Dynamic Mechanical Properties and Adhesive Strengths of Epoxy Resins Modified with Liquid Rubber. I. Modification with ATBN

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Synopsis

The dynamic mechanical properties and the adhesive strengths of Epikote 828 and Epikote 828-ATBN blend systems were investigated. The ATBN blend systems were proved to be completely incompatible with the dynamic mechanical measurement and also fitted well with Takayanagi's model which was designed for completely incompatible two-phase systems. The epoxy resin had a nonreacted part when cured at room temperature. The blending of ATBN reduced the nonreacted part of the epoxy resin, and made contributions to the adhesive strengths. In the case of tensile test of crosslap specimens using aluminium as adherends, the adhesive strengths of ATBN blend systems were almost 1.5-fold of those of epoxy resin without blending of ATBN. As for wood adherends, the maximum of the adhesive strengths was found at 60°C for epoxy resin without blending of ATBN, and at 0°C for ATBN blend systems. The facts meant that there were mutual interactions between the adhesive strengths and the viscoelastic behavior of the adhesive polymers in the two-phase systems as observed in completely miscible polymer blends. There was not pronounced distinction between epoxy resins without blending of ATBN and ATBN blend systems, as to the shear adhesive strengths.

INTRODUCTION

It was reported that the adhesive strengths are closely associated with the mechanical properties of the adhesive polymers.[1,2] We have reported that the strengths of bonded wood joints are governed by the rheological porperties of the adhesive such as the moduli and the damping behavior.[3-7] In our work a series of adhesives gradually differing in mechanical properties were prepared by blending PVC [poly(vinyl chloride)] and NBR (nitrile–butadiene rubber) systems of which were known as completely miscible ones.[5] The temperature corresponding to the absorption peak in loss modulus at 110 Hz, $T(E''_{max})$, could be made to vary at any levels between -9 and 70°C, depending on the blend ratio. Furthermore, we investigated, with a procedure similar to the one described above, completely miscible epoxy resin–epoxy resin blend.[6] In both cases the tests of adhesive strengths were carried out only at the constant temperature of 20°C. On the other hand, the adhesive strengths and the mechanical behaviors for PVAc [poly(vinyl acetate)] over a temperature range from -150 to $+150$°C were evaluated, and the result indicated the close interaction between the adhesive strengths and the mechanical properties of the polymers.[7] This method could be considered to be prominent in changing rheological properties

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of polymers without altering chemical components of polymers.

Epoxy resins are widely used in various fields of coating, adhesion, lamination, molding, and so on. When used as adhesives, epoxy resins have generally high adhesive strengths. Epoxy resins, however, are apt to bring about a poor impact strength or peeling strength. In order to improve these disadvantages, liquid poly(butadiene–acrylonitrile) copolymers have been added to epoxy resins.[8-10] General use of this polymer blend is made on mixing epoxy resins and CTBN (carboxy-terminated copolymer of butadiene–acrylonitrile), and curing with piperidine or some tertiary amines at high temperatures. According to the literature, this system is completely incompatible, which is determined with dynamic mechanical spectroscopy. This method, because it requires high curing temperatures, cannot be practically applied as adhesives for wood.

For that reason, we used ATBN (amine-terminated butadiene–acrylonitrile copolymers) whose primary amino groups were expected to react with epoxide groups at room temperature. HMDA was used as room temperature curing agent which also has primary amino groups. There has not been report of epoxy resin–ATBN blend cured at room temperature either to apply for adhesives or to measure the mechanical properties. In addition epoxy resin–ATBN blends were proved to be incompatible in this work; that is to say, they had two independent phases, and we have never dealt with such kind of polymer blend systems for wood adhesions.

This paper deals with the mechanical properties and the adhesive strengths of these blend systems over a wide range of temperatures.

EXPERIMENTAL

Materials

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-hydroxy phenol)propane and epichlorohydrin. ATBN (HYCAR ATBN 1300X16, Ube Industries Ltd.) was used as the rubber polymer whose molecular weight was about 3400. As a curing agent, HMDA (hexamethylenediamine) was employed. Against 100 parts of Epikote 828, 10 and 20 parts of ATBN were blended, then mixed with stoichiometric amount of HMDA, and successively cured for more than 1 day at room temperature. These blends were referred as ATBN-10 and ATBN-20, respectively, and Epikote 828 alone system was referred as ATBN-O.

Mechanical Properties

To study mechanical properties, films of 1.0–1.5 mm in thickness were made by casting onto a Teflon sheet. Two types of curing were carried out; one was cured at room temperature; the other cured at 130°C for 8 h after curing at room temperature. The dynamic relaxation behavior were measured with Rheovibron DDV-III (Toyo Baldwin Co.), at a frequency of 110 Hz and heating rate of 1°C min over a temperature range from −120 to 160°C.

Adhesive Strengths

Two types of testing methods were applied for these polymers. One was the crosslap tensile testing method the design of which was referred to by Marra,[11-13] and the other, the tensile shear testing method. Adherends used were Kaba (*Betula maximowicziana* Regal) and aluminium. But in the case of aluminium, only the crosslap tensile testing method was employed. The sizes of specimens and bonding areas were as follows: 80 mm (length) $\times$ 25 mm (width) $\times$ 5 mm (thickness), 3.75 cm^2 for shear test of wood; 65 $\times$ 25 $\times$ 25, 6.25 cm^2 for crosslap test of wood; 65 $\times$ 25 $\times$ 15, 6.25 cm^2 for crosslap test of aluminium. The aluminium specimens were polished by Pical (Nihon Maryo-Kogyo Co.), and then washed with acetone and trichloroethylene successively before bonding.

The bonding conditions were as follows: open and closed assembly time, 0 and 2–5 min, respectively; bonding pressure, 10 kg/cm^2; pressure time, 2 days. The specimens were conditioned at 20°C and 65 RH for around 1 week before tested.

The adhesive strengths were measured with a Tensilon tensile testing machine (Toyo Baldwin Co.) equipped with a temperature control chamber over temperatures from -120 to $+120$°C, and crosshead speed was 10 mm/min. Temperature control was performed by a combination of liquid nitogen cooling and an electric heater.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

Figures 1 and 2 illustrate the temperature dependence of the storage moduli E' and loss moduli E'' for ATBN-0 and ATBN-20, respectively, which were cured at room temperature. Figures 3 and 4 show also the temperature
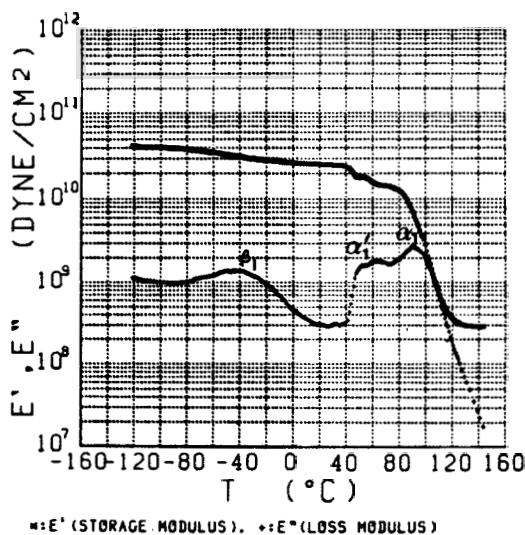

■:E'（STORAGE MODULUS）, ◆:E"（LOSS MODULUS）

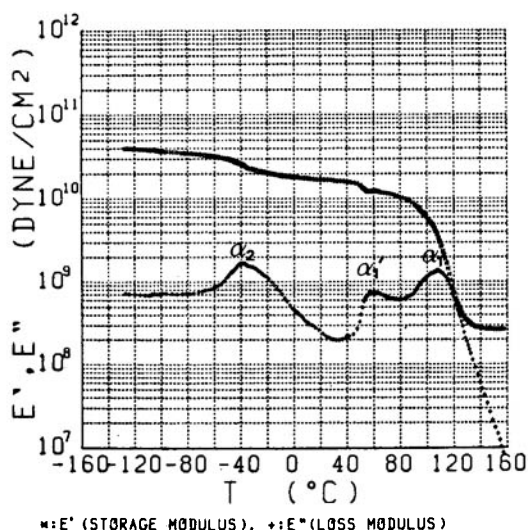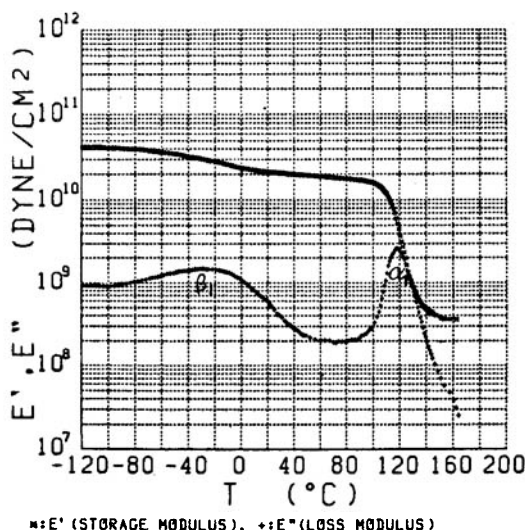Fig. 1. Dynamic mechanical data for ATBN-0 cured with HMDA at room temperature.

Fig. 2.   Dynamic mechanical data for ATBN-20 cured with HMDA at room temperature.

dependences of the dynamic mechanical properties for ATBN-0 and ATBN-20, respectively, cured at 130°C for 8 h after curing at room temperature. Each peak temperature is summarized in Table I.

In Figures 3 and 4 the peaks of 120°C correspond to the micro-Brownian motion of the epoxy resin's main chain, which is called α_1 transition. There is another peak (α_2 transition) in the lower temperature around $-40°C$ in Figure 4 which is due to the micro-Brownian motion of the ATBN's main chain. The lower relaxation in Figure 3 is derived from the secondary transition of the epoxy resin (β_1 transition). The peaks (α_1, α_2) never shift to the inner side of each other, which suggests that these blend systems

Fig. 3.   Dynamic mechanical data for ATBN-0 with HMDA at 130°C for 8 h after curing at room temperature.

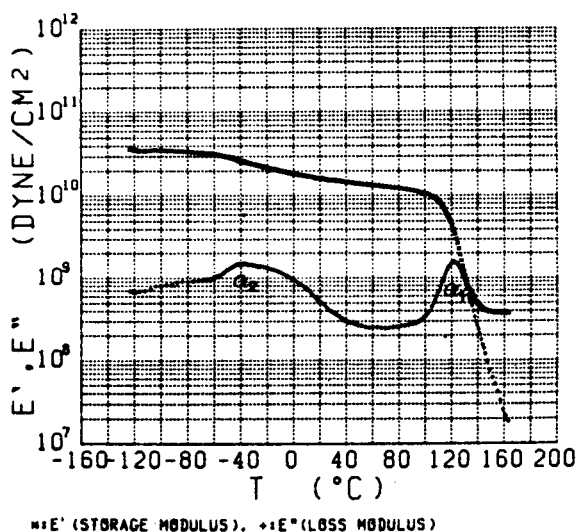**:E' (STORAGE MODULUS), +:E"(LOSS MODULUS)

Fig. 4. Dynamic mechanical data for ATBN-20 cured with HMDA at 130°C for 8 h after curing at room temperature.

are completely incompatible. If only the systems were somewhat compatible, α_1 transition would be lower and α_2 transition higher as the ATBN content increases.

We also made an analysis using models proposed by Takayanagi et al.[14] Figure 5 illustrates the mechanical equivalent models for the completely incompatible two-phase system wherein P and R are the continuous phase and the dispersed phase, respectively. Complex moduli of the composite are defined by the following equations:

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

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

where E_P^* and E_R^* are the complex moduli of epoxy resin (continuous phase) and ATBN (dispersed phase), respectively, the parameters λ and φ define the state of dispersion, and $\lambda \cdot \varphi$ is equal to despersed phase. Figures 6 and

TABLE I
Transition Temperatures of Polymers

Samples	α_2 transition[a]	α_1' transition[a]	α_1 transition[a]
ATBN-0	—	50°C	90°C
130°C cure	—	—	117°C
ATBN-10	−40°C	55°C	92°C
130°C cure	−45°C	—	120°C
ATBN-20	−40°C	60°C	110°C
130°C cure	−42°C	—	121°C

[a] Three transitions, α_1, α_1', and α_2, are referred to in Figures 1–4.
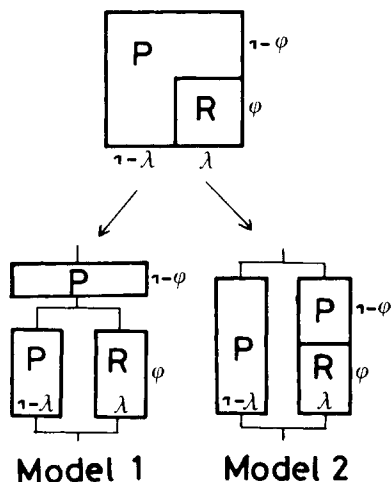
Fig. 5. The schematic models for completely incompatible two-phase polymer system proposed by Takayanagi.

7 are plots of the calculated moduli of ATBN-20, which were determined by solving simultaneously the above formula at 5°C intervals between −120 and 160°C, and numbered curves correspond to combinations of λ and φ in Table II. The calculated moduli in Figure 6, in the case of λ = 0.167 and φ = 1.0, fit well to the observed one (Fig. 4). Furthermore, in Figure 7, when λ = 0.2 and φ = 0.833, they also fit well. These facts mean that the epoxy resin-ATBN blend systems are thoroughly incompatible.

In Figures 1 and 2, strange peaks are present between 50 and 60°C, which we named α_1' transition, and these peaks are supposed to arise from a nonreacted part of the epoxy resin. It can be said that the epoxy resin cured at room temperature would not always be cured perfectly, which affects
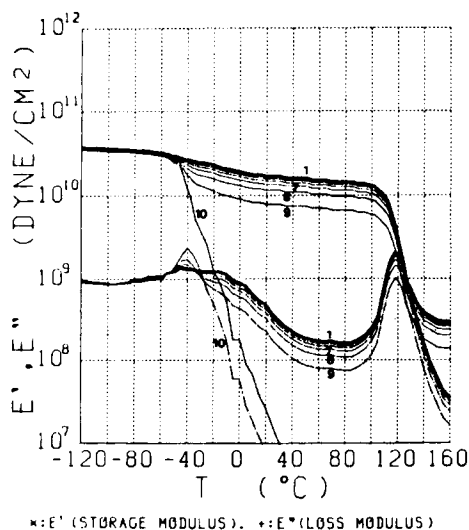

Fig. 6. Calculated moduli for ATBN-20 by Takayanagi's model 1.

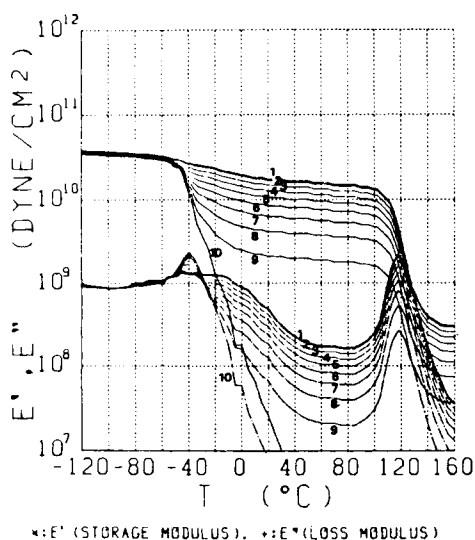*:E' (STORAGE MODULUS), *:E"(LOSS MODULUS)

Fig. 7. Calculated moduli for ATBN-20 by Takayanagi's model 2.

the dynamic mechanical properties to a great extent. At a lower temperature, the relaxation behavior of the epoxy resin cured at room temperature is similar to the behavior of those cured at 130°C for 8 h. A broad transition at around $-40°C$ is seen in Figure 1, which is the secondary transition of the epoxy resin (β_1 transition), and in Figure 2 the absorption of ATBN (α_2 transition) is observed at around $-40°C$ more distinctly. As discussed above, the temperature of E'' max, $T(E''_{max})$, corresponding to the micro-Brownian motion of the epoxy resin's main chain for ATBN-0 and ATBN-20 cured at 130°C is the same temperature of 120°C, but in the case of curing at room temperature $T(E''_{max})$ shifted as ATBN is increases. Those of ATBN-0, ATBN-10, and ATBN-20 are 90, 92, and 110°C, respectively. It indicates that the addition of ATBN raises T (E''_{max}). In the case of ATBN-20, $T(E''_{max})$ becomes 110°C, which is near the real $T(E''_{max}) = 120°C$ in the case of curing at 130°C for 8 h (Fig. 4). In a word, the blending of ATBN reduces the quantity of the nonreacted part of the epoxy resin cured at room temperature. If the reaction is not carried out completely, the adhesive strengths would be lower. Consequently, in the case of wood adhesion, when curing at room

TABLE II
Combinations of Parameters in Calculation of Figures 6 and 7

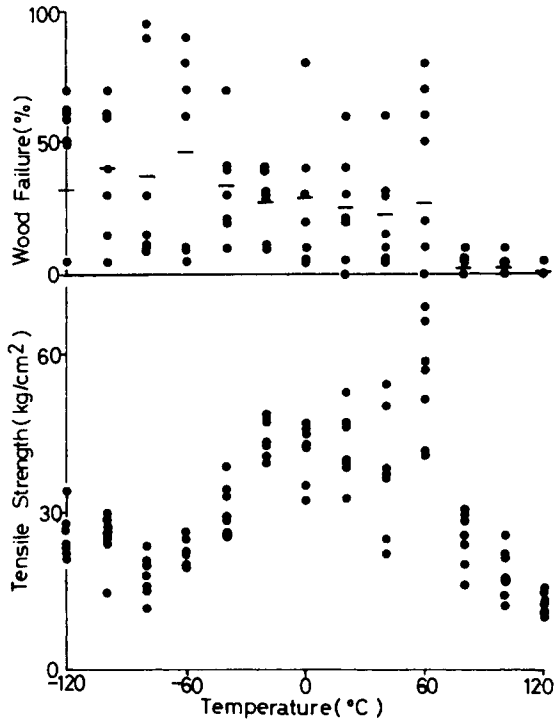|	λ	φ
1	0.167	1
2	0.2	0.833
3	0.3	0.566
4	0.4	0.417
5	0.5	0.333
6	0.6	0.278
7	0.7	0.238
8	0.8	0.208
9	0.9	0.185
10	1.0	0.167

Fig. 8. Temperature dependences of adhesive crosslap tensile strengths for ATBN-0 cured with HMDA using Kaba as adherends.

temperature is especially needed, the blending of ATBN is considered to encourage the increase of the adhesive strengths.

Crosslap Tensile Strengths

The temperature dependences of adhesive crosslap tensile strengths, using Kaba as adherends for ATBN-0, ATBN-10, and ATBN-20 are shown in Figures 8, 9, and 10, respectively. Both ATBN-0 and ATBN blends maintain high adhesive strengths over a wide temperature range between −40 and 80°C. In the case of ATBN-0, the temperature of the maximum adhesive strengths is about 60°C. This fact may correspond to the dynamic mechanical absorption at 50°C, which is due to the relaxation of the nonreacted part of epoxy resin (Fig. 1). In contrast there is a significant difference as for ATBN blends, whose temperatures of the maximum adhesive strengths are about 0°C (Figs. 9 and 10). The storage moduli at the temperature for the maximum adhesive strengths are about 2.0×10^{10} dyn/cm^2 in both case, as shown in Figures 1 and 2. It would be considered as follows: the adhesive strengths are governed by the polymer's cohesion in the region where the modulus is lower than 2.0×10^{10} dyn/cm^2; in the region where the modulus is higher than that, the micro-Brownian motion is fixed, and the adhesive strengths are governed by the anchor effect, to which the crosslap tensile testing method is not very sensitive; in the region where the modulus is about 2.0×10^{10} dyn/cm^2, the micro-Brownian motion of the polymer begins and the adhesive polymer exerts the adhesive strengths on the surface of
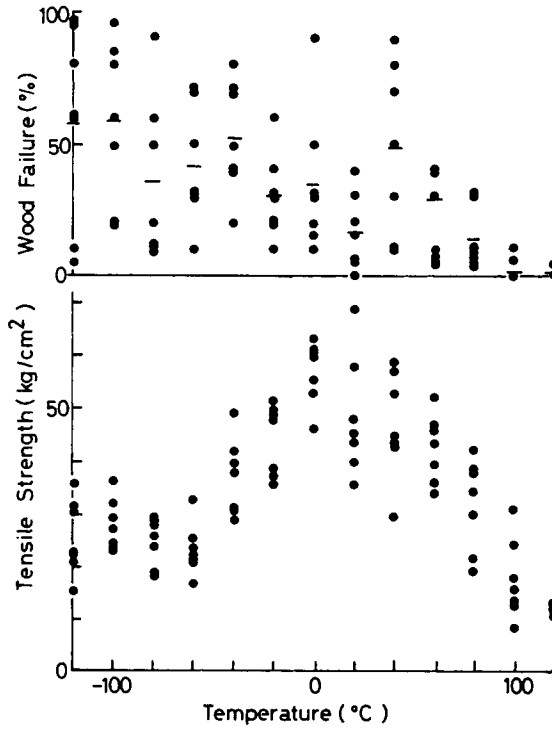
Fig. 9. Temperature dependences of adhesive crosslap tensile strengths for ATBN-10 cured with Kaba as adherends.
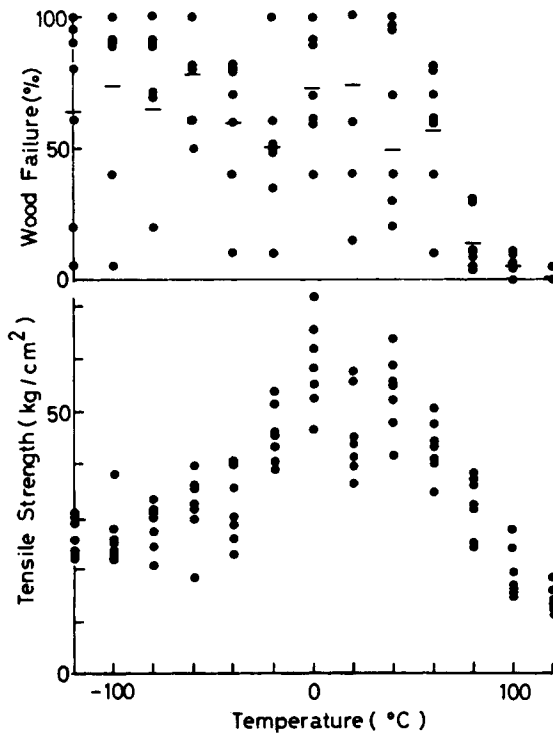

Fig. 10. Temperature dependences of adhesive crosslap tensile strengths for ATBN-20 cured with HMDA using Kaba as adherends.
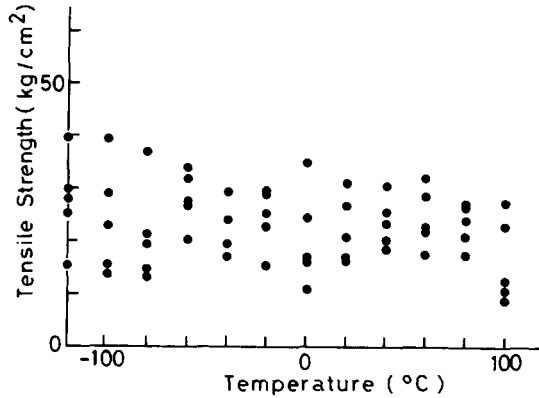
Fig. 11. Temperature dependences of adhesive crosslap tensile strengths for ATBN-0 cured with HMDA using aluminium as adherends.

adherend through the boundary surface. Especially in the case of ATBN-0, having maximum adhesive strengths at 60°C is thought to be the synergistic effect between α'_1 transition at 50°C and the storage modulus of 2.0 $\times$ 10^{10} dyn/cm^2 at 60°C. The concept described above accords very well with the result of completely compatible systems on which we reported before.[5,6]

With respect to the wood failure, in the lower temperature below 0°C, the values are considerably high. So it can be said that the real adhesive strengths are higher in that region, and the adhesive strengths themselves are slightly higher when there is blending of ATBN. But blending more than 20 phr of ATBN is not practically applicable for the adhesive because of high viscosity.

Figures 11 and 12 show the temperature dependences of the adhesive crosslap tensile strengths, using aluminium as adherends. There are not marked tendencies between ATBN-0 and ATBN-20. To sum up, the maximum adhesive strengths were not observed, and the strengths are not so high as in the case of wood adherends. It is thought that there is less anchor
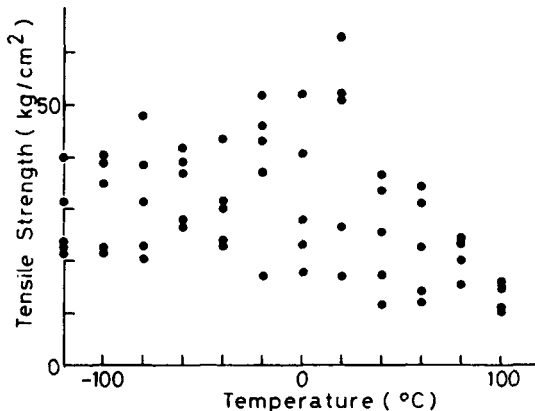

Fig. 12. Temperature dependences of adhesive crosslap tensile strengths for ATBN-20 cured with HMDA using aluminium as adherends.
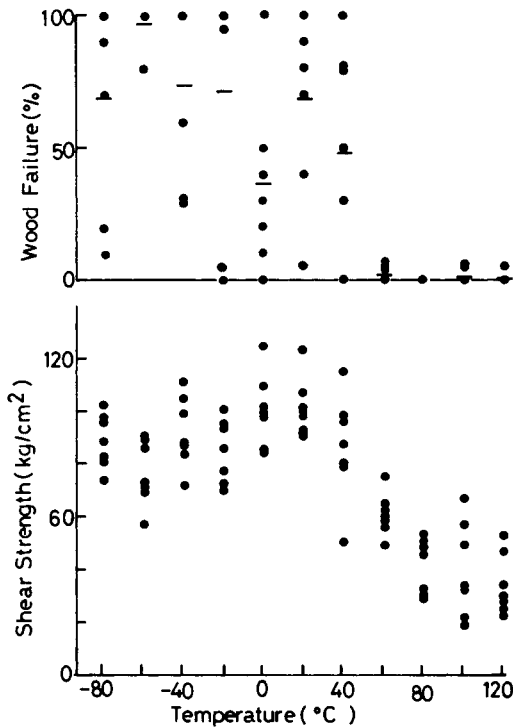
Fig. 13.   Temperature dependences of adhesive tensile shear strengths for ATBN-0 cured with HMDA using Kaba as adherends.

effect when compared with Kaba adherends. Nevertheless, with increasing ATBN's content, the adhesive strengths approach high values. In the case of ATBN-20 (Fig. 12), the strength are almost 1.5-fold of those of ATBN-0 (Fig. 11) over a full range of temperatures. It can be considered that, in the case of aluminium for adherends, a more complete cure must be needed, e.g., curing at high temperatures, and that also in this case ATBN reduces the amount of the nonreacted part of the epoxy resin. In other word, with increasing ATBN, the more perfect cure can be completed.

Tensile Shear Strengths

Next we deal with the shear adhesive strength, using Kaba for adherends, which are shown in Figures 13, 14, and 15. There are not distinguished differences between ATBN-0 and ATBN blend systems. But in the temperature region below −40°C, the more ATBN is added, the higher the adhesive strengths are. This effect is also considered due to the less nonreacted part of epoxy resin. However, in the temperature region above 60°C, the less ATBN is added, the higher the adhesive strengths, which is supposed to be reasonable. The drop in strengths is not observed in the lower temperature below 0°C, compared with the crosslap tensile strengths. This result is considered to be due to the anchor effect.[15] We have reported that the anchor effect is more evident in the shear test whose fracture mechanism is to pull the anchor at right angle, than in the crosslap test whose fracture mechanism is to pull vertically.
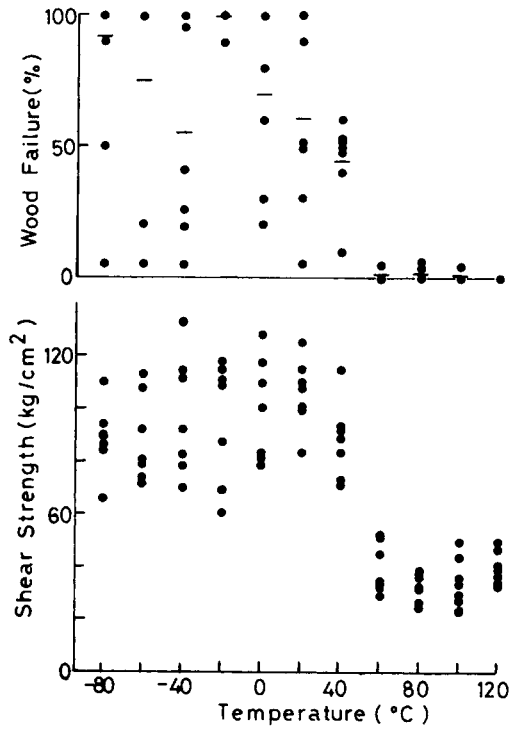
Fig. 14. Temperature dependences of adhesive tensile shear strengths for ATBN-10 cured with HMDA using Kaba as adherends.
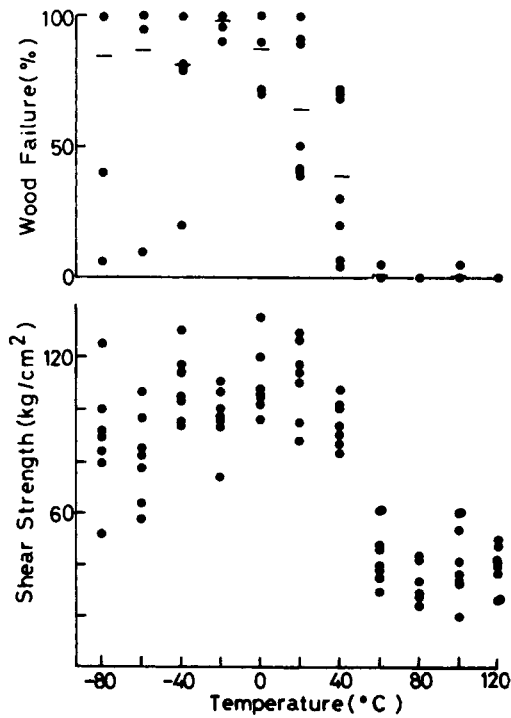

Fig. 15. Temperature dependences of adhesive tensile shear strengths for ATBN-20 cured with HMDA using Kaba as adherends.

CONCLUSION

The dynamic mechanical measurement and indirectly Takayanagi's models showed that epoxy resin–ATBN blend systems were proved to be completely incompatible. The epoxy resin cured at room temperature had a nonreacted part. The blending of ATBN showed similar mechanical properties of the polymer cured at high temperatures. It was considered that the blending of ATBN reduced the nonreacted part of the epoxy resin, which contributed to the increasing of the adhesives strengths.

As to the temperature dependencies of the crosslap tensile strengths, the temperature of the maximum adhesive strengths for ATBN-0 was 60°C, which gave good agreement with the presence of the peak of ATBN-0, while those of ATBN blend systems were around 0°C. But the storage moduli at the temperature for the maximum adhesive strengths were about 2.0×10^{10} dyn/cm^2 in each case. These facts meant that the completely incompatible systems in the present paper behaved in the same way with the completely compatible systems, as we have reported already.

About the tensile shear strengths, large differences were not observed between ATBN-0 and ATBN blend systems. In the lower temperature, the adhesive strengths did not fall compared with the crosslap strengths, which was thought to be due to the anchor effect.

As a whole, the blending of ATBN made fairly large contributions to the adhesive strengths, which is attributed to the reduction of the nonreacted part of the epoxy resin.

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