Korea Polymer Journal, Vol. 5, No. 4, pp 256-261 (1997)

Relationship Between Strain Energy Release Rate in Mode I Fracture and Adhesive Tensile Strength for Adhesives Having Different Molecular Structure

Won Woo Lim* and Hiroshi Mizumachi

Division of Polymeric Materials, Department of Bio-material Science, Graduate School of Agricultural and Life Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Received June 17, 1997

Abstract: It is well known that the adhesive strength of adhesive related to dynamic mechanical properties shows temperature or rate dependence. Similar dependencies were also found in the strain energy release rate of adhesive joints. However, when two values were compared in detail, a complicate correlation between two values occur. In this study, the strain energy release rate(G_{IC}) in opening mode (mode I) for wood/adhesive joints bonded with different type of typical adhesives was measured. In addition, an extensive comparison between the G_{IC} and adhesive tensile strength in the similar deformation mode was presented.

Introduction

Adhesives have been used in many industrial fields. Various practical performances are demanded according to their applications. Adhesives are polymeric materials, and it is well known that their physical properties depend upon chemical and supermolecular structures. Generally, the performance of adhesives, especially, the adhesive strength is evaluated by the standard testing method for adhesive. The adhesive strength depends on testing methods and is defined by the load at failure of adhesive joints divided by the adhesive area or the width. The cohesive fracture of adhesives and adherend, interfacial fracture, and fractures in mixed modes are usually observed under the various testing conditions. The physical meaning of the adhesive strength is not yet well defined. Furthermore, the value of external force per unit area or width is ambiguous in terms of mechanics. In spite of this, when the adhesive strength is measured by changing the viscoelastic properties of the adhesives, some types of general empirical rules could be found.[1-7] Also, several approaches to explain these rules by a simple rheological model have been investigated.[7,8] It was true that many characteristics of temperature and rate dependencies of adhesive strength could be explained qualitatively with this model. However, it was also found that some of results of calculation with this model were not in agreement with the experimental results. This discrepancy strongly suggested the importance of stress concentration inside the adhesive joints.

In fracture mechanics, criteria for initiation and propagation of crack are described in terms of stress field near the crack-tip of material and it is well known that fracture toughness(K_C or G_C) is an appropriate parameter to describe the fracture characteristics.

Mostovoy *et al.*[10-13] had applied fracture mechanics to aluminium DCB (Double Cantilever Beam) specimen bonded with epoxy resins. They examined the effect of the shape and dimension of specimens on the fracture toughness and also proposed a method for measuring the critical strain energy release rates in the opening mode (G_{IC}) and in the plane shearing mode (G_{IIC}). Many studies on the fracture mechanics testing methods of adhesive joints were summarized by Kinloch.[14] Even if the shape and the dimension of specimen were the same, there was a case where the value of fracture toughness was different with the testing methods. The important factors involved in this fracture toughness are temperature, rate, fracture type, thickness of adhesive layer, environmental testing conditions, and molecular structure and properties of the adhesive itself. Lim *et al.*[15-18] have studied fracture toughness for a series of wood/adhesive joints. They confirmed the experimental condition for estimating G_{IC}, G_{IIC}, and G_{IIIC}, in dependent of shape and dimensions of the specimen. They also evaluated the critical strain energy release rates as a function of temperature and rate, using some typical adhesives having glass transition temperatures. They applied the temperaturerate superposition procedure to obtain a continuous master curve from the data. They pointed out that there is a significant correlation between the strain energy release rate and the adhesive strength. They also clarified that G_{IC} and adhesive tensile strength showed a maximum value at $\Delta T = 40$ °C, $E' = 1.0 \times 10^{10}$ dyne/cm^2, $E'' = 6.0 \times 10^8$ dyne/cm^2 and $\tan\delta = 0.1$, where ΔT is the difference between glass transition temperature(T_g) of an adhesive and testing temperature. It was found that the correlation between adhesive tensile strength and $\sqrt{G_{IC}}$ was different if viscoelastic properties of the adhesives and fracture mode were different. That is, when adhesives were in the glassy state, a linear correlation exists between the two values. On the other hand, when adhesives were in the rubbery state, the correlation was expressed by a quadratic curve, and a significant correlation was not found in the transition region. However, a positive correlation was found between adhesive shear strength and $\sqrt{G_{IIC}}$, although data were scattered.

In this study, we measured the strain energy release rate in opening mode for wood/adhesive joints bonded with typical adhesives which had different molecular structures and physical properties. The strain energy release rate was compared with the adhesive tensile strength.

Experimental

Materials. Adhesives used in this study were polyvinyl acetate(PVAc(S), DP = 1400 - 1600, Wako Junyaku Kogo Co., Ltd.) and rubber-modified epoxy resin(Epikote 828(epoxy value 190, Shell Chemical Co.)-ATBN(amine-terminated butadiene acrylonitrile copolymer, HYCAR ATBN 1300 × 16, amine value 900, Ube Industries Ltd.)). PVAc(S) is a linear polymer made by the solution polymerization. PVAc(S) dissolved in some amount of MeOH, was spreaded onto a Teflon sheet and PVAc(S) film was obtained by evaporating solvent completely. Epikote 828-ATBN epoxy resin is a cross-linked polymer. Epikote 828 and ATBN were homogeneously mixed in the ratio of 80/20, then cured by adding HMDA(amine value 27, Wako Junyaku Kogo Co., Ltd). It is known that the epoxy resin and rubber phases were separated in a cured film. Wood adherend used in this work was Kaba (*Betula maximowiczana* Regel) and its physical properties were listed in Table I.

Measurement of Strain Energy Release Rate in Opening Mode of Adhesive Joints. As shown in Figure 1, wood specimens with grain angle of 5° were prepared for fracture mechanics tests. The angle is necessary to prevent wood-failure along the grain prior to joint fracture. A precracked length was 8 cm[15] and for the case where rubber-modified epoxy resins adhesive was used, the amount of adhesive applied was 250-300 g/cm^2. The specimen was pressed under 10 kgf/cm^2 (Figure 1) and cured at 20 °C, R.H.65% for 4 days. For PVAc(S), the 1.0 mm thickness of film prepared was inserted between adherends (Figure 1) and kept in an oven at 100 °C for 1 hour. The specimens were taken out, pressed at 10 kg/cm^2, and kept at 20 °C, 65% R.H. for 4 days. A fracture mechanics test was carried out with the crosshead speed of 10 mm/min. at various temperatures by using Tensilon (Orientec Co.). A strain energy release rate, G_{IC}, in opening mode was evaluated by the compliance method using the fol-

Table I. Characteristics of Adherend

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

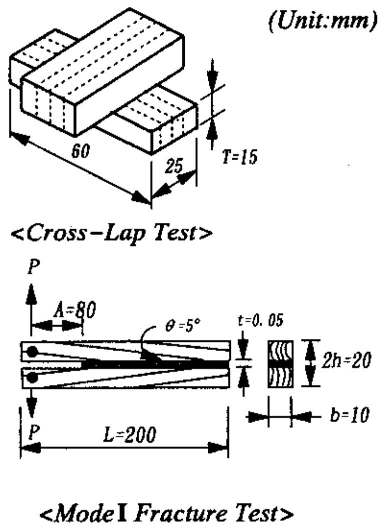

Figure 1. The geometry of specimens for adhesive tensile strength and mode I fracture test.

lowing equation:[11,12]

$$G_{IC} = \frac{4P_c^2}{b^2E}\left(\frac{3A^2}{h^3} + \frac{1}{h}\right)$$

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

Measurement of Adhesive Tensile Strength. The specimen for the cross-lap test was prepared as shown in Figure 1. The adhesion condition such as spread amount of adhesive and bonding pressure was the same as that of the case of fracture mechanics test described above. The measurement of adhesive tensile strength was carried out with the crosshead speed of 10 mm/min. at various temperatures using Tensilon.

Observation of Fracture Surface. Crack tip was cut from a specimen after the fracture test, coated with silver, and then the fracture surface was observed by means of SEM.

Results and Discussion

Dynamic mechanical properties of PVAc(S) confirmed that the primary absorption appears at around 52℃, and that a significant secondary absorption was not found.[7] Epikote 828/ATBN20 is a cross-linked polymer with two phase structure. For this adhesive, E'' peaks corresponding to the primary absorption of the epoxy-rich matrix phase and rubber-rich dispersed phase were observed at 100℃ and -40℃, respectively.[22] In this study the fracture toughness of wood/adhesive joints was compared with the adhesive tensile strength. The adhesives used in this work had different chemical structure, phase structure and viscoelastic properties.

Figure 2 shows the temperature dependence of strain energy release rate (G_{IC}) in opening mode for adhesive joints bonded with PVAc(S). This is a typical fracture toughness curve for the adhesive joints bonded with adhesive of a linear polymer. When the adhesive is in glassy state, G_{IC} is nearly constant and the modulus is sufficiently high. When an external force is applied to the adhesive joints, stress must be concentrated at the crack tip and fracture occurs at the interface. In Figure 3, the characteristic brittle fracture was observed in the stress-strain curves measured at -16℃~20℃ and 64℃ and it is evident that linear fracture mechanics can be applied. When temperature is elevated up to the vicinity of T_g of the adhesive, the value of G_{IC} becomes very high. Since the mod-

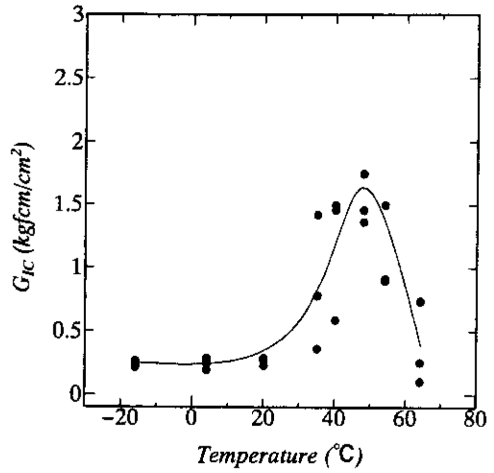

Figure 2. Temperature dependence of G_{IC} for adhesive joint bonded with PVAc(S).

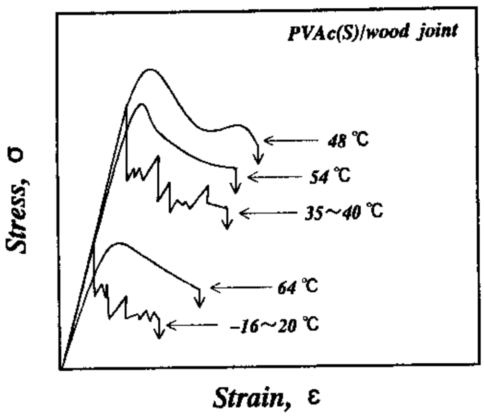

Figure 3. Stress-strain curve for PVAc/wood joint.

ulus of the adhesive decreases in this temperature region, a small plastic deformation is found. The stress-strain curve measured at 48 ℃ showed that a typical ductile fracture occurred during crack propagation. It is described in ASTM that fracture toughness can be evaluated even in the case of plastic deformation if the compliance(C_C) at crack initiation is within 5% of the compliance at yielding.[19] In this work, G_{IC} was calculated after confirming this fact. Figure 4 shows the temperature dependence of G_{IC} for wood/Epikote 828-ATBN 20 joints. It is shown with the SEM observation that a phase separation occurred irregularly in the cured adhesive. Temperature dependence of G_{IC} is complicated, reflecting the complexity of structural properties of the adhesive. A similar result was obtained by Bascom *et al.*[20,21] Their study on CTBN-modified epoxy joints showed that the rubber phase was uniformly separated when CTBN was added to Epoxy resin up to 15 wt%. For higher percentage, the rubber phase was heterogeneously separated. The fracture mode also changed in a complicated manner according to the change of temperature or strain rate. G_{IC} decreases at around -120 ℃ and peaks of G_{IC} are seen at -20 ℃ and 70 ℃. G_{IC} then gradually decreases at temperatures above 60 ℃, as shown in Figure 4. Judging from the viscoelastic data, both epoxy-rich matrix phase and rubber-rich particle phase are in a glassy state below -40 ℃. In the temperature region of -40 ℃ to 110 ℃, rubbery particles are dispersed in the glassy matrix. Above 110 ℃, both phases are in rubbery or flowing state. It is difficult to find out any simple correspondence between these situations and temperature dependence curve of G_{IC}. The reason for this is not yet evident.

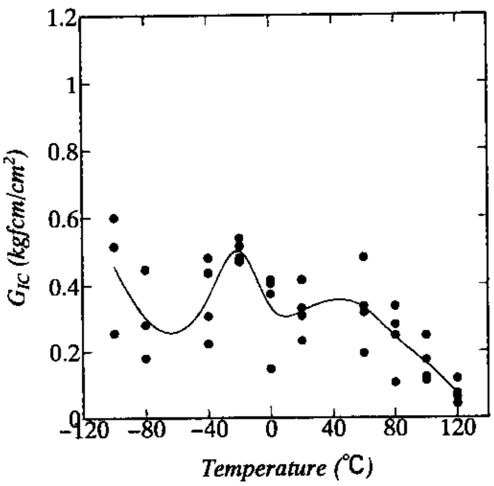

Figure 4. Temperature dependence of G_{IC} for wood/Epikote 828-ATBN 20 joint.

Stress-strain curves in Figure 5 shows that stick-slip brittle fracture occurred and the crack propagated through a complicated pathway in the glassy adhesive. The stick-slip phenomenon becomes less pronounced at higher temperatures, and stable ductile fracture occurred when the temperature became sufficiently high. Some SEM photographs show that a com-

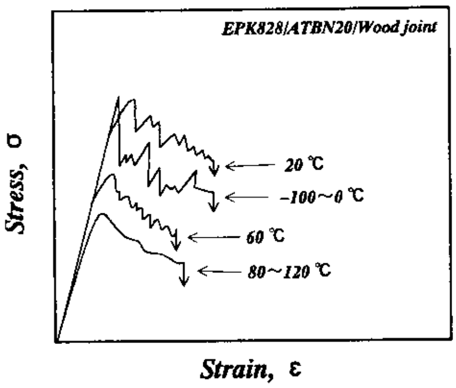

Figure 5. Stress-strain curve for wood/Epikote 828-ATBN 20 joint.

plicated interfacial fracture occurred below T_g and a cohesive fracture of the adhesive occurred above T_g. Kobayashi *et al.*[7] and Takemura *et al.*[22] measured the adhesive tensile strength as a function of temperature using the wood specimen bonded with the same adhesive used in this work. Adhesive area in their studies was 2.5 cm × 2.5cm, and crosshead speed was 10 mm/min.

G_{IC} obtained in this work is compared with their adhesive tensile strength in Figures 6 and 7 for PVAc(S) and Epikote 828/ATBN 20, respectively. For PVAc(S), adhesive tensile strength and G_{IC} had almost constant value of 35 kgf/cm^2 and 0.25 - 0.35 kgfcm/cm^2, respectively, at a temperature lower than the room temperature. A significant correlation between adhesive tensile strength and G_{IC} was not found in the transient region around T_g. When the adhesive is in a rubbery or flowing state at elevated temperature, a positive correlation between the two values could be found. A correlation between the two values might be described as a loop for the whole data, and the experimental data moved clockwise on the loop as the adhesive changes from a glassy to a rubbery state. A similar correlation was found in other adhesive joints.[16,17]

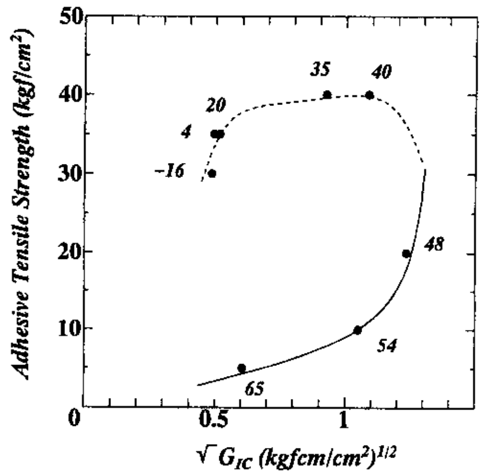

Figure 6. Relationship between adhesive tensile strength and $\sqrt{G_{IC}}$ for wood/PVAc(S) joint.

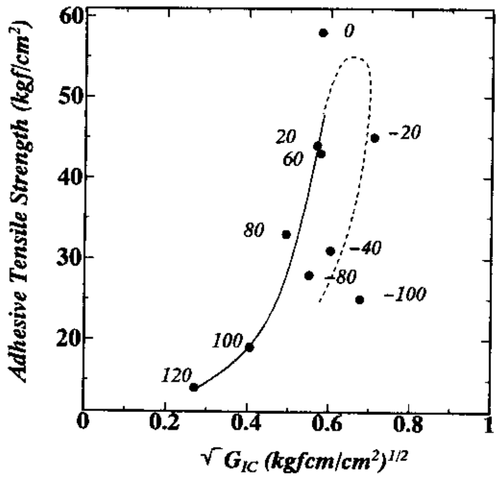

Figure 7. Relationship between adhesive tensile strength and $\sqrt{G_{IC}}$ for wood/Epikote 828-ATBN 20 joint.

For Epikote 828/ATBN 20 adhesive joints, the correlation between the two values is described by a curve although data were scattered. Homogeneous structure of PVAc(S) and two phase structure of Epikote 828/ATBN 20 showed a significant difference in the fracture behavior. The reasion for this fact, however, is not clarified yet. Further investigation of the crack propagation in microscopic scale will be needed.

Conclusions

PVAc(S) adhesive is a linear polymer and has a homogeneous structure. G_{IC} of adhesive joints bonded with the PVAc(S) was a constant value at the glassy state. Stress-strain curve gave the evidence related to an unstable brittle fracture. SEM photographs showed that crack propagated sharply and interfacial fracture occurred. When temperature was elevated and then reached at the vicinity of T_g, G_{IC} became maximum value. When temperature was higher than T_g, and the adhesive was in a rubbery or flowing state, a ductile cohesive fracture occurred and an apparent G_{IC} decreased. It could be considered that the temperature dependence of G_{IC} reflected directly viscoelastic properties of the adhesive. When the same adhesive was used to adhesion test, a positive correlation between adhesive tensile strength and G_{IC} was found at a temperature higher than T_g, while a significant correlation was not found at lower temperature.

On the other hand, Epikote 828/ATBN 20 is a cross-linked polymer and has two phase structure. For this adhesive joints, G_{IC} showed a very complicated change reflecting the complication of inner structure of the adhesive, and it was difficult to find any simple correlation between G_{IC} curve and viscoelastic properties of the adhesive. It was found that there was a correlation between adhesive tensile strength and G_{IC} for the same adhesive which was described by a loop with data scattering. A further detailed study requires to clarify the reason why there is such a difference between the two adhesives used in this study.

References

(1) Y. Yamagishi, Y. Hatano and H. Mizumachi, *Holzforschung,* **34**, 169 (1980).

(2) K. Taki, B. Tomita and H. Mizumachi, *Mokuzai Gakkaishi,* **28**, 143 (1982).

(3) Y. Hatano, B. Tomita and H. Mizumachi, *Mokuzai Gakkaishi,* **29**(9), 578 (1983).

(4) H. Mizumachi, Y. Hatano and Y. Yamagishi, *Holzforschung,* **34**(5), 169 (1991).

(5) L. D.Turreda, Y. Hatano and H. Mizumachi, *Holzforschung,* **45**(5) 371 (1991).

(6) K. Motohashi, B. Tomita and H. Mizumachi, *Wood and Fiber Sci.,* **16**(1), 72 (1984).

(7) T. Kobayashi, Y. Hatano and H. Mizumachi, *Mokuzai Gakkaishi,* **37**, 331 (1991).

(8) Y. Hatano and H. Mizumachi, *Mokuzai Gakkaishi,* **35(3)**, 243 (1989).

(9) T. Hata, *Zairyo,* **17**, 322 (1968).

(10) E. J. Ripling, S. Mostovoy and R.L.Tatrick, *ASTM, STP,* **360**, 5 (1963).

(11) S. Mostovoy and E. J. Ripling, *J. Appl. Polym. Sci.,* **10**, 1351 (1966).

(12) S. Mostovoy and E. J. Ripling, *J. Appl. Polym. Sci.,* **13**, 1083 (1969).

(13) S. Mostovoy and E. J. Ripling, *J. Appl. Polym. Sci.,* **15**, 661 (1971).

(14) A. J.Kinloch and S. J. Shaw, *Development in Adhesives-2,* chap.3, 1981.

(15) W. W. Lim, Y. Hatano and H. Mizumachi, *J. Appl. Polym. Sci.,* **52**, 967 (1994).

(16) W. W. Lim and H. Mizumachi, *J. Appl. Polym. Sci.,* **57**, 55 (1995).

(17) W. W. Lim and H. Mizumachi, *J. Appl. Polym. Sci.,* **63**, 835 (1997).

(18) W. W. Lim and H. Mizumachi, *J. Appl. Polym. Sci.,* **66**, 525 (1997).

(19) ASTM standard E399-74: Standard method of test for plane-strain fracture toughness of metallic materials: American Society of Testing Materiasls, 1974.

(20) W. D. Bascom, R. L. Cottington, R. L. Jones and P. Peyer, *J. Appl. Polym. Sci.,* **19**, 2545 (1975).

(21) W. D. Bascom and R. L. Cottington, *J. Adhesion,* **7**, 333 (1976).

(22) A. Takemura, B. Tomita and H. Mizumachi, *J. Appl. Polym. Sci.,* **30**, 4031 (1985).