Rheology of SiO₂/(Acrylic Polymer/Epoxy) Suspensions. II. Nonlinear Stress Relaxation

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Rheology of SiO_2 /(Acrylic Polymer/Epoxy) Suspensions.

II. Nonlinear Stress Relaxation

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Abstract Large deformation, nonlinear stress relaxation modulus $G(t, \gamma)$ was examined for the SiO₂ suspensions in a blend of acrylic polymer (AP) and epoxy (EP) with various SiO₂ volume fractions (ϕ) at various temperatures (T). The AP/EP contained 70 vol% of EP. At $\phi \leq 30$ vol%, the SiO₂/(AP/EP) suspensions behaved as a viscoelastic liquid, and the time-strain separability, $G(t, \gamma) = G(t)h(\gamma)$, was applicable at long time. The $h(\gamma)$ of the suspensions was more strongly dependent on γ than that of the matrix (AP/EP). At $\phi = 35$ vol% and $T = 100^\circ\text{C}$, and $\phi \geq 40$ vol%, the time-strain separability was not applicable. The suspensions exhibited a critical gel behavior at $\phi = 35$ vol% and $T = 100^\circ\text{C}$ characterized with a power-law relationship between $G(t)$ and t ; $G(t) \propto t^{-n}$. The relaxation exponent n was estimated to be about 0.45, which was in good agreement with the result of linear dynamic viscoelasticity reported previously. $G(t, \gamma)$ also could be approximately expressed by the relation $G(t, \gamma) \propto t^{-n'}$ at $\phi = 40$ vol%. The exponent n' increased with increasing γ . This nonlinear stress relaxation behavior is attributable to strain-induced disruption of the network structure formed by the SiO₂ particles therein.

Keywords Nonlinear stress relaxation · Time-strain separability · Sol-gel transition · Critical gel point · Critical exponent · SiO₂ suspension

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. Low expansion coefficient is achieved by adding high volume fraction of SiO_2 . In a previous paper (Uematsu et al. 2009), we reported that the linear viscoelasticity of the (AP/EP) medium drastically changed by adding SiO_2 particles and the suspensions showed a sol-gel transition with increasing SiO_2 concentration.

Suspensions of weakly attracted particles exhibit the critical gel behavior at sufficiently high volume fraction, though strongly attractive particles form gel at low volume fraction. 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 like 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 gelatin to the interparticle attraction 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. They found that the suspensions exhibited sol-gel transition as increasing volume fraction ϕ of CB and the ϕ_{gel} at the gelation point decrease with increasing T (Aoki and Watanabe 2004; Aoki 2007).

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:

$$G'(\omega) = G''(\omega) / \tan \delta \propto \omega^n \quad (1)$$

$$\tan \delta = \tan (n\pi/2) \quad (2)$$

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. Using the relation each of $G'(\omega)$, $G''(\omega)$ and a relaxation modulus, $G(t)$ (Ferry 1980), $G(t)$ at the critical gel point can be expressed by Eq. (3).

$$G(t) = St^{-n} \quad (3)$$

S is called the strength of the network at gel point or the GP-strength.

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 or 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 . Despite these studies, the rheology of sol-gel transition of weakly attractive particles has not been fully elucidated. Especially, reports of rheological behavior under large deformation for the suspensions are very few.

In general, $G(t, \gamma)$ of entangled homopolymers can be expressed by

$$G(t, \gamma) = G(t)h(\gamma) \quad t > \tau_K \quad (4)$$

where $G(t)$ is the linear relaxation modulus, $h(\gamma)$ is the damping function and τ_K is the appropriate time for constricted chain to return to equilibrium length. $h(\gamma)$ is a universal function of γ for a entangled flexible polymer and expresses the degree of shrinkage for polymer chain (Doi and Edwards 1986). In homopolymers, time-strain separability is satisfied above τ_K (Osaki et al. 1982, Isaki et al. 2003). Large deformation shear relaxation modulus $G(t, \gamma)$ is one of the most important nonlinear viscoelastic quantities. For respective materials of our interest, we will examine the time-strain separability and the damping function of particle filled polymer melt/solution systems.

In the previous paper (Uematsu et al. 2009), we prepared a new suspension system consisting of SiO_2 particles in an acrylic polymer (AP)/epoxy (EP) medium, and reported the linear viscoelastic properties of SiO_2 /(AP/EP) suspensions at various particle volume fractions ϕ and temperatures T as described at the beginning. We found 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 %. At critical gel point, the critical relaxation exponent was found to be 0.45. The rheological behavior of sol-gel transition of weakly attractive particles is indicated in our suspension system. We have concluded that the optimal volume fraction is 35~40 vol% for the adhesive film for stacking IC chip from the result of linear viscoelasticity. It is also very important to investigate the nonlinear rheological behavior $\text{SiO}_2/(\text{AP}/\text{EP})$, because the adhesive film undergoes large strain at high strain rates in the actual processing.

From the academic point of view, it is very interesting to investigate nonlinear viscoelasticity of weakly attractive particle system. Pham et al. (2006, 2008) have reported nonlinear viscoelasticity for depletion gels, however, such studies are few compared with linear viscoelastic measurements. The investigation of nonlinear viscoelasticity using our suspension system ($\text{SiO}_2/(\text{AP}/\text{EP})$) is of great significance in industrially and academically.

In this paper, we focus on the effect of SiO_2 on larger deformation, nonlinear stress relaxation modulus $G(t, \gamma)$ and damping function $h(\gamma)$ of the $\text{SiO}_2/(\text{AP}/\text{EP})$ suspensions having various ϕ . Details of the nonlinear stress relaxation 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 for L-epo. The content of EP in (AP/EP) was 70 vol%. Volume fractions of SiO_2 particles were 0, 20, 30, 35 and 40 vol %. 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 were described previously (Uematsu et al. 2009).

Stress relaxation measurements

Step-shear stress relaxation measurements were carried out with a strain-controlled rheometer (ARES, TA Instruments) at several temperatures between 60 and 120 °C. A parallel-plate geometry with 8 mm diameter was used. The shear relaxation modulus $G(t, \gamma)$ was corrected with following the equation (Soskey and Winter 1984),

$$G(t, \gamma) = G_a(t, \gamma)(1 + d \ln G_a(t, \gamma) / 4d \ln \gamma) \quad (5)$$

where $G_a(t, \gamma)$ is a apparent stress relaxation modulus measured with parallel plate. Applicability of this correction has already been demonstrated by former experiments (Yoshikawa et al. 1990a, b). Since the yield behavior was not shown in our suspensions, $G(t, \gamma)$ of suspension was corrected using eq 5. The time needed to impose the step strain was less than 0.1s. The stress relaxation behavior was measured until about 100s,

because the experimental error became larger. The shear strain ranged from 0.01 to 8.0. All of the measurements were performed under nitrogen atmosphere.

Results and discussion

$G(t, \gamma)$ at the sol state ($\phi \leq 30$ vol %)

For the $\text{SiO}_2/(\text{AP/EP})$ suspensions with various particle concentrations, $\phi = 0$ and 20 vol %, Figs. 1a,b show the nonlinear relaxation modulus $G(t, \gamma)$ at 80 °C, and Figs. 2a,b show $G(t, \gamma)$ of suspensions having $\phi=0$ and 30 vol% of SiO_2 at 100°C. To confirm the linearity for small γ , we also present the linear relaxation modulus $G(t)$ calculated from the G' and G'' data (see in inset in Fig.1 (a)) reported in our previous paper (Uematsu et al. 2009). The solid curves represent this $G(t)$ obtained with the method of Schwarzl (1975).

$$G(t) = [G'(\omega) - 0.56G''(0.5\omega) + 0.200G''(\omega)]_{\omega=1/t} \quad (6)$$

Eq.6 is an approximate formula of $G(t)$ obtained from the dynamic viscoelastic modulus G' and G'' . For the medium $\phi = 0$ vol% (Figs. 1a and 2a), the $G(t, \gamma)$ curves for $\gamma < 0.5$ are very close to each other and agree with the linear $G(t)$ curve. This $G(t, \gamma)$ decreases with increasing $\gamma > 0.5$, and the nonlinearity prevails. For the $\text{SiO}_2/(\text{AP/EP})$ suspension having $\phi = 20$ vol%, the $G(t, \gamma)$ curves for $\gamma < 0.3$ are very close to linear $G(t)$ curve and deviate from linear $G(t)$ above $\gamma > 0.3$. For the suspension having $\phi = 30$ vol%, the linear region is limited $\gamma < 0.1$. From the result of dynamic strain sweep test, we found

that linear region for 20 and 30 vol% suspension is limited $\gamma \leq 0.2$ and $\gamma \leq 0.1$, respectively. Therefore, it is confirmed that the linear region in stress relaxation behavior for suspensions agreed with those dynamic strain sweep test.

It is known that for strongly flocculated systems in the medium having a poor affinity the linear region becomes tremendously narrows than that of homogeneous polymer systems. It is reported that the linear strain region is smaller than 0.01 (Onogi and Matsumoto 1981; Amari and Watanabe 1983; Aoki et al. 2003). This strong nonlinearity is caused by deformation/flow of the network-type agglomerate of the particles. As compared with these reports, the linear strain regions in our suspension system are more extensive. From the report of Aoki et al. (2003) for weakly flocculated and well dispersed system, it is confirmed that the linear region for their suspensions quantitatively agree with our results. Therefore, it is suggested that the SiO_2 particles in the (AP/EP) medium are comparatively dispersed. More importantly, these $G(t, \gamma)$ of the suspension exhibit damping in a manner similar to matrix AP/EP. For these $G(t, \gamma)$ data, validity of the time-strain separability is examined below.

In Fig. 3 and 4, the $G(t, \gamma)$ curves for $\phi = 0\sim 30$ vol% at 80°C and 100°C , respectively, are shifted vertically (in the double-logarithmic scales) to be superposed on respective reference curves obtained for the smallest γ . As seen in Fig. 3a and 4a, the reference curve is in good agreement with the linear $G(t)$ curves at $t \geq \tau_k$. In other words, time-strain separability for matrix (AP/EP) is valid. We tried the time-strain separability for suspensions. If τ_k is chosen as $12.5 \pm 2.5\text{s}$ and $5.5 \pm 1.5\text{s}$ at 80°C and 100°C in the suspension system, respectively, time-strain separability is approximately satisfied as shown in Figs. 3b and 4b.

$G(t, \gamma)$ at the sol state ($\phi=35$ vol% at $T<100^\circ\text{C}$)

In Figure.5, the solid line represents the linear relaxation modulus $G(t)$ calculated from the G' and G'' data (see in inset in Fig.5). As seen in Fig.5, the $G(t, \gamma)$ curves for $\gamma \leq 0.05$ agree with the linear $G(t)$ curve. This $G(t, \gamma)$ decreases with increasing $\gamma (> 0.05)$, and the nonlinearity prevails. We evaluated $h(\gamma)$ from the data using Eq.4. We applied time-strain separability for the suspension. It is confirmed that time-strain separability is approximately satisfied above $12.5 \pm 2.5\text{s}$.

Our interest in this paper is placed on the nonlinear damping behavior of the suspension systems. In this paper, we evaluate the damping function for these samples as

$$h(\gamma) = G(t, \gamma) / G(t) \quad (t > \tau_k) \quad (7)$$

As seen in Figs. 3 and 4, $G(t, \gamma)$ curves for suspensions could be superposed above τ_k within the range of the experimental error. When time-strain separability for suspensions is assumed to be approvable, damping function $h(\gamma)$ could be summarized as follows. Figure 6 illustrates the damping function $h(\gamma)$ of the AP/EP and the suspensions. $h(\gamma)$ data for the AP/EP monotonically decrease with increasing of strain. On the other hand, strain dependency of $h(\gamma)$ becomes stronger with increasing SiO_2 .

Aoki et al. have reported that strong damping was related to filler effect (Aoki et al. 2001). For well-dispersed particle system, they discussed the strong damping in terms of local strain γ_{local} and external strain γ_{Ex} . To examine this expectation, we evaluated γ_{local} for the case of the simplest filler effect (Guth and Cold 1938),

$$\gamma_{local} = [1 + 2.5\phi + 14.1\phi^2] \gamma_{Ex} \quad (8)$$

where γ_{Ex} is the externally applied (nominal) strain, and ϕ is the volume fraction of the SiO_2 particles. Eq. 8 was derived from taking into account the mutual disturbance caused by a pair of particles of laminar stream for high concentration of suspensions by Guth and Gold (1938). In Fig.7, the $h(\gamma)$ data of the suspensions are plotted against γ_{local} thus evaluated. The plots for various ϕ approximately agree with each other and coincide with that of AP/EP.

$G(t, \gamma)$ at the critical gel state ($\phi = 35 \text{ vol } \%, T=100^\circ\text{C}$)

Figure 8 shows the nonlinear relaxation modulus $G(t, \gamma)$ of the $\text{SiO}_2/(\text{EP}/\text{AP})$ suspensions having $\phi = 35 \text{ vol } \%$ at 100°C . As seen in Fig.8, $G(t, \gamma)$ of suspension agree with the linear relaxation modulus $G(t)$ calculated from the G' and G'' data (see in inset in Fig.5) at $\gamma \leq 0.05$. This $G(t, \gamma)$ decreases with increasing $\gamma (> 0.05)$, and the nonlinearity prevails. We should note that it was impossible to evaluate $h(\gamma)$ because time-strain separability could not be applicable for the suspensions anymore. A decrease of the linear strain region and failure of time-strain separability is discussed below.

In general, it is known that the relaxation modulus $G(t)$ at the gel point is expressed by a power law (Eq. 3). Especially, the magnitude of n agrees with the critical gel exponent n at critical gel temperature. We found that the gradient of $G(t)$ is 0.45 in Fig. 8. It is suggested that critical gel behavior is exhibited in Fig. 8 because the

slope of $G(t)$ in the double-logarithmic scales agrees with the critical gel exponent ($n=0.45$) calculated from linear viscoelasticity at 35 vol% (Uematsu et al. 2009).

$G(t, \gamma)$ at the gel state ($\phi = 35$ vol% at $T > 100^\circ\text{C}$, $\phi = 40$ vol%)

Figure 9 shows the nonlinear stress relaxation modulus $G(t, \gamma)$ of the $\text{SiO}_2/(\text{AP}/\text{EP})$ suspension having $\phi = 35$ vol% at 120°C (a) and 40 vol% at 80°C (b) and 100°C (c) plotted against t at various γ . The linear relaxation modulus $G(t)$ calculated from the G' and G'' data (see in inset in Fig.5 and 9 (b)) are plotted as solid line in Fig.9. As well as the result of 35 vol% suspension at 100°C , the $G(t, \gamma)$ curves decrease with increasing γ (>0.01), and the nonlinearity prevails. It is also impossible to satisfy the time-strain separability for nonlinear $G(t, \gamma)$ data and strong damping is confirmed as compared with low SiO_2 suspensions in Fig. 6.

As seen in Fig. 8 and 9, the nonlinear relaxation modulus $G(t, \gamma)$ is expressed by power law in the critical gel states and gel state in spite of nonlinear region. We focus on these interesting results. Gel stiffness (S) and power law index (n') for $\phi = 35$ and 40 vol% are plotted as a function of γ using the data of 100°C in Figure 10a, b, respectively. In Fig.10a, both of S for suspensions decreases with increasing γ . This result means the fractal network structure is broken with increasing of strain. So, the time-strain separability is not satisfied due to changing of network structure in each strain. It is also confirmed that the magnitude of S for the 40 vol% suspension is larger than that of 35 vol% suspension. The slope of S for 40vol% suspension is almost the same as

compared with that of 35 vol% suspension. This result means that the fragility of the gel structure for 35 and 40 vol% suspensions is almost the same. As seen in Fig. 10b, n' of suspensions increases with increasing γ . The value of n' of 35 vol% suspension is mostly comparable with the 40 vol% suspensions. This fact suggests that the fractal network structure hardly depends on volume fraction of SiO_2 in our case. This figure also shows that the structure for suspensions is assumed a fractal network structure despite of broken for network structure. If the structure of the suspension having $\phi = 35$ or 40 vol% could be observed dynamically with light scattering method, the relationship between the gel strength (S) and fractal dimension (n') might be clarified. It is future work for us to quantify the relationship between fractal network and rheological behavior.

Conclusion

We measured the nonlinear stress relaxation modulus of $\text{SiO}_2/(\text{AP/EP})$ suspensions with various SiO_2 volume fractions (ϕ) at various temperatures (T), and investigated the effects of the SiO_2 particles on the time-strain separability and damping function $h(\gamma)$. At $\phi \leq 30$ vol%, the time-strain separability for nonlinear relaxation modulus $G(t, \gamma)$ was satisfied in the suspension systems and the characteristic time τ_k , which is the appropriate time for constricted chain to return to equilibrium length, was hardly influenced on SiO_2 particles. These $h(\gamma)$ of the suspensions were more strongly dependent on γ than that of the matrix AP/EP. This result quite possibly reflects the filler effect in these suspensions. In contrast, the time-strain separability was not applied at $\phi = 35$ vol%, $T=100^\circ\text{C}$. The slope of linear $G(t)$ in the double-logarithmic scales agrees with the critical gel exponent n calculated from the result of linear viscoelasticity. It was also found that the time-strain separability was not satisfied at $\phi=35$ vol% at $T>100^\circ\text{C}$ and $\phi=40$ vol%. The important result is that the nonlinear relaxation modulus $G(t, \gamma)$ is expressed by power law in the critical gel and gel state in nonlinear γ region; $G(t, \gamma) = St^{-n'}$, where S is stiffness of gel network and n' is power law index. This nonlinear stress relaxation behavior is attributable to strain-induced disruption of the network structure of the SiO_2 particles therein.

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Figure Captions

Fig. 1 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 0$ vol % (a) and 20 vol% (b), respectively, at 80°C . The Solid curves indicate the linear relaxation modulus calculated from the G' and G'' data. In (a), the inset shows the result of linear viscoelasticity for suspension having $\phi \leq 30$ vol % reduced at 80°C (Uematsu et al. 2010)

Fig. 2 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 0$ vol % (a) and 30vol % (b), respectively, at 100°C . The Solid curves indicate the linear relaxation modulus calculated from the G' and G'' data.

Fig. 3 Plots of $G(t, \gamma)/h(\gamma)$ against time for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 0$ vol % (a) and 20 vol% (b), respectively, at 80°C .

Fig. 4 Plots of $G(t, \gamma)/h(\gamma)$ against time for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 0$ vol % (a) and 30vol % (b), respectively, at 100°C .

Fig. 5 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 35$ vol % at 80°C . The Solid curves indicate the linear relaxation modulus calculated from the G' and G'' data. The inset shows the result of linear viscoelasticity for suspension having $\phi = 35$ vol % (Uematsu et al. 2010)

Fig. 6 Damping function $h(\gamma)$ of $\text{SiO}_2/(\text{AP/EP})$ suspensions having different SiO_2 volume fraction.

Fig. 7 Plot of $h(\gamma)$ of $\text{SiO}_2/(\text{AP/EP})$ suspensions with various SiO_2 volume fraction against local strain γ_{local} .

Fig. 8 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 35$ vol % at 100°C . The Solid curves indicate the linear relaxation modulus calculated from the G' and G'' data.

Fig. 9 Stress relaxation modulus $G(t, \gamma)$ at various strain γ obtained for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 35$ vol% at 120°C (a), $\phi = 40$ vol% at 80°C (b) and 100°C (c), respectively. The Solid curves indicate the linear relaxation modulus calculated from the G' and G'' data. In (b), the inset shows the result of linear viscoelasticity for suspension having $\phi = 40$ vol % (Uematsu et al. 2010)

Fig. 10 Plot of the gel stiffness S (a) and power law index n' (b) against strain γ at 100°C for $\text{SiO}_2/(\text{AP/EP})$ suspensions having $\phi = 35$ and 40 vol%.

Inset shows the phase diagram of the $\text{SiO}_2/(\text{AP/EP})$ suspensions.

(a)

Fig. 1 (Uematsu, et al.)

(b)

Fig. 1 (Uematsu, et al.)

(a)

Fig. 2 (Uematsu, et al.)

(b)

Fig. 2 (Uematsu, et al.)

(a)

Fig. 3 (Uematsu, et al.)

(b)

Fig. 3 (Uematsu, et al.)

(a)

Fig. 4 (Uematsu, et al.)

(b)

Fig. 4 (Uematsu, et al.)

Fig. 5 (Uematsu, et al.)

Fig. 6 (Uematsu, et al.)

Fig. 7 (Uematsu, et al.)

Fig. 8 (Uematsu, et al.)

(a)

Fig. 9 (Uematsu, et al.)

(b)

Fig. 9 (Uematsu, et al.)

(c)

Fig. 9 (Uematsu, et al.)

(a)

Fig. 10 (Uematsu, et al.)

(b)

Fig. 10 (Uematsu, et al.)