The Effect of Modification of an Epoxy Resin Adhesive with ATBN on Peel Strength

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PLEASE SCROLL DOWN FOR ARTICLE

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The effects of rubber content, rate of peel and temperature on peel strength of ATBN modified DGEBA based epoxy resin adhesives have been investigated. The fracture surfaces of peel test specimens and the distribution of rubber particles in cured bulk epoxy resin have been observed with SEM and TEM, respectively. The mechanical properties of bulk rubber modified epoxy resin have been also measured. The peel strengths increased with increasing rubber content, peel rate, and decreasing temperature. The peel strengths were superposed as a function of rate and temperature. Plots of the shift factors against temperature gave two straight lines, which followed an Arrhenius relationship. The region of temperature below the intersection of the two straight lines, temperature somewhat lower than T_g of epoxy adhesive, gave markedly high peel strengths and a stick-slip failure due to plastic deformation of the adhesive, and a number of micro holes produced by the rupture of rubber micro particles on the fracture surface. The region of temperature above the intersection gave lower peel strengths and an apparent interfacial failure with ductile fracture of the adhesive, and larger, shallow holes or no holes. From these results, the marked increase of peel strength was concluded to be mainly attributed to the plastic or viscoelastic deformation of epoxy matrix, the strong bond at the interface between rubber particles and epoxy matrix, and the dilation and rupture of a number of rubber particles.

KEY WORDS Superposition of peel strength; ATBN modified epoxy resin; morphology; mechanical properties; distribution of rubber particles; toughening mechanism.

1 INTRODUCTION

Epoxy resins have been widely used as adhesives because of their high shear strength, but low peel, flexural, impact, and fatigue performances (the so-called toughness parameters) are the disadvantages of unmodified epoxy resin adhesives. In order to improve the toughness of epoxy resin adhesives, modification with liquid nitrile rubber has been employed, and these rubber modified epoxy resins have been used as structural adhesives for aerospace and so on.[1]

Many papers have been published on the modification of epoxy adhesives with

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liquid nitrile rubber.[2] Most of these papers have discussed carboxyl-terminated butadiene acrylonitrile rubber (CTBN), however, there have been a few papers on amine-terminated butadiene acrylonitrile rubbers (ATBN).[3,4,5,6] In most papers on modified epoxy resin adhesives, the toughness has been described by K_{IC} (stress intensity factor or fracture toughness) or G_{IC} (strain energy release rate or fracture energy) by the procedures of fracture mechanics. Papers on the practical bond strength such as shear or peel have been very limited.[7,8,9,10] Therefore, we have investigated the peel and shear strengths of ATBN modified epoxy resin adhesives. In the present paper, the peel strength is reported.

In general, the bond strength varies dramatically with test temperature and rate, even if the same materials, geometries and bonding conditions were used. Consequently, it is impossible to predict the bond strengths over a wide range of temperature and rate from the measurements at a single set of test conditions. Hence, the temperature-rate superposition of the peel strengths has been examined. A master curve thus obtained will give much information on the peel strengths over a wide range of temperature and rate.

In addition, the mechanism of marked high peel strength of ATBN modified epoxy resin has been discussed from the mechanical properties of the adhesives, and the observations with a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

2 EXPERIMENTAL

2.1 Materials

As an adhesive, a blend of the following materials was used: Epoxy resin; diglycidyl ether of bisphenol A (DGEBA, Yuka-Shell Epoxy Co., Epikote 828), Hardener; polyamide (Henkel-Hakusui Co., Versamid 125), Modifier; liquid amine-terminated butadiene acrylonitrile rubber (B.F. Goodrich Co.-Ube Industry Co., Hycar ATBN 1300X16). The structural formulas and some physical properties of the epoxy resin and ATBN used are given in Fig. 1. Versamid 125, hàving the amine value of 345, is a typical polyamide hardener, and is said to be the reaction product of a dimer acid (dimer of unsaturated fatty acid) with polyamines.

As an adherend, a high purity, bright aluminum sheet (purity: 99.99%, thickness: 0.3 mm) was used. Before bonding, the sheet was degreased with trichloroethylene, polished with No. 240 sand paper, cleaned again with trichloroethylene, and stored in a desiccator containing P_2O_5.

This dead soft aluminum was used because of the easy operation in the peel test and its purity. The surface treatment such as FPL etching or phosphoric acid anodizing was not adopted because of the very strict regulation of the waste of the Cr compounds. If the strong aluminum alloy and the better surface treatment are used, a different result from this study may be obtained.

2.2 Peel Test

The blend of epoxy resin, hardener, and ATBN was applied on the aluminum sheet, deaerated in vacuo at 20~25°C for 30 min. Then, the laminate of two aluminum

(1) Epikote 828

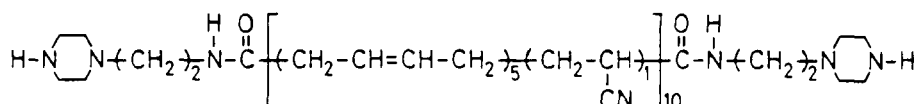$$CH_2-CH-CH_2 \left[O-\text{⬡}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\text{⬡}-O-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2 \right]_{0.09} O-\text{⬡}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\text{⬡}-O-CH_2-CH-CH_2$$
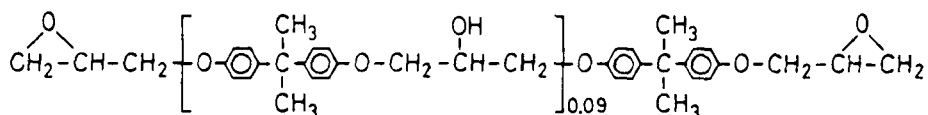
$\overline{Mn} \doteqdot 380$, Epoxy Equivalent Weight $= 184 \sim 194$ g/mol

(2) ATBN 1300 X16

$$H-N\underset{\smile}{\frown}N-(CH_2)_2^-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}\left[(CH_2-CH=CH-CH_2)_5(CH_2-\overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle CN}{|}}{CH}})_1\right]_{10}\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_2N\underset{\smile}{\frown}N-H$$

$\overline{Mn} = 3500$, AN Content $\doteqdot 17$ %

FIGURE 1   Some characterizations of epoxy resin and ATBN used.

sheets bonded with the adhesives was pressed at 100°C for 60 min. The thickness of adhesive layer was controlled to be about 0.3 mm using a 0.3 mm thick spacer. The blend ratio of epoxy resin, hardener, and ATBN was 100/50/5~60 parts. The T-peel strength of the bonded laminate was measured according to ASTM D 1876.

2.3 Morphology

The fracture surface after peel test was observed with a SEM (JEOL, JSM-T20). Before the observation with a SEM, gold of about 500 Å thickness was vapor-deposited on the fracture surface of the specimen.

The distribution and size of rubber particles dispersed in cured epoxy matrix resin were examined with TEM. For the observation with TEM, ultra-thin sections of cured rubber modified epoxy resin adhesives were made by the following procedure: Two aluminum sheets were bonded with adhesives using the same method as described in the preparation of bonded specimen for peel test, except for treatment of aluminum sheet surfaces with a fluoro-resin release agent before bonding. The about 300 μm thick sheet of cured modified epoxy resin was easily peeled from the two aluminum sheets, because of the fluoro-resin treatment. Utrathin sections were microtomed from the modified epoxy resin sheet as shown in Fig. 2. and then stained with osmium tetraoxide (O_sO_4). As well known, ATBN containing double bond is stained with O_sO_4. However, the double bond contained in the Versamid is also stained.

2.4 Mechanical Properties

The tensile dynamic mechanical properties of bulk rubber modified epoxy resin were measured with a Rheolo Graph-Piezo (Toyo Seiki Co.) under the conditions of 3 H_z and heating rate of 2°C/min. The specimens were prepared by using the same method as described in the preparation of the TEM specimen.
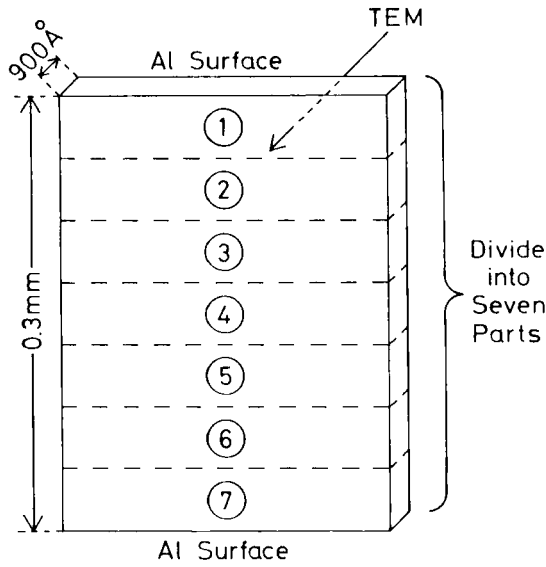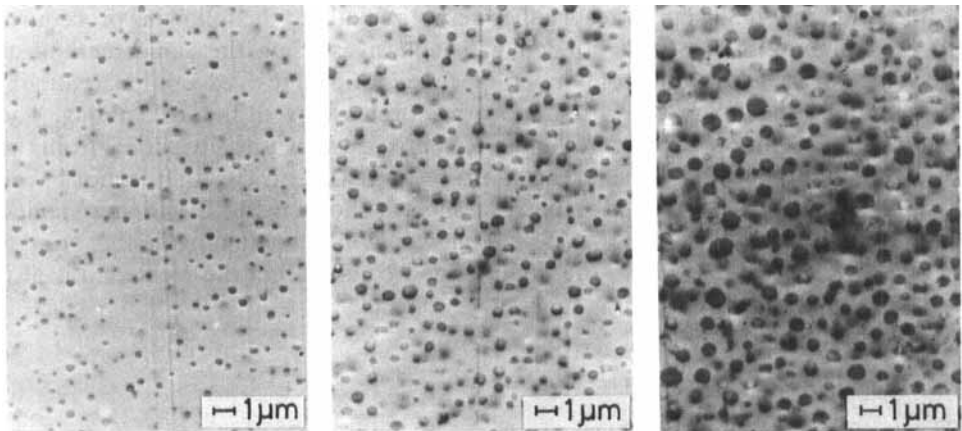
FIGURE 2   Location photographed with TEM in adhesive layer.

3   RESULTS AND DISCUSSION

3.1   Dispersion of Rubber Particles in Cured Bulk Epoxy Resin

Fig. 3-a, b and c show the TEM photographs of cross sections of cured epoxy resin containing ATBN of 5, 30 and 50 phr, respectively. All photographs are those of

(a) ATBN : 5 phr   (b) ATBN : 30 phr   (c) ATBN : 50 phr

FIGURE 3   TEM photographs of DGEBA epoxy adhesives modified with 5, 30 and 50 phr ATBN.

the division 4 in Fig. 2, which is located in the center region of adhesives layer between two aluminum sheets. These photographs demonstrate that the numerous micro rubber particles are dispersed in the epoxy resin matrix, and the size and number of rubber particles increase with increasing content of rubber. The TEM photographs similar to those have been presented by Kunz, et al.[3]

3.2 Dynamic Mechanical Properties of Rubber Modified Epoxy Resins

In Fig. 4, the dynamic mechanical properties of unmodified and rubber modified epoxy resins are shown. With increasing contents of rubber, the storage moduli E' of rubber modified epoxy resins were gradually decreased. It is clear that this phenomenon is derived from the increase of the size and number of rubber particles in epoxy matrix, shown in Fig. 3.

For the unmodified epoxy resin, the tan δ peak at higher temperature of about 104°C is assigned to the α-transition, that is, T_g, and that at lower temperature of about −63°C, the β-transition. For the epoxy resins modified with rubber of 30 and 60 phr, these tan δ peaks at lower temperature of about −49°C and −47°C seem to indicate the overlaps of the tan δ peak of β-transition of unmodified epoxy resin
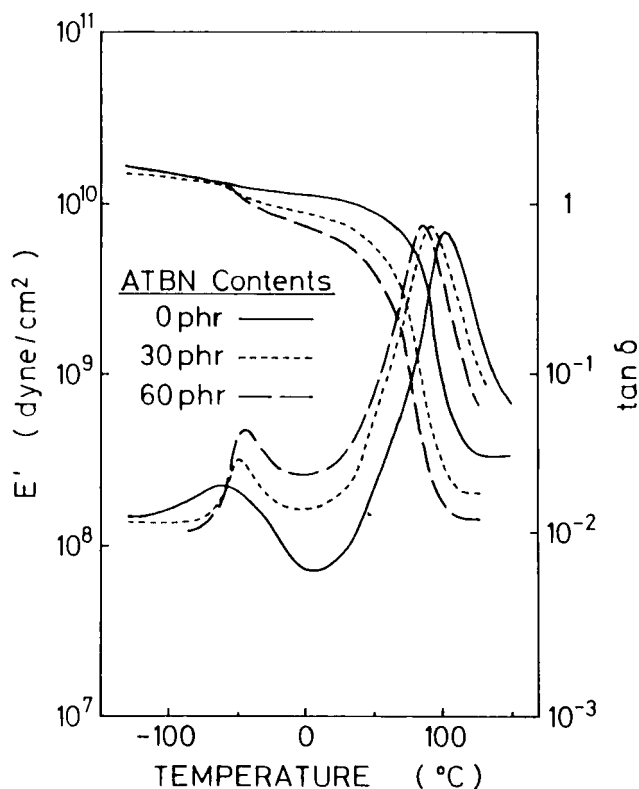

FIGURE 4   Dynamic storage modulus, E', and loss tangent, tan δ, of unmodified and ATBN modified DGEBA epoxy resins.

and that of ATBN. This overlap of tan δ peaks at lower temperatures was pointed out by Kalfoglou[11] and Kinloch,[12] with regards to CTBN modified epoxy resin.

These tan δ curves indicate that the two phases of rubber and epoxy resin are separated on the whole in the rubber modified epoxy resins, shown in Fig. 3. The tan δ peak of epoxy resin shifted slightly to the lower temperature side, and that of ATBN, to the higher temperature side, with increasing ATBN content. This shows that there is some compatibility between the epoxy resin and ATBN. Regarding CTBN modified epoxy resin, Sayre, et al.[13] revealed by use of TEM and NMR that there is some compatibility between epoxy resin and CTBN.

3.3 Effects of ATBN Content and Rate on Peel Strength

As shown in Fig. 5, the peel strengths at 20°C increased with increasing ATBN contents over peel rates less than 300 mm/min. The peel strengths at a peel rate of 1000 mm/min were slightly less than those at 300 mm/min over all ATBN contents.
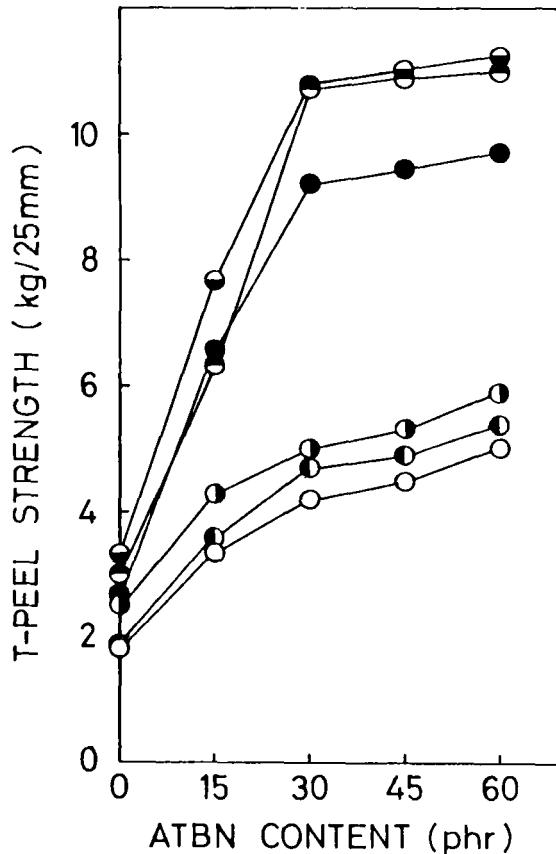

FIGURE 5   Effects of ATBN content and rate on T-peel strength: Cross-head speeds (mm/min); ○ 3, ◐ 10, ◑ 30, ◒ 100, ◓ 300, ● 1000.
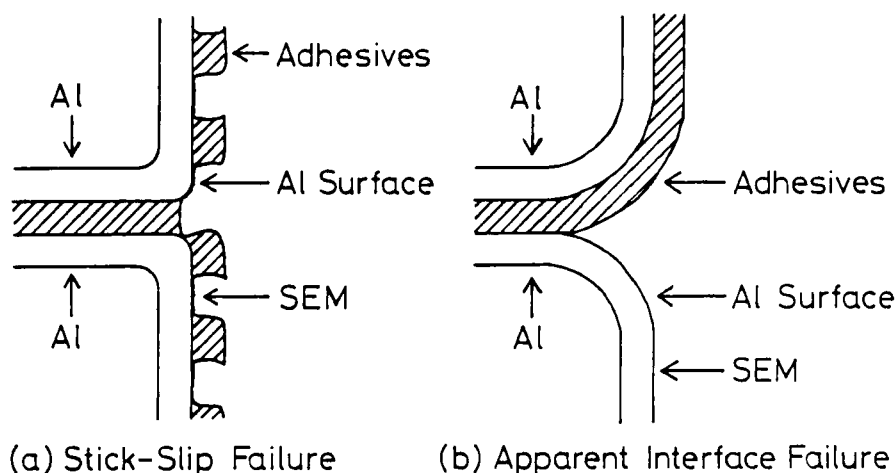
FIGURE 6   Failure modes in T-peel test and locations photographed with SEM.

At higher peel rates ranging from 100 to 1000 mm/min, peel strengths higher than 6 kg/25 mm were obtained, and the modes of failure were all stick-slip failures (Fig. 6-a), except for the case of 0 phr ATBN. At lower peel rates ranging from 3 to 30 mm/min, peel strengths less than 6 kg/25 mm were obtained, and the modes of failure were interfacial over all ATBN contents, according to visual observation (Fig. 6-b). From the observation with a SEM, however, it was revealed that very thin fragments of fractured adhesives were deposited here and there on the aluminum surface. Consequently, the true modes of fracture are not complete interfacial failures, but are the mixed modes of cohesive and interfacial failures. In this paper, such failure modes are called "apparent interfacial failure".

As illustrated in Fig. 6-a, in the stick-slip mode, the fracture plane propagates in the adhesive layer only a short distance before being stopped, and shifts after each such localized fracture from near one adherend interface to near the opposite interface. Such shifts of fracture plane are regularly repeated in the adhesive layer. In the case of stick-slip mode, the surface of the adhesive near the aluminum interface was photographed with SEM, as shown in Fig. 6-a. Fig. 7-a, b, c and d show the SEM photographs of fracture surfaces of specimens after peel tests at a peel rate of 300 mm/min. Fig. 7-a (ATBN: 0 phr) indicates a brittle fracture of epoxy resin. In Fig. 7-b (ATBN: 30 phr), numerous micro holes of average diameter of about 0.7 μm are observed. Fig. 7-c (ATBN: 60 phr) indicates a number of relatively larger micro holes. The increases of size and number of micro holes with increasing rubber content observed with SEM correspond roughly to those of micro rubber particles observed with TEM (Fig. 3). Consequently, it is clear that these micro holes arose from rubber micro particles on fracturing the rubber modified epoxy adhesive. Furthermore, in some cases for 60 phr ATBN, a coarse surface having relatively large micro hillocks and depressions was observed (Fig. 7-d). There may be rubber particles under these hillocks. The coarse fracture surface appears to be produced by ductile fracture of the rubber modified epoxy adhesive, considering a significant

(a) ATBN : 0 phr

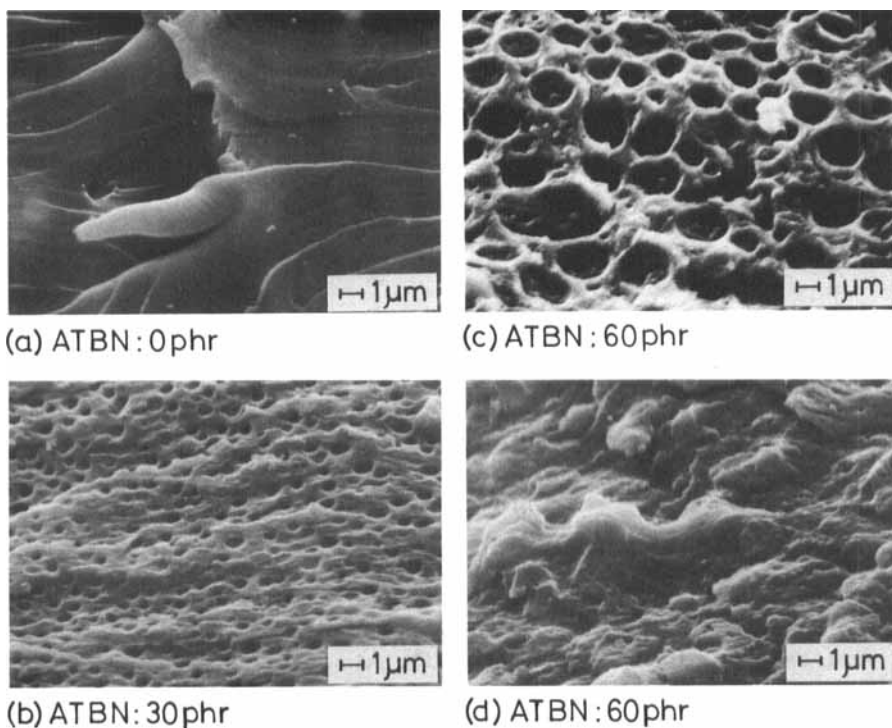(c) ATBN : 60 phr

(b) ATBN : 30 phr

(d) ATBN : 60 phr

FIGURE 7   SEM photographs of fracture surfaces after peel test: Peel test conditions; 20°C, 300 mm/min.

decrease in the modulus of an epoxy resin modified with 60 phr ATBN as shown in Fig. 4. Therefore, the transition of fracture features from a surface having numerous micro holes to a coarse one may occur near an ATBN content of 60 phr under the peel conditions of 20°C and 300 mm/min.

3.4 Effects of Temperature and Rate on Peel Strength

In general, it is well known that the temperature-rate superposition can be applied to the bond strengths such as peel and shear. However, the application of the temperature-peel rate superposition to the peel strength of the ATBN modified DGEBA epoxy adhesive has not been reported. Therefore, it has been investigated whether this superposition is valid or not.

For epoxy adhesive modified with 30 phr ATBN, the relationship between peel strength and test temperature or rate is shown in Fig. 8. The peel strength increased with decreasing temperature or increasing rate, except for some decrease of peel strength under the test conditions of 0°C~60°C and 1000 mm/min. Then, by shifting horizontally these curves, these peel strengths were superposed as a function of temperature and rate, and a master curve was obtained, except for peel strengths at 0°C~60°C and 1000 mm/min (Fig. 9). From the results, it was concluded that, in this bond system under these test conditions employed, the peel strength increases
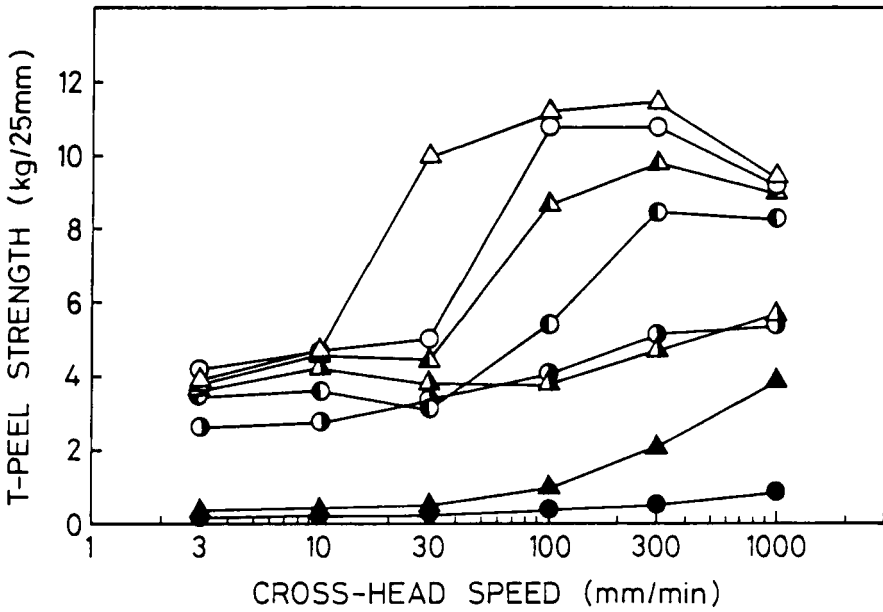
FIGURE 8   Effects of temperature and rate on T-peel strength: Temperatures (°C); △ 0, ○ 20, ▲ 40,
◑ 60, ▲ 80, ◑ 100, ▲ 120, ● 140.

with decreasing temperature or increasing rate, having some exceptions. Since the
application of the temperature-rate superposition is essentially limited to thermo-
rheologically simple polymer system, these exceptional peel strengths may be attrib-
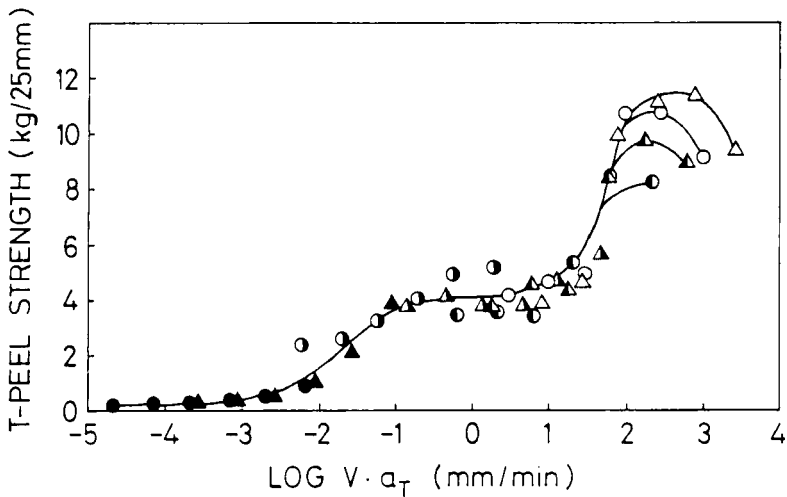uted to the behavior of the adhesive outside this limit under these test conditions.

FIGURE 9   Master curve of T-peel strengths for DGEBA epoxy adhesives modified with 30 phr ATBN:
Temperatures (°C); △ 0, ○ 20, ▲ 40, ◑ 60, ▲ 80, ◑ 100, ▲ 120, ● 140.

It is well known that the superposition is generally unable to be applied to thermo-plastic polymers below T_g.

On plotting the shift factors, a_T, against temperature, two straight lines are given (Fig. 10). Consequently, the relationship between log a_T and T is not a WLF type but is an Arrhenius type. Then, the activation energies, ΔE, were estimated using the Arrhenius equation.

$$\log a_T = \frac{\Delta E}{2.303\, R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

where T is test temperatures, and R is Gas constant. As a standard temperature, T_o, 20°C was arbitrarily employed. The value for ΔE was 6.9 kcal/mol for temperatures lower than the intersection of the two straight lines and 41.9 kcal/mol for temperatures higher than that. The superpositions of some mechanical properties in terms of temperature and time or frequency were discussed in detail by Hunston, et al.[14,15,16] Hunston, et al.[15] also reported that the plot of log a_T against $1/T$ for some mechanical properties of bulk CTBN modified epoxy resins gave two straight lines and their intersection was near 60°C. The activation energy of the Arrhenius type relationship below 60°C was 160.5 kJ/mol (38.4 kcal/mol) ranging from 5.0 to 17.5 phr CTBN.
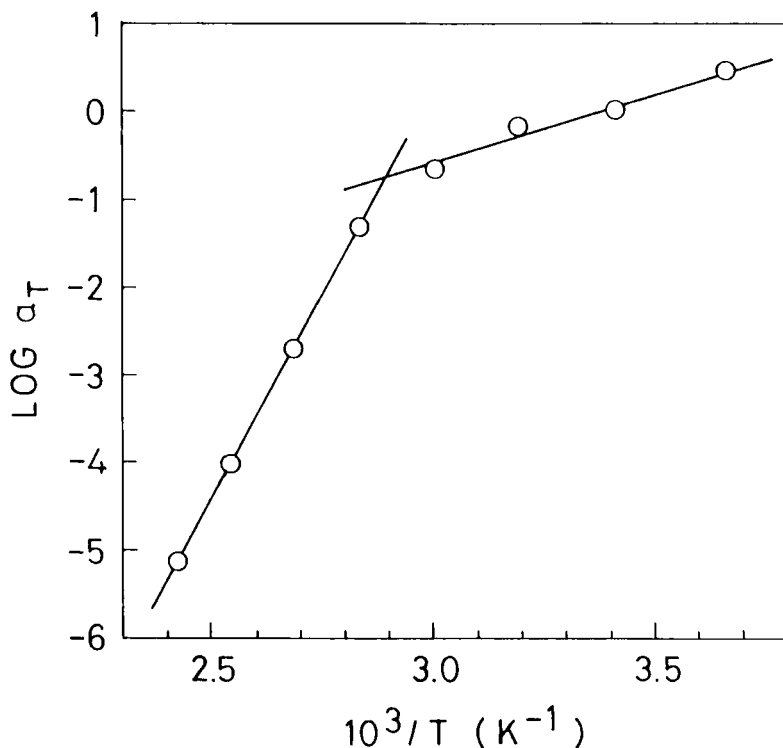

FIGURE 10   Arrhenius plot of shift factors against temperature.

It is clear that the fracture mechanism at higher temperatures above the intersection is different from that at lower temperatures below the intersection. The fracture modes were a stick-slip failure for lower temperatures and higher rates, but, an apparent interfacial one for higher temperatures or lower rates. The peel strengths were higher than about 8 kg/25 mm for the former, but, lower than 8 kg/25 mm for the latter. The temperature of the intersection was about 73°C. As shown in Fig. 4, the T_g of the adhesive containing 30 phr ATBN is about 94°C, and the modulus at 73°C is low, being near 10^9 dyne/cm^2.

The observation with SEM of aluminum surfaces after the peel test revealed that the size of micro holes for apparent interfacial failures was somewhat larger than that for stick-slip one, and the density of micro holes for the former was somewhat lower than that for the latter. For example, the SEM photographs of aluminum surfaces after peel test are shown in Fig. 11. Fig. 11-a, an example of stick-slip failure (peel conditions: 20°C, 1000 mm/min.), indicates that the holes are small in size (about 0.7 μm) and numerous. The photograph suggests that the fracture of adhesive is due to plastic deformation near brittle fracture. Three examples of apparent interfacial failure are shown in Fig. 11-b, c and d. In Fig. 11-b (20°C,

(a) 20°C, 1000mm/min.

(c) 140°C, 1000mm/min.

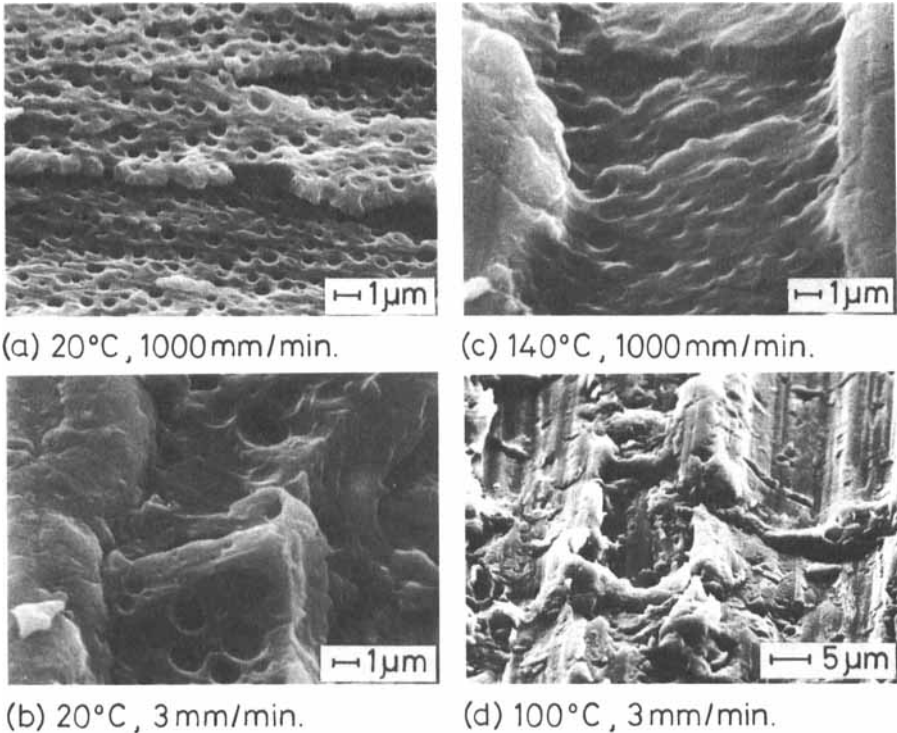(b) 20°C, 3mm/min.

(d) 100°C, 3mm/min.

FIGURE 11   SEM photographs of fracture surfaces after peel test: ATBN content; 30 phr.

3 mm/min), almost naked aluminum surface and fragments of adhesive are observed, which have a smaller number of somewhat larger holes (about 1.5 μm) than those for stick-slip failure. The fracture surface of adhesive seems to indicate plastic deformation. Also in Fig. 11-c (140°C, 1000 mm/min), almost naked aluminum surface and fragments of adhesive are shown, which have a smaller number of somewhat larger and shallow micro depressions, and some micro hillocks. The fracture mode of adhesive is highly ductile. Fig. 11-d (100°C, 3 mm/min) demonstrates nearly naked aluminum surface and fragments of adhesive having few holes. The fracture surfaces of the adhesive suggest plastic deformation. These observations with SEM indicate that the fracture of the adhesive under study is due to the plastic deformation near brittle fracture at the temperatures lower than the intersection, the highly plastic deformation at the temperatures higher than the intersection, and the plastic deformation near the intersection or T_g, giving the transition region of fracture.

3.5 Distribution of Rubber Micro Particles and Course of Fracture

Even if the same rubber, epoxy resin and hardener are used, the size and density of rubber particles in the cured epoxy resin matrix depend on the blend ratio,[3,17,18] cure conditions[6,19] and the procedures from blending to curing. As mentioned above, for the bonded specimens using the same materials, cure conditions and procedure, it has been revealed that the size and density of holes on the fracture surface after peel test differ by fracture modes. Why does such phenomenon occur?

In Fig. 12, the TEM photographs of epoxy adhesive modified with 50 phr ATBN are shown. Fig. 12-a, b and c correspond the divisions—1, 4 and 7 in Fig. 2, respec-
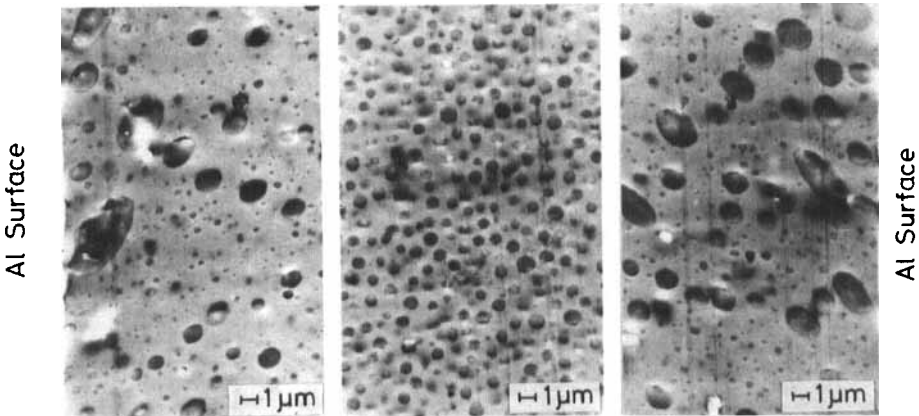

(a) Division-1   (b) Division-4   (c) Division-7 in Fig.2

FIGURE 12   TEM photographs of DGEBA epoxy adhesives modified with 50 phr ATBN.

tively. Fig. 12-a and c are those of the most outside surface layer of adhesive contacting with aluminum surfaces. Fig. 12-b is that of the center region of adhesive. Comparing Fig. 12-b with Fig. 12-a and c, it is clear that the rubber particles of surface layer have larger size and lower density than those of the center region. Such a trend becomes marked with increasing ATBN contents,[19] and so here TEM photographs of ATBN of 50 phr in place of 30 phr have been employed to help the clearer understanding. Consequently, it appears that, for stick-slip failure, the fracture plane propagates in the adhesive layer containing rubber particles of small size and high density with the shift from near one interface to near the opposite interface, and, for apparent interfacial failure, propagates along interface, as illustrated in Fig. 13-a. In the case of stick-slip failure, numerous small holes derived from the breaking of the rubber particles were observed (Fig. 11-a). Therefore, it seems that, at low temperature or high peel rate (Fig. 13-b-1), the fracture plane passes through the centers of rubber particles, because of the low plastic deformation near to brittle fracture of the epoxy resin.

On the contrary, in the case of apparent interfacial failure, a smaller number
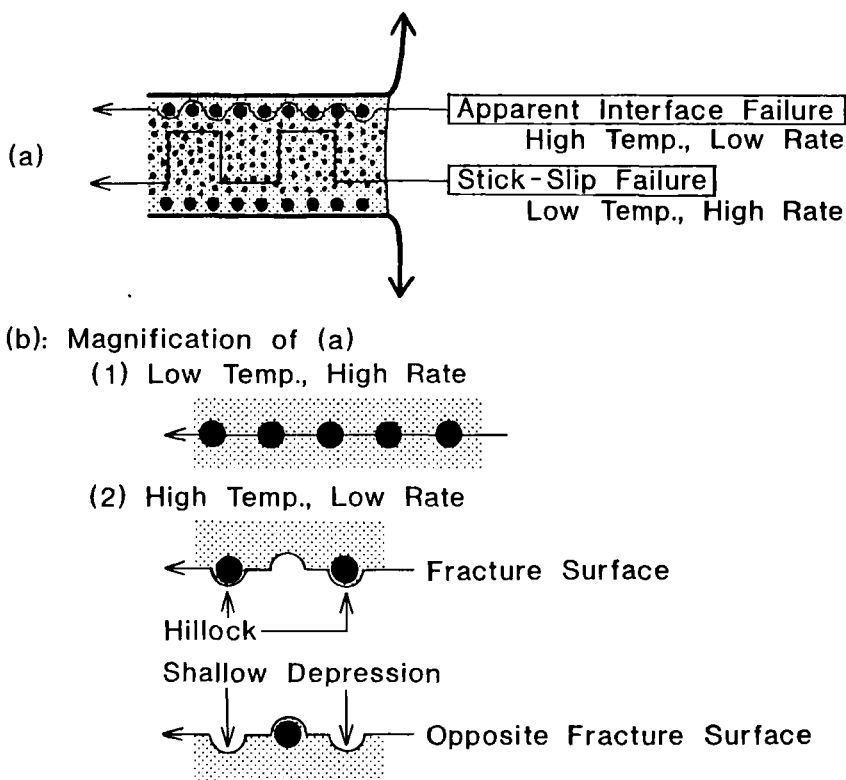
Black: Rubber, Shadow: Epoxy Resin Matrix

FIGURE 13   Course of fracture propagation in DGEBA/ATBN adhesives.

of somewhat larger, shallow depressions and hillocks were observed (Fig. 11-c). Therefore, it is supposed that, at high temperature or low peel rate (Fig. 13-b-2), the fracture plane passes through epoxy resin around rubber particles, because of ductile fracture of epoxy resin. Effects of cure conditions on the distribution of size and density of rubber particles in the epoxy matrix were investigated in detail.[19] As a result, it is revealed that this distribution becomes uniform with increasing temperature of curing. The mechanism of the distribution is not yet clear and under investigation. These results will soon be published in another paper.

3.6 Toughening Mechanism

Concerning the toughening of epoxy resin, that is, the increase of K_{IC} or G_{IC}, by modifying with CTBN, many mechanisms have been presented, for example, elongation and tearing of rubber particles,[18,20] crazing of epoxy resin matrix,[21,22] yield and plastic flow[23,24,25] and triaxial dilation.[23,24,26] The T-peel strength is different from K_{IC} or G_{IC} in the test method, though both data have been used for the evaluation of the toughness of adhesive. Hence, the values obtained with these test methods are unable to be directly compared. It may be possible, however, to discuss fracture mechanisms from these test methods, particularly T-peel and TDCB tests, in a similar manner, since these test methods are based on a cleavage fracture.

3.6.1 Stretching and tearing of rubber particles   Why are a number of holes observed only for high peel strength?

With the fracture process on loading uniaxial tension on a butt joint, it was revealed that first a triaxial stress arose and caused local yield, and then crack and void at the center region of adhesive layer, which dilated with enlarging void, and finally ruptured.[27]

For the T-peel test also, similar phenomena to those in a butt joint test may occur, except for the effect of rubber particles. Hence, the fracture of the T-peel specimen will initiate and propagate through the following process:

On applying a load to a T-peel specimen, the epoxy resin matrix shell around the spherical rubber particle dilates by a triaxial stress. With the dilation of the epoxy resin, the rubber also dilates, if the bond between rubber and epoxy resin is strong (Fig. 14). Their dilation causes the collapse of both epoxy resin and rubber.

On fracturing, the rubber particle bonded strongly to the epoxy matrix shell is
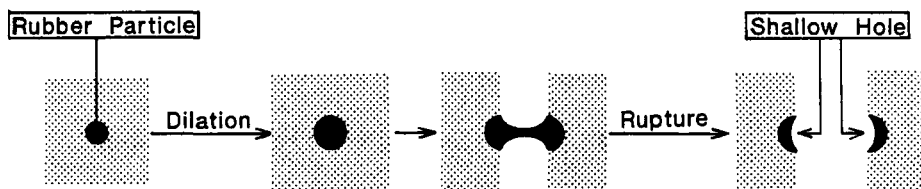
Black: Rubber, Shadow: Epoxy Matrix Shell

FIGURE 14   Mechanism of rupture of rubber particle in DGEBA/ATBN adhesives.

stretched and torn. The two fragments of torn rubber come back and fill the insides of the hemispherical epoxy matrix shells broken into two parts (Fig. 14). This hollow hemisphere of epoxy resin is still enlarged as a result of the preceding dilation, but, on the contrary, rubber contracts to the original volume after fracture. This appears to be the reason for the production of the shallow hole.

As mentioned above, the large dissipation of energy for the plastic deformation and fracture of the epoxy matrix and numerous rubber particles caused by triaxial stress may be an important reason for the remarkable increase of the peel strength of the DGEBA/ATBN adhesive.

3.6.2 Yield and plastic flow of epoxy resin As described in the preceding paragraphs, the superposition of peel strength is, on the whole, governed by plastic or viscoelastic deformation of the ATBN modified epoxy adhesive (Fig. 9). Furthermore, the peel strengths were high at the temperatures lower than the T_g of the adhesive and at high peel rate. The fracture mode was a stick-slip failure of the adhesive, due to the plastic deformation near brittle fracture (Fig. 11-a). In view of these facts, the marked increase of peel strength in a stick-slip failure region may be, on the whole, attributed to the shear yield and plastic flow of the epoxy matrix.

The important role of shear yield and plastic flow of the epoxy matrix acting on the toughness of DGEBA/CTBN system has been discussed in detail by Kinloch, et al.[24,25] Regarding the remarkable increase of peel strength of the DGEBA/ATBN adhesive also, it seems that the shear yielding is the main source of energy dissipation and increased toughness.

4 CONCLUSION

The effects of content, peel rate and temperature on peel strength of ATBN modified DGEBA epoxy resin adhesive have been investigated. The fracture surfaces of specimens after a peel test and the distributions of rubber particles in cured bulk epoxy resin have been observed with SEM and TEM, respectively. The mechanical properties of bulk rubber modified epoxy resin have been also measured.

The observation with TEM demonstrated that the size of micro rubber particles dispersed in the epoxy matrix increased with increasing rubber content. The measurement of mechanical properties revealed that the moduli of the DGEBA/ATBN system and T_g of the epoxy resin decreased gradually with increasing rubber content. The peel strengths at 20°C increased with increasing rubber content or peel rate. The higher rates gave remarkably high peel strengths with a stick-slip failure and a large number of micro holes produced by the rupture of rubber particles on the fracture surface. With increasing rubber content, the size of the holes increased. This reflects the observation with TEM.

In the case of rubber content of 30 phr, the peel strengths increased with decreasing temperature or increasing rate. These peel strengths were superposed as a function of temperature and rate. Plotting of the shift factors against temperature gave two straight lines, which followed an Arrhenius relationship. This shows that the fracture mechanism differs for regions of temperatures below and above

the intersection of two straight lines, which occurs at the temperature somewhat lower than T_g. The former gave marked high peel strengths with a stick-slip failure due to plastic deformation of the adhesive, and a number of holes were observed. The latter gave lower peel strengths with an apparent interfacial failure having some adhesive fragments produced by highly ductile fracture and larger, shallow holes or no holes were observed. The observation with TEM illustrated that the size of particles in the most outside region of adhesive nearest aluminum interface was larger than that in the inside region. These results show that the peel strength and fracture mechanism depend upon rate and temperature of fracture, that is, plastic or viscoelastic deformation of the adhesive, and that the fracture propagates in the adhesive at lower temperature but along the interface at higher temperature.

Finally, the marked increase of peel strength of DGEBA epoxy adhesive modified with ATBN was concluded to be mainly attributed to the following: (1) The plastic or viscoelastic deformation of epoxy matrix, (2) The strong bond between rubber particles and epoxy matrix, (3) The dilation and rupture of a number of rubber particles.

Acknowledgements

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