

Toughening Bismaleimide Resins by Reactive Liquid Rubbers

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Synopsis

The modification of bismaleimide resins with carboxyl-terminated butadiene-acrylonitrile rubbers (CTBN) was studied. The effects of the rubbers on mechanical and thermal properties such as flexural strength, tensile strength, fracture toughness, glass transition temperature, and decomposition temperature of the rubber-modified bismaleimide resins are discussed. The morphology of these resins were investigated by means of scanning electron microscopy and dynamic mechanical analysis. Addition of the rubbers improved the toughness of the bismaleimide resins without significant reductions in heat resistance of the resins.

INTRODUCTION

Bismaleimides afford crosslinked resins with high-temperature resistance. The cured bismaleimide resins, however, are extremely brittle because of the highly crosslinked structure. This disadvantage of the resins have been improved by chain-extended bismaleimide prepolymer molecules, prepared by the Michael addition reaction of bismaleimides with diamines¹⁻⁴ or dithiols.^{5,6} The chain extension of bismaleimides, however, induces a reduction in thermal properties such as decomposition temperature, glass transition temperature, and thermal stability.

It is well known that the addition of a reactive liquid rubber can improve the toughness of epoxy resins without significant reductions in thermal and mechanical properties. Only a few papers on the modification of bismaleimide resins with rubbers have been reported, although there are many papers on rubber-modified epoxy resins.⁷⁻¹¹

St. Clair and St. Clair¹² have reported an increase in the adhesive fracture energy of nadic-terminated polyimides, LARC-13, by the addition of amine-terminated silicone rubbers, whereas Varma et al.¹³ have reported an increase in short beam shear strength of bismaleimide resins by the addition of amine-terminated rubbers. Shaw and Kinloch¹⁴ observed a significant increase in the fracture energy of bismaleimide resins by the modification with a carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber.

Recently new bismaleimides containing ether linkages were prepared and characterized.¹⁵ Mixture systems of two bismaleimide species that form a eutectic mixture become too easy to handle because of their low melting point and long pot life.

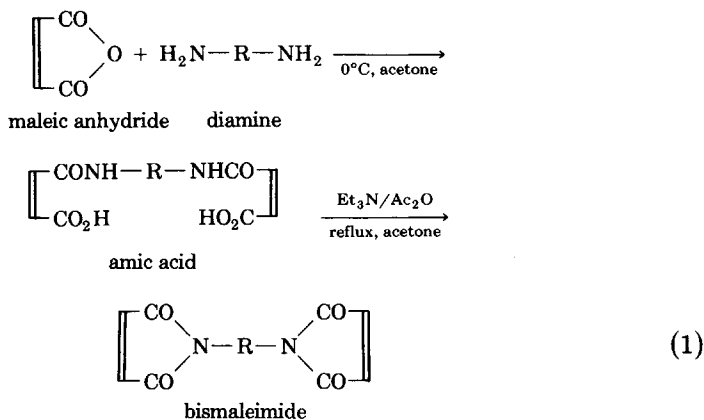
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In this paper, we report on the modification of these mixture systems with CTBN. The thermal and mechanical properties of the modified resins were studied as a function of the amount of and the composition (acrylonitrile content) of the added rubbers, and a relationship between the morphology and the fracture energy of the modified resins was also discussed.

EXPERIMENTAL

Materials

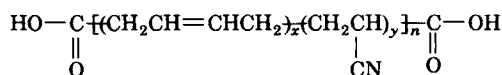
Various kinds of bismaleimides were prepared according to:



Name	R
BDM	
BPPP	
3,3'-BPPS	

2,2-Bis[4-(4-maleimidophenoxy)phenyl] propane (BPPP) was prepared¹⁵ from the corresponding diamine and maleic anhydride: mp 119–120°C. Bis[4-(3-maleimidophenoxy)phenyl] sulfone (3,3'-BPPS) was prepared¹⁵ from the corresponding diamine and maleic anhydride: mp 104–108°C. A commercial bismaleimide, 4,4'-bismaleimidodiphenylmethane (BDM), was recrystallized from 1 : 1 CHCl₃/MeOH: mp 159–160°C (Lit. 157–158°C).¹

The rubber modifiers employed are low-molecular-weight copolymers of butadiene and acrylonitrile manufactured by B. F. Goodrich Co. under the trade name Hycar CTBN:



Four rubbers of varying acrylonitrile content were employed. Hycar CTB corresponding to the acrylonitrile content zero wt % is carboxyl-terminated

TABLE I
Properties of Reactive Liquid Rubbers^a

Hycar	CTBN 1300 × 13	CTBN 1300 × 8	CTBN 1300 × 31	CTB 2000 × 162
Molecular weight	3500	3500	3500	4800
Acrylonitrile content (wt %)	27	17	10	0
Viscosity, Brookfield (cP), 27°C	625,000	125,000	55,000	40,000
Solubility parameter	9.14	8.77	8.45	8.04

^a Materials and data supplied by B. F. Goodrich Co.

polybutadiene rubber. Chemical and physical properties of these rubbers supplied by the manufacturer are listed in Table I.

The prereaction was carried out by adding the liquid rubber to the molten basic bismaleimide resins for 5 h at 130°C. Specimens of the CTBN-modified bismaleimide resins were molded by means of a press for 2 h at 200°C and cured in an oven for 10 h at 250°C.

Measurement of Mechanical Properties

Flexural testing and tensile testing (JIS K6911) were conducted on a Shimadzu Model S-500 Autograph. Fracture properties were determined by using compact-tension specimens (Fig. 1).¹⁶ A sharp razor blade was used to indicate a starting crack. The specimen was mounted in a Toyo Baldwin Model Tensilon VTM1-500BW and was loaded at a constant crosshead rate 1 mm/min. A load P was recorded and the value of the stress-intensity factor,

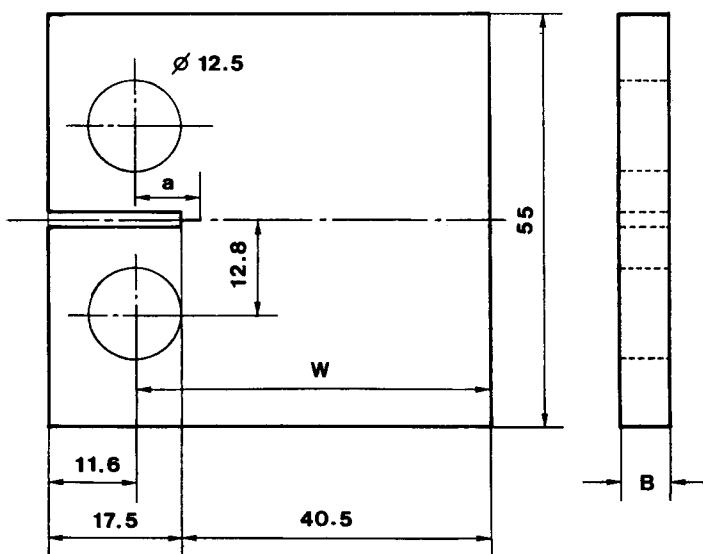


Fig. 1. Schematic diagrams; compact-tension specimen.

K_{IC} , was calculated with

$$K_{IC} = P_C \times Y \times a^{1/2} / (B \times W) \quad (2)$$

$$Y = 29.6 - 185.5(a/w) + 655.7(a/w)^2 - 1017(a/w)^3 + 638.9(a/w)^4 \quad (3)$$

where P_C = load at crack initiation; B = thickness of specimen (6.5 mm); W = width of specimen (46.4 mm); and a = crack length. The K_{IC} values were converted to fracture energy G_{IC} by eq. (4), where ν is Poisson's ratio (0.35):

$$G_{IC} = K_{IC}^2(1 - \nu^2)/E \quad (4)$$

Measurement of Thermal Properties

Differential scanning calorimetry (DSC) was accomplished with a Du Pont Model 910 at a heating rate of 10°C/min in air.

Thermogravimetric analysis (TGA) was accomplished with a Shimadzu Model TG-20 at a heating rate of 10°C/min in air or in a nitrogen atmosphere.

Thermomechanical analysis (TMA) was conducted with a Rigaku Denki Model TMA8140 at a heating rate of 10°C/min in air.

TABLE II
Thermal Properties of Bismaleimides

Bismaleimide	mp ^a (°C)	T_1^b (°C)	T_{exo}^c (°C)	T_2^d (°C)	GT ^e (s)
BDM	158	174	233	316	130
BPPP	121	203	302	344	510
3,3'-BPPS	104	198	211, 272	330	1060
PB resin	92-136	185	249	344	720
SB resin	94-135	171	238	328	1650

^aMelting point by DSC.

^bOnset temperature for curing reaction by DSC.

^cExothermal peak temperature by DSC.

^dTemperature for completion of reaction by DSC.

^eGel time at 200°C.

TABLE III
Thermal Properties of Cured Bismaleimide Resins

Cured resin	T_d^a		T_g^b (°C)
	In air (°C)	In N ₂ (°C)	
BDM	416	500	342
BPPP	412	464	312
3,3'-BPPS	414	436	288
PB resin	413	482	340
SB resin	418	465	340

^aInitial weight loss temperature of bismaleimide resin, cured for 10 h at 280°C, by TGA.

^bGlass transition temperature of bismaleimide resin, cured for 10 h at 280°C, by TMA.

Dynamic Mechanical Analysis (DMA)

DMA was conducted on rectangular strip measuring $40 \times 10 \times 2$ mm by using a Du Pont Model 982 between -150 and 400°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Scanning Electron Micrographs (SEM)

SEM was obtained on fracture surfaces of cured rubber-modified bismaleimide resins with a Hitachi Model S-450.

RESULTS AND DISCUSSION

Preparation of CTBN-Modified Bismaleimide Resins

Tables II and III show the thermal properties of bismaleimides used in this study and their cured resins. The preparation of new bismaleimides, 2,2-bis[4-(4-maleimidophenoxy)phenyl] propane (BPPP) and bis[4-(3-maleimidophenoxy)phenyl] sulfone (3,3'-BPPS) is described elsewhere.¹⁵ These bismaleimides containing aromatic ether bonds had long gel times, and these cured resins showed high temperature resistance.

The basic bismaleimide resins employed are PB resin and SB resin: PB resin is a mixture of BDM 50 wt % and BPPP 50 wt %; SB resin is a mixture

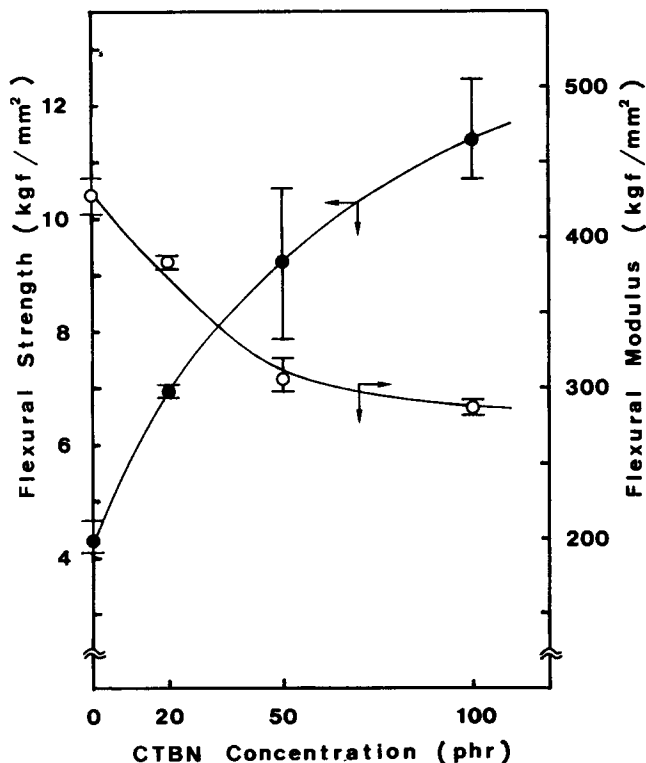


Fig. 2. Effect of CTBN concentration of CTBN-modified PB resin on flexural strength and flexural modulus: PB resin, cured for 10 h at 280°C , and CTBN-modified PB resin, cured for 10 h at 250°C , were tested.

of BDM 50 wt % and 3,3'-BPPS 50 wt %. The prereaction of CTBN with bismaleimides is needed to improve the properties of the modified resins. The two basic resins formed a eutectic mixture, resulting in low melting points and long gel times (long pot life of melt), as shown in Table II. This made it possible to do the prereaction of CTBN with the basic resins in molten states without using solvents. If the prereactions are carried out in solution, it is difficult to remove the solvents.

As the prereaction proceeded, the compatibility of CTBN and the basic resins increased. This result suggests that the bismaleimides are reacted (copolymerized) with CTBN in this stage. The compatibility was dependent on the acrylonitrile (AN) content of CTBN. The rubber of higher AN content (27 wt %) was more compatible than the rubber of lower AN content (10 wt %).

The prereaction was followed by the analysis of the carboxyl functions of CTBN. When a mixture of PB resin and CTBN 1300 \times 8 (100 phr) was heated for 5 h at 130°C, the carboxyl content hardly changed compared with the original one, indicating that the carboxyl functions did not add to the maleimide group via a Michael reaction. It is known that polyisoprene is radically crosslinked in the presence of catalytic amounts of bismaleimide: The crosslinked network contains linkages between the allylic carbon of the rubber and the maleimide C—C double bonds.¹⁷ These results suggest that

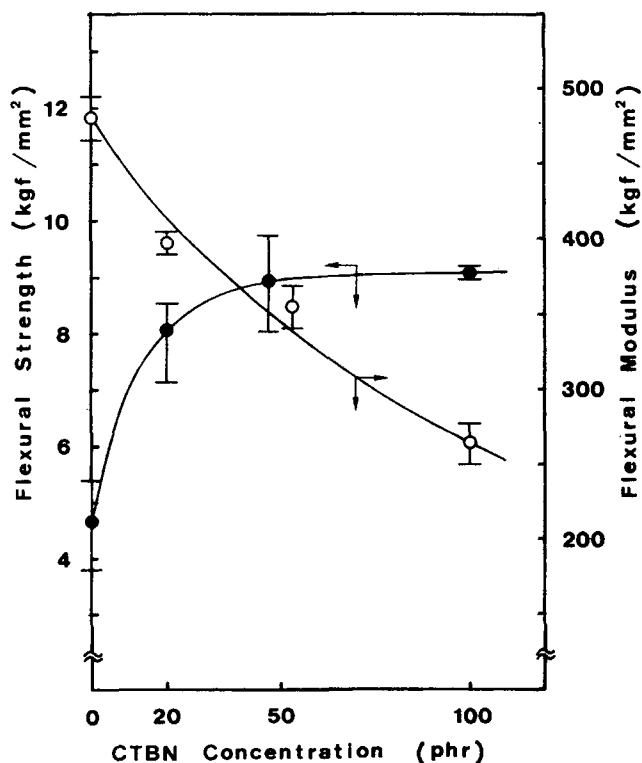


Fig. 3. Effect of CTBN concentration of CTBN-modified SB resin on flexural strength and flexural modulus: SB resin, cured for 10 h at 280°C, and CTBN-modified SB resin, cured for 10 h at 250°C, were tested.

the prereaction of the bismaleimides and CTBN yields products (copolymers) with a structure in which the maleimide C—C double bonds have coupled with the reactive sites, presumably the allylic carbon, of CTBN.

Mechanical Properties of CTBN-Modified Bismaleimide Resins

Figures 2 and 3 show the results of flexural tests of PB and SB resins modified with CTBN 1300 × 8. The flexural strength of the modified resins increased with increasing CTBN concentration. The flexural strength of PB resin modified with 50 phr of CTBN was about twice greater than that of unmodified PB resin. The flexural modulus of the CTBN-modified resins reduces as CTBN concentration increases.

Figure 4 shows the result of tensile tests of PB resin modified with CTBN 1300 × 8. The tensile strength and elongation at break increased with increasing CTBN concentration. In the case of the resin modified with 50 phr of CTBN, the tensile strength and the elongation at break are about 3 times and 4 times, respectively, greater than those of the basic resin.

These results indicate that the basic bismaleimide resins (PB resin and SB resin) are toughened by the modification with the reactive liquid rubber CTBN.

Thermal Properties of CTBN-Modified Bismaleimide Resins

Figure 5 shows the effect of CTBN concentration on initial weight loss temperature T_d for PB and SB resins modified with CTBN 1300 × 8. The increased rubber concentration resulted in a small reduction in T_d ; e.g., the value of T_d changes from 465°C for unmodified SB resin to 437°C for the CTBN (20 phr)-modified resin.

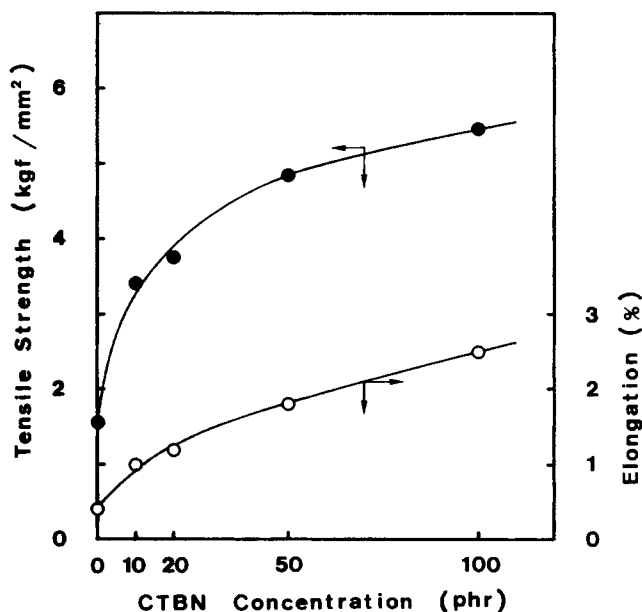


Fig. 4. Effect of CTBN concentration of CTBN-modified PB resin on tensile strength and elongation at break: PB resin, cured for 10 h at 280°C, and CTBN-modified PB resin, cured for 10 h at 250°C, were tested.

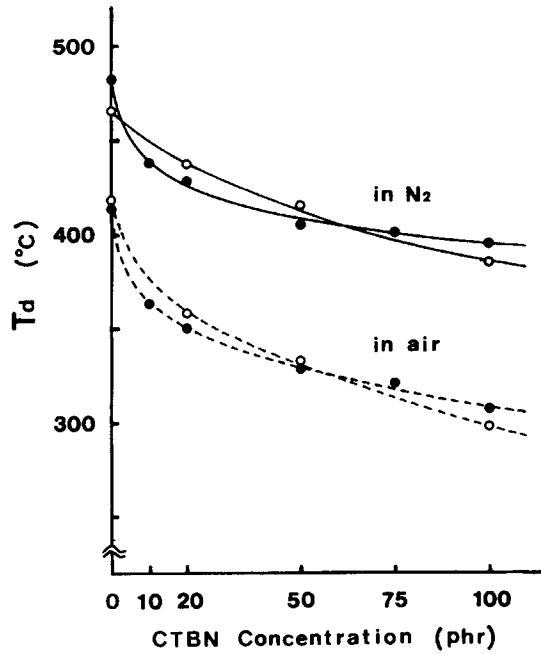


Fig. 5. Effect of CTBN concentration on initial weight loss temperature T_d of CTBN-modified PB resin and SB resin: (●) CTBN-modified PB resin; (○) CTBN-modified SB resin.

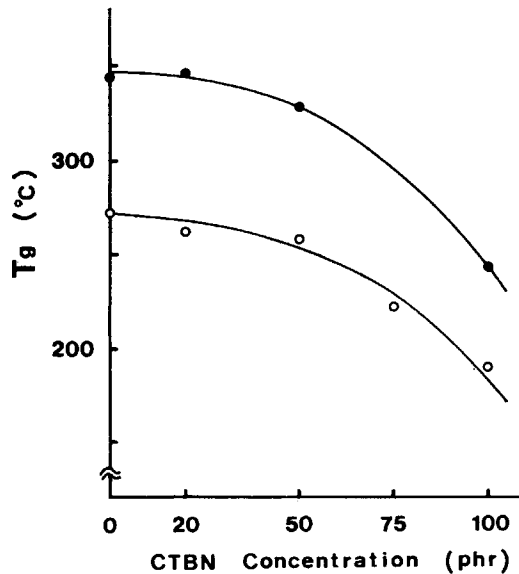


Fig. 6. Effect of CTBN concentration on glass transition temperature T_g of CTBN-modified PB resin; T_g was obtained from TMA. Curing condition: (○) 250°C, 5 h; (●) 280°C, 10 h.

The influence of CTBN concentration on glass transition temperature T_g obtained from TMA is indicated in Figure 6. The value of T_g for the modified resins, cured for 5 h at 250°C, scarcely decreased up to 50 phr of CTBN. The modified resins which were postcured for 10 h at 280°C showed a similar trend. As expected, the postcured resins exhibited higher T_g .

Consequently, the bismaleimide resins modified with 20–50 phr of CTBN as well as the unmodified resins have high heat resistance.

Dynamic Mechanical Analysis (DMA) of the CTBN-Modified Bismaleimide Resins

The dynamic mechanical properties of PB resin modified with CTBN 1300 × 8 are indicated in Figures 7 and 8. The $\tan \delta$ peak at -55°C for the basic resin is ascribed to the β -relaxation of the cured bismaleimide. The α -relaxation (T_g) of the cured bismaleimide, however, was not observed within the temperature range of DMA. The α -relaxation of the resins modified with

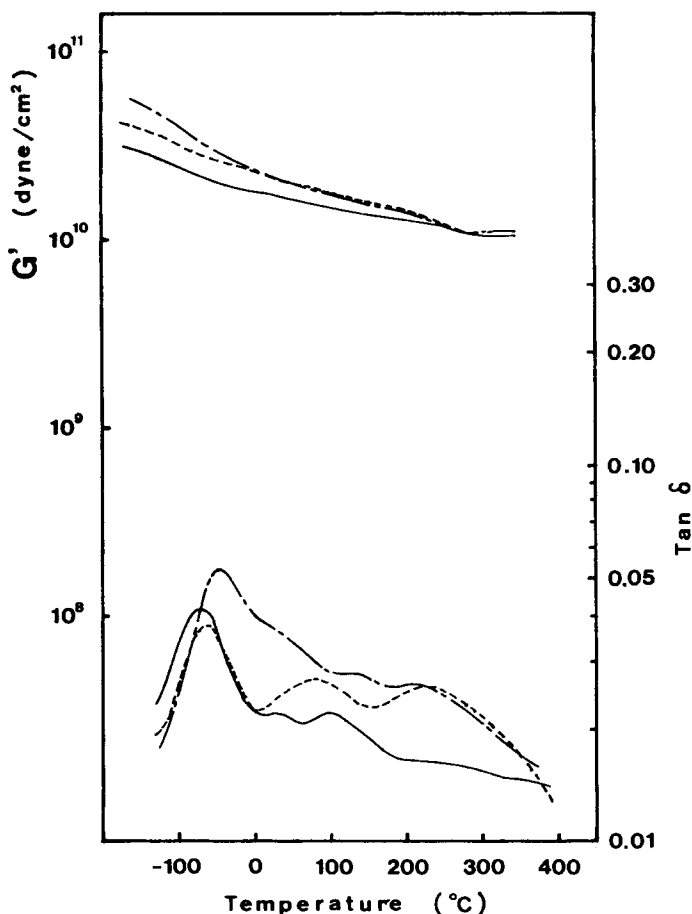


Fig. 7. DMA results for the CTBN-modified PB resin. CTBN concentration, curing condition: (—) 0 phr, 250°C, 24 h; (---) 10 phr, 250°C, 5 h; (- - -) 20 phr, 250°C, 5 h.

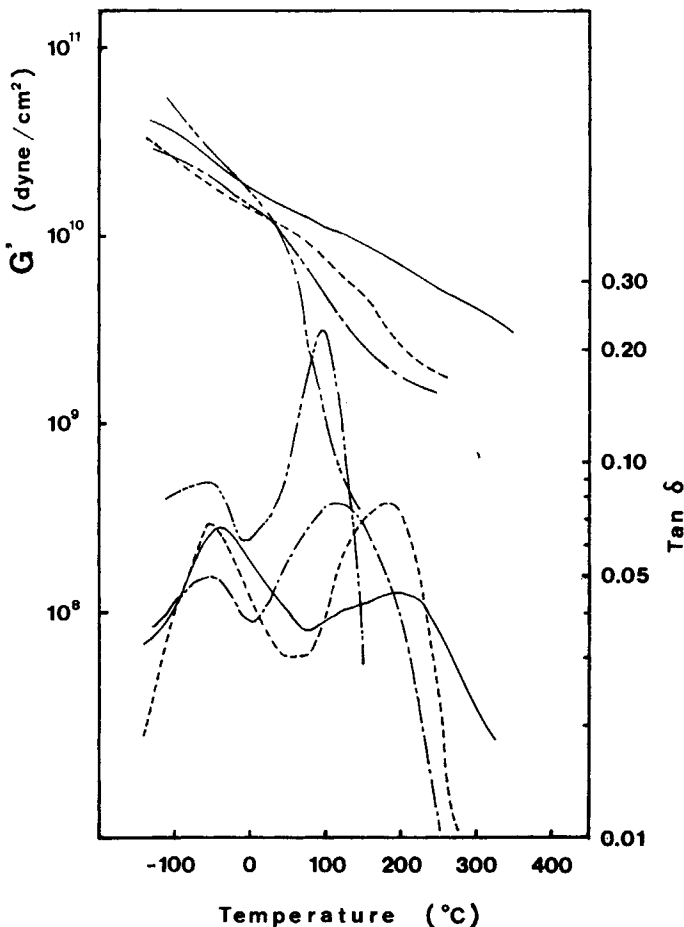


Fig. 8. DMA results for the CTBN-modified PB resin. CTBN concentration, curing condition: (—) 50 phr, 250°C, 5 h; (---) 75 phr, 250°C, 5 h; (- - -) 100 phr, 250°C, 5 h; (----) 200 phr, 250°C, 5 h.

10–20 phr of CTBN was not observed either. The α -relaxation temperatures for these resins may be above 400°C.

In the case of the resin modified with 50 phr of CTBN, the new $\tan \delta$ peak appeared at 202°C. This peak may be attributed to the α -relaxation for the copolymer of CTBN and the bismaleimide. As the rubber concentration increases over 50 phr, the peak temperatures in $\tan \delta$ for the copolymers become lower—202, 186, 115, 96°C—and the intensity of the peaks becomes larger. This result suggests that both the copolymer contents in the rubber-modified resins and CTBN content in the copolymer increase with suggesting CTBN concentration.

The dynamic modulus G' remained constant up to 50 phr of CTBN, indicating that the resins retain good mechanical properties at high temperature.

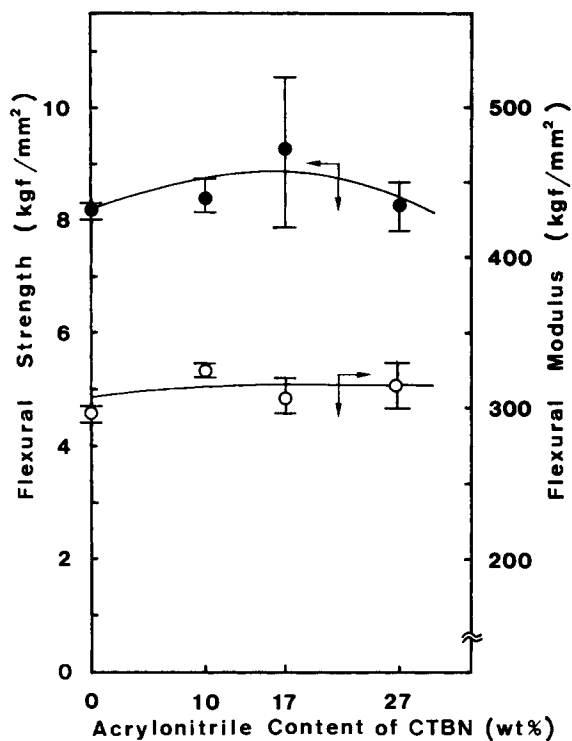


Fig. 9. Effect of acrylonitrile content of rubber on flexural strength and flexural modulus; CTB- or CTBN-modified PB resin containing 50 phr rubber were tested.

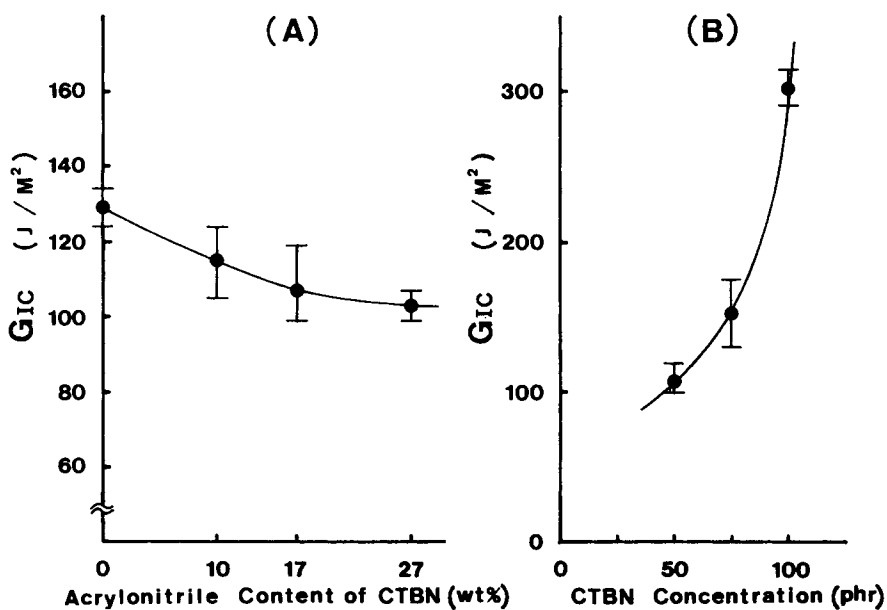
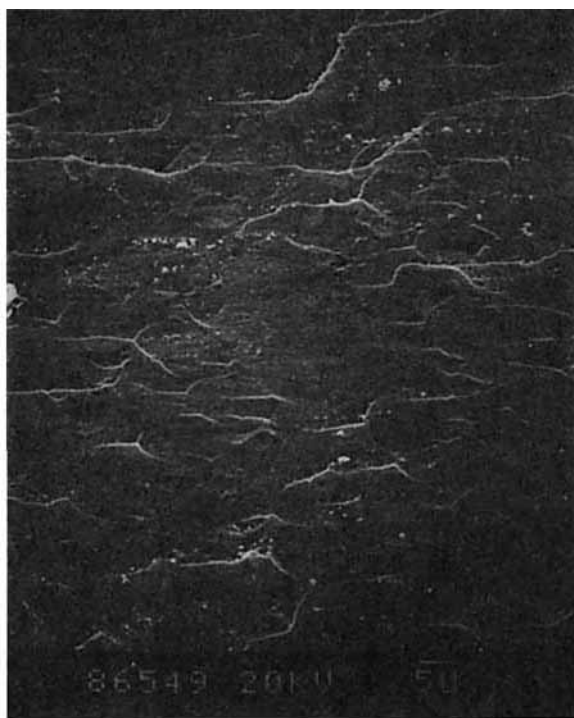


Fig. 10. Fracture energy G_{IC} of rubber-modified PB resin: (A) Effect of acrylonitrile content of rubber; rubber-modified PB resin containing 50 phr rubber; (B) Effect of CTBN (AN 17 wt %) concentration.



(a)

10 μm

Fig. 11. SEM micrograph of fracture surface of CTB- or CTBN-modified PB resin containing 50 phr rubber: (a) AN 0 wt % (CTB 2000 \times 162); (b) AN 10 wt % (CTBN 1300 \times 31); (c) AN 17 wt % (CTBN 1300 \times 8); (d) AN 27 wt % (1300 \times 13).

Effect of Acrylonitrile Content of CTBN on Mechanical Properties and Morphology of the Modified Resins

Figure 9 shows the results of flexural test of PB resin modified by use of the rubbers with various acrylonitrile (AN) contents. The flexural strength and modulus were independent of the AN content, when the resins were modified with 50 phr of the rubber.

The dependence of the fracture energy G_{IC} of the modified resin on the AN content is presented in Figure 10(A). The G_{IC} of the resins increases with a decrease in the AN content of the rubber. On the other hand, when 100 phr of CTBN (AN 17 wt %) was added to PB resin, the G_{IC} of the modified resin was about three times greater than that of the resin modified with 50 phr of CTBN, as shown in Figure 10(B). The compact-tension specimens containing less than 50 phr of CTBN could not be prepared because of their brittleness.

The scanning electron micrographs for the fracture surface of the rubber-modified resins are shown in Figure 11. In the case of the resin modified with



(b) 
10 μm

Fig. 11. (Continued from the previous page.)

the rubber containing no AN unit (CTB), the existence of the microphase separation in the resin was clearly visible [Fig. 11(a)]. The particles with sizes of 5–15 μm dispersed in the resin matrix. A similar microphase separation was also observed for the resin modified by use of CTBN with 10 wt % of AN content [Fig. 11(b)]. The particle size was over the range of 2–5 μm . These dispersed particles would be composed of the copolymer of CTBN and the bismaleimide. In the case of the rubber with 17 wt % of AN content, the interface between the particle and the matrix was not clearly visible [Fig. 11(c)]. As CTBN containing 27 wt % of AN unit was added to the basic resin, the microphase separation in the modified resin was not visible, that is, this resin was homogeneous [Fig. 11(d)].

The result shown in Figure 11 concludes that the increased AN content of the rubber enhances its compatibility with the bismaleimide resin. This behavior can be reasonably explained in terms of the solubility parameter (SP). The SP value of 4,4'-bismaleimidodiphenylmethane, which is calculated on the basis of Hoy's method,¹⁸ is 11.0, whereas the SP values of the rubbers are 8.04–9.14, as shown in Table I. Therefore, the higher polar rubber with higher AN content is more compatible with the bismaleimide.



(c)

10 μm

Fig. 11. (Continued from the previous page.)

The flexural strength and modulus of CTB- and CTBN-modified PB resins were independent of the morphology of these resins, whereas the fracture energy G_{IC} of the resin modified with the rubber of lower SP (lower AN content) was greater than that of the resin containing the rubber with higher SP (higher AN content) on account of the microphase-separated structure. In general, microphase-separated structure of resins can improve toughness of resins,^{9-11,19,20} because the rubber particles enhance the extent of plastic shear deformations in the matrix at the crack tip due to interactions between the stress field ahead of the crack and the rubber particles, and in this case is also.

The mechanical and thermal properties of the commercial bismaleimide resin, Kerimide 601, were studied in order to compare with those of the CTBN-modified PB and SB resins. The properties of Kerimide 601 and the modified resins were summarized in Table IV. The flexural strength of Kerimide 601 was about twice as great as those of PB and SB resin modified with 50 phr of CTBN. The fracture toughness of PB resin modified with 50 phr of CTBN, however, was greater than that of Kerimide 601. The increased fracture toughness is due to the morphology, that is, the microphase-separated structure.



(d) 
10 μ m

Fig. 11. (Continued from the previous page.)

TABLE IV
Thermal and Mechanical Properties of Kerimide 601 and CTBN-Modified Resins

Resin	T_d^a		T_g^b (°C)	Flexural strength ^c (kgf/mm ²)	Flexural modulus ^c (kgf/mm ²)	G_{IC}^d (J/m ²)
	In air (°C)	In N ₂ (°C)				
Kerimide 601	378	402	300	16.3	434	106
CTBN 1300 × 31 (50 phr) modified PB resin	322	412	328	8.4	324	115
CTBN 1300 × 8 (50 phr) modified SB resin	333	415	—	9.0	345	—

^aInitial weight loss temperature of the resin, cured for 10 h at 250°C, by TGA.

^bGlass transition temperature of the resin, cured for 10 h at 280°C, by TMA.

^cThe resin, cured for 10 h at 250°C, were tested (JIS K6911).

^dThe resin, cured for 10 h at 250°C, were tested.¹⁶

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