

Modification of Epoxy Resin with Polyether-grafted-Polysiloxane and Epoxy-Miscible Polysiloxane Particles

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Abstract: Polyether-grafted-polysiloxane (FPMS) and epoxy-miscible polysiloxane particles (EMPP) were prepared to improve the toughness of epoxy resin. The chemical structures of the products were characterized by FTIR, ¹H NMR, ²⁹Si NMR, and gel permeation chromatography (GPC). The morphology of the EMPP was analyzed by transmission electron microscopy (TEM). The thermal and mechanical properties and morphologies of the polysiloxanes modified epoxy networks were examined by differential scanning calorimetry (DSC), tensile and impact testing, and scanning electron microscopy (SEM). Microspheres were observed in the EMPP modified epoxy network, whereas irregular particles were obtained for the FPMS modified epoxy resin. The FPMS and EMPP effectively improved the tensile and impact strength of the cured epoxies, while the glass transition temperatures (*T_g*s) were depressed slightly. Moreover, with the same content of modifiers, the EMPP-modified epoxy network exhibited higher impact strength and lower *T_g*s than the FPMS-modified epoxy network.

Keywords: epoxy resin, polysiloxanes, polyether, toughness, microsphere, miscible.

Introduction

Epoxy resins are widely used in diverse areas such as coatings, adhesives, and electronic polymeric materials, especially in electronic packaging materials because of their superior mechanical properties, excellent thermal resistance, and good processability.¹⁻³ However, these products tend to be rather brittle due to their high cross-link density and are therefore prone to fracture and hard to meet the requirements of the rapid developing electronic devices. Thus, a considerable amount of work has been undertaken in an attempt to enhance the toughness of these materials.⁴

It has been suggested that polysiloxanes are proper toughening agents due to their low glass transition temperature, good thermal and oxidative stability, low surface tension as well as high flexibility and good weather ability.⁵ However, pure poly(dimethylsiloxane) (PDMS) had very little use as a toughening agent because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy which largely resulted from the lack of hydrogen bonding.⁶ To improve the compatibility of polysiloxane with epoxy matrix, a great deal of researches have been conducted, including using silane coupling agents,^{7,8} utilizing modified PDMS (such as capped with amino,^{9,10} epoxy^{11,12} and isocy-

anate group¹³), making use of sol-gel method to bridge polysiloxane and epoxy monomers,¹⁴ and adding block containing silicone to make polysiloxane homogeneously dispersed in the matrix.¹⁵⁻¹⁷

Nevertheless, the flexibility of modified epoxy resin is influenced by many factors, such as the particle size, distribution, and the content of elastomer in the epoxy resin matrix.¹⁸⁻²¹ Introduction of predispersed polysiloxane particles into modify epoxy resin can keep the size of particles stable before and after curing, which may be a good attempt to improve the toughness of the epoxy resins. To the best of our knowledge, there are few reports on using predispersed polysiloxane particles to modify epoxy resins.²²

Polyether has good miscibility with epoxy resins, and polyether-grafted polysiloxanes can be homogeneously dispersed in epoxy resins.²³ And double bond containing siloxane from the sol-gel of the γ -methacryloxypropyl trimethoxy silane contains terminal double bond which can react with Si-H; and the polar groups such as Si-OH and C=O, increase the interaction with epoxy resins; furthermore, the molecular weight and microstructures can be easily controlled by optimizing the synthetic parameters, such as concentration, water/alkoxide ratio, temperature, pressure, type of catalyst, and solvent. Based on these, we used the polyether to improve the miscibility of polysiloxane with epoxy resin, and used double bond containing siloxane from the sol-gel

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of the γ -methacryloxypropyl trimethoxy silane as nucleating agent to prepare polysiloxane particles.

In order to clarify the difference between the predispersed particles and curing-reduced particles modified epoxy resins, we used polyether grafted polysiloxane and predispersed polysiloxane particles to modify epoxy resin, respectively. The effects of the content of modified polysiloxanes on the mechanical properties and glass transition temperature of the cured resins were investigated. The morphologies of the cured resins were studied as well.

Experimental

Materials. Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 185-205 g/eq. was purchased from Shell Chemical Co., Holland. The curing agent is 4,4-diaminodiphenylmethane (DDM), supplied by Shanghai SSS Reagent Co., Ltd., China. Poly(methylhydrosiloxane) (PMHS, average molecular weight, $M_n=7,266$, polydispersity index, $PDI=1.57$, and hydrogen amount=0.186 wt%) was from Jiangxi Xinghuo Chemical Works, China. Allyl polyoxyethylene polyoxypropylene ether (F6, average molecular weight, $M_n=1,200$) was purchased from Yangzhou Chenhua Science and Technology Group Co., Ltd., China and vacuum-dried prior to use. γ -Methacryloxypropyl trimethoxy silane was from WD Silicone Co., Ltd., China. Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Chloroplatinic acid (H_2PtCl_6) was from Shanghai NO.1 reagent plant, China and its isopropanol solution (0.025 g/mL) was used as catalyst in hydrosilylation.

Preparation of Polyether-grafted-Polysiloxane (FPMHS). Polyether-grafted-polysiloxane was prepared by the reaction of poly(methylhydrosiloxane) (PMHS) with allyl polyoxyethylene polyoxypropylene ether (F6) using H_2PtCl_6 as catalyst. 100 g PMHS, 100 g F6 and 200 g toluene were placed in a three-necked round-bottomed flask with magnetic stirring, thermometer and reflux condenser, after purging with nitrogen at 75 °C for 30 min, 0.20 mL H_2PtCl_6 isopropanol solution (0.025 g/mL) was added to the flask, and reacted at 110 °C for 4 h under the protection of nitrogen, the FPMHS toluene solution was obtained. Then superfluous *n*-propanol was added and kept at 100 °C for 2 h under the protection of nitrogen to consume the unreacted Si-H bonds. Obtained solution was dialyzed in toluene by dialysis bag for 72 h. The solvent were removed by a rotary evaporator. The obtained product (FPMS) was light yellow transparent oil liquid. The synthetic scheme is shown in Figure 1.

Preparation of Double Bond Containing Siloxane (KSO). The double bond containing siloxane (KSO) was prepared by sol-gel of the γ -methacryloxypropyl trimethoxy silane using dibutyltin dilaurate as catalyst. 100 g γ -methacryloxypropyl trimethoxy silane, 43.5 g THF, 21.7 g distilled water and 1.0 g dibutyltin dilaurate were poured into a two-necked

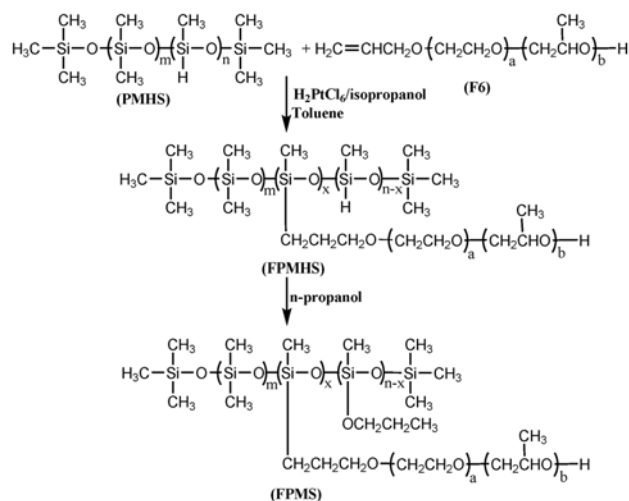


Figure 1. The synthesis of polyether-grafted-polysiloxane.

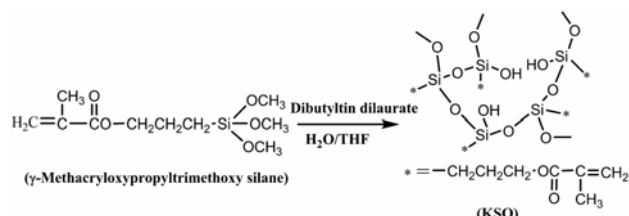


Figure 2. The synthesis of double bond containing siloxane (KSO).

round-bottomed flask with magnetic stirring, thermometer and reflux condenser. After mixing the reactants and solvent by vigorous stirring for 10 min, the mixture were heated to about 70 °C, and refluxed for 5 h. The solvent, water and other small molecules were removed by a rotary evaporator. The obtained product was colorless and transparent viscous liquid. The synthetic scheme is shown in Figure 2.

Preparation of Epoxy-Miscible Polysiloxane Particles (EMPP). The epoxy-miscible polysiloxane particles were synthesized by hydrosilylation between the above resultant FPMHS and double bond containing siloxane (KSO). 50 g FPMHS and 100 g toluene were placed in a four-necked round-bottomed flask with magnetic stirring, thermometer and reflux condenser, after purging with nitrogen at 75 °C for 30 min, 0.3 mL H_2PtCl_6 isopropanol solution (0.025 g/mL) was added to the flask, and the mixture was heated to 110 °C, then 25 mL KSO toluene solution (0.02 g/mL) was added dropwise into the reaction mixture. After the addition of KSO toluene solution (about 2 h), the reaction kept at 110 °C for 3 h under the protection of nitrogen. Finally, superfluous *n*-propanol was added and kept at 100 °C for 2 h under the protection of nitrogen to consume the unreacted Si-H bonds. Obtained solution was dialyzed in toluene by dialysis bag for 72 h. The solvent were removed by a rotary evaporator. A clear and light yellow viscous product (EMPP) was obtained. The synthetic scheme is shown in Figure 3.