in the examples.

15 The catalyst (e.g. ionic liquid) and solvent can be removed by washing with water, to afford a pale brown resin powder comprising of a branched oligomeric resin (e.g. if the polymer was PET, then the resin will be oligomeric PET) that can be hot processed into films or used directly as binders for composite materials. The extracted catalyst (e.g. ionic liquid) and solvent can be readily recovered for reuse, with negligible decrease in catalytic activity.

20 Thus, in certain embodiments, the method disclosed above may include a further step of quenching the mixture into water with stirring after the period of time to precipitate out the oligomers derived from the depolymerisable condensation polymer to provide a branched oligomeric resin after collection of the precipitated oligomers derived from the depolymerisable condensation polymer. As will be appreciated, this resin may then be used in further processes, depending on the desired application for the resulting oligomeric resin.

Any suitable condensation polymer (or oligomer in need of further depolymerisation) may be used herein provided that it can be depolymerised into oligomers of the original polymeric length. The weight average molecular weight of the initial polymers may be from 50 kDa to 300 kDa and the resulting oligomers may have a weight average molecular weight that exceeds 0.5 kDa, such as from 500 Da to 10,000 Da. Examples of suitable condensation polymers include, but are not limited to a thermoplastic polyamide, a thermoplastic polyester, a thermoplastic polyurethane, a crosslinked polyurethane and combinations thereof. It will be appreciated that the polymers disclosed herein may be formed from a single monomer or from a plurality of monomers (i.e. 2, 3, or 4 monomers).

Particular examples of depolymerisable condensation polymers that may be mentioned herein includes, but is not limited to a polyurethane, nylon 6,6, nylon 6, polyethylene terephthalate, polylactic acid, elastane and combinations thereof. For example, the depolymerisable condensation polymer may be selected from one or more of the group consisting of nylon 6,6,
5 nylon 6, polyethylene terephthalate, and polylactic acid.

As noted hereinbefore, the cleaving agent is a polyol compound. Any suitable polyol material may be used in this method. Examples of suitable polyol materials include, but are not limited to glycerol, ethylene glycol, propylene glycol, tris(hydroxymethyl)aminomethane,
10 tris(hydroxymethyl)methane, pentaerythritol, sugar alcohols and combinations thereof. Examples of sugar alcohols that may be mentioned herein include, but are not limited to erythritol, threitol, arabitol, xylitol, ribitol, mannitol, galactitol, fucitol, iditol, inositol, volemitol, isomalt, maltitol, lactitol, maltotriitol, maltotetraitol, polyglycitol, sorbitol, and combinations thereof (e.g. the sugar alcohol may be sorbitol).

15 The purpose of the cleaving agent is to cleave the chemical linkage within the polymers, giving lower molecular weight polymers described as oligomers. As noted above, the cleaving agent may be a multifunctional alcohol, otherwise described as a polyol. Glycerol, in particular, is a biobased molecule that is a by-product from biodiesel refining with little commercial value due to its relative low purity (<99%) and presence of contaminants such as methanol, surfactants and minerals in significant quantities. While this chemical grade of glycerol is unsuitable for
20 high value applications such as pharmaceuticals, it is sufficient as a cleaving agent for the depolymerization of condensation polymers from plastic waste.

25 Any suitable material may be used as the catalyst, for example, the catalyst may be selected from one or more of the group consisting of an ionic liquid, a secondary amine, a tertiary amine, a heterocyclic amine, an organometallic compound, a metal salt, and combinations thereof. In particular embodiments of the invention, the catalyst may be selected from one or more of the group consisting of an ionic liquid, a tertiary amine and a metal salt.

30 In embodiments of the invention that may be mentioned herein, the ionic liquid may be an imidazolium-based ionic liquid. The imidazolium-based ionic liquid in such embodiments may be formed from 1-alkyl-3-methylimidazolium cations having an alkyl chain length of from C1 to C8. The anionic component of the ionic liquid may be selected from one or more of
35 acetate, chloride, bromide, iodide, methyl sulfate, benzenesulfonate, tetrachloroferrate, tetrachloroaluminate, tetrafluoroborate, dicyanamide, tetrachlorozincate and chlorocuprates.

Specific catalysts that may be mentioned herein include, but are not limited to hexamethylenetetramine, ZnCl_2 , 1-ethyl-3-methylimidazolium (e.g. 1-ethyl-3-methylimidazolium chloride), and combinations thereof.

- 5 In yet more particular embodiments of the invention, the catalyst may be an ionic liquid. For example, the catalyst may be 1-ethyl-3-methylimidazolium chloride.

In certain embodiments that may be mentioned herein, the cleaving agent and the catalyst may be the same material. For example, the catalyst and the cleaving agent may be
10 tris(hydroxymethyl)aminomethane, which is both a polyol and an amine. As such, while the cleaving agent and catalyst may be separate components, they may in some instances be provided in a single substance that has the required features for both the catalytic function and as a cleaving agent. Such substances may be a polyol that also incorporates an amino moiety.

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Without wishing to be bound by theory, it is believed that the catalyst and the polar aprotic solvent form a co-catalytic mixture that enables the depolymerisation reaction to take place much more readily than would be the case without the use of these components.

- 20 Again, without wishing to be bound by theory, it is believed that the polar aprotic solvent may function as a co-catalyst in combination with the ionic liquid by two mechanisms:

I. swelling, plasticizing and dissolving the polymer of interest to reveal and increase availability of reaction sites; and

II. forming a Lewis acid-base pair with the ionic liquid to form a co-catalytic pair that is
25 more efficient at catalysing transesterification reactions.

It is believed that similar co-catalytic pairs are formed with the other combinations discussed herein.

- 30 The amount of the catalyst relative to the polar aprotic solvent may be any suitable ratio. For example, the catalyst may form from 0.1 to 90 percent by weight of the combined weight of the catalyst and polar aprotic solvent alone, with the remainder being formed from the high-temperature polar aprotic solvent.

- 35 When the catalyst is an ionic liquid, the ionic liquid/solvent containing reaction product was observed to gel readily upon cooling to provide an ionogel. Thus, in certain embodiments of the method, when the catalyst is an ionic liquid, the process may involve a subsequent step

of cooling the mixture after the period of time to provide an ionogel. This ionogel may then be used in a range of different applications, as discussed in more detail hereinbelow.

5 The period of time used in step (b) of the method may be any suitable period of time as determined by a person skilled in the art for the desired degradation of the polymer into oligomeric fragments. However, suitable periods of time that may be mentioned herein include, but are not limited to from 3 hours to 48 hours, such as from 4 hours to 24 hours, such as from 5 hours to 18 hours.

10 Any suitable polar aprotic solvent may be used in the process. The only requirement is that the polar aprotic solvent used (or the solvent within the mixture) have a boiling point that is higher than the selected temperature for step (b) of the method. For example, the polar aprotic solvent may be selected from one or more of the group including, but not limited to, N-methyl-2-pyrrolidone (NMP), dimethyl Sulfoxide (DMSO), acetamide, dimethyl formamide (DMF),
15 cyrene, cyclohexanone, dimethyl Acetamide (DMAc) and combinations thereof.

As noted hereinbefore, the temperature applied to the mixture in step (b) of the method is a temperature of from greater than 150 °C to less than 200 °C. For example, the temperature may be from 155 °C to 195 °C, such as from 170 °C to 190 °C, such as about 180 °C.

20 Any suitable stoichiometric ratio of the depolymerisable condensation polymer to the cleaving agent may be used herein. For example, the stoichiometric ratio of the depolymerisable condensation polymer to the cleaving agent may be from 1.25:1 to 10:1, such as from 5:3 to 5:1, such as about 5:2. As described in the examples hereinbelow, there may be a correlation
25 between oligomer molecular weight and the amount of cleaving agent used. For ionogels, the optimal ratio may be 5:1, based on the examples provided below, but this may differ depending on the specific cleaving agents used. In general, there is no particular matching between the cleaving agents and any particular polymer. For example, ethylene glycol or glycerol could be used as cleaving agent for any type of polyester, polyamide or polyurethane.

30 As will be appreciated, the disclosed method provides either a resin formed from oligomeric materials or, when treated with an ionic liquid as catalyst, an ionogel. These materials may have a number of downstream uses and so the methods disclosed herein may be extended to cover these potentially desired uses.

35 For example, an ionic liquid containing recyclate can be film casted and dried to form films that can be used as high strength adhesives due to its branched oligomeric morphology.

Reinforcements such as structural fibres can be incorporated into the recyclate to fabricate composite materials that can be used for structural applications.

Thus in embodiments of the invention where an ionogel is provided by the method, the resulting ionogel may be used in further processing steps to provide a reinforced composite material, which additional steps include:

- (ai) providing a plurality of glass fiber meshes coated in the ionogel; and
- (a ii) stacking the plurality of glass fiber meshes coated in an ionogel and subjecting the resulting stack to heat and pressure to provide a reinforced composite material.

10

In alternative embodiments of the invention where an ionogel is provided by the method, the resulting ionogel may be used in further processing steps to provide a composite product, which additional steps include:

- (ai) applying the ionogel to a first substrate to form a coated surface and pressing a second substrate against the coated surface to form a pre-adhered composite material; and
- (a ii) heating the pre-adhered composite material to an elevated temperature for a period of time to substantially remove the solvent in the ionogel and provide the composite material.

15

Ideally, recycled plastics should be of the same grade as virgin resin materials and could be directly used as such. However, it is not an economically feasible approach due to the capital- and labour-intensive recycling process coupled with the low price of virgin resin making it impossible to balance the cost and value. By simplifying the waste sorting process, costs involved can be significantly reduced. The process does not strive to achieve virgin-grade recyclates, but instead aims to directly upcycle the recyclate into valuable functional materials.

20

As discussed above, the catalyst (e.g. ionic liquid) can be removed from the recyclate to isolate the branched oligomeric recycled resin product. The recycled resin can be hot processes similarly to virgin materials to obtain films with excellent optical transparency. The recycled resin could either be applied directly in powder coatings for anti-corrosion applications or be reincorporated at high loading into virgin resin without significant loss in material properties.

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In embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a transparent film coating, which additional steps include:

- (bi) melting the branched oligomeric resin; and
- (b ii) applying the melted branched oligomeric resin onto a surface to provide a transparent film coating upon cooling.

30

In other embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a blended material suitable for use in coating, which additional steps include:

- 5 (ci) forming a mixture comprising the branched oligomeric resin, an isocyanate resin and a solvent; and
(cii) removing the solvent to provide a blended material suitable for coating.

10 In embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a crosslinked material suitable for use in coating, which additional steps include:

- (ci) forming a reaction mixture comprising the branched oligomeric resin, an triglycidyl isocyanurate epoxy crosslinker and a solvent, which is allowed to react for a period of time; and
15 (cii) removing the solvent to provide a crosslinked material suitable for use in coating.

In embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a vitrimer material, which additional steps include:

- 20 (di) providing a melted mixture of the branched oligomeric resin, an anhydride material (e.g. maleic anhydride) and a metal salt (e.g. zinc acetate);
(dii) subjecting the melted mixture to extrusion to provide a vitrimer material.

25 In embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a vitrimeric resin, which additional steps include:

- (ei) forming a reaction mixture comprising the branched oligomeric resin, a dicarboxylic acid (e.g. succinic acid), a metal salt (e.g. zinc acetate) and a solvent;
(eii) quenching the reaction mixture by using a water and/or an alkyl alcohol (e.g. isopropyl
30 alcohol) and then collecting a precipitated material, which is the vitrimeric resin. In certain embodiments, the vitrimeric resin may further be melted and subjected to extrusion to provide an extruded vitrimeric material.

35 In embodiments of the invention where an oligomeric resin is provided by the method, the resulting oligomeric resin may be used in further processing steps to provide a solid-state electrolyte, which additional steps include:

- (fi) providing an ionogel slurry comprising the branched oligomeric resin, an ionic liquid (e.g. 1-ethyl-3-methylimidazolium chloride), a first solvent (e.g. propylene carbonate) and a second solvent (e.g. ethyl acetate); and
- (fii) film casting the ionogel slurry onto a substrate and drying the slurry to provide a solid electrolyte.

In addition, the ionogel and the oligomeric resin may have uses associated with these materials directly.

- For example, the ionogel can be used directly as a solid-state electrolyte for batteries and supercapacitors due to its high ionic conductivity.

As noted above, an ionogel may be formed by directly incorporating oligoesters (or other suitable oligomeric materials) into a liquid electrolyte to form an ionogel for various metal ion batteries. Depending on the relevant ionic chemistry of the metal ion battery type, the corresponding metal salt can be dissolved into a polar aprotic solvent, with or without additional ionic liquid to form a gel electrolyte (i.e. ionogel) with added branched oligoesters. For example, a lithium salt such as lithium chloride or lithium bis(trifluoromethanesulfonyl)imide can be used for lithium-ion battery, and similarly a zinc salt such as zinc chloride or zinc acetate can be used for zinc-ion battery.

A typical composition of the gel electrolyte may include:

- (ia) an oligomer comprising between 5-50 percent by weight;
- (ib) a metal salt comprising between 0.1-25 percent by weight;
- (ic) a polar, aprotic solvent including but not limited to ethylene carbonate, dimethyl carbonate, propylene carbonate, N-methyl pyrrolidone, comprising between 5-50 percent by weight; and
- (id) an ionic liquid comprising 0-50 percent by weight. Examples of ionic liquid includes but not limited to 1-alkyl-3-methylimidazolium cations with alkyl chain length between C1 to C8.
- The anionic component of the ionic liquid includes but not limited to acetate, chloride, bromide, iodide, methyl sulfate, benzenesulfonate, tetrachloroferrate, tetrachloroaluminate, tetrafluoroborate, dicyanamide, tetrachlorozincate and chlorocuprates.

Alternatively one may directly incorporate an oligomer into a liquid electrolyte to form a gel electrolyte for electrochemical supercapacitors.

The typical composition of the gel electrolyte for this use may include:

- (iia) an oligomer comprising between 5-50 percent by weight;
- (iib) a metal salt comprising between 0-25 percent by weight;
- (iic) a polar, aprotic solvent including but not limited to ethylene carbonate, dimethyl carbonate, propylene carbonate, N-methyl pyrrolidone, comprising between 5-50 percent by weight; and
- (iid) an ionic liquid comprising 0-50 percent by weight. Examples of ionic liquid includes but not limited to 1-alkyl-3-methylimidazolium cations with alkyl chain length between C1 to C8. The anionic component of the ionic liquid includes but not limited to acetate, chloride, bromide, iodide, methyl sulfate, benzenesulfonate, tetrachloroferrate, tetrachloroaluminate, tetrafluoroborate, dicyanamide, tetrachlorozincate and chlorocuprates.

For applications of the resin one may chemically react the oligomer with a multifunctional crosslinker to form a covalently crosslinked thermosetting network. The crosslinked thermoset network can be used as binder resins for composites or coatings.

15

Applicable crosslinkers include the following:

- (iia) molecules containing multiple glycidyl moieties including but not limited to Bisphenol A diglycidyl ether, Glycerol triglycidyl ether, polyethylene glycol diglycidyl ether, Trimethylolpropane triglycidyl ether and Butanediol diglycidyl ether;
- (iib) molecules containing single or multiple anhydride moieties including but not limited to Maleic anhydride, Phthalic anhydride, Tetrahydrophthalic anhydride, Hexahydrophthalic anhydride, Methyl-tetrahydrophthalic anhydride, Methyl-hexahydrophthalic anhydride, Nadic methyl anhydride, Hexachloro Endomethylene Tetrahydrophthalic anhydride, Pyromellitic dianhydride and Benzophenone tetracarboxylic dianhydride;
- (iic) molecules containing multiple isocyanate moieties including but not limited to Methylenediphenyl diisocyanate, Toluene diisocyanate, Isophorone diisocyanate, Hexamethylene diisocyanate, Phenyl diisocyanate, Methylenebis(cyclohexyl isocyanate) and their related dimers and trimers; and
- (iid) molecules containing multiple carboxylic acid moieties including but not limited to malonic acid, succinic acid, maleic acid, fumaric acid, oxalic acid, glutaric acid, adipic acid, pimelic acid, furan dicarboxylic acid, phthalic acid, itaconic acid, citraconic, citric acid, isocitric acid, aconitic acid, propane-1,2,3-tricarboxylic acid and trimesic acid.

- Polar, aprotic solvents including but not limited to chloroform, dichloromethane, tetrahydrofuran, acetone, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), acetamide, dimethyl formamide (DMF), ethylene carbonate, dimethyl carbonate, propylene

carbonate, cyrene, cyclohexanone, dimethyl acetamide (DMAc) and combinations thereof may be used as a processing aid to dissolve and facilitating chemical crosslinking reaction.

For alternative applications of the resin one may chemically react the oligomer with a multifunctional crosslinker to form a dynamic covalent network based on vitrimer chemistry. The thermosetting material based on dynamic covalent network can be used as binder resins for composites or coatings. An advantage of a dynamic covalent network includes enhanced mechanical damping ability, improved recyclability, repairability and self-healing capability.

Applicable crosslinking strategies to impart dynamic covalent bonds include the following:
(iva) By incorporating a transition metal salt comprising between 0.01-25 percent by weight and a molecule containing single or multiple anhydride moieties comprising between 0.01-25 percent by weight, with the remainder comprising of the oligomer.

The molecule containing single or multiple anhydride moieties includes but not limited to Maleic anhydride, Phthalic anhydride, Tetrahydrophthalic anhydride, Hexahydrophthalic anhydride, Methyl-tetrahydrophthalic anhydride, Methyl-hexahydrophthalic anhydride, Nadic methyl anhydride, Hexachloro Endomethylene Tetrahydrophthalic anhydride, Pyromellitic dianhydride and Benzophenone tetracarboxylic dianhydride.

The transition metal salt includes but not limited to the corresponding chlorides, acetates, acetylacetonates, glycolates, glycerolates, carbonates, sulfates, nitrates, phosphates, citrates, carboxylates, fluorides and bromides of the respective transition metals including Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc.

(ivb) By incorporating a transition metal salt comprising between 0.01-25 percent by weight and a molecule containing multiple carboxylic acid moieties comprising between 0.01-25 percent by weight, with the remainder comprising of the oligomer.

The molecule containing multiple carboxylic acid moieties including but not limited to malonic acid, succinic acid, maleic acid, fumaric acid, oxalic acid, glutaric acid, adipic acid, pimelic acid, furan dicarboxylic acid, phthalic acid, itaconic acid, citraconic, citric acid, isocitric acid, aconitic acid, propane-1,2,3-tricarboxylic acid and trimesic acid.

The transition metal salt includes but not limited to the corresponding chlorides, acetates, acetylacetonates, glycolates, glycerolates, carbonates, sulfates, nitrates, phosphates, citrates, carboxylates, fluorides and bromides of the respective transition metals including Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc.

Polar, aprotic solvents including but not limited to chloroform, dichloromethane, tetrahydrofuran, acetone, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), acetamide, dimethyl formamide (DMF), ethylene carbonate, dimethyl carbonate, propylene carbonate, cyrene, cyclohexanone, dimethyl acetamide (DMAc) and combinations thereof may be used as a processing aid to dissolve and facilitating chemical crosslinking reaction.

Further aspects and embodiments of the invention will be further described by the following non-limiting examples.

10

Examples

Materials

Virgin grade PET pellets (Ramapet N1) were obtained from Indorama Ventures. N-methyl pyrrolidone (NMP), glycerol (GLY), ethyl acetate, dichloromethane, chloroform and propylene carbonate (PC) were obtained from Tedia Company, Inc. 1-ethyl-3-methylimidazolium chloride (EmimCl), potassium bromide, tris(hydroxymethyl)aminomethane (TRIS), zinc chloride, hexamethylenetetramine, zinc acetate, succinic acid, pentaerythritol (PEN) and hexafluoroisopropanol were obtained from Sigma Aldrich. Triglycidyl isocyanurate, maleic anhydride and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were obtained from Tokyo Chemical Industries. Ethylene glycol (EG) and isopropyl alcohol were obtained from Aik Moh Singapore. Samples of Nylon 6,6 (DuPont™ Zytel®) were provided by DuPont Singapore. Samples of isocyanate resin (Desmodur® N 3580 BA) were provided by Bayer Singapore. PU foam was obtained from discarded sofa cushion. Mixed polyester/elastane textile was obtained from discarded clothing waste. Carbon-coated aluminium electrode sheet, stainless-steel plate, coin cell, aluminium strips and glass fibre mesh were purchased from ANR Technologies.

20

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General procedure for preparing PET powder

PET powder was obtained by cryo-milling of virgin grade PET pellets using a SPEX 6875 cryogenic grinder.

30

Analytical techniques

FTIR

A Perkin-Elmer Frontier FTIR was used, and the analysis was performed at a 4 cm⁻¹ resolution averaged over 32 scans from 400-4000 cm⁻¹ wavenumber range. For PET powder, it was mixed with dry potassium bromide powder and cold pressed into pellets for FTIR analysis.

35

Ionic conductivity

A TA instruments DHR-3 rheometer with dielectric accessory connected to a Keysight E4980A LCR meter and 25 mm parallel plate geometry fixture was used in this analysis. The ionogel were sandwiched between the parallel plates and dielectric frequency scan was performed between 20 Hz – 20 kHz at 1 V amplitude.

DSC

A TA Q10 DSC was used in this analysis. About 5 mg of sample was encased within a sealed hermetic aluminium pan for each DSC analysis. The analysis was performed under 50 cc/min flowing nitrogen gas, and at 5 °C/min heating ramp from 100 °C to 300 °C.

DLS

A Malvern Nano ZS (ZEN3600) DLS was used in this analysis. About 0.5 g of each ionogel sample was precipitated in excess water, filtered and oven-dried. The oligomer precipitate was then redissolved in chloroform/hexafluoroisopropanol (98/2 wt%) solvent to form a 0.001 wt% solution for DLS analysis.

Dynamic mechanical analysis (DMA)

A TA Q800 DMA with double cantilever fixture was used in this analysis. The branched oligomer resin or vitrimer samples was cold pressed in a steel mould under 5 tons of pressure to form a rectangular bar 60 mm long, 5 mm wide and 3 mm thick. The sample bar was affixed within the double cantilever fixture clamp, and the temperature ramp analysis was performed at 1 Hz frequency and 20 µm amplitude, at a heating rate of 3 °C/min.

25

Example 1. Demonstration of Catalytic Partial Depolymerisation (CPD) Process to obtain ionogel from PET polymer

In a 3-neck round bottom flask, PET pellets (14 g) was dissolved in NMP (22 g) solvent at 180 °C in an oil bath under magnetic stirring. EmimCl (14 g) and GLY (0.45 g) were then added into the PET/NMP solution to initiate the depolymerisation reaction under reflux typically for 5 hours. The reaction was terminated simply by cooling the reaction mixture to room temperature to obtain an ionogel. The PET repeating unit to GLY hydroxyl ratio in this example is 5:1. The PET-GLY ratio can be adjusted by controlling the addition of GLY to facilitate molecular weight control of the oligomer and depolymerisation reaction time would also influence the degree of molecular weight reduction as demonstrated in the following examples.

An oligomer with lower molecular weight will result in a softer ionogel due to lower molecular weight.

FIG. 1A is a reaction schematic describing the catalytic transesterification depolymerisation between PET and a hydroxyl-containing cleaving agent compound in the presence of catalyst and solvent under heating while FIG. 1B is a schematic drawing describing the possible molecular structures of oligomers obtained using different multifunctional alcohols. Increasing hydroxyl groups can be expected to correspond to a higher degree of branching in the oligomer obtained.

10

Characterization

The IL-containing recyclate was observed to be able to form gel upon cooling without any further separation or purification process. FIG. 2B shows the FTIR analysis of the PET oligomer obtained after CPD, compared to neat PET powder. No observable change was reported in the PET fingerprint region between 500-200 cm^{-1} after the CPD process, indicating that the product still comprised of PET. The larger absorbance in the 3000-3800 cm^{-1} can be attributed to the increase in hydroxyl end-groups due to incorporation of GLY into the oligomer during depolymerisation.

20 **Example 2. Viscosity change during the CPD process**

Depolymerisation simulation study to determine viscosity change

A TA instruments DHR-3 rheometer with environmental test chamber and 25 mm parallel plate geometry fixture was employed for this depolymerisation simulation study. The process simulation consists of applying a constant heating ramp from ambient to 160 °C, followed by a short isothermal phase. PET powder (0.1 g), GLY (3 mg) and NMP (1 g) solvent were mixed into a slurry paste using a spatula and for 10 secs. The slurry paste was then sandwiched between the two parallel plates of the parallel plate rheometer. In a separate experiment, EmimCl (0.1 g, IL catalyst) was combined with PET powder (0.1 g), GLY (3 mg) and NMP (1 g) solvent to form a slurry mixture using a spatula and for 10 secs. The slurry mixture was then sandwiched between the two parallel plates of the parallel plate rheometer, and subjected to the same simulation process as aforementioned.

Results and discussion

FIG. 2A describes the viscosity change during the CPD process. The initial viscosity of the slurry mixture was low due to sedimentation of the PET powder and thus, the viscosity

reflected mainly the contribution by the NMP/GLY solvent component. As the temperature increases, PET starts to dissolve into the solvent, leading to an increase in viscosity measured.

5 In the presence of IL catalyst, PET was still observed to dissolve into the solvent but no appreciable increase in viscosity was observed due to the simultaneous depolymerisation of high molecular weight PET into short chain oligomers. The CPD process is thus shown to possess high depolymerisation rates when performed in a co-catalytic IL/solvent system.

10 **Example 3. Effect of GLY cleaving agent concentration and depolymerisation reaction time over the molecular weight and architecture of the ensuing ionogel**

Shear modulus

The shear modulus of the extracted ionogel product was measured using TA instruments DHR-3 rheometer with a 25 mm parallel plate geometry fixture in an oscillatory measurement
15 mode at 1% strain and 1 Hz at ambient condition.

Effect of CPD reaction time on ionogel properties

To study the effect of CPD reaction time on ionogel properties, samples at different reaction times were prepared by following the protocol in Example 1 except approximately 5 g of
20 reaction product was extracted from the reaction vessel after 0.5, 1, 2, 3, 5 and 18 hours. The samples were directly used for ionic conductivity measurements.

Effect of PET to GLY-hydroxyl ratio on ionogel properties

To study the effect of PET to GLY-hydroxyl ratio on ionogel properties, samples with different
25 PET to GLY-hydroxyl ratios were prepared by following the protocol in Example 1 except one of 0.22 g (10:1), 0.45 g (5:1), 0.89 g (5:2) and 1.34 g (5:3) of GLY was added into the PET/NMP solution.

Results and discussion

30 Using PET and GLY as example, the molecular weight and architecture of the ensuing branched oligomer product can be controlled by varying the stoichiometric ratios of PET repeating unit to cleaving agent or reaction time, as described in FIG. 3.

FIG. 3A describes the decrease in colloidal particle size with increasing GLY content during
35 depolymerisation. The colloidal particle size correlate with the average molecular weight of the oligomers, which is expected to decrease with increasing cleaving agent used. FIG. 2C and 3B describe the decrease in shear modulus of the depolymerisation ionogel product with

increasing cleaving agent content as expected due to lower molecular weight of the oligomer. In all cases, the storage modulus remained larger than the loss modulus, which indicates that the depolymerisation product remained as a gel-like state. FIG. 2D is a photograph showing the gel state of the ionogel product, which is mouldable by casting in a Teflon mould. FIG. 3C describes the ionic conductivity of ionogel product at different cleaving agent content. The ionogel obtained at 5:1 PET to GLY hydroxyl ratio possesses the optimal ionic conductivity likely due to the largest intramolecular free volume available for unhindered diffusion of ionic species. As expected, the gel modulus and ionic conductivity vary with different PET/GLY stoichiometric ratios. Therefore, by only varying the PET repeating unit to GLY cleaving agent hydroxyl molar concentration, it was demonstrated that the molecular weight, architecture, and polydispersity can be controlled.

Similarly, depolymerisation reaction time have been shown to influence the molecular weight, architecture, and polydispersity of the oligomers. Initially, GLY cleaves the PET polymer chains and remains as a terminal end group with 2 free hydroxyl moieties. Over time, as transesterification proceeds, the terminal dihydroxyl is able to further cleave and incorporate new branches, as depicted in FIG. 4. FIG. 4 shows a simple schematic of the change in molecular weight and degree of branching due to incorporation of multifunctional cleaving agents into the polymer. This will further reduce molecular weight and polydispersity as described in FIG. 3D. FIG. 3D describes the decrease in colloidal particle size with increasing depolymerisation reaction time. The colloidal particle size correlate with the degree of branching of the oligomers as longer reaction time would facility a greater degree of transesterification exchange between the hydroxyl end-groups and the ester moieties along the polymer backbone. FIG. 3E describes the decrease in shear modulus of the depolymerisation ionogel product with increasing depolymerisation reaction time which is expected due to lower crystallinity with increasing degree of branching. The extent of transesterification appears to reach a plateau after 5 hours. FIG. 3F describes the ionic conductivity of ionogel product with increasing depolymerisation reaction time. The initial increase in ionic conductivity is due to the increase in degree of branching and thus, free volume. However, the high depolymerisation reaction temperatures would lead to the degradation of the IL which result in decrease in ionic conductivity measured. Hence, depolymerisation reaction time will influence the molecular weight and degree of branching which subsequently affect the chain packing ability of the oligomers which influences its ability to form chain entanglements with neighbouring macromolecules and also the available intramolecular free volume.

Example 4. Simple symmetric capacitor cell with ionogel

FIG. 5A is a schematic drawing explaining the mobility of ions within the ionogel comprising of branched oligomers due to the high free volume when coupled with an appropriate IL and aprotic solvent to maximise swelling of the oligomer.

5

Preparation of simple symmetric capacitor cell with ionogel

The ionogel prepared in Example 1 was sandwiched between 2 pieces of stainless-steel plate and sealed with a coin cell to form a simple symmetric capacitor cell. FIG. 5B is a photograph showing a circuit setup using a 9 V battery to light an LED diode.

10

Results and discussion

A container in the circuit functions as a switch when filled with the ionogel, thereby demonstrating the ionic conductivity of the ionogel. The ionic conductivity of the as-obtained ionogel within the coin cell was measured to be within the range of $10^{-3} \text{ S.cm}^{-1}$. Therefore, due to the presence of the IL, the material possesses excellent ionic conductivity that lends itself to be incorporated into energy storage devices such as batteries and supercapacitors as solid electrolyte as described in FIG. 5A-B.

15

Example 5. Symmetric electrochemical double layer supercapacitor utilising ionogel

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FIG. 5C is a schematic layout for a symmetric electrochemical double layer supercapacitor utilising ionogel obtained from depolymerised PET.

Fabrication of ionogel membrane composite separator

25

The ionogel membrane composite separator can be fabricated by simple film casting of the hot ionogel solution prepared in Example 1, and cooling it to form a gel film, which can then be sandwiched between carbon coated current collectors to assemble the supercapacitor.

Results and discussion

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FIG. 5D describes the nominal specific capacitance performance of the symmetric electrochemical double layer supercapacitor. The wide potential window is due to the use of IL and aprotic solvent instead of traditional aqueous acids.

Example 6. Demonstration of CPD Process to obtain ionogel from PU foam and mixed polyester/elastane textile

35

PU foam waste

In a 3-neck round bottom flask, EmimCl (14 g) and GLY (1 g) were dissolved in NMP (50 g) solvent at 180 °C in an oil bath under magnetic stirring. PU foam waste (14 g) was shredded into 0.5 cm sized bits and gradually added into the IL/GLY/NMP solution to undergo depolymerisation reaction under reflux typically for 5 hours. The reaction was terminated simply by cooling the reaction mixture to room temperature to obtain an ionogel.

Mixed polyester/elastane textile

Ionogel from mixed polyester/elastane textile was obtained by following the PU foam waste protocol above except shredded mixed polyester/elastane textile waste (14 g) was used instead of PU foam waste.

Results and discussion

FIG. 6A describes the depolymerisation of PU foam from waste cushions into ionogel using the same CPD process and reagents as described in FIG. 2A. FIG. 6B describes the depolymerisation of mixed polyester and PU from waste textile into ionogel using the same CPD process and reagents as described in FIG. 2A.

Comparative Example 1

The CPD in Example 1 was compared to the established BHET approach for PET depolymerisation.

Results and discussion

FIG. 7 describes the comparison between the CPD approach with the established BHET approach for PET depolymerisation. The BHET approach utilises far excess amount of EG to function as both depolymerisation reactant and solvent for PET depolymerisation. There is a need for multiple process steps to concentrate, separate and purify the BHET to make suitable for subsequent repolymerisation and thus, reuse. In contrast, the CPD approach utilises less process steps and the obtained oligomeric product could directly be reused in various applications.

Example 7. Demonstration of ionogel from PET as adhesive

On a strip of 2 mm thick aluminium plate of width 2.5 cm, ionogel (0.2 g) prepared in Example 1 was spread thinly using a spatula across an area of 2.5 cm by 2.5 cm on one end of the plate. The coated aluminium plate was dried in an oven at 80 °C for 2 hours to dry off the NMP solvent. Another strip of 2 mm thick aluminium plate of width 2.5 cm was pressed against the

coated surface and both aluminium strips were clamped together between 2 pieces of glass microscope slides using a 1-inch binder clip (FIG. 8A). The clamped specimen was heated in an oven at 250 °C for 30 mins, before being allowed to cool down to ambient temperature by removing it from the oven. Then, the clamp was removed. One end of the specimen was
5 attached to a 500 g weight to show the adhesive strength of the ionogel from PET.

Results and discussion

First, a simple tug/pull by hand was done to judge if the strips were bonded. The 2 aluminium strips were observed to be strongly bonded to each other as the strips were not easily peeled
10 apart without bending the aluminium strip. Next, one end of the specimen was attached to a 500 g weight. As demonstrated in FIG. 8B, the ionogel from PET has strong adhesive strength.

Example 8. Demonstration of ionogel from PET for fibre reinforced composite

15 Reinforcements, such as structural fibres, can be incorporated into the recyclate to fabricate composite materials that can be used for structural applications.

Preparation of fibre reinforced composite

On 10 pieces of 15 cm-by-15 cm glass fibre meshes, the ionogel prepared in Example 1 was
20 spread thinly using a spatula across the entire area. The ionogel-coated glass fibre mesh was dried in an oven at 80 °C for 2 hours to dry off the NMP solvent. Subsequently, the 10 pieces of dried ionogel coated glass mesh was stacked upon each other and compacted using a hot press at 250 °C and 300 kPa for 5 mins. Upon removal from the hot press and allowed to cool to ambient temperature.

25

Results and discussion

A densified fibre reinforced composite board was obtained (FIG. 9).

Example 9. Obtaining branched oligomeric resin from ionogel via controlled 30 depolymerisation of PET using GLY in aprotic solvent catalysed by IL

The branched oligomeric resin was prepared from PET pellets (50 g), NMP (100 g) solvent, EmimCl (2.5 g) and GLY (1.6 g) by following the protocol in Example 1 except the reaction was under reflux typically for 18 hours, and the reaction was terminated by quenching the
35 reaction product in deionised (DI) water under strong stirring to induce precipitation of the branched oligomeric resin. The precipitated resin was filtered and washed repeatedly using DI water thrice, followed by ethyl acetate twice. The washed branched oligomeric resin was

then dried in an oven at 80 °C overnight to give a pale brown resin powder. The PET repeating unit to GLY-hydroxyl ratio in this example is 5:1.

Results and discussion

- 5 The EmimCl IL catalyst was recovered by distilling away water from the precipitation bath to give a clear yellow solution of NMP/EmimCl. The NMP/EmimCl solution was further distilled to remove the NMP solvent for reuse, leaving behind EmimCl in form of a dark brown liquid. This dark brown liquid was subsequently reused as catalyst for repeated controlled depolymerisation for a further 3 times with no observable changes in depolymerisation yield.

10

Example 10. Obtaining branched oligomeric resin via controlled depolymerisation of PET using EG or PEN in aprotic solvent catalysed by IL

Cleaving agent: EG

- 15 The branched oligomeric resin was prepared by following the protocol in Example 9 except EG (1.6 g) was used instead of GLY. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown powder. The PET repeating unit to ethylene glycol-hydroxyl ratio in this experiment is 5:1.

Cleaving agent: PEN

- 20 The branched oligomeric resin was prepared by following the protocol in Example 9 except PEN (1.8 g) was used instead of GLY. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown powder. The PET repeating unit to ethylene glycol-hydroxyl ratio in this experiment is 5:1.

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Results and discussion

- Using PET as example, through the use of different cleaving agents including EG, GLY (described in Example 9) and PEN, the molecular weight and architecture of the ensuing branched oligomer product can be controlled, as described in FIG. 10. After depolymerisation into branched oligomers, the crystallinity of the PET polymer was greatly suppressed, due to the large polydispersity, low molecular weight and branched molecular architecture.

- FIG. 10A shows the FTIR analysis of the PET oligomer obtained after depolymerisation with GLY, EG and PEN, compared to neat PET powder. No observable change was reported in the PET fingerprint region between 500-200 cm⁻¹ after the depolymerisation process, indicating that the product still comprises of PET. Therefore, the FTIR analysis indicate that the ester linkages of PET are intact, which is expected since the depolymerisation proceeds

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by a transesterification mechanism and thus, the branched oligomer can still be considered to be PET chemically. The larger absorbance in the 3000-3800 cm^{-1} can be attributed to the increase in hydroxyl end-groups due to incorporation of cleaving agents into the oligomer during depolymerisation.

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FIG. 10B shows the DSC of the PET oligomer obtained after depolymerisation, compared to neat PET powder. Compared to neat PET which shows a distinctive crystallite melting peak at 240 °C, the various oligomers did not display any distinct melting peak. Instead, all three oligomers show broadened melting endotherm at temperatures below 200 °C, describing the reduced crystallinity due to lower molecular weight and increased degree of branching. The melting peak of the three oligomers was compared: EG > PEN > GLY.

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The branched oligomers possessed increased solubility in solvents, including HFIP/chloroform mixtures, which was subsequently used to monitor, via DLS, the differences in molecular weight and architecture due to different cleaving agents. FIG. 10C shows the DLS showing the dispersion of 0.001 wt% depolymerised oligomers in chloroform/hexafluoroisopropanol (98/2wt%) solvent. Neat PET did not dissolve in the chloroform/hexafluoroisopropanol (98/2wt%) solvent. GLY as the cleaving agent resulted in the smallest colloid size due to the highest degree of polymer branching leading to lower solvodynamic radius. The oligomer dispersion and size of the three oligomers were compared: EG > PEN > GLY.

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FIG. 10D shows the ionic conductivity of the as obtained ionogels using different cleaving agents extracted before precipitation in water. All ionogel samples possessed excellent ionic conductivity due to excellent ion mobility within the large free volume of the ionogel. The ionic conductivity of the three oligomers was compared: GLY > PEN > EG.

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As mentioned previously, the ensuing IL/solvent-containing branched oligomer gel product with GLY obtained directly after depolymerisation was observed to form gel readily upon cooling to room temperature. In contrast, the PET reaction product with EG was observed to crystallise into a waxy solid upon cooling and thus, the resistance to crystallization and gel forming ability of PET/GLY is another feature of the branched architecture which is unique among recycled polymers. Hence, it is demonstrated here that the molecular weight and architecture of branched oligomers during depolymerisation can be controlled simply via the intelligent selection of cleaving agents.

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Example 11. Obtaining branched oligomeric resin via controlled depolymerisation of PET using GLY in aprotic solvent catalysed by tertiary amine or metal salt

Tertiary amine

The branched oligomeric resin was prepared by following the protocol in Example 9 except hexamethylenetetramine (2.5 g) was used instead of EmimCl, and the reaction was under
5 reflux typically for 72 hours. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown resin powder. The PET repeating unit to GLY-hydroxyl ratio in this example is 5:1.

Metal salt

10 The branched oligomeric resin was prepared by following the protocol in Example 9 except zinc chloride (2.5 g) was used instead of EmimCl, and the reaction was under reflux typically for 24 hours. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown resin powder. The PET repeating unit to GLY-hydroxyl ratio in this example is 5:1.

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Example 12. Obtaining branched oligomeric resin via controlled depolymerisation of PET using TRIS in aprotic solvent without added catalyst

The branched oligomeric resin was prepared by following the protocol in Example 9 except
20 TRIS (2.1 g) was used, and neither EmimCl nor GLY was used in the reaction. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown resin powder. The PET repeating unit to TRIS-hydroxyl ratio in this example is 5:1.

**Example 13. Obtaining branched oligomeric resin via controlled depolymerisation of
25 Nylon 6,6 using GLY in aprotic solvent catalysed by IL**

The branched oligomeric resin was prepared by following the protocol in Example 9 except EmimCl (5 g) and Nylon 6,6 pellets (30 g) instead of PET pellets, were used. The washed
30 branched oligomeric resin was then dried in an oven at 80 °C overnight to give a brown resin powder. The Nylon 6,6 repeating unit to GLY-hydroxyl ratio in this example is 5:1.

Example 14. Controlled depolymerisation of PET using GLY in water-immiscible carbonate solvent catalysed by IL or metal salt*IL catalyst*

35 In a 3-neck round bottom flask, PET pellets (50 g) were dissolved in PC (100 g) solvent at 180 °C in an oil bath under magnetic stirring. EmimCl (2.5 g) and GLY (1.6 g) were then added

into the PET/PC solution to initiate the depolymerisation reaction under reflux typically for 18 hours. The reaction was terminated by quenching the reaction product in isopropyl alcohol under strong stirring to induce precipitation of the branched oligomeric resin. The precipitated resin was filtered and washed repeatedly using isopropyl alcohol thrice, followed by ethyl acetate twice. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a pale brown resin powder. The PET repeating unit to GLY-hydroxyl ratio in this experiment is 5:1.

Metal salt

The branched oligomeric resin was prepared by following the IL catalyst protocol above except zinc chloride (2.5 g) was used instead of EmimCl. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a milky white resin powder. The PET repeating unit to GLY-hydroxyl ratio in this experiment is 5:1.

Example 15. Crosslinking of branched oligomeric resin using isocyanates to form coatings

Crosslinking of branched oligomeric resin using isocyanates

5 g of the resin product prepared in Example 9 was dispersed in dichloromethane (5 g) to form a slurry. Isocyanate resin (1 g) was mixed into the slurry mixture using a spatula and for 10 secs, and the slurry mixture was allowed to dry by evaporation of dichloromethane in a fumehood. The dried product remained as a powdery resin blend.

Fabrication of transparent film coating

About 0.1 g of the powdered resin blend prepared above was deposited onto a 2 mm thick aluminium plate. The substrate was then heated using a gas burner stove to melt the resin powder before being removed from the flame and allowed to cool. Upon heating, the powdered resin was observed to melt and fuse into a thin, homogeneous liquid coating. Upon cooling to ambient temperature, the resin coating was observed to remain clear and transparent.

Results and discussion

DSC and rheology analysis indicate that minimal crosslinking have resulted from the mixing procedure and drying steps. The resin blend needed to be heated above 200 °C to melt the oligomer in order to facilitate reaction with the isocyanate component. The coating was scratched using a metal spatula and it did not crack or delaminate. Droplets of water were dripped onto the coated aluminium plate and it was tilted to allow the droplets to readily run off. Therefore, the coating was observed to be scratch-resistant, hydrophobic, and based on

visual observation, it has excellent optical transparency. The coating was not soluble when immersed in hot NMP.

Example 16. Crosslinking of branched oligomeric resin using epoxies to form coatings

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Crosslinking of branched oligomeric resin using epoxies

5 g of the resin product prepared in Example 9 was dispersed in dichloromethane (5 g) to form a slurry. Triglycidyl isocyanurate (0.5 g) epoxy crosslinker was mixed into the slurry mixture using a spatula and for 10 secs, and the slurry mixture was allowed to dry by evaporation of dichloromethane in a fumehood. The dried product remained as a powdery resin blend.

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Fabrication of transparent film coating

About 0.1 g of the powdered resin blend prepared above was used to prepare a transparent film coating by following the protocol in Example 15.

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Results and discussion

DSC and rheology analysis indicate that minimal crosslinking have resulted from the mixing procedure and drying steps. The resin blend needed to be heated above 200 °C to melt the oligomer in order to facilitate reaction with the glycidyl epoxy component. The coating scratched using a metal spatula and it did not crack or delaminate. Droplets of water were dripped onto the coated aluminium plate and it was tilted to allow the droplets to readily run off. Therefore, the coating was observed to be scratch-resistant, hydrophobic, and based on visual observation, it has excellent optical transparency. The coating was not soluble when immersed in hot NMP.

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Taken together, the isolated branched oligomeric recycled resin can be chemically crosslinked using either epoxies, anhydrides, carboxylic acids or isocyanates to improve its mechanical, thermal stability and chemical resistance properties. The crosslinked resin based on oligomeric recyclates could either be applied directly in powder coatings for anti-corrosion applications or as binders for composites including fibre reinforced panels.

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Example 17. Incorporating recyclate into virgin resin

3 g of the powdered resin prepared in Example 9 was dry mixed into virgin grade PET pellets (7 g). The blended resin mixture was then dried in an oven at 120 °C for 2 hours. The dried resin mixture was then compounded using a twin-screw extruder operating at 250 °C.

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Results and discussion

The viscosity of the resulting polymer melt was visually observed to be significantly lower compared to the virgin resin, allowing for extrusion at lower torque. Based on hands on observation of the extrudate product, no significant deterioration in mechanical properties was observed on the 30% recyclate polymer blend. Therefore, the recycled resin can be reincorporated at high loading into virgin resin without significant loss in material properties.

Example 18. Formation of vitrimers from branched oligomeric resin and anhydrides catalysed by metal salt

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10 g of the resin product from Example 9 was dry mixed with maleic anhydride (1 g) and zinc acetate (0.19 g) to form a powdery resin blend. This resin blend was introduced into a twin-screw extruder operating at 220 °C with extrusion cycle time of 10 mins before material expulsion.

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Results and discussion

The extruded material appeared glassy. It was taken for DMA studies and was found to be mechanically tougher than the extruded branched oligomeric resin recyclate product prepared in Example 17. DMA studies indicate that the glassy extruded product can be described as a Vitrimer.

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Example 19. Formation of vitrimers from branched oligomeric resin and carboxylic catalysed by metal salt

In a 3-neck round bottom flask, 10 g of the resin product prepared in Example 9 was combined with succinic acid (1.2 g) and zinc acetate (0.19 g). NMP solvent (25 g) was added and the mixture was heated at 150 °C in an oil bath under magnetic stirring and reflux for 2 hours. Then, the reaction mixture was quenched into an isopropyl alcohol under strong stirring to induce precipitation of the vitrimer resin. The precipitated resin was filtered and washed repeatedly using isopropyl alcohol three times followed by ethyl acetate twice. The washed branched oligomeric resin was then dried in an oven at 80 °C overnight to give a brown resin powder. The vitrimer resin was introduced into a twin-screw extruder operating at 220 °C with extrusion cycle time of 2 mins before material expulsion.

Results and discussion

The extruded material appeared glassy. It was taken for DMA studies and was found to be mechanically tougher than the extruded branched oligomeric resin recyclate product prepared

in Example 17. DMA studies indicate that the glassy extruded product can be described as a Vitrimer.

Therefore, taken together, the isolated branched oligomeric recycled resin can be chemically crosslinked using either anhydrides or carboxylic acids with a transition metal salt as catalyst to form a vitrimer with improved mechanical, thermal stability, and chemical resistance properties. The vitrimer resin based on oligomeric recyclates could either be applied as high strength adhesives with ability to be detached conveniently, or as binders for composites including fibre reinforced panels that could be repairable and recyclable.

Example 20. Formation of ionogel as lithium-ion-containing solid-state electrolyte for Li-polymer batteries

5 g of the resin product prepared in Example 9 was combined with EmimCl (5 g) and LiTFSI (5 g, 1 M) in PC solution. Anhydrous ethyl acetate (10 g) was added into the reaction mixture, followed by centrifugal mixing in a planetary centrifugal mixer at 2000 RPM for 5 mins to obtain an ionogel slurry. The ionogel slurry was film casted onto a carbon-coated aluminium electrode sheet and dried in a vacuum oven at 80 °C for 18 hours. The dried ionogel coated electrode sheet was then incorporated as the anode into a self-assembled lithium polymer laminated pouch battery.

Example 21. Formation of ionogel as lithium-ion-containing solid-state electrolyte for electrochemical supercapacitors

The ionogel slurry was prepared and film casted onto a carbon-coated aluminium electrode sheet by following the protocol in Example 20. Then, 2 pieces of the dried ionogel coated electrode sheet was sandwiched together with gel-side facing inwards and laminated within a self-assembled aluminised PET-film pouch to form a symmetric supercapacitor.

Claims

1. A method of partially depolymerising a depolymerisable condensation polymer, the method comprising the steps of:

- (a) forming a mixture comprising a depolymerisable condensation polymer, a polar aprotic solvent, a catalyst and a cleaving agent;
- (b) heating the mixture to a temperature from greater than 150 °C to less than 200 °C and allowing the depolymerisation reaction to take place for a period of time to provide oligomers derived from the depolymerisable condensation polymer, wherein the cleaving agent is a polyol compound.

2. The method according to Claim 1, wherein the process involves quenching the mixture into water with stirring after the period of time to precipitate out the oligomers derived from the depolymerisable condensation polymer to provide a branched oligomeric resin after collection of the precipitated oligomers derived from the depolymerisable condensation polymer.

3. The method according to any one of the preceding claims, wherein the polyol compound is selected from one or more of the group selected from glycerol, ethylene glycol, propylene glycol, tris(hydroxymethyl)aminomethane, tris(hydroxymethyl)methane, pentaerythritol, and sugar alcohols (e.g. one or more of the group consisting of erythritol, threitol, arabitol, xylitol, ribitol, mannitol, galactitol, fucitol, iditol, inositol, volemitol, isomalt, maltitol, lactitol, maltotriitol, maltotetraitol, polyglycitol, and sorbitol). 4. The method according to Claim 3, wherein the catalyst is selected from one or more of the group consisting of an ionic liquid, a secondary amine, a tertiary amine, a heterocyclic amine, an organometallic compound, and a metal salt.

5. The method according to Claim 4, wherein the catalyst is selected from one or more of the group consisting of an ionic liquid, a tertiary amine and a metal salt, optionally wherein the catalyst is an ionic liquid.

6. The method according to Claim 5, wherein the catalyst is selected from one or more of the group consisting of hexamethylenetetramine, ZnCl_2 and 1-ethyl-3-methylimidazolium chloride, optionally wherein the catalyst is 1-ethyl-3-methylimidazolium chloride.

7. The method according to any one of Claims 1 and 3 to 6, wherein, when the catalyst is an ionic liquid, the process involves a subsequent step of cooling the mixture after the period of time to provide an ionogel, suitable for use as a solid-state electrolyte.

8. The method according to any one of the preceding claims, wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of a thermoplastic polyamide, a thermoplastic polyester, and a thermoplastic and/or crosslinked polyurethane.

9. The method according to Claim 8, wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of a polyurethane, nylon 6,6, nylon 6, polyethylene terephthalate, polylactic acid, and elastane, optionally wherein the depolymerisable condensation polymer is selected from one or more of the group consisting of nylon 6,6, nylon 6, polyethylene terephthalate, and polylactic acid.

10. The method according to any one of the preceding claims, wherein the period of time is from 3 hours to 48 hours, such as from 4 hours to 24 hours, such as from 5 hours to 18 hours.

11. The method according to any one of the preceding claims, wherein the temperature is from 155 °C to 195 °C, such as from 170 °C to 190 °C, such as about 180 °C.

12. The method according to any one of the preceding claims, wherein the stoichiometric ratio of the depolymerisable condensation polymer to the cleaving agent is from 1.25:1 to 10:1, such as from 5:3 to 5:1, such as about 5:2.

13. The method according to any one of Claims 7 to 12 as dependent upon Claim 7, wherein the ionogel is used in further processing steps to provide a reinforced composite material, which additional steps include:

- (ai) providing a plurality of glass fiber meshes coated in the ionogel; and
- (aii) stacking the plurality of glass fiber meshes coated in an ionogel and subjecting the resulting stack to heat and pressure to provide a reinforced composite material.

14. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a transparent film coating, which additional steps include:

- (bi) melting the branched oligomeric resin; and

(bii) applying the melted brached oligomeric resin onto a surface to provide a transparent film coating upon cooling.

15. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a blended material suitable for use in coating, which additional steps include:

- (ci) forming a mixture comprising the branched oligomeric resin, an isocyanate resin and a solvent; and
- (cii) removing the solvent to provide a blended material suitable for coating.

16. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a crosslinked material suitable for use in coating, which additional steps include:

- (ci) forming a reaction mixture comprising the branched oligomeric resin, an triglycidyl isocyanurate epoxy crosslinker and a solvent, which is allowed to react for a period of time; and
- (cii) removing the solvent to provide a crosslinked material suitable for use in coating.

17. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a vitrimer material, which additional steps include:

- (di) providing a melted mixture of the branched oligomeric resin, an anhydride material (e.g. maleic anhydride) and a metal salt (e.g. zinc acetate);
- (dii) subjecting the melted mixture to extrusion to provide a vitrimer material.

18. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a vitrimeric resin, which additional steps include:

- (ei) forming a reaction mixture comprising the branched oligomeric resin, a dicarboxylic acid (e.g. succinic acid), a metal salt (e.g. zinc acetate) and a solvent;
- (eii) quenching the reaction mixture by using a water and/or an alkyl alcohol (e.g. isopropyl alcohol) and then collecting a precipitated material, which is the vitrimeric resin.

19. The method according to Claim 18, wherein the vitrimeric resin is further melted and subjected to extrusion to provide an extruded vitrimeric material.

20. The method according to any one of Claims 2 to 6 and 8 to 12 as dependent upon Claim 2, wherein the branched oligomeric resin is used in further processing steps to provide a solid-state electrolyte, which additional steps include:

(fi) providing an ionogel slurry comprising the branched oligomeric resin, an ionic liquid (e.g. 1-ethyl-3-methylimidazolium chloride), a first solvent (e.g. propylene carbonate) and a second solvent (e.g. ethyl acetate); and

(fii) film casting the ionogel slurry onto a substrate and drying the slurry to provide a solid electrolyte.

21. The method according to any one of Claims 7 to 12 as dependent upon Claim 7, wherein the ionogel is used in further processing steps to provide a composite product, which additional steps include:

(ai) applying the ionogel to a first substrate to form a coated surface and pressing a second substrate against the coated surface to form a pre-adhered composite material; and

(aii) heating the pre-adhered composite material to an elevated temperature for a period of time to substantially remove the solvent in the ionogel and provide the composite material.