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PREPARATION AND CHARACTERIZATION OF POLYURETHANES/ALLYL NOVOLAC RESIN SIMULTANEOUS INTERPENETRATING NETWORK

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Abstract—A series of interpenetrating networks (IPNs) of polyurethanes (PU) and allyl novolac resin were successfully prepared by mixing all the essential components at the same time so that these two polymer networks were constructed simultaneously. The major components included PU prepolymers and allyl novolac resin. The former components were prepared by reacting 4,4′-diphenyl methane diisocyanate (MDI) with poly (tetramethylene oxide) (PTMO) whose molecular weight range falls in 600–700 (for convenience this polymer is called as UT1), 900–1050 (UT2) and 1900–2100 (UT3) separately, and the latter component was synthesized by substituting the hydroxy group of phenolic resin with allyl group. The phenomena of phase mixing for these IPN polymers were investigated and confirmed through dynamic mechanical analysis (DMA), differential scanning calorimetric analysis (DSC) and transmission electric microscopy (TEM) analysis. The tensile strength of these IPNs was improved and was in accordance well with their structures, viscoelastic properties and morphology.

INTRODUCTION

PU has been widely investigated and utilized for its high tensile strength, processability and mechanical properties. Therefore, the IPNs of PU with different kinds of polymers have been widely studied and used as industrial materials [1–3]. Phenolic resins were commercialized long ago and have been widely used as paints, adhesives, coupling agents and various moulding materials because of their excellent mechanical and thermal properties.

Nevertheless there is little reported about PU/phenolic resin IPNs because of the inherent incompatibility between these two polymers. There can be two approaches concerning preparing a composite of PU/phenolic resin. One approach uses a phenolic resin as the polyol to modify the PU; the main proponents are James *et al.* [4], Billy *et al.* [5], Eugene *et al.*, [6–8] and the Hodogaya Chemical Co. [9]. James oxyalkylized the resole resin by using alkylene oxide as polyol which can improve the mechanical properties of PU. Billy directly synthesized novolac resin as polyol in PU foam and the resultant polyol increased the foam's non-burning ability. Eugene incorporated aniline as well as propylene oxide into the phenolic resin and the polyol so formed made the urethane foam have excellent resistance to changes in volume and density after cold and humid aging. These desirable properties improve the structural and insulating applicability of the foam. The Hodogaya Chemical Co., used formaldehyde-phenol copolymers or formaldehyde-p-nonyl phenol copolymers as polyols to enhance the mechanical properties of PU. The other approach is to utilize phenolic resin as the PU crosslinking agent. For instance, Antoine *et al.* [10] synthesized polyoxyl allyloxy benzene as PU crosslinker from trimethylol phenol which was derived from formaldehyde-phenol and this PU crosslinker could increase the curing rate of PU so that a good quality semi-rigid cellular foam was produced.

The methods, as mentioned above, would more or less sacrifice the elastic or mechanical properties of the resultant polymer. Using the IPN technique, however, one can retain the different characteristics of the two different polymers. There are several methods for constructing an IPN structure; the simultaneous interpenetrating network (SIN) represents a special case of the IPNs. The SIN involves mixing all components simultaneously and both polymer networks are constructed independently at the same time. Since one network is formed by a chain growth mechanism and the other by a step growth mechanism, the possibilities of grafting occurring between the homopolymer networks are minimized [11].

It is well known that segmented PUs with a two phase structure have been widely used as biomedical or gas/liquid separation membrane materials. However, further increasing the heterogeneity of PU to meet the biomedical demand will result in the mechanical strength severely decreasing. The purpose of this study was to develop suitable membrane materials which have sufficient tensile strength and heterogeneity for biomedical or separation membrane application. Therefore, we introduce rigid phenolic resin into PU to enhance the material's heterogeneity. In doing so we must maintain the system's compatibility to maintain the necessary mechanical strength. Thus, we modified the phenolic resin by substituting

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the hydroxy group in novolac resin to form allyl novolac resin [12] which can be crosslinked by a free radical initiator to improve the compatibility between phenolic resin and PU. Then we apply a SIN technique to synthesize the IPNs of PU/allyl novolac resin. The PUs were prepared from polyol of a different chain length to investigate the effect of the length of soft segment to the SINs tensile strength. These PU/allyl novolac resin SINs were subjected to DMA, DSC and a tensile strength test to investigate their structure and mechanical properties.

EXPERIMENTAL

Materials

4,4′-diphenyl methane diisocyanate (MDI), produced by Tokyo Kasei Corp., was melted at 60°C and the liquid part was used without further purification. Poly(tetramethylene oxide) (PTMO), supplied by Du Pont Chemical Corp., with $M_n = 600$–700 (UT1), $M_n = 900$–1050 (UT2), and $M_N = 1900$–2100 (UT3), was degassed before use. 1,4-butane diol (BD) and trimethylol propane (TMP), obtained from Tokyo Kasei Corp., were used as PU chain extender and crosslinker respectively. Phenol, trioxane, allyl chloride, ethanol, KOH, benzoyl peroxide (BPO), acetic acid and $HClO_4$ were used without further purification. The N,N-dimethyl formamide (DMF) was dried and used as a reaction solvent.

Preparation of allyl novolac resin

The synthesis procedures of PU/phenolic resin SINs are shown in Scheme 1. Phenol (47 ml), allyl chloride (50 ml), ethanol (100 ml) and KOH (28 g) were added into a two-neck flask which was stirred and refluxed for 4 hr at 50°C. The resultant product (I) was washed with distilled water and dried. Product (I) (60 g), trioxane (20 g) and acetic acid (200 ml) were added into a two-neck flask. Then $HClO_4$ (70%, 25 ml) was added dropwisely during an hour. The reaction temperature was held at 45°C for 3 hr. The reaction mixture was extracted with $CHCl_3$ to obtain product (II).

Preparation of PU/allyl novolac resin IPNs

1 mol of degassed UT1, UT2, or UT3 and 2 mol of MDI were added into a 4-neck flask equipped with mechanical stirrer. After 2–3.5 hr under N_2 stirring at 65–70°C, the PU prepolymer (III) was obtained. Product (III) and product (II) were mixed by the ratio of 100/0, 75/25, 50/50, 25/75 separately and were dissolved in DMF at 75–80°C. Then, the resultant solutions were added with PU's chain extender BD (IV), crosslinking agent TMP (V), and allyl novolac resin's initiator BPO (VI) at the same time. The ratio of TMP/BD was 1/4. After 2 hr mixing, the solution was cast onto Petri dishes and post-cured in a 60°C oven for 24 hr followed by 70°C in a vacuum oven for 12 hr.

MEASUREMENTS

Glass transition behaviour and tensile properties

The glass transition temperature (T_gs) was determined by DSC (Du Pont 910). The measurements were carried out with 10 mg samples from −100 to 250°C at a scanning rate of 10°C/min under a nitrogen atmosphere. The tensile strength and elongation to break were measured at room temperature on an Instron Tester at a cross-head speed of 50 mm/min (ASTM D638).

Electron microscopy

Ultrathin sections of the bulk specimens, which were embedded in epoxy resin, (approx. 800 Å thick) were obtained at room temperature using a Lica Ultratome microtome. The sections supported on 300 mesh grids were exposed to RuO_4 vapours in a desiccator containing a few millilitres of the 0.1% RuO_4 solutions. Stained sections were observed in a JEOL JEM-1200 EX III TEM or a HITACHI H-7100 TEM at 80 kV.

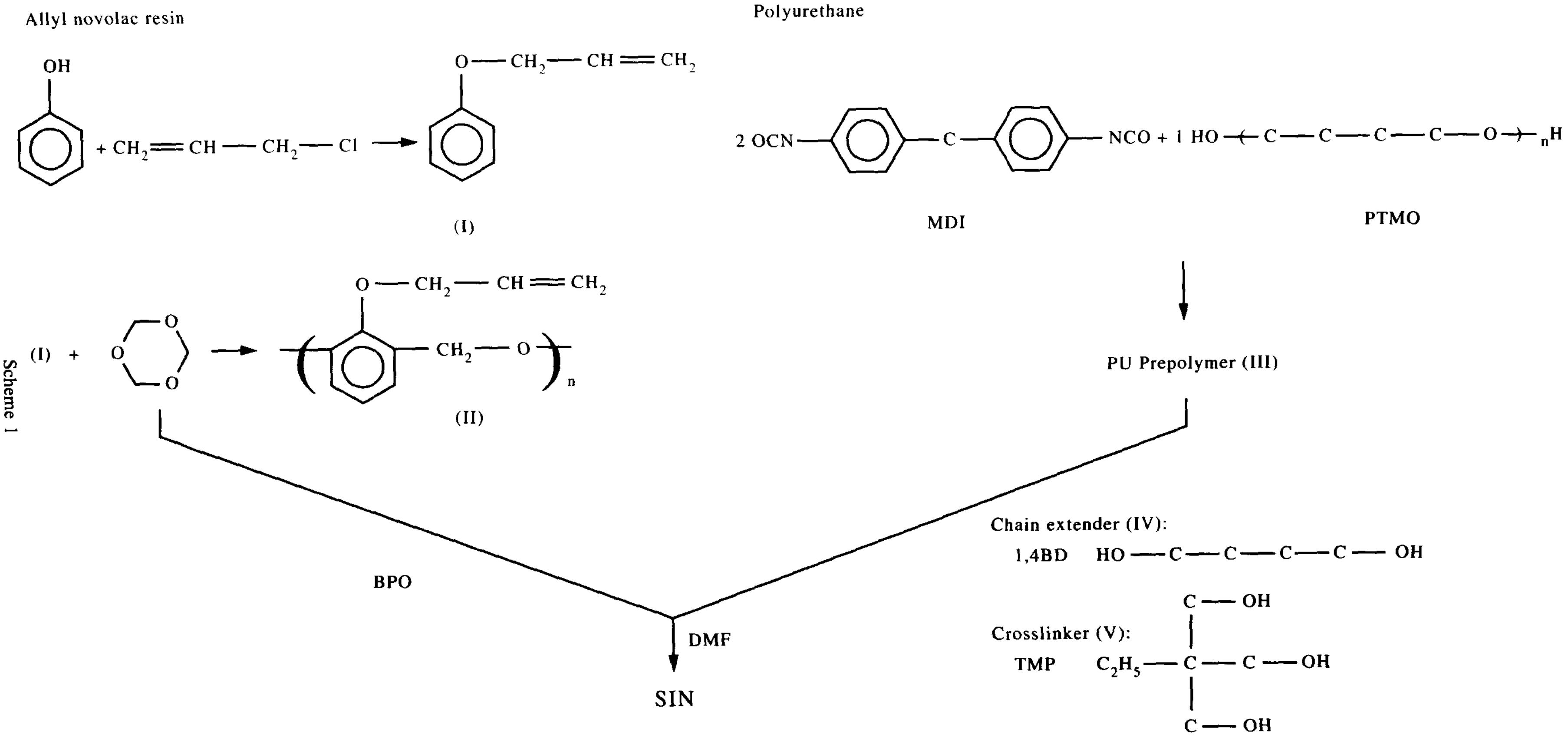
Dynamic mechanic analysis (DMA)

Results for tan δ, E′ and E″ were obtained with 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 and a temperature interval of 3°C.

RESULTS AND DISCUSSION

One of the problems in our research in PU/phenolic resin SINs was the formation of phenolic resin which would interrupt the chain extension reaction of PU. It is because the hydroxyl group in the phenolic resin would react with the isocyanate group in the PU. Then we changed the isocyanate group of PU into a double bond by using 2-hydroxyethyl methacrylate as the chain extender in the second stage of the PU chain growth reaction to avoid the disturbance from phenolic resin's hydroxy group. However, such a modification would cause severe phase separation and the resultant film exhibited poor mechanical properties. Basically, these problems were caused by the inherent incompatibility between PU and phenolic resins. Therefore, we modified the phenolic resin by substituting its hydroxy group with an allyl group and the mode of propagation of phenolic resin changed from condensation to free radical chain growth reaction thus eliminating the interference in PU formation. Finally, we successfully synthesized the PU/phenolic resin SINs film which exhibit excellent mechanical properties.

It is conventional that the compatibility of a system of two components is investigated by dynamic mechanical analysis (DMA). Generally, phase-separated materials exhibit two glass transitions, one for each phase. Moreover, shifting and broadening of transition temperatures are indicative of the degree of phase mixing. The magnitude of each damping peak, tan δ, is a characteristic of the relative concentrations of the two components [13]. In our system, the effect of sample structure on the dynamic mechanical properties of the SINs is shown in Figs 1–3. It is clear that the lower peak temperature which corresponds to the glass transition temperature of the soft segment of PU moves towards higher temperature and its magnitude decreased as the component of allyl novolac resins ratio increases. Likewise, the peak magnitude at a higher temperature which corresponds to the glass transition temperature of allyl novolac resins increases with the ratio of allyl novolac resins increasing. Furthermore, the peak broadening shown in these figures means that extensive interpenetration between the two components apparently occurs. Since the specimens composed by 50% wt of allyl novolac resin in each series of SINs had a broadened damping peak, it means that these specimens had a higher degree of phase mixing and these phenomena would be further explained by the results of DSC, TEM and mechanical measurements.


Allyl novolac resin
OH
+ CH2=CH—CH2—Cl
O—CH2—CH=CH2
(I)
(I) +
O
O
O
CH2—O
n
(II)
Polyurethane
2 OCN
C
NCO + 1 HO—(C—C—C—C—O)nH
MDI
PTMO
PU Prepolymer (III)
Chain extender (IV):
1,4BD HO—C—C—C—C—OH
Crosslinker (V):
TMP C2H5—C—C—OH
C—OH
C—OH
BPO
DMF
SIN

Scheme 1

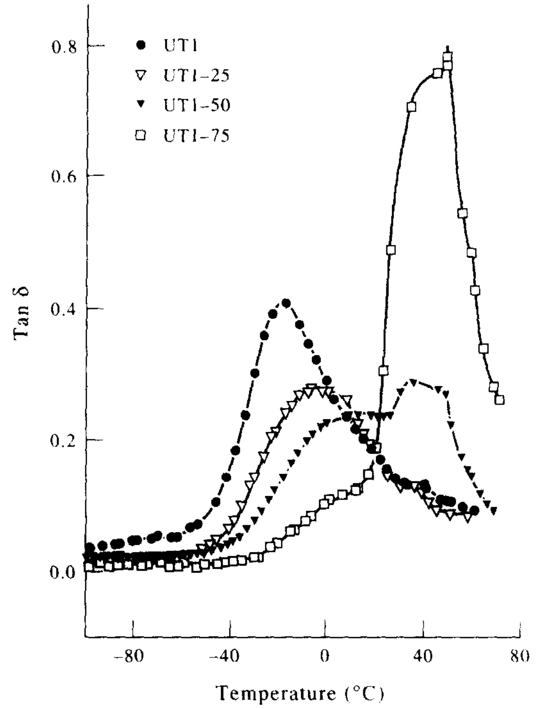


Fig. 1. Loss tangent of UT1 series SINs as a function of temperature.

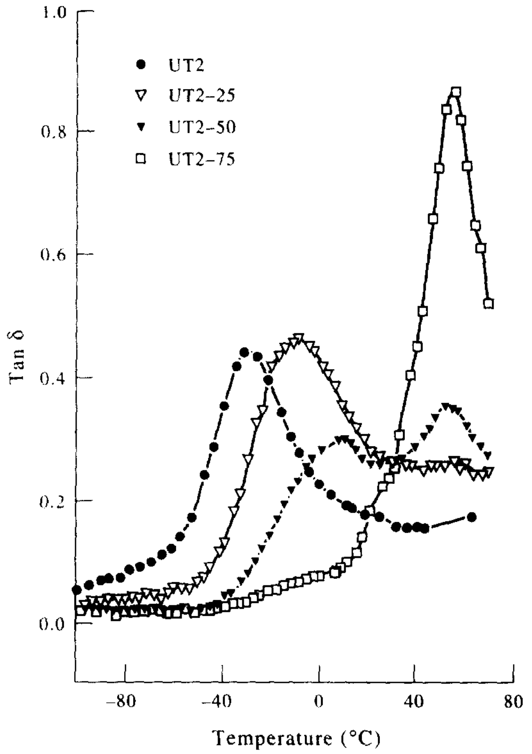


Fig. 3. Loss tangent of UT3 series SINs as a function of temperature.

Figure 4 presents the ultimate mechanical properties of the whole range of specimens. As stated above, all the IPNs show the tendency of superior tensile strength than pure PU, and the pure allyl novolac resin cannot be formed into a film because of its brittleness. The relatively high tensile strength of UT1 SIN series which correspond to the PU component derived from the shortest polyol is probably due to the higher crosslinking density of the network. The

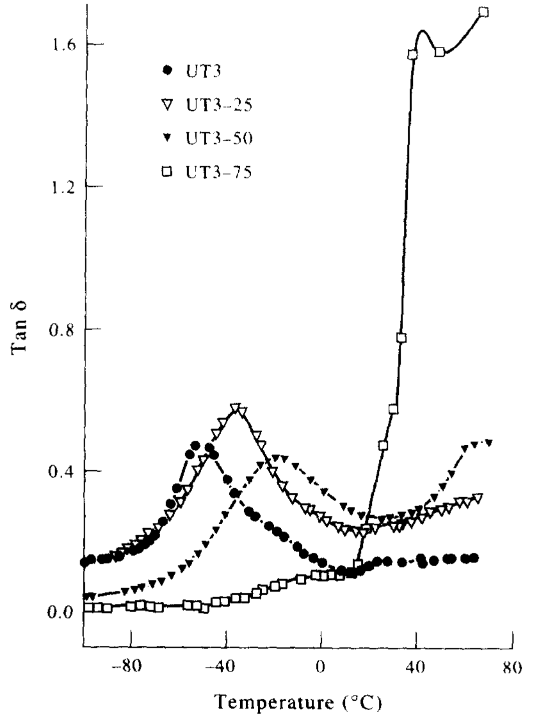


Fig. 2. Loss tangent of UT2 series SINs as a function of temperature.

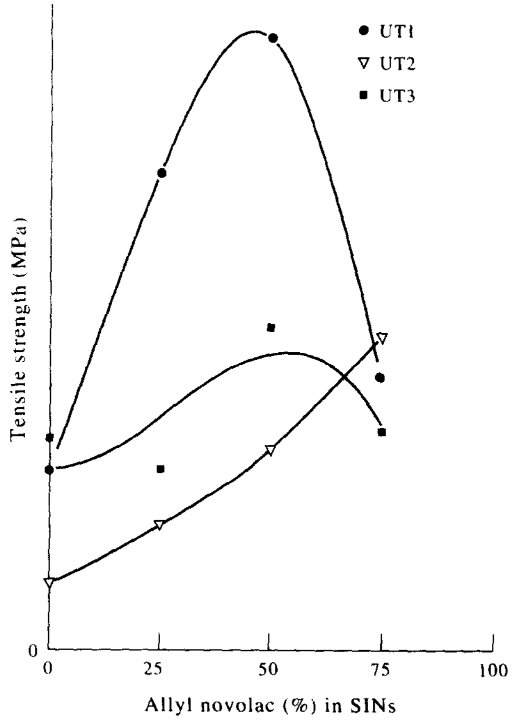


Fig. 4. Tensile strength of various novolac resin content of the SINs (ASTM D638).

Table 1. Mechanical properties and transition temperature obtained from DSC of SINs

Designation	Allyl novolac resin (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	Transition region measured by DSC (°C)		
UT1	0	5.41	106	17.34	−28	—	—
UT1-25	25	14.38	362	46.96	−28.6	—	—
UT1-50	50	18.42	352	37.66	−18.6	26.5	—
UT1-75	75	8.20	222	43.01	−22.5	25.5	—
UT2	0	1.97	97	12.66	−51	26	—
UT2-25	25	3.79	277	12.05	−47	26	48
UT2-50	50	6.12	585	24.87	−38	30	50
UT2-75	75	9.54	320	49.13	−20	36	—
UT3	0	6.49	1545	4.74	−64	−10	16
UT3-25	25	5.53	1395	3.73	−54	—	—
UT3-50	50	9.79	669	6.51	−54	36	—
UT3-75	75	6.61	418	30.82	−26	26	—

higher degree of crosslinking of UT1 SIN series was supported by the higher damping peak temperature of the PU component than those of the UT2 and UT3 SIN series as shown in Figs 1–3 [14]. In addition, with varying the allyl novolac resin's composition, one can find an optimal tensile strength, which can be accounted for by the synergistic effect of IPNs [8]. However, the unclear trend in the tensile strength of the UT2 series could probably be explained in terms of lower crosslinking density and less entanglement effect. Further studies of the UT2 series will be made for investigating the dependence between molecular structure, crosslinking density and entanglement effect.

Table 1 lists the component compositions and the results of mechanical properties and transition temperatures obtained from DSC. The DSC results of the UT3 SINs series are shown in Fig. 5. As indicated by arrows, the SINs exhibit two T_gs when the novolac resin's content is relatively high. The lower transition temperature is the PU soft segment's T_g, i.e. the polyol, which was the indicator for the degree of phase separation [15]. Comparing various allyl novolac resins composition, one can find the soft segment's T_g to increase from pure PU through UT3-25 to UT3-50 and then decrease at UT3-75. The highest T_g of UT3-50 revealed that this IPN had the highest degree of phase mixing; therefore, the highest compatibility between PU and allyl novolac resin. The similar DSC results for UT1 and UT2 SIN are shown in Table 1. Again, these DSC data were consistent with the results of the DMA analysis.

The TEM micrographs shown in Fig. 6 are the phase morphologies of UT3-25 (a), UT3-50 (b), and UT3-75 (c). The dark domain is allyl novolac stained by RuO_4. The allyl novolac resin domain size changed from 1–1.5 μm (a), 0.1–0.2 μm (b), to 3.5–4 μm (c) which indicates the changes of the extent of phase mixing between PU and allyl novolac resin apparently according to the increase of component ratio of allyl novolac resin. These micrographs provided more direct evidence that the UT3-50 had highest phase mixing as mentioned above.

According to Fig. 5 it is obvious that the pure UT3 possesses crystalline structure while the UT3 SIN series do not have crystalline structure. However, in Fig. 4, we find that the tensile strength of these SINs are apparently higher than the pure UT3. This means

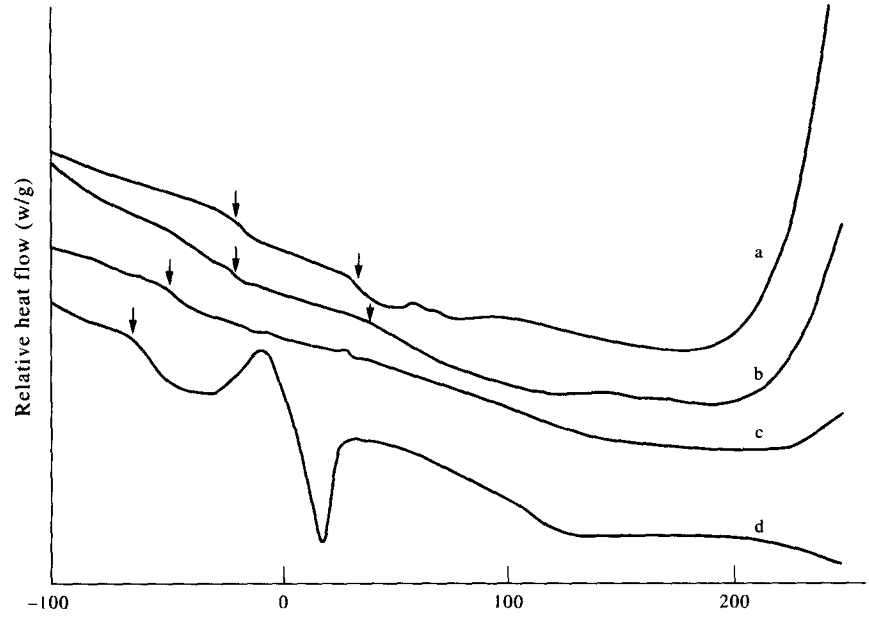


Fig. 5. DSC curves of the UT3 SINs series: (a) UT3-75; (b) UT3-50; (c) UT3-25; and (d) UT3.

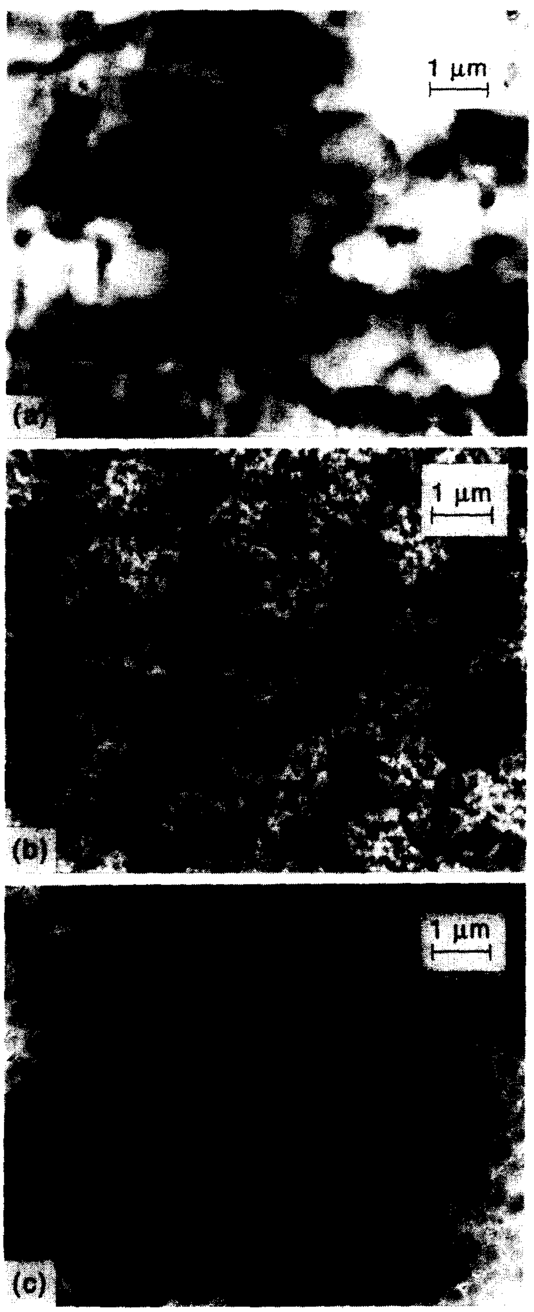


Fig. 6. TEM of UT3 series SINs: (a) UT3-25; (b) UT3-50; and (c) UT3-75.

the improved mechanical strength of these SINs does not arise from the crystalline structure and the reasonable explanation for this phenomenon is the interpenetrating structure between PU and allyl novolac resin.

CONCLUSION

This study has shown that the compatibility between PU and novolac resin can be significantly improved by changing the hydroxy group of the novolac resin into an allyl group. Based on the results of the thermal, mechanical and viscoelastic analysis and morphology studies, we conclude that the excellent mechanical properties of the PU/allyl novolac resin SINs are caused by the effect of entanglement (UT3 series) and the increasing of crosslinking density (UT1 series), respectively. For the UT1 and UT3 series, the SINs composed of 50% wt of allyl novolac resin exhibits the best phase mixing and mechanical properties. These SINs may be considered promising candidates for separation membrane and biomedical applications.

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REFERENCES

1. H. L. Frisch, K. C. Frisch and D. Klempner. *CHEMTECH*, 188 (1977).
2. K. C. Frisch, D. Klempner and H. L. Frisch. *Polym. Engng Sci.* **22**, 17, 1143 (1982).
3. L. H. Sperling. *CHEMTECH*, 104 (1988).
4. J. L. McFarling. Granvill, U.S. 3,770,671 (1973).
5. B. D. Davis *et al.* U.S. 3,598,771 (1971).
6. E. F. Cox *et al.* U.S. 3,245,924 (1966).
7. E. F. Cox *et al.* U.S. 3,436,373 (1969).
8. E. F. Cox *et al.* U.S. 3,186,969 (1965).
9. Hodogaya Chemical Co. Ltd. Japanese Kokai Tokky Koho, Jp 58-57,418 (1983).
10. A. Khawam. Arbutus, U.S. 3,063,964.
11. N. Devia, J. A. Manson and L. H. Sperling. *Macromolecules*, **12**, 3360 (1979).
12. Japanese Kokai Tokky Koho Jp 59-168,019 (1984).
13. Takayuki Murayama. In *Dynamic Mechanical Analysis of Polymeric Materials*. Elsevier, Amsterdam (1978).
14. L. E. Nielsen. In *Mechanical Properties of Polymers and Composites*. Dekker, New York (1974).
15. B. Hartmann *et al. J. appl. Polym. Sci.* **35**, 1829 (1988).