Rheology of SiO2/(Acrylic Polymer/Epoxy) Suspensions.III. Uniaxial Elongational Viscosity

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Rheology of SiO$_2$/(Acrylic Polymer/Epoxy) Suspensions.

III. Uniaxial Elongational Viscosity

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Abstract   Uniaxial elongational viscosity of $SiO_2/(AP/EP)$ suspensions with various SiO_2 volume fractions (ϕ) in a blend of acrylic polymer (AP) and epoxy (EP) was investigated at various temperatures (*T*).   The matrix polymer ((AP/EP) blend) contained 70 vol.% of EP.   At $\phi \leq 35$ vol.% at $T \leq 80^{o}C$, where the suspensions were in sol state, strain hardening behavior was observed.   This strain hardening of the suspensions is attributable to the elongational flow properties of (AP/EP) medium.   At critical gel state ($\phi = 35$ vol.% and $T = 100^{o}C$) and in gel state ($\phi \geq 40$ vol.%) the elongational viscosity exhibited the strain softening behavior.   These results strongly suggest that the strain softening results from the strain-induced disruption of the network structure of the SiO_2 particles therein.

Introduction

In a semiconductor industry, IC chips are three-dimensionally integrated in order to increase the capacity of memory without a change of size.   The IC chips are stacked on a wafer using an adhesive film.   Our adhesive film consists of three components; epoxy resin (EP), non-crystalline acrylic polymer (AP) and silica particle SiO_2.   In a certain IC package, the bonding wire which interconnects IC chips with substrates is embedded in the adhesive layer.   Since a presence of void gives rise to serious damage such as electrical short, the adhesive material has to fill the space around the thin wire also.   Therefore, we have to investigate the nonlinear viscoelasticity for SiO_2/(AP/EP) suspension system because adhesive film is undergone large deformation in actual staking process.   In a previous paper (Uematsu et al. 2010a), we reported that the linear viscoelasticity of the (AP/EP) medium drastically changed by adding SiO_2 and the suspensions showed a sol-gel transition with increasing SiO_2 concentration and temperature.   From the result, our suspension system is categorized as weakly flocculated system.

The rheological behavior of suspensions changes with affinity of suspending medium (Larson 1999, Aoki et al. 2003).   Three different types of the behavior are observed.   The first is "well dispersed systems"; in the medium having a high affinity toward the particles, the particles are randomly dispersed without large agglomerates. The slow relaxation of the suspension is attributable to diffusion of the particles (Russel 1980 and Shikata et al. 1994).   The second is "weakly flocculated systems"; in the medium having a moderate affinity, the particles form fragmented network-like structures

that grow to a self-similar, fractal network. Correspondingly, a power-law type relaxation similar to that of critical gels is observed at high particle volume fraction where the fractal network is formed (Rueb and Zukoski 1998 and Aoki and Watanabe 2004). The third is "strongly flocculated systems"; in the medium having a poor affinity, the particles form well-developed network-like structures. This network structure provides the suspension with highly nonlinear, elasto-plastic features. This type of rheological behavior has been extensively investigated for many suspensions, because the affinity of the medium and particles is generally poor in simple blend system (Onogi and Matsumoto 1981 and Amari and Watanabe 1983).

As we mentioned, the SiO_2/(AP/EP) suspension is a weakly flocculated system. The linear viscoelasticity of the sample have been reported (Uematsu et al. 2010a). We found that the SiO_2/(AP/EP) suspension exhibited a liquid-like behavior at $\phi \leq 30$ vol.%, the critical gel behavior at $\phi = 35$ vol. % at $100^{\circ}C$, and a solid-like behavior at $\phi \geq 40$ vol.%. At the critical gel point, the critical relaxation exponent was found to be 0.45. We also investigated the nonlinear stress relaxation behavior of SiO_2/(AP/EP) (Uematsu et al. 2010b). In the sol state, the SiO_2/(AP/EP) suspensions behaved as a viscoelastic liquid, and the time-strain separability, $G(t,\gamma) = G(t)h(\gamma)$, where $G(t,\gamma)$ is nonlinear relaxation modulus, $G(t)$ is linear relaxation modulus and $h(\gamma)$ is damping function, was applicable above τ_k, which is the appropriate time for constricted chain to return to equilibrium length. On the other hands, the time-strain separability was not applicable at critical gel and gel state. This nonlinear stress relaxation behavior is attributable to strain-induced disruption of the network structure formed by the SiO_2 particles therein. The investigation of elongational flow behavior for SiO_2/(AP/EP) is

also of considerable significance because SiO_2/(AP/EP) suspension undergoes large deformation of free surface in stacking process of wafers. The bonding wire which interconnects IC chips with substrates is embedded in the adhesive layer. The flow around these wires is restricted and the large elongational strain is generated in stacking process. The embedding behavior of adhesive film around wire could be practically controlled with temperature and volume fraction of each component. Therefore, the investigation of elongational flow for SiO_2/(AP/EP) suspension is very important to perform the material and process designs.

Elongational flow behavior of strongly flocculated or well dispersed system has been done in earlier reports. Tanaka and White (1980) reported the elongational flow behavior of PS reinforced by carbon black (CB), titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$). These systems exhibited yield values generated by breaking of a network structure formed by filler in elongational flow. Takahashi et al. (1999) investigated the strain hardening properties of LDPE composites, which consisted of various fillers (particle, talc, and fiber). The strain hardening of these composites became weaker than that of the matrix with increasing in aspect ratio of fillers. Ferec (2009) investigated the effect of the structure for the glass fiber on the elongational viscosity for PP. Le Meins et al. (2003) also reported the same effect of particle size and volume fraction on elongational viscosity in well disperse system. Chellamuthu et al have investigated the effect of clusters composed with nanoparticle on extensional rheology for poly (propylene glycol) (2009). These studies suggest that the elongational viscosity of suspension depends on the dispersibility of filler. However, the study of elongational flow behavior for weakly attractive particle system has hardly been reported.

The investigation of elongational flow behavior for our suspension system $(SiO_2/(AP/EP))$ is of great significance from academic point of view also.

In this paper, we investigated the uniaxial elongational behavior for $SiO_2/(AP/EP)$ suspensions having various ϕ. We focus on the effect of the volume fraction of SiO_2 and temperature on nonlinearity for uniaxial elongational viscosity $\eta_E^+(t,\dot{\varepsilon})$. Details of the uniaxial elongational viscosity behavior are presented in this paper.

Experimental methods

Sample preparation

Blend of an acrylic polymer (AP) with linear chain and low molecular weight epoxy (EP) was used as suspending medium. Both AP and EP were provided from Hitachi Chemical Co. Ltd. The weight-averaged molecular weight, M_w, and heterogeneity index, M_w/M_n, of AP are 360,000 and 2.2, respectively, where M_n is the number-average molecular weight. EP consists of bisphenol f diglycidylether (L-epo), cresol novolac type epoxy resin (S-epo) and bisphenol A novolac (CA). The composition ratio of L-epo and CA is equal and that of S-epo is one third of L-epo. The content of EP in (AP/EP) was 70 vol%. Volume fractions of SiO_2 particles which are provided from Admatechs Co. Ltd. were 0, 20, 30, 35 and 40 vol.%. The SiO_2 particles were produced by a vaporized metal combustion (VMC) method. The average diameter of SiO_2 was 0.5 μm. The surface of SiO_2 was treated with epoxy silane coupling agent

to prevent agglomeration of SiO_2 particles. Details of this preparation method are described previously (Uematsu et al. 2010a).

Uniaxial elongational viscosity measurements

Measurements of uniaxial elongational viscosity $\eta_E^+(t, \dot{\varepsilon})$ at constant strain rates were carried out with ARES (TA Instruments) using elongational viscosity mode at several temperatures (60, 80 and 100 °C). The strain rates $\dot{\varepsilon}$ were from 0.01 to 1.0 s^{-1}. All of the measurements were performed under nitrogen atmosphere.

Results and discussion

In a previous paper (Uematsu et al. 2010a), we reported that the SiO_2/(AP/EP) suspensions exhibited a liquid-like behavior at $\phi \leq 30$ vol.%, the critical gel behavior at $\phi = 35$ vol.% at 100°C, and a solid-like behavior at $\phi \geq 40$ vol. %. In this paper, we investigated the $\eta_E^+(t, \dot{\varepsilon})$ for the SiO_2/(AP/EP) suspensions in three kinds of states. $\eta_E^+(t, \dot{\varepsilon})$ for the suspensions in sol state is reported in the beginning.

Uniaxial elongational viscosity $\eta_E^+(t, \dot{\varepsilon})$ at the sol state ($\phi \leq 30$ vol.%, $\phi = 35$ vol.% at T < 80°C)

Figure 1 shows the uniaxial elongational viscosity $\eta_E^+(t, \dot{\varepsilon})$ for the (AP/EP) medium ($\phi = 0$ vol.%) and the SiO_2/(AP/EP) suspension with particle concentrations of

$\phi = 35$ vol.% at 60$^{\mathrm{o}}$C.   In Fig.1, the numerals denote strain rate $\dot{\varepsilon}$ and the solid lines indicate $3\eta_{\mathrm{s}}$, where η_{s} is the linear shear viscosity measured under steady and transient flow.   The $\eta_E^+(t, \dot{\varepsilon})$ increased with two steps: gradual increase (strain rate $\dot{\varepsilon}$ independent linear elongational viscosity) and rapid increase ($\dot{\varepsilon}$ dependent nonlinear elongational viscosity).   Usually, $\dot{\varepsilon}$ independent linear elongational viscosity is in good agreement with $3\eta_{\mathrm{s}}$ (Trouton law) (1906).

$\eta_E^+(t, \dot{\varepsilon})$ of the medium ($\phi = 0$ vol%) follows the linear shear viscosity $3\eta_{\mathrm{s}}$ over the short time scale measured as shown in Fig.1.   In contrast, $\eta_E^+(t, \dot{\varepsilon})$ of AP/EP medium drastically increases at large strain region ($\varepsilon \geq 1.0$).   The strain hardening appears in (AP/EP) medium above 0.01s^{-1}.   In our suspension system, linear elongational viscosities of the suspensions ($\phi = 20, 30$, and 35 vol.%) are also in good agreement with $3\eta_{\mathrm{s}}$ for each sample at small strain.   We have to note that the steep increases of $\eta_E^+(t, \dot{\varepsilon})$ for the suspensions also can be confirmed above 0.01 s^{-1}.   This is unusual behavior for suspensions with high volume fraction of particles.   It has been reported that the strain hardening is suppressed by adding of particle (Takahashi et al. 1999 and Le Meins et al. 2003).

Figures 2 and 3 show the $\eta_E^+(t, \dot{\varepsilon})$ for $\phi = 0, 20$ and 30 vol.% at 80$^{\mathrm{o}}$C and 100$^{\mathrm{o}}$C, respectively.   As seen in Fig. 2 and 3, the data of the suspensions having $\phi = 0{\sim}30$ vol.% agree with $3\eta_{\mathrm{s}}$ in the small strain region at T=80$^{\mathrm{o}}$C and 100$^{\mathrm{o}}$C.   The rapid increasing of $\eta_E^+(t, \dot{\varepsilon})$ for the (AP/EP) medium is observed above 0.1 at 80$^{\mathrm{o}}$C and 0.3 s^{-1} at 100$^{\mathrm{o}}$C, respectively. $\eta_E^+(t, \dot{\varepsilon})$ of the suspensions is very similar to that of the medium.   The tendency of nonlinear behavior for the suspensions coincides with that of

the medium. Therefore, strain hardening of the suspensions is attributable to the elongational flow properties of the (AP/EP) medium.

It was found from the result of nonlinear stress relaxation behavior that characteristic time τ_k, which is the relaxation time for constricted chain to return to equilibrium length, was almost independent of SiO_2 content (Uematsu et al. 2010b). The magnitude of τ_k was found to be 12.5 ± 2.5 s at $80^{\circ}C$ and 5.5 ± 1.5 s at $100^{\circ}C$, respectively, in the suspension system. From these results, we notice that the strain hardening emerges at $\dot{\varepsilon}\tau_k >> 1$ in Figs. 2 and 3. Thus, it is suggested that the strain hardening of the suspensions results from enough stretching of polymer chain regardless of a presence of the particles.

Time temperature superposition

In order to confirm the effect of temperature on the dispersibility of SiO_2 particle, master curves of $\eta_E^+(t, \dot{\varepsilon})$ measured at $60\sim100^{\circ}C$ were investigated. Figure 4 shows the master curves of the (AP/EP) medium (a) and $\phi = 30$ vol.% suspension (b) reduced at $80°C$. The shift factor a_T of the suspensions having $\phi = 0\sim30$ vol.% is represented by the WLF equation (Ferry 1980) as indicated by the solid line in Fig. 5

$$\log a_T = \frac{c_1(T-T_r)}{c_2+(T-T_r)} \tag{1}$$

The closed and open symbols denote the a_T obtained from elongational viscosity and linear viscoelasticity (Uematsu 2010a), respectively. The solid line calculated with WLF equation ($c_1 = 5.75$ and $c_2 = 128.9$) represents in Fig.5. As seen in Fig.5, a_T of

the suspensions are described with c_1 and c_2 of the (AP/EP) medium. It is confirmed that the temperature dependence of a_T determined form elongational viscosity agree with that of linear viscoelasticity.

What is significant in this argument is that the time temperature superposition principle could be applied to the $\eta_E^+(t, \dot{\varepsilon})$ $\phi \leq$ 30 vol.%, as already observed by Li et al. (1988, 1990) and Takahashi et al. (1993). In other words, the particle structure in the suspensions does not change with T and the motion of the particles is governed by the chain friction of the medium like homo-polymer. From these results, it could be interpreted that the strain hardening for the suspensions is attributable to enough stretching of polymer chain as well as the medium. However, , as we discuss later, time temperature superposition could not be applied in suspension having $\phi = 0.35$ vol.%

$\eta_E^+(t, \dot{\varepsilon})$ at the critical gel state (ϕ = 35 vol.%, T=100°C) and the gel state (ϕ = 40 vol.%)

Figure 6 shows the $\eta_E^+(t, \dot{\varepsilon})$ of the SiO$_2$/(AP/EP) suspension having ϕ = 35 vol.% at 100°C. As seen in Fig.6, linear $\eta_E^+(t)$ of the suspension agrees with the $3\eta_s$. However, we should note that $\eta_E^+(t, \dot{\varepsilon})$ deviates downwards from linear viscoelastic regime at large strain region. It is clear that the strain softening is observed in the SiO$_2$/(AP/EP) suspension having $\phi = 35$ vol.% at 100°C.

Figure 7 shows the $\eta_E^+(t, \dot{\varepsilon})$ for ϕ = 40 vol.% suspension at 80°C (a) and 100°C (b) plotted against t at various $\dot{\varepsilon}$, respectively. As seen in Fig. 7, the linear

$\eta_E^+(t)$ coincided to $3\eta_s$. As well as the result of 35 vol.% suspension at 100 °C, $\eta_E^+(t, \dot{\varepsilon})$ deviated from $3\eta_s$ at small strain region and strong strain softening is exhibited at 80 and 100°C.

In SiO$_2$/(AP/EP) having ϕ = 35 vol.% system at 60°C, the strain hardening could be observed with same strain rate region as well as the (AP/EP) medium (Fig.1). The steep increase of elongational viscosity results from extension of polymer chain in suspension. On the other hand, the strain hardening for the medium became very weak at 100°C due to reduced the relaxation time (Fig.3 (a)). It is likely that the effect of SiO$_2$ on the nonlinearity for elongational viscosity is dominant at 100°C (Fig.6 (a)). That is also considered similarly in SiO$_2$/(AP/EP) having ϕ = 40 vol% system

In our suspension, we found that the SiO$_2$/(AP/EP) suspensions exhibited the critical gel behavior at ϕ = 35 vol.% at 100°C, and a gel-like behavior at $\phi \geq$ 40 vol.% (Uematsu et al. 2010a). In the small strain region, the $\eta_E^+(t, \dot{\varepsilon})$ coincided to $3\eta^+(t)$, which was calculated from *G'* and *G"* using an approximate equation proposed by Osaki et al. (1976) in Fig.6 and 7 (not shown here) However, $\eta_E^+(t, \dot{\varepsilon})$ deviates downwards from linear viscoelasticity at ε > 0.1 in suspension system having ϕ = 35 40 vol.%. From this result, it is reasonable to suppose that the strain softening could be developed by broken of network structure above critical strain.

In staking process of IC chip, the result leads to our presumption that the strain softening is effective for embedding of SiO$_2$/(AP/EP) around wire. Therefore, we can conclude that the optimum volume fraction of SiO$_2$ is 35~45 vol.% and the stacking of IC chip should be done above 100°C to control the processability.

Conclusion

We measured the uniaxial elongational viscosity of $SiO_2/(AP/EP)$ suspensions with various SiO_2 volume fractions (ϕ) at various temperatures (T), and investigated the effects of the SiO_2 particles on the nonlinear properties. At $\phi \leq 30$ vol.% and $\phi = 35$ vol.% at $T \leq 80^{\circ}C$, strain hardening was observed as well as AP/EP medium ($\phi = 0$ vol.%). The time temperature surperposition was valid for $\phi \leq 30$ vol.%. The a_{T} of the suspensions were described by WLF equation with general WLF constant c_1 (5.75) and c_2 (128.9) calculated from the master curve of the medium (AP/EP). Therefore, strain hardening for the suspensions is attributable to enough stretching of polymer chain. In contrast, nonlinear behavior for $\phi = 35$ and 40 vol.% suspensions exhibited the strain softening at $T = 100^{\circ}C$, where is critical gel and gel state, respectively. The strain softening is exhibited by strain-induced disruption of the network structure of the SiO_2 particles.

Acknowledgment

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Figure Captions

Fig. 1   Time dependence of uniaxial elongational viscosity at various strain rates for SiO$_2$/(AP/EP) suspensions having ϕ =0 vol.% (a) and 35 vol.% (b), respectively, at 60$^{\mathrm{o}}$C. The solid lines represent 3$\eta_{\mathrm{s,}}$ where η_{s} is the linear shear viscosity.

Fig. 2   Time dependence of uniaxial elongational viscosity at various strain rates for SiO$_2$/(AP/EP) suspensions having ϕ =0 vol.% (a) and 20 vol.% (b), respectively, at 80$^{\mathrm{o}}$C. The solid lines represent 3$\eta_{\mathrm{s,}}$ where η_{s} is the linear shear viscosity.

Fig. 3   Time dependence of uniaxial elongational viscosity at various strain rates for SiO$_2$/(AP/EP) suspensions having ϕ =0 vol % (a) and 30 vol % (b), respectively, at 100$^{\mathrm{o}}$C. The solid lines represent 3$\eta_{\mathrm{s,}}$ where η_{s} is the linear shear viscosity.

Fig. 4   Master curves of the uniaxial elongational viscosity for the SiO$_2$/(AP/EP) suspensions having ϕ = 0 vol.% (a) and 30 vol.% (b) reduced at 80 °C. The solid lines represent 3$\eta_{s,}$ where η_{s} is the linear shear viscosity.

Fig. 5   Temperature dependence of the shift factors a$_{\mathrm{T}}$ of the SiO$_2$/(AP/EP) suspension having $\phi \leq$ 30 vol %. The closed and open symbols represent the $a_{_T}$ obtained from elongational viscosity and linear viscoelasticity (Uematsu 2010a), respectively.

Fig. 6   Time dependence of uniaxial elongational viscosity at various strain rates for the SiO$_2$/(AP/EP) suspension having ϕ = 35 vol.% at 100$^{\mathrm{o}}$C, respectively. The solid lines represent 3$\eta_{\mathrm{s,}}$ where η_{s} is the linear shear viscosity.

Fig. 7   Time dependence of uniaxial elongational viscosity at various strain rates for the SiO$_2$/(AP/EP) suspension having ϕ = 40 vol.% at 80$^{\mathrm{o}}$C (a) and 100$^{\mathrm{o}}$C (b), respectively. The solid lines represent 3$\eta_{\mathrm{s,}}$ where η_{s} is the linear shear viscosity.
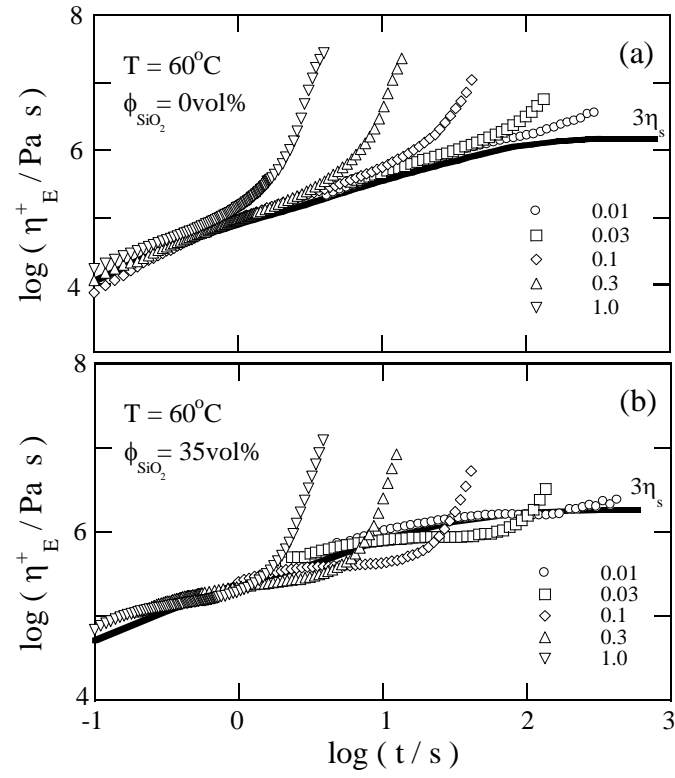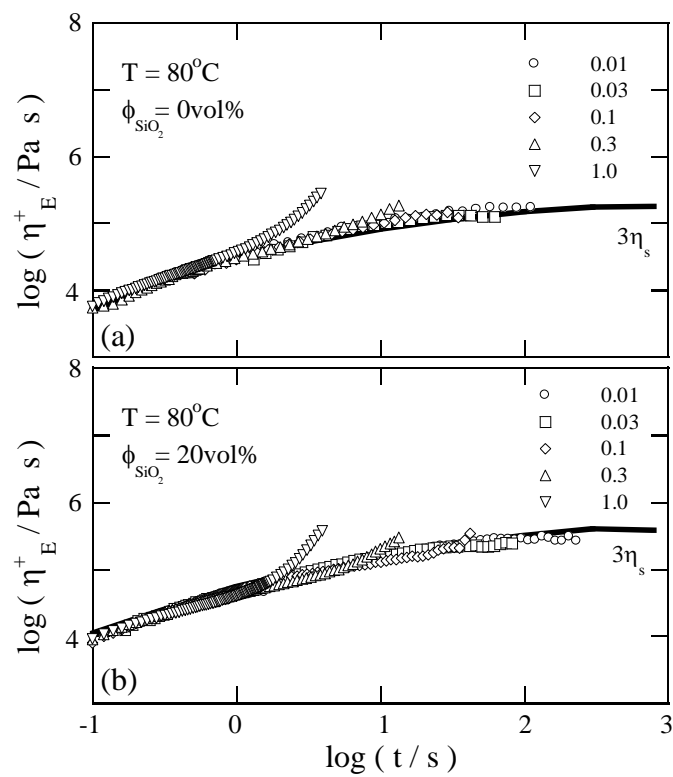
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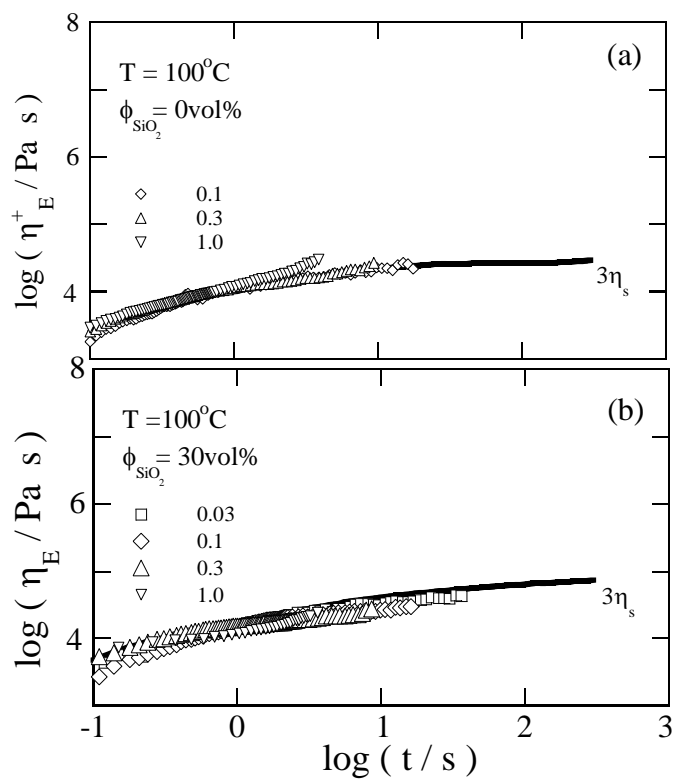
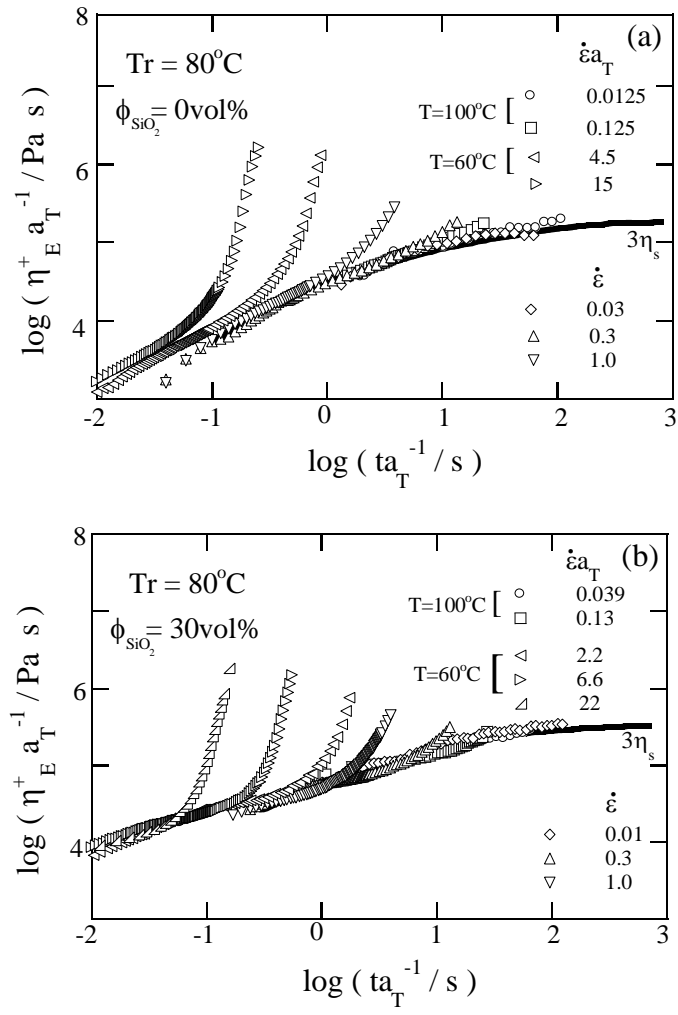Fig. 2   (Uematsu, et al.)

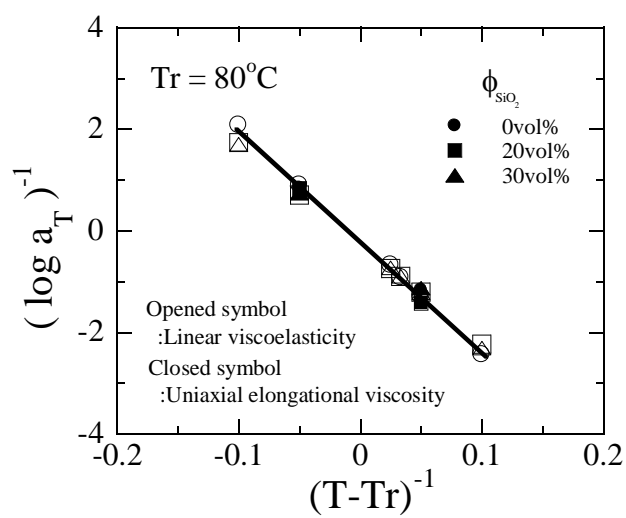Fig. 3　　(Uematsu, et al.)

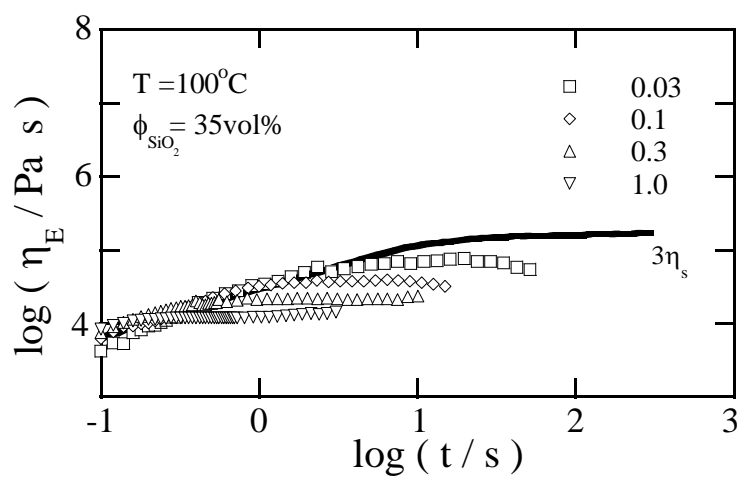Fig. 4   (Uematsu, et al.)

Fig. 5   (Uematsu, et al.)
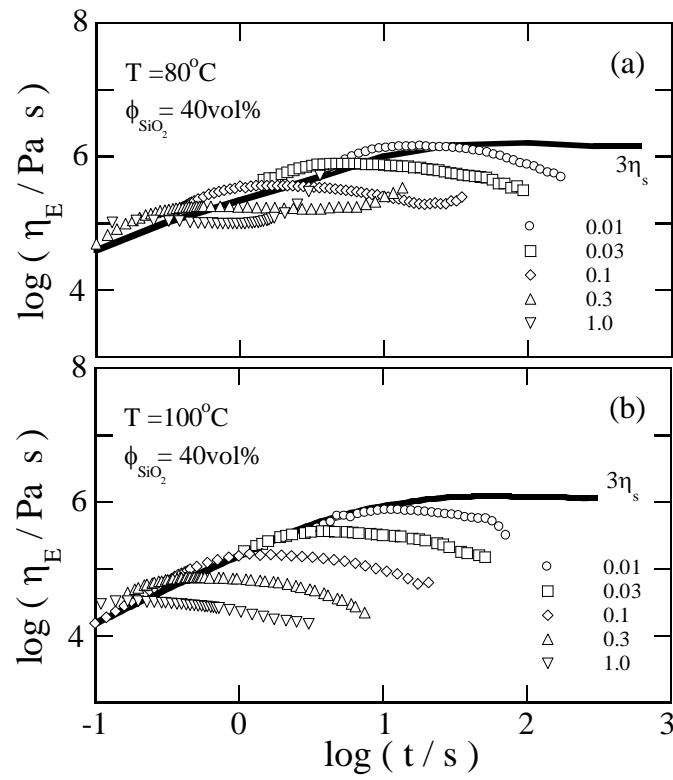
Fig. 6   (Uematsu, et al.)

Fig.7   (Uematsu, et al.)

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