Performance Improvement of Rubber-Modified Polybenzoxazine

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ABSTRACT: Polybenzoxazine as a noble phenolic resin was modified with amine-terminated butadiene acrylronitrile rubber (ATBN) and with carboxyl-terminated butadiene acrylronitrile rubber (CTBN) in order to improve its mechanical properties. The fracture toughness, flexural modulus, and flexural strength of rubber-modified polybenzoxazine were measured to investigate the effect of rubber modification. In fracture toughness, ATBN is more effective than CTBN. ATBN-modified polybenzoxazine showed better distribution of rubber particles in matrix phase than did CTBN-modified polybenzoxazine. The cure rates in these systems were monitored by differential scanning calorimetry to investigate the effect of cure rate on rubber size. The change of glass transition temperatures of rubber-modified polybenzoxazine was measured with a dynamic mechanical thermal analyzer to explain the variation of mechanical properties. In addition, the relationship between mechanical properties and the morphology of rubber-modified polybenzoxazines was also undertaken. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1–10, 1998

Key words: polybenzoxazine; rubber modification; fracture toughness; flexural strength

INTRODUCTION

Phenolic polymers have been used in construction and electrical applications because of their good mechanical properties, heat resistance, flame resistance, and dielectric insulation property.[1] They also have a low cost/performance index because of their cheap raw materials and easy synthesis. However, they release volatile by-products during the curing process, so it is hard to control their micro voids. Designing their molecular structure is also hard, and their brittleness is bad for construction.

The synthesis of the novel phenolic polymer has been studied to overcome these shortcomings. The phenolic polymer with a benzoxazine ring was synthesized for this purpose. However, the monomer of the first synthesized phenolic polymer with a benzoxazine ring was monofunctional, so its mechanical properties were not sufficient compared with phenolic polymers such as novolac and resol.[2] In order to improve the mechanical properties, the polyfunctional monomer of phenolic polymer was synthesized by Ning and Ishida.[3,4] The polymerization of the monomer is synthesized by Ning and Ishida is initiated by heat, and the reaction type of polymerization is addition, so there is no volatile curing reaction. In addition, it has good dimensional stability because of the ring opening cure process and low viscosity to make complicated shapes easily.[5,6] However, it has a very brittle property, as is usual for phenolic materials, and this limits its application.

The modification of brittle materials has been conducted by adding tough materials such as rubber and thermoplastics.[7–10] However, the viscosity of the novel phenolic polymer is very low and curing is slow, so solid additives such as solid rubber and thermoplastics precipitate during cure.

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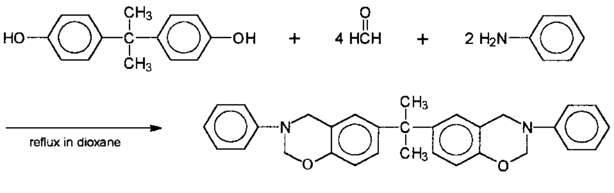
Therefore, the liquid rubber, which is commonly used for epoxy modification, is appropriate to apply to the novel phenolic polymer because it is easy to handle because of its low viscosity and to control the polarity of rubber by changing the ratio of polybutadiene and acrylronitrile rubber. The polarity control of additives is important because polarity has an effect on rubber distribution in matrix. In rubber toughening, it was reported that the phase separation of rubber and matrix is necessary and the size of the distributed particle has to be $10^2 \sim 10^3$ nm to obtain substantial improvement in toughness.[11] In addition, the novel phenolic polymer has many functional groups, and the reactive functional group of commercial liquid rubber has many chances to form chemical bonds.

In this article, the mixed systems of noble phenolic resin with benzoxazine ring structure (abbreviated as polybenzoxazine) and reactive liquid rubber (amine-terminated butadiene acrylronitrile rubber [ATBN], carboxyl-terminated butadiene acrylronitrile rubber [CTBN]) were studied for the purpose of improving the toughness of polybenzoxazine. The special catalysis effect can be expected by the reactive functional groups of liquid rubber, because it is possible for acid and base to accelerate the curing reaction of polybenzoxazine. The stress intensity factor and other mechanical properties of these systems were also investigated for the application of polybenzoxazine.

EXPERIMENTAL

Materials and Preparation

The monomer of polybenzoxazine was synthesized with bisphenol A, formaldehyde, and aniline. The raw materials were purified according to reference 12. The monomer was synthesized as shown in Scheme 1.[4] The characterization of synthesized monomer was conducted by nuclear magnetic resonance spectroscopy and infrared spectroscopy, and these results are shown in Figures 1 and 2.



Scheme 1. Synthetic scheme of monomer of novel phenolic resin.

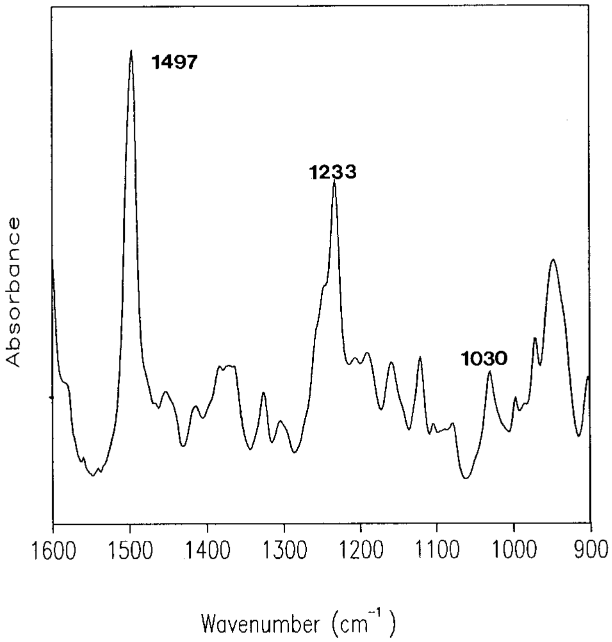


Figure 1 Fourier Transform Infrared (FTIR) spectrum of benzoxazine monomer (1497 cm^{-1}: trisubstituted benzene ring mode, 1233 and 1030 cm^{-1}: the ether linkage in benzoxazine ring).

The CTBN and ATBN used as tougheners were Hycar 1300 × 13 and Hycar 1300 × 16, respectively, and they were purchased from BF Goodrich Co. The properties of these two materials are shown in Table I.

Rubber modification of polybenzoxazine was carried out by adding liquid rubber to molten monomer at 120°C and by mixing with a mechanical stirrer. The molten mixture was cast in silicon rubber open mold and cured according to the following procedure. First, the mixtures were degassed in a vacuum oven at 120°C for 1 h. Curing was carried out at 180°C for 1 h and then at 225°C for 2 h. In this study, the formulations of the ATBN and CTBN series were varied with 0, 1, 3, 5, 10, 15, and 20 wt %, respectively.

Mechanical Properties

A three-point bending flexural test was performed with a Universal Testing Machine (Instron 4201) according to ASTM 790. The specimen dimension was 50 × 25 × 2 mm, and the crosshead speed was 1 mm/minute.

A fracture test was conducted according to ASTM D5045. Specimen geometry was single-edge-notch bending (SENB); its dimension was

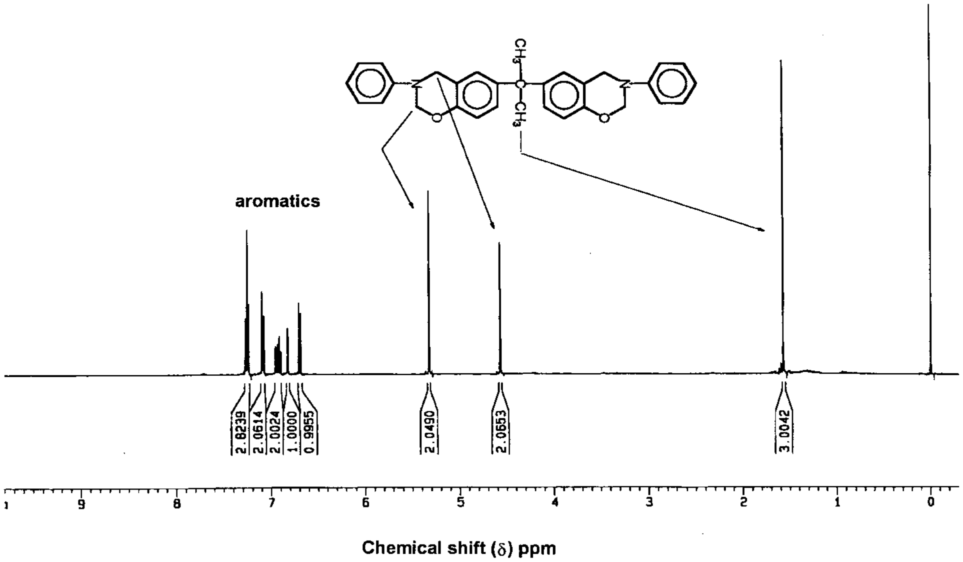


Figure 2 Nuclear magnetic resonance spectrum of benzoxazine monomer.

35 × 8 × 4 mm, and the crack length was the half of its width. The specimens were cut from cast sheets, and cutting by saw was conducted in the middle of specimens. A final sharp crack was carefully introduced by tapping a fresh razor blade. Span length was 32 mm, and crosshead speed was 10 mm/minute.

The value of the stress-intensity factor, K_{Ic}, was calculated by the following equation:

$$K_{IC} = \frac{Pc}{BW^{1/2}} f(x) \qquad (1)$$

where $(0 < x < 1)$:

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1 - x) \times (2.15 - 3.93x + 2.7x^2)]}{(1 + 2x)(1 - x)^{3/2}} \qquad (2)$$

and Pc is the load at break (kN), B is the specimen thickness (cm), S is the span (cm), W is the specimen width (cm), a is the crack length (cm), and $x = a/W$.

Table I The Physical and Chemical Properties of ATBN and CTBN

Properties	1300X16 (ATBN)	1300X13 (CTBN)
Acrylonitrile content (%)	18	26
Brookfield viscosity (cP at 21°C)	200,000	500,000
Specific gravity (g/mL at 25°C)	0.956	0.96
Functionality	—	1.8
Molecular weight (M_n)	—	3,150
Glass transition temperature (T_g) (°C)	−51	−39

The validity of this test was confirmed by the following equation:

$$B, a\ (W - a) > 2.5(K_{Ic}/\sigma_y)^2 \qquad (3)$$

where

$$\sigma_y = \text{yield stress.}$$

Thermal Properties

A dynamic mechanical thermal analyzer (DMTA; Rheometric Science Co. MKIII) was used to determine the T_g of rubber-modified polybenzoxazine. A bar-type DMTA specimen was used for three-point bending. The heating rate was 2°C/min, and the frequency was 4 Hz.

To investigate the curing peak temperature of rubber-modified polybenzoxazine, a dynamic experiment was conducted by differential scanning calorimetry (DSC; Perkin Elmer DSC 2). The heating rate was 5°C/min, and the temperature range was from 170 to 270°C.

Fractography

To investigate the fracture surfaces of rubber-modified polybenzoxazines, a scanning electron microscope (JEOL-35CF) was used. The specimens resulting from the SENB test were used,

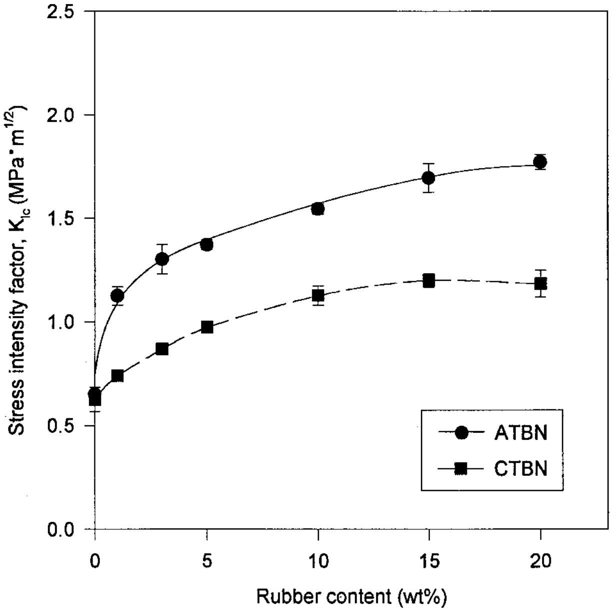


Figure 3 Stress intensity factor, K_{Ic}, of rubber-toughened polybenzoxazine as a function of rubber content.

and the rubber phase of the specimens was extracted with benzene for 1 day. Gold was coated on its surface to improve conductivity. The magnification was ×4000.

RESULTS AND DISCUSSION

Figure 3 shows the stress intensity values (K_{Ic}) of rubber-modified polybenzoxazine. The K_{Ic} of polybenzoxazine increased from 0.6 MPa · m$^{1/2}$ to 1.8 MPa · m$^{1/2}$ with the increase of rubber content. This shows that ATBN is better for toughness improvement than CTBN. Observing Figure 3, the trend of K_{Ic} values with the rubber content was different in both cases. In the case of ATBN, K_{Ic} values increased abruptly up to 5 wt % and then the increment of K_{Ic} values was alleviated. However, in the case of CTBN, the K_{Ic} values increased smoothly with increasing rubber content. The fractographical analysis was performed to explain these results.

The fracture surfaces of rubber-modified polybenzoxazines are shown in Figures 4 and 5. In Figure 4, the fracture surface of neat polybenzoxazine was clear and monotonous. This means that the crack propagation rate is very fast in neat polybenzoxazine as a result of the highly crosslinked structure. However, a rough fracture surface was observed in both CTBN and ATBN cases. This rough morphology was believed to be caused by multiple crack initiation. In addition, several different features were observed in the morphologies of CTBN- and ATBN-modified cases.

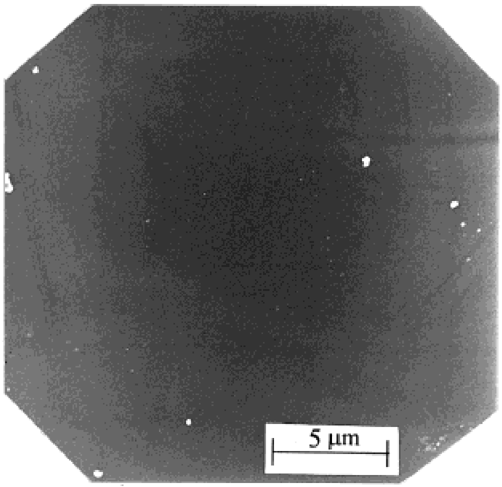
In the case of CTBN (Fig. 4), the rubber domain was obviously observed and the particle size increased as the content of rubber increased. This is attributed to the increase of the probability for rubber dissolved in the matrix phase to meet the rubber previously separated from the matrix phase. Considering the ATBN-modified cases (Fig. 5), the rubber particle size is very small compared with that in the CTBN-modified cases. This suggests that the separation rate of ATBN is slower than that of CTBN. This phenomenon is caused by the difference in compatibilities of polybenzoxazine and two types of modifiers.

The dispersed rubber particles play an important role in toughness improvement. Rubber particles blunt the sharp crack tip and disperse the stress concentrated on the equator of the rubber particle in many directions to induce the localized shear yielding. Through this process, the improvement of fracture toughness is achieved. Stress whitening and micro void, which can lower the degree of local constraint and allow further shear yielding to occur, were not observed in our study. With the viewpoint of dispersed rubber particles, it can be expected that the K_{Ic} values of the CTBN-modified polybenzoxazine should be larger than those of the ATBN-modified case. However, the trend of K_{Ic} values did not coincide with the above explanation.

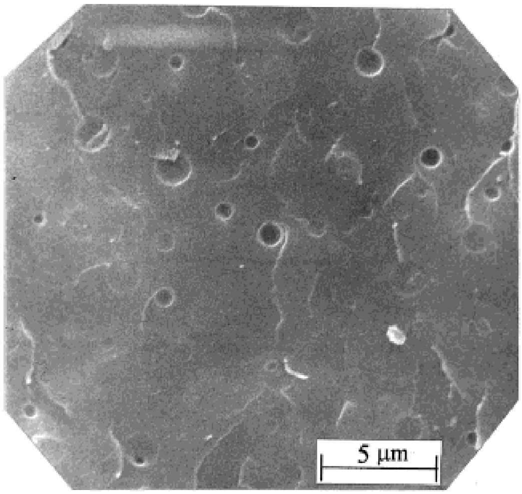
On the other hand, in rubber toughening, it was known that rubber dissolved in matrix phase as well as rubber particles finely distributed in matrix contributed to the increase of K_{Ic}. Therefore, it is necessary to calculate the amount of dissolved rubber to understand the K_{Ic} values shown in Figure 3. The amount of dissolved rubber was calculated on the basis of eq. (4). This equation was previously used in a rubber-toughened epoxy case by Chan et al.[13]

$$\frac{1}{T_g} = \frac{(1 - w_R)}{T_{gP}} + \frac{w_R}{T_{gR}} \tag{4}$$

Figure 4 Scanning electron microscopy photos of fracture surface of rubber-modified polybenzoxazine: (a) neat polybenzoxazine; (b) CTBN, 5 wt %; (c) CTBN, 10 wt %; (d) CTBN, 15 wt %; (e) CTBN, 20 wt %.



(a)



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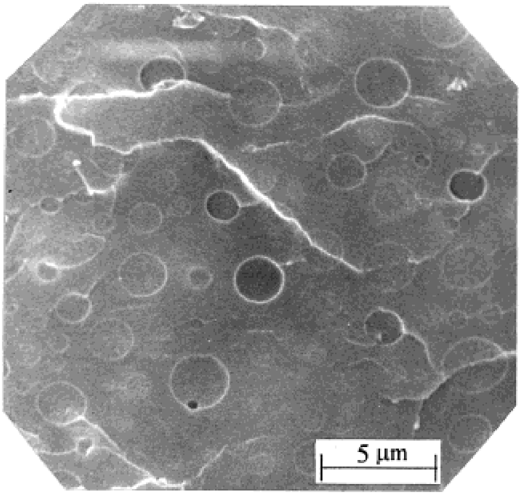

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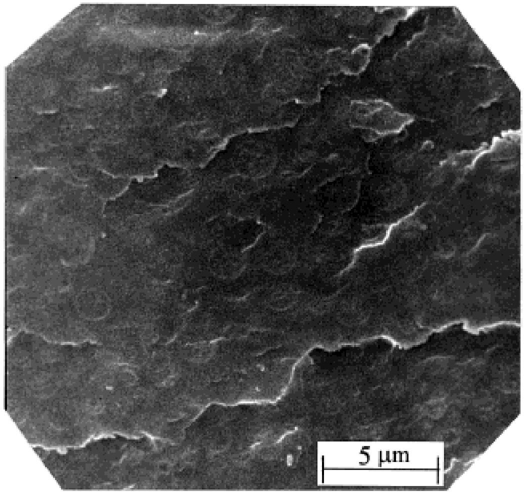

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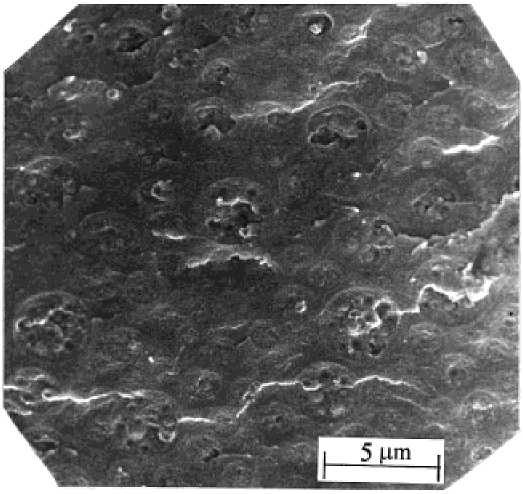

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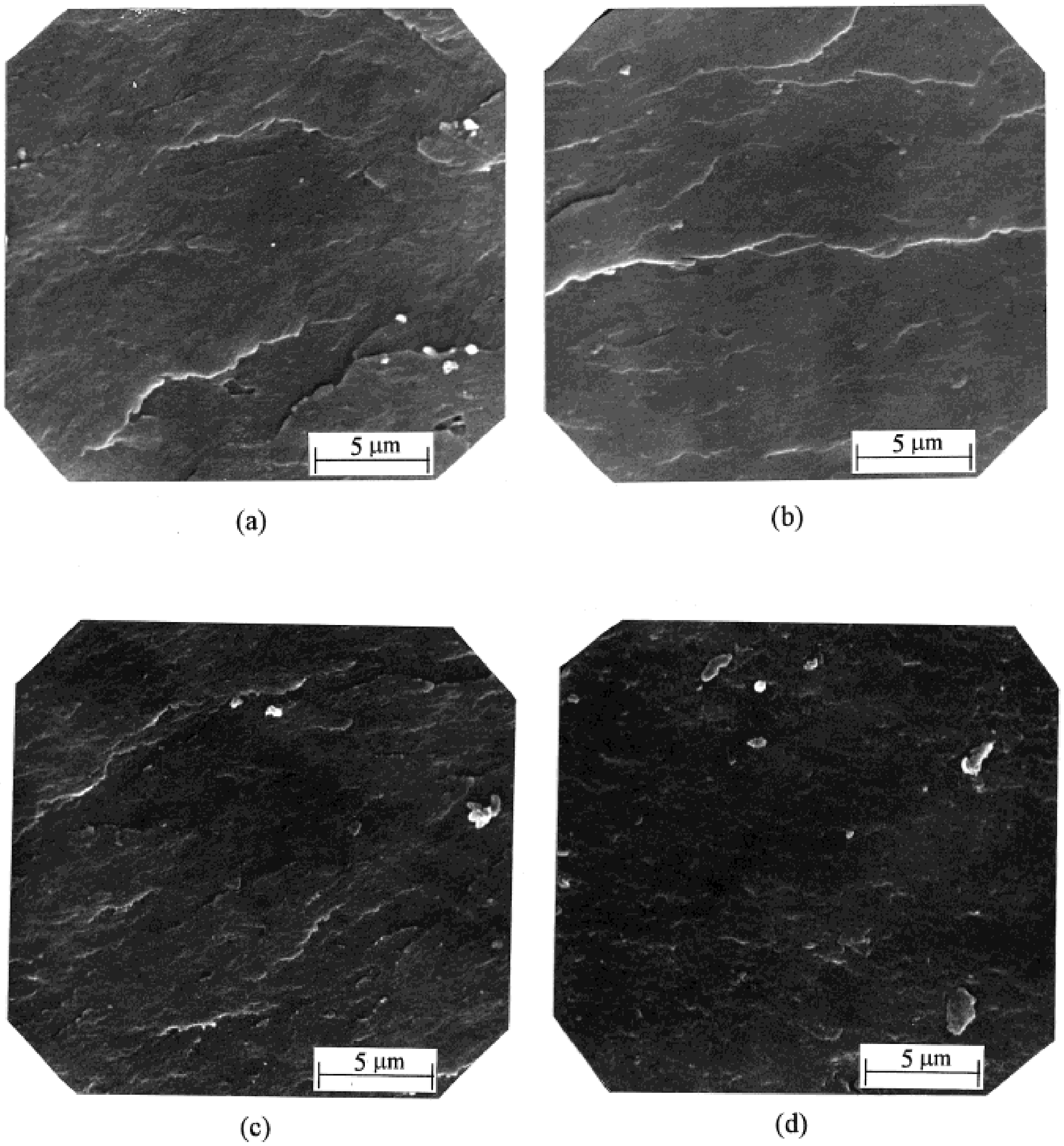

(a) (b) (c) (d)

Figure 5 Scanning electron microscopy photos of fracture surface of rubber-modified polybenzoxazine: (a) ATBN, 5 wt %; (b) ATBN, 10 wt %; (c) ATBN, 15 wt %; (d) ATBN, 20 wt %.

W_R is weight fraction of dissolved rubber, T_g is the T_g of modified polybenzoxazine, T_{gP} is the T_g of pure polybenzoxazine, and T_{gR} is the T_g of rubber. Before the above calculation was made, the glass transition temperatures of polybenzoxazine were measured as a function of rubber content and the results are given in Figure 6. It was observed that the T_g of matrix decreased as rubber content increased. This depression results from the presence of dissolved or finely dispersed rubber in matrix. The values calculated using eq. 4 were shown in Table II. In general, the rubber particles that separated perfectly have little effect on the T_g of the mixed system. Therefore, ATBN-modified polybenzoxazine has a lower T_g than that in the CTBN-modified case. From these two results, it can be shown that ATBN is more miscible with polybenzoxazine than is CTBN. The difference in miscibility is caused by the fact that ATBN has a low nitrile content and lower viscosity.

Considering Figure 3 and Table II, it can be shown that the K_{Ic} values have some relation to the amount of dissolved rubber. As particle size decreases, the K_{Ic} becomes higher. This could be explained as follows. Although the stress field near a particle is independent of particle diame-

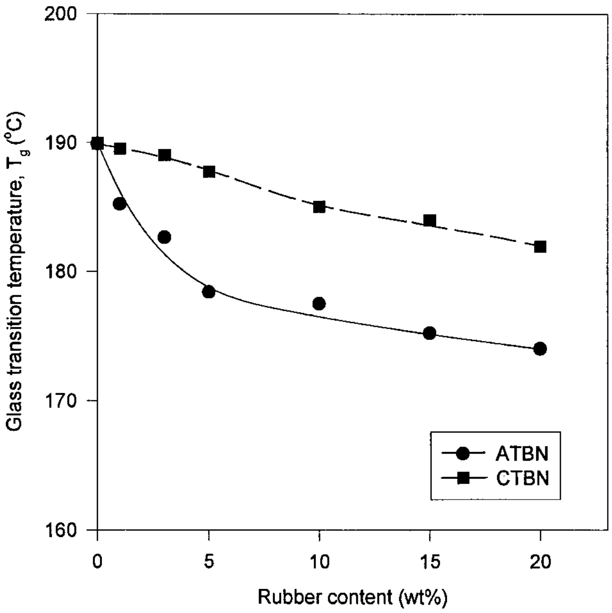

Figure 6 T_g trends in rubber modification of polybenzoxazine with CTBN and ATBN.

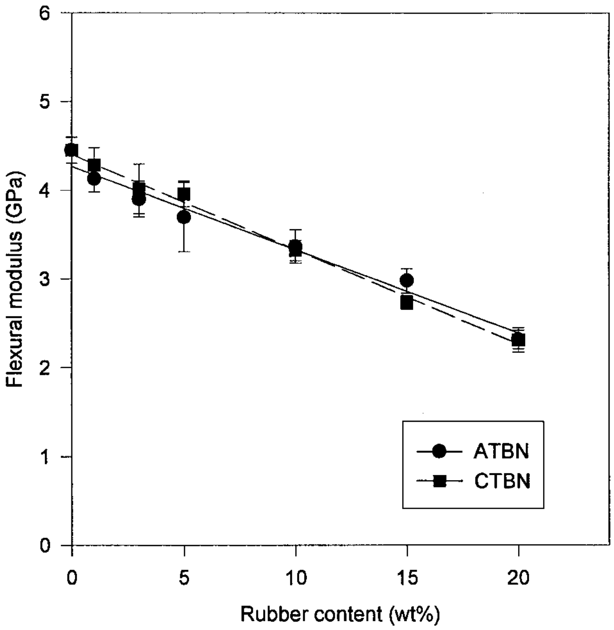

Figure 7 Flexural modulus of rubber-modified polybenzoxazine as a function of rubber content.

ter, the volume of matrix which undergoes stress concentration increases as particle diameter increases. Therefore, when a large crack is included in the stress concentration area, it acts as a strong weak point of the matrix. It reduces the K_{Ic} of the matrix according to Griffth's theory.[14] For this reason, the CTBN-modified polybenzoxazine does not show dominant improvement compared with the ATBN-modified case. In addition, because the ATBN-modified polybenzoxazine has more particle equator to form more rough surface because of its small particle size, its K_{Ic} is higher than that of the CTBN-modified polybenzoxazine. As a result, it can be concluded that the amount of dissolved rubber is more important to the toughness improvement of polybenzoxazine than is the size of dispersed rubber particles. In each rubber, it was observed that the increase of K_{Ic} is alleviated with the increase of rubber content as a result of the decrement of particle surface area.

Table II The Rubber Content Soluted in Polybenzoxazine Phase

Rubber Content in Rubber-Modified Polybenzoxazine (wt %)	ATBN Content Soluted in Polybenzoxazine Phase (wt %)	CTBN Content Soluted in Polybenzoxazine Phase (wt %)
0	0	0
1	0.94	0.09
3	1.48	0.20
5	2.35	0.49
10	2.54	1.09
15	3.03	1.33
20	3.28	1.80

The brittle characteristic of polybenzoxazine can be reduced by rubber modification. However, polymer undergoes reduction of modulus as a result of the addition of rubber. Modulus is regarded as an important mechanical property in structural materials.

Figure 7 shows the flexural modulus of rubber-modified polybenzoxazine as a function of rubber content. As the rubber content increases, the flexural modulus of rubber-modified polybenzoxazine decreases linearly. Although the terminal group and modulus of CTBN and ATBN are different, flexural moduli of rubber-modified polybenzoxazine are nearly the same. This is attributed to the fact that in determining the modulus of rubber-modified polymer, the modulus of matrix is the more important than that of rubber because rubber has a poor modulus.

The size of the rubber particle increases as rubber content increases in the modification with CTBN, but the modulus of CTBN-modified polybenzoxazine decreases linearly. This suggests that there is a good interfacial bond between CTBN and matrix. If the interface between CTBN and matrix has poor interfacial bond strength, the increase of particle size, which is not linear, will

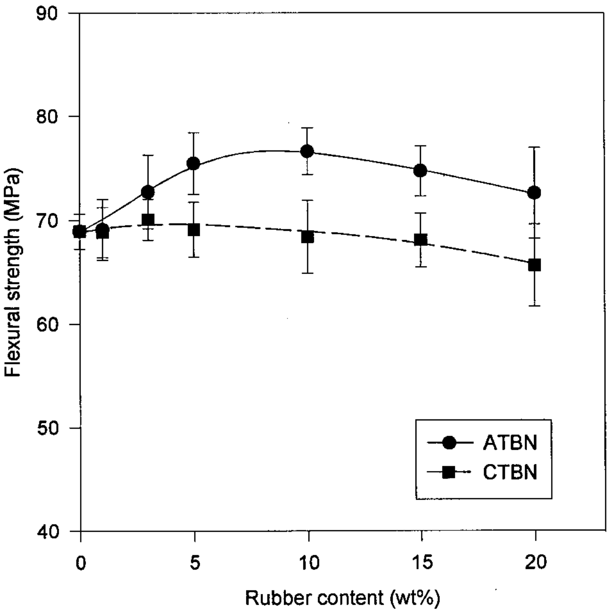

Figure 8 Yield strength change as a function of rubber content.

cause the nonlinearity in modulus change as a result of the nonlinearity of the shear stress increment. If plain stress is applied, shear stress takes place at the interface between rubber and matrix. The decrement of the moduli of the two systems can be affected by the resistance to shear stress that is introduced by rubber particles. Interfacial bonding between matrix and rubber is very important in the modulus of rubber-modified polybenzoxazine for this reason.[15] In spite of different particle sizes, the same moduli of the ATBN-modified polybenzoxazine and the CTBN-modified polybenzoxazine can be explained in this way.

In this system, the functional groups of matrix, which can react with the terminal group of rubber, are abundant. CTBN has carboxyl groups at its chain ends, and these functional groups can react with activated phenolic hydroxyl groups in polybenzoxazine to form ester linkage at high curing temperature and hydrogen bonds. Therefore, the interfacial bond of rubber and matrix will be sufficiently strong. ATBN has amino groups at its chain ends, which can react with imines created during the curing step. This reaction is easy because imine is very electrophilic and the amino group is very nucleophilic. The amino groups in ATBN can also form hydrogen bonds with activated phenolic hydroxyl groups in polybenzoxazine. The good chemical bond at the interface between rubber and matrix sufficiently transfers the stress to the rubber phase. Therefore, each rubber particle can absorb stress equally even though more rubber is added. The rule of mixture can be applied to these systems.

From Figure 8, it can be shown that the flexural strength of the ATBN-modified polybenzoxazine increases with the increase of rubber content, but that of CTBN-modified polybenzoxazine decreases slightly. Usually, when rubber is added to matrix, the flexural strength of the mixed system decreases by rule of mixture, that is, volume fractional average of two components, as a result of the poor strength of rubber. However, ATBN-modified systems show the opposite result.

Polybenzoxazine has a high modulus and a very brittle characteristic. Brittle materials are very sensitive to internal flaw. When specimens are tested by the three-point bending mode, the internal flaw can act as a stress concentration point and fracture can initiate from this point. Consequently, brittle fracture can occur at small load. However, when rubber is added to polybenzoxazine, the content of rubber dissolved in polybenzoxazine increases. The dissolved rubber modifies the brittleness of polybenzoxazine, and this reduces the flaw sensitivity of polybenzoxazine. The modification of brittleness can be seen in Figure 9. As rubber content increases, the yield strain of modified polybenzoxazine increases to double at 20 wt % of rubber content. Therefore, modified polybenzoxazine becomes more resistant to load.

In the modification with 5 wt % of ATBN, flexural strength shows a maximum. This can be explained by the T_g trend in Figure 6. In Figure 6,

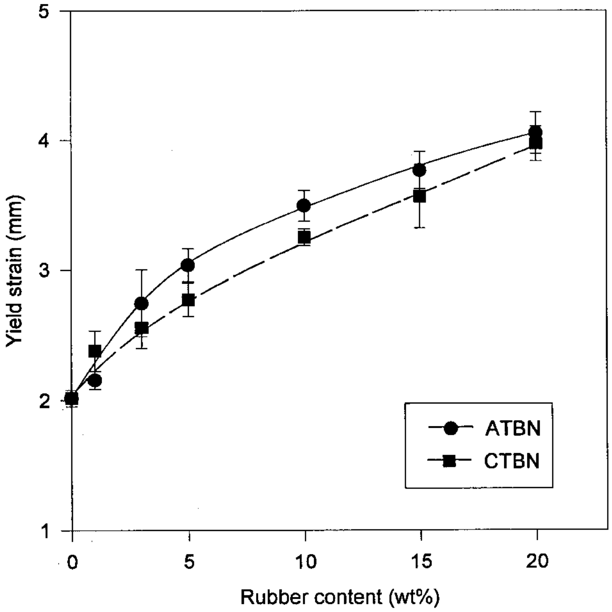

Figure 9 Yield strain of rubber-modified polybenzoxazine as a function of rubber content.

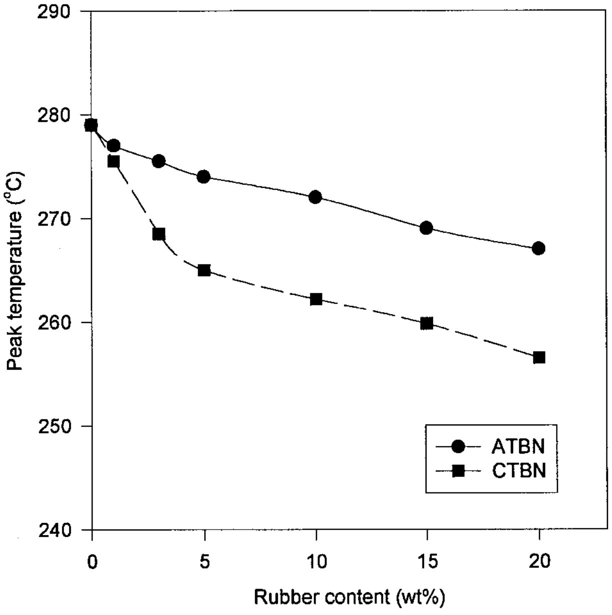

Figure 10 Cure peak temperature change as a function of rubber content.

there is a steep decrease in T_g up to 5 wt %. This means that the amount of rubber dissolved in the polybenzoxazine phase increases steeply up to 5 wt % and that the increment of rubber dissolved in polybenzoxazine decreases above 5 wt %. As mentioned above, the brittleness modification of matrix is predominantly conducted by dissolved rubber in polybenzoxazine, so 5 wt % is competition criterion between brittleness modification and strength reduction, which is caused by rule of mixture as a result of the poor strength of rubber. Compared with the CTBN-modified polybenzoxazine, the ATBN-modified polybenzoxazine has higher flexural strength. This can also be explained by the dissolved rubber content in view of T_g, as mentioned above.

The curing peak temperatures of the polybenzoxazine/rubber system from the dynamic DSC experiment are shown in Figure 10. When rubber is added to polybenzoxazine, the peak temperature of curing decreases. This is caused by their terminal groups. The reaction mechanism of polybenzoxazine was studied by Gu et al.[16] According to that article, the reaction is initiated by the ring-opening reaction of the benzoxazine structure. The six-membered ring is very stable, so the ring-opening reaction is the rate-determining step in the curing of benzoxazine. CTBN added to polybenzoxazine is thought to act as an acid catalyst. It helps ring opening by dint of making phenolic oxygen very electrophilic by the addition of hydrogen ion to oxygen. This effect reduces the reaction constant of benzoxazine, so the peak temperature decreases. However, there is no acid in ATBN, so the above mechanism cannot apply to the decrease of peak temperature of the polybenzoxazine/ATBN system. ATBN does not act as a catalyst, but it acts as a stabilizer of the ring-opened compound. The nonpaired electrons in the amine group of ATBN can react with unstable imine in the ring-opened compound, so the concentration is lower in the ATBN-added case than in the neat polybenzoxazine case. The reaction is driven by this decrease of concentration, so the curing peak temperature decreases. In view of rubber particle size, the gelation time is important because the gelation forbids the precipitation of rubber dissolved in the matrix phase. However, the increment of curing rate is not fast enough to prevent rubber dissolved in polybenzoxazine from precipitating. Considering Figure 4, the rubber particle size was not maintained with increasing the rubber content and the size of rubber particles in CTBN modification was the larger.

CONCLUSIONS

The K_{Ic} of polybenzoxazine increased from 0.6 to 1.8 MPa · m$^{1/2}$ with the increase of rubber content. The modification with ATBN showed the larger increase in fracture toughness than the modification with CTBN. In toughening polybenzoxazine with liquid rubber, the particle size and the content of rubber dissolved in matrix phase are the main factors of the toughness improvement. In modification with ATBN, the rubber particle diameter was nearly 0.2 μm, and in the modification with CTBN, it was 2.5 μm. The smaller particle size, which means good distribution of rubber and the more dissolved rubber, showed a better toughening effect. The size of the rubber particle and the content of rubber dissolved in matrix phase depend on the solubility of rubber. The flexural strength of polybenzoxazine increased slightly or was maintained, and its flexural modulus decreased up to 2.4 GPa as rubber content increased.

The adding of CTBN or ATBN accelerated the cure rate of polybenzoxazine. However, in this study, this result nearly affected the precipitation rate of rubber, which is important for particle size because cure rate was not sufficiently fast.

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