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Synthesis and properties of maleimide-terminated polyurethane AB crosslinked polymers
I. Polyurethane/allyl nonyl novolac resin ABCPs

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Abstract

Polyurethane (PU) and phenolic resin were prepared to form maleimide-terminated PU/allyl nonyl novolac resin ABCPs. The polyurethane was prepared from 4,4′-diphenyl methane diisocyanate (MDI) and poly(tetramethylene oxide) [PTMO] of various molecular weights. The composition, compatibility, mechanical and thermal properties of these inhomogeneous network polymers were investigated through differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), the tensile strength tester and transmission electron microscopy (TEM) micrographs. The results reveal that the miscibility makes only a little improvement but the tensile strength has clear improvement when the PU's soft segment, i.e. PTMO, is higher, because of the entanglement between components.

1. Introduction

When two or more polymers are mixed, the resulting composition can be called a multicomponent polymer material. In this multicomponent field, polymer blends, blocks, graft, AB cross-linked polymers (ABCPs), and interpenetrating polymer networks (IPNs) involves techniques which have been widely investigated in both academia and industry for years. ABCPs are a structure in which two polymers are grafted together to form one network. Polymer B is bonded to polymer A at both ends or at various points along the main chain. Although bonded primarily to polymer B, polymer A is not cross-linked to itself [1].

Most multicomponent systems undergo phase separation because their positive mixing enthalpies result in low entropy of mixing. Morphological features have been the central issue in the study of the multicomponent system because their domain sizes, shapes, and interfacial bonding characteristics determine the mechanical properties. A proper understanding of these features often allows one to develop synergistic behavior [2].

Our previous papers [3–10] on polyurethane (PU) based IPNs and ABCPs, which have been studied for years, discovered that maleimide-terminated PU based ABCPs are good in either miscibility or mechanical properties [10]. In this study, PU based ABCPs will be investigated in terms of their definition, types, theories, and thermal and mechanical results.

2. Experimental

2.1. Materials

The raw materials and reagents for synthesis are listed in Table 1. 4,4′-diphenyl methane diisocyanate

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Table 1
Raw materials and their abbreviation

Designation	Name and description	Source
PTMO	Poly(tetramethylene oxide), Mw = 650, 1000, 1400, 2000, 2900	Du Pont Chemicals
MDI	4,4′-diphenylmethane diisocyanate	Tokyo Kasei Chemicals
Nonyl phenol	extra pure reagent	Wako Pure Chemicals
Trioxane	1,3,5-trioxane	FLUKA Chemicals
Acetic acid	solvent grade	Wako Pure Chemicals
DMF	*N*, *N*-dimethyl formamide	Wako Pure Chemicals
KOH	extra pure reagent	Wako Pure Chemicals
Ethanol	dried, 99.5%, solvent grade	SCI chemicals
$HClO_4$	perchloric acid (70%)	Wako Pure Chemicals
Allyl chloride	extra pure reagent	Wako Pure Chemicals
BPO	benzyl peroxide, initiator	Wako Pure Chemicals
MI	maleimide	Tokyo Kasei Chemicals
Chloroform	solvent grade	Wako Pure Chemicals

(MDI), produced by the Tokyo Kasei Corporation, Japan, was melted at 60°C and the liquid part was used without further purification. Poly(tetramethylene oxide) (PTMO), supplied by Du Pont, with Mn = 600–700, 900–1050, 1350–1450, 1900–2100, and 2825–2975, was degassed by vacuum pump before use. The *N*, *N*-dimethyl formamide (DMF) was dried and used as a reaction solvent. Nonyl phenol, trioxane, allyl chloride, ethanol, KOH, benzoyl peroxide (BPO), acetic acid and $HClO_4$ were used without further purification.

2.2. Preparation of polyurethane prepolymer

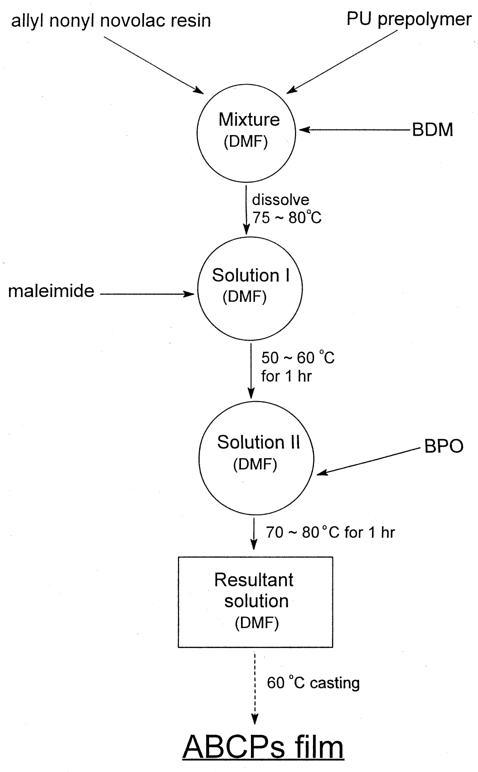
One mole of degassed PTMO and 2 moles of melted MDI were added to a four-necked flask equipped with a mechanical stirrer. After 3–4 h under N_2 stirring at 65–70°C, a white fluid PU prepolymer was obtained.

2.3. Preparation of allyl nonyl novolac resin

The synthesis procedure can be separated into two parts: firstly, changing the OH group of the phenol into the allyl group. Nonyl phenol and allyl chloride were added into a two-necked flask which contained a proper solvent, ethanol, at a 1:1 ratio by mole. Then an equal mole mount of the initiator, KOH, was added, stirred and refluxed for 4 h at 50°C. The resultant solution was changed to pH 7 with HCl, and then extracted with distilled water. An orange color liquid was obtained after drying. Secondly, the polymerization of allyl nonyl novolac resin. Allyl nonyl phenyl ether (60 g), trioxane (10.34 g) and acetic acid (200 ml) were added into a two-necked flask, then $HClO_4$ (70%, 25 ml) was added drop-wise over an hour. The reaction temperature was held at 70°C for 8 h. The reaction mixture was extracted with methanol and then desolvented with a vacuum to obtain a dark brown powder [11].

2.4. The PU/allyl nonyl novolac resin ABCPs films

The whole synthesis procedure is shown in Scheme 1.



Scheme 1. The synthesis procedures of the PU/allyl nonyl novolac resin/BDM ABCPs (PND series).

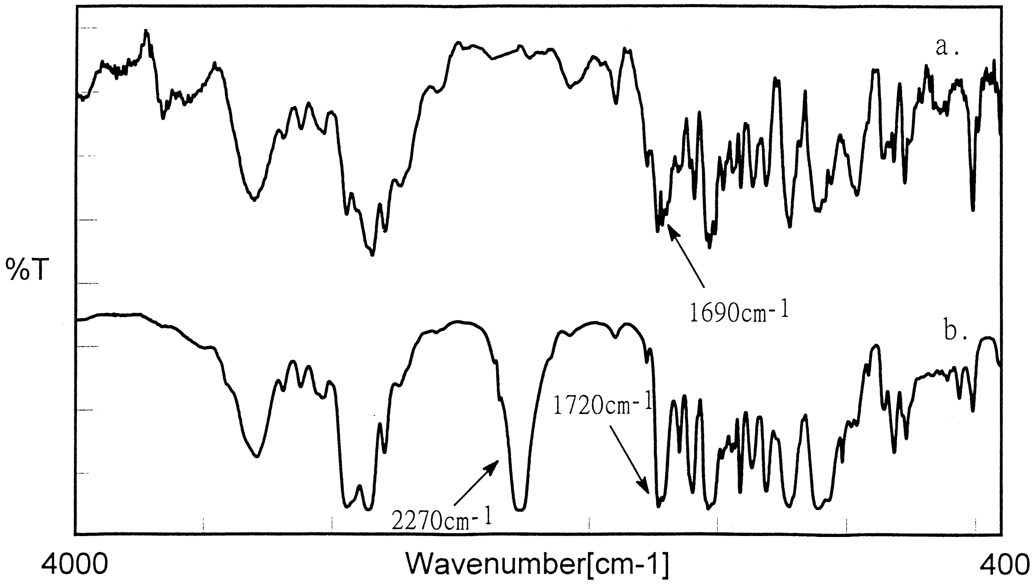


Fig. 1. The FTIR spectra of maleimide-terminated PU prepolymer (a) and PU prepolymer (b).

The PU prepolymer and the allyl nonyl novolac resin were mixed at a ratio by weight of 100/0, 75/25, 50/50 and 25/75 separately, and were dissolved in DMF at 75–80°C. Then the resultant solutions were added with the end-capped agent, maleimide (double the amount of the PU prepolymer by mole), and were left to react for a further 1 h at 50–60°C. Subsequently, the initiator, BPO (3% in weight of the reagent), was added for another hour of reaction at 70–80°C. Finally, the resultant solution was cast onto Petri dishes and postcured in a 60°C oven for 24 h, followed by 70°C in a vacuum oven for 12 h.

3. Measurements

Fourier transform spectra were obtained at room temperature on a JASCO 300E FTIR spectrometer with a KBr reference. The element analysis was tested on a Perkin–Elmer 2400 type. The tensile strength and

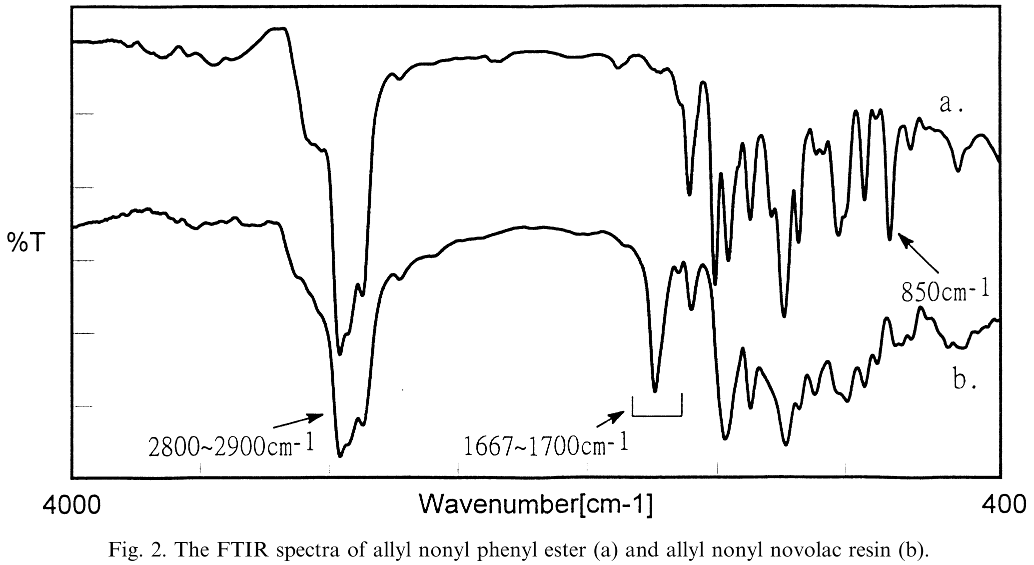


Fig. 2. The FTIR spectra of allyl nonyl phenyl ester (a) and allyl nonyl novolac resin (b).

Table 2
The element analysis result of allyl nonyl phenyl ether and allyl nonyl novolac resin

	Theoretical			Experimental		
	H%	O%[a]	C%	H%	O%	C%
Allyl nonyl phenyl ether	10.76	6.18	83.06	10.33	6.98	82.69
Allyl nonyl novolac resin	9.71	11.13	79.16	9.54	11.55	78.91

[a] The O% data are estimated from the equation: 100% − (H% + C%).

elongation to break-point were measured at room temperature on a tensile strength tester (Lloyd, LRS-250 type, UK) at a crosshead speed of 50 mm/min with a model of ASTM D638. The glass transition temperature (T_g) 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 flow rate of 30 ml/min. Ultra thin sections (approximately 90 nm thick) of the bulk specimens, which were embedded in epoxy resin (Spi-chem Spurr, PA, USA), were obtained at room temperature using a Leica Ultratome microtome. The section supported on a 300 mesh grid was exposed to RuO_4 vapors in a desiccator containing a few milliliters of the 0.1% RuO_4 solutions. Stained sections were observed in a Hitachi H-7100 transmission electron microscopy at 80 kV. The tan δ, E' and E'' were obtained by Du Pont DMA 2980. The measurements were carried out from −120 to 100°C at a frequency of 26 Hz, and a heating rate of 3°C/min.

4. Results and discussion

ABCP, a kind of IPN, is a somewhat complicated polymer structure. The polymer structure will be more complicated and difficult to confirm as soon as ABCPs are formed. An important structure of the PU prepolymer end-capped with maleimide is analyzed in an FTIR spectrum, as shown in Fig. 1. The spectrum indicated as "b" is the PU prepolymer synthesized from PTMO and MDI at a mole ratio of 1:2. The car-

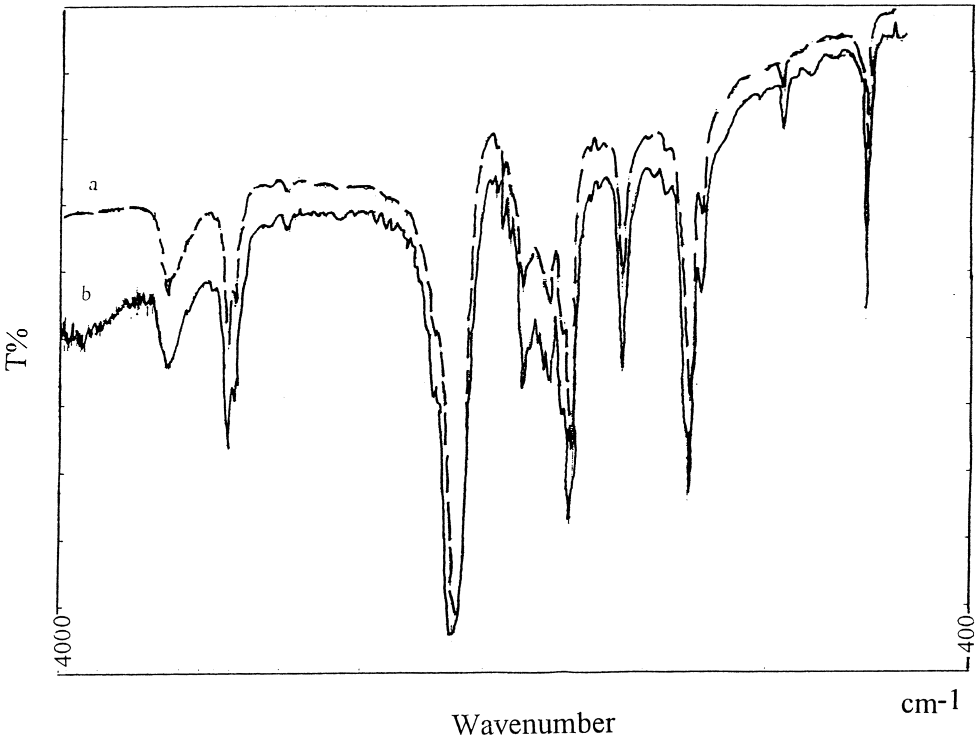


Fig. 3. The FTIR spectra of the reaction of maleimide with allyl nonyl novolac resin, the initial reactant (a); the 70 min latter (b).

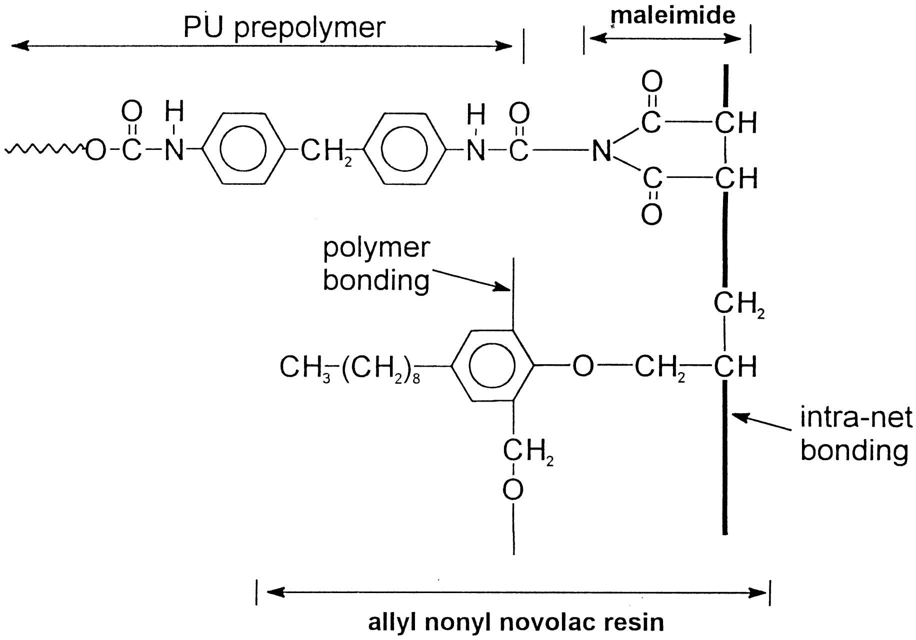


Fig. 4. The proposed structure of PN series ABCPs.

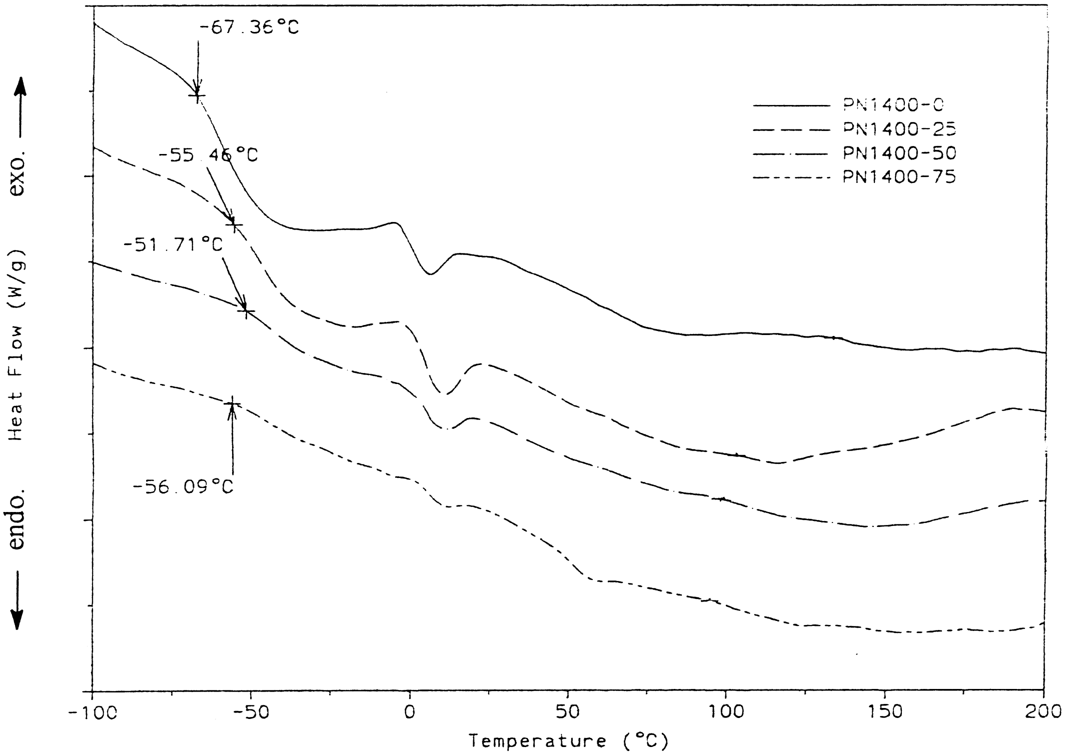


Fig. 5. The DSC curves of the PN1400 series ABCPs.

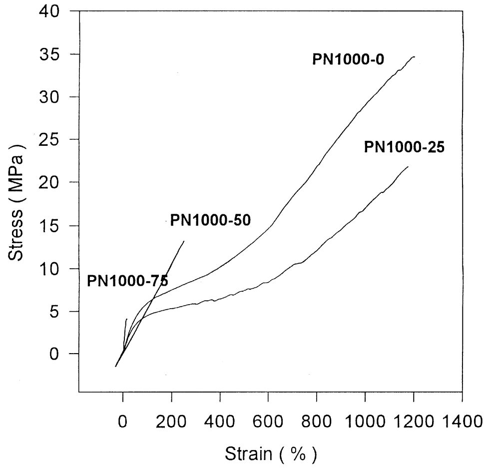


Fig. 6. The stress–strain curves of various allyl nonyl novolac resin contain of the PN1000 series ABCPs.

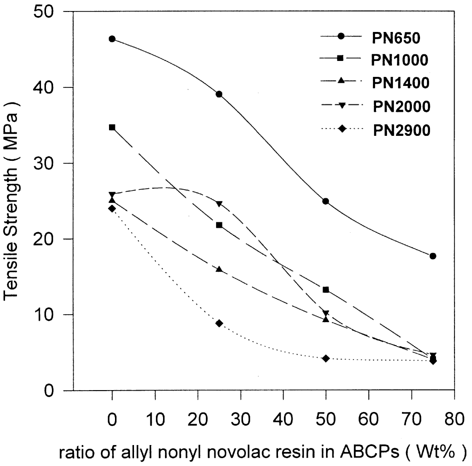


Fig. 7. Tensile strength of PN series ABCPs.

bamate group's absorption peak (1720 cm^{-1}) reveals the forming of the PU, and a strong absorption peak of the isocyanate group at 2270 cm^{-1} proved the isocyanate-terminated PU prepolymer. After 1 h of reaction with the maleimide, the absorption peak of the isocyanate group disappeared, as shown by spectrum "a", and the amide absorption peak appeared (1690 cm^{-1}). It means that the maleimide is successfully connected to the two ends of the PU prepolymer. The maleimide-terminated PU has been formed. On the other hand, the allyl novolac resin is modified by a long soft chain, nonane, to form allyl nonyl novolac resin, In the course of the synthesis of allyl nonyl novolac resin, the final step, in which the polymeriz-

Table 3
Mechanical properties, transition temperature and average relative molecular weight between cross-links of PN series ABCPs

Designation	Nonyl allyl novolac resin (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	Transition region measureed by DSC (°C)	Average relative MW between cross-links, M_c [a] (g/mole)
PN650-0	0	46	887	8	−47.9	1002
PN650-25	25	39	802	6	−25.4	1193
PN650-50	50	25	447	23	−30.4	294
PN650-75	75	17	6	309	−22.9	25
PN1000-0	0	34	1197	5	−66.7	1525
PN1000-25	25	21	1174	4	−55.5	1905
PN1000-50	50	13	531	5	−58.6	1368
PN1000-75	75	4	16	28	−60.5	276
PN1400-0	0	25	1079	3	−67.4	2399
PN1400-25	25	15	1195	2	−55.5	2678
PN1400-50	50	9	943	7	−51.7	1102
PN1400-75	75	4	295	16	−56.1	471
PN2000-0	0	25	1175	1	−72.4	4066
PN2000-25	25	24	1515	2	−64.2	3859
PN2000-50	50	10	684	5	−62.4	1308
PN2000-75	75	4	239	7	−57.3	973
PN2900-0	0	24	1415	3	−73.6	2199
PN2900-25	25	8	852	0.5	−71.7	13395
PN2900-50	50	4	898	0.4	−59.2	19694
PN2900-75	75	3	520	4	−32.0	1823

[a] The average relative molecular weight between cross-links. These values are theoretically estimated by the equation, $M_c = 3\rho RT/E'$.

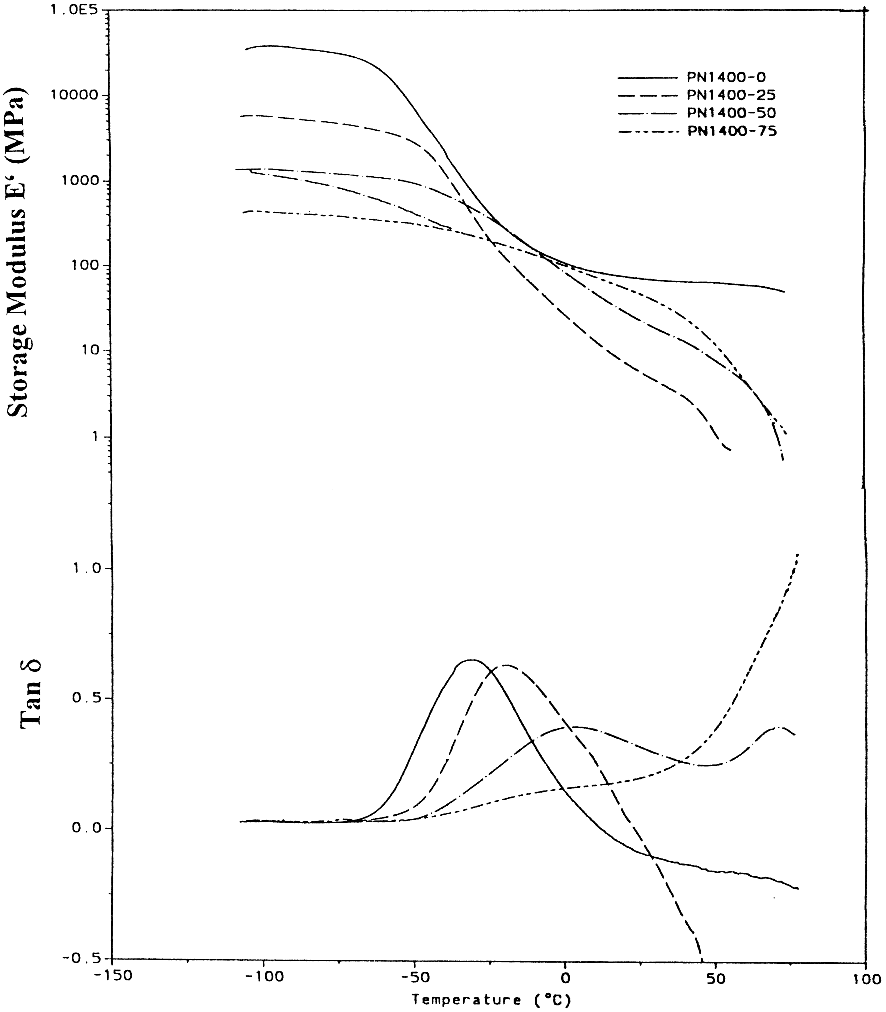


Fig. 8. The DMA modulus of the PN1400 series ABCPs.

ation of allyl nonyl novolac resin takes place, is the point we are concerned about. In Fig. 2, the spectrum indicated as "a" is allyl nonyl phenyl ether, an early product, and the "b" spectrum is allyl nonyl novolac resin, a late product. One can notice that the para-substitute absorption peak (850 cm^{-1}) in a spectrum disappears and the tetra-substitute absorption peak's overtone (1667–1700 cm^{-1}) appears in the "b" spectrum. It means that the formation of allyl nonyl novolac resin is complete. Table 2 gives an element analysis of these two products, and the experimental obtained data are close to the theoretical ones. The discrepancies are in the range of permission. Fig. 3 is the IR spectrum of maleimide and allyl nonyl novolac resin 70 min reaction. No clear difference between these two spectra means that the two components will not react in this situation described above. The cross-linking phenomena can, therefore, take place simultaneously.

Once ABCPs is formed, the linked network structure inside can be thought of as shown in Fig. 4. Theoretically, the double bond of maleimide, which is connected at the end of the PU prepolymer, and the allyl group of the allyl nonyl novolac resin, are combined with each other by a single covalent bond with an initiator, BPO. These two networks, therefore, are linked by a single bond, as shown by the bold line in the figure.

4.1. Differential scanning calorimetry (DSC)

The DSC results of the PN1400 ABCPs series are shown in Fig. 5. These ABCPs exhibit two transition temperatures, as indicated by arrows, except the pure PU. The lower one is the T_g of the PU soft segment, i.e. the PTMO, which is the indicator for the degree of phase separation [12], the other is for that of the allyl nonyl novolac resin. One can notice that the whole T_gs of the soft segment are higher than the PTMO, −85°C. Furthermore, these T_gs increase from pure PU through the specimens whose ratio of allyl nonyl novolac resin is 25% and the 50% to the 75%. It means that the miscibility has improved with the increase in the degree of the intermolecular interaction between two components in ABCPs. The placement of the lower T_gs (the higher transition temperature are too broad and difficult to identify exactly) also shows the degree of miscibility. The specimens which have a high PTMO molecular weight ratio show poor miscibility. A comparison with the previous study in Ref. [10] reveals that the PN series is a little more compatible when the molecular weight of PTMO is lower than 2000. The attempt to improve entanglement by using the nonyl group on the phenolic resin ABCPs has been made, but when the soft chain of the PU is high, the phase separation happens.

4.2. Mechanical properties

Fig. 6 shows the stress–strain curves of the PN1000 series ABCPs. To the soft, elastic PU is added a hard, brittle novolac resin; therefore, the curves change from one which possesses the yield point, to a straight line in stress–strain curve figures. However, when the PU soft chain is long enough, the phenomena change. The specimens become elastomers. The strengths decrease as the content of allyl nonyl novolac resin increases, because of the inherent incompatibility between maleimide-terminated PU and allyl nonyl novolac resin. These results can also be seen in Fig. 7. The chain length of the PU's soft segment plays an important role in the tensile strength of the specimen. The strength decreases as the chain length increases. The short chain length possesses higher tensile strength because of its higher cross-linking density, i.e. lower molecular weight between cross-links. On the other hand, the longer chain length can improve the entanglement, but it can also cause phase separation. That is the reason for the phenomena of the PN2900 series. The PN2000 series have handled the entanglements and the compatibilities, their properties are better than others.

Table 3 summarizes the component compositions and the results of mechanical properties, transition temperature obtained from DSC, and the average molecular weight between cross-links, M_c, which indicate the cross-linking density in ABCPs.

4.3. Dynamic mechanical analysis (DMA)

The damping peak, tan δ, and storage modulus curves to temperature phenomena of the PN1400 series ABCPs, are shown in Fig. 8. The whole specimens which contain allyl nonyl novolac resin less than 25% show one damping peak. It means that the resultant ABCPs have higher miscibility between the two components. Moreover, the peak position shifts right proportionately to the increase of the composition ratio of allyl nonyl novolac resin, and the damping peaks also broaden. However, as the contents of allyl nonyl novolac resin rise to 50%, the two damping peaks show up; the greater the length of the PTMO, the clearer the phenomenon. The reason is the occurance of the phase separation. These results, which is also consistent with the DSC and tensile strength measurements.

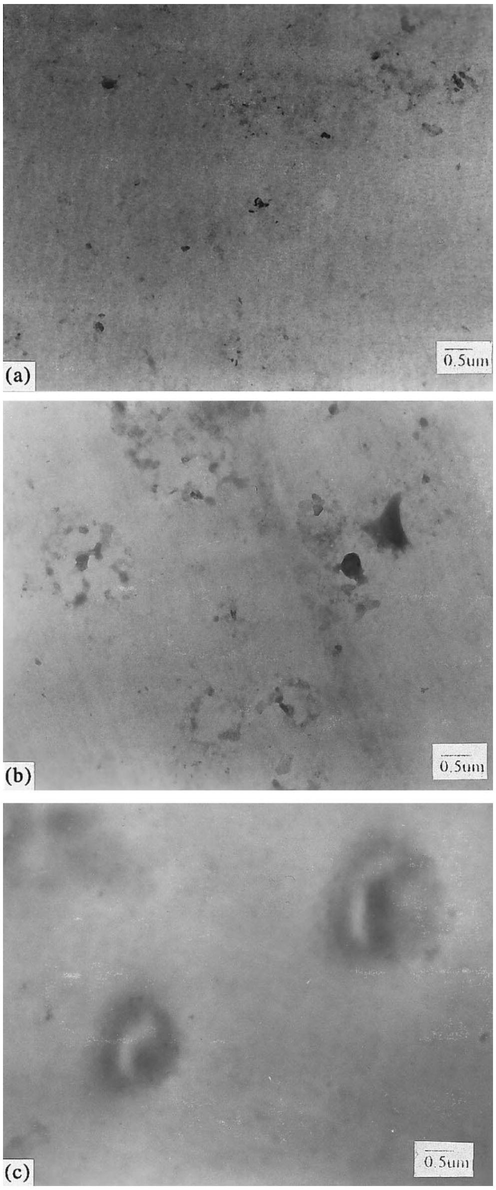


Fig. 9. Transmission electron micrographs of PN1400 series ABCPs: (a) PN1400–25, (b) PN1400–50 and (c) PN1400–75.

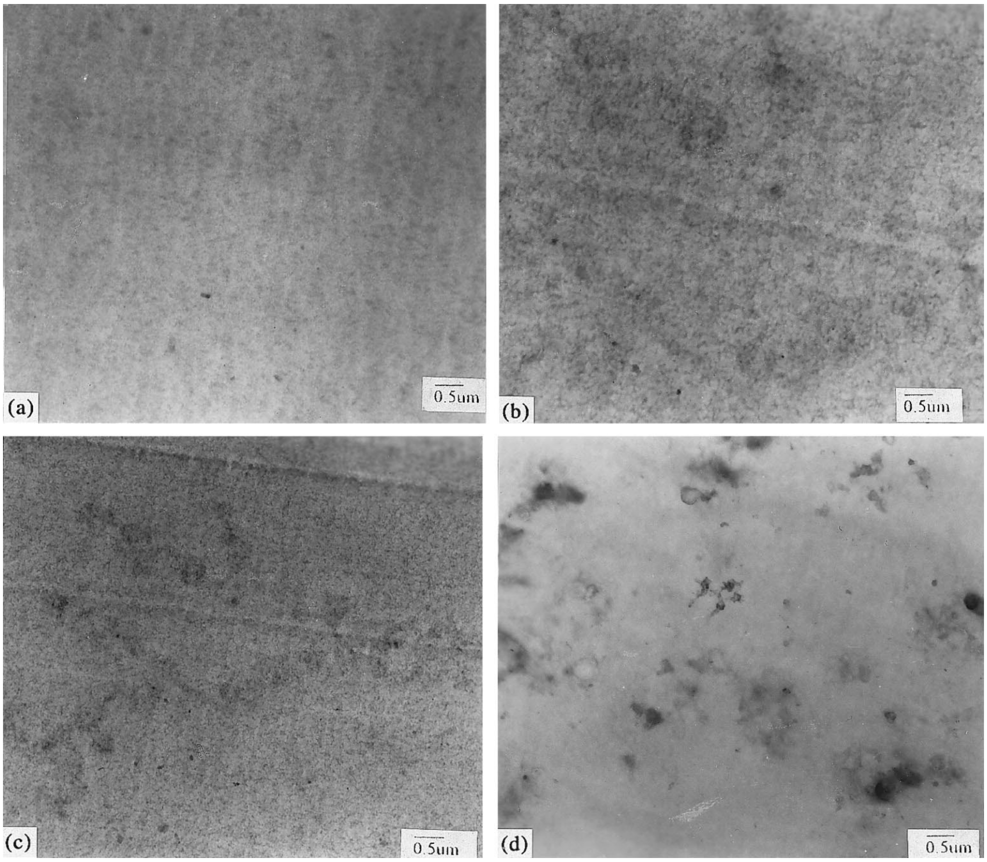


Fig. 10. Transmission electron micrographs of PN series ABCPs: (a) PN650–25, (b) PN1000–25, (c) PN2000–25 and (d) PN2900–50.

4.4. Morphological observation

The TEM micrographs are shown in Figs. 9 and 10. The dark domain is allyl nonyl novolac resin stained by RuO_4. Fig. 9 indicates the micrographs of the PN1400series, (a) PN1400-25, (b) PN1400-50 and (c) PN1400-75, the allyl nonyl novolac resin domain size change from (a) 0.05–0.15 μm and (b) 0.15–0.25 μm to (c) 0.8–0.9 μm, which means that there are changes in the extent of phase mixing between PU and allyl nonyl novolac resin. These micrographs provide more direct evidence that the specimens which contain 25% of allyl nonyl novolac resin has the highest phase mixing.

Fig. 10 lists the micrographs of specimens which contain different PTMO molecular weights, (a) PN650-25, (b) PN1000-25, (c) PN2000-25 and (d) PN2900-25, but have the same PU contents. These micrographs reveal that the effect of the molecular weight of the PU soft segment, i.e. the molecular weight of PTMO, is also a factor contributing to the miscibility in ABCPs. As the micrographs show, the lower MW of PTMO, which is used as a PU soft segment, has a smaller domain size in the TEM micrograph than that of the higher MW of PTMO.

5. Conclusion

According to the previous study of maleimide-terminated PU ABCPs [8], it is clear that the newly modified ABCPs structure possesses higher performance. In this study, the component, allyl nonyl novolac resin, which has an extra long soft chain to allyl novolac resin, is able to improve the ABCPs' compatibility by the entanglement effect exerted by this soft long chain. A comparison with the data from DSC, DMA, tensile strength and TEM micrographs, reveals that the miscibility has slight improvement, and that the tensile strength has clear improvement when the PU's soft segment, i.e. PTMO, is higher than 2000 in MW, a result of the entanglement between the two components, as mentioned above.

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