Interpenetrating polymer networks of polyurethane cross-linked epoxy and polyurethanes

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1. Introduction
Viscoelastic polymeric materials are capable of attenuating the sound and damping the vibration. As the temperature or frequency varies, the loss modulus ($E''$) and loss tangent ($\tan \delta$) show a peak value, where damping reaches a maximum [1]. Therefore, the polymers are usually used as damping materials near their glass transition temperatures [2]. The ability for a polymer to dissipate sound and vibrational mechanical energy into heat depends on the intensity of loss modulus or $\tan \delta$ value at the applying temperature. Generally, the damping peaks of homopolymers ranged only 20–30 °C, which is rather narrow for practical applications [3]. However, the temperature range for a good damping material is required to be at least 60–70 °C. In order to broaden the damping peaks and improve the damping behaviour, damping polymers of polyblends, copolymer, or interpenetrating polymer networks (IPNs) [4–10] were developed. In recent years, interpenetrating polymer networks have been widely applied as a damping material with satisfactory properties, for instance, poly(methyl methacrylate)/polyurethane (PU), and epoxy/PU IPN systems [11–19].

Two types of polyurethanes (polyether or polyester) cross-linked epoxy were introduced into polyurethane matrix to prepare the PU cross-linked epoxy/PU IPNs. In this paper, the LA (loss modulus area), TA ($\tan \delta$ area) were measured to characterize damping property of the IPNs. The effect of the epoxy content in the IPNs and the type of PU cross-linked epoxy/PU IPNs on the damping behaviour, mechanical properties, dynamic mechanical properties, and morphology were investigated.

2. Experimental procedure
2.1. Materials
The materials used, and their designations, are listed in Table I. The polyl (PPG1000, PPG400, PBA1000, PPG3000 (polytriol) and epoxy (diglycidyl ether of bisphenol A) were degassed at 80 °C with magnetic stirring in the flask for at least 12 h and the 4,4'-diphenyl methane diisocyanate (MDI) was melted at 70 °C before they were used. The 2,4,6, tri(dimethyl aminomethyl) phenol (TDMP) used as a catalyst of epoxy was employed without further purification.

2.2. Preparation of polyurethane prepolymer
The polyurethane prepolymer were prepared by two equivalents of MDI and one equivalent of polyl (PPG1000 or PBA1000). The reaction of MDI and polyl was carried out at 70 °C under dry nitrogen.
The reaction was stopped, when the \( -\text{NCO} \) content, which was determined by the di-\( n \)-butylamine titration method [20], reached the theoretical value.

2.3. Preparation of polyurethane cross-linked epoxy

PU (PPG1000 or PBA1000) prepolymer was put into a reaction kettle which was maintained at about 70 °C under dry nitrogen. A suitable amount of epoxy (the equivalent ratio of \( -\text{NCO} \) group of the PU prepolymer and hydroxyl group of the epoxy is 1.05) was then poured into the kettle under vigorously mixing. The cross-linking reaction occurred between the pendant hydroxyl groups of the epoxy resin and the isocyanate groups of polyurethane prepolymer. Several drops of dibutyltin dilaurate (DBTDL) were added and vigorously agitated with the mixture to accelerate the reaction for several hours. The intensity of the infrared spectrum absorption peak (2270 cm\(^{-1}\)) of the isocyanate was measured periodically to detect the degree of reaction. When the \( \text{NCO}^- \) absorption peak at 2270 cm\(^{-1}\) disappears, it indicates that the pendent hydroxyl groups of epoxy completely react with the isocyanate groups of the polyurethane prepolymer.

To cure PU cross-linked epoxy by 3 phr (per hundred resin) of catalyst (TDMP) was added and followed by vigorously stirring with the PU cross-linked epoxy for 60 s with high torque mechanical stirrer at about 60 °C. It was then poured into a hot mould at 90 °C and cured in a hot press under pressure of 13.7 MPa for 2 h. The sample was then postcured at 110 °C for 24 h.

2.4. Preparation of PU cross-linked epoxy/PU IPNs

The preparation of PU cross-linked epoxy/PU IPNs was carried out with the polyurethane (PU) synthesized via a one-shot method. The IPNs were prepared by mixing two components together; one component consisted of PU (PPG1000 or PBA1000) cross-linked epoxy and MDI, the other one contained the mixture of the PPG400, PPG3000 and TDMP. The mixture was vigorously stirred for 60 s with high torque mechanical stirrer at about 60 °C. The curing steps of the IPNs are the same with the preparation of PU cross-linked epoxy, as described previously. Finally, the samples were removed from the mould and placed in a desiccator, where the relative humidity was maintained at 50%, for at least 3 days before they were tested.

2.5. Testing method

The tensile strength and modulus were measured by using a Tensilon (Mode: TCF-RC). The test procedure followed the specifications of ASTM D412-Die C type with strain rate of 100% min\(^{-1}\) and at least five specimens were tested for the test.

The dynamic mechanical analysis (DMA) was carried out on a Perkin-Elmer DMA-7 form −100 °C to 150 °C with a heating rate of 3 °C min\(^{-1}\). The measurement was performed on the extension mode with fixed dynamic and static stress with force control. The frequency was set at 1 Hz. The dimensions of the specimens were approximately 5 \( \times 1.5 \times 1 \) mm.

The loss modulus area (LA) under the curve of loss modulus versus temperature and the tan δ area (TA) under the curve of tan δ versus temperature are calculated by integrating from −70 to 60 °C.

Morphological studies were performed by using scanning electron microscopy (SEM). Microphotographs were taken on the surface which was made by breaking the specimen in liquid nitrogen and then coated with gold powder.

3. Results and discussion

3.1. Dynamic mechanical properties

Fig. 1 illustrates the loss moduli (\( E'' \)) from dynamic mechanical analysis of the epoxy cross-linked with polyurethane (PU) based on polyether (PPG)- and polyester (PBA)-type polyols. Two distinct transition peaks of the neat epoxy are observed at −88 °C (\( T_{el} \)) and 91 °C (\( T_{sh} \)). Both the \( T_{el} \) and \( T_{sh} \) of the epoxy shift to higher temperatures when the epoxy is cross-linked with polyether-type PU. This behaviour indicates that both the soft and hard domains of the epoxy dissolves in the soft and hard segments of the PU respectively to form another hard-segment domain and soft segment domains containing both polymer components [21]. Another PU cross-linked epoxy based on polyester-type PU shows that the \( T_{el} \) and \( T_{sh} \) move inward and the intensity of the high transition peak show much higher. It may show the more compatible nature of polyester-type PU with the hard and soft segments of epoxy results in shifting inward of the two transition peaks. In the other words, it indicates that the PU dissolves in hard and soft segment domains of