MULTIFUNCTIONAL EPOXY RESIN FOR STRUCTURAL SUPERCAPACITORS

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Abstract

Polymer-based electrolytes based on commercially available epoxy resins were prepared through the addition of a liquid electrolyte, a solution of a lithium salt in an ionic liquid. The polymer monoliths were characterized using impedance spectroscopy, 3-point bending test, scanning electron microscopy (SEM) and nitrogen adsorption (BET). The balance of ionic conductivity and flexural modulus is crucially dependent on the relative proportions of epoxy resin to electrolyte. Also the effect of the liquid electrolyte on curing kinetics and processing was assessed by complex viscosity measurements and differential scanning calorimetry (DSC). Only one out of the three resins investigated exhibited a significant acceleration effect.

1 Introduction

Materials which can perform two or more functions simultaneously have received widespread attention due to the potential benefits from their application in the number of areas from biomedical to aerospace [1]. Energy storage is one of the areas where the introduction of multifunctional materials is expected to save weight and volume by combining the features of structural materials with materials providing the electrochemical performance [2].

Our focus is on developing new composite materials for energy storage applications. We expect particular benefits from mobile energy applications where weight savings are particularly valuable. Amongst the different types of energy storage, we chose supercapacitors for this initial investigation as we regard their more robust mode of energy storage to provide a better fit with the demands on processing placed by carbon fibre composite materials. Our typical composite structure is shown in Figure 1. Layers of carbon fibre mats are separated by layers of insulating glass fibre weaves infused throughout by a multifunctional nanostructured polymer matrix. This is by design a well established carbon fibre composite architecture, which was adopted to minimise changes and modifications

which are potentially required when introducing new materials. A further reason for our supercapacitor architecture is the opportunity of improving independently the performance through modification of both carbon fibre and the polymer matrix.
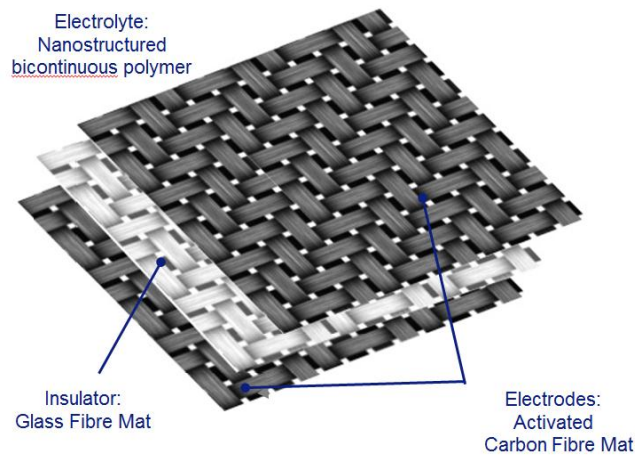
Figure 1. Structural Power Supercapacitor – Device concept.

Work is ongoing in both areas, modification of carbon fibres to increase their surface area translating into an increase in energy density and the development of ionically conducting resins. In this paper we concentrate on the polymer matrix and will discuss one of our approaches to equip the polymer matrix with high ionic conductivity while retaining the maximum of mechanical performance provided by the parent epoxy resin. It chimes with our supercapacitor architecture approach that we try and make use of commercially available epoxy resins, trying to find ways in which we can add, in our case the ionic conductivity functionality, whilst minimising the need to establish completely new processing conditions.

Conceptually we wanted to explore the possibility of producing bicontinuous polymer matrices in which one phase would be responsible for ionic conductivity and a second phase for mechanical properties. Routes to bicontinuous polymer morphologies are well known. Employing templates such as surfactants and block copolymers is very well established though requires careful study and tuning of the phase behaviour of the system [3-7]. Non-templating approaches widely used for the synthesis of (macro)porous polymer networks appeared to offer a more general strategy which we followed [8-9]. In this approach monomers and electrolyte form a solution at the initial stage. Polymerisation of the epoxy network means that the growing polymer will become insoluble as the polymerisation (curing) progresses and ultimately the polymer phase separates from the electrolyte phase. Three high performing fully formulated commercial epoxy resins (VTM266, MVR444 and MTM57 (UMECO)) were chosen for the polymer matrix and as electrolyte we opted for an ionic liquid doped with a lithium salt (EMIM TFSI and LiTFSI). The choice of epoxy resins reflected differences in resin type, cure rate and viscosity. An ionic liquid was chosen as electrolyte doped with a lithium salt as it offers advantages of low vapour pressure and high thermal stability while possessing high ionic conductivity and a large electrochemical window [10].

2 Materials and testing methods
2.1 Materials
Three fully formulated commercially available epoxy resins with trademarks MVR444, MTM57 and VTM266 were prepared at ACG. MVR444 is a low viscosity resin (14.7 Pa·s)

used in the composite manufacturing *via* resin infusion. VTM266 and MTM57 have much higher viscosity 1400 Pa·s and 4835 Pa·s and used in the composite manufacturing *via* prepreg route. Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL, ≥98% (H-NMR)) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, puriss., ≥99.0% (19F-NMR) were purchased from Sigma-Aldrich and used as received.

2.2 Preparation of epoxy resin based electrolytes
The general preparation procedure is as follows: After dissolving LiTFSI in IL, an epoxy resin was added and all components were stirred until a homogeneous mixture was formed. The mixture was poured into a mould and cured using a time and temperature profile specific for each resin. Samples for detailed characterization (ionic conductivity at different temperatures and mechanical properties were cured using the following cure cycles: for MVR444 based formulations it was 18 hours at 100°C, for MTM57 based - 1 hour at 120°C and for VTM266 based - 1 hour at 120°C. Samples were cured in the shape on flat plaques with thickness of 2.5-3 mm.

2.3 Characterization of uncured and cured formulations
A differential scanning calorimeter TA Q2000 (TA Instrumental, USA) was employed to study the curing kinetics between - 100°C to + 350°C (for formulations based on MVR444) and to 250°C (for formulations based on MTM57, VTM266) at a heating rate of 5°C/min. Ionic conductivity of the cured formulations was studied using impedance spectroscopy.

To characterize mechanical performance of the cured formulations three point bending tests was carried out, using a "Zwick" testing frame with a 1kN force transducer and a "Heidenhein" displacement transducer.

With the three point bending test it is possible to characterize mechanical properties such as the bending modulus E_b in GPa, which for isotropic materials is similar to the Young's modulus In order to characterize the influence of the deformation rate to the mechanical properties of polymers, the peripheral strain rate must be constant during the tests. To get a constant strain rate the anvil speed v must be adjusted to the sample geometry by the following equation.

$$v = \frac{\dot{\varepsilon}_{dot} l^2}{6h} \text{ [mm/min]} \quad (\varepsilon_{dot} \text{ dimensionless - not in \% -, span } l \text{ and height } h \text{ in mm})$$

To study morphology and surface area of the obtained formulations, IL and LiTFSI were extracted from the cured formulations as follows. About 0,5-1.0 g of the sample were placed in ethanol and washed extensively and later dried in a vacuum oven at 70°C under reduced pressure until constant weight. In all cases at least 97 wt.% of IL + LiTFSI was removed from the monolithic polymer networks.

The surface area of extracted samples was determined by physical adsorption and capillary condensation of N_2 using a surface area and porosity analyser Tristar 3000 (Micrometrics, Dunstable, UK) applying the Brunauer–Emmett–Teller (BET) model.

SEM images of extracted samples were recorded on a (Jeol JSM 5610 LV) with an accelerating voltage of 15 kV. All samples were gold coated for 120 s in an argon atmosphere (Emitech 550, Emitech Ltd., Ashfort, UK).

3 Results and Discussion

Optimum compositions of fully formulated resins and IL electrolyte were established by varying the resin content between 75 wt.% to 25 wt.%. Samples were screened for homogeneity post curing both visually and by measuring the ionic conductivity of sample discs which were cut from both the top and bottom part of monolithic specimen. The results are shown in the Figure 2. Homogeneous samples were was obtained using as little as 30 wt.% MVR444 while for VTM266 and MTM57 50 wt.% of resin were required to insure sample homogeneity.
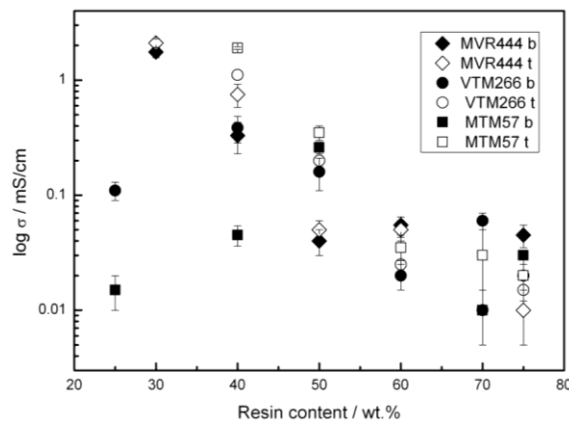
Figure 2. Effect of the resin content on the ionic conductivity value for three different resins, MTM57, VTM266, MVR444; "t" is top part of the sample and "b" is bottom part of the sample.

For the five most promising formulations, selected on the basis of high ionic conductivity and toughness (by physical inspection), the temperature dependence of their ionic conductivity was studied in detail and is shown in Figure 3. A typical increase of ionic conductivity with temperature was found for all samples. The sample with the highest ionic conductivity across the temperature was MVR444/30. Already at -20 ^{o}C the ionic conductivity was 0.05 mS/cm. This value is similar to a reported bicontinuous system which exhibits much lower mechanical performance [11]. Room temperature conductivity is near 1 mS/cm a value also suitable to consider films of the resins as Li ion battery separator membranes.
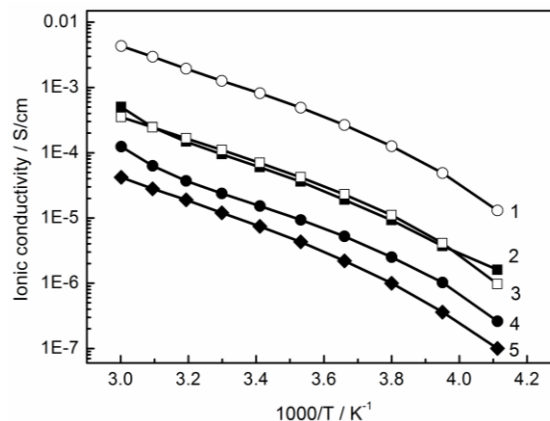

Figure 3. Temperature dependence of ionic conductivity of samples; 1: 30 wt.% MVR444; 2: 50 wt.% MTM57; 3: 40 wt.% MVR444; 4: 50 wt.% VTM266; 5: 50 wt.% MVR444.

Formulation containing 50 wt.% of resin were selected to study in more detail the effect of resin type on the mechanical properties of the uncured and cured samples. Figure 4 illustrates the relationship between ionic conductivity and flexural modulus of MVR444, VTM266 and MTM57 all present at 50.wt%. It can be seen that samples with highest ionic conductivity (MTM57/50) has lowest flexural modulus and sample with lowest ionic conductivity (MVR444/50) has highest flexural modulus. However the relative tradeoff between ionic conductivity and the flexural modulus is different for each resin indicating that the optimum formulation for each resin has to be established individually. To what extent there may be a trend between different resins which would reduce the effort needed for individual optimization is the subject of ongoing investigations.
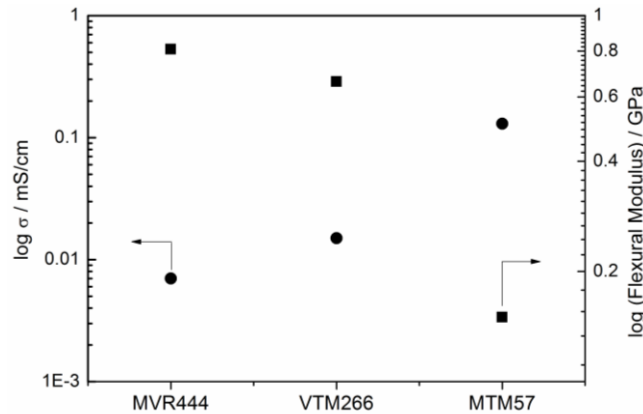

Figure 4. Ionic conductivity and flexural modulus of samples MVR444/50, VTM266/50 and MTM57/50. Flexural modulus of the neat epoxy resins are 3.22 GPa, 2.66 GPa and 2.73 GPa for MVR444, VTM266 and MTM57 respectively.

The morphology of each of the three samples as shown by SEM images suggests significant differences amongst them (Figure 5). For MVR444/50 it is not sufficiently clear if a bicontinuous morphology is present. VTM266/50 on the other hand can be clearly described as possessing a bicontinuous morphology whereas in the case of MTM57/50 an "inverted" phase structure of connected beads is present, which could explain the lower flexural modulus found for this formulation (Figure 4).
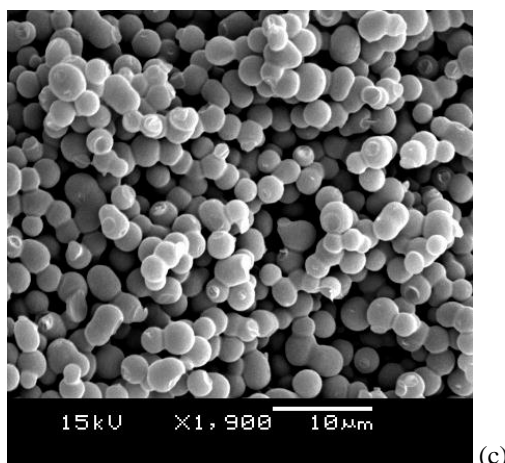

(a)

(b)

(c)
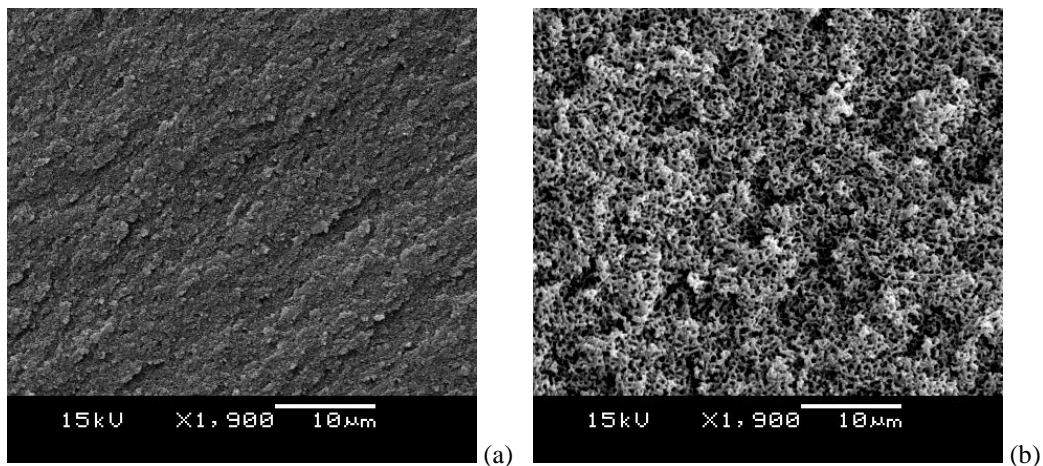
Figure 5. SEM micrographs of epoxy resins MVR444/50 (a); VTM266/50 (b); MTM57/50 (c), (electrolyte removed in all cases)

With the help of nitrogen absorption measurements MVR444/50 was found to possess a surface area of close to 30 m^2g^{-1} (Figure 6) which indicates and open pore structure which is further supported by the ability to remove at least 97 wt.% of the liquid electrolyte after curing. It is likely that the pore morphology of MVR444/50 is similar to VTM266/50 but with much smaller pore sizes.
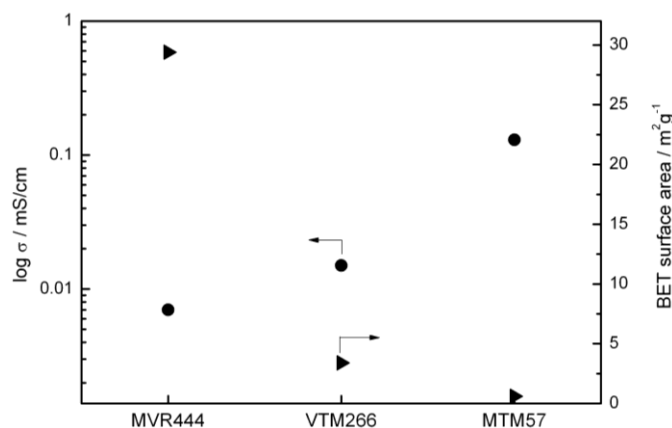

Figure 6. Correlation between ionic conductivity and specific surface area of the samples containing 50 wt.% of resin.

It was important to identify any changes in the curing behavior between the unmodified fully formulated epoxy resins and those containing the IL based liquid electrolyte, especially as it is known that IL can be used as a latent initiator for epoxy resin[12]. Thus we carried out complex viscosity and DSC studies on MVR444, VTM266 and MTM57 without and with addition of liquid electrolyte to establish the magnitude of the effect on curing kinetics and the onset of curing (Figure 7). The addition of the liquid electrolyte to MVR444 had a significant accelerating effect not seen for the other two epoxy resins (Figure 7a). For MVR444/50 the curing already started close to room temperature reached a viscosity value of 10 Pa·s at 70°C whereas the parent resin would have to be heated to about 180°C to reach the same level of viscosity. In the case of MTM57 and VTM 266 the effect of the liquid electrolyte addition can be interpreted as a simple dilution effect lowering the viscosity throughout the curing process (Figure 7b,c).
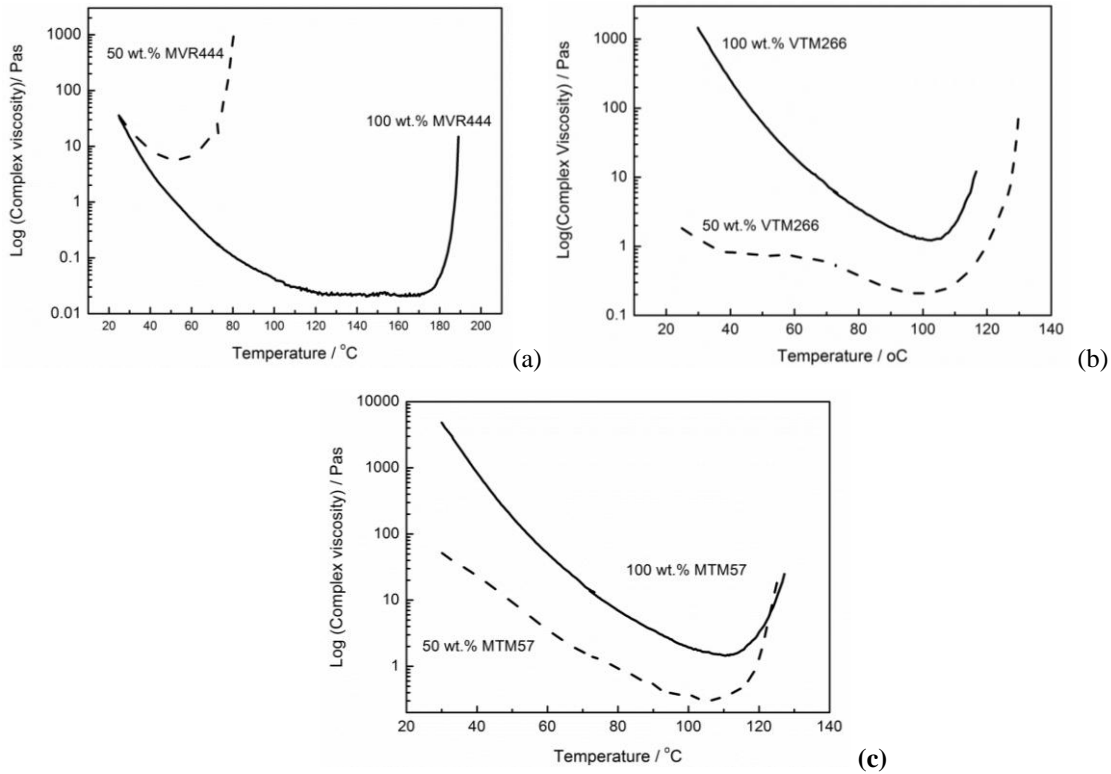
(a)

(b)

(c)

Figure 7. Influence of an addition of liquid electrolyte on complex viscosity of MVR444 (a); VTM266 (b) and MTM57 (c) based formulations

The complex viscosity data was consistent with data obtained from DSC measurements on the same formulations. Figure 8 shows the comparison of the onset temperature (T_{onset}) of the curing process for the neat resins side by side that of the three resin formulations containing 50 wt.% of a resin in each case. Clearly the onset temperature of MVR444 is much lower with the addition of the IL electrolyte (by ~ 120°C) whereas for VTM266 and MTM57 the difference between neat resin and the formulations containing liquid electrolyte was less than 10°C in both cases.
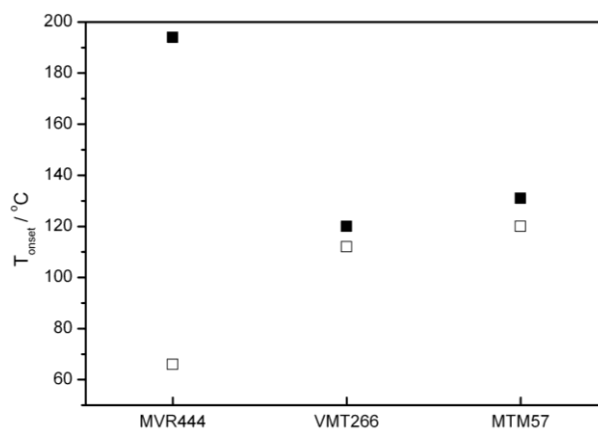

Figure 8. Effect of liquid electrolyte presence (IL+LiTFSI) on the onset of the curing temperature of neat resins (■) and formulations with 50 wt.% resin (□).

4 Conclusions

Structural polymer-based electrolytes based on three commercially available epoxy resins were prepared through the addition of a liquid electrolyte, a solution of a lithium salt in an ionic liquid. It was found that effect of the addition of the liquid electrolyte on properties of the cured formulation, such as ionic conductivity, mechanical properties, morphology, was different for each resin For formulations containing 50 wt.% of resin ionic conductivity values varied from 0.007 mS/cm for MVR444/50 to 0.13 mS/cm for MTM57/50 and flexural moduli from 0.81 GPa for MVR444/50 to 0.15 GPa for MTM57/50. The effect of the liquid electrolyte on curing kinetics and processing, assessed by complex viscosity measurements and DSC, showed that two of the three resins can be processed in much the same way as their parent resins.

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