

Effect of Epoxy Oligomer on Viscoelasticity of Acrylic Polymer

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ABSTRACT: Linear and nonlinear viscoelasticity of an adhesion material for integrated circuit chips were investigated to control the processability. The material consists of acrylic polymer (AP) and epoxy oligomer (EP). EP content in AP/EP blend is 70 vol %. From the linear viscoelasticity, it was found that the iso-free volume state of AP/EP blend was 20°C lower than that of AP and the entanglement molecular weight M_e of AP/EP was three times higher than that of AP. Nonlinear stress relaxation modulus $G(t, \gamma)$ showed that the time-strain separability, $G(t, \gamma) = G(t)h(\gamma)$, was applicable at long time above a characteristic time τ_k , where $G(t)$ is linear relaxation modulus and $h(\gamma)$ is the damping function. The τ_k value was estimated to be 10 s for AP/EP and below 0.1 s for AP at an iso-free volume state.

($h(\gamma)$ for AP and AP/EP behaved like a usual linear homopolymer.) The time evolution of the elongational viscosity $\eta_E(t)$ of each sample showed that AP/EP system exhibited strong strain hardening at $\dot{\epsilon} \geq 0.3 \text{ s}^{-1}$, although AP did not show strain hardening at strain rate measured, when the data were compared at an iso-free volume state. These results strongly suggest that the strain hardening behavior of AP/EP is attributable to enhancement of the stretch of AP polymer chains by diluting EP oligomer chains. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1316–1321, 2011

Key words: adhesive film; low molecular weight component; uniaxial elongational viscosity; strain hardening; characteristic time

INTRODUCTION

In a semiconductor industry, integrated circuit (IC) chips are three-dimensionally integrated to increase the capacity of memory without a change of size. The IC chips are stacked on a wafer using an adhesive material. This stacking process is carried out at temperature above the glass transition temperature (T_g) of the adhesive material, followed by complete curing at higher temperature to enhance the interface adhesion. Our adhesive material consists of two components; (1) epoxy resin (EP) to exert the adhesion strength and the heat resistance and (2) acrylic polymer (AP) having low T_g for elasticity and toughness at room temperature. It is possible to prevent the crack of adhesive film by adding AP. The handling of the adhesion film is also excellent at room temperature. In a certain IC package, adhesion film undergoes large deformation because the bonding wire which interconnects IC chips with substrates is embedded in the adhesive layer. So far, the investigation of the nonlinear rheological behavior for adhesion film is important.

One of the rheological measurements in large deformation is stress relaxation test. The material can be characterized with nonlinear stress relaxation behavior. The significance of the chain shrink is recognized with respect to the shear modulus, $G(t, \gamma)$, at high magnitude of strain, γ , for polymer solutions or melts. It can be factorable as follows:

$$G(t, \gamma) = G(t)h(\gamma)(t > \tau_k) \quad (1)$$

where $G(t)$ is the linear relaxation modulus, $h(\gamma)$ the damping function, and τ_k characteristic time. $h(\gamma)$ is a universal function of γ for entangled flexible polymers and expresses the degree of shrinkage for polymer chain.¹ In homopolymers, time-strain separability is satisfied above τ_k .^{2,3} It is well known that τ_k correspond to the appropriate time for constricted chain to return to equilibrium length. So, large deformation shear relaxation modulus $G(t, \gamma)$ is one of the most important nonlinear viscoelastic quantities.

Another large deformation test is uniaxial elongational measurement. The elongational flow behavior of polymer melts is very important for their application to polymer processing including melt spinning, foaming, bottle blowing, and so on. The interesting and important phenomena are nonlinear properties such as strain hardening which correlate with molecular weight distribution,⁴ molecular architecture,^{5–7}

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copolymerization,^{8,9} and compounding.^{10,11} It is understood that the nonlinearity is enlarged with increasing of zero-shear viscosity.^{12,13} A unique characteristic of the elongational viscosity is that the strain hardening property is enhanced by a small amount of ultra high-molecular-weight (UHMW) polymer. Munstedt¹⁴ reported the evidence of a dramatic strain hardening increase by a high-molecular-weight segment. Takahashi et al.¹⁵ compared the strain hardening properties of the three types of polymer blend (i.e., homogeneous, miscible, and immiscible) by incorporation of a small amount of UHMW chains and revealed the effect of miscibility on the strain hardening property. Minegishi et al.¹⁶ demonstrated the effect of content of UHMW component. They concluded that the strong strain hardening is enhanced when the number of entanglement among UHMW chain exceeds 2. Sugimoto et al.¹⁷ have improved strain hardening of polypropylene (PP) by adding tiny amount of UHMW polyethylene (PE), which generally exhibits low-melt strength and weak-strain hardening behavior. The important point in these reports is that the strain hardening could be improved without change of linear viscoelasticity. The productivity might be poor if the high-molecular-weight material is used. Therefore, the control of strain hardening by adding of a small amount of UHMW polymer is very useful in the industrial point of view.

Our adhesive film for electronic device is composed of high-molecular-weight component (AP) and low-molecular-weight component (EP). The flow property of adhesive film (AP/EP) is higher than AP because AP chain is diluted with EP component. Therefore, the load to substrate and wafer is reduced and the high productivity is practically realized in stacked process. Moreover, the functionality of integrated chip was not degraded when the burr and drooping of adhesion film are generated between IC chips. It is especially necessary to control the elongational viscosity because the outside of adhesion material undergoes free surface deformation. The linear and nonlinear rheological flow behavior of adhesion material has never been reported though the investigation of the elongational viscosity for adhesion material is important for processability.

In this study, the rheological behavior of adhesive material which is used in actual products was investigated. The effect of EP component on nonlinear viscoelastic properties of AP/EP is discussed. Details of these results are presented in this article.

EXPERIMENTAL

Acrylic polymer (AP) and epoxy component (EP) provided by Hitachi Chemical Co. Ltd. were used. EP consists of bisphenol diglycidylether (L-epo) in

TABLE I
Molecular Characteristic of Each Component

	M_w (g/mol)	M_w/M_n
L-epo	300	1.05
S-epo	2200	1.53
CA	1200	1.17
AP	298,000	1.97

liquid form at ambient temperature, cresol novolac-type epoxy resin (S-epo) in solid form, and bisphenol A novolac (CA) as a curing agent. Table I shows the molecular characteristics of the samples. The weight-average-molecular weight (M_w) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) made by Showa Denko K. K. M_w and M_w/M_n of AP/EP were measured with GPC after rheological tests. GPC measurements confirmed that M_w and M_w/M_n of the polymeric components in AP/EP were almost the same comparing with that of AP and molecular architecture of AP chain was hardly changed.

The samples were prepared according to the industrial process. Blends of AP/EP were made by casting from cyclohexanone solutions. The solutions were evaporated at 120°C for 30 min to volatilize cyclohexanone. Thermogravimetric analysis (TGA) confirmed that the cyclohexanone in the sample was almost disappeared. The composition ratio of L-epo was equal parts of CA and that of S-epo was one third of L-epo. The content of EP in AP/EP was 70 vol %.

Viscoelastic measurements were carried out at various temperatures T from 60 to 120°C with a strain-controlled rheometer (ARES, TA Instruments) using parallel plate for fixture. Parallel plates with 8 mm in diameter were used for the frequency ω sweeps. The ω dependencies of the storage (G') and loss (G'') moduli were measured in the frequency range from 0.1 to 100 rad/s. The strain was 0.1 in the linear viscoelastic criterion of AP and AP/EP systems.

Measurements of stress relaxation were carried out using ARES (TA Instruments) with parallel plate of 8-mm diameter at several temperatures between 60 and 120°C. The shear relaxation modulus $G(t, \gamma)$ was corrected with following the equation,¹⁸

$$G(t, \gamma) = G_a(t, \gamma)(1 + d \ln G_a(t, \gamma)/4d \ln \gamma) \quad (2)$$

where $G_a(t, \gamma)$ is measured apparent stress relaxation modulus with parallel plate. Applicability of this correction has already been demonstrated by former experiments.^{19,20} The time needed to impose the step strain was less than 0.1 s. Strain was from 0.1 to 8.0.

Measurements of uniaxial elongational viscosity at constant strain rates were carried out using ARES (TA Instruments) with elongational viscosity mode

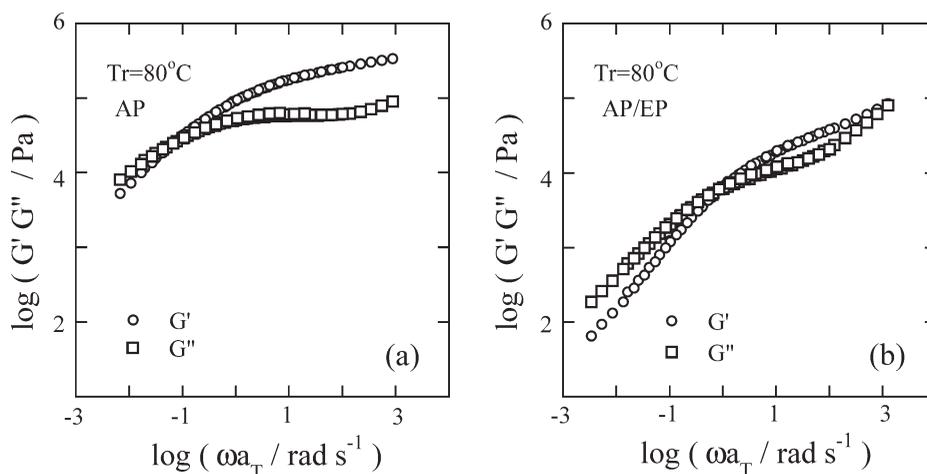


Figure 1 Master curves of the storage modulus G' and loss modulus G'' plotted against angular frequency ω for (a) AP and (b) AP/EP at 80°C.

at several temperatures between 60 and 120°C. Strain rates were from 0.01 to 3.0 s⁻¹. All of the viscoelastic measurements were performed under nitrogen atmosphere.

RESULTS AND DISCUSSION

Linear viscoelasticity

The storage modulus (G') and loss modulus (G'') versus ω curves at various T were excellently superimposed into a master curve by shifting along the ω axis by a factor a_T . Figure 1(a,b), respectively, show the master curves for AP and AP/EP at 80°C. The principle of time-temperature superposition was valid for these samples from 60 to 120°C. However, at high temperature ($T > 140^\circ\text{C}$), time-temperature superposition for both samples were not valid because AP gradually reacts on itself without any initiator. The shift factors (a_T) (T : 60–120°C) were represented by the following WLF equation²¹:

$$\log a_T = \frac{-8.86(T - T_s)}{101.6 + (T - T_s)} \quad (3)$$

where T_s is the reference temperature. Figure 2 shows $\log a_T$ plotted against $T - T_s$ for AP and AP/EP. When the reference temperatures were chosen at 56°C and 36°C for AP and AP/EP, respectively, both curves could be expressed in a single WLF equation denoted by the dotted line. This result indicates that the iso-free volume state of AP/EP is 20°C lower than that of AP.

The plateau modulus G_N^0 was determined as the storage modulus G' in the plateau zone at the frequency where $\tan \delta$ is at a minimum.²² The entanglement molecular weight (M_e) was evaluated by the following equation:

$$M_e = \frac{\rho RT}{G_N^0} = \frac{cRT}{G_N^0} \quad (4)$$

where ρ , R , T , and c are the density, gas constant, absolute temperature, and volume fraction of polymer. M_e of AP and AP/EP was calculated to be 9200 and 25,000, respectively. This result implies that AP chain is sufficiently diluted with EP component.

It is necessary to compare the viscoelasticity for polymer and diluted polymer at iso-free volume state f because the molecular mobility could be changed by adding another component. According to Ferry,²¹ f could be calculated with a_T . It was already discussed that f of AP/EP at 80°C is equal that of AP at 100°C. Accordingly, the effect of low-molecular-weight component on nonlinear viscoelasticity was carried out at iso-free volume state as examined below.

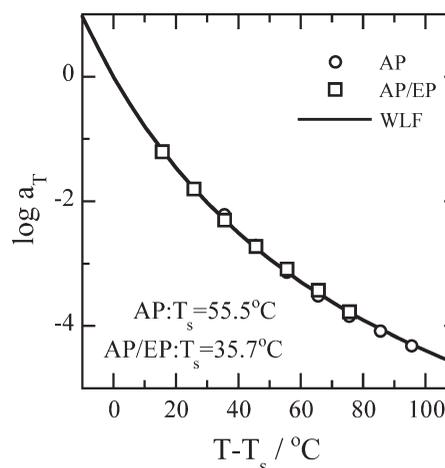


Figure 2 Temperature dependence of the shift factor a_T plotted against $(T - T_s)$ for the AP and AP/EP.

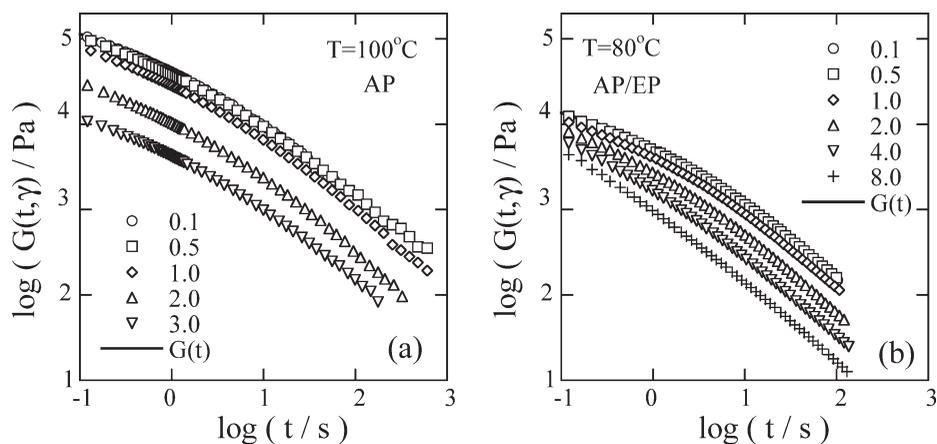


Figure 3 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for (a) AP at 100°C and (b) AP/EP at 80°C, respectively. The solid curves indicate the linear relaxation modulus calculated from the G' and G'' data.

Nonlinear stress relaxation modulus

Figure 3(a,b) show the nonlinear relaxation modulus $G(t, \gamma)$ of AP and AP/EP samples at 100 and 80°C, respectively. The solid curves represent the linear $G(t)$ obtained with the method of Schwarzl.²³

$$G(t) = [G'(\omega) - 0.56G''(0.5\omega) + 0.200G''(\omega)]_{\omega=1/t} \quad (5)$$

Both $G(t, \gamma)$ curves of AP and AP/EP agreed with the linear $G(t)$ curve at $\gamma < 0.5$. These $G(t, \gamma)$ decreases with increasing γ (> 0.5) and the nonlinearity becomes pronounced. For these $G(t, \gamma)$ data, validity of the time-strain separability [Eq. (1)] is examined below.

In Figure 4(a,b), $G(t, \gamma)$ curves for AP and AP/EP at 100°C and 80°C, respectively, were shifted vertically (in the double-logarithmic scales) to be superposed on respective reference curves obtained for the smallest γ . The shifted curves for AP were in good agreement with the linear $G(t)$ curves in our experimental window. On the other hand, the data of AP/EP was superimposed on well a single curve only at $t \geq 10$ s. It is said that time-strain separability is valid above a

critical time τ_k .¹ Therefore, τ_k of AP/EP system can be evaluated to be 10 s. Figure 5 illustrates the damping function $h(\gamma)$ of AP and AP/EP. $h(\gamma)$ data for AP and AP/EP monotonically decreased with increasing strain. The strain dependency of $h(\gamma)$ of AP system was slightly stronger than the predicted curve calculated from Doi and Edwards¹ theory for a narrow distributed polymer. On the other hand, $h(\gamma)$ of AP/EP coincided with the predicted curve.

Osaki²⁴ pointed out that the apparent damping becomes significant when a slip between material and wall surface or the instability of deformation in the material arises. In highly entanglement systems, the slip happens at material/wall interface, and $h(\gamma)$ is stronger than the predicted curve. If the entanglement number is decreased, $h(\gamma)$ is approached with the universal function of the Doi-Edwards tube model theory.^{24,25} Therefore, we consider that the reason why $h(\gamma)$ of AP showed remarkable decrease of $h(\gamma)$ is resulted to a slip between a material and plates in large strain. On the contrary, we note that the slip was prevented with adding to low-molecular-weight component in AP/EP system. The

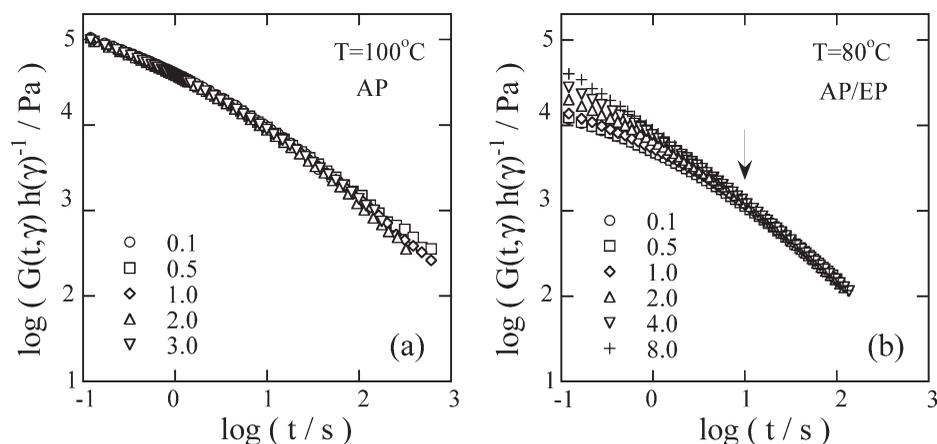


Figure 4 Plots of $G(t, \gamma)/h(\gamma)$ against time for (a) AP at 100°C and (b) AP/EP at 80°C, respectively.

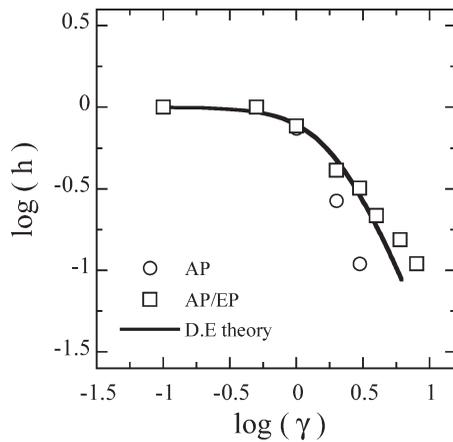


Figure 5 Damping function $h(\gamma)$ for AP and AP/EP. Solid curve represents the theoretical value due to the Doi-Edwards theory.

important result is that nonlinear relaxation modulus $G(t, \gamma)$ for AP and AP/EP behaves like a homopolymer.

Uniaxial elongational viscosity

Figure 6(a,b) show a uniaxial elongational viscosity ($\eta_E^+(t, \dot{\epsilon})$) of AP and AP/EP at 100°C and 80°C, respectively. In these figures, the numerals denote strain rates and the solid lines indicate $3\eta^+(t)$. Here, $\eta^+(t)$ is the shear stress growth function in the linear viscoelastic region calculated from the G' and G'' using an approximate equation proposed by Osaki et al.,²⁶

$$\eta^+(t) = t[G''(\omega) + 1.12G'(\omega/2) - 0.200G'(\omega)]_{\omega=1/t} \quad (6)$$

This equation was adopted to the linear elongational viscosity by use of the Trouton law (linear $\eta_E^+(t) = 3\eta^+(t)$).²⁷ The $\eta_E^+(t, \dot{\epsilon})$ increased with two steps: gradual increase (strain rate $\dot{\epsilon}$ independent linear

elongational viscosity) and rapid increase (strain rate dependent nonlinear elongational viscosity). Usually, $\dot{\epsilon}$ independent linear elongational viscosity is found to be in good agreement with the prediction curve ($3\eta^+(t)$). The steep increase of $\eta_E^+(t, \dot{\epsilon})$ above $3\eta^+(t)$ is called strain hardening.

The $\eta_E^+(t, \dot{\epsilon})$ of AP followed the linear viscoelastic function $3\eta^+(t)$ over the entire time scale measured. The strain hardening for AP was slightly observed at 3.0 s⁻¹. Linear elongational viscosity of AP/EP was in good agreement with the prediction for these samples at small strains ($\dot{\epsilon} \leq 0.3$). Steep increase in $\eta_E^+(t, \dot{\epsilon})$ for AP/EP could be observed at 1.0 s⁻¹. The point that should be paid attention is that AP/EP exhibited the stronger strain hardening than AP.

Recently, Nielsen et al.²⁸ investigated the uniaxial elongational viscosity for highly entangled polyisoprene with three type rheometers (Sentmanat extensional rheometer (SER), extensional viscosity fixture (EVF), and filament stretching rheometer (FSR)). They reported that it is difficult to discuss the steady state in the high-strain region ($\gamma > 1.2$) because the experimental error occurs depending on aspect ratio (height-to-thickness ratio) of the sample. However, we discuss the tendency about the steep increase of elongational viscosity at various strain rates in the uniform deformation region. Moreover, we have confirmed the uniform deformation at each strain (1.0, 2.0, and 3.5), when we obtained the results of Figure 6(a,b). Therefore, we believe that our elongational data were reliable.

Takahashi et al.²⁹ reported that the strain hardening is observed when the strain rate exceeds the contraction (retraction) rate τ_{eq}^{-1} . They also reported that an experimental relation between τ_{eq} and τ_k is obtained as follows:

$$\tau_{eq} \cong \tau_k/4.4 \quad (7)$$

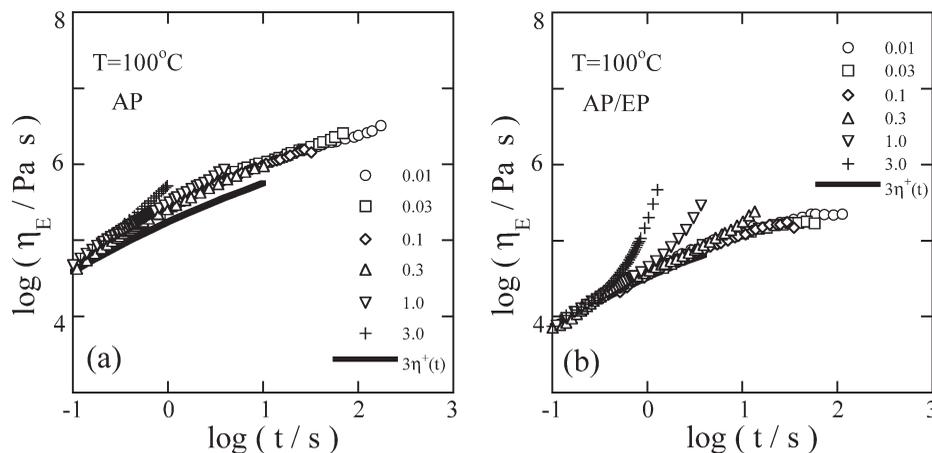


Figure 6 Time dependence of uniaxial elongational viscosity at various strain rates for (a) AP at $T = 100^\circ\text{C}$ and (b) AP/EP at $T = 80^\circ\text{C}$, respectively. The solid lines represent $3\eta^+(t)$ of AP and AP/EP calculated from dynamic viscoelastic data.

The τ_{eq} value of AP/EP can be estimated to be about 2, when the above relation is applicable to AP/EP. According to the Doi-Edwards theory,¹ strain hardening behavior of $\eta_E^+(t, \dot{\epsilon})$ is expected, when the strain rate is high enough for the primitive chain to extend. Our results indicate that the strain hardening of AP/EP was observed at $\dot{\epsilon} > \tau_{eq}^{-1}$. The characteristic time of polymer chain stretching obtained from the stress relaxation measurements was in excellently agreement with that from the elongational viscosity measurements.

We have studied the effect of low-molecular-weight component on uniaxial elongational viscosity in polystyrene (PS)/PS oligomer system³⁰ and confirmed that strain hardening properties of PS was enhanced by adding PS oligomer as well as that of AP/EP system. These facts indicate that the polymer chain becomes easy to be stretched in low-entanglement system though we can not have direct evidence. In other words, the stretching of polymer chain is remarkable in diluted system. It is a useful method to improve the strain hardening to dilute polymer chain by adding a low-molecular-weight component in an industrial point of view.

CONCLUSIONS

We studied the rheological behavior of an adhesive material used for electric device. Linear and nonlinear viscoelasticity of acrylic polymer (AP) and blend of AP and epoxy component (EP) system (AP/EP), which contained 70 vol % of EP, were investigated. From the linear viscoelasticity, it was found that time-temperature superposition of storage modulus G' and loss modulus G'' was satisfied, and the iso-free volume state of AP/EP blend was 20°C lower than that of AP. The entanglement molecular weight of AP and AP/EP was determined in the plateau zone of G' . It was confirmed that AP chain is sufficiently diluted with EP components. In the investigation of nonlinear stress relaxation modulus $G(t, \gamma)$, time-strain separability, $G(t, \gamma) = G(t)h(\gamma)$ was well-satisfied at long time above a characteristic time τ_k . The τ_k value was estimated to be 10 s for AP/EP and below 0.1 s for AP. The $h(\gamma)$ data for the AP and AP/EP monotonically decreased with increasing strain and behave like a usual polymer system. The time evolution of the elongational viscosity $\eta_E(t)$ of each sample followed the linear viscosity growth function $3\eta^+(t)$ at linear strain. AP/EP exhibited strong strain hardening at $\dot{\epsilon} \geq 1.0$, although AP did not show strain hardening at strain measured. These results imply that the stretch of polymer chain is remarkable in diluted polymer chain systems. Therefore, the adding of EP component enables not only the decrease of linear viscosity but also the enhance-

ment of strain hardening. It is concluded that the productivity of electric device is improved without breaking of device, and the dimension of adhesive layer is stabilized in free surface deformation area by adding EP component.

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