

Relationship between Structure and Mechanical Property for Bismaleimide–Biscyanamide Resin

Bismaleimides, which may be classified into addition-type polyimides, are well known as high-temperature resistant polymers. Their cured products, however, are extremely brittle because of their high crosslinking density. So the most important problem in technical application is toughening bismaleimides without decreasing their heat resistance.^{1,2}

Recently we reported on the modification of N,N-bismaleimidediphenylmethane (BMI) with bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM), and the characterization of the cured resin systems.³ We found their properties, such as glass transition temperature, crosslinking density, dielectric constant, and decomposition temperature, changed with the molar ratio of BMI and BCMM. We attributed these changes to a variation of chemical structure at different molar ratios.

In this note, we report on the mechanical property of the modified resins as a function of the amount of biscyanamide for the purpose of correlating macroscopic behavior and the resin's chemical structure.

EXPERIMENTAL

Materials and Sample Preparation

Figure 1 shows the materials used. The prepolymers were prepared from BMI (Mitsui Toatsu Chemical) and BCMM, which was synthesized according to the literature^{4,5} at several molar ratios (Table I). Prepolymerization was done as follows: A 200-mL, four-necked flask with a reflux condenser was charged with N,N-dimethylformamide (DMF, Wako Pure Chemical) and BMI. The amount of DMF was determined to get a 50 wt % prepolymer solution. The solution was heated at 120°C, using an oil bath for 20 min, while stirring. Then, BCMM solid was added into the flask and the solution was held at 120°C for 20 min. The product solution was then cooled to room temperature and was coated lightly on polyester films. The DMF was removed by holding the polyester films in a thermostated oven at 150°C for 10 min.

The prepolymer powder was placed in a heated molding press, with a 1 mm spacer, and was cured under a pressure of 40k gf/cm². The molding temperature was first held at 170°C for 5 min, and then was raised to 220°C and held for 2 h.

Measurements

The densities of the cured products were evaluated using a bromoform- (d: 2.9) toluene (d: 0.86) mixture at 25°C. The density of the corresponding mixture was measured on a Anton Parr precision density meter (Model DMA-02C). Dynamic mechanical analysis (DMA) was done using an Iwamoto Seisakusho device (Model RPX-706), ranging from -180 to 400°C at a heating rate of 5°C/min, and determined by means of an instrument employing a forced longitudinal vibration at 10 Hz. The samples were rectangular strips, 40 × 4 × 1 mm. Flexural testing by the procedure of JIS-K6911 was conducted on a Shimadzu Autograph (Model DDS-5000) at room temperature.

RESULTS AND DISCUSSION

Crosslinking Densities

The crosslinking densities (ν) were obtained from the experimental equilibrium rubber modulus using the same method as our former report.³ The resin components and crosslinking densities of cured resins are listed in Table I. Crosslinking densities of the cured resins became the lowest at the ratio of BCMM/BMI = 50/50.

Room Temperature Flexural Modulus

The flexural moduli at room temperature of formulations 2 through 7 showed a significant drop as compared with formulation 1, BMI alone, as presented in Figure 2. In general, crosslinking density affects several properties of cured resin, including moisture absorption, yield stress, tensile modulus above T_g , creep, density, and impact

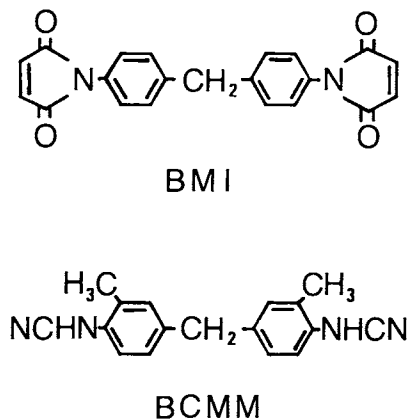


Figure 1 Structures of materials.

strength. The data in Table I showed that the formulations with different BCMM/BMI ratios had different crosslinking densities, so there may be a corresponding relationship between crosslinking densities of this system and the flexural modulus. For the thermoset networks that we investigated, there was a weak correlation between crosslinking density and the room temperature flexural modulus, as shown in Figure 3. On the other hand, the flexural modulus at room temperature correlated well to bulk density, as shown in Figure 4.

One group has reported that the glassy state moduli of a series of chemically similar networks were independent of crosslinking density,⁶ but two other groups^{7,8} have found that the higher the crosslinking density, the lower the modulus of the studied epoxy system. In these cases, because the epoxy system did not obtain a high bulk density by cramp for crosslinking, the moduli decreased with increasing crosslinking density. For our systems, the bulk density was weakly affected by crosslinking density, as shown in Figure 5, so flexural moduli were a function of crosslinking density.

Table I Formulations and Their Crosslinking Density

Formulation	BCMM/BMI (Molar Ratio)	$\log \nu$ (mol/cc)
1	0/100	—
2	20.1/79.9	-2.08 ^a
3	25.0/75.0	-2.14 ^a
4	30.0/70.0	-2.08
5	40.0/60.0	-2.26
6	50.0/50.0	-2.47
7	60.0/40.0	-2.29
8	100/0	—

^a Estimated value following Ref. 3.

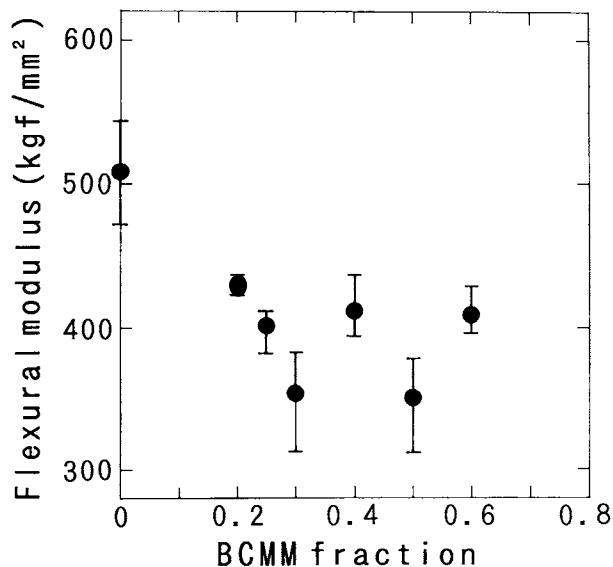


Figure 2 Flexural modulus vs. BCMM fraction.

Flexural Strength

The introduction of biscyanamide improved the flexural strength of cured resins, as shown in Figure 6. These resins are suitable for industrial use.

Hasumi and Kataoka⁹ have investigated the mechanical property of maleimide polymers prepared from BMI and 4,4'-diaminodiphenylmethane (DMA). They achieved the highest tensile strength and elongation when the molar ratio of BMI/DMA was 1.2, and they explained it as follows. If only a Michael addition reaction occurred between BMI and DMA at BMI/DMA = 1.0, the resins obtained

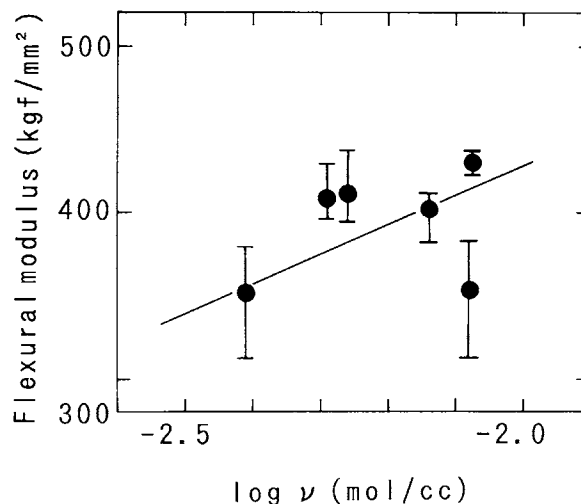


Figure 3 Flexural modulus vs. $\log \nu$.

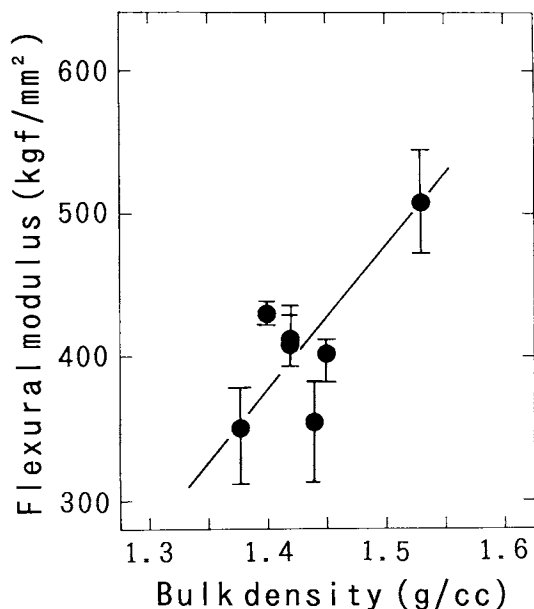


Figure 4 Flexural modulus vs. bulk density.

would ideally be a long chain and the mechanical property would be a maximum. However, at 1.0, self condensation of BMI and a crosslinking reaction occurred, and there were some unreacted amine groups, so the property was not maximized. However, at the 1.2 ratio, where BMI was present in a larger amount than DMA, there were no unreacted amine groups and the mechanical property was a maximum.

The room temperature flexural strength vs. logarithmic crosslinking density is shown in Figure 7. Generally, the flexural strength in glass regions is affected by crosslinking density.⁸ As crosslinking density increased with formulations 6 < 7 < 5, the break strength increased. However, as crosslinking density continued to increase, break strength dropped off slowly. In this region, crosslinking

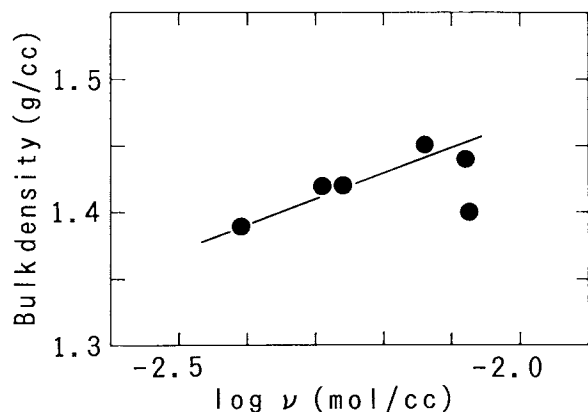


Figure 5 Bulk density vs. log ν.

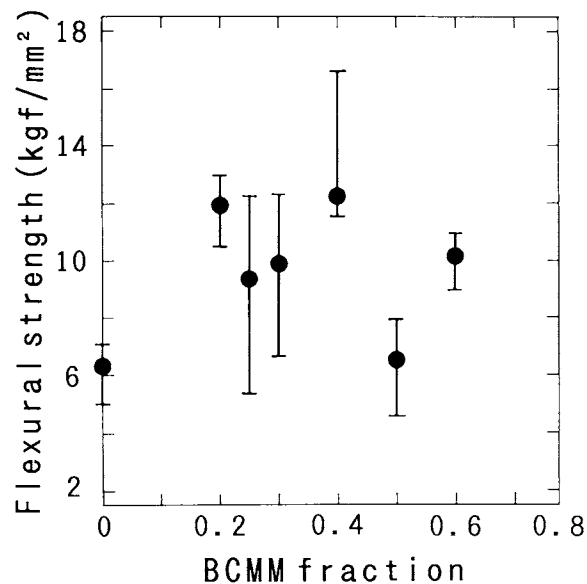


Figure 6 Flexural strength vs. BCMM fraction.

densities were like that of cured BMI (formulation 1), so the network structure become very rigid and the cured resins were brittle.

CONCLUSION

The introduction of bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM) to N,N-bismaleimidediphenyl-

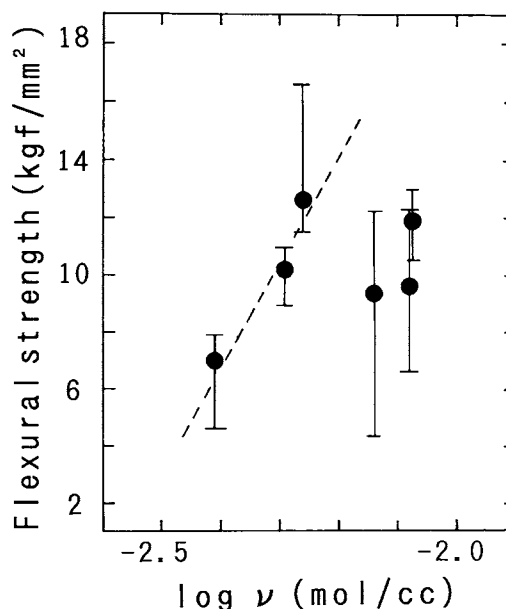


Figure 7 Flexural strength vs. log ν.

methane (BMI) could improve the mechanical property of cured resins. The flexural modulus at room temperature of this system showed a significant drop as compared with BMI alone. A weak correlation of the room temperature modulus to crosslinking density was found, because there was a weak correlation between bulk density and crosslinking density. In addition, flexural strength of cured resin was shown to change with crosslinking density. In the region where crosslinking density was low, the strength was improved with increasing crosslinking density. However, in the region where crosslinking density was high, the network structure became very rigid and the cured resins were brittle.

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