Study on epoxy resin modified by polyether ionic liquid

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Abstract. Chloride 1-carboxyl polyether-3-methyl imidazole ionic liquid (PIIL) was synthesized. Then blended with epoxy resin(EP) to prepare the composite materials of PIIL/EP, which cured with aniline curing agent. The structure and curing performance of PIIL/EP were determined by FT-IR and DSC. The effects of the content of PIIL on strength of EP were studied. The results show that the PIIL was the target product. The strength was improved significantly with increase of the PIIL content. The obvious rubber elasticity of PIIL/EP after cured was showed when the content of PIIL accounts for 40% and the impact strength was up to 15.95kJ/m².

1. Introduction
Epoxy resin (EP) is one of the most widely used thermosetting resins. The toughening modification has been the focus of research at home and abroad. The most traditional methods of toughening epoxy resins are the so-called "soft toughening" and "hard toughening"[1]. New modification methods appear continuously. Such as National Taiwan University Hsieh et al[2] ,who studied the graft interpenetrating polymer networks (EP) and polyurethane elastomers (PUR) The tensile strength of EP was improved, and the epoxy polyurethane acrylic acid (IPN) coating was synthesized by Shah et al[3]. The tensile strength and bond strength of the coating were improved by the excellent corrosion resistance of the coating. Yang Weijiang et al[4] optimized the synthesis of epoxy acrylate resin emulsion by changing the glass transition temperature (Tg) and thermal decomposition temperature (Td).

Ionic liquids have been widely utilized in the fields of organic synthesis, separation, and extraction, as well as in material preparation, because of their excellent performance. The structure of green solvent ionic liquid has a unique "tailored" design[5] if we can design a rational structure, it can react with epoxy groups with long chain ionic liquids, prepared with epoxy resin modified with long chain structure, its impact toughness will be greatly improved in theory, at the same time the thermal properties and processing performance can be improved. Therefore, this article on the existing research and synthesis of novel functional ionic liquids - carboxyl polyether ionic liquid, the E-44 type epoxy resins curing under the action of a small amount of aniline. Preparation of polyether ionic liquid / epoxy resin composite material (PIIL/EP), and the performance of heat shock. Study on toughness of polyether ionic liquid for epoxy resins, and expounds its toughening mechanism.

2. Experimental
2.1. Reagents and instruments
Materials and equipments: Epichlorohydrin (AR), N- methyl imidazole (AR), epoxy resin, E-44 (6101), aniline (content above 99.5%), ethylene glycol (AR), three boron fluoride ether (content 47.5%). MAGNA-IR750 infrared spectrometer (FTIR), Mettler 821e/400 DSC differential thermal scanner, 2-XZ-4 type rotary vane vacuum pump, XJJ-50 Charpy impact test machine, SFX-2L type DF-101S instrument, rotary evaporation magnetic stirrer, DZF-6050 type vacuum drying box.

2.2. Preparation of polyether ionic liquid
Hydroxyl-terminated polyepichlorohydrin was prepared by the cationic ring-opening polymerization of epichlorohydrin[6], and chloroacetic acid was added into a three-neck flask with a condenser pipe (molar ratio of 1:2.2), with acetonitrile as the solvent. After mixing at 80 °C for 1 h, a small amount of Na₂CO₃ was placed into the system in batches until insolubility, with continuous reaction for 6 h to 8 h. Hydrochloric acid was dripped into the reaction system to regulate the system for acerbity. The solvent was removed by rotary evaporation under the conditions of 70 °C, 0.09 MPa. The excess chloroacetic acid was removed by washing with deionized water for 3 to 5 times. A small amount of water was removed under the conditions of 70 °C and 0.09 MPa by rotary evaporation again. The carboxyl-terminated polyepichlorohydrin intermediate was then obtained.

The above intermediate and N-methylimidazole were added to the three-neck flask at a molar ratio of 1:1 and mixed in a 80 °C thermostatic waterbath for 24 h. The reaction was then stopped. The product was washed with ethyl acetate for 3 times and vacuum dried for 12 h. Finally, the [HOOC-PECH-MIM]Cl catalyst, which is a yellow-brown sticky liquid, was obtained. The yield was 74%. Its chemical structure is shown in Figure 1.

![Figure 1. Chemical structure of [HOOC-PECH-MIM]Cl.](image)

2.3. Preparation and curing of PIIL/EP
The 50g epoxy resin was mixed with a certain amount of polyether ionic liquid (10%, 20%, 30%, and 50%, respectively) for the epoxy resin, and then was mixed into the round bottom flask while stirring at 2h for 80 °C. The reaction system into brown viscous, adding 5g aniline curing agent, its quality for the added weight of the epoxy resin 10% with stirring to cast. For the stage of curing it was 100-150 °C, the curing process below 100°C for 1h, 120 °C for 2h and 150 °C for 1h.

3. Results and discussions
3.1. Chemical structure and characterization of PIIL/EP
Fourier transform infrared spectroscopy was used to characterize the chemical structure of the epoxy resin before and after modification. The results are shown in Figure 2.
3.2. Determination of thermal properties of PIIL/EP

The curing properties of epoxy resin were tested by DSC before and after the modification. DSC data was taken on a Mettler 821e/400 DSC instrument over a temperature range 25-350 °C at a heating rate of 10 °C·min⁻¹. The results are shown in Figure 3.

**Figure 2.** IR spectrum of EP (a) and PIIL/EP (b) (a-EP; b-40%PIIL/EP).

Figure 2 is the EP and polyether ionic liquid modified PIIL/EP composite system (PIIL content of 40%) infrared spectrum. Figure indicates that the polyether ionic liquid has a strong and broad hydroxyl absorption peak near 3501 cm⁻¹. In the vicinity of the 1115 cm⁻¹, the absorption peak of the in-plane symmetric stretching vibration of the 2922 cm⁻¹ is observed. The in-plane shear vibration absorption peak of 1429 cm⁻¹ appears in the vicinity of C-O. You can see from curve B did not change the basic peak and absorption peak of 2822 cm⁻¹, 1429 cm⁻¹, 1115 cm⁻¹. Absorption peak and absorption peak of 3480 cm⁻¹ decreased significantly and widely, and moving towards the lower wavenumber towards 908 cm⁻¹ characteristic absorption peaks of epoxy group which indicated that the polyether ionic liquid has been transformed into the most epoxy group.
The DSC spectra of EP and P PIL/EP are blended in Figure 3. The peak temperature of the decomposition of pure epoxy resin is 395 DEG C, and the endothermic peak temperature of PIIL/EP blends (b) with a small amount of ionic liquid. The results showed that in the blend system, all of the polyether ionic liquids were received on the epoxy resin and epoxy resin became a single system. With the increase of the ionic liquids, PIIL/EP blends (c) endothermic peak temperature is reduced to 252 DEG C, which may be the introduction of polyether ionic liquid. Its hydroxyl terminated epoxy resin has formed ring opening reaction of crosslinking and copolymerization. Hydroxyl has a certain role in the curing epoxy resin, so the endothermic peak temperature of the decomposition decreases. When the ionic liquid dosage is too large, the ionic liquid and the epoxy resin cannot be excessive reaction, which leading to the endothermic reaction of blends complexly and no obviously endothermic peak, the curve of 160 DEG C should be excess decomposition temperature of ionic liquid.

3.3. Determination of impact properties of PIIL/EP

The impact test machine was used to test the impact bar, and the effect of the addition of polyether ionic liquid on the impact strength of epoxy resin was studied. The results are shown in Table 1.

| Sample | 1   | 2   | 3   | 4   | 5   | 6   |
|--------|-----|-----|-----|-----|-----|-----|
| PIIL content (%) | 0   | 10  | 20  | 30  | 40  | 50  |
| Impact strength (kJ/m²) | 2.13 | 5.23 | 9.52 | 14.22 | 15.95 | 15.98 |

According to the data in Table 1, the impact strength of the unmodified epoxy resin is only 2.13 kJ/m². After ionic liquid was modified, the impact strength increased significantly. With the increasing content of ionic liquid, the impact strength increased. When the percentage of ionic liquid for epoxy resin quality reached 40%, the impact of strength was up to 14.21kJ/m² while the content of ionic liquid was 40%, the increasing impact modified epoxy resin strength of the amplitude tends to be...
stable. The results show that the bigger ionic liquid content is the longer the curing time of epoxy resin. Therefore, it can be concluded that the imidazole type polyether ionic liquid is a very effective toughening agent for epoxy resin, and its content is no more than 40%.

The polyether ionic liquid has active hydroxyl terminated reaction with epoxy resin and a flexible long chain structure. It is liquid at room temperature, with high boiling point and low volatility, its structure of hydrophilic lipophilic group indicates that ionic liquids have very good solubility and compatibility of polymers with the coupling effect during the curing process. It can be uniformly dispersed in the polymer resin; the improvement of impacted strength is conducive. The ionic liquid simultaneously was connected to long chain with the structure of the epoxy resin. It will make epoxy resin glass transition temperature decreased and the active groups of ionic liquids will make certain cross-linked epoxy resin. The improvement of the impact toughness of polymers was conducive. However, when the ionic liquid reaches a certain use level, the crosslinking degree of epoxy resin reaches the maximum value, and the toughness of epoxy resin is no longer obviously.

Therefore, the compatibility and curing properties of epoxy resin toughened by imidazole type polyether ionic liquid are much better than that of traditional toughening agent. This study provides a good theoretical basis and broad prospects for the development of functionalized ionic liquids in the preparation of high performance environmental friendly polymer materials.

4. Conclusions

In this article, the synthesis of imidazole based ionic liquids and the modification of epoxy resin were studied. The conclusions are as follows:

(1) Results of IR and TG analysis show that the chemical reactions of imidazole based ionic liquid polyether and epoxy resin or the polyether ionic liquid modified EP has good toughness, with the increase of the amount of ionic liquid, the decomposition temperature after heat modified by epoxy resin decreased gradually.

(2) Modification of epoxy resin with the use of imidazole type ionic liquid, the impact strength increased significantly. With the increasing amount of ionic liquid, the impact strength increases, but the amount of ionic liquid is 40%, the impact strength of the modified epoxy resin can be as high as 15.95kJ/m².

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