Fracture Toughness of Adhesive Joints. III. Temperature and Rate Dependencies of Mode II Fracture Toughness and Adhesive Shear Strength

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ABSTRACT: Adhesive strength shows temperature and rate dependencies that reflect viscoelastic properties of an adhesive. Similarly, a critical strain energy release rate is expected to show temperature and rate dependencies because deformation and fracture of the adhesive occur at the time of the measurement of the strain energy release rate, which is a kind of fracture mechanical parameter for adhesive joints. In this study, the critical strain energy release rate (G_{IIC}) of a plane-shear mode was measured over a wide range of temperatures and rates, and then a master curve was obtained by applying the temperature-rate superposition principle to the obtained data. The relation between G_{IIC} and adhesive shear strength was also investigated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 835–841, 1997

INTRODUCTION

A polymer used as an adhesive is a viscoelastic material, and its mechanical properties are dependent on experimental conditions, especially the temperature and time scale (strain rate, frequency). A series of time-scale dependencies on the linear viscoelastic properties of the polymer were measured at various temperatures, and a master curve was then obtained by applying the time–temperature superposition principle to the obtained data. We also obtained viscoelastic functions over a wide range of time scales from the master curve. A shift factor, a_T, used to obtain the master curve, was expressed by the WLF (Williams, Landel and Ferry equation) or Arrhenius equation.[1–4]

The ultimate stress and failure strain of polymer materials depends on the intrinsic structure and physical properties of the materials, and at the same time microvoids inside the materials and the other flaws largely alter the fracture behavior. Recently, the fracture mechanical approach has been frequently tried with emphasis on the latter. Bitner et al.,[5] Huang and Kinloch,[6] and Hunston and Bullman[7] showed that the fracture energy of rubber-modified epoxy could be described as a function of temperature and time to failure, and they clarified that the master curve was obtained by applying the temperature-rate superposition principle to these data.

It was also experimentally confirmed that the adhesive strength measured by the standardized test methods shows systematic temperature and rate dependencies in most cases. Application of the temperature and rate superposition principle to this complicated behavior was also attempted by many researchers, and it was found that the

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Table I Description of Adhesives KU661/2

	KU661	KU662
Component	Polyester(polyol)	Polyisocyanates
Specific gravity	1.13	1.23
Viscosity (cps at 25°C)	6000–15,000	100–250
Mixing ratio, parts by weight	100	100
Work life at 20°C		30–40 min(mixture)

Table II Characteristics of Adherend

	Specific Gravity			Young's Modulus (10^5 kgf/cm^2)
Adherend	Air	Dry	Moisture Content (%)	E_1
Kaba	0.88	0.78	14.9	1.16

shift factor just changed according to the change of the fracture modes.[8–13]

In fracture tests of adhesive joints, there are opening, plane-shear, and tearing-shear modes; their critical strain energy release rates are G_{IC}, G_{IIC}, and G_{IIIC}, respectively. We studied the rheological characteristics of these critical strain energy release rates. A critical strain energy release rate (G_{IC}) in the opening mode for the adhesive joints bonded with polyurethane adhesive showed temperature and rate dependencies reflecting viscoelastic properties of the adhesive. We showed that the master curve was obtained by applying the temperature-rate superposition principle to these data. In an Arrhenius plot of a shift factor, we obtained two straight lines, which suggests the fact that two different fracture mechanisms exist. Furthermore, a positive correlation between the square root of G_{IC} and the adhesive tensile strength was confirmed in a higher temperature region, and no clear correlation was found in a lower temperature region.[14]

On the other hand, the data on the critical strain energy release rate (G_{IIC}) of the plane-shear mode for the adhesive joints have not been studied sufficiently. Gent and Kinloch[15] measured adhesive fracture energy (ϕ) as a function of temperature and rate of deformation for a copolymer of butadiene and styrene/

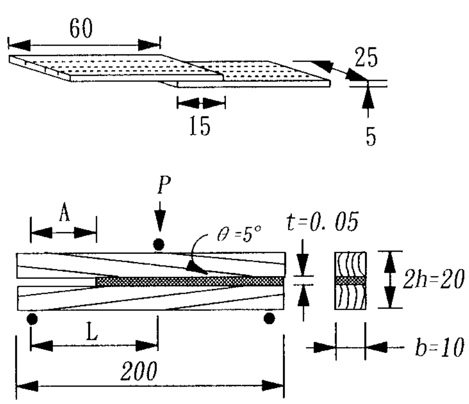

Figure 1 The geometry of specimens for adhesive shear strength and mode II fracture test.

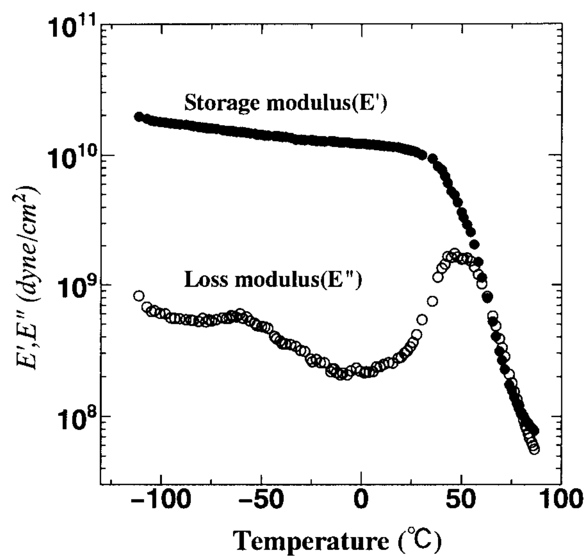

Figure 2 Dynamic mechanical properties of the adhesive.

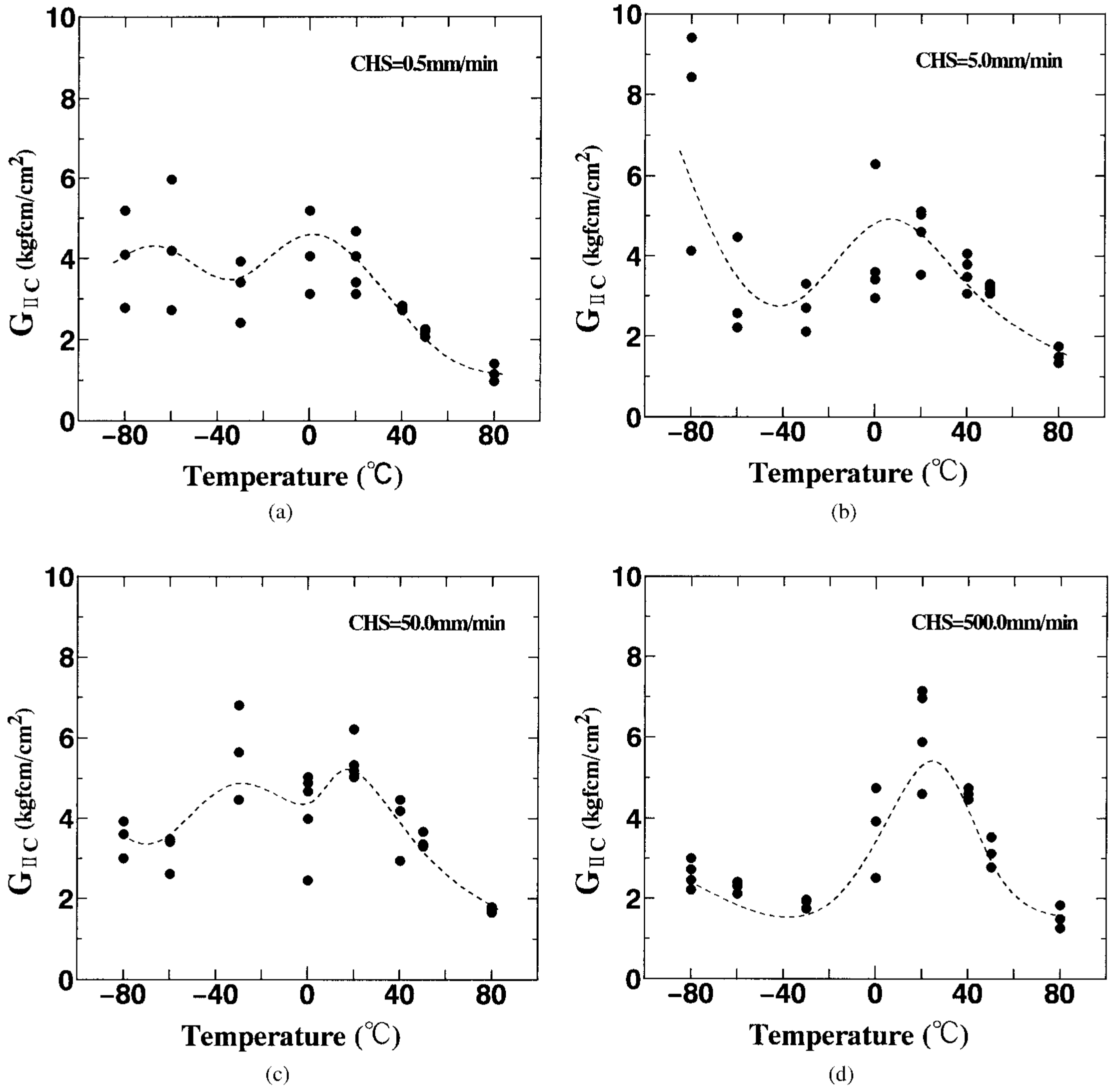

Figure 3 Temperature dependencies of G_{IIC} for adhesive joints bonded with polyurethane adhesives. CHS, crosshead speed.

Mylar-coated steel joints and obtained the master curve by applying the WLF equation to these data. They also confirmed that the energy criterion could be applied to the fracture of the adhesive joints. In our previous work[16] we clarified the fundamental conditions to experimentally estimate the strain energy release rates in three different fracture modes.

In this study, the G_{IIC} of the plane-shear mode was measured over a wide range of temperatures and rates for a specimen prepared according to our previous work.[16] Then, we examined whether or not the temperature-rate superposition principle could be applied to the obtained data. And we examined the relation between G_{IIC} and the adhesive shear strength, both of which have similar deformation modes.

EXPERIMENTAL

Materials

Polyurethane adhesives KU661 and KU662 (Konishi Company) were used in this work. The adhesives consist of polyester(polyol) (KU661) and

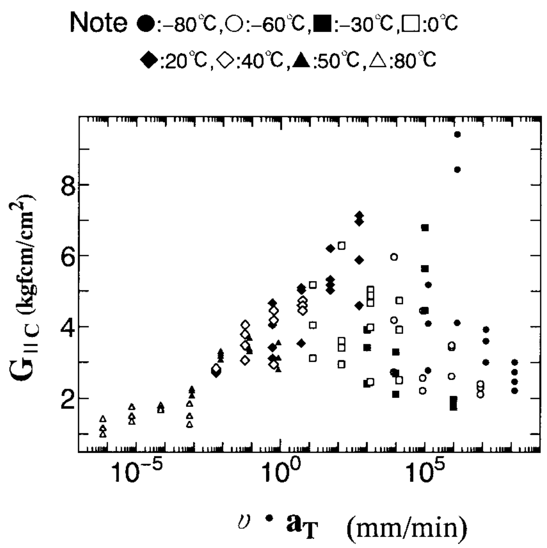

Figure 4 Master curve of G_{IIC} for adhesive joints bonded with polyurethane adhesives reduced to 20°C.

polyisocyanates (KU662). The characteristics of the adhesives are summarized in Table I.

Kaba (Japanese birch, *Betula maximowiczana regel*) finished with a surface planer (Hitachi Co.), was used as an adherend. Its physical properties are shown in Table II.

Measurement of Dynamic Mechanical Properties

The cured polyurethane film was prepared by casting the mixture of KU661 and KU662 on a Teflon sheet and curing the mixture at room temperature and 65% relative humidity (RH) for 5 days. Dynamic mechanical properties of the film were measured by means of a Rheovibron DDV-II (Toyo Baldwin Co., Ltd.) at 110 Hz with an average heating rate of 1°C/min.

Measurement of G_{IIC} for Adhesive Joints

Wood specimens for fracture mechanical tests were prepared with grain angle of 5° as shown in Figure 1, which is the angle necessary to prevent wood failure along the grain prior to fracture. Precrack length was 4 cm, as in our previous work.[16] The amount of adhesive employed was 250–300 g/cm^2, and the specimen was assembled as shown in Figure 1.

The specimen was pressed under 10 kg/cm^2 and kept at 20°C and 65% RH for 4 days for curing. A fracture mechanical test was carried out with crosshead speeds of 0.5, 5.0, 50.0, and 500.0 mm/min over a range of −60 to 80°C by means of a Tensilon testing machine (Orientec Co.). A critical strain energy release rate, G_{IIC}, was determined by the compliance method according to the following equation[15,17]:

$$G_{IIC} = \frac{P_c^2}{2b}\left(\frac{\partial C}{\partial A}\right), \qquad (1)$$

where P_C and E are failure load and Young's modulus of the adherend, respectively, and the other parameters are shown in Figure 1.

Measurement of Adhesive Shear Strength

The specimen for the shear-lap test was prepared as shown in Figure 1. The adhesion conditions, such as the spread amount of the adhesive and bonding pressure, was the same as that of the fracture mechanical test described above. The measurement of adhesive shear strength was carried out with crosshead speeds of 0.5, 5.0, 50.0, and 500.0 mm/min over a range of −60 to 80°C using the Tensilon testing machine.

RESULTS AND DISCUSSION

Temperature and Rate Dependencies of G_{IIC}

Figure 2 shows the dynamic mechanical properties of the adhesive used in this work.[14] α and β

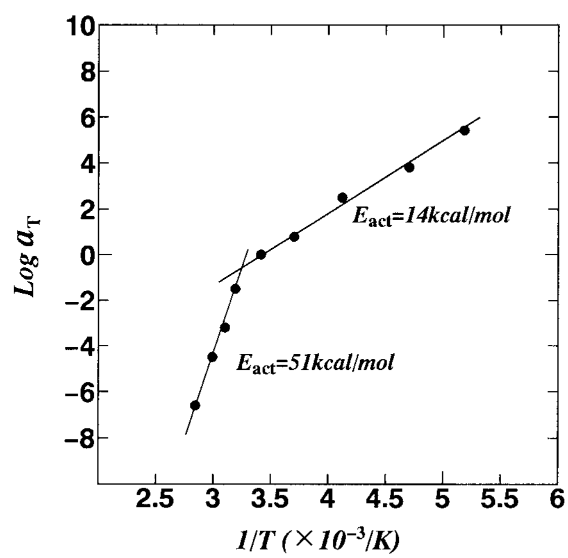

Figure 5 Arrhenius plot of shift factor, α_T, used to obtain the master curve.

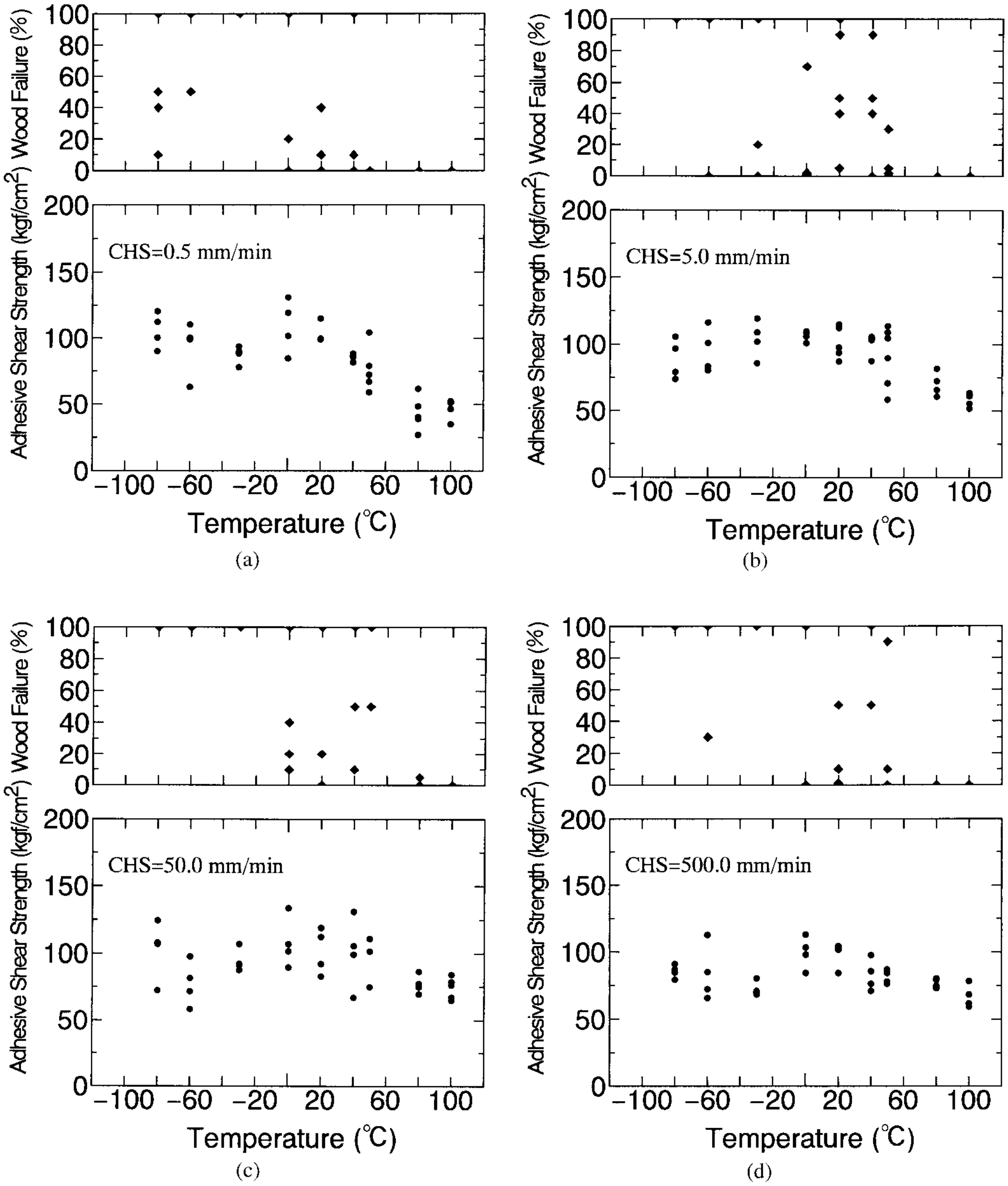

Figure 6 Temperature dependencies of adhesive shear strength for adhesive joints bonded with polyurethane adhesives. CHS, crosshead speed.

relaxations appeared at 46 and −60°C, respectively. It was assumed that the viscoelastic properties of the adhesive strongly affected the fracture mechanical properties of the adhesive joints because the fracture phenomena of the joints involved deformation of the adhesive layer.

Figure 3 shows the temperature dependence of G_{IIC} for the adhesive joints. G_{IIC} showed a higher value or a peak around the glass transition temperature, T_g. This result suggested that the mechanical relaxation mechanism of the adhesive reflects in the fracture. In the temperature region over T_g, G_{IIC} decreased with an increase of temperature. It was not clarified in this work why G_{IIC} showed a higher value at −80°C at a crosshead speed of 5.0 mm/min. The curve of G_{IIC} shifted to a higher temperature region with the increase of crosshead speeds.

Equation (2) holds for G_{IIC} of the adhesive joints bonded with viscoelastic adhesive,[14]

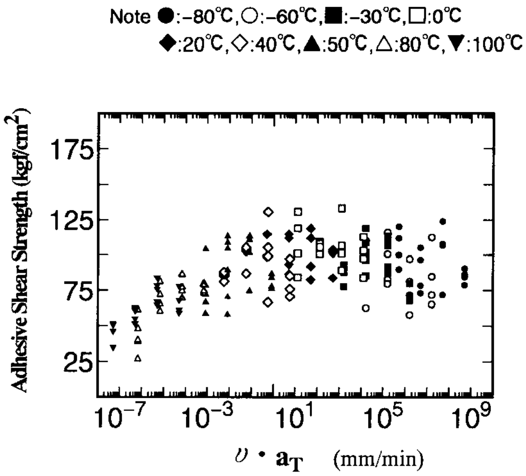

Figure 7 Master curve of adhesive shear strength for adhesive joints bonded with polyurethane adhesives reduced to 20°C.

$$G_{IIC}(v) = \left(\frac{T}{T_0}\right)^2 G_{IIC0}(va_T), \qquad (2)$$

where v is the rate, a_T is a shift factor, and G_{IIC} and G_{IIC0} are critical strain energy release rates at temperatures T and T_0, respectively.

Figure 4 shows the master curve of G_{IIC} reduced to 20°C by applying the temperature-rate superposition principle to the obtained data. We obtained information on G_{IIC} over a very wide range of rates from this master curve. The peak of G_{IIC} centered at around $v \cdot a_T = 1.0 \times 10^3$ mm/min was considered to correspond to an α relaxation of the adhesive polymer. The scatters of G_{IIC} at higher rates indicated that the fracture behavior at higher rates and lower temperatures was unstable and complicated. Criterion for the crack propagation strongly depended on interfacial structures because stress concentration was occurred easily in flaws of the interface between the adhesive and the substrate. The surface of the wood was a bumpy structure with voids, and tissue and quantities of the structure were not uniform. Critical criterion of the crack propagation was dependent on this heterogeneous interfacial structure. This resulted in great scatters of G_{IIC}.

The Arrhenius plot of the shift factor, a_T, which had been used to obtain the master curve, is shown in Figure 5. Two straight lines were clearly observed, which suggests that there were two different fracture mechanisms.

The peak of the curve of G_{IIC} appeared in a lower temperature region or a higher rate region than that of G_{IC}.[14] Similar behavior was found between adhesive tensile strength and shear strength.[9,18,19]

Temperature and Rate Dependencies of Adhesive Shear Strength

Figure 6 shows the temperature dependence of the adhesive shear strength. The value of adhesive shear strength was almost constant in a temperature region lower than T_g and then decreased with increasing temperature. As crosshead speeds increased, the curve of the adhesive shear strength tended to shift to a higher temperature region.

Applying the temperature-rate superposition principle using the shift factor shown in Figure 5 to these data, a master curve was obtained as shown in Figure 7. The adhesive shear strength increased with increasing crosshead speed and approached a constant when the crosshead speed was over 1.0×10^{-1} mm/min.

Observation of the fracture surface showed that mixed modes of the cohesive fracture of the adherend and interfacial fracture occurred in a lower temperature region, and cohesive fracture of the adhesive layer mostly occurred in a higher temperature region.

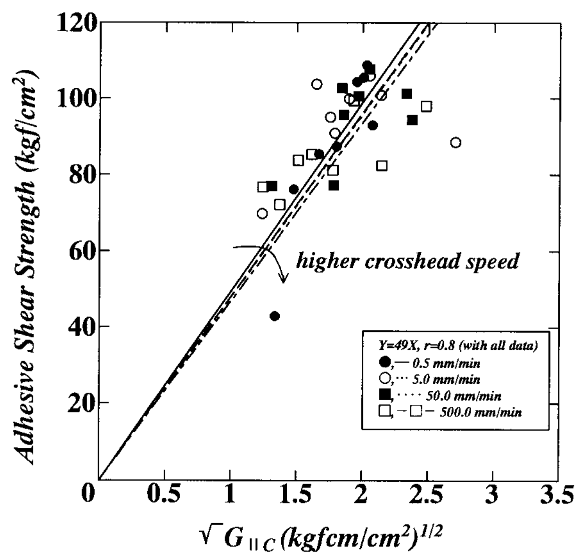

Figure 8 Relationship between adhesive shear strength and $\sqrt{G_{IIC}}$.

Relationship Between G_{IIC} and Adhesive Shear Strength

Figure 8 shows the relationship between the G_{IIC} and the adhesive shear strength of the specimens bonded with polyurethane adhesive. A positive correlation with a correlation coefficient of 0.8 was found between the square root of G_{IC} and adhesive tensile strength. Furthermore, the slope of the recurrence line tended to be gentle with increasing crosshead speeds. In a lower temperature region or a higher rate region, cohesive fracture of the adherend mostly occurred at the adhesive shear strength test, and interfacial fracture occurred at the fracture mechanical test. In the higher temperature region or the lower rate region, mostly cohesive fracture of the adhesive layer occurred. Although the fracture mechanism in both tests was different, it is interesting to note that there is a certain correlation between the two values. And it is evident that the viscoelastic properties of the adhesive are significantly related to the fracture of the adhesive joints.

CONCLUSION

G_{IIC} and adhesive shear strength of adhesive joints bonded with polyurethane adhesives varied as a function of temperature and rate, reflecting the viscoelastic properties of the adhesives. G_{IIC} and adhesive shear strength became a maximum or a higher value at a certain temperature region or a rate region. This showed that the mechanical relaxation mechanism of the adhesive was strongly dependent on these two tests. Applying the temperature-rate superposition principle to the experimental data, we obtained the master curves of G_{IIC} and adhesive shear strength. Performing an Arrhenius plot with the shift factor, a folded line was observed. This fact indicates that different fracture mechanisms existed.

A positive correlation was confirmed between the square root of G_{IIC} and adhesive shear strength. Furthermore, a slope of the recurrence line tended to be gentle with increasing crosshead speeds. In a lower temperature region, interfacial properties between adherend and adhesive strongly affected the fracture mechanism of the adhesive joints.

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