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Synthesis and properties of simultaneous interpenetrating networks based on poly(urethane-epoxy)/allyl novolac resin

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Poly (urethane-epoxy)/allyl novolac resin simultaneous interpenetrating networks (SINs) were prepared by crosslinking urethane-epoxy adduct with diamino diphenylmethane (DDM) and allyl novolac resin simultaneously. An urethane-epoxy adduct was synthesized by terminating the urethane prepolymer composed of 4,4′-diphenyl methane diisocyanate (MDI) and poly (tetramethylene oxide) (PTMO), whose molecular weight range falls in 600–700 (UT1), 900–1050 (UT2) and 1900–2100 (UT3) with glycidol (GL). The allyl novolac resin was derived from novolac type phenolic resin by substituting the hydroxy group on the aromatic ring with the allyl group. The thermal, mechanical and dynamical characteristics of these SINs were measured by differential scanning calorimetry (DSC), Instron tester and dynamical mechanical analysis (DMA), and correlated well enough with morphological observations from transmission electron microscopy (TEM). All these SINs exhibit a two-phase structure and a reasonable explanation is provided for the correspondence of the phase mixing and the specific mechanical properties.

1. Introduction

Among contemporary composite techniques, the interpenetrating network structure (IPN) is a newer blending technique to improve the blending system's compatibility, as well as physical and chemical properties [1]. An IPN is defined as any material containing two polymers which have been synthesized or crosslinked in the immediate presence of each other. SIN is constructed by mixing all components at an early stage, followed by the simultaneous formation of both networks via independent reaction processes; one by a chain growth mechanism and the other by a step growth mechanism.

Because its structural formation can be easily controlled and it has good mechanical properties, polyurethane (PU) has been widely investigated and utilized in the laboratory and industry. Therefore, the IPNs of PU with different kinds of polymers have been widely studied and used as industrial materials [2–7]. Phenolic resins were commercialized long ago and have been widely used in industry for their significant mechanical and thermal properties [8]. Epoxy resins are a family of oligomeric materials that can be further reacted to form thermoset polymers possessing flexibility, impact resistance, good electrical properties, a high degree of chemical and solvent resistance, outstanding adhesion to a broad range of substrates, and a low order of shrinkage on cure.

Recently, there have been many investigative studies on PU-epoxy IPN polymers. Among these, the study goals can be divided into three areas: (i) theoretical study of the toughness mechanism [9–12] and mechanical properties [13–18], (ii) damping behaviour and energy absorption [19–24], and (iii) structural modification (involving the three component IPNs) [25–32]. Also there were some investigations based on PU and epoxy polymer with GL mentioned, especially as a modifier with end-capping PU in epoxy resins [33], but there were fewer studies on PU-epoxy/phenolic IPNs. The aim of this study was to construct heterogeneous materials for ethanol/water separation or biomaterial applications using the IPN technique. In our previous studies [34–37], we overcame the inherent incompatibility between PU and phenolic resin to synthesize successfully a series of new PU/allyl novolac resin SINs. To identify the effect of GL on our synthesized specimen, we investigated the compatibility and morphology between PU and allyl novolac resin. The network component of PU was substituted by poly(urethane-epoxy), which was prepared by introducing the epoxide group into the chain structure of PU, i.e. the PU prepolymer was end-capped with GL, and then crosslinked with DDM to form a network structure. Thermal as well as thermodynamic analysis, mechanical tests and morphological observations were carried out to confirm the function of the epoxide group, GL while the network structure was being constructed.

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2. Experimental details

2.1. Materials

MDI (TOKYO KASEI Co. Ltd.) was melted at 60 °C in an oven and its liquid fraction was used to avoid dimers and trimers. UT1, UT2 and UT3 were dried under vacuum overnight. GL (SIGMA Chem. Co. Ltd), DDM (Fluca Chem. Co. Ltd.), benzoyl peroxide (BPO), trioxane, EtOH, allyl chloride, KOH, chloroform, acetic acid, dimethyl formamide (DMF) and $HClO_4$ were used without further purification.

2.2. Preparation of allyl novolac resin

47 ml phenol (0.5 mole), 50 ml allyl chloride (0.65 mole), 100 ml ethanol and 28 g KOH (0.5 mole) were added into a two-neck flask equipped with a temperature controller, mechanical stirrer and reflux condenser. The reaction mixture was stirred under a reflux for 4 h at 50°C, was washed with distilled water and was dried under vacuum produced by a water pump. The product (I), 60 g, trioxane 20 and acetic acid 200 ml were added to a two-neck flask, then 70% $HClO_4$ 25 ml was added drop by drop for 1 h. The reaction temperature was held at 45°C for 3 h. The product (II), identified by infrared (IR) spectroscopy, was washed by using distilled water/$CHCl_3$ with the ratio at 1/2, and the solvent was removed by vacuum. The preparation scheme is shown in Fig. 1.

2.3. Preparation of poly(urethane-epoxy)/allyl novolac resin IPNs

Degassed UT1, UT2, or UT3, and MDI were added into a four-neck flask equipped with a mechanical stirrer, nitrogen inlet and temperature controller. After 2–3.5 h under N_2 mixing at 65–70°C, the PU prepolymer (III) was obtained in NCO/OH = 1:1.05. With various weight ratios: 100/0, 75/25, 50/50, 25/75, the PU prepolymer and previously synthesized allyl novolac resin were weighed and were dissolved in DMF at 70–75°C, then an equal molar quantity of GL (IV) was added into the reaction solution for 1–1.5 h. The crosslinking agent (V) for the allyl novolac resin, BPO, and for the urethane-epoxy adduct, DDM, were added in the following procedures. After 1.5 h mixing, the solution was cast on Petri dishes and post-cured at 60 °C in an oven for 24 h and at 70 °C in a vacuum oven for 12 h. The preparation scheme is shown in Fig. 1.

3. Measurements

3.1. Glass transition behaviour and tensile properties

The glass transition temperature (T_g) was determined by DSC (Du Pont 910 with Thermal Analyst 2000 coprocessor). The measurements were carried out using 10 mg samples from -100 to 250 °C at a scanning rate of 10 °C min^{-1} under a nitrogen atmosphere. The tensile strength and elongation to break were measured at room temperature on an Instron Tester at a crosshead speed of 50 mm min^{-1} (ASTM D638).

3.2. Dynamic mechanic analysis (DMA)

Values for tanδ, E' and E'' were obtained using a GABO Qualimeter (West Germany). The measurements were carried out from -120 to 80 °C with a frequency of 26 Hz, a heating rate of 3 °C min^{-1} and a temperature interval of 3 °C.

3.3. Electron microscopy

Ultrathin sections (approximately 80 nm thick) of the bulk specimens, which were embedded in epoxy resin,

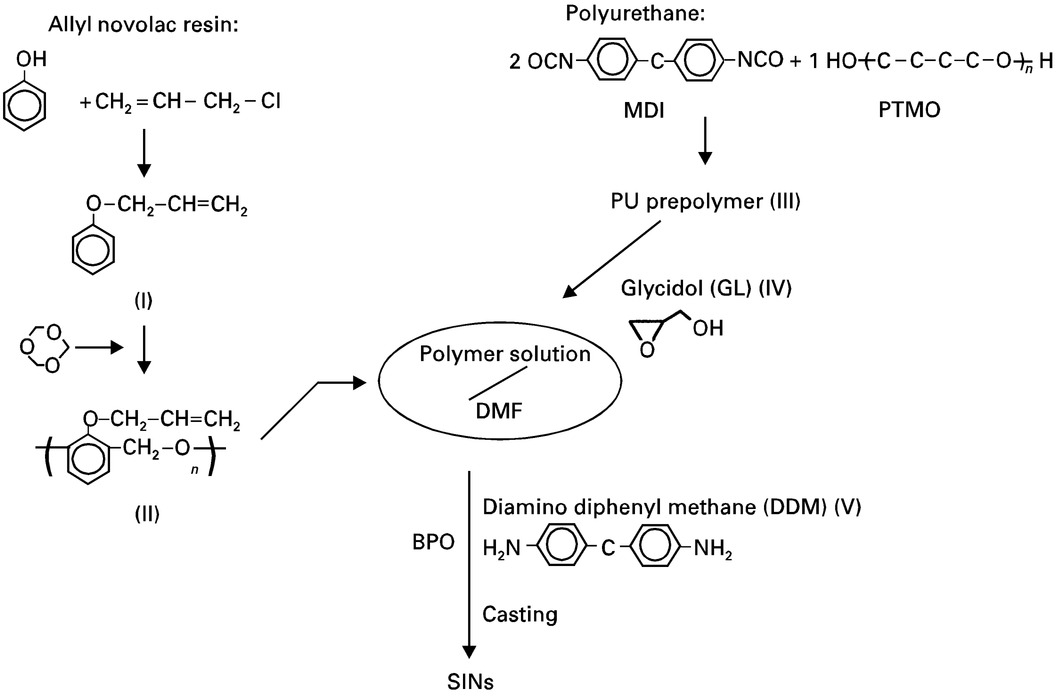

Figure 1 Preparation of allyl novolac resin.

were obtained at room temperature using a Lica Ultratome microtome with a diamond knife. The sections, supported on 300 mesh grids, were exposed to RuO_4 vapours in a desiccator containing a few millilitres of 0.1% RuO_4 solution. Stained sections were observed in a Jeol JEM-1200 EX III transmission electron microscope or a Hitachi H-7100 transmission electron microscope at 80 kV.

4. Results and discussion

The detailed properties of the modified phenolic resin, allyl novolac resin, and PU SINs are described elsewhere [34–37]. The object of this study was to find out a possible route to construct heterogeneous structured polymers with special functionality. Because of the vast use of GL in PU, GL was chosen as an end-capping reagent in the hope that it could be more effective in increasing the compatibility or the tensile strength of the SINs.

Like most phase-separated materials, the IPNs exhibit two loss tangent peaks in the DMA spectrum; each peak is characteristic of the glass-transition temperature of one of the components. Moreover, the height and width of the peak are relative not only to the properties of the selected material but also to the miscibility and the phase separation of the IPNs [38]. As shown in Figs 2–4, the lower peak temperature, which corresponds to the glass transition temperature of the soft segment of PU, evidently does not move towards a higher temperature; in fact, the peak of SUT2 series SINs shifts to lower temperature (see Fig. 3). The change definitely implies poor compatibility between the components of those poly (urethane-epoxy)/allyl novolac resin SINs. In addition, all of these synthesized SINs exhibited a heterogeneous structure, a fact also confirmed by the observation of the domain size and distribution from TEM micrography, and by the results of DSC and mechanical strength measurements.

Table I summarizes the designation, the component compositions, and the mechanical properties from the Instron results and the transition temperature obtained from DSC observation. The composition ratio of poly(urethane-epoxy): allyl novolac resin (25:75) of these SINs was too brittle and could not be tested by Instron and DMA measurement. The molecular weight between crosslinking point ($\bar{M}_c$) was evaluated according to the equation shown below [39]:

$$E' = 3\rho RT/\bar{M}_c$$

where the Young's modulus was directly measured on the Instron test.

The DSC thermogram obtained from these poly(urethane-epoxy)/allyl novolac resin SINs versus temperature are shown in Figs 5–7. As mentioned above, all of the SINs showed two glass transition temperatures (T_gs), with one at a lower temperature, designated T_{g_l}, which was caused by the local motion of the PU soft segment, and the other at high temperature, designated T_{g_h} caused by the thermal motion of the allyl novolac resin. The T_{g_h}s of these SINs in different chain lengths of the PU soft segment, i.e. different molecular weights of PTMO, became more evident when the ratio of allyl novolac resin increased. Hartmann *et al.* [40] reported that the position and intensity of the T_{g_l}s in PU related polymers could be treated as an indicator of the degree of phase separation. As shown in Fig. 5, the T_{g_l}s of the SUT1 series SINs decreases initially and then increases when the weight ratio of allyl novolac resin increases. The shift means that the phase mixing of those SINs increases when the composition ratio of allyl novolac resin

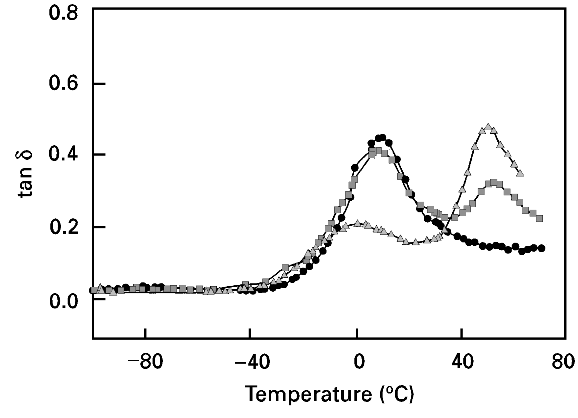

Figure 2 Loss tangent of SUT1 series SINs as a function of temperature: ● SUT1; ■ SUT1-25; △ SUT1-50.

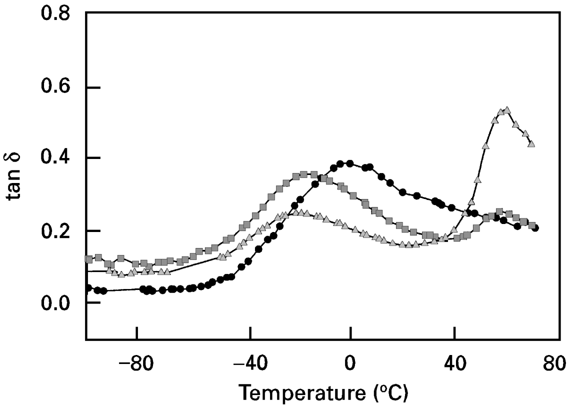

Figure 3 Loss tangent of SUT2 series SINs as a function of temperature: ● SUT2; ■ SUT2-25; △ SUT2-50.

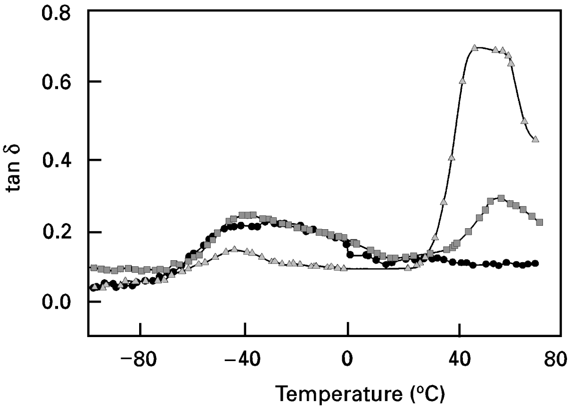

Figure 4 Loss tangent of SUT3 series SINs as a function of temperature: ● SUT3; ■ SUT3-25; △ SUT3-50.

TABLE I Mechanical properties and transition temperature obtained from DSC of SINs

Designation	Allyl novolac resin (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	$\bar{M}_c$ $\times 10^{-2}$	Transition region measured by DSC (°C)		
SUT1	0	4.4	305	17.74	4.70	− 17		
SUT1-25	25	5.3	136	86.53	0.99	− 24	60	
SUT1-50	50	12.9	42	100.19	0.85	− 36	49	
SUT2	0	5.6	539	13.80	5.98	− 34		
SUT2-25	25	2.1	122	16.42	5.03	− 44	− 22	41
SUT2-50	50	3.6	64	29.81	2.64	− 49	− 22	51
SUT3	0	6.3	854	11.40	6.65	− 69	13	
SUT3-25	25	8.7	947	17.38	5.05	− 62	15	53
SUT3-50	50	9.0	903	49.82	1.69	− 62	12	53

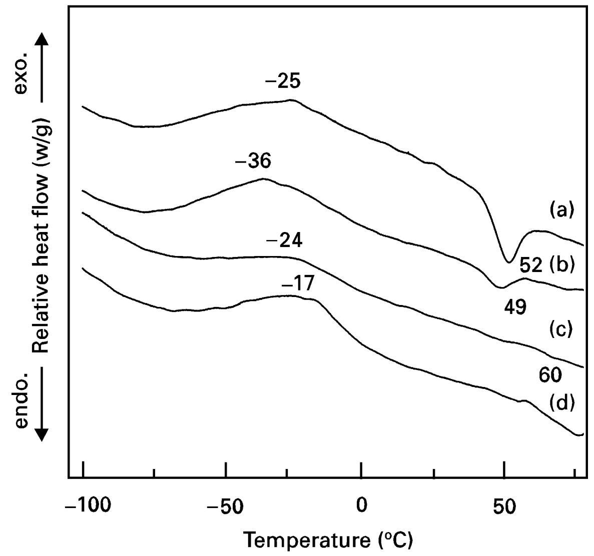

Figure 5 DSC traces of the SUT1 SINs series: (a) SUT1-75, (b) SUT1-50, (c) SUT1-25, and (d) SUT1.

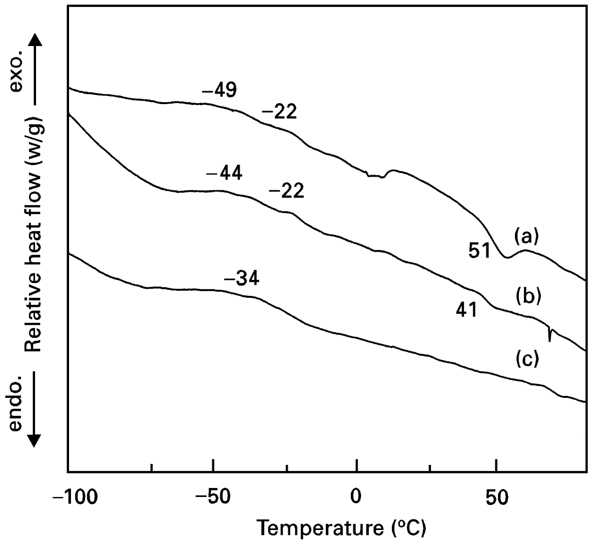

Figure 6 DSC traces of the SUT2 SINs series: (a) SUT2-75, (b) SUT2-50 and (c) SUT2-25.

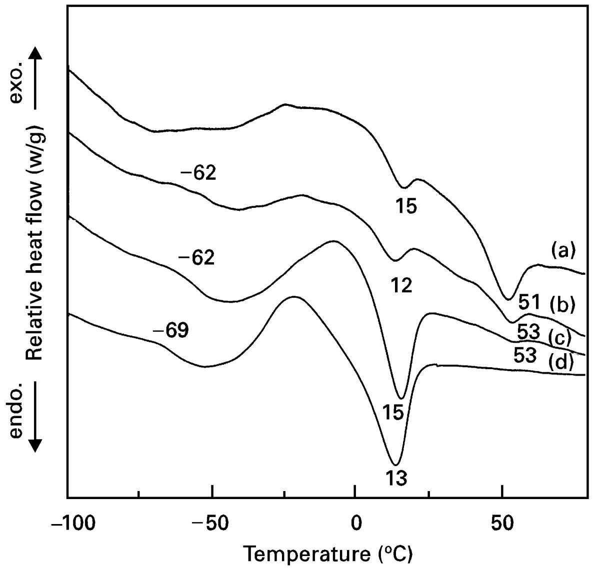

Figure 7 DSC traces of the SUT3 SINs series: (a) SUT3-75, (b) SUT3-50, (c) SUT3-25, and (d) SUT3.

increases from 50% to 75%. However, the shifts toward the lower temperature region of the T_{g_1}s of the SUT2 and SUT3 series SINs were different from that of the SUT1 series SINs; in fact, the tendency to move toward lower temperature regions of the SUT2 series SINs was especially obvious. The difference means that the phase mixing of the SUT2 and SUT3 series SINs, especially SUT2 series SINs, shows no improvement over that of the SUT1 series SINs. This result is also consistent with the observations from TEM micrographs.

The morphology of the SINs herein was observed using TEM as shown in Fig. 8. The dark domain on the photographs is the allyl novolac resin networks, which were vapour-stained by RuO_4 for 8–10 min, while the white domain is the PU networks. As seen from the photographs, both samples have two-phase structures. However, the separated phase structure of the SUT1 series SINs is certainly different from that of the SUT3 series SINs. The former has a phase inversion structure, i.e. the PU network components change from being the continuous phase to the dispersion phase as the ratio of the allyl novolac resins is raised from 25% to 50%; on the other hand, the latter has two continuous phase structures, even the ratio of the allyl novolac resins is just 25%.

Among these three series of poly(urethane-epoxy)/allyl novolac resin SINs, the tensile strength varies as the ratio of the allyl novolac resin increases (see Fig. 9).

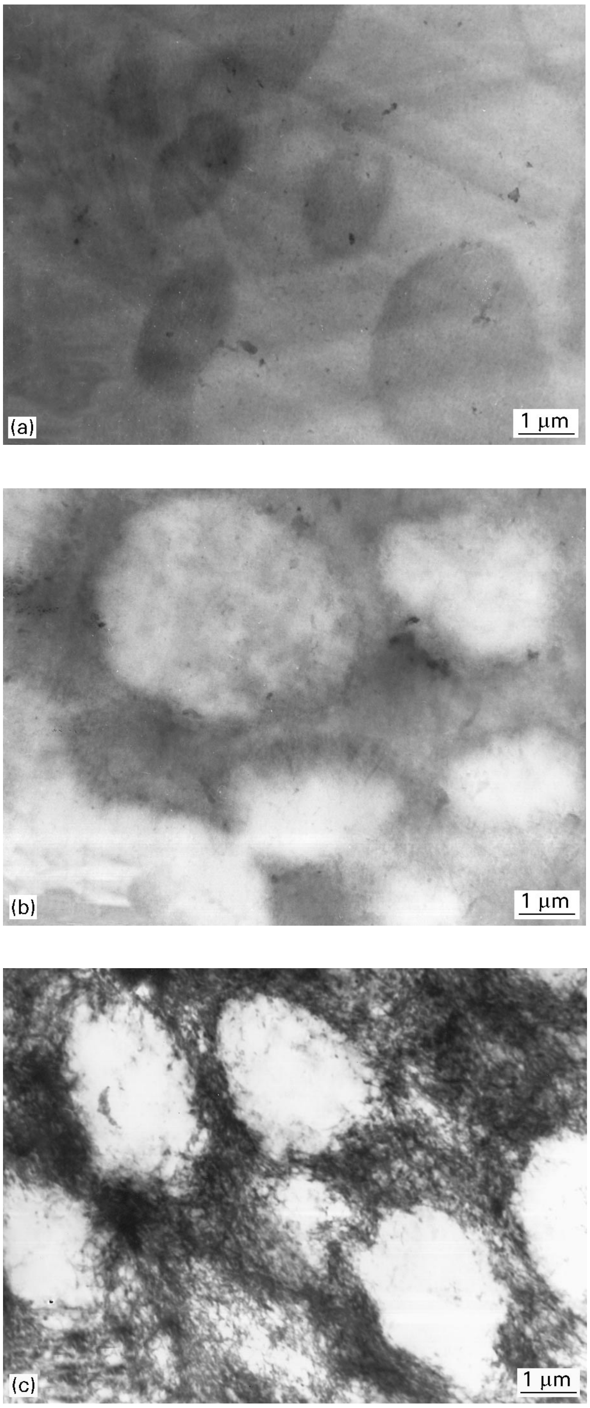

Figure 8 Transmission electron micrographs of the SINs: (a) SUT1-25, (b) SUT1-50, (c) SUT3-25.

One possible explanation for this change may lie in the effect of the improvement of phase mixing or the chain entanglement of the network components of SINs. As a result of its higher phase mixing, as compared to the other two series SINs, the SUT1 series SINs exhibit better mechanical strength. The improvement on phase mixing of the SUT1 series SINs stems from the increase in crosslinking density which results from the short chain segment used as the PU soft segment, i.e. the MW of PTMO is 650. The estimated value of $\bar{M}_c$, shown in Table I, also confirms the changes of crosslinking density. The other important effect is the chain entanglement from the network components. As seen from Fig. 9, the SUT3 series SINs seems to maintain certain mechanical properties, such as tensile strength within 6–8 MPa and elongation of about 900% when the wt % of the allyl novolac resin varies from 0 to 50%. The TEM photographs, as shown in Fig. 8, demonstrate that these SUT3 series SINs have two continuous phase structures even in the SUT3-25 specimen. These two phenomena could thoroughly elucidate the influence of chain entanglement, i.e. the effect of interpenetration. The mechanical properties of the SUT2 series SINs deteriorate when the composition ratio of allyl novolac resin increases, resulting in lower crosslinking density and absence of chain entanglement.

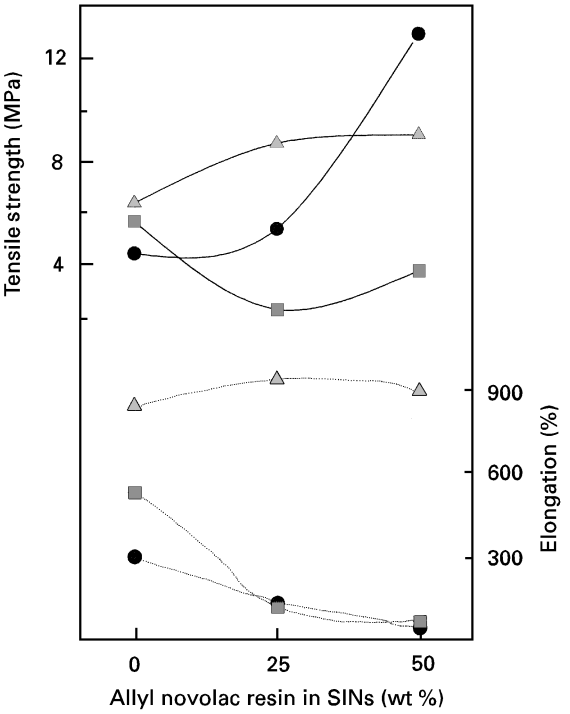

Figure 9 Tensile strength and elongation of the SINs: ● SUT1; ■ SUT2; ▲ SUT3.

5. Conclusion

Poly(urethane-epoxy)/allyl novolac resin SINs were synthesized based on a poly(urethane-epoxy), which was composed of urethane prepolymer, terminated by GL and crosslinked by DDM, and allyl novolac resin. All of the SINs exhibit a two-phase structure. There are two important factors which affect the morphology and mechanical properties of the SINs: crosslinking density and chain entanglement. When the crosslinking density is high, i.e. the SUT1 series SINs, the specimen exhibits dispersed–continuous phase structure and shows higher mechanical strength than other SINs. When the molecular weight of polyol in the PU soft segment is larger (i.e. SUT3 series SINs), which would make the chain entangled, the SINs show two continuous phase domains and maintain the value of mechanical properties as the composition ratio of allyl novolac resin changes from 0 to 50 wt %.

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