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Miscibility and Kinetic Behaviour of Cyanate Resin/Polysulfone Blends

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SUMMARY: A dicyanate ester resin was modified by blending with polysulfone (PSF) and cured at different temperatures with or without cobalt catalyst. Size exclusion chromatography was used to determine the cyanate conversion until the gel point. The morphology of the cured samples, characterised by scanning electron microscopy, varied from PSF particle structure to a combined particle structure.

Introduction

Polycyanate resins belong to technologically important thermosets due to their low dielectric loss, high temperature service and good mechanical performance [1,2]. The cyanate monomer undergoes polycyclotrimerization upon heating to form highly crosslinked polycyanurates [3-5]. In industrial practice, transition metal cations with an active hydrogen initiators are usually added to the resin in order to increase trimerization rate, which leads to reduction of losses by volatilization and the increase of the degree of conversion [3,6-9].

Plain polycyanates are brittle and their modification is desirable to improve their mechanical performance. It was found that modification by introduction some thermoplastics into the liquid resin prior to cure leads to the improvement of the fracture toughness [10-12]. The toughening mechanism generally depends on a process of phase separation occurring when an originally miscible liquid mixture of the cyanate monomer and a thermoplastic polymer is transformed into a cross-linked modified cyanate network. Prediction and control of the phase morphology of the thermoplastic-modified polycyanate, which determines the final properties of the cured material, is quite complicated.

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The cure reactions transform an initially homogeneous liquid blend into a crosslinked network of thermoplastic-incorporated polycyanate. For thermoplastic modified thermosetting systems, phase separation is influenced not only by thermodynamic factors but also by kinetic factors such as gelation/vitrification of the thermosetting component during cure [10,13,14]. In most cases, however, the phase separation resulting from these two driving forces remains incomplete. The final morphology of the modified matrix depends on the balance of both thermodynamic and kinetic factors. Therefore, it is difficult to establish general structure-property relationships applicable to such systems.

In previous work [15], we have studied the kinetics of polycondensation by size exclusion chromatography (SEC) of a dicyanate ester monomer in presence or absence of cobalt catalyst. In the present work an attention was focused on the kinetic and miscibility behaviour of dicyanate resin modified with polysulfone (PSF). Size exclusion chromatography was used to evaluate the cyanate conversion until the gel point, while the final morphology of the resin was probed with scanning electron microscopy.

Experimental Part

In this study, a bisphenol-A dicyanate, (BADCy) monomer was used (trade name AroCy B10, 99.5% purity, gently supplied by Ciba-Geigy). The complex of cobalt (II) acetylacetonate, $Co(AcAc)_2$, (99%, Aldrich) with the co-catalyst nonylphenol, NP (technical grade, Aldrich) formed the catalyst system used. The thermoplastic selected was a commercial grade of polysulfone, PSF, (Amoco UDEL P-1700, M_w/M_n: 63000/38000).

For curing purposes, PSF-cyanate resins were prepared according to the following procedure: PSF was dissolved in the molten dicyanate monomer at 80°C with continuous stirring until a homogeneous mixture was obtained. Air bubbles were removed from the mixture under vacuum at 90°C. Modified cyanate resins containing 0-20 wt% PSF were blended, if desired, with the catalytic system (360 ppm by weight of $Co(AcAc)_2$ +2% of the total resin weight of nonylphenol) at 90°C prior to cure. The blend was stored in the refrigerator in a desiccator to avoid moisture absorption.

A set of tubes, each containing about 30 mg of mixture, was placed in an oil bath at the curing temperature (selected within the range from 140°C to 220°C). Tubes were removed from the bath after various time of residence, and then the reaction was stopped by rapid cooling in an ice bath. THF was added to each tube in order to make a 1% (w/v) solution, which was injected into the chromatograph. The moment when an insoluble fraction appeared for the first time demonstrated that gelation has been attained.

The polycondensation kinetics up to the gelation was followed by size exclusion chromatography (SEC) of samples reacted partially at the selected temperature. The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector (Waters, Milford MA, USA). Detection was carried out with a refractive index (RI) detector Model 2410 (Waters). Data collection and handling were carried out using Millennium^{32} Chromatography Manager (Waters). The system was equipped with μ-styragel columns (30cm length and 0.78cm ID) filled with highly crosslinked styrene-divinylbenzene copolymer of 10^3 and 100 Å nominal pore size (Waters). Polystyrene standards were used for column calibration. Chromatograms were obtained at a flow rate of 1.0 mL min^{-1} by injection of 100 μL of 1.0 % (w/v) solutions in THF. From these chromatograms the kinetic in the pregel stage can be determined on the basis of the height of AroCy B10 peak, decreasing with the increase of reaction time. The overall conversion of dicyanate groups was evaluated under assumption of equal reactivity of the cyanate groups and absence of any substitution, which lead to the formula [16]:

$$x=1-(h/h_0)^{1/2}$$

where h/h_0 is the ratio of the peak height at a given time to the initial peak height. Gelation was noticed during sample preparation before injection. The corresponding gel-point conversion was determined from the residual monomer peak.

FTIR studies were performed using a Perkin-Elmer spectrophotometer, model FT-IR 16PC equipped with a temperature-controlled sample holder, which allowed *in-situ* analysis of the curing reaction. Peak areas were calculated for the cyanate vibration at 2270 cm^{-1}. The C-H stretch vibration at 2950 cm^{-1} was used as the reference peak. Assuming that peak areas are directly proportional to the concentration, the normalised cyanate concentration at any time was calculated as:

$$C(t)=\frac{A(t)_{2270}A(0)_{2950}}{A(0)_{2270}A(t)_{2950}}$$

where $A(t)_{2270}$ and $A(t)_{2950}$ is the absorbance at 2270 and at 2950 cm^{-1} at the time t, respectively; $A(0)_n$ is the initial absorbance and C(t) is the fraction of unreacted cyanate.

The morphology of the cured PSF-modified resins was examined with scanning electron microscope (SEM) Hitachi S-4100. The samples of PSF-modified dicyanate designed for SEM observations were prepared by curing at 200°C for 4 hours and then post-cured at 220°C for 2 hours or at 250°C for 1 hour in the mould coated with Frekote 44. After solidification by cooling down to the room temperature, they were fractured at the liquid nitrogen temperature. The fractured specimens were coated with gold by ion-sputtering.

Results and Discussion

In order to monitor the cure reaction, we have determined the dependence of the cyanate conversion on temperature and percentage of PSF for the uncatalysed and cobalt catalysed systems by liquid chromatography until the gel point. Evaluation based on the measurement of the height of the dicyanate monomer peak in the elution profiles, under assumption that the monomer concentration is proportional to height of the monomer peak. Such an assumption was previously tested for the unmodified resin [15]. Figure 1a shows the refractive index (RI) detector response to injection of THF solutions of 10%PSF/AroCy B10 sample with the concentration ranging from 0.001 to 0.015 g/mL (chromatograms from bottom to top). The dicyanate monomer shows a single peak at an elution volume, V_e= (17.3 ± 0.1) mL, which indicates an absence of high molecular weight impurities. The PSF elutes at (10.3 ± 0.1) mL, far apart from the monomer peak and its monitoring does not pose any difficulties. Both, the area and the height of the peak registered by the RI detector show a good linear dependence with AroCy B10 and PSF concentration in the mixture (see Figure 1b), and could be used to study the consumption of the dicyanate monomer during polymerisation. Calibration curves for AroCy B10 in THF, as well as PSF in THF were prepared. Every point in Figure 1b corresponds to the peak in each chromatogram plotted in Figure 1a. Heights of these peaks demonstrated a good linear correlation with concentration of either AroCy B10 or PSF, respectively.

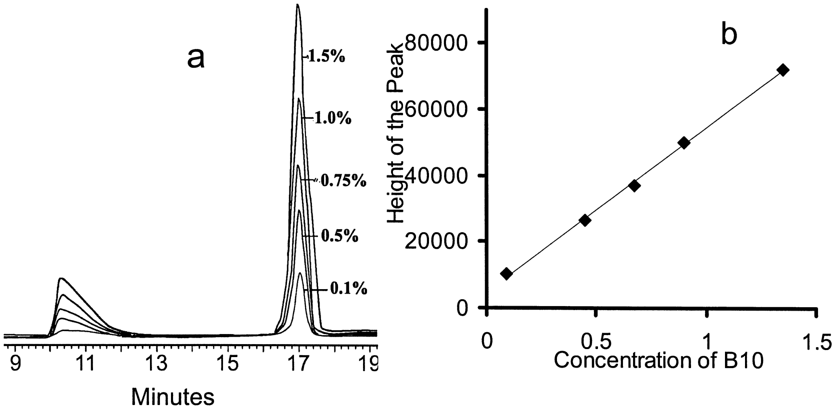

Figure 1. (a) Elution profiles for 100 μL of 10%PSF/Arocy B10 at different concentrations in %(w/v). Eluent: THF; RI detector; (b) Height of the AroCy B10 peak against the injected monomer concentration, RI detector.

Under isothermal conditions, curing of dicyanate monomer leads to a cross-linked network built up of triazine rings. The monomer conversion can be followed by size exclusion chromatography (SEC) since the monomer peak become to decline and higher molar mass species appear with increasing reaction time. As an example, the RI detector response during polycondensation of dicyanate modified with 10% of PSF in the pre-gel state at different reaction times cured at 180 °C is shown in Figure 2a. The peaks from right to left correspond to the monomer and to the trimer at the elution volume of 17.3 mL and around 15.9 mL, respectively (identification based on the calculated respective molar mass versus elution time calibration). The other peak on the left side might correspond to the formation of five- or higher order oligomeric species. The PSF peak remained isolated during reaction and did not interfere with cyanate groups. The above spectra evidence that trimerisation is the dominant reaction pathway (approx. 90%), which agrees with previous findings [17]. As the curing process develops, reactions between growing chains and with the monomer result in appearance of a wide range of oligomeric species. The overall distribution of species becomes broader as the system approaches gelation, more accentuated for the catalysed system. Figure 2b depicts the cyanate conversion for 10%PSF/AroCy B10 system obtained from chromatograms similar to those presented in Figure 1a, for samples cured at different temperatures. Cure temperature higher than 200°C has to be also used for the curing time to be reduced below 100 min and obtain a high degree of conversion for industrial purposes.

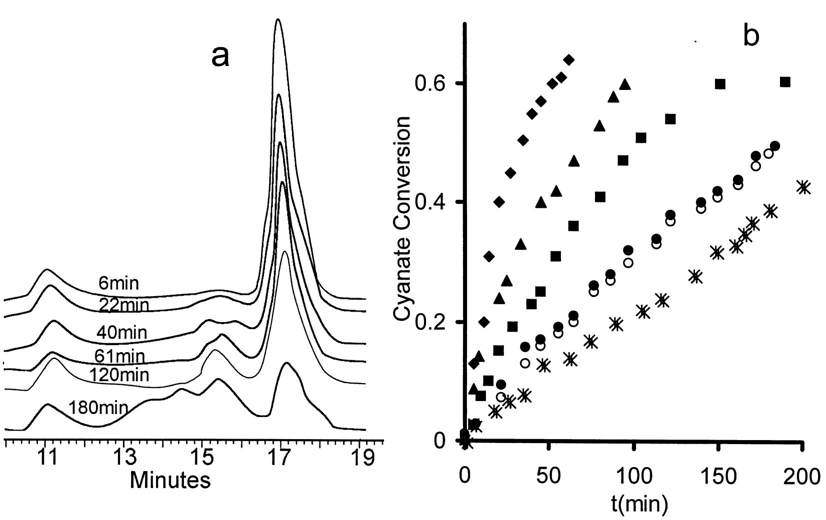

Figure 2. Isothermal curing of 10%PSF modified AroCy B10: (a)Elution profiles during the cure at 180°C; (b) conversion of cyanate groups as a function of time at different curing temperatures: (*)170, (•)180, (■)190, (▲) 200 and (◆) 220°C. For comparison conversion data for the cure of the neat resin at 180°C has been included (o).

Figure 3 shows the evolution of conversion degree with curing time at different temperatures determined for dicyanate modified with 20% of PSF and cured in the absence (part a) and presence of catalyst (part b). The catalyst is normally used for industrial purposes because the rate of trimerization of cyanates in absence of catalyst is low and is a function of the concentration of active hydrogen impurities. Therefore, this reaction is usually catalysed by a mixture of metal cations and active hydrogen initiators, such as nonylphenol, which lowers the curing temperature necessary to yield a high conversion degree, and reduces losses by volatilization.

Data obtained for the PSF-modified cyanate system do not show a significant difference with the neat system. This is demonstrated in Figures 2 and 3 where data collected with the same technique for the cure of unmodified resin [15] were plotted for

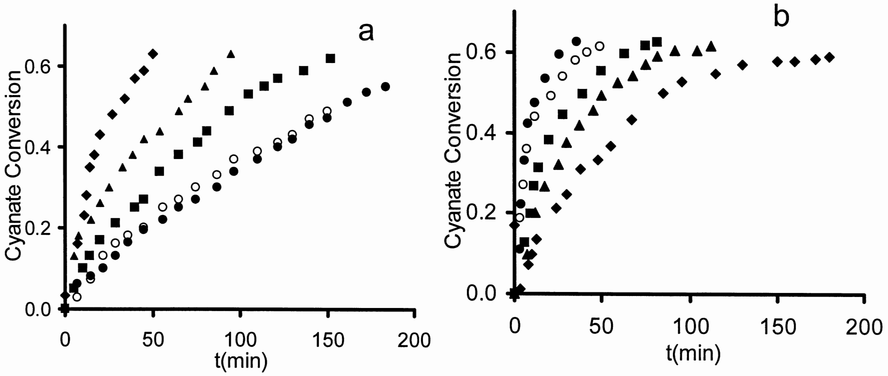

Figure 3. Conversion of cyanate groups as a function of time for the curing of 20%PSF modified AroCy B10 system at different curing temperatures: (a) without catalyst: (●) 180, (■) 190, (▲) 200 and (◆) 220 °C, and (b) catalysed with cobalt/nonylphenol catalyst at (◆) 140, (▲) 150, (■) 160 and (●) 180 °C. For comparison conversion data for the neat resin at (○) 180 °C is also included.

comparison. It is seen that addition of PSF does not influence the kinetic of polycondensation, in contrast to Hwang et al.[18], who found on the basis of DSC studies that the rate of cyanate conversion increases in presence of PSF by the use of a lower molar mass of PSF and a different mixing procedure.

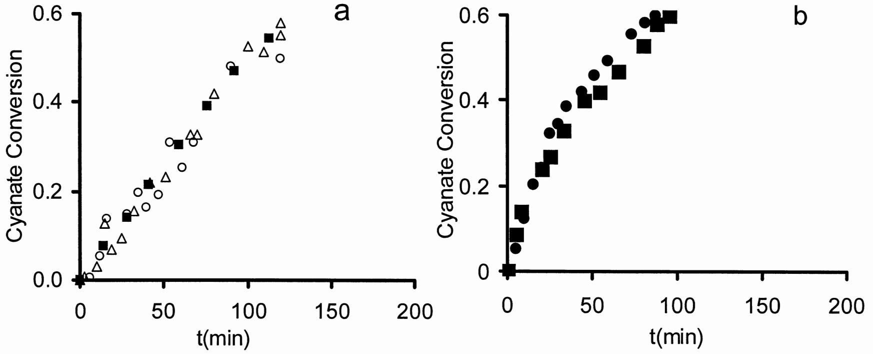

Figure 4. Conversion of cyanate groups as a function of time for the curing of AroCy B10 with 10%PSF (a) reproducibility of the SEC technique at 190°C and (b) comparison of dicyanate conversion obtained by SEC (■) and FTIR (●) at 160 °C for the catalysed system.

Figure 4a depicts a good reproducibility of the SEC technique for the systems studied showing as an example the results obtained in several independent experiments of curing of AroCy B10 modified with 10% of PSF performed at 190°C. To prove an accuracy of this technique, Figure 4b shows conversion data for curing temperature 160°C obtained from FTIR and from SEC measurements. It demonstrates a good agreement of both data sets. Similar results were obtained for other curing temperatures.

The experimental data of cyanate conversion until the gel point obtained in this work were fitted with a second order kinetic expression with respect to the consumption of monomer, $\frac{dx}{dt} = k(1-x)^2$, where k is the rate constant. The fit with this second order kinetic equation appeared pretty good until the gel point, where the reaction is considered to be kinetically controlled. This agrees with literature data [3,9,19], where the rate of the reaction is also found to be controlled kinetically.

For each system the rate constants, k, shows an Arrhenius type temperature dependence, therefore a linear fit of logarithm of apparent rate constant vs. reciprocal cure temperature is attained. From such linear fit the activation energy, E_a, and the pre-Arrhenius frequency factor, A, of the process were estimated. The calculated values of E_a were equal to 78 kJ/mol, 77 kJ/mol and 62 kJ/mol and $A = 6.76 \times 10^6$, 4.95×10^6 and 9.20×10^4 $g^{-1}mol^{-1}$ for 10%PSF/AroCy B10, 20%PSF/AroCy B10, and cobalt catalysed 20%PSF/AroCy B10 systems, respectively. These values agree with those reported in previous studies [3,8,9,19]. In the future work theoretical determinations of E_a and A will be carried out.

Monitoring of the gel time of these systems (i.e. time at which one observes a first appearance of insoluble particles, indicating that a 3-dimensional network started to form) is crucial since it determines the processability time limit for the resin. The gel times estimated for the studied systems demonstrate a good linear Arrhenius-type dependence with activation energy of 80, 78 and 70 kJ/mol for 10%PSF/AroCy B10, 20%PSF/AroCy B10, and cobalt catalysed 20%PSF/AroCy B10, respectively. The calculated cyanate conversion degree at gelation point is within the range of 0.51-0.60. It is slightly higher than the mean-field prediction but of the same order of magnitude as compared to the most of previous works [17,20-22].

The content of thermoplastic component and the curing temperature are two main factors determining the morphology of thermoset/thermoplastic blends, and therefore, the final material properties [10,11,18]. The morphology observations with scanning electron microscope provide a direct visualisation of the phases, their degree of mixing and their continuities. Figure 5 shows SEM micrographs of cryo-fractured surfaces of samples of AroCy B10 blends with 10wt.% and 20wt.% of PSF, cured at 200°C for 4 hours (upper row), cured at 200°C for 4 hours and then post-cured at 220°C for 2 hours (center row) as well as cured at 200°C for 4h and then post-cured at 250°C for 1h (lower row). The blend modified with 10% of PSF demonstrates a matrix-particle morphology. On the other hand, the system modified with 20% of PSF shows a more complicated double-dispersion morphology with visible interpenetration of components. Phase separation is controlled by the competition between kinetics and miscibility (thermodynamics). Since the degree of conversion changes with time in a similar way in both systems, the thermodynamic factors had to determine the final morphology. Although the systems were initially miscible (prior to curing), they moved into the two-phase region on the phase diagram due to the increase of molar mass of the resin and decrease of its solubility parameter with increasing conversion. The phase morphology of the blends changes at a composition between 10 and 20wt.% of PSF from continuous matrix and separated inclusions to the dual continuous phases formed by both the thermosetting and thermoplastic components. After 100 min of curing at 200°C gelation of the matrix was attained and the observed morphology was similar to that present in sample cured for 4 hours. This indicates that the final phase morphology was formed and fixed already at the gel point. These blends have to be specially treated in the sense that the thermosetting component is reacting and changing from a low-viscosity liquid to a highly cross-linked network. In future work, we will study deeper the phase separation process.

Conclusions

Several features related with PSF and thermosetting AroCy B10 cyanate blends were studied. The conversion of cyanate groups, followed by size exclusion chromatography until the gel point, does not show any significant difference from the conversion of the neat resin. The SEC technique has been proven to be a good technique to follow the cyanate conversion. The same conclusions can be drawn for the cobalt catalysed system. Both systems have similar activation energies. The morphology of the cured system changes from the matrix-inclusions morphology at the content of PSF of 10wt.% to a dual-dispersion and co-continuous phases at 20wt.% of PSF.

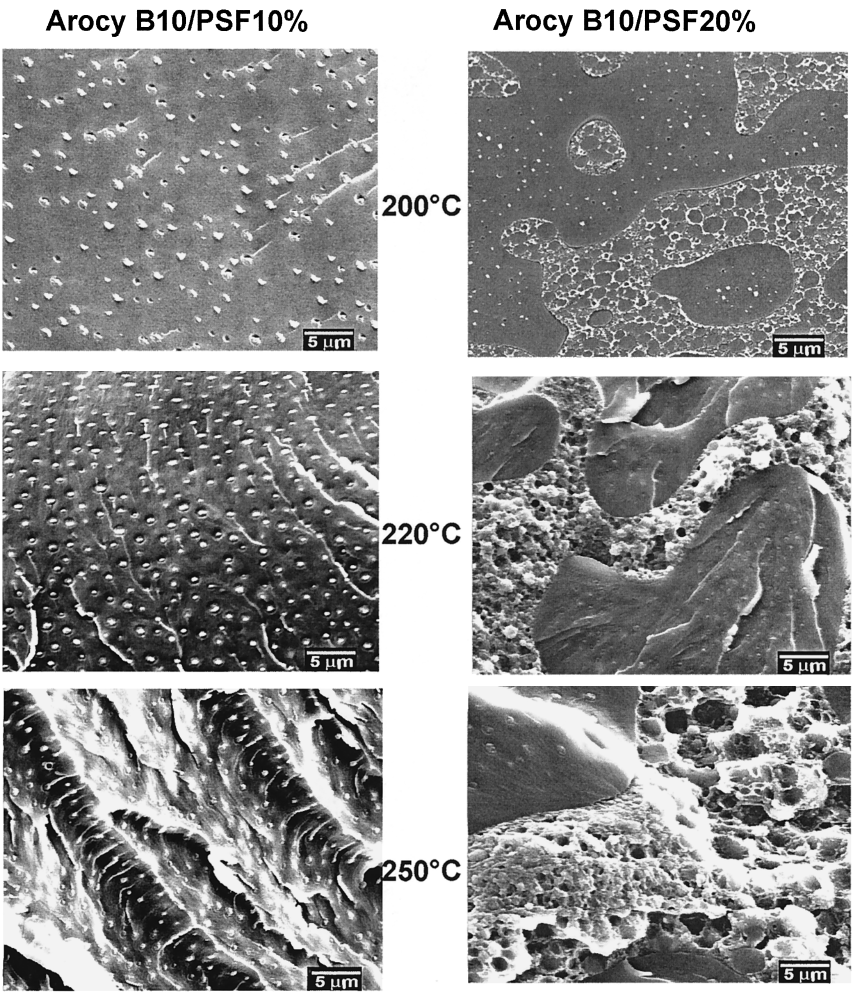

Figure 5. SEM micrographs of the uncatalysed PSF modified Bisphenol A dicyanate cured at 200 °C for 4 hours and post cured at 220°C for 2 hours or at 250 °C for 1 hour.

Acknowledgements

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