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

I. Linear Viscoelasticity

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Abstract   Linear viscoelastic properties of SiO_2/(AP/EP) suspension with various SiO_2 volume fractions (ϕ) in a blend of acrylic polymer (AP) and epoxy (EP) were investigated at various temperatures (T).   The AP/EP contained 70 vol% of EP.   The SiO_2 particles were treated with epoxy silane coupling agent.   The effects of the SiO_2 particles are more pronounced in the terminal zone: a transition from viscoelastic liquid ($\phi \leq 30$ vol %) to viscoelastic solid ($\phi \geq 40$ vol %) was observed which can be interpreted as a critical gelation occurring at a critical particle content and critical gel temperature.   The SiO_2/(AP/EP) systems exhibited a critical gel behavior at $\phi \cong 35$ vol % and $T \cong 100$ °C characterized with a power-law relationship between the storage and loss moduli (G' and G'') and frequency (ω); $G' = G''/\tan(n\pi/2) \propto \omega^n$.   The critical gel exponent (n) was estimated to be about 0.45.   The gelation occurred with increasing T.

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. This stacking process is carried out at temperature above the glass transition temperature (T_g) of the adhesive film, followed by complete curing at higher temperature to enhance the interface adhesion. Our adhesive film consists of three components; 1) epoxy resin (EP) to exert the adhesion strength and the heat resistance, 2) acrylic polymer (AP) having low T_g for elasticity and toughness at room temperature, 3) SiO_2 particles to keep the linear expansion coefficient low. It is possible to prevent the crack of adhesive film by adding AP. So far the handling of adhesive film is advanced at room temperature. Low expansion coefficient is often achieved by adding high volume fraction of SiO_2. It is reported that rheological behavior of the (AP/EP) medium drastically changes by the adding of SiO_2 particle. Especially, we focus on the relationship rheological behavior and affinity of polymeric material and rigid particle to consider the rheological behavior of SiO_2/(AP/EP) 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. First is "well dispersed systems"; in the medium having a high affinity toward the particles, the particles are randomly dispersed to form no larger agglomerates. The slow relaxation is attributable to diffusion of the particles. 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 this fractal network is formed. 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 medium affinity is generally poor (Onogi and Matsumoto 1981; Amari and Watanabe 1983).

Suspensions of weakly attractive particles, exhibiting the critical gel behavior at sufficiently high particle volume fraction, have been attracting industrial as well as academic interest. Recently, a number of studies of "weakly flocculated systems" have been reported. Most of the rheological studies for such suspensions were devoted to elastic properties of the gels (Grant and Russel 1993; Rueb and Zukoski 1997; Yanez et al. 1999; Trappe and Weitz 2000; Wu and Morbidelli 2001) and to gelation process (In and Prud'homme 1993; Jokinen et al. 1998; Tokumoto et al. 2000). Rueb and Zukoski (1998) investigated the rheology of silica suspensions in decalin and tetradecane and found that the particles interact like hard spheres at high temperature (T) but the gelation due to the interparticle attraction occurred at low T.

Recently, Aoki et al. studied the linear viscoelastic behavior of carbon black (CB) suspensions in the medium having moderate affinity toward CB particles and found that the suspensions exhibited sol-gel transition on an increase in volume faction ϕ of CB and the ϕ_{gel} at the gelation point decrease with increasing T (Aoki and Watanabe 2004; Aoki 2007). This T dependence of ϕ_{gel} is opposite to the dependence seen for gelling systems as compared with past reports (Jansen et al. 1986a,b,c,d; Rueb and Zukoski 1998).

The application of sol-gel transition to suspension systems should result in a much deeper understanding of the rheology of suspensions. Winter and Chambon (Winter and Chambon 1986; Chambon and Winter 1987) found that the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ follow power laws with the same exponent n at the gel point. The gel point corresponds to the state where $G'(\omega)$ and $G''(\omega)$ parallel each other over the experimentally accessible range of ω, and is characterized by a single exponent n which is called the critical relaxation exponent that ranges between 0 and 1:

$$G'(\omega) = G''(\omega)/\tan \delta \propto \omega^{n} \tag{1}$$

$$\tan \delta = \tan (n\pi/2) \tag{2}$$

The loss tangent $\tan \delta$ is independent of the frequency. Eq. (2) is of importance, because Eq. (2) allows the precise value of the gelation point to be determined.

The experimentally determined relaxation exponent n was reported to be around 0.75 for zirconium alkoxide (In and Prud'homme 1993), silica gels (Jokinen et al. 1998), and SnO_2 suspensions (Tokumoto et al. 2000), and 0.13 and 0.15 for TiO_2 suspensions (Pontom et al. 1999). In the previous papers, Aoki et al. (2003, 2004, 2007) reported that the critical exponent n of CB/varnish suspensions was near 0.7 at 40 °C and was increased with elevating T.

In the processing of stacking IC chip, it has been empirically found that the processability such as burr between IC chip and wafer depends on the volume fraction of SiO_2 within the matrix polymer (AP/EP). So far the rheological behavior of this complex system has never been reported. It is very important to investigate the rheological behavior of $SiO_2/(AP/EP)$ to improve the processability. The purpose of our

study is to investigate the effect of SiO_2 particles on the rheological behavior for the adhesive film to improve the processability.

We investigated the linear viscoelastic properties of SiO_2/(AP/EP) suspensions at various particle volume fractions ϕ and temperature T.   We found that the SiO_2/(AP/EP) suspensions exhibited a liquid-like behavior at low ϕ ($\phi \leq 30$ vol %), the critical gel behavior at $\phi = 30$ vol %, and a solid-like behavior at $\phi \geq 40$ vol %.   Details of these results 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 for L-epo. The content of EP in (AP/EP) was 70 vol%.   Volume fractions of SiO_2 particles which is provided from Admatechs Co. Ltd. were 0, 20, 30, 35 and 40 vol%.   This SiO_2 particles made by 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.   Each of the components was dissolved homogeneously in cyclohexanone.   The concentration of total components in the

solution was about 20 vol%.   Cyclohexanone in solution was evaporated at 120°C for 30 minutes.   It was confirmed by thermo-gravimetric analysis (TGA) that the cyclohexanone in the sample was almost disappeared.   The M_w and radius of gyration of AP, respectively, were found to be the same before and after evaporation of cyclohexanone by GPC/MALS measurements.   The measurement of M_w of EP was difficult because the detection limit of GPC ($M_w <$ 3,000g/mol).   The sample made from EP without AP showed a Newtonian flow behavior and the magnitude of viscosity was about 7 Pas at 60 $^{\circ}$C.   Accordingly, EP was thought to be oligomer.   Chemical reaction of AP or EP with SiO_2 surface was checked by TGA.   TGA results verified that neither AP nor EP reacted to SiO_2 because weight decrease was less than 0.003% for the SiO_2 particles after centrifugation.

Linear viscoelasticity measurements

Dynamic viscoelastic measurements were carried out at various T from 60 °C to 120 °C with a strain-controlled rheometer (ARES, TA Instruments) using parallel plate fixture.   Parallel plates with 8 mm in diameter were used for the frequency ω sweeps. The ω dependencies of the storage and loss moduli, G' and G'', were measured in the frequency range from 0.1 to 100 rad/s.   The strain was 0.004 in the linear viscoelastic criterion of AP/EP and SiO_2/(AP/EP) systems.   All of the viscoelastic measurements were performed under nitrogen atmosphere.

Results and discussion

Viscoelasticity at the sol state ($\phi \leq 30$ vol %)

For the SiO_2/(AP/EP) suspensions with various particle concentrations, $\phi = 0$, 20, 30 vol%, Figure 1 shows the master curves of G' (a) and G'' (b) reduced at 80 °C. Figure 2 shows the shift factor a_T for the suspensions and medium utilized for constructing the master curves.

The temperature dependence of the shift factors (a_T) was almost the same irrespective of ϕ. The a_T of the SiO_2/(AP/EP) suspensions was well described by the WLF equation (Ferry 1980), as indicated by the solid line in Fig. 2.

$$\log a_T = \frac{c_1(T - T_r)}{c_2 + (T - T_r)} \tag{3}$$

As seen in Fig.2, a_T of the suspensions are described by c_1 (5.75) and c_2 (128.9) calculated from the master curve of matrix AP/EP.

It should be emphasized that viscoelastic properties of the SiO2/(AP/EP) suspensions below $\phi \leq 30$ vol % obey the time-temperature superposition and the temperature dependences of a_T were identical with each other; see Figure 2. These data indicate that the particle structure in the suspensions does not change with T and the motion of the particles is governed by the friction from the medium. In other words, the suspensions include no agglomerates structure that changes with T. These results strongly suggest that the behavior of the SiO_2/(AP/EP) suspensions below $\phi \leq 30$ vol % can be very well described as the behavior of good suspension systems.

In the range of our experimental window, the (AP/EP) medium behaves as a viscous fluid having $G'' >> G'$, although the terminal tails ($G' \propto \omega^2$ and $G'' \propto \omega$) cannot be observed. The G' and G'' of the SiO_2/(AP/EP) suspensions decrease with lowering of

frequency.   The slopes of G' and G'' of the SiO_2/(AP/EP) suspensions become weak with increasing ϕ.   These results also indicate that the SiO_2 particles in the (AP/EP) medium are considered to form a good dispersed system.

Viscoelasticity at the critical gel state ($\phi = 35$ vol %)

Figure 3 shows the ω dependence of the G' and G'' of the SiO_2/(AP/EP) suspensions having $\phi = 35$ vol%.   In the lower temperature range below 90 °C, the suspension exhibits the flow behavior like low ϕ suspensions; the G' and G'' decrease with lowering of ω.   However, at 100 °C, the suspension exhibits the power-law type ω dependence of G' and G''.   This power-law behavior is characteristic of a critical gel consisting a self-similarly branched fractal network, as described in Introduction. Above 110 °C, the suspension behaves as a well-developed gel; the G' and G'' tend to level off with decreasing ω and exhibit a plateau at low ω.   This behavior suggests that a network structure of SiO_2 particles is formed in the suspension.

Figure 4 shows the plot of tan δ versus ω at various T for the SiO_2/(AP/EP) suspensions having $\phi = 35$ vol%.   Specifically, it suggests that the ω-independent tan δ is observed at 100 °C.   This flat phase angle region covers a wide ω window, as marked by a horizontal line.   From the ω-independent tan δ point, the critical gel temperature (T_{gel}) and the n value can be determined.   It is found that $T_{gel} = 100$ °C and $n = 0.45$.

This SiO_2/(AP/EP) suspension exhibits heat-induced gelation.   Such a behavior has been reported only a few systems (Horn and Patterson 1997; Aoki and Watanabe 2004; Aoki 2007).   The heat-induced gelatin should result from an enhancement of the

attraction between the particles with increasing T.   Aoki and Watanabe (2004) discussed the mechanism of heat-induced gelation of CB/varnish system, and proposed that this enhancement was due to the affinity change of the polymeric component in the varnish. Our suspending medium (AP/EP) is a complicated polymer solution.   We speculate that the change of the affinity to the particles influences the particle agglomeration.

Viscoelasticity at the gel state ($\phi = 40$ vol %)

Figure 5(a), (b) and (c) ,respectively, shows the G', G'', and tan δ of the SiO_2/(AP/EP) suspension having $\phi = 40$ vol % plotted against ω at various temperatures. The suspension behaves as a well-developed gel; the G′ and G″ tend to level off with decreasing ω and exhibit a plateau at low ω.   With elevating T, the slopes of the G' and G'' become small and tan δ values decrease.   This behavior suggests that a network structure of SiO_2 particles is formed in the suspension and grows up to more dense structure.

Mechanism of heat-induced gelation

Figure 6 shows the phase diagram of the SiO_2/(AP/EP) suspensions.   As seen in Fig. 6, the suspensions exhibit heat-induced gelation.   This type of behavior has been reported only for a few systems (Horn and Patterson 1997; Aoki and Watanabe 2004; Aoki 2007) and is the opposite to the behavior of the majority of gelling systems in thermoplastic/particle system.   We should note that this heat-induced gelation is also to be thermally reversible within the temperature range from 60 to 120°C. G' and G'' curves roughly trace the data during heating process when cooling from 120 to 60°C.

The heat-induced gelation should result from an enhancement of the attraction among SiO_2 particles with increasing T because it is confirmed that neither AP nor EP reacts to SiO_2 surface by analyzing TGA.   Therefore, it is suggested that observation of sol-gel behavior is related with physical interaction between SiO_2 and polymeric components.   In the medium having a moderate affinity, the particles form fragmented network-like structure and sol-gel transition depending on T is observed.   In other words, sol-gel transition is originated with changing of the affinity between rigid particle and polymeric components.   A key factor for this enhancement can be due to the composition of the medium (AP/EP) in our studies.   The medium consists of complicated components.   We consider that AP/EP have a temperature-sensitive affinity toward the SiO_2 particles treated with epoxy silane coupling agent.   If the affinity of AP towards SiO_2 decreases as increasing temperature, it would lead to enhancement of the adsorption of EP component on the SiO_2 particles.   The adsorbed component would bridge neighboring particles and enhance the gelation.   At present, we do not have direct evidence for changed affinity of EP with SiO_2.   It is, however, found that the sol-gel transition behavior can never been observed without EP component.   It may be reasonable to say that, the heat-induced gelation of the SiO_2/(AP/EP) suspension appears to be attributable to this adsorption/bridging.   Thus we should note that a present of the EP plays a very important role in the sol-gel transition behavior of the AP/EP/SiO_2 system.

If the IC chip is stacked with adhesive film which contained 35~40 vol% of SiO_2 at $100^{o}C$, it is not only easy to attach adhesive film to IC chip or wafer due to decreasing of viscosity but also the dripping of adhesive film or burr between IC chip and wafer is

prevented by gelation.   Therefore, we can conclude that the optimal volume fraction is

35~40 vol% for the adhesive film from this study.

Conclusion

We investigated the linear viscoelastic properties of SiO_2/(AP/EP) suspensions with various SiO_2 volume fractions (ϕ) at various temperatures (T). We found that the effects of the SiO_2 particles are more pronounced in the terminal zone: a transition from viscoelastic liquid ($\phi \leq 30$ vol %) to viscoelastic solid ($\phi \geq 40$ vol %) was observed which can be interpreted as a critical gelation occurring at a critical particle content and critical gel temperature. The SiO_2/(AP/EP) systems exhibited a critical gel behavior at $\phi \cong 35$ vol % and T $\cong 100$ °C characterized with a power-law relationship between the G' and G'', and ω, $G' = G''/\tan(n\pi/2) \propto \omega^n$. The critical gel exponent (n) was estimated to be about 0.45 at $\phi = 35$ vol %. The gelation occurred with increasing T. This heat-induced gelation is opposite to the usual gelling systems. Nonlinear rheology such as nonlinear stress relaxation and elongational viscosity will be reported in near future.

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Figure Captions

Fig. 1   Master curves of the storage and loss moduli: (a) G'; (b) G'' for the SiO_2/(AP/EP) suspensions having $\phi \leq 30$ vol % reduced at 80 °C

Fig. 2   Temperature dependence of the shift factors a_T of the SiO_2/(AP/EP) suspensions having $\phi \leq 30$ vol %

Fig. 3   Frequency (ω) dependence of the linear viscoelastic modulii: (a) G'; (b) G'' of the SiO_2/(AP/EP) suspension having $\phi = 35$ vol %

Fig.   4   tan δ plotted against temperature (T) for the SiO_2/(AP/EP) suspension having ϕ = 35 vol %

Fig. 5   Frequency (ω) dependence of the linear viscoelastic modulii: (a) G'; (b) G'' and tan δ (c) of the SiO_2/(AP/EP) suspension having $\phi = 40$ vol %

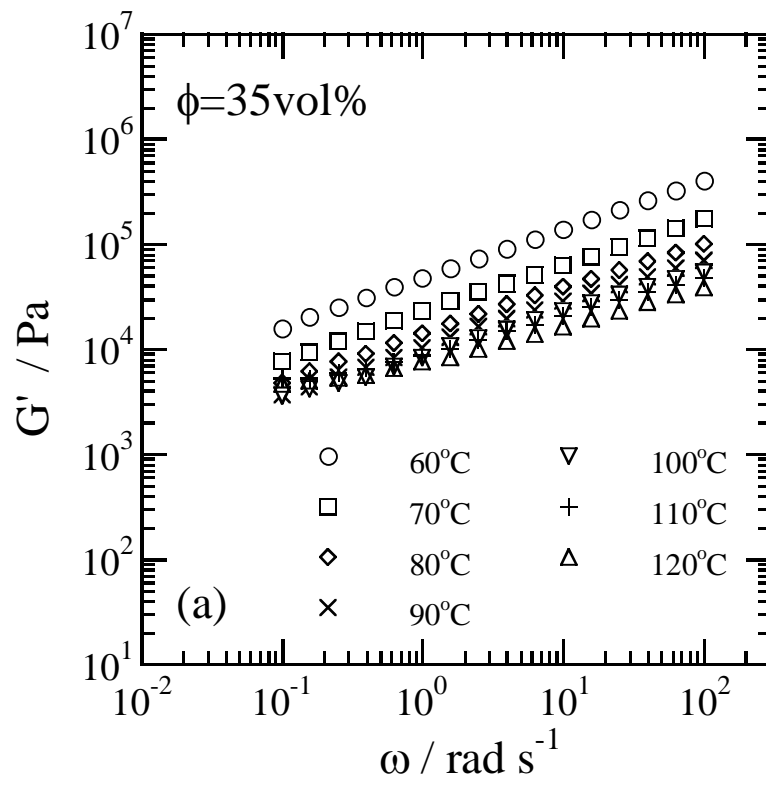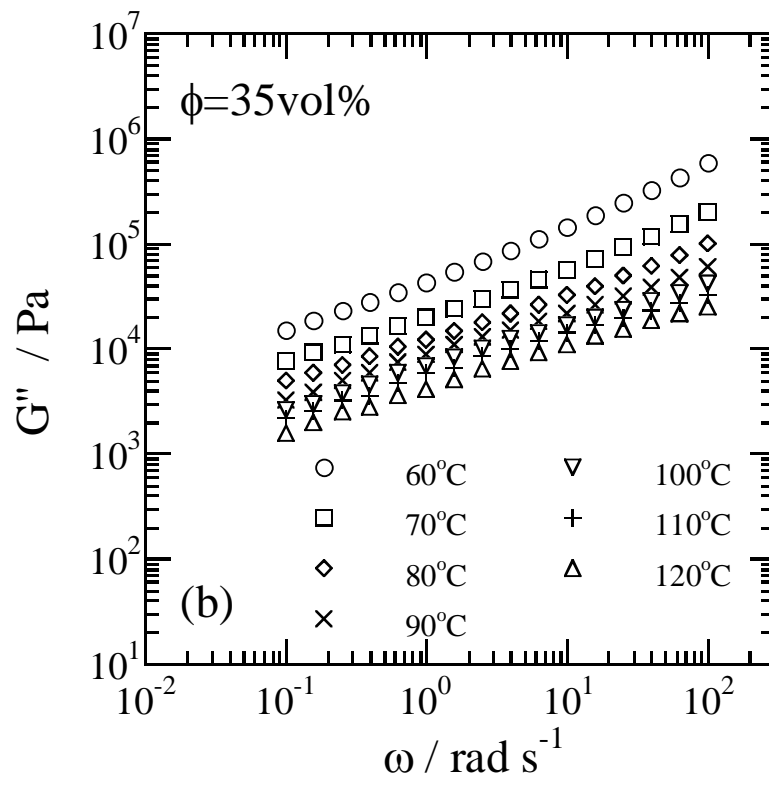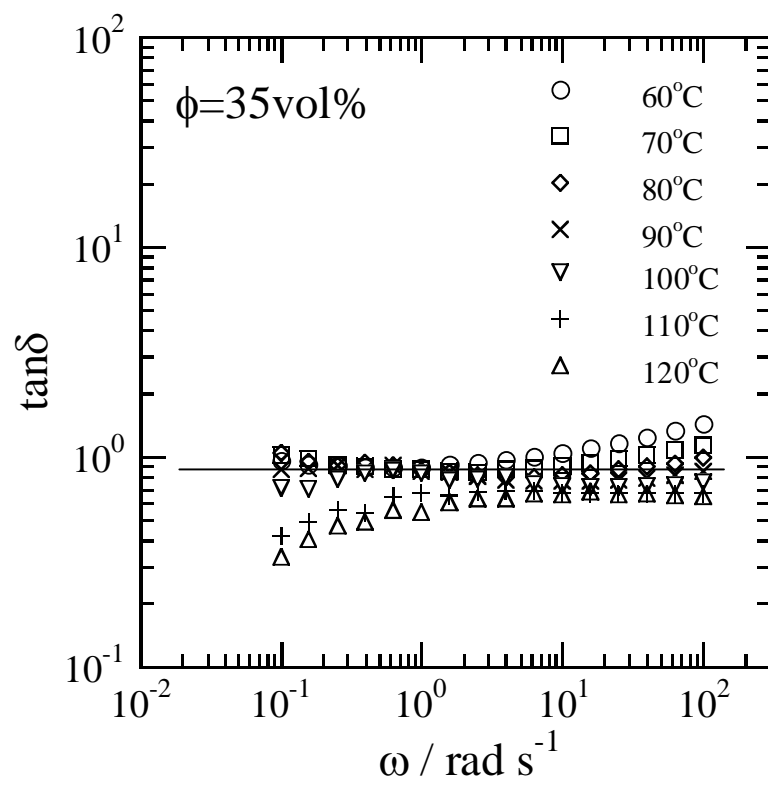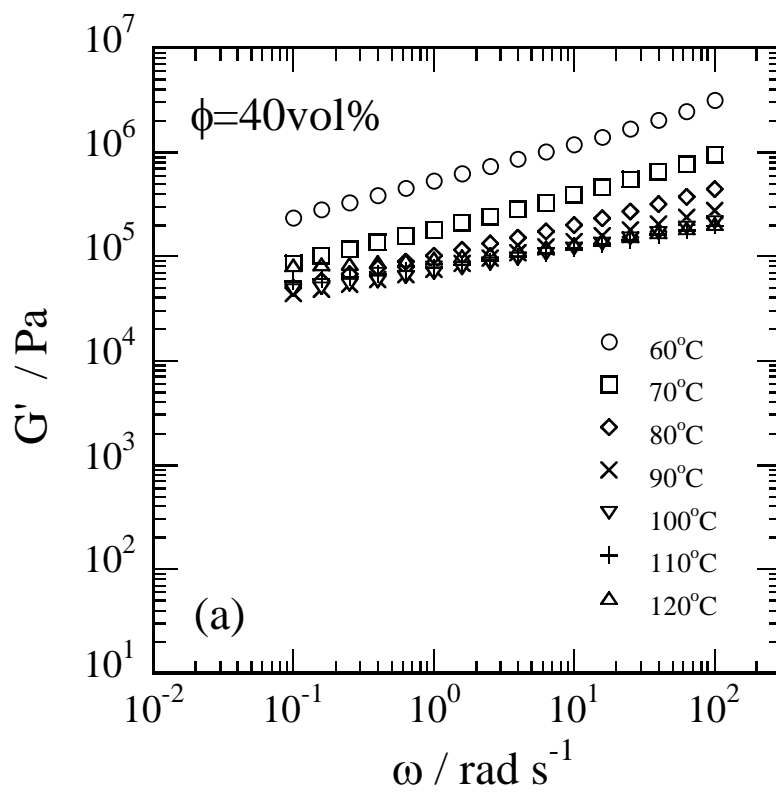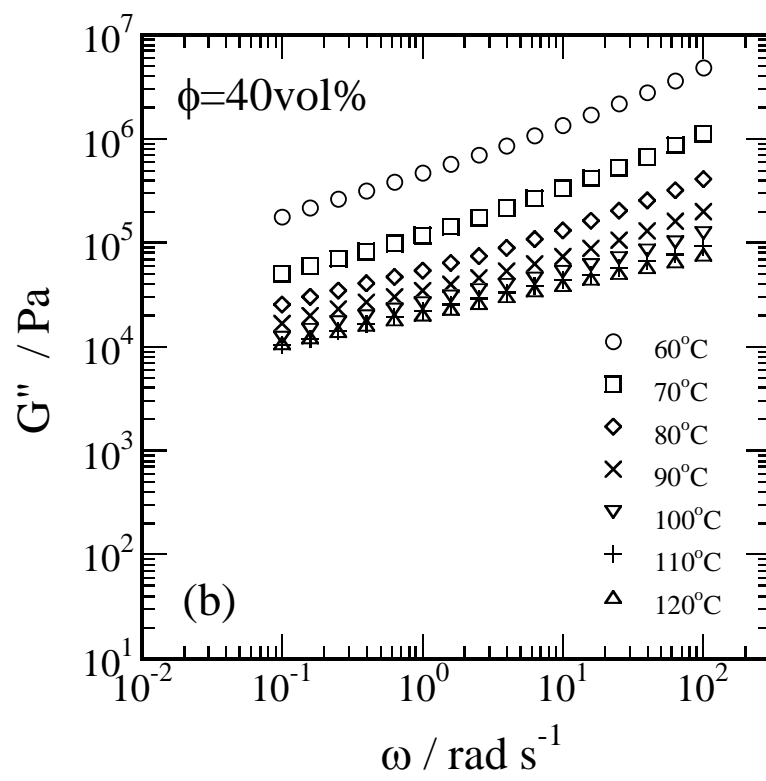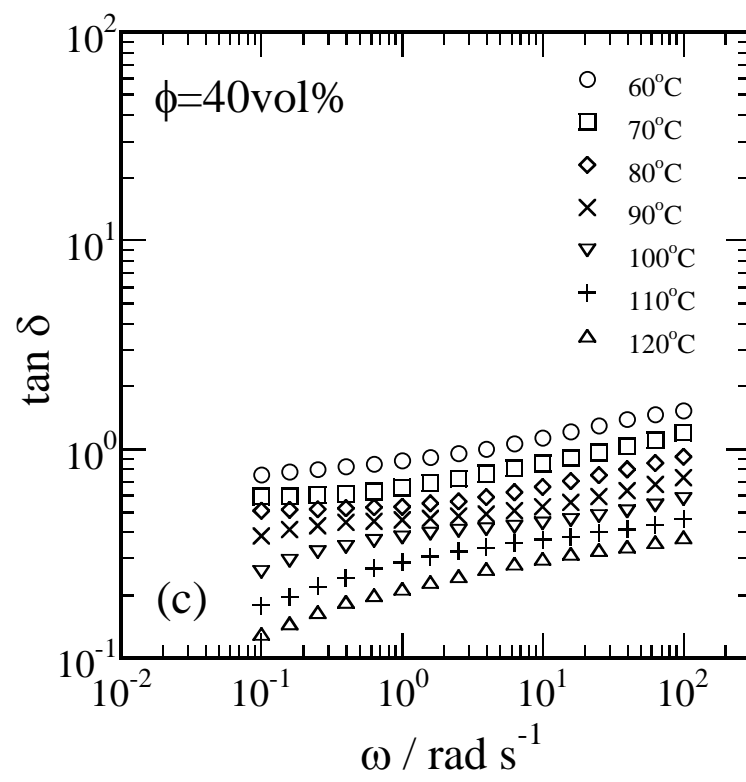Fig. 6   Phase diagram of the SiO_2/(AP/EP) suspensions
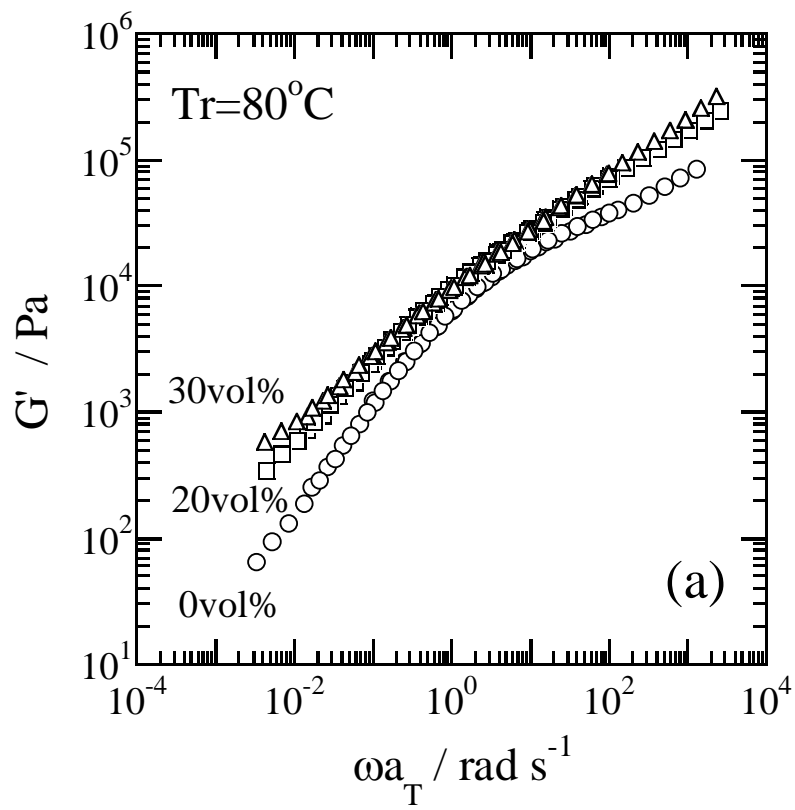
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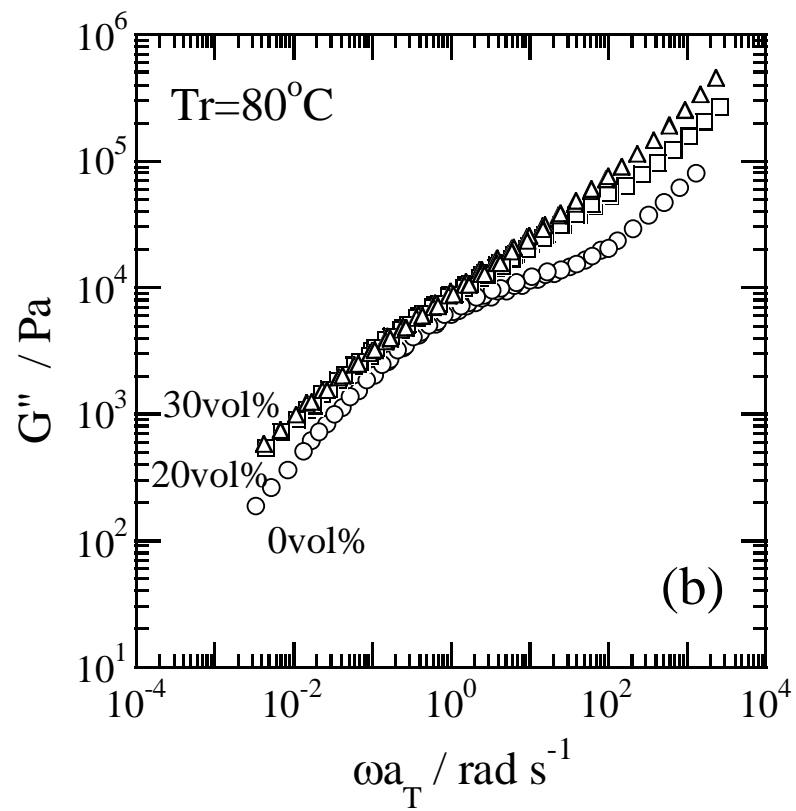
Fig. 1   (Uematsu, et al.)

Fig. 2 (Uematsu, et al.)

ϕ=35vol%

G' / Pa

10^7

10^6

10^5

10^4

10^3

10^2

10^1

○ 60°C ▽ 100°C
□ 70°C + 110°C
◇ 80°C △ 120°C
× 90°C

(a)

10^{-2} 10^{-1} 10^0 10^1 10^2

ω / rad s^{-1}
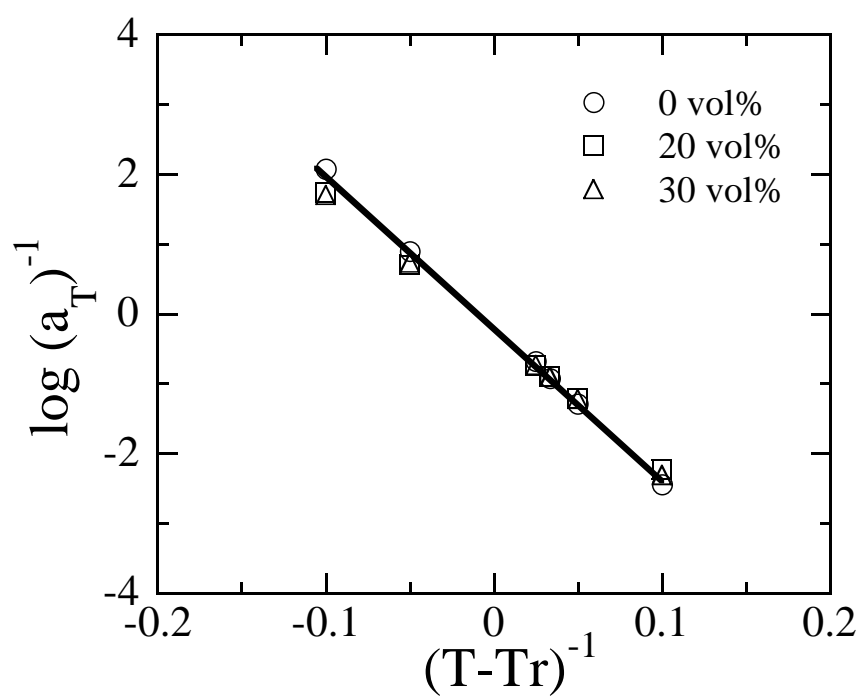
Fig. 3 (Uematsu, et al.)

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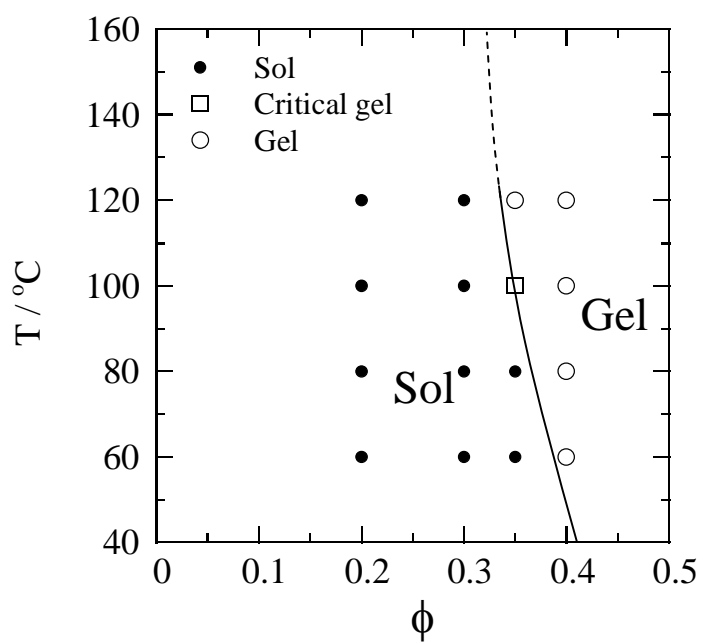
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