Materials and Design 104 (2016) 126–133

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Co-continuous structural electrolytes based on ionic liquid, epoxy resin and organoclay: Effects of organoclay content

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ARTICLE INFO

Article history:
Received 6 March 2016
Received in revised form 1 May 2016
Accepted 4 May 2016
Available online 6 May 2016

Keywords:
Structural electrolyte
Organoclay
Mechanical properties
Ionic conductivity

ABSTRACT

As a vital part of structural power composites, structural electrolyte should achieve ionic conducting and load bearing functions simultaneously. In the present work, a novel method was established for optimizing the morphology and multifunctionality of a liquid/epoxy based structural electrolyte by adding different contents of organoclay (organically modified layered silicates, OLS). The OLS content had a substantial effect on the liquid/epoxy co-continuous morphology. The introduction of OLS changed the epoxy microstructure from the interconnected flakes to the parallel ridges. The increase of OLS content led to a more compact epoxy network and a more interpenetrated conductive phase. However, an excessive amount of OLS could cause the agglomeration and make the morphology parallel interconnected bars. The variation in morphology accounted for the multifunctionality increase in the structural electrolytes. The optimal formulation was determined with the best properties of 211 MPa in tensile modulus and 0.09 mS/cm in ionic conductivity, approaching the inferior limit of the multifunctional performance for a structural electrolyte. As a promising candidate for structural power composites, this co-continuous structural electrolyte containing ionic liquid, epoxy resin and OLS shows great potential to be used in the multifunctional energy storage devices.

1. Introduction

Broad efforts have been devoted to lightweight and multifunctional materials for the reduction of the energy consumption in many engineering applications [1]. The structural power composite (SPC) can simultaneously realize the goals of load bearing and energy storage and is considered as one of the most promising alternative materials for manufacturing energy storage devices [1–3]. The structural electrolyte, typically modified polymer materials, is a vital component in SPC to provide high ionic conductivity as well as the ability to transfer load [4,5,6]. Apart from the conventional research approaches of polymer matrix, the investigations on the electrochemical performances such as the ionic conductivity and dielectric properties are also utilized for the development of the structural electrolytes [7–10].

Studies have been mainly focused on two major strategies for the applications of the polymer electrolyte systems: One is the development of polyethylene oxide (PEO) based solid polymer electrolytes where the ions move via the local relaxation and segmental motion of the PEO chains, the other is the preparation of epoxy resin blended with gel or liquid electrolyte to achieve the mechanical and electrochemical functions separately in one polymer system. Since Wright [11] firstly discovered that the complex of PEO and alkaline salts has the ability of ionic conductivity in 1973, numerous researchers have deeply investigated the ionic conduction mechanisms and multifunctional performance of PEO based electrolytes. Given the potential use of the vinyl ester derivatives of poly(ethylene glycol) (PEG), Snyder and co-workers formulated random copolymers containing ethylene oxide (EO) groups [12–14]. In this way a structural scaffold is generated through crosslinking while the PEG sidechains can enhance the ion transport. Willgert et al. [15] also conducted a systematic study on photoinduced curing of PEO-dimethacrylate/PEO-monomethacrylate lithium salt mixtures to form thermoset electrolytes and addressed the importance of seeking for an acceptable balance between mechanical and conductive properties. However, despite the advantage that the manufacture process for the vinyl ester derivatives of PEG is simple, the trade-off between mechanical and conductive properties makes it very difficult for the PEO based electrolytes to satisfy the inferior limit of the multifunctional performance for the SPC [13–16]. Epoxy resin is one class of the most used structural polymer matrices with high mechanical modulus and strength. Adding the immiscible electrolyte into epoxy/amine system can generate the co-continuous phase structure, with the epoxy networks providing the load-bearing function while the electrolyte phase supplying the ion mobility [17,18]. Recently, poly(ethylene-glycol) (PEG) or propylene carbonate (PC) as the additive was explored to form a bicomponent structural electrolyte [16]. Low multifunctional performance was obtained due to a combination

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http://dx.doi.org/10.1016/j.matdes.2016.05.004

of plasticization of the structural network and limited percolation of the liquid network. Besides, several authors chose ionic liquids (ILs) as the ionic conducting agents for the polymer electrolytes and highlighted the influence of the ILs on the dual-phase formation and structuration [19–23]. The addition of ILs led to a good multifunctionality with a room temperature ionic conductivity reaching 0.8 mS/cm and a Young's modulus of 180 MPa [21]. Gienger et al. compared the properties of the in-situ cured electrolyte and the porous epoxy resin backfilled with liquid electrolyte. The latter showed a better multifunctional performance with a room temperature ionic conductivity reaching 1.5 mS/cm and a Young's modulus of 120 MPa [18]. In summary, only when the formation and the control of the interconnected microstructure are well realized, can the multifunctional performance of the epoxy modified electrolyte be improved greatly. Thus the epoxy modified electrolyte has shown great potential to be the component of energy storage devices.

It is well acknowledged that the addition of particle fillers into epoxy based hybrids are beneficial to the miscibility, phase separation and morphology with the fracture toughness being improved simultaneously [24–28]. As a result, incorporating nanoparticles into epoxy-based multi-phase blends is considered as the most effective method to phase separation and morphology controlling. Tanaka and the co-workers employed glass spheres into the polymer blends to affect the dynamic coupling between phase separation and wetting, and indicated the possibilities to control the final domain size in phase separation and the final morphology [24]. Zhang et al. devoted their efforts to the modification of the epoxy/PEI resin using nano-scale silica particles. The dispersion of the silica particles led to the occurrence of phase inversion structure and the size change of the secondary epoxy rich phase [25]. In recent years, there has been a growing interest in the utilization of organoclays (organically modified layered silicates, OLS) to control the morphology and phase separation kinetics for its distinctive intercalated and/or exfoliated structures [26–29]. The onset of phase separation and the gelation or vitrification time were greatly brought forward and the periodic distance of phase-separated structure was reduced when OLS was incorporated [28]. The phase diagram of epoxy blend was indicated to shift to a higher temperature with the increase in OLS content due to the easy penetration of the blends into the clay galleries [29]. Hence OLS has a dramatic impact to the phase separation process and the final phase morphology of binary polymer mixtures. However, to the best of our knowledge, these studies are mainly focused on the application of OLS into the thermoplastic/thermosetting mixtures but no literature is available regarding the effects of OLS on the morphology and multifunctional performance of the liquid/polymer co-continuous system.

In the present paper, the effects of OLS content on the multifunctional performance of the structural electrolytes were discussed. Epoxy was blended with liquid electrolyte and OLS to form the co-continuous microstructures. Bisphenol A epoxy/polyether amine resin system was utilized to form the crosslinked network for load-bearing, and IL dissolved with PC and lithium salt as the liquid phase provided the ionic conductivity. We optimized the phase separation and final microstructure by the addition of different mass contents of nano-scaled OLS, and evaluated the morphology, mechanical and conductive properties of the structural electrolytes. The influence of OLS content on the multifunctional performance was summarized and the optimal formulation of the structural electrolyte based on ionic liquid, epoxy resin and OLS was determined.

2. Experimental

2.1. Materials

The epoxy resin system used in this study was composed of liquid diglycidyl ether of bisphenol A (DGEBA) type epoxy resin E51 with an epoxy value of 0.51 from Lanxing Wuxi Resin Co. Ltd. and tetrafunctional epoxy resin AG-80 with an epoxy value of 0.85 from Shanghai Huayi Resin Co. Ltd. The curing agent was JEFFAMINE D400 polyetheramine bought from Huntsman International LLC, with an amine hydrogen equivalent weight of 115. The organoclay (Nanomer® I.·30P from Nanocor Inc.) employed in this work was a montmorillonite with octadecylamine modified as the intercalation reagent. The mixture of 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (EMIM-Tf_2N, 99%, Shanghai Cheng Jie Chemical Co. Ltd.) and propylene carbonate (PC, 99%, Kuer Chemistry Co. Ltd.) was utilized as the liquid electrolyte with the corresponding lithium salt of lithium bis(trifluoromethanesulphonyl)imide ($LiTf_2N$, 99.9%, Chinese Special Gases Department of Purification Equipment Research Institute). All these materials were kept in a vacuum drier at ambient temperature in order to avoid absorbing moisture.

2.2. Polymer preparation

The liquid electrolyte component was prepared with $LiTf_2N$ dissolved in the mixture of 99 wt.% EMIM-Tf_2N and 1 wt.% PC at the concentration of 2.3 mol/L. E51, AG80 and the liquid electrolyte were roughly blended following the component ratio listed in Table 1 and placed in an oven at 55 °C for 5 min in order to decrease the viscosity. The OLS was dispersed finely in the preheated blends by high-shear mixer at 8000 rpm for 1 h in an external ice bath to keep the system from local overheating before the formulated addition of D400. Finally all the components were stirred using a power mixer until a uniform solution was obtained.

The resin plaques with the thickness of 2 mm were manufactured using two paralleled glass plates separated by a silicone spacer. The two glass plates were treated with the mold release agent and clamped by bulldog clips. The cylindrical spacer with a diameter of 2 mm was placed in a U-shape between the glass plates, as shown in Fig. 2. The

Table 1
Compositions and multifunctional performances of the structural electrolytes based on ionic liquid, epoxy resin and OLS.

Sample label	Structural phase				Liquid phase			Multifunctional performance		
	E51 (g)	AG-80 (g)	D400 (g)	OLS (g)	EMIM-Tf_2N (g)	PC (g)	$LiTf_2N$ (g)	Tensile modulus (MPa)	Tensile strength (MPa)	Ionic conductivity (mS/cm)
S	70	30	73.49	0 (0 wt.%)	128.81	1.30	56.14	373.25 ± 36.71	9.27 ± 1.34	$(5.67 \pm 0.42) \times 10^{-2}$
A	70	30	73.49	8.99 (2.5 wt.%)	128.81	1.30	56.14	136.89 ± 7.88	9.75 ± 0.80	$(4.74 \pm 0.30) \times 10^{-2}$
B	70	30	73.49	17.99 (5.0 wt.%)	128.81	1.30	56.14	211.57 ± 11.10	10.92 ± 0.35	$(8.97 \pm 0.54) \times 10^{-2}$
C	70	30	73.49	26.98 (7.5 wt.%)	128.81	1.30	56.14	198.94 ± 9.67	9.07 ± 0.09	$(8.42 \pm 0.41) \times 10^{-2}$
Epoxy-S	70	30	73.49	0 (0 wt.%)	–	–	–	2800.69 ± 24.28	52.93 ± 0.43	–
Epoxy-A	70	30	73.49	8.99 (2.5 wt.%)	–	–	–	2753.75 ± 52.23	44.20 ± 0.21	–
Epoxy-B	70	30	73.49	17.99 (5.0 wt.%)	–	–	–	3024.64 ± 57.56	47.32 ± 0.25	–
Epoxy-C	70	30	73.49	26.98 (7.5 wt.%)	–	–	–	3115.89 ± 57.72	44.84 ± 0.33	–
Ionic liquid	–	–	–	–	128.81	–	–	–	–	7.01 ± 0.03
Conductive phase	–	–	–	–	128.81	1.30	56.14	–	–	1.66 ± 0.02

The concentration of $LiTf_2N$ in the liquid phase was kept constant at 30.14 wt.% and weight ratio (E51 + AG-80 + D400): (PC + EMIM-Tf_2N) at 100:75.