

Dynamic Mechanical Properties and Adhesive Strengths of Epoxy Resins Modified with Liquid Rubber. II. Modification with CTBN

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Synopsis

The dynamic mechanical properties and the adhesive strengths of epoxy resins-CTBN blend systems and epoxy resins-CTBNX blend systems were investigated.

Both CTBN blend and CTBNX blend systems were proved to be partially compatible with the dynamic mechanical measurement. In the case of CTBN blend systems, the more blending of CTBN, the more the compatibility increased. On the other hand, CTBNX-20 was more compatible than CTBNX-30 but less than CTBNX-40. In any case, the blending of CTBN or CTBNX reduced the nonreacted part of the epoxy resins cured at room temperature.

The adhesive strengths were evaluated as a function of the storage modulus with altering temperature and altering rubber content. Both procedures were proved to be equal.

INTRODUCTION

Several reports have pointed out the intimate relationship between the dynamic mechanical relaxation behavior of the adhesive polymers and the adhesive mechanism.¹⁻⁷ The application of polymers with broad relaxation in a wide range of temperature is considered to be as profitable as adhesives.

As the polymers described above, interpenetrating polymer networks (IPNs) have been reported recently.⁸ Generally, it can be said that an IPN is prepared only when two networks are synthesized in close interaction with each other. However, an ideal IPN has no chemical bonds but mechanical entanglements between two networks. IPNs are synthesized through several procedures. Simultaneous interpenetrating networks (SINs) are one of the varieties of IPNs that are prepared by two networks synthesized at once with different reaction mechanisms. Among many kinds of IPNs, the SINs are considered to have practical advantages as adhesives.

In the previous paper,⁹ the mechanical properties and the adhesive strengths of the epoxy resin-ATBN (amine-terminated copolymer of butadiene-acrylonitrile) polymer blends were studied. The blend systems were proved to be completely incompatible, and the addition of ATBN reduced the nonreacted parts of epoxy resins cured at room temperature and contributed to the adhesive strengths to a great extent. It was confirmed that the moduli and the relaxations of adhesive polymers were correlated with the adhesive strengths as observed in the completely compatible polymer blend systems.

Many papers have been published concerning epoxy resins toughened

with CTBN (carboxy-terminated copolymer of butadiene-acrylonitrile).¹⁰⁻¹⁶ In most of them, the improvement of toughness, impact strengths, tearing resistance, or fatigue resistance were reported. In the present paper, we wish to discuss the epoxy resin-CTBN polymer blends, which are not IPN strictly, through its mechanical properties and the adhesive strengths. Carboxyl groups do not react with epoxide at room temperature, although primary and secondary amines are reactive with epoxide at ambient temperature. This study was intended to synthesize practical polymers for wood adhesion. Prepolymers of epoxy resin-CTBN or CTBNX blends were synthesized at elevated temperature and then cured with cross-linker at room temperature. These blend systems were proved to be partially compatible, which we have never investigated as wood adhesives. We focused both on the temperature dependencies of the adhesive strengths for CTBN blend systems and on the relation between the adhesive strengths and the storage modulus for CTBNX blend systems.

EXPERIMENT

Preparation of Prepolymers

The materials were obtained from the following sources and used without further purification. The epoxy resin used was Epikote 828 (Shell Chemical Co.), a condensation product of 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin. CTBN 1300X8 and CTBNX 1300X9 (Ube Industries Ltd.) were used as rubber polymers; the number-average molecular weights were both about 3400. Their functionalities were 1.9 and 2.4, respectively. As a curing agent, HMDA (hexamethylenediamine) was employed. The prepolymers were synthesized by mixing Epikote 828 and CTBN or CTBNX and then reacting at 170°C for 1.5 h. The reactions between epoxide and carboxyl group were completed more than 95%, which was confirmed by titration of carboxyl groups. Against 100 parts of epoxy resins, CTBN of 10, 20, and 30 parts were blended and termed CTBN-10, CTBN-20, and CTBN-30, respectively. CTBNX was also blended in an amount of 5, 10, 20, 30, and 40 phr. We named them similarly as CTBNX-05, CTBNX-10, CTBNX-20, CTBNX-30, and CTBNX-40, respectively. The prepolymers were then cured with a stoichiometric amount of HMDA at room temperature.

Preparation of Films and Dynamic Mechanical Test

Films were prepared by mixing prepolymer and HMDA, then casting onto a Teflon sheet at room temperature. Some films were further allowed to cure at 130°C for 8 h after curing at room temperature. The dynamic mechanical spectroscopy was measured with a Rheovibron DDV-III (Toyo Baldwin Co. Ltd.) at a frequency of 110 Hz with a heating rate of about 1°C/min over a temperature range between -120° and +160°C.

Adhesive Strengths Test

Birch (*Betula Maximowicziana* Regal; Japanese *Kaba*) was used as adherend. The shapes of specimens were referred in the previous paper.⁹

The bonding conditions were as follows: open and closed assembly time,

0 and 2–5 min, respectively; bonding pressure, 10 kg/cm². The specimens were bonded under pressure for 7 days and conditioned at 20°C at 65% RH for more than 7 days. The adhesive strength tests were carried out by Tensilon (Toyo Baldwin Co. Ltd.) equipped with a temperature control chamber over a temperature from -120° to +120°C using a crosshead speed of 10 mm/min. Temperature control was performed by a combination of liquid nitrogen cooling and an electric heater.

RESULTS AND DISCUSSION

Dynamic Mechanical Spectroscopy

Figure 1 shows the temperature dependencies of dynamic storage moduli (E') and dynamic loss moduli (E'') of the Epikote 828 alone system (CTBN-0) and CTBN-30 cured at room temperature. The relaxation temperatures are summarized in Table I. The primary dispersions (α_1 transitions) of CTBN-10, 20, and 30, which are derived from the micro-Brownian motion of the main chain in the matrix, are observed at 100, 85, and 80°C, respectively. The dispersion temperatures go down as the content of CTBN increases. The α_2 transitions, which arise from the micro-Brownian motion of CTBN in dispersed phase, are observed at around -40°C in a similar manner through all polymer blends. The α_1' transitions, which we discussed in the previous paper,⁹ are derived from the nonreacted part of the epoxy resins. This dispersion temperature becomes higher—50, 55, and 60°C—when the content of CTBN increases. The relative intensity of α_1' transition becomes smaller with higher content of CTBN, which suggests that blending

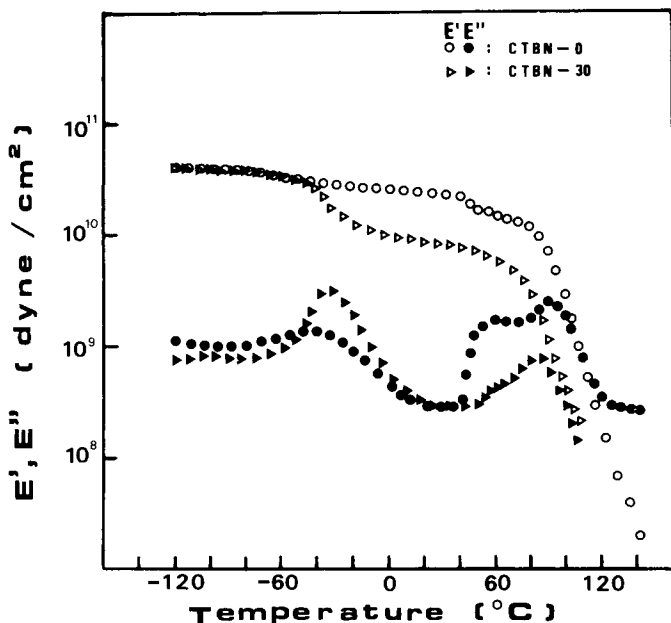


Fig. 1. Dynamic mechanical data for CTBN blend systems cured with HMDA at room temperature.

TABLE I
 Transition Temperatures of CTBN Blend Systems

Samples	Condition ^a	α_2 Transition (°C)	α_1' Transition (°C)	α_1 Transition (°C)
CTBN-0	A	—	50	90
	B	—	—	117
CTBN-10	A	-40	50	100
	B	-45	—	110
CTBN-20	A	-40	55	85
	B	-45	—	100
CTBN-30	A	-40	65	80
	B	-40	—	100

^a Condition A: cured at room temperature.

Condition B: cured at 130°C for 8 h after curing at room temperature.

CTBN reduces the nonreacted parts of the epoxy resins cured at room temperature. Figure 2 shows the dynamic mechanical data for a CTBN blend cured at 130°C for 8 h after curing at room temperature, and there are no α_1' transitions. The α_1 transition shifts lower—117, 110, 100, and 100°C—as the content of CTBN increases. Further, the α_2 transition shifts slightly higher—-45, -45, and -40°C. From the results obtained above, the blend systems can be called partially compatible two-phase systems. This is most distinguishable from ATBN blend systems.⁹

Takayanagi et al.¹⁷ proposed a theory of calculating dynamic moduli in completely incompatible systems. Complex moduli of the composite are defined by the equations

$$E^*(\text{model 1}) = \left(\frac{\phi}{\lambda E_R^* + (1 - \lambda) E_P^*} + \frac{1 - \phi}{E_P^*} \right)^{-1}$$

$$E^*(\text{model 2}) = \lambda \left(\frac{\phi}{E_R^*} + \frac{1 - \phi}{E_P^*} \right)^{-1} + (1 - \lambda) E_P^*$$

where E_P^* and E_R^* are complex moduli of epoxy resin (continuous phase) and CTBN (dispersed phase), respectively, and parameters λ and ϕ define the state of dispersion; $\lambda\phi$ is equal to the dispersed phase. Figures 3 and 4 are plots of the calculated moduli of CTBN-30 for models 1 and 2, respectively, and the numbered curves correspond to the parameter set of λ and ϕ in Table II. In the case of epoxy resin-ATBN blend systems, the moduli observed fit well with the calculated moduli when choosing appropriate values of λ and ϕ . In the present systems, they never fit at all. The most different point is that the transition temperatures of observed curves shift to the inner side against those of calculated curves. The fact described above means that the blend systems are not completely incompatible.

Table III shows each transition temperature of epoxy resin-CTBNX blend systems. The α_2 transition temperature goes up with increase in CTBNX, which is similar to CTBN blend systems. Nevertheless, the α_1 transition temperature reveals a temporary minimum when CTBNX is 20 phr and immediately rises at CTBNX-30. Then it goes down at CTBNX-40, which

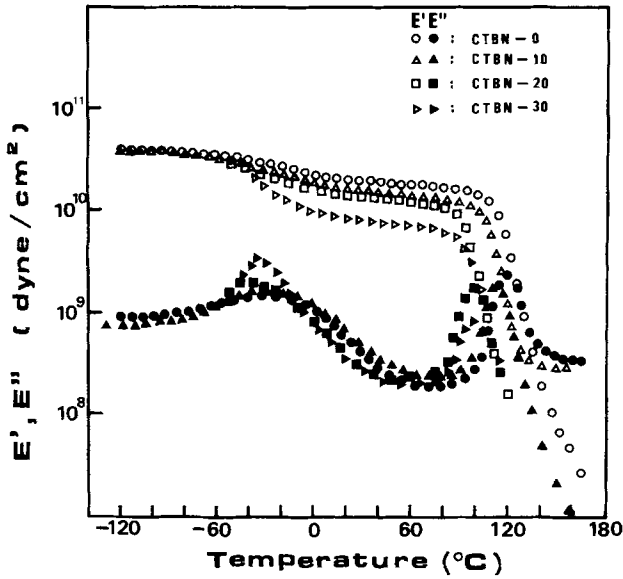


Fig. 2. Dynamic mechanical data for CTBN blend systems cured with HMDA at 130°C for 8 h after curing at room temperature.

is the most remarkable feature of these blend systems; this is, CTBNX-20 is more compatible than CTBNX-30 but less than CTBNX-40.

Temperature Dependencies of Adhesive Strengths

Figures 5 and 6 show the temperature dependencies of cross-lap tensile strengths for CTBN-20 and CTBN-30, respectively. The adhesive strengths for CTBN-0 should be referred to Figures 8 and 11 in the previous paper

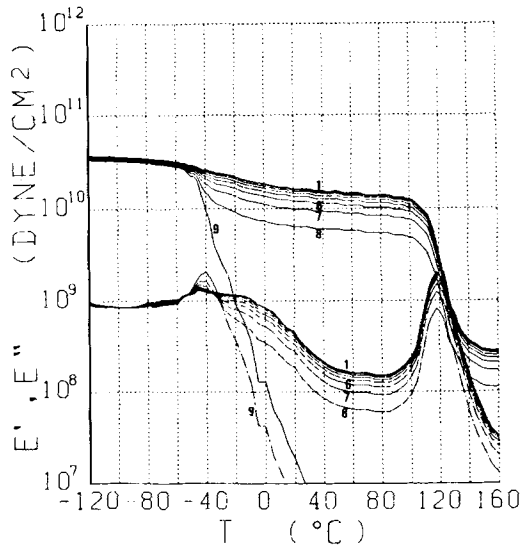


Fig. 3. Calculated moduli for CTBN-30 by Takayanagi's model 1. Solid line: E' (storage modulus). Broken line: E'' (loss modulus).

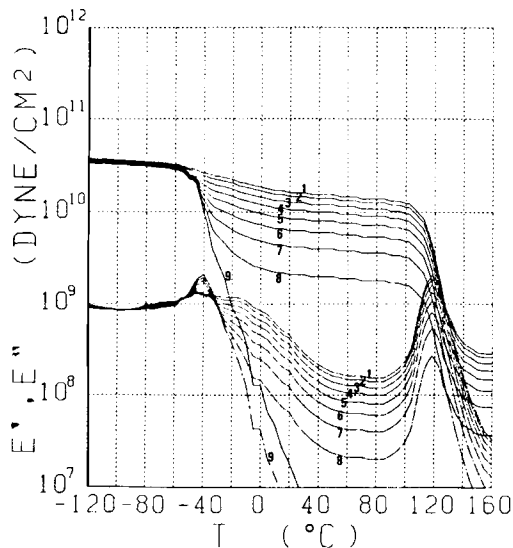


Fig. 4. Calculated moduli for CTBN-30 by Takayanagi's model 2. Solid line: E' (storage modulus). Broken line: E'' (loss modulus).

(CTBN-0 is equal to ATBN-0). The wood failure percentage is not so high over the whole temperature range, and accordingly the adhesive strengths should be considered real themselves. It is understandable that the blend systems have maximum adhesive strengths around -20°C , which is common to CTBN-10 (not shown as a figure). On the other hand, it is observed around 60°C for CTBN-0. The storage moduli corresponding to the temperature at the maximum adhesive strengths for CTBN-0, CTBN-10, CTBN-20, and CTBN-30 are 2.0 , 2.2 , 1.9 , and 1.2×10^{10} dyn/cm², respectively. That cross-lap tensile strengths have a maximum around 2.0 – 1.2×10^{10} dyn/cm² of the storage modulus accords with our data in both completely compatible systems and completely incompatible ones.⁹ The absolute value for the adhesive strengths increases as the content of CTBN through the whole temperature range, which is considered to be due to the decrease of the nonreacted parts of the epoxy resins cured at room temperature. This is common with the case for ATBN blend systems.

TABLE II
Combinations of Parameters in Calculation of Figures 3 and 4

	λ	ϕ
1	0.231	1.0
2	0.3	0.769
3	0.4	0.577
4	0.5	0.462
5	0.6	0.385
6	0.7	0.330
7	0.8	0.288
8	0.9	0.256
9	1.0	0.231

TABLE III
Transition Temperatures of CTBNX Blend Systems

Samples	Condition ^a	α_2 Transition (°C)	α_1' Transition (°C)	α_1 Transition (°C)
CTBNX-10	A	-39	58	103
	B	-40	—	111
CTBNX-20	A	-39	60	77
	B	-39	—	87
CTBNX-30	A	-32	60	86
	B	-33	—	91
CTBNX-40	A	-28	—	52
	B	-31	—	78

^a Condition A: cured at room temperature.

Condition B: cured at 130°C for 8 h after curing at room temperature.

In the shear adhesive strength tests, there certainly is a peak between -40 and -20°C for CTBN-30 (Fig. 7). On the other hand, there is no marked tendency for ATBN blend systems or CTBN-10 (not shown) and CTBN-20 (Fig. 8) in the lower temperature. This tendency is probably due to the anchor effects. Adding up to 30 phr of CTBN is thought to bring about essential CTBN properties and to give this result even if the anchor effects should occur.^{9,18}

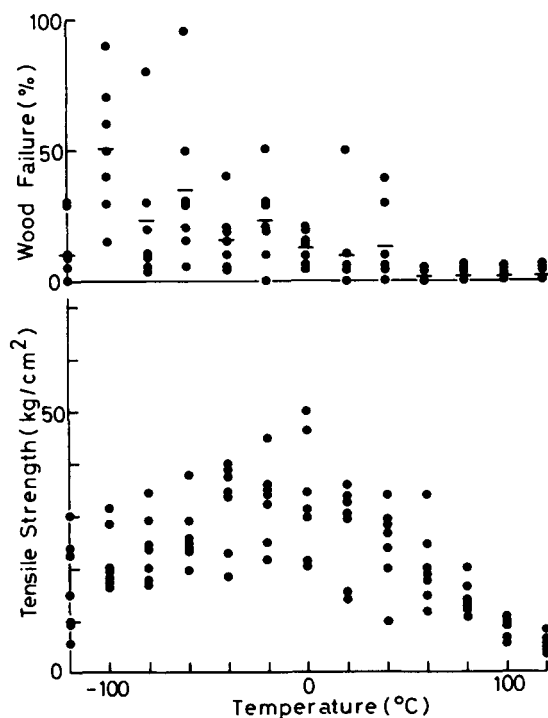


Fig. 5. Temperature dependencies of adhesive cross-lap tensile strengths for CTBN-20 cured with HMDA using Kaba as an adherend.

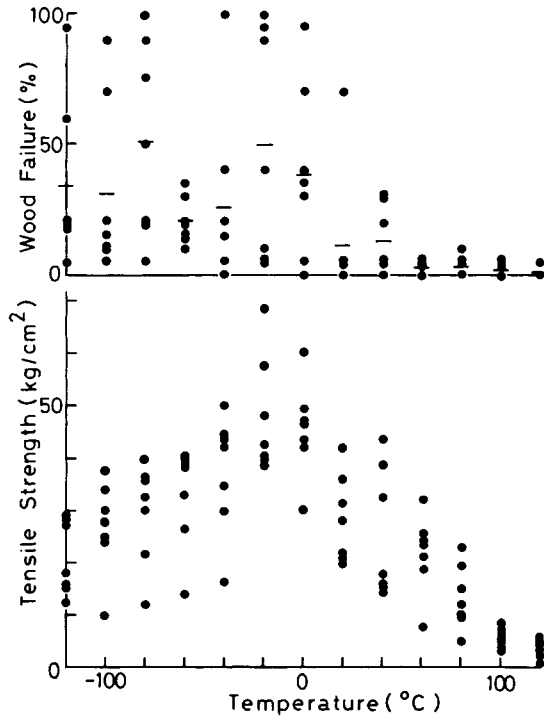


Fig. 6. Temperature dependencies of adhesive cross-lap tensile strengths for CTBN-30 cured with HMDA using Kaba as an adherend.

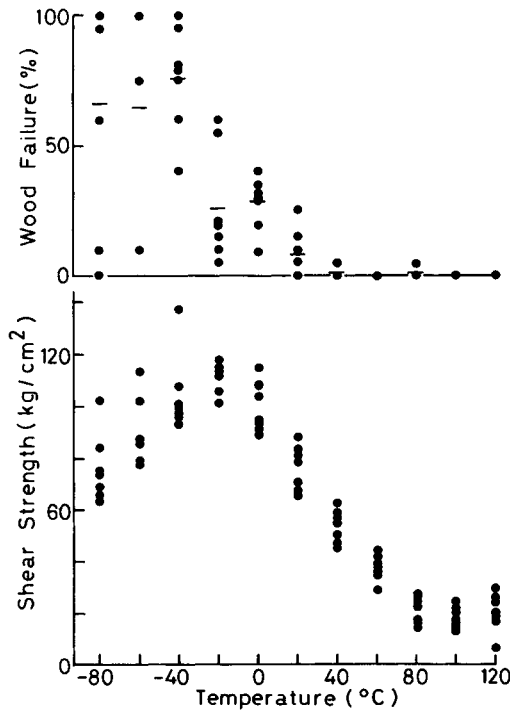


Fig. 7. Temperature dependencies of adhesive tensile shear strengths for CTBN-30 cured with HMDA using Kaba as an adherend.

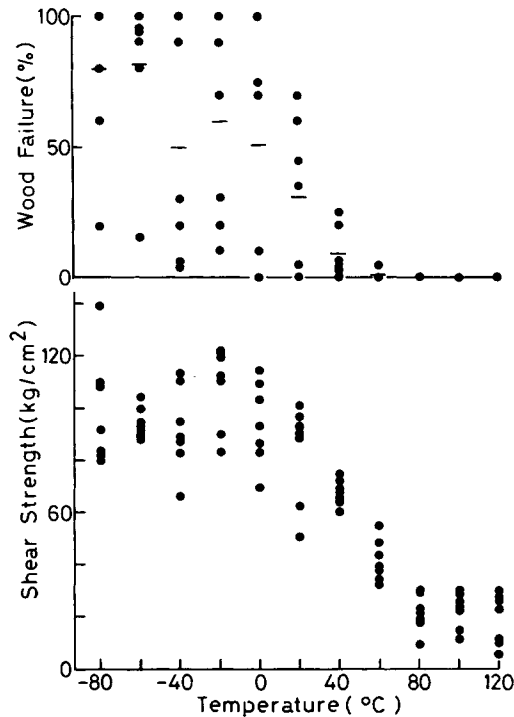


Fig. 8. Temperature dependencies of adhesive tensile shear strengths for CTBN-20 cured with HMDA using Kaba as an adherend.

In the temperature dependencies of the adhesive strengths, the temperature at the maximum of strengths for shear test is lower than those for the cross-lap test. In other words, the storage modulus at the temperature of the maximum strengths for shear test is higher than for the cross-lap test. This also agrees with our past data.^{6,7,9}

Relationship Between Adhesive Strengths and Storage Modulus

In the previous paper and previous section, we investigated adhesive strengths as a function of the storage modulus with altering temperature. In the present section, the adhesive strengths as a function of the storage modulus by changing CTBNX content are discussed. Figure 9 shows the storage modulus at 20°C for a series of various CTBNX blend systems. The storage modulus against CTBNX content is found to be linear.

Figures 10 and 11 show the adhesive cross-lap tensile strengths and the adhesive tensile shear strengths for CTBNX-0, 05, 10, 20, 30, and 40 at 20°C at 65% RH, respectively. It can be seen from Figure 10 that the adhesive strengths show a maximum between CTBNX-10 and 20. This means that the adhesive strengths by cross-lap test become maximum when the storage moduli at 20°C for these systems (Fig. 11) are between 2.1 and 1.4×10^{10} dyn/cm². This tendency coincides with the results of the temperature dependencies of the adhesive strength, which were investigated in the previous section.

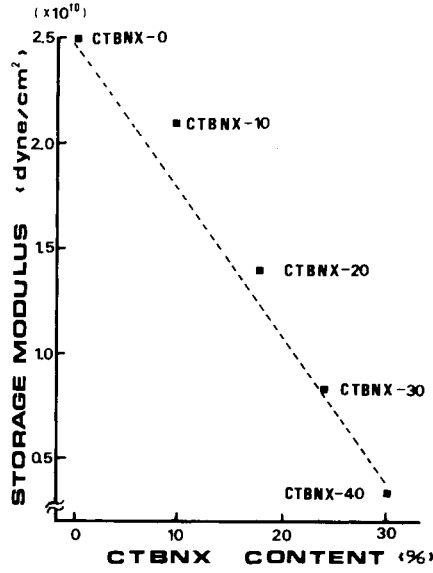


Fig. 9. Storage modulus at 20°C for a series of CTBNX blend systems.

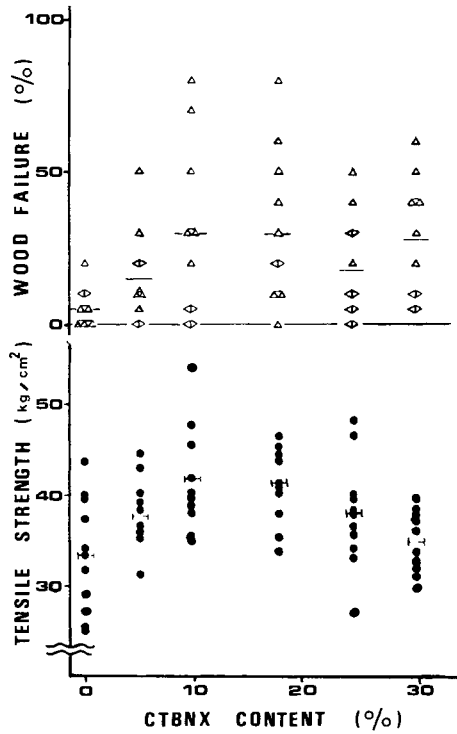


Fig. 10. Adhesive cross-lap tensile strengths at 20°C/65% RH for a series of CTBNX blend systems.

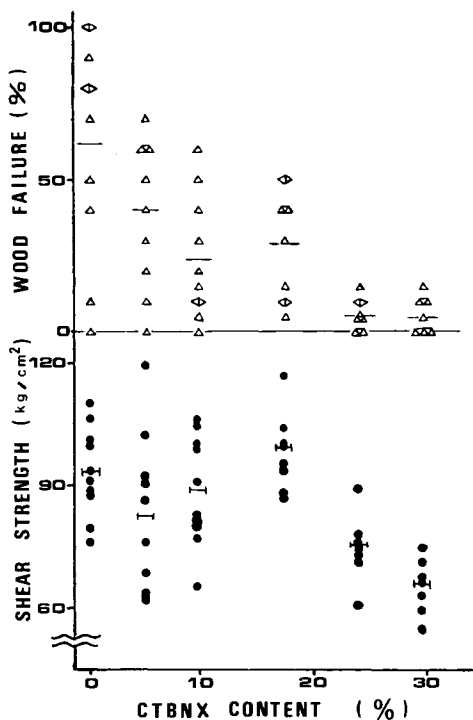


Fig. 11. Adhesive shear strengths at 20°C/65% RH for a series of CTBNX blend systems.

As to the shear strengths, it is difficult to define tendency between the adhesive strengths and CTBNX content. At first glance the adhesive strengths for CTBNX-20 are the largest of all. However, the adhesive strengths for CTBNX-0 seem to be larger than those for CTBNX-20, as the average wood failure for CTBNX-0 is larger than those of other CTBNX blend systems. Considering this, our philosophy that the modulus at the maximum adhesive strengths for the shear test is higher than that for the cross-lap test is also thought to be proper in this case.

CONCLUSIONS

Dynamic mechanical measurement showed that the epoxy resin-CTBN blend systems were partially compatible. In this case, the more blending of CTBN, the more the compatibility increased. The glass transition temperature (T_g ; E''_{max}) decreased with the blending of CTBN. The calculated data of the Takayanagi model never did fit the observed data. The blending of CTBN reduced the nonreacted parts of the epoxy resins in the same way as ATBN blend systems. The CTBNX blend systems behaved in a different way compared with CTBN blend systems. Thus, CTBNX-20 was more compatible than CTBNX-30 but less than CTBNX-40.

Concerning the temperature dependencies of the cross-lap tensile adhesive strengths, the storage moduli corresponding to the temperature at the maximum adhesive strengths for CTBN blend systems were between 2.2 and 1.2×10^{10} dyn/cm². This meant the adhesive strengths became max-

imum in that region. Such behavior was also observed in both the completely incompatible and compatible blend systems.

As to the temperature dependencies of the shear strengths, there was a peak between -40 and -20°C for CTBN-30. There were no such peaks for CTBN-10, 20, or ATBN blend systems, which was thought due to the anchor effects. That the storage modulus at the temperature corresponding to the maximum strengths for the shear test is higher than those for the cross-lap test agreed well with our past data.

From the results of the adhesive strengths for CTBNX blend systems, it was shown that the modulus at the maximum adhesive strengths is between 2.1 and 1.4×10^{10} dyn/cm² in the cross-lap test and that the modulus at the maximum adhesive strengths by shear test is higher than that by cross-lap test.

We investigated the temperature dependencies of the adhesive strengths and the adhesive strengths with altering CTBNX content. It was demonstrated that changing rubber content is equal to changing temperature of fracture test in terms of altering the magnitude of the storage modulus for the adhesive polymer.

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