〈연구논문〉

모드 I의 변형 에너지 해방율과 인장 접착강도에 미치는 접착제 고분자의 유변 특성의 영향

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Influence of Rheological Properties of Adhesive Polymer on Strain Energy Release Rate of Mode I and Adhesive Tensile Strength

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요 약

접착강도는 접착제의 점탄성을 반영한 온도 · 속도 의존성을 나타낸다는 것이 잘 알려져 있다. 특히 유리전이온도(T_g)에서의 역학적 완화기구가 접착층의 변형을 수반하는 접착강도에 크게 영향을 미치고 있다. 또한 접착계의 모드I의 변형 에너지 해방율(G_{IC})를 측정할 때에도 접착제의 변형과 파괴가 발생하기 때문에 접착제의 점탄성이 그 값에 어떠한 영향을 미치는 지에 흥미가 깊다. 본 연구에서는 2종류의 에폭시 수지를 블랜드한 접착제를 이용하여 일정한 측정조건에서 인장 접착강도와 G_{IC}를 측정하고 이들의 값에 영향을 미치는 접착제의 점탄성 함수의 영향을 조사하였다. 또한 인장 접착강도와 G_{IC}의 상관관계에 대하여서도 토론하였다.

Abstract — It is well known that adhesive strength shows temperature- and rate-dependencies reflecting viscoelastic properties of an adhesive used. Especially, mechanical relaxation mechanism around glass transition temperature(T_g) has a strong effect on the adhesive strength which involves deformation of the adhesive layer. In addition, it is very interesting to know how viscoelastic properties of the adhesive affect the value of strain energy release rate since deformation and failure of the adhesive occur at measurement of strain energy release rate for adhesive joints. In this study, adhesive tensile strength and strain energy release rate(G_{IC}) in opening mode were measured under a constant experimental condition using the adhesives consisting of two types of epoxy resins, and the influence of viscoelastic properties on these two values was investigated, and we discussed on the relationship between the adhesive tensile strength and G_{IC}.
Keywords: Viscoelastic properties, fracture toughness, strain energy release rate, adhesive tensile strength.

1. Introduction

Adhesives are polymeric materials. The mechanical properties of the materials vary with their chemical and supermolecular structures. Because linear viscoelastic functions such as relaxation modulus, creep compliance, and complex modulus change greatly according

to temperature and time-scale(i.e., deformation rate, frequency, and time), it is necessary to know whether a polymer is in a glassy state, rubbery state, or in flowing state under any conditions by measuring the value of the functions. It is known that temperature and rate(time or frequency) superposition procedure holds for the linear viscoelastic functions over a wide range of temperature and time-scale, and a smooth master curve is obtained [1,2,3]. The same procedure can not be applied in a strict sense to the fracture of polymeric materials because large deformation as well as initiation and propagation of crack are involved in the phenomena.

However, T.L.Smith[4] has pointed out the fact that the temperature and rate superposition principle apparently holds for the data of stress and strain at failure of rubbers which he obtained over a wide range of temperature and deformation rate(R). A master curve of failure stress(σ_B) plotted against log(1/R) is a sigmoid and that of failure strain(ε_B) is a curve with a single peak. He also showed that the shift factor, log(a_T) in this case followed WLF equation. A general curve of σ_B plotted against ε_B was called the failure envelope. Hata[5] explained qualitatively the characteristics of failure envelope in terms of a simple mechanical model and two failure criteria.

Adhesive strength is defined as a value of an external force(or stress) at failure but its physical meaning is not necessarily clear because cohesive fracture of adhesive and adherend, interfacial fracture, and the mixed mode fractures occur in the adhesion tests. Neverthless it is sometimes pointed out that there is a correlation between the physical properties of a polymer and adhesive strength. Some try to understand temperature- and rate- dependencies of

adhesive strength in relation to viscoelastic properties of adhesive[6,7]. Hatano *et al.*[8] measured adhesive tensile strengh of crosslap joints of wood bonded with epoxy resins and found that adhesive strength is very low when modulus of the adhesive is either too high or too low, and a maximum value is obtained at around $E'=1.0 \times 10^{10}$ dyne/cm². Similar behaviors were found also in the other adhesive joints [9-12].

In many standards for testing materials, adhesive strength is defined as an external force to break the joints, which is devided by a bonding area or a width. When the external force is applied to the adhesive joints, complicated stress and strain distributions will generally be generated within the specimens, including the interface, adhesive layer, and adherend. Accordingly, mechanical approach with emphasis on stress concentraion is needed for adhesive joints in order to describe fracture behavior in terms of physically defined quantities. In fracture mechanics, stress concentration near crack-tip of materials is related to the criteria of initiation and propagation of crack, and fracture toughness, K_C and G_C are defined.

Mostovoy and Ripling[13,14] studied on fracture mechanics for aluminium/epoxy resins joints and confirmed that strain energy release rate of adhesive joints could be easily measured if a proper shape and dimensions of a specimen are designed. Chai[15] also studied on fracture mechanical properties of steel specimens bonded with amorphous thermosetting resin, and semicrystalline thermoplastic resin and found the fact that strain energy release rates for three modes of deformation, G_{IC}, G_{IIC}, G_{IIIC}, depend upon thickness (t) of adhesive layer in different way. A value of G_{IC} was constant independently of t, and both G_{IIC}, and G_{IIIC} in-

creased with increase of t and then reached a plateau when t is over thickness(t_L). Lim et al. [16,17] studied on fracture toughness of a series of wood/adhesive joints. First, they confirmed experimental conditions to estimate G_{IC}, G_{IIC}, and G_{IIIC} which are not affected by the shape and dimension of specimen. Second, they studied on the temperature and rate dependencies of strain energy release rate for typical adhesives. Finally, they applied the temperature-rate superposition procedure to the obtained data in order to get a continous master curve. They also examined the relationship between strain energy release rate and adhesive strength.

In this study, we measured both strain energy release rate(G_{IC}) of opening mode and adhesive tensile strength using a series of epoxy resins with different glass transition temperatures. And we tried to clarify the influence of viscoelasticity of adhesives on the correlation between the two values.

2. Experimental

2.1. Material

Adhesives used in this work are blends of two epoxy resins, Epikote828(Shell Chemical Co.) and Epikote871(Shell Chemical Co.). The blended epoxy resins are apparently transparent at room temperature. The adhesives are cured by adding stoichiometric amount of diethylene tetramine(DETA) to the blends.

Japanese birch, Kaba(*Betula maximowiczana* Regel) is used as an adherend, physical properties of which are shown in Table 1.

Table 1. Characteristics of Adherend

| Adherend	Specific Gravity		Moisture content (%)	Young's modulus, $E(\times 10^5 \text{ kgf/cm}^2)$
	Air	Dry		
Kaba	0.88	0.78	15	1.16

2.2. Measurement of dynamic mechanical properties

The cured film was prepared by casting the mixture of Epikote828 and Epikote871, and DETA on a teflon sheet, and keeping the mixture at room temperature and R.H.65% for 5days. Chemical structures of Epikote828 and Epikote871 were shown in Fig. 1. The blend ratio of Epikote871/Epikote828 ranged from 0/100 to 50/50, and the films were postcured at 60~80℃ for 2 hrs. Dynamic mechanical properties of the films were measured by means of a Rheovibron DDV-II(Toyo Baldwin Co., LTD) at 110 Hz with an average heating rate of 1℃/min.

2.3. Measurement of strain energy release rate of adhesive joints

Wood specimens for fracture mechanical tests were prepared with grain angle of 5℃ as shown in Fig. 2 in order to prevent woodfailure along the grain. Precrack length was 8 cm, referring to our previous work[16]. Amount of adhesive employed in this work was 250~300 g/cm^2, and the specimen was assembled as shown in Fig. 2.

The specimen was pressed under 10 kgf/cm^2, and was kept at 20℃, R.H.65% for 4 days for curing. The bonded specimen were postcured at 60~80℃ for 2 hrs. Fracture mechanical test was carried out with a crosshead speed of 10.0
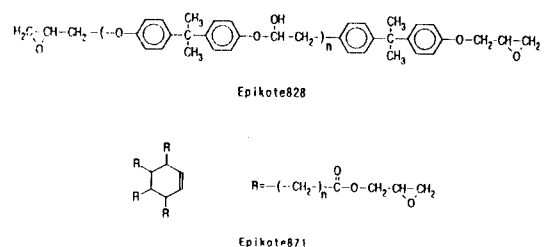
Fig. 1. Chemical structures of Epikote828 and Epikote 871.

mm/min over a range of $-60°C \sim +80°C$ by means of Tensilon(Orientec Co.) A strain energy release rate, G_{IC}, was determined by the compliance method according to the following equation:

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

where P_C and E are failure load and Young's modulus of the adherend, respectively and the other parameters are shown in Fig. 2.

2.4. Measurement of adhesive tensile strength

The specimen for cross-lap test was prepared as shown in Fig. 2. The adhesion condition such as spread amount of adhesive and bonding pressure was the same as that of the case of fracture mechanical test described above. The measurement of adhesive tensile strength was carried out with the crosshead speed of 10.0 mm/min over a range of $-60°C \sim +$

(Unit:mm)

<Cross-Lap Test>

<Mode I Fracture Test>

Fig. 2. Geometry of test specimens.

80°C using Tensilon.

3. Results and discussion

Dynamic mechanical properties of cured films of adhesives are shown in Fig. 3. When two types of epoxy resins, Epikote871 and Epikote 828, were blended at various ratios and cured with a common hardner DETA, a series of polymers with different mechanical properties were obtained. Curves of storage modulus(E'), loss modulus(E''), and tanδ plotted as a function of temperature shifted toward high temperature as Epikote828 content increased. That might suggest that the two epoxy compounds were mixed at cured state to a considerable extent. However, there were cases where double peaks or shoulder were found in the E'' and tanδ curves especially in the intermediate blend ratios. Epikote871 and Epikote828 were molecularly miscible with each other in the liquid state, but as the blends were cured with DETA, phase separation might have occured to some extent, although such phenomena had not been visualized in this study. Suzuki[18] also pointed out the possibility of phase separation in the same blend systems in his mechanical study on adhesive strength of scarf and butt joints where steel was bonded using the same adhesives.

Glass transition temperature, E', E'' and tanδ at room temperature were plotted against blend ratio in Fig. 4. It is interesting to notice that T_g of the film changes almost linearly with blend ratio. This trend can be described approximately in terms of either Gordon-Taylor[19] equation or Fox[20] equation, which are derived for T_g of the miscible blends. Storage modulus at room temperature was almost constant when the Epikote871 content was between 0% and 40% and decreased gradually as the content exceeded 40%. Loss modulus increased at first
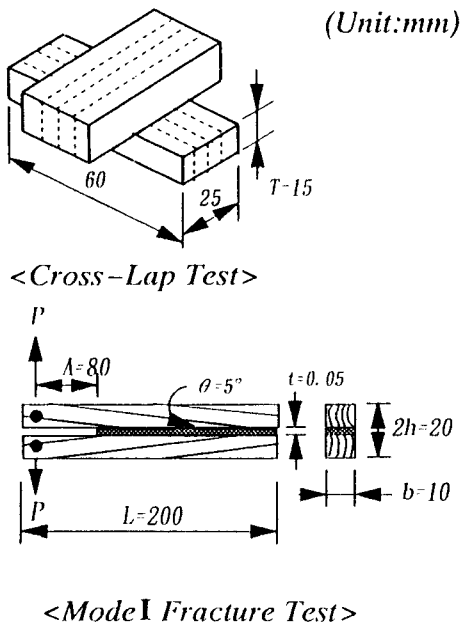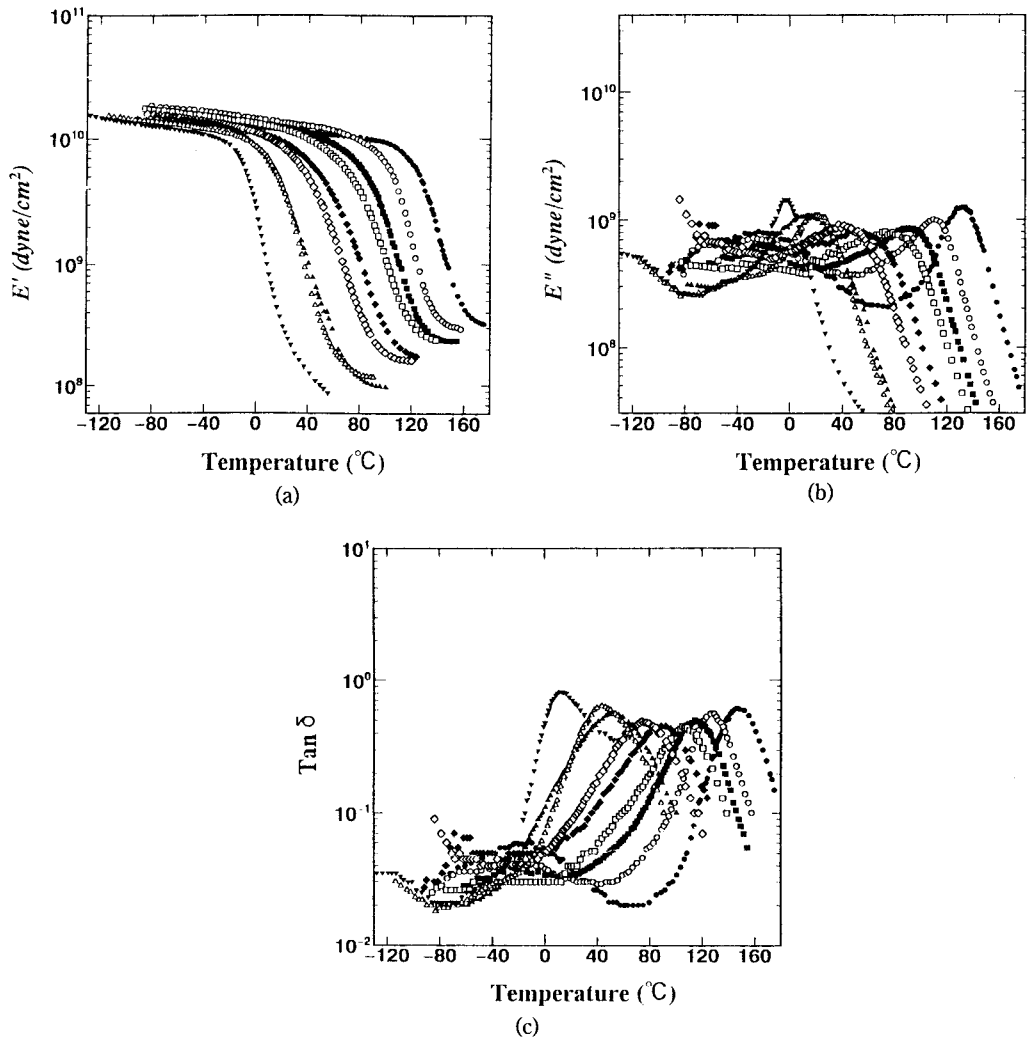
Fig. 3. Dynamic mechanical properties of cured films of of adhesives: ○ : 0, ● : 02, ■ : 0.3, □ : 0.4, ◆ : 0.5, ◇ : 06, ▲ : 0.7, △ : 0.8, ▼ : 1.0 (Epikote 871/Total epoxy).

and then decreased through a maximum as Epikote871 content increased or storage modulus decreased. It was known that tanδ was almost constant when the Epikote871 content was between 0% and 40%, but increased linearly when the content increased over 40%. From these facts, it was known that epoxy resins with various blend ratios used in this work were in glassy state at room temperature when Epikote871/Epikote828 ratio was low, and then

in transient state, and in rubbery state as the ratio increased. It was considered that these viscoelastic properties of adhesives would affect the adhesive strength and strain energy release rate(G_c).

Fig. 5 shows the dependence of adhesive tensile strength on the blend ratio. In the case where Epikote871 content was very high and the modulus of adhesives was low, the adhesive strength was very low. Fracture

mode was cohesive fracture of adhesive layer with little wood failure. However, adhesive tensile strength increased as modulus of adhesives increased with increasing Epikote828
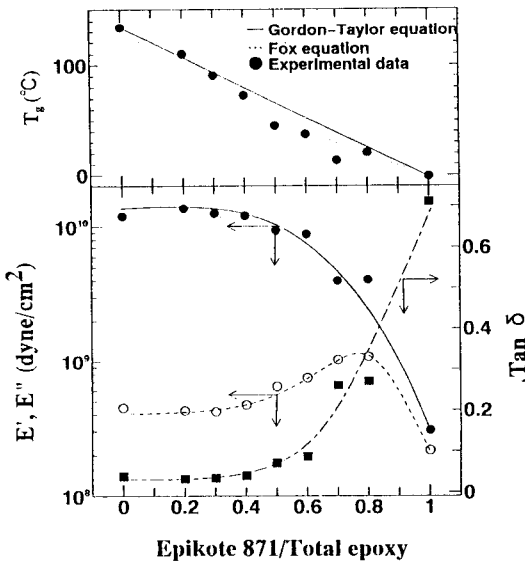

Fig. 4. Glass transition temperature, E', E'' and tan δ at room temperature with various blend ratio.
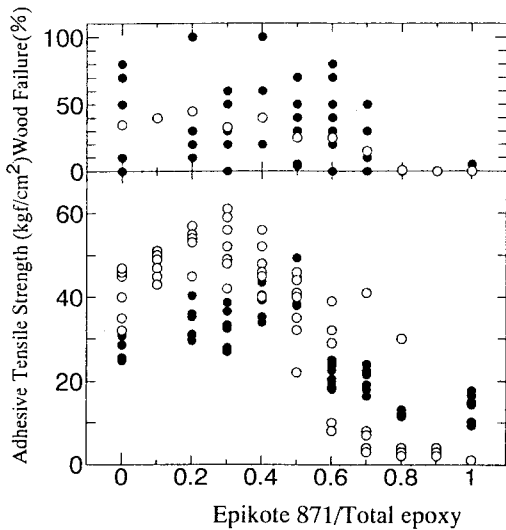

Fig. 5. Dependence of adhesive tensile strength on blend ratio; ● measured in this work, ○ measured by Y. Hatano[12] under the same condition as this work.

content. It showed a maximum when E' was around 1.0×10^{10} dyne/cm^2 and then slightly decreased when the adhesives was well in the glassy state(E'>1.0×10^{10} dyne/cm^2). When adhesive tensile strength was high, wood failure was naturally high, but at the same time there were much scatters of points. When adhesives were well in the glassy state, fracture mode was complicated in a sense that both cohesive fracture and interfacial fracture were seen. Hatano *et al.* described these characteristics in detail. Similar phenomenon has also been found in other adhesive joints[9, 10, 11, 12, 21].

Fig. 6 shows the dependence of G_{IC} on blend ratio. These values were almost constant when Epikote871 content was in the region of 0%–40%, which means the fact that no toughening effect is recognized at all in case where brittle component(Epikote828) is blended with soft component(Epikote871) in molecular scale. However, G_{IC} was high when Epikote871 content was 50–60%. Toughening mechanism of homogeneous blends must be different from that of rubber-toughened plastics. When Epi-
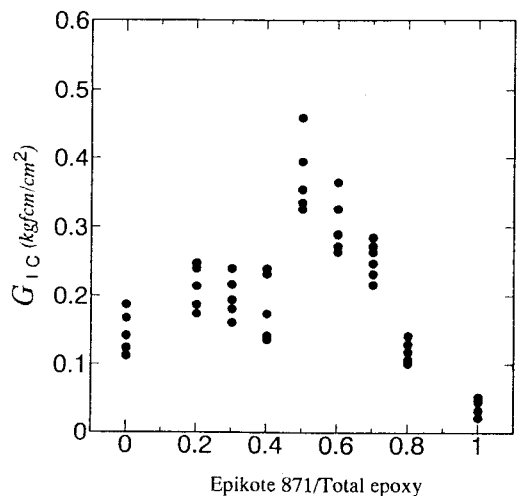

Fig. 6. Dependence of G_{IC} on blend ratio.

kote871 content increased further, adhesives became softer and their cohesive strength decreased further, and at the same time G_{IC} decreased because resistance against crack propagation decreased.

Stress-strain curves on fracture mechanical test changed reflecting change of viscoelastic properties of adhesives. Some typical examples are shown in Fig. 7. When Epikote871 content was in region of 0%-40%, such curve as shown in Fig. 7(a) was obtained. This was a characteristic curve of brittle fracture. When a crack initiated, it propagated quickly and then stick-slip behavior occurred. Also, when the content was in region of 50%-60%, brittle fracture was retarded and crack propagation did not occur very quickly. That is a typical crack propagation behavior of a toughened material. As expected, crack propagation behavior was complicated as shown in Fig. 7(b). As the content increased further, adhesives became softer, and resistance against external force at crack-tip decreased. Crack propagation rate was slow and the curve became smooth. That is typical characteristics of ductile fracture.

Fig. 8 shows the dependence of adhesive tensile strength upon ΔT ($= T\text{-}T_g$, T and T_g are room temperature and glass transition temperature, respectively), E', E'' and $\tan\delta$ at room temperature. Adhesive tensile strength was low when T_g of adhesives was sufficiently lower than room temperature(experimental temperature) and increased with increasing T_g. However, interfacial fracture occurred and the adhesive tensile strength became low in case where T_g is much higher than room temperature. This figure shows that adhesive tensile strength had a peak at ΔT=-20°C. Because E', E'' and $\tan\delta$ at room temperature changes with the change of T_g of adhesives, each curve had a peak. The figure shows adhesive tensile strength was a maximum approximately at $E' = 1.0 \times 10^{10}$ dyne/cm^2, E''=6.0$\times 10^8$ dyne/cm^2, and $\tan\delta$=0.1.

Fig. 9 shows similar plots for G_{IC}. Almost the same trend could be confirmed qualitatively for the dependence of G_{IC} on viscoelastic properties of adhesives. Fig. 10 shows the relationship between adhesive tensile strength and $\sqrt{G_{IC}}$. It seems that the correlation between the two values is rather complicated. In case where adhesives were in glassy state, a positive correlation between adhesive tensile strength and $\sqrt{G_{IC}}$ was confirmed. In this region, cohesive fracture of adherend mostly occurred in adhesive strength test, but on the other hand interfacial fracture occurred in fracture mechanical test. Also, in the region
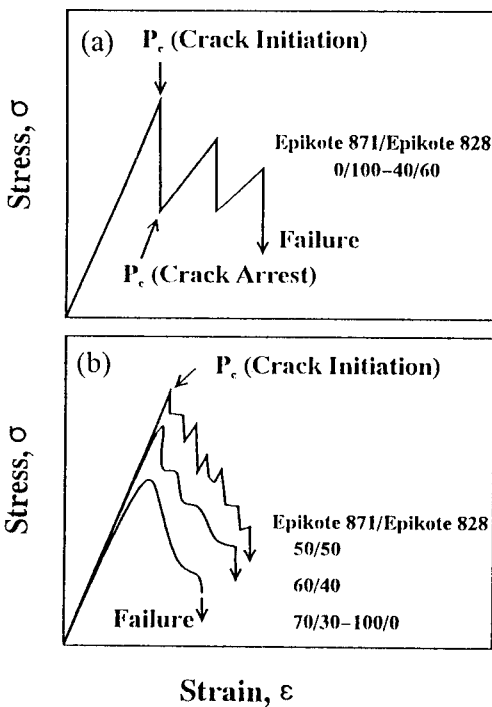

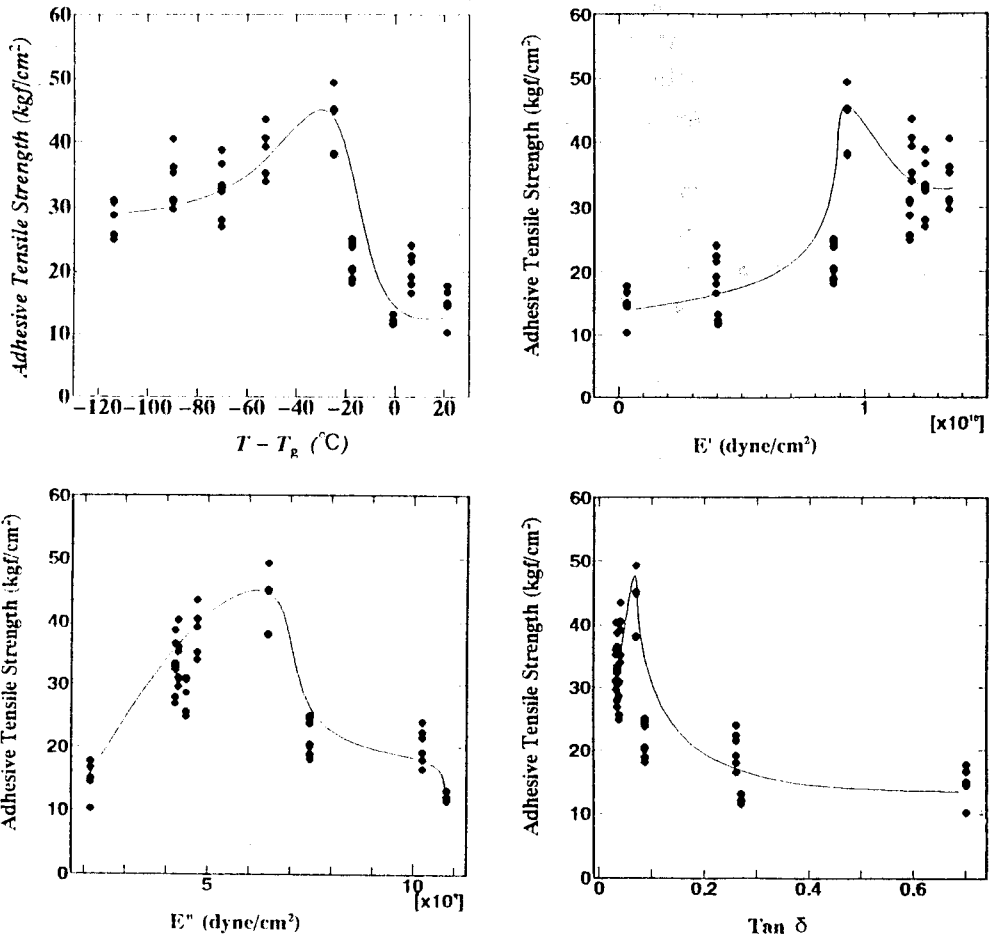Fig. 7. Stress-strain curves on fracture mechanical test with various blend ratio.

Fig. 8. Dependence of adhesive tensile stength upon Δ T, E', E'' and tant δ at room temperature.

where the adhesives changes from glassy to rubbery state, a complicated fracture mode was found in both tests, and the corelation between adhesive tensile strength and $\sqrt{G_{IC}}$ was not siginficant. Namely $\sqrt{G_{IC}}$ increased, whereas adhesive tensile strength was almost constant because it was near tensile strength of adherend itself. When the adhesives became rubbery state, cohesive fracture of the adhesives mainly occurred in both tests reflecting the decrease of cohesive strength of the adhesives. In this region, the higher $\sqrt{G_{IC}}$ is, the higher adhesive tensile strength is, but

the correlation between the two values was shown as a curve. Accordingly, it was considered that totally the correlation between the two values is shown by a loop in a wide range of temperature.

4. Conclusion

When Epikote827 and Epikote871 were blended with various ratios and cured with a common hardner DETA, a series of polymers which ranged from glassy to rubbery state at room temperature were obtained. Adhesive tensile strength and G_{IC} of wood/adhesive joints bonded
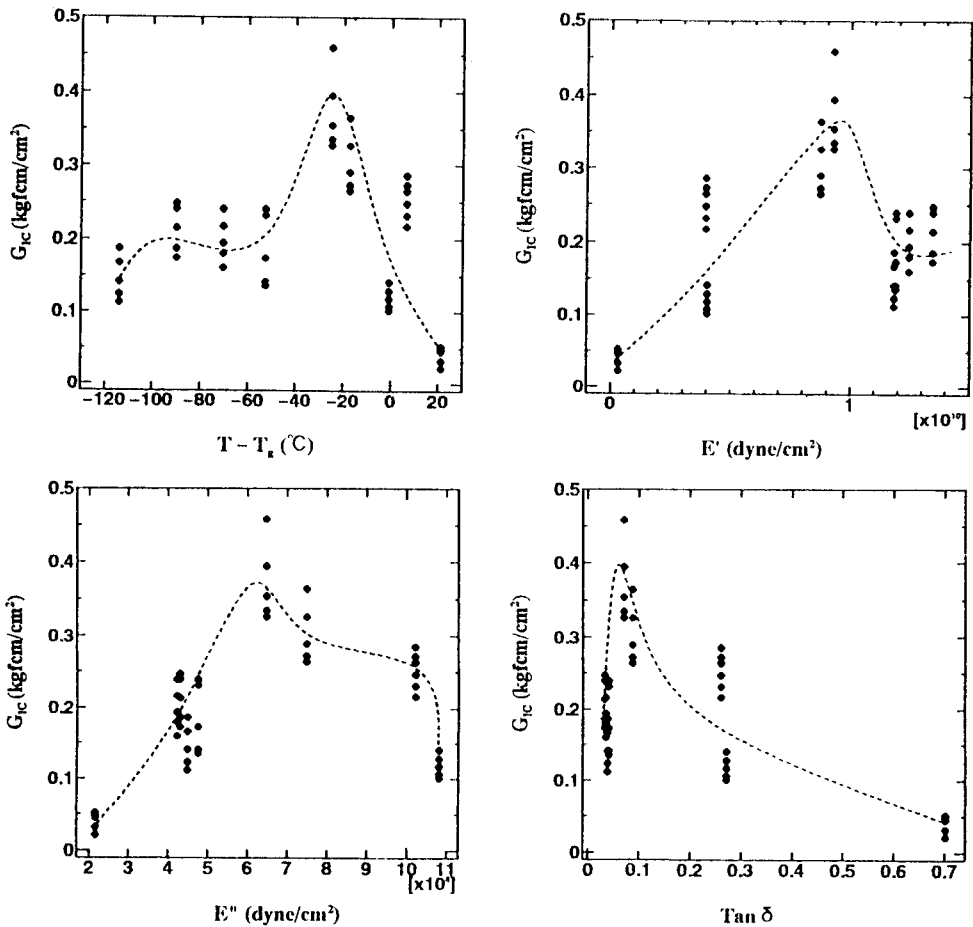
Fig. 9. Dependence of G_{IC} upon ΔT, E', E'' and tan δ at room temperature.
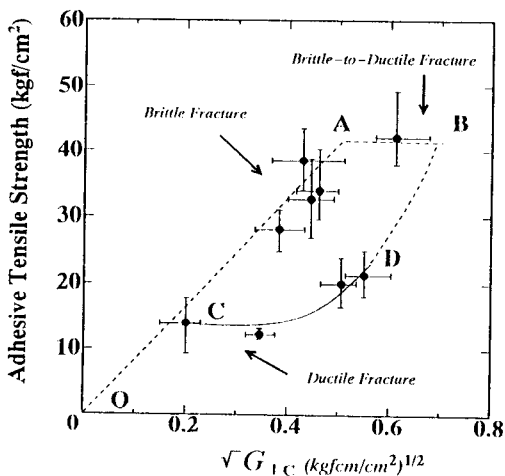

Fig. 10. Relationship between adhesive tensile strength and $\sqrt{G_{IC}}$.

with these polymers were measured.

Adhesive tensile strength and G_{IC} became a maximum approximately at $T_g = 40°C$, $E' = 1.0 \times 10^{10}$ dyne/cm^2, $E'' = 6.0 \times 10^8$ dyne/cm^2, and tan$\delta = 0.1$.

Relationship between adhesive tensile strength and $\sqrt{G_{IC}}$ changed with viscoelastic properties of adhesives. When the adhesives were in glassy state, the linear correlation between the two values was found. On the other hand, the correlation was described by a curve at rubbery state. In transition region, the significant correlation between the two values was not confirmed.

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