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The effect of chain length of flexible diacid on morphology and mechanical property of modified phenolic resin

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Abstract

Adipic acid (DA4), suberic acid (DA6), sebacic acid (DA8), and dodecanedioic acid (DA10) were used to improve the brittleness of resol type phenolic resin (PF). Chemical reaction of PF with diacid was manifested by a shift of carbonyl stretching peak of diacid to a higher frequency in FT-IR spectra. The modified PF with diacid showed an optimum content (0.0014 mol) and an optimum chain length of diacid ($n = 6$, i.e. DA6) to improve effectively its brittleness. The highly cured phenolic resins with DA4 and DA6 were found to have homogeneous morphologies, but those with DA8 and DA10 had phase-separated morphologies in scanning electron microscopy (SEM) images. The slightly cured PFs with DA4, DA8, and DA10 exhibited phase-separated morphologies, but that with DA6, a homogeneous morphology on SEM micrographs. Furthermore, the latter was confirmed by a proton spin–lattice relaxation time (T_1^H) measurement on solid-state ^{13}C NMR spectra. It was found by X-ray diffraction and differential scanning calorimeter that the phase-separated part of modified phenolic resin was a crystalline phase of unreacted diacid. The highly improved toughness of modified PF with DA6 was attributed to the inherently homogeneous morphology with domain sizes around 20–30 nm scale found by the T_1^H measurement.

Keywords: Resol type phenolic resin; Diacid; Homogeneous morphology

1. Introduction

Phenolic resin has been indeed an irreplaceable material for selective high technology applications offering high reliability under severe circumstances. It has been widely used in thermal insulation materials, molding compounds, foundry, wood products industry, coatings, and composite materials due to its excellent ablative property, structural integrity, thermal stability and solvent resistance [1–6].

In general, thermoset resins such as phenolic resin and epoxy, etc. are inherently brittle due to their high cross-link density. Furthermore, the highly brittle fillers such as carbon or glass fiber, etc. tend to make the composite materials based on these kinds of thermoset resins more brittle. Consequently, the composites with brittle thermoset resins as a matrix have limited use in applications requiring high impact strength. Recently, thermoset resins have been modified with flexible elastomers and/or thermoplastic polymers to improve their brittleness. However, most of them have focused on epoxy resins because a versatile amine modifier and the high reactivity of epoxide ring are allowed to modify easily the epoxy resins. A lot of groups have obtained the improved impact resistance of epoxy resin by simple or chemical blending of elastomers [7–12] or thermoplastic polymers [13–18] with the brittle epoxy resin.

There are two types of phenolic resins, i.e. novolac and resol type of resin. Novolac resin is almost unable to cross-link without curing agent, which is allowed to modify the novolac resin by melt blending with flexible thermoplastic polymers. Recently, some approaches have been proposed to improve the toughness of novolac resin. In most of the cases, novolac resins were modified by blending with thermoplastic homopolymers or copolymers [19–26]. In contrast to the novolac resin, resol resin can be cured only by heating, which makes it very difficult to obtain the blend with other thermoplastic polymers. However, resol resin has many reactive hydroxyl groups. This advantage was adopted to modify the resol resin by chemical reaction with polyurethane and nitrile rubber [27,28]. Like the high molecular weight polymers, a small molecule can also be

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used to improve the brittleness of resol type phenolic resin [29]. In this case, the processing window can be wider since the small molecules usually have a low glass transition or melting temperature and a low viscosity.

In this study, we tried to modify the resol type phenolic resin with a low molecular weight flexible diacid by inducing a chemical reaction between them to form an ester linkage during the cure of phenolic resin. We investigated the morphology of the modified phenolic resin with diacids of different chain length by using scanning electron microscopy (SEM), X-ray diffraction, differential scanning calorimeter (DSC), solid-state ^{13}C NMR. Also, we observed the mechanical properties of the modified phenolic resin.

2. Experimental

2.1. Materials

Resol type phenolic resin used in this study was obtained from Kolon Chemical Co., Ltd and its commercial name was KRD-HM2. It was a mixture of 60 wt% phenolic resin and 40 wt% methanol. Its density was 1.063 g/cm^3 and gel time was 52 s at 150 °C. The pure phenolic resin (PF) was prepared by removing the methanol with distilled water at 25 °C. The PF was dried in a vacuum oven at 25 °C to remove the remaining methanol and water. The phenolic resin was pulverized mechanically into fine particles and further dried in a vacuum oven at 25 °C for several days. Flexible diacids were adipic acid (DA4), suberic acid (DA6), sebacic acid (DA8), and dodecanedioic acid (DA10) purchased from Aldrich. The suffix figure (n) indicates the number of methylene unit for each diacid, i.e. diacid chain length. All reagents were used without further purification. All diacids were incorporated by mole relative to 1 g of PF. Modified phenolic resins with each diacid were referred to PFDA4, PFDA6, PFDA8, and PFDA10, respectively. Also, a PFDA8 sample containing 0.0014 mol of DA8 relative to 1 g of PF (DA8 0.0014 mol/PF 1 g) was referred to PFDA8-14, etc.

2.2. Reaction of phenolic resin with diacid

One gram of PF and 0.0014 mol of DA6 were mixed in methanol and stirred for 1 h at room temperature. A PFDA6 film used for FT-IR measurement was prepared by casting the solution on the Krs-5 window. FT-IR spectra were averaged over 20 scans at 4 cm^{-1} resolution in the absorption mode on a Bomem MB 102 FT-IR spectrometer. In order to investigate the reaction of PFDA6, we monitored the FT-IR spectra with the temperature in situ under nitrogen atmosphere with a heating cell accessory. The FT-IR spectra were collected from the same sample by heating from room temperature to 300 °C with a heating rate of 4 °C/min. During each data collection at a temperature, no further heating was applied to keep the temperature.

2.3. Mechanical property of modified phenolic resin

DA8 was used in order to observe the effect of diacid content on the mechanical properties of modified phenolic resin. Fine particles of PF (1 g) and DA8 (0.0007–0.0028 mol) were mechanically mixed and molded with a dumbbell-shaped molder on hot press. PFDA8 samples were cured at 140 °C for 1 h followed by curing at 160 °C for 1 h.

The effect of diacid chain length on the mechanical properties of modified phenolic resin was investigated with DA4, DA6, DA8, and DA10. Each diacid (0.0014 mol) and PF (1 g) were mechanically mixed, and molded by a dumbbell-shaped molder for tensile test and a rectangular-shaped molder with a dimension of 5 mm × 2.5 mm × 2 mm for flexural test on hot press. For each sample, the curing condition was same as the earlier. Tensile and flexural test were performed at room temperature on Instron tester (model 4201) according to ASTM 638-94 and ASTM D 790M-93, respectively. At least, five specimens were tested for each set of samples and the mean values were reported.

2.4. Morphology of modified phenolic resin

The fracture surface of modified phenolic resin was coated with thin layer of a gold–palladium alloy to image its morphology on an Akashi model SX-30E SEM.

X-ray diffraction spectra were obtained by a Rigaku X-ray generator (Cu Kα radiation with $\lambda = 0.15406$ nm) at room temperature to analyze a crystalline phase of diacid in the modified phenolic resin. The diffractograms were scanned in a 2θ range of 5–40° at a rate of 4°/min.

DSC (Du Pont model 910 thermal analyzer) was used to observe the melting behavior of diacid in the modified phenolic resin under nitrogen atmosphere. A typical sample weight was about 10 mg and the scan speed was 10 °C/min.

To investigate the initial morphology of modified phenolic resin, phenolic resin was blended with diacids and cured slightly at 140 °C for 5 min followed by quenching to room temperature. The morphology was obtained on SEM and X-ray diffraction. Also, high resolution solid-state ^{13}C CP/MAS NMR spectra on a Bruker DSX-400 spectrometer were obtained at resonance frequency of 5 kHz for ^{13}C to measure the proton spin–lattice relaxation time (T_1^{H}) indirectly via observation of phenolic ring carbon at 130 ppm using inversion recovery pulse sequence. The data were obtained using ^{1}H decoupling and delay time (τ) ranging from 1 ms to 20 s with contact time of 1.0 ms.

3. Results and discussion

3.1. Reaction of phenolic resin with diacid

The brittleness of phenolic resin can be improved by the incorporation of flexible unit between phenolic resin cross-linkers. Diacids with flexible unit can be inserted into the brittle phenolic resin by the simultaneous process of curing

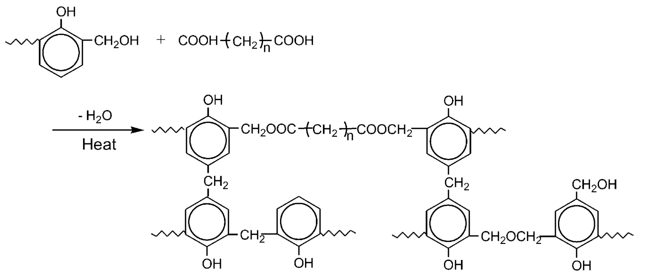

Fig. 1. The reaction of phenolic resin with diacid.

and chemical reaction between methylol groups of phenolic resin and acid groups of diacid to form an ester linkage as shown in Fig. 1.

The curing behavior and chemical reaction of phenolic resin with diacid were investigated at various curing temperatures by an in situ method with FT-IR. In Fig. 2, the spectrum at 50 °C indicates a simple mixture of PF and DA6 (unreacted sample). Broad peak around 3200–3700 cm^{-1} is the characteristic for the –OH stretchings of phenolic ring, methylol group of phenolic resin, and diacid. Small peaks around 2800–3060 cm^{-1} are associated with the –CH stretchings of phenolic ring, methylene ($-CH_2-$) and dimethylene ether ($-CH_2OCH_2-$) bridges of phenolic resin, and methylene unit ($-CH_2-$) of diacid. A signal at 1610 cm^{-1} is the characteristic for the elongation of the aromatic ethylene bond (C=C) of phenolic ring. The regions of 753–794, 820–855, and 912–917 cm^{-1} can be assigned to *ortho* and *para* substitution and ring deformation of a phenolic ring, respectively. Peak around 1200 cm^{-1} is associated with –CO stretchings of phenolic ring, dimethylene ether bridge, and diacid. The band at 1500 cm^{-1} is assigned to a phenolic ring substituted in *ortho* or *para* positions. A peak around 1700 cm^{-1} corresponds to the –C=O stretching of diacid. Upon elevating the temperature above 120 °C, the intensity of the band at 1500 cm^{-1} decreases, suggesting the depletion of mono- and di-substituted phenolic rings due to the initiation of cross-linking reaction. Also, the phenolic ring deformation peaks in the regions of 753–794, 820–855, and 912–917 cm^{-1} decrease in intensity. Probably, these behaviors are attributed to the difficulty of phenolic ring deformation when it is highly cross-linked [5]. The –OH peaks around 3200–3350 cm^{-1} become small and eventually almost disappear above 200 °C. It indicates the disappearance of methylol groups of phenolic resin and acid groups of diacid due to the curing reaction of phenolic resin and the chemical reaction between phenolic resin and diacid. Furthermore, the carbonyl signal shifts to a higher frequency with the curing reaction (see the arrow in Fig. 2), which evidently indicates that carboxylic acid is transformed into ester linkage to react with methylol group of phenolic resin [30]. Also, Pizzi and Stephanou [31] reported a lower shift of –C=O signal at 1800 cm^{-1} when propylene carbonate was hydrolyzed to form other carboxylic compound.

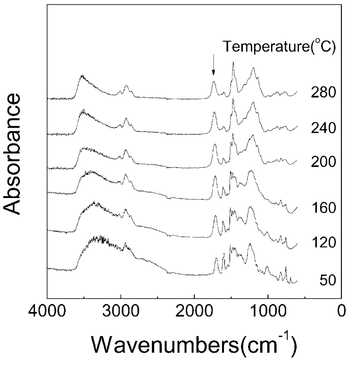

Fig. 2. FT-IR spectra of curing behaviors of phenolic resin with DA6 at various temperatures.

3.2. Determination of the optimum diacid content

Before investigating the effect of diacid chain length on the mechanical property of modified phenolic resin, we should find an optimum content of diacid. To determine the optimum diacid content, we investigate the tensile property of modified phenolic resin with DA8 content. Tensile properties of the modified phenolic resin are illustrated in Table 1. Tensile strength, toughness, and elongation at break of PFDA8 increase with the DA8 content, but decrease generally over 0.0014 mol of DA8. Even though the increment of tensile property is not significant, it indicates that the brittleness of phenolic resin is improved by the incorporation of flexible unit of DA8. The decrease in the tensile properties of PFDA8 over 0.0014 mol of DA8 probably suggests the enough incorporation of DA8 to degrade the original property of phenolic resin or the function of unreacted DA8 as a defect associated with a phase-separation [32]. Some thermoset resins modified with elastomers and/or thermoplastic polymers showed an optimum content of modifier to have the highest improved mechanical properties [32,33]. However, the tensile modulus of PFDA8 continually decreases with the DA8 content, which is also frequently shown in other systems [19]. Probably, the flexible unit inserted between cross-linkers of phenolic resin lowers the cross-link density and thus the high original modulus of phenolic resin.

The morphology can significantly affect the mechanical property. SEM image of PFDA8-07 shows a homogeneous morphology like PF as shown in Fig. 3(a) and (b). However, PFDA8 shows the phase-separation over 0.0014 mol of DA8. Specifically, PFDA8-28 exhibits a significantly phase-separated morphology, almost a co-continuous morphology. It is noted that the phases are dispersed irregularly as shown in Fig. 3(e). Probably, the phase dispersed discontinuously may be a crystalline phase of the unreacted DA8. This morphology is very different from those of thermoset resins modified with elastomers and/or thermoplastic polymers, which had a sea-island or a dual phase morphology [13,14,32].

Table 1
Mechanical properties of modified phenolic resin cured at 140 °C for 1 h followed by curing at 160 °C for 1 h as a function of DA8 content

Code	DA8 content[a] (mol)	Tensile strength (MPa)	Tensile modulus (GPa)	Toughness (MJ/m^3)	Elongation at break (%)
PF	0.0000	29.38 ± 1.00	2.44 ± 0.11	39.86 ± 2.01	2.53 ± 0.03
PFDA8-07	0.0007	30.18 ± 1.15	1.89 ± 0.13	42.50 ± 1.50	2.63 ± 0.03
PFDA8-14	0.0014	32.11 ± 0.98	1.72 ± 0.08	46.27 ± 2.12	2.86 ± 0.05
PFDA8-21	0.0021	25.36 ± 2.03	1.05 ± 0.10	26.84 ± 1.22	2.02 ± 0.02
PFDA8-28	0.0028	23.27 ± 1.50	0.93 ± 0.14	28.48 ± 1.06	2.16 ± 0.07

[a] Mole of DA8 relative to 1 g of PF (DA8 mol/PF 1 g).

In order to confirm that the phase is a crystalline state of DA8, we used DSC. PFDA8-28 shows a prominent melting behavior at 132 °C as shown in Fig. 4. This melting temperature of PFDA8-28 is almost coincident with that of DA8, i.e. 133–138 °C. The slightly lower melting temperature of PFDA8-28 is probably attributed to the difficulty of fully crystallization of DA8 due to the reduced mobility of DA8 in rigid phenolic resin matrix when cured. The exothermic peak around 190–250 °C corresponds to the curing reaction of uncured phenolic resin and/or the chemical reaction of phenolic resin with unreacted DA8. Thus, the significant reduction in tensile properties of PFDA8 over 0.0014 mol of DA8 is attributed to the phase-separated morphology. The optimum content is determined to 0.0014 mol of DA8. Assuming that this optimum content (0.0014 mol) can be applicable to all the diacids, we investigated the effect of diacid chain length on the mechanical property of modified phenolic resin to find an optimum diacid chain length.

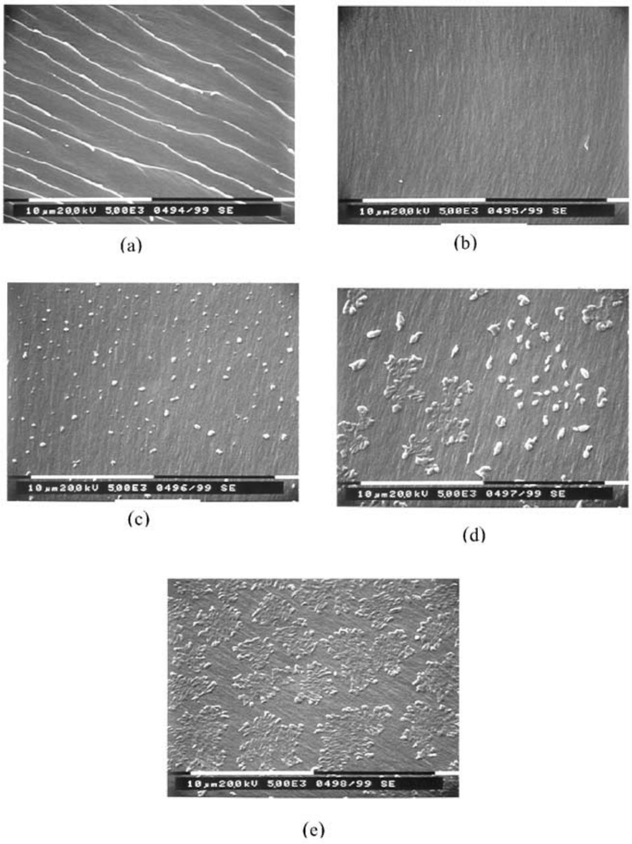

Fig. 3. SEM micrographs of phenolic resin and modified phenolic resin cured at 140 °C for 1 h followed by curing at 160 °C for 1 h as a function of DA8 content. (a) PF, (b) PFDA8-07, (c) PFDA8-14, (d) PFDA8-21, and (e) PFDA8-28.

3.3. Effect of diacid chain length on mechanical property and morphology of modified phenolic resin

To determine the optimum diacid chain length based on the optimum content of diacid (i.e. 0.0014 mol), we investigated the tensile and flexural properties of modified phenolic resin. Figs. 5 and 6 show tensile and flexural properties of the modified phenolic resin with diacids (0.0014 mol) having different flexible chain length, respectively. Tensile strength and toughness increase with the diacid chain length, but decrease over $n = 6$ of diacid chain length. Elongation at break shows the highest value when diacid chain length is $n = 8$. However, tensile modulus decreases continuously with the diacid chain length, which is probably attributed to the gradual decrease in cross-link density of phenolic resin with increasing flexible chain length. Flexural strength and maximum strain of modified phenolic resin exhibit the highest values for the diacid chain length of $n = 6$ like the tensile property. Flexural modulus shows a similar behavior to tensile modulus. Thus, from the overall features of tensile and flexural properties, the optimum chain length is determined as $n = 6$. The modified phenolic resin with DA6 having the optimum chain length shows the

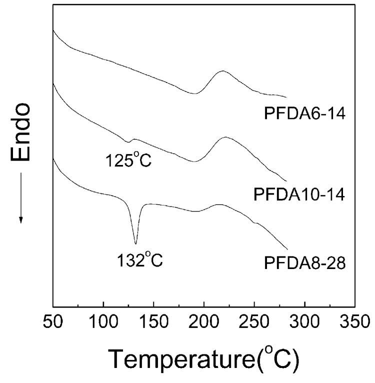

Fig. 4. DSC thermograms of PFDA6-14, PFDA10-14, and PFDA8-28 cured at 140 °C for 1 h followed by curing at 160 °C for 1 h.

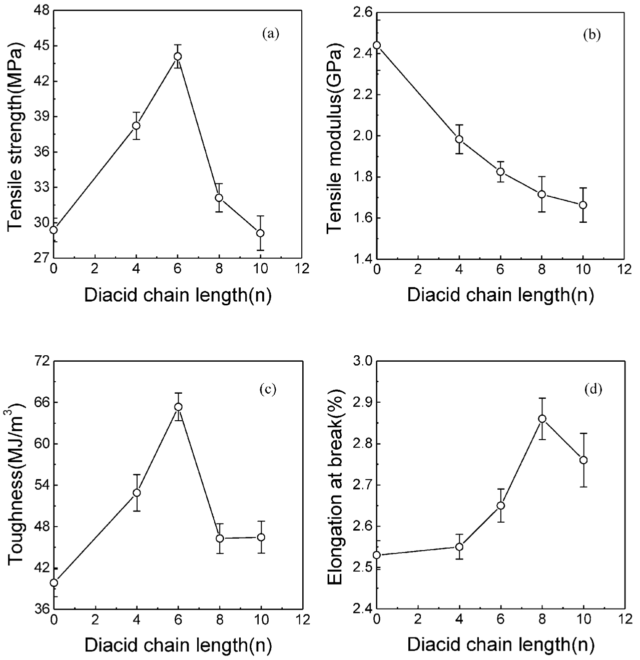

Fig. 5. Tensile properties of modified phenolic resin with diacids cured at 140 °C for 1 h followed by curing at 160 °C for 1 h as a function of diacid chain length. (a) Tensile strength, (b) tensile modulus, (c) toughness, and (d) elongation at break ($n = 0$ indicates pure phenolic resin). Each error bar shows the standard deviation.

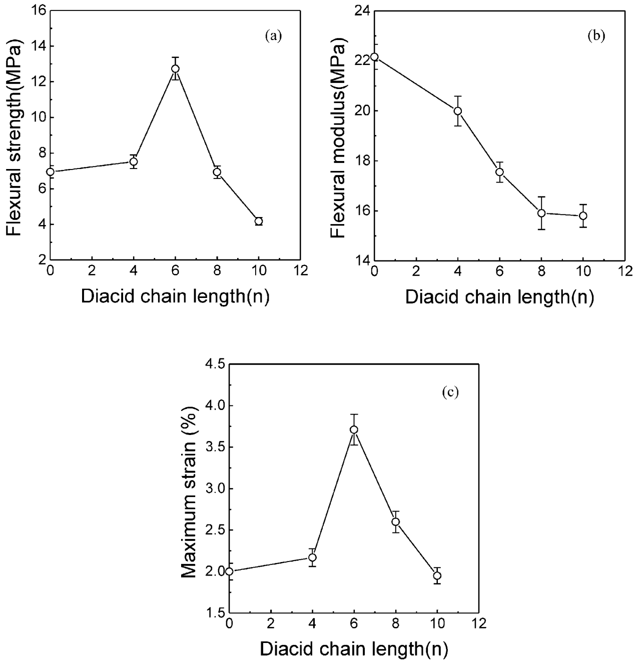

Fig. 6. Flexural properties of modified phenolic resin with diacids cured at 140 °C for 1 h followed by curing at 160 °C for 1 h as a function of diacid chain length. (a) Flexural strength, (b) flexural modulus, and (c) maximum strain ($n = 0$ indicates pure phenolic resin). Each error bar shows the standard deviation.

increased tensile strength and toughness by about 54 and 64%, respectively, as well as the almost two times increased flexural strength and maximum strain when compared to the unmodified phenolic resin. These behaviors indicate that the incorporation of small molecule, DA6 clearly improves the brittleness of phenolic resin.

The diacid chain length may also affect the morphology of modified phenolic resin. PFDA4-14 and PFDA6-14 show homogeneous morphologies as shown in Fig. 7(a) and (b), but PFDA8-14 and PFDA10-14, the phase-separated morphologies. This morphological evidence explains why the tensile strength and toughness decrease with the diacid chain length over $n = 6$. The phase-separation is the main factor in the reduction of mechanical properties of modified phenolic resin. The domain of discontinuously dispersed phase may act as a stress concentration portion. On the contrary to our systems, a thermoset resin modified with elastomer showed the increase in mechanical property with the domain size of phase-separated part [12]. In the system, the rubber domain had a flexible and tough characteristic. However in our system, the crystalline part of unreacted diacid is very brittle, and thus acts as a defect instead of participating in a toughening process of phenolic resin (see later). This phase-separated part is confirmed to be a crystalline phase of diacid by observing melting behavior of diacid. In Fig. 4, PFDA6-14 having the homogeneous morphology shows no melting behavior, but PFDA10-14 having the immiscible morphology shows a melting point at 125 °C. This melting temperature of PFDA10-14 is similar to that of pure DA10, i.e. 128–130 °C.

Some blends of novolac type phenolic resin with thermoplastic polymers such as poly(ethylene oxide), ethylene vinyl acetate resin, etc. showed also a melting temperature depression when they had a homogeneous morphology due

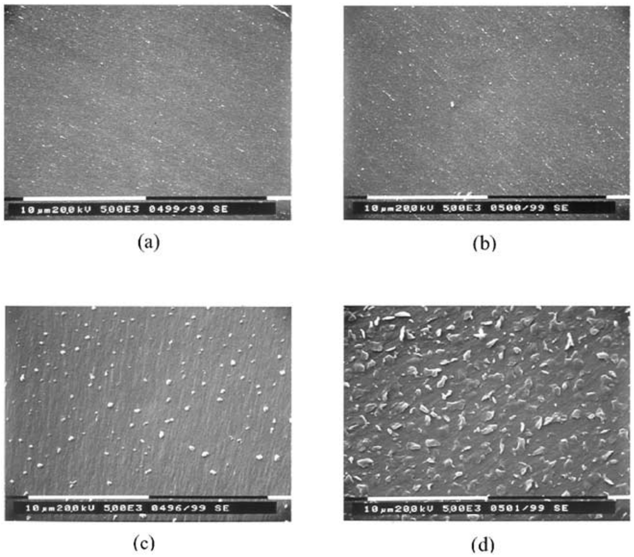
(a) (b)
(c) (d)

Fig. 7. SEM micrographs of modified phenolic resin with diacids of different chain length cured at 140 °C for 1 h followed by curing at 160 °C for 1 h. (a) PFDA4-14, (b) PFDA6-14, (c) PFDA8-14, and (d) PFDA10-14.

to a favorable intermolecular interaction, i.e. hydrogen bonding [22]. The homogeneous morphologies of PFDA4-14 and PFDA6-14 (Fig. 7(a) and (b)) are probably attributed to the chemical reaction of phenolic resin with diacids, which induces a permanent dispersion of diacid in cured phenolic resin and reduces the mobility for crystallization. The final morphology of modified phenolic resin may be much dependent on the initial miscibility of each component.

3.4. Initial morphology of modified phenolic resin with diacids

To investigate the initial miscibility of phenolic resin with diacids, we prepared a sample slightly cured at 140 °C for 5 min followed by quenching to room temperature. The initial morphology of phenolic resin with diacids of different chain length is shown in Fig. 8. PFDA4-14, PFDA8-14, and PFDA10-14 show remarkable phase-separations, which indicates that the phenolic resin does not favorably interact and is immiscible with the unreacted diacids. The diacids in the separated phase would crystallize when quenched. However, the slightly cured PFDA6-14 has a homogeneous morphology in Fig. 8(b) like the highly cured PFDA6-14 as shown in Fig. 7(b). This means that phenolic resin and DA6 favorably interact, and are miscible at the initial state.

The initially homogeneous morphology of PFDA6 is almost unchangeable even when they are highly cured (Fig. 7(b)). It is noted that the initially phase-separated morphology of the slightly cured PFDA4-14 transforms to the homogeneous morphology when highly cured as shown in Figs. 7(a) and 8(a). Also, the domain sizes of diacids in PFDA8-14 and PFDA10-14 become smaller as they are cured (Figs. 8(c) and (d) → 7(c) and (d)). It indicates that the amount of unreacted diacid is reduced significantly by the reaction with phenolic resin and the morphology becomes homogeneous. To confirm that the phase-separated domain of SEM images in Fig. 8 is a crystalline phase of unreacted diacid, X-ray diffraction method is used. As shown in Fig. 9, PFDA6-14 having a homogeneous morphology exhibits no crystal peak suggesting that it has almost amorphous phase. All systems except for PFDA6-14 show crystal peaks at $2\theta = 20$–$25°$. Probably, PFDA10-14 has the most complex crystal structures since crystal peaks are shown at $2\theta = 20$–$25°$ as well as $2\theta = 7°$. Thus, it is concluded that the initially homogeneous morphology and the amorphous phase of PFDA6-14 are due to the favorable interaction of phenolic resin with DA6.

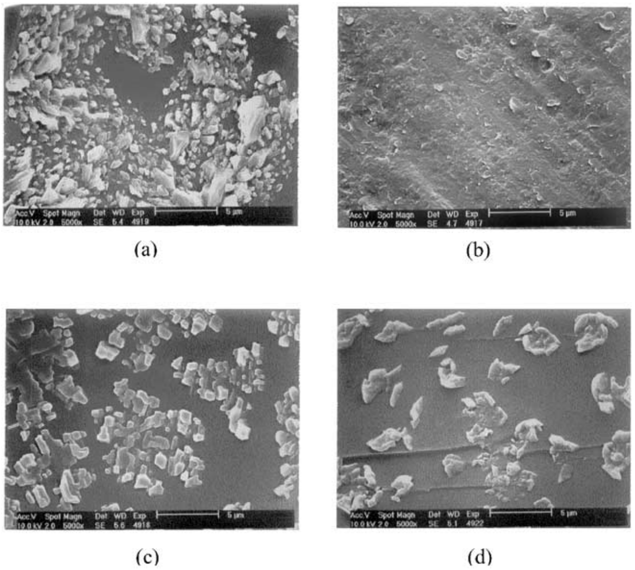

Fig. 8. SEM micrographs of modified phenolic resin with diacids of different chain length slightly cured at 140 °C for 5 min followed by quenching to room temperature. (a) PFDA4-14, (b) PFDA6-14, (c) PFDA8-14, and (d) PFDA10-14.

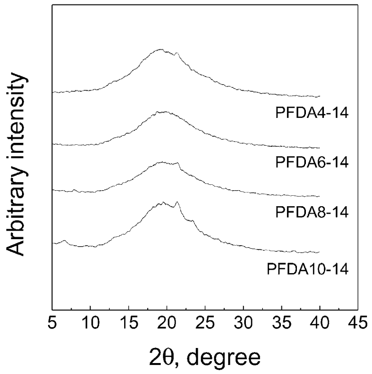

Fig. 9. X-ray diffraction patterns of modified phenolic resin with diacids of different chain length slightly cured at 140 °C for 5 min followed by quenching to room temperature.

A spin–lattice relaxation time (T_1) measurement of NMR has been widely used to observe the microstructure of a blend system, i.e. a miscibility of physical or chemical polymer blends and a surface state of organic–inorganic composite [21,34–36]. Here, we investigated more closely the initial morphology of phenolic resin with diacids by measuring a proton spin–lattice relaxation time (T_1^{H}) indirectly via observation of phenolic ring carbon at 130 ppm. Fig. 10 shows a semi-log plot of carbon signal intensity as a function of delay time (τ) for the slightly cured phenolic resin with diacids of different chain length. The unmodified PF exhibits a single exponential decay with T_1^{H} of 19.3 ms (Table 2). PFDA6-14 has a slightly higher T_1^{H} of 19.4 ms than PF, but shows a single exponential decay like PF. This behavior indicates that the proton spin diffusion of phenolic resin is not interfered with DA6 in the relaxation, and PFDA6-14 maintains the good miscibility of PF with DA6. This result reveals that the domain size of diacid in PFDA6-14 is on the scale of 20–30 nm, which is the characteristic maximum spin diffusion path length during relaxation time (T_1^{H}).

However, PFDA10-14, which has the significantly phase-separated morphology as shown in Fig. 8(d), exhibits a double exponential relaxation behavior. PFDA10-14 first

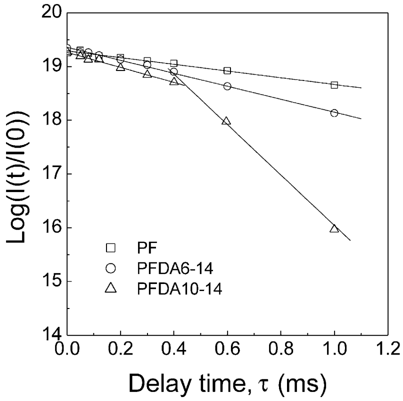

Fig. 10. The semi-logarithmic plots of the magnetization intensities at 130 ppm (benzene ring of phenolic resin) versus the delay time for pure phenolic resin (PF) and modified phenolic resin (PFDA6-14 and PFDA10-14) with diacids of different chain length slightly cured at 140 °C for 5 min followed by quenching to room temperature.

relaxes with the similar relaxation time of 19.5 ms to PF and PFDA6-14, but abruptly with a higher relaxation time of 20.8 ms. This behavior suggests that the spin diffusion within T_1^H cannot efficiently average out the whole relaxation process. The domain size of PFDA10-14 would be much larger than the scale of 20–30 nm. PFDA10-14 has the crystalline phase of DA10 (Figs. 8(d) and 9). Thus, the abrupt slow relaxation behavior of PFDA10-14 is attributable to the interference of the rigid crystalline domain of DA10. The double relaxations of PFDA10-14 measured from T_1^H coincide well with the phase-separated morphology in Fig. 8(d).

From these results, we can conclude that the blend of phenolic resin with DA6 has a homogeneous morphology independent of curing reaction and is inherently miscible. This homogeneous morphology of PFDA6 system is allowed to improve significantly the brittleness of phenolic resin.

Table 2
T_1^H values (ms) of phenolic resin with diacids of different chain lengths slightly cured at 140 °C for 5 min followed by quenching to room temperature (indirectly measured values with intensity at 130 ppm of benzene ring of phenolic resin)

PF[a]	PFDA6-14[a]	PFDA10-14[b]
19.3	19.4	19.5, 20.8

[a] Single exponential decay.
[b] Double exponential decay.

4. Conclusions

The initial morphology of slightly cured phenolic resin with diacids was investigated by using SEM, X-ray, and a proton spin–lattice relaxation time measurement of solid-state ^{13}C NMR. Phenolic resin was initially miscible with DA6, but immiscible with DA4, DA8, and DA10. The initially immiscible morphology of phenolic resin with DA4 became homogeneous during curing reaction, but the domain sizes of diacids in PFDA8-14 and PFDA10-14 became only smaller. The phenolic resin modified with DA6 maintained the initially homogeneous morphology when it was highly cured. It was suggested that the blend of phenolic resin with DA6 was inherently miscible.

PFDA6-14, inherently miscible system, exhibited highly improved tensile toughness and maximum strain. Thus, it was concluded that the mechanical properties of modified phenolic resin with diacids were significantly dependent on the diacid chain length affecting the miscibility. The brittleness of phenolic resin could be improved by the incorporation of flexible diacids with small molecular weight. This toughened phenolic resin with flexible diacids can be used as a matrix resin of composite materials.

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References

[1] Knop A, Scheib W. Chemistry and application of phenolic resins. New York: Springer, 1979.
[2] Zaks Y, Lo J, Raucher D, Pearce EM. J Appl Polym Sci 1982;27:913.
[3] Choi MH, Jeon BH, Chung IJ. Polymer 2000;41:3243.
[4] Ishida H, Allen DJ. J Polym Sci, Polym Phys 1996;34:1019.
[5] Choi MH, Chung IJ, Lee JD. Chem Mater 2000;12:2977.
[6] Byun HY, Choi MH, Chung IJ. Chem Mater 2001;13:4221.
[7] Subramanian M, Malhotra SK, Krishnamurthy R. J Mater Sci Lett 1996;15:576.
[8] Bagheri R, Pearson RA. Polymer 1996;37:4529.
[9] Pearson RA, Yee AF. J Mater Sci 1989;24:2571.
[10] Kim SC, Ko MB, Jo WH. Polymer 1995;36:2189.
[11] Daghyani HR, Ye L, Mai Y, Wu J. J Mater Sci Lett 1994;13:1330.
[12] Bagheri R, Pearson RA. Polymer 2000;41:269.
[13] Kim YS, Kim SC. Macromolecules 1999;32:2334.
[14] Bonnet A, Pascault JP, Sautereau H, Taha M, Camberlin Y. Macromolecules 1999;32:8517.
[15] Clark JN, Daly JH, Garton A. J Appl Polym Sci 1984;29:3381.
[16] Cardwell BJ, Yee AF. J Mater Sci 1998;33:5473.
[17] Jang J, Shin S. Polymer 1995;36:1199.
[18] Pasquale GD, Motta O, Recca A, Carter JT, McGrail PT, Acierno D. Polymer 1997;38:4345.
[19] Matsumoto A, Hasegawa K, Fukuda A, Otsuki K. J Appl Polym Sci 1992;44:205.
[20] Kim BS, Nakamura G, Inoue T. J Appl Polym Sci 1998;68:1829.
[21] Chu PP, Wu HD. Polymer 2000;41:101.
[22] Ma CM, Wu HD, Lee CT. J Polym Sci, Polym Phys 1998;36:1721.
[23] Zhong Z, Guo Q. J Polym Sci, Polym Phys 1999;37:2726.
[24] Wu HD, Chu PP, Ma CC. Polymer 1998;39:703.
[25] Kwei TK. J Polym Sci, Polym Lett 1984;22:307.
[26] Ma CM, Wu HD, Chu PP, Tseng HT. Macromolecules 1997;30:5443.

[27] Wu HD, Lee MS, Wu YD, Su YF, Ma CM. J Appl Polym Sci 1996;62:227.

[28] Achary PS, Ramaswamy R. J Appl Polym Sci 1998;69:1187.

[29] Choi MH, Chung IJ. Submitted for publication.

[30] Pavia DL, Lampman GM, Kriz Jr GS. Introduction to spectroscopy: a guide for students of organic chemistry. Philadelphia: Harcourt Brace College Publishers, 1996.

[31] Pizzi A, Stephanou A. J Appl Polym Sci 1993;49:2157.

[32] He J, Raghavan D, Hoffman D, Hunston D. Polymer 1999;40:1923.

[33] Pasquale GD, Motta O, Recca A, Carter JT, McGrail PT, Acierno D. Polymer 1997;38:4245.

[34] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1991;24:5756.

[35] Zhang X, Takegoshi K, Hikichi K. Macromolecules 1992;25:2336.

[36] Powell DG, Mathias LJ. J Am Chem Soc 1990;112:669.