# Effect of Blending Polyethersulfone on the Cure Kinetics and Physical Properties of Dicyanate Resin

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**ABSTRACT:** The curing behavior and thermomechanical properties of dicyanate/polyethersulfone (PES) blends were investigated. Differential scanning calorimetry (DSC) was used to study the curing behavior of the dicyanate/PES blends. A second-order autocatalytic reaction mechanism was used to describe the cure kinetics of the blends. The reaction kinetic parameters were determined by fitting DSC conversion data to the kinetic equation. The main glass-transition temperatures of the blends decreased with increasing PES content. Two glass-transition temperatures indicating phase-separated morphology of the blends were observed. The thermal decomposition behavior of the blends was measured using thermogravimetric analysis. Mechanical and electrical properties of the blends were investigated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1952–1962, 2001

**Key words:** cure kinetics; dicyanate; polyethersulfone; blend; physical property

## INTRODUCTION

In the design of thermoset polymers for printed circuit board substrates, the thermal stability, glass-transition temperature ($T_g$), moisture resistance, and electrical insulating properties of the polymers are considered. The need for increased circuit densities, increased operating temperatures, and more stringent electrical insulation has prompted investigations into alternate polymeric materials such as dicyanate resin systems.[1–3]

Dicyanate resins are low-viscosity resins that can crosslink to form polycyanurates by forming cyclic triazine rings.[4] Cured dicyanate resins have high glass-transition temperatures (250–280°C), low water absorption, excellent electrical properties, high mechanical strength, and excellent com-

patibility with carbon fibers.[5] Dicyanate resins combine the processing advantages and the handling convenience of epoxies, the fire resistance of phenolics, and the high-temperature performance of polysulfones or polyimides. The excellent properties of dicyanate resins make them attractive in the area of circuit board fabrication and high-performance composites and differentiate them from standard epoxy resins and bismaleimides. Some recent studies have focused on their applications in circuit board fabrications and advanced composites.[6–10]

Modification of the dicyanate resin by introducing a thermoplastic results in a semi-IPN, which has been proven to show a considerable improvement in toughness. The toughening mechanism generally depends on the morphology developed during phase separation, which occurs as an originally miscible liquid mixture of the dicyanate resin and thermoplastic is transformed into a crosslinked network. The phase-separated morphology has been found to significantly influence

the fracture toughness and other properties of the thermoplastic-modified dicyanate resins.[11] The concept of semi-IPN has been successfully applied to develop toughened high-temperature matrix resins for use in advanced reinforced composites.[12–17] Such high-performance semi-IPNs can be processed like a thermoset and show notable improvement in fracture toughness of fiber-reinforced composites over that of unmodified thermosetting composites.[18]

PES resins are rigid and tough thermoplastics with glass-transition temperatures of 180–250°C. Rigidity is derived from the inflexible and immobile phenyl and $SO_2$ groups, and toughness from the connecting ether oxygens. These groups also impart the thermal stability and chemical inertness that characterize these resins.[19]

The polymerization kinetics of a thermoset resin can be affected by incorporating a thermoplastic. The cure kinetics of rubber-toughened epoxy systems was considerably affected by incorporating a rubber.[20] A study on the reaction kinetics of a semi-IPN system is very important both to optimize the processing conditions and to maximize the physical properties of polymer composites comprising the semi-IPN. Therefore, semi-IPN systems based on a dicyanate resin and a high-performance thermoplastic PES have been developed in this work, and the effect of semi-IPN composition on the curing behavior, thermal property, and both thermomechanical and electrical properties of the dicyanate/PES semi-IPN systems were analyzed.
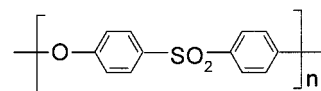
## EXPERIMENTAL

### Materials

The dicyanate resin used in this study was 1,1-bis(4-cyanatophenyl) ethane (Arocy L-10 from Ciba Specialty Chemical, Summit, NJ). The amorphous thermoplastic polymer used to modify the dicyanate resin was polyethersulfone (Ultrason E 6020 P from BASF, North Mount Olive, NJ). The weight-average molecular weight of the PES was 58,000. The two resins were used as received. Figure 1 shows the chemical structures of the resins. Methylene chloride ($CH_2Cl_2$; Junsei Chemical Co., Japan) was used as a cosolvent to make a homogeneous resin mixture because the molecular weight of the PES was too high. The resin content in the solution was 30 wt %.
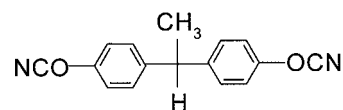


1,1-bis(4-cyanatophenyl) ethane (Arocy L-10)



Polyethersulfone (Ultrason E 6020 P)

**Figure 1** Chemical structures of the dicyanate and the PES used in this study.

## Thermal Analysis

### *Differential Scanning Calorimetry (DSC)*

To obtain experimental reaction kinetic data to analyze the curing behavior of the dicyanate/PES blends, DSC 2910 (TA Instruments, New Castle, DE) was employed. The samples for the DSC experiments were prepared according to the following sequences: (1) the dicyanate resin and the PES resin were mixed in a beaker at room temperature; (2) a homogeneous solution was prepared by adding methylene chloride to the resin mixture and stirring the solution sufficiently at room temperature; (3) the solution was degassed sufficiently in a vacuum oven at 60°C for 4 h to obtain a homogeneous solvent-free dicyanate/PES resin mixture. About 10 mg of the blend was placed in a hermetic aluminum pan and tested immediately after sealing. The amount of PES in the dicyanate/PES blend was varied from 0 to 25 phr. Each sample was cured dynamically with different heating rates of 5, 10, and 20°C/min, respectively. The dynamic scanning temperature range was from room temperature to 350°C and each DSC scan was carried out under nitrogen gas atmosphere ($N_2$ purge rate = 50 mL/min). To measure the glass-transition temperature of each blend dynamic DSC second scans were carried out at a heating rate of 10°C/min. The isothermal curing behavior of the blend containing 15 phr PES was investigated at three isothermal curing temperatures of 280, 300, and 320°C, respectively.

### *Thermogravimetric Analysis (TGA)*

TGA experiments were performed using SDT 2960 (TA Instruments) to investigate the thermal

decomposition behavior of the cured dicyanate/PES blends. Each TGA scan was carried out at a heating rate of 10°C/min from room temperature to 700°C under nitrogen gas atmosphere ($N_2$ purge rate = 110 mL/min). The cured blend samples for the TGA experiments were taken from the specimens prepared for dynamic mechanical analysis.

### Dynamic Mechanical Analysis (DMA)

DMA experiments were carried out to measure the modulus (stiffness) and damping (energy dissipation) properties of the cured dicyanate/PES blends. DMA experiments were performed using DMA 2940 (TA Instruments) in a single cantilever mode. Each sample specimen was prepared by pouring the dicyanate/PES mixtures into a rectangular mold cavity (35 × 13 × 3.2 mm) composed of a silicon rubber spacer and two steel plates and curing them at 180°C for 15 h in an oven. The specimens were postcured at 270°C for 10 h in a hot press. In DMA experiments, the frequency was 1 Hz and the heating rate was 5°C/min. The scanning temperature range was from room temperature to 350°C.

### Thermomechanical Analysis (TMA)

To measure thermal expansion properties of the blends thermomechanical analysis was performed using TMA 2940 (TA Instruments). Disk-shape sample specimens (diameter, 7 mm; height, 3.2 mm) were prepared using the cured blend sheets for DMA experiments. The frequency was 1 Hz and the heating rate was 5°C/min. The scanning temperature range was from room temperature to 320°C.

### Dielectric Analysis (DEA)

Electrical properties of the cured dicyanate/PES blends were investigated using DEA 2970 (TA Instruments) at several frequencies between 1 and 10,000 Hz. A parallel plate–type sensor was installed to the DEA. Each sample was made according to the same procedure and conditions used in DMA experiments except for the mold cavity size (25 × 25 × 0.5 mm). The scanning temperature range was from room temperature to 320°C and the heating rate was 3°C/min. Each scanning was carried out under nitrogen gas atmosphere ($N_2$ purge rate = 500 mL/min). To maintain tight contacts between sensors and sample surfaces during experiments the ram force pressing the sensors and sample was set at 300 N.

## RESULTS AND DISCUSSION

### Reaction Kinetics

The curing condition affects not only the cure kinetics but also the physical properties of the resulting material. The curing behavior of dicyanate resins has been studied by several researchers.[21–27] They found that the reaction kinetics of dicyanate resins can be described by a second-order reaction kinetic equation in the kinetic controlled regime for the catalyzed systems.

Osei–Owusu et al.[21] reported that the observed reaction rate showed a first-order dependence on the initial catalyst concentration. For the uncatalyzed systems, the kinetics was described by a second-order autocatalytic model. They also proposed a reaction scheme to describe the trimerization reaction, which consisted of four elementary reaction steps involving the monomer, the metal (catalyst), and the cyanate/metal complexes. Their reaction scheme indicated that the trimerization reaction could be described by second-order kinetics with respect to monomer concentration and first-order kinetics in terms of catalyst concentration.

To analyze the reaction kinetics of dicyanate resins, several authors[23,24,28,29] used the following autocatalytic kinetic equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1 - \alpha)^p \qquad (1)$$

where $\alpha$ is chemical conversion, $n + p$ is the overall reaction order, and the reaction rate constants $k_1$ and $k_2$ are usually assumed to have an Arrhenius temperature dependence. The overall reaction rate order ($n + p$) was assumed to be 2 in this study, and this assumption was successful in analyzing reaction kinetics of similar dicyanate resin systems.[23,29] The parameters $k_1$ and $k_2$ were found to follow an Arrhenius dependence on temperature and could be described as follows:

$$k_1 = k_{10}\exp\left(-\frac{E_1}{RT}\right) \qquad (2)$$

$$k_2 = k_{20}\exp\left(-\frac{E_2}{RT}\right) \qquad (3)$$
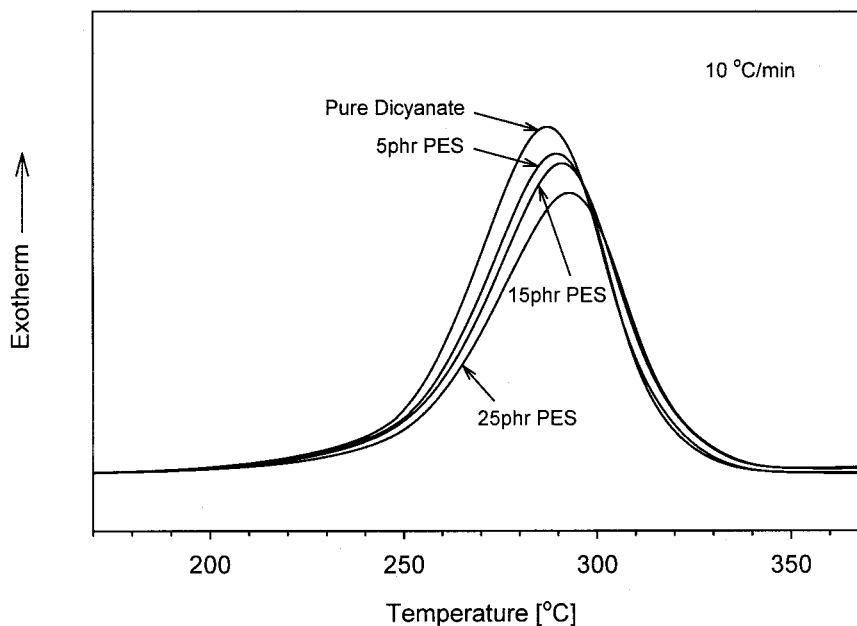
**Figure 2**   Dynamic DSC thermograms of the blends containing various PES contents.

where $k_{10}$ and $k_{20}$ are frequency factors, $E_1$ and $E_2$ are activation energies, and $R$ is the ideal gas constant.

By combining eqs. (1)–(3), a second-order autocatalytic reaction kinetic equation can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{1}{Sr}\,(k_1 + k_2\alpha^n)(1 - \alpha)^{2-n} \qquad (4)$$

$$Sr = \frac{dT}{dt} \qquad (5)$$

The dynamic DSC method was used to obtain experimental conversion data needed in determining the kinetic parameters of the reaction kinetic equation. The conversion was assumed to be the ratio of the heat generated until $T$ ($H_T$) to the heat of reaction at complete conversion $H_{rxn}$, as follows:

$$\alpha = \frac{H_T}{H_{rxn}} \qquad (6)$$

The $H_{rxn}$ for the curing reaction of each dicyanate/PES blend was measured by integrating dynamic DSC exotherm curves.

Figure 2 shows the dynamic DSC thermograms obtained at 10°C/min for the dicyanate/PES blends containing various PES contents. The exo-

therm curves slightly shifted to a higher temperature region as PES content was increased. This result shows that the curing rate of the blend decreased as PES content was increased. The reason for the decrease of reaction rate with increasing PES content in the blend is thought to be attributed to the mobility decrease of the reacting medium because the viscosity of PES is very high compared to that of the dicyanate resin.

The data points plotted in Figure 3 show conversion data calculated from the dynamic DSC thermograms shown in Figure 2. The reaction kinetic parameters were determined by fitting the dynamic DSC experimental conversion data to the reaction kinetic equation using Marquardt's multivariable nonlinear regression method and Runge–Kutta integration.[30] The conversion curves determined by fitting agree well with the experimental data. This agreement between DSC conversion data and the kinetic model showed that the proposed reaction kinetic model could well describe the reaction kinetics of the dicyanate/PES blends. The reaction kinetic parameters ($k_{10}$, $k_{20}$, $E_1$, $E_2$, and $n$) for each dicyanate/PES blend were determined by this way and are listed in Table I.

Glass-transition temperatures of the cured dicyanate/PES blends were measured using DSC at a heating rate of 10°C/min. Figure 4 shows that glass-transition temperatures of the dicyanate/PES blends decreased as PES content was in-
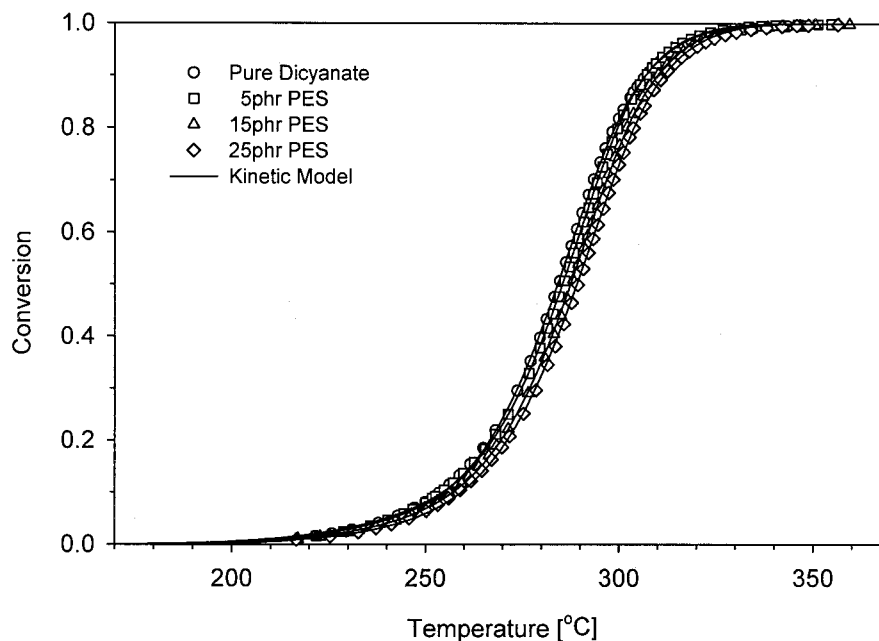
**Figure 3**   Comparison between conversion data measured from DSC (data points, indicated by various open symbols) and those calculated from the kinetic model (lines) for the blends containing various PES contents.

creased. The result is reasonable because the $T_g$ of PES is lower than the $T_g$ of pure dicyanate resin. Two glass transitions showing phase-separated morphology were not observed by DSC for the blends containing PES less than 15 phr; however, for the blend containing 25 phr PES, two glass transitions indicating phase-separated morphology were observed by DSC. The lower $T_g$ corresponds to the glass transition in the PES-rich phase, whereas the higher $T_g$ corresponds to the glass transition in the dicyanate-rich phase.

Figure 5 shows DSC thermograms of the dicyanate/PES blend containing 15 phr PES for various scanning rates. The peak temperature denoting maximum reaction rate increased with increasing scanning rate. The peak temperature shift resulting from the increasing scanning rate depends on the

activation energy associated with each reaction. Based on this peak-shifting phenomenon, there have been two methods used to calculate the activation energy associated with each reaction: Kissinger's method[31] and the method suggested by Ozawa[32] and Flynn.[33] Even though the area under the curve appears to increase with increasing scanning rate, the overall heat of reaction determined by integrating reaction exotherms with time, not temperature as shown in Figure 5, is constant and independent of scanning rate.

Figure 6 shows that the conversion data calculated from the dynamic DSC thermograms in Figure 5 agree well with the conversion curves calculated from the reaction kinetic equation determined by the fitting method for the dicyanate/PES blend containing 15 phr PES. This result

**Table I   Values of Reaction Kinetic Parameters for the Dicyanate/PES Systems Containing Various PES Contents**

| PES Content [phr] | $k_{10}$ [1/s] | $k_{20}$ [1/s] | $E_1$ [J/mol] | $E_2$ [J/mol] | $n$ |
|---|---|---|---|---|---|
| 0 | $7.19 \times 10^5$ | $1.13 \times 10^6$ | $7.74 \times 10^4$ | $6.57 \times 10^4$ | 0.86 |
| 5 | $1.50 \times 10^6$ | $1.82 \times 10^6$ | $7.91 \times 10^4$ | $6.82 \times 10^4$ | 0.92 |
| 15 | $2.07 \times 10^6$ | $1.20 \times 10^6$ | $8.24 \times 10^4$ | $6.65 \times 10^4$ | 0.89 |
| 25 | $4.62 \times 10^7$ | $7.42 \times 10^5$ | $9.46 \times 10^4$ | $6.49 \times 10^4$ | 0.90 |
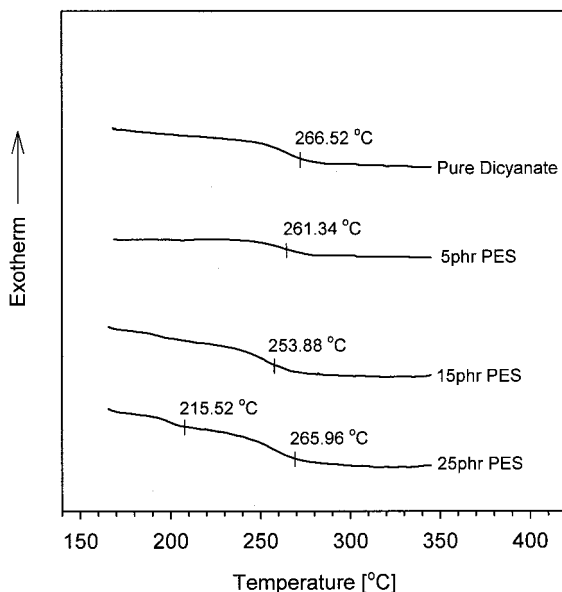
**Figure 4** Glass transitions of the blends containing various PES contents.

also shows that the proposed second-order auto-catalytic reaction kinetic model could well describe the reaction kinetics of the dicyanate/PES blends. The reaction kinetic parameters ($k_{10}$, $k_{20}$, $E_1$, $E_2$, and $n$) for the dicyanate/PES blend containing 15 phr PES are listed in Table I. Three dynamic DSC thermograms for each blend were used in determining the reaction kinetic parame-

ters of each blend to improve accuracy of the reaction kinetic equation.

It is important to check the coincidence between the dynamic DSC scanning data and isothermal DSC curing results. The isothermal DSC thermograms of a blend containing 15 phr PES for various curing temperatures of 280, 300, and 320°C are shown in Figure 7. Each curve shows a rapid increase in the heat output followed by an exponential decrease with time, ending in a flat line. With decreasing isothermal curing temperature, a decrease in the maximum exothermic peak value and its shift to longer times were observed. The bell shape of these isothermal curing curves suggested that the autocatalytic reaction mechanism could be used to analyze the reaction kinetics of the dicyanate/PES blends.

The conversion change with time during curing at an isothermal curing temperature can be calculated using the reaction kinetic equation determined from the dynamic DSC thermograms. Figure 8 shows the conversion change with time at various isothermal curing temperatures for the dicyanate/PES blend containing 15 phr PES. The figure shows how much the reaction rate of the blend can be affected by changing isothermal curing temperature. It shows good correlation with Figure 7.

**Thermal Stability**

Thermal stability is an important property of a polymeric material because it determines the us-
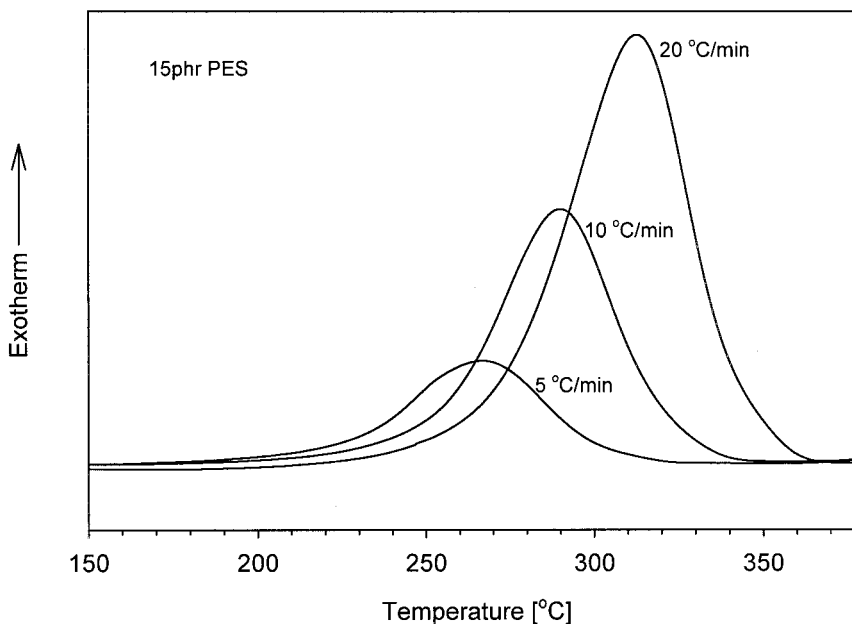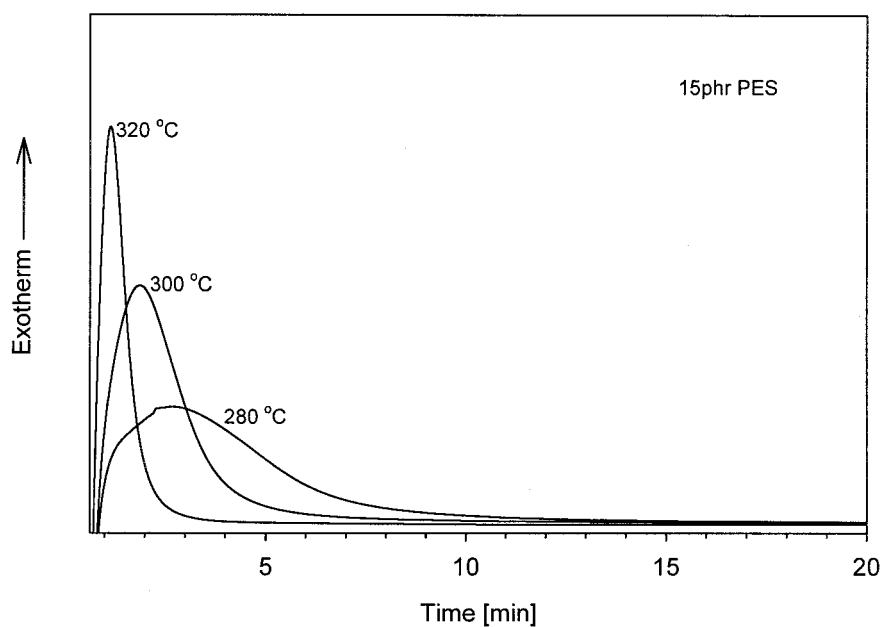


**Figure 5** Dynamic DSC thermograms of the blend containing 15 phr PES.
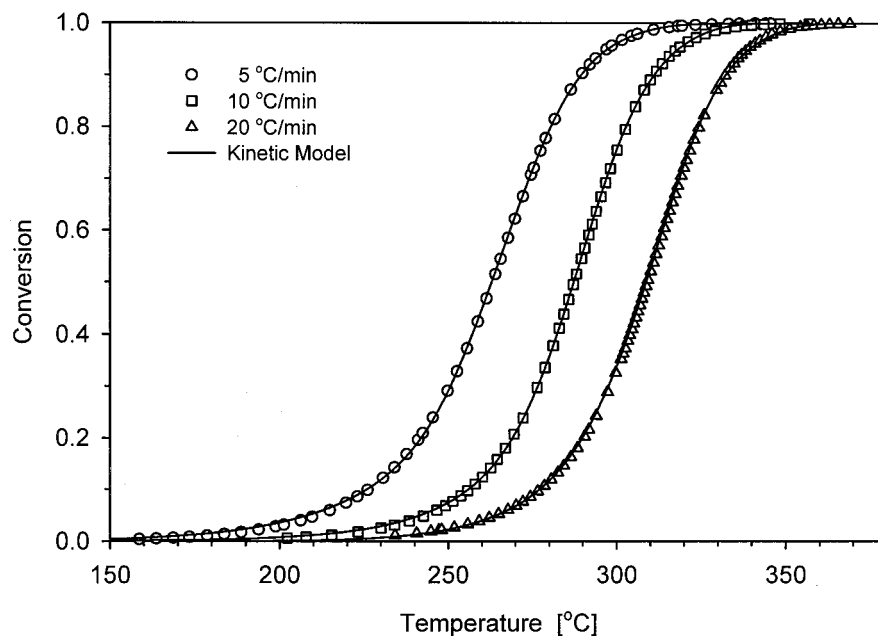
**Figure 6** Comparison between conversion data measured from DSC (data points, indicated by various open symbols) and those calculated from the kinetic model (lines) at various heating rates for the blend containing 15 phr PES.

able temperature limit of the material. Thermogravimetric analysis is sensitive to the degradation process, which involves weight loss that occurs during depolymerization and volatilization. Figure 9 shows TGA thermograms of the cured dicyanate/PES blends containing various PES contents measured at 10°C/min. The onset temperature of weight loss was hardly affected by the blend composition. The thermal stability of the blend increased slightly with increasing PES con-



**Figure 7** Isothermal DSC thermograms of the blend containing 15 phr PES for various isothermal curing temperatures.
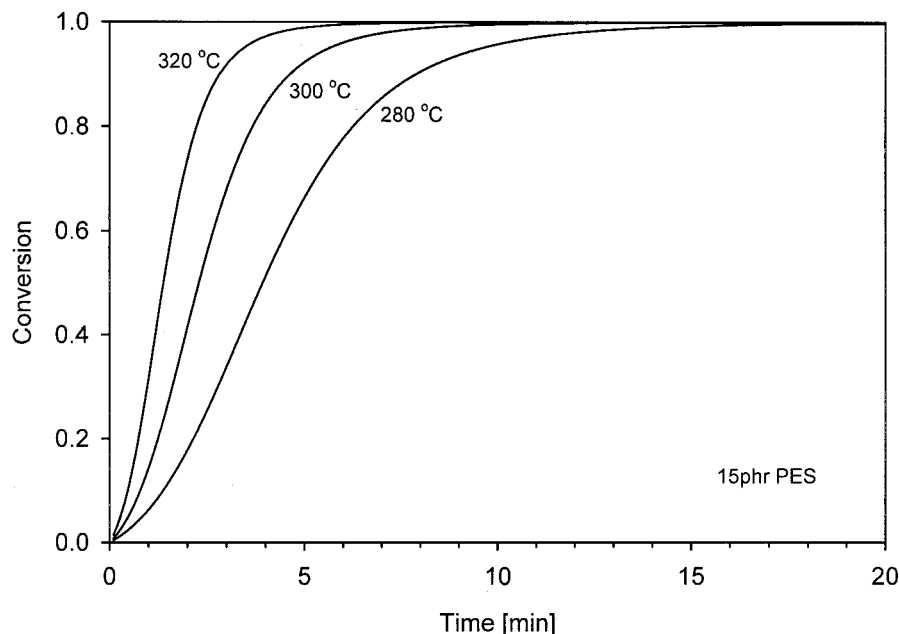
**Figure 8** Calculated conversion changes with time at various isothermal curing temperatures for the blend containing 15 phr PES.
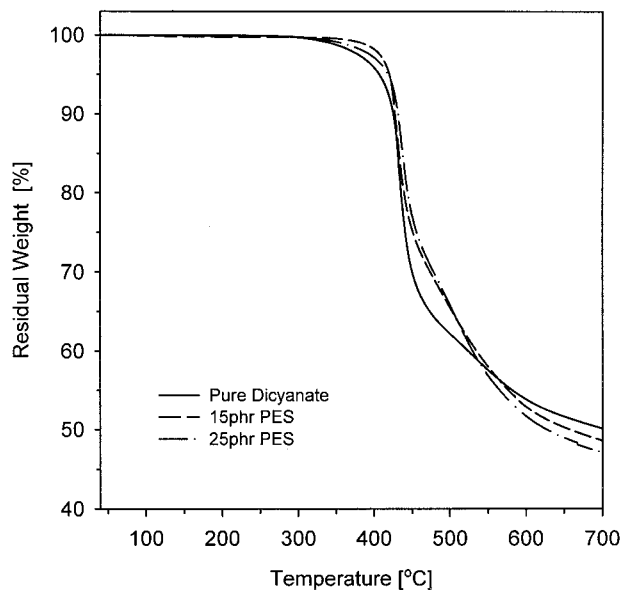
tent because the weight loss process retarded slightly as PES content was increased. The cured blends were thermally stable up to about 410°C.

### Thermomechanical Properties

Dynamic mechanical analysis, which usually measures the viscoelastic and rheological proper-



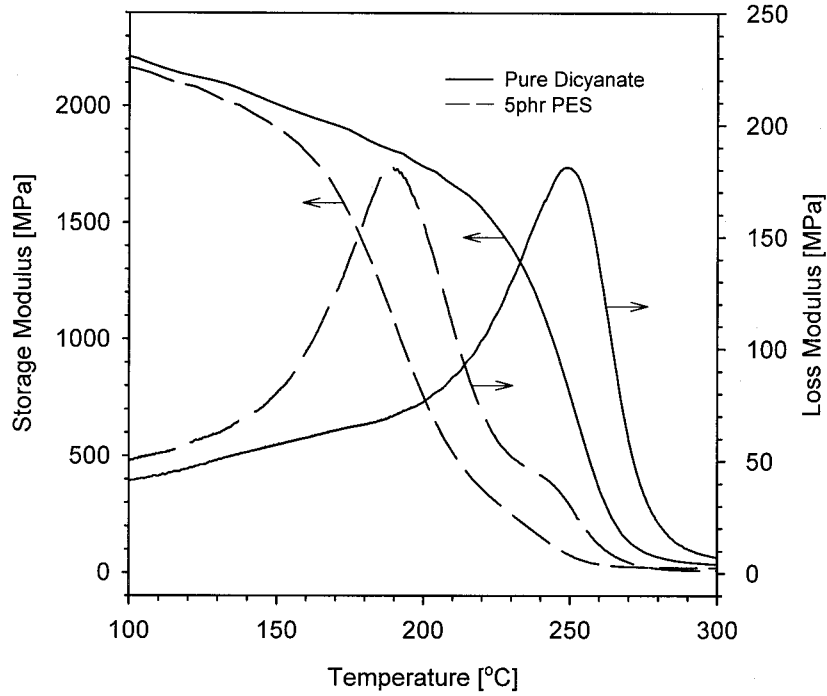**Figure 9** TGA thermograms of cured blends containing various PES contents.

ties of materials under application of a periodic stress or strain, is also valuable in determining glass-transition temperatures as well as the thermomechanical properties of the cured dicyanate/ PES blends. Figure 10 shows the storage modulus and loss modulus of the blend containing 5 phr PES. For comparison, Figure 10 also shows the storage modulus and loss modulus of cured pure dicyanate resin. The glass-transition temperature of the blend containing 5 phr PES, which is determined from the sharp decrease region in the storage modulus or the maximum peak in the loss modulus, was considerably low compared to that of pure dicyanate.

Figure 11 shows tan δ data of the two resin systems as a function of temperature. The tan δ curve for pure dicyanate resin shows only one damping peak, showing one glass transition, whereas there are two damping peaks for the dicyanate/PES blend containing 5 phr PES, showing that two glass transitions resulted from the phase-separated morphology of the blend. The lower $T_g$ corresponds to the glass transition in the PES-rich phase, whereas the higher $T_g$ corresponds to the glass transition in the dicyanate-rich phase. The DSC thermogram in Figure 4 shows only one glass transition for the blend containing 5 phr PES because sensitivity of DSC is generally lower than that of DMA in determining transition temperatures by 10-fold.
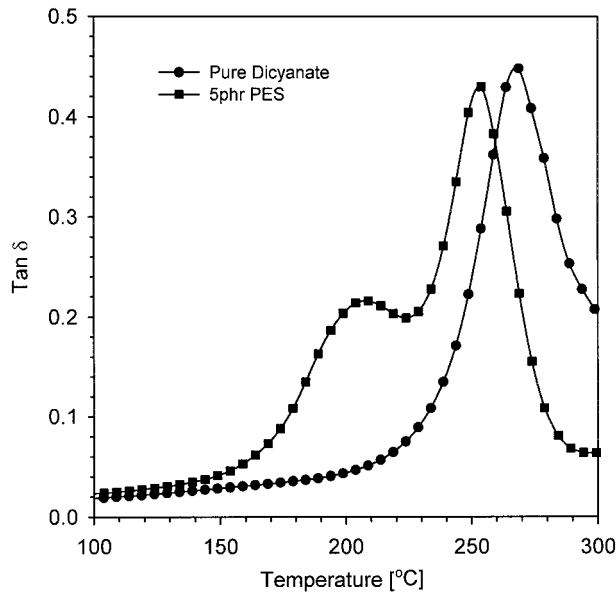
**Figure 10** Storage modulus and loss modulus curves for the blend containing 5 phr PES and pure dicyanate.

Figure 12 shows dimension change with temperature for pure dicyanate and the dicyanate/PES blend containing 5 phr PES, respectively. Each data curve was obtained at a heating rate of 5°C/min. Dimensional stability of the dicyanate resin increased slightly by blending a small amount of PES. This result seems to be ascribed to the fact that the coefficient of linear thermal expansion (CLTE) of the PES is smaller than that



**Figure 11** Tan δ curves for the blend containing 5 phr PES and pure dicyanate.
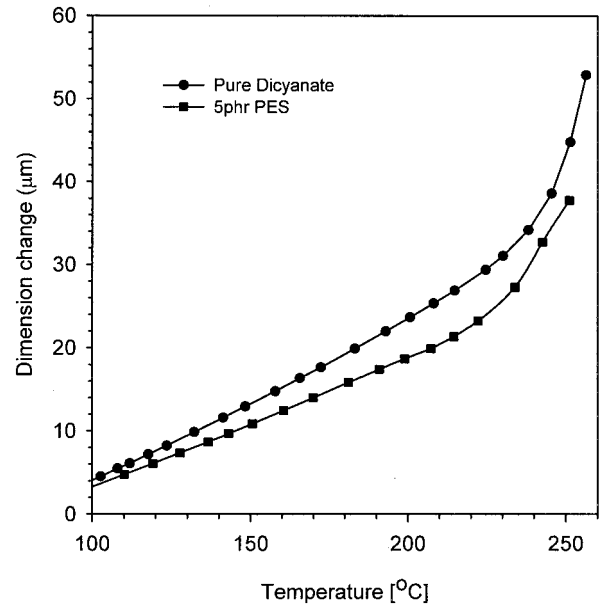


**Figure 12** Dimension change with temperature for the blend containing 5 phr PES and pure dicyanate.

of the cured dicyanate resin. For a polymeric material, CLTE over $T_g$ is greater than CLTE below $T_g$. Therefore, glass-transition temperatures can be obtained by taking the inflection point of the curves shown in Figure 12. The blend containing 5 phr PES showed one glass-transition temperature like that of the DSC result. The glass-transition temperature of the dicyanate resin decreased by incorporating 5 phr PES because the $T_g$ of PES is lower than the $T_g$ of pure dicyanate resin.

### Dielectric Properties

The capacitive nature of a material is its ability to store electric charge and dominates the properties at temperatures below the glass transition. The conductive nature is the ability to transfer electric charge and generally dominates the electrical response at temperatures above $T_g$. These electrical properties can be correlated to molecular activity.

The permittivity (or dielectric constant) of a material is the sum of permittivities resulting from both induced dipoles and alignment of dipoles. Permittivity is low for polymers at low temperature (i.e., below $T_g$) because the molecules are frozen in place and the dipoles cannot move to align themselves with the electric field. For the same reasons permittivity is low for highly crosslinked resins. The loss factor represents the energy required to align dipoles below and through $T_g$.

Figure 13 shows loss factors of pure dicyanate and the blend containing 15 phr PES, which were measured at 30 Hz. The loss factor increased abruptly around their glass-transition temperatures because an increase in molecular mobility above $T_g$ increased the alignment of the molecular dipoles. The glass-transition temperature of pure dicyanate resin decreased by blending it with 15 phr PES. The loss factor of each material was almost constant at temperatures below $T_g$ because the crosslinked network restricted molecular mobility.

### CONCLUSIONS

The effect of blending polyethersulfone on the curing behavior and physical properties of dicyanate resin was studied by thermal analyses. The curing rate of the dicyanate/PES blend decreased as PES content was increased. The reaction ki-
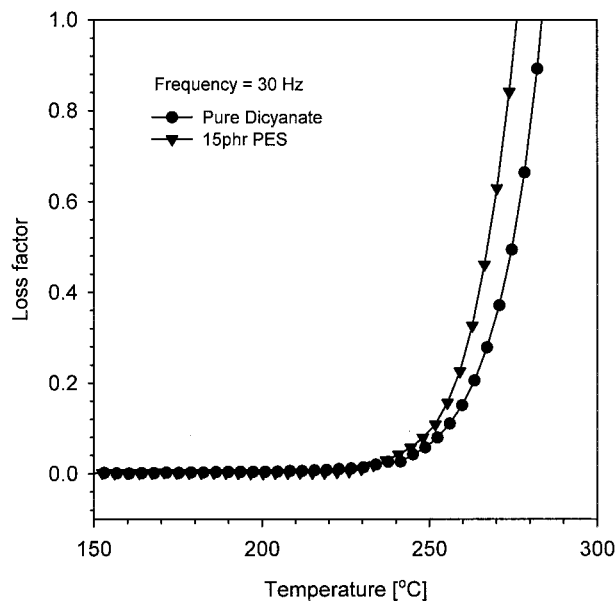


**Figure 13**  Loss factor for the blend containing 15 phr PES and pure dicyanate.

netics of the blend could be well described by the second-order autocatalytic kinetic equation. Several reaction kinetic parameters were determined by fitting DSC conversion data to the kinetic equation. The weight decrease of the blends with increasing temperature retarded slightly as PES content was increased. The effect of blending PES on the dynamic mechanical properties of the dicyanate resin was considerable. The glass-transition temperature of the dicyanate/PES blends measured by DSC decreased with increasing PES content. Two glass transitions, indicating phase-separated morphology of the blends, were observed in DMA. The dimensional stability of the dicyanate resin improved slightly by incorporating PES, whereas the electrical property of the dicyanate resin was hardly affected by blending with PES.

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