Properties of Epoxy Molding Compound According to the Pretreatment Method of an Amino-Silane Coupling Agent on Epoxy or Phenol Resin

Jung-Hyun Lee, Hyo-Chang Yoon

Central Research Institute, KCC Corporation, 85, Mabook-ri, Kuseong-up, Yongin, Kyunggi, 449-910, Korea

Received 22 December 2004; accepted 22 August 2005
DOI 10.1002/app.23615
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An amino-functional silane coupling agent, which is an important component for epoxy molding compound (EMC), has been used by diverse methods, such as integral addition into a mixed powder and pretreatment on silica or on resin. However, the homogeneous dispersion of the amino-functional silane coupling agent in mixed powder is limited with integral addition, and the possibility of white gel formation, sometimes causing gate blocking during the transfer-molding process, due to the aggregation of silica with the coupling agent cannot be completely removed by it. The pretreatment of the amino-functional silane coupling agent on silica has been adopted as an alternative process, but the process is expensive and limited in mass production. Although the pretreatment of the coupling agent on resin as another method has also been used by some EMC manufacturing companies, it has hardly been known in which resin phase, the epoxy or hardener, the silane coupling agent should be pretreated for better mechanical properties of EMC. In this study, the pretreatment of the amino-functional silane coupling agent on epoxy or phenol resin, essential components of EMC, has been investigated with respect to the reaction during the pretreatment and the properties of EMC according to the different pretreatment methods. In the case of the pretreatment on epoxy, the amino-functional silane coupling agent rapidly forms an adduct with epoxy via a ring-opening reaction, whereas its alkoxy groups are well preserved. The glass-transition temperature and flexural strength of the EMC by the application of the pretreatment method on epoxy are lower than those by the pretreatment on phenol. It is thought that the degree of linkage between the resin matrix and silica becomes lower because of the confinement of aminopropyltriethoxy silane (APTS) within the epoxy matrix through an irreversible reaction with epoxy in advance. In the case of the pretreatment on phenol, most of the alkoxy groups in the coupling agent are assumed to be replaced with protonic nucleophiles such as phenol, generating an equivalent amount of alcohol. Because the adduct between the phenol and amino-functional silane coupling agent can be easily regenerated during the manufacturing process, it is thought that the pretreatment method of APTS on phenol helps APTS disperse well within EMC. Actually, the glass-transition temperature and flexural strength of EMC by the application of the pretreatment method on phenol are higher than those by the integral addition method and the pretreatment on epoxy. However, they become lower as the degree of reaction of silane with phenol increases. The pretreatment of the amino-functional silane coupling agent on phenol shows lots of advantages over the previous methods. From the viewpoint of the process, the homogeneous dispersion of the coupling agent can be obtained with consistency, and the possibility of white gel formation can also be completely removed by it. From the perspective of properties, through a controlled pretreatment on phenol resin, better mechanical properties of EMC can be obtained than those through the pretreatment on epoxy. In addition, the pretreatment process on phenol is simple and feasible for mass production. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2171–2179, 2006

Key words: composites; mechanical properties; resins

INTRODUCTION

An epoxy molding compound (EMC), a typical organic and inorganic hybrid composite, is widely used in the field of encapsulating semiconductors for protecting and electrically insulating semiconductor chips from their surroundings and effectively ejecting heat during operation because of its low cost and effective mass production.[1–4]

Recently, for the demanding Pb-free soldering process, package reliability related to moisture absorption via EMC has become a critical issue.[5–9] Hence, many efforts to modify EMC to enhance package reliability not only in formulation aspects, such as increasing the filler loading,[10] introducing a new resin system,[11–15] and modifying the silica surface,[16–19] but also in process modification have constantly been carried out. Among those efforts, a silane coupling agent as an important component of EMC has intensely been studied to establish strong adhesion between the resin and silica.[20–22] The pretreatment of the coupling agent on silica has long been used for that purpose,[17–19] but the process has

Correspondence to: J. H. Lee (leejhy@kccworld.co.kr).

Journal of Applied Polymer Science, Vol. 100, 2171–2179 (2006)
© 2006 Wiley Periodicals, Inc.

TABLE I
Structures of the Raw Materials

Component	Chemical structure/name	Grade name (maker)
Epoxy	$-(CH_2-C_6H_4-C_6H_4-CH_2-C_6H_3(OCH_2-CH(O)CH_2))_n-$ (OCH$_2$—CH—CH$_2$ with O bridging the epoxide)	NC-3000 (Nippon Kayaku Co.)
Hardener	$-(CH_2-C_6H_4-CH_2-C_6H_3(OH))_n-$	MEH-7800-4S (Meiwa Kasei Co.)
Coupling agent	$(CH_3O)_3SiC_3H_6OCH_2CH—CH_2$ (with O bridging CH—CH$_2$)	KBM-403 (Shinetsu Chemical Co.)
	(C2H5O)$_3$SiC$_3$H$_6$-NH$_2$	KBE-903 (Shinetsu Chemical Co.)
Filler	Fused and spherical silica	FB-24R (Denki Kagaku Co.)
Accelerator	Phosphonium salt	TPP-K (Hokko Chemical Co.)

a limitation due to its high cost and process complexity in application to mass production. Instead of the treatment of the coupling agent on the silica, integral addition into a mixed powder with a spray facility has also been widely applied.[23] However, the homogeneous dispersion of the silane coupling agent over the mixed powder is hardly obtained because of the small dose of the silane coupling agent. Moreover, in the mass production of EMC, integral addition increases the possibility of generating a white gel, an aggregation of silica with the silane, which causes gate blocking during transfer molding. Therefore, as another economical approach not only reducing the generation of white gel but also enhancing the linkage between the resin and silica, the pretreatment method of the silane coupling agent on resin has been adopted by some EMC manufacturing companies. Nevertheless, it is hardly known in which resin phase, the epoxy or hardener, the silane coupling agent should be pretreated for better mechanical properties of EMC.

In this study, the pretreatment of the silane coupling agent on an organic resin was carried out not only to effectively disperse the silane coupling agent within the organic resin by the control of the degree of reaction but also to prevent white gel formation due to the aggregation of silica with the silane coupling agent. Epoxy and phenol as base resins and an amino-functional silane coupling agent were selected, and the reaction mechanism was examined with H-NMR spectroscopy. Furthermore, the effects of the pretreatment of the silane coupling agent on the organic resin were investigated in comparison with previous methods, such as integral addition and treatment on silica.

TABLE II
Design of the Experiments for the Pretreatment of the Amino-Functional Silane Coupling Agent

Treated phase	Reaction time (min)	Vacuum during the reaction	Notation (phase, vaccum time)
Epoxy resin	15	X	EX-15
	300	X	EX-300
	15	O	EO-15
	300	O	EO-300
Phenol resin	30	X	PX-30
	600	X	PX-600
	30	O	PO-30
	600	O	PO-600
Silica/epoxy resin	Silica (1.0[a])[b] + EX-15 (2.4[a])[c]		SE-15
Silica/phenol resin	Silica (1.0[a])[b] + PX-30 (2.4[a])[d]		SP-30

[a] Presented in parts by weight based on 100 parts of the epoxy resin.
[b] Denotes the amount of the amino-silane coupling agent treated in silica.
[c] Denotes the amount of the amino-silane coupling agent treated in epoxy resin.
[d] Denotes the amount of the amino-silane coupling agent treated in phenol resin.

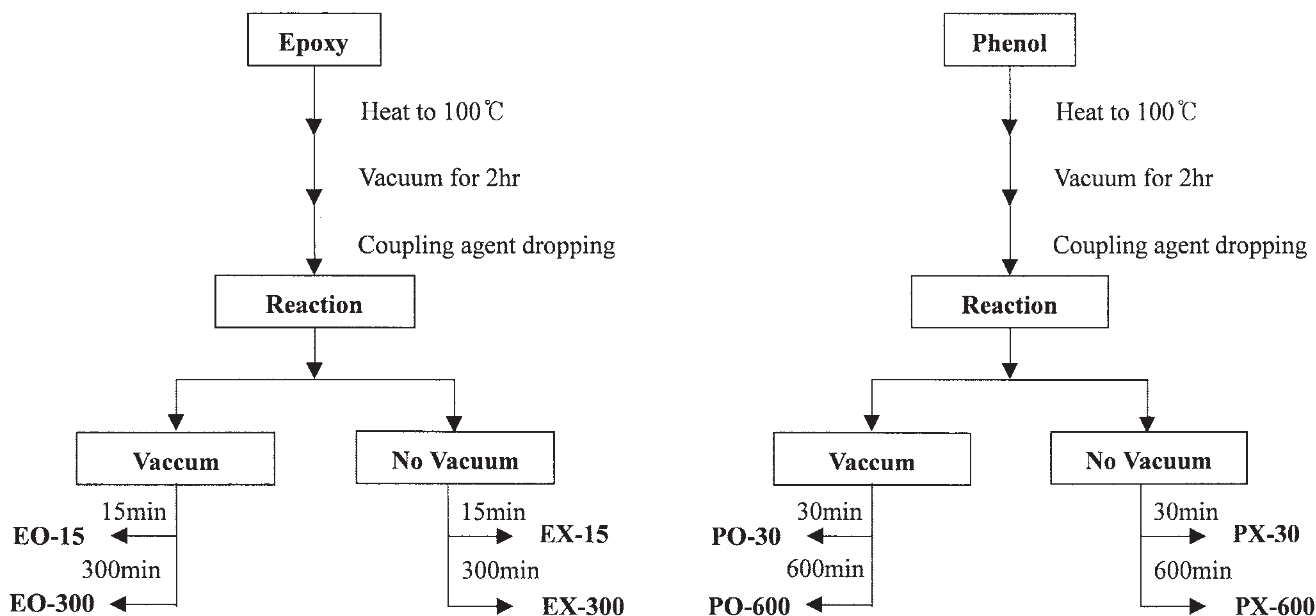

Figure 1 Design of the experiments for the pretreatment of the amino silane coupling agent.

EXPERIMENTAL

Materials

The epoxy resin used in this study was a biphenyl-type epoxy [epoxy equivalent weight (EEW) = 260–280 g/equiv] obtained from Nippon Kayaku Co., and the phenol resin used as a hardener was an aralkyl-type phenol (hydroxyl equivalent weight = 175–180 g/equiv) obtained from Meiwa Kasei Co. The filler, fused and spherical silica (mean diameter = 12 μm, specific surface = 4.6 m^2/g), was produced by Denki Kagaku Co. Phosphonium salt made by Hokko Chemical Industry Co. was used without purification as an accelerator. γ-Glycidoxypropyltrimethoxy silane (GPTS; KBM403) and γ-aminopropyltriethoxy silane (APTS; KBE903) made by Shinetsu Chemical Co. were used without purification. The detailed structures and properties of the raw materials are summarized in Table I.

Pretreatment methods of the silane coupling agent (APTS)

The pretreatment of APTS on epoxy or phenol was carried out with the following procedure. Epoxy or phenol was melted via heating at 100°C with N_2 purging, and then a vacuum (<30 Torr for 2 h) was applied to remove moisture. APTS (5 wt % per epoxy or phenol resin) was dropped for 1 min with vigorous stirring and N_2 purging. After the coupling agent was dropped, a vacuum (<30 Torr for 0.5 h) was selectively applied to investigate the effect of removing the volatile substance as a product by the reaction. Reacted intermediates were sampled at a constant time interval and analyzed with a cone-and-plate viscometer, EEW, and H-NMR spectroscopy. In addition, the trapped substance at the condenser during the vacuum process was analyzed with H-NMR spectroscopy to verify the reaction mechanism.

The pretreatment of APTS on silica was performed with the following procedure. Under room temperature, fused silica was inserted into a ball-mill mixer, and 0.1 wt % APTS per silica was sprayed on the silica. Ball milling for 10 min at 10 rpm was carried out with N_2 purging for removing the volatile substance. The detailed design of the experiments is described in Table II and Figure 1.

TABLE III
Basic Formulation of the EMC

Component	Grade name	Parts by weight
Epoxy resin	NC-3000	100
Phenol resin	MEH-7800-4S	76.8
Filler	FB-24R	1153
Accelerator	TPP-K	4.2
Coupling agent	KBM-403	3.4
	KBE-903	3.4 (variable according to the treatment)
Releasing agent	Carnauba wax	2.7

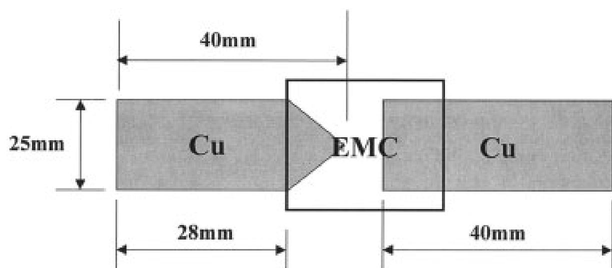

Figure 2 Dimensions of the test specimen for the adhesion strength.

EMC sample preparation

All the ingredients, including the epoxy, phenol, silica (no silica for the neat resin system), and additives such as the releasing agent, flame retardant, colorant, and epoxy-functional silane coupling agent, except for the amino-functional silane coupling agent (APTS), were premixed in a Henshel mixer for 5 min. APTS was introduced into the Henshel mixer in four different ways: integral addition, pretreatment on epoxy, pretreatment on phenol, and pretreatment on silica. The mixed powder was melt-mixed in twin-screw kneader at 115–120°C, cooled and crushed into a powder, and molded into a test specimen. The detailed formulation in this study is described in Table III.

Measurement

Adhesion strength on a Cu plate

The adhesion strength between the EMC and Cu plate was examined in the 180° pulling-out mode, as shown in Figure 2. Coupled with the pentagon and rectangle types of Cu plates, the specimens (thickness = 0.5 mm) were molded by EMC at 175°C for 90 s and then heated in an oven at 175°C for 6 h. The adhesion strength was measured at a test speed of 2.8 mm/min and at 260°C with a universal test machine (Shimazu Co.)

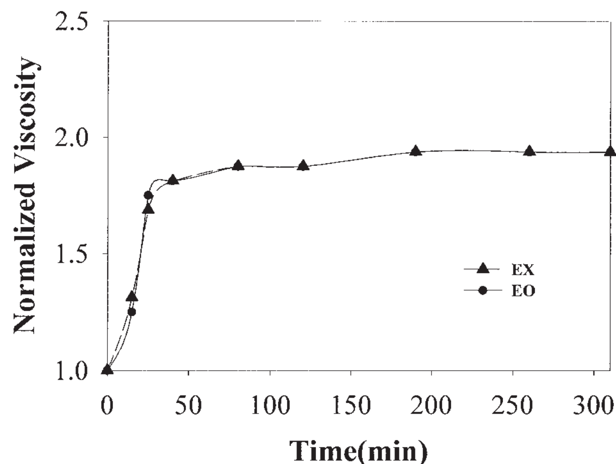

Figure 4 Viscosity change of APTS with epoxy as a function of the reaction time.

Flexural strength

The specimens ($6.4 \times 12.7 \times 127$ mm^3) were molded at 175°C for 90 s and heated in an oven at 175°C for 6 h. The flexural strength was measured in the three-point-bending mode with a span width of 100 mm and a test speed of 2.8 mm/min at 260°C with a universal test machine (Shimazu) in accordance with ASTM D 790.

Glass-transition temperature (T_g)

The specimens ($3 \times 40 \times 10$ mm^3) were molded at 175°C for 90 s and heated in an oven at 175°C for 6 h. Then, T_g was estimated from the peak point temperature of tan δ with a dynamic mechanical temperature analyzer (Rheometric Scientific) under a resonance

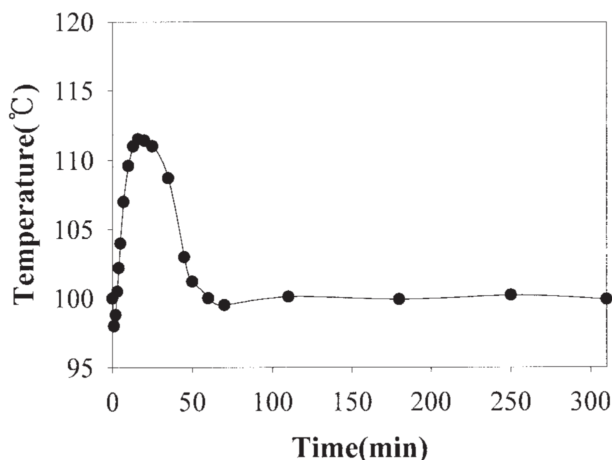

Figure 3 Reaction temperature of APTS with epoxy as a function of the reaction time.

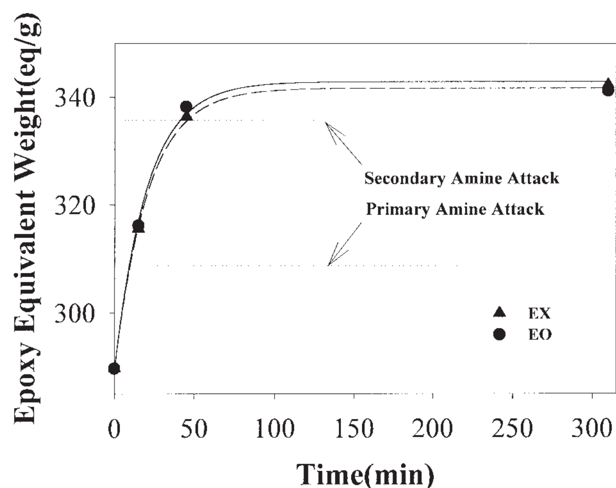

Figure 5 EEW of reacted intermediates between APTS and epoxy as a function of the reaction time.

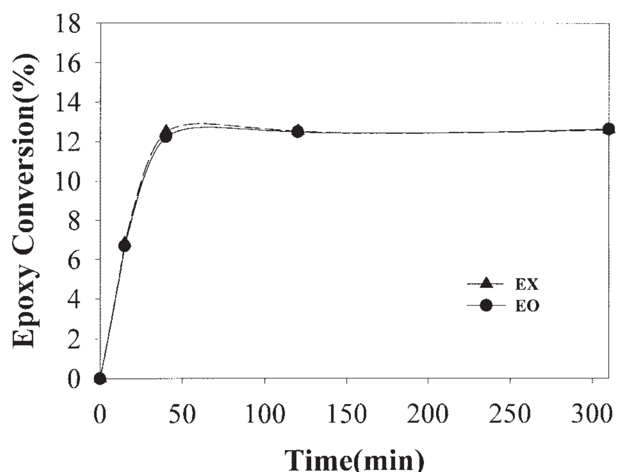

Figure 6 Conversion of epoxy groups in the reaction of APTS with epoxy as a function of the reaction time.

frequency of 1 Hz with the temperature increasing at 5°C/min. The range was room temperature to 250°C.

RESULTS AND DISCUSSION

Reaction mechanism in the pretreatment of the silane coupling (APTS) agent on epoxy

The reaction temperature and viscosity change were monitored as a function of the reaction time after APTS was dropped into melted epoxy and are shown in Figures 3 and 4, respectively.

The reaction temperature rapidly increased upon the dropping of APTS from 98 to 112°C within 20 min and then returned to the initial value of 100°C after 1 h. This implies that the reaction rate of APTS with epoxy is quite fast with an exothermic nature, which is typically observed in the reaction of amine with epoxy.

The viscosity of the reacted intermediates rapidly increased to twice the initial value within 30 min and then reached a steady state within 60 min. The tendency of the viscosity, as shown in Figure 4, can be understood as the increasing molecular weight of the reacted intermediates by the addition of APTS to epoxy. The viscosity of intermediates was not affected by the vacuum process reaction.

EEW of the reacted intermediates was measured by a titration method and is shown in Figure 5. EEW increased with the reaction time from 290 to 340 eq/g, and then no further increment was observed. The final EEW, 340 eq/g, implies that the secondary amine in the adduct of the epoxy with the primary amine of APTS sequentially attacked the epoxy into the new epoxy adduct; otherwise, the final EEW had to be 305 eq/g. In addition, no quaternary ammonium salt formed.

To investigate the reaction mechanism of APTS with epoxy, the number of epoxy groups in epoxy resin and ethoxy groups in APTS of the intermediate was monitored and analyzed with H-NMR spectroscopy. H-NMR peaks at $\delta = 2.9$ ppm and $\delta = 1.2$ ppm were selected for the quantitative analysis of epoxy and ethoxy, respectively, and are shown in Figure 6. In this study, the diminution of the ethoxy groups of the intermediate nearly did not occur, and ethanol, which was produced by the cleavage of ethoxy groups, was nearly not trapped during the vacuum process with the reaction, as shown in Table IV. However, the epoxy conversion rapidly increased up to 12%, and then no further increment was observed. The theoretical epoxy conversion was calculated to be 6% when the primary amine in APTS reacted with epoxy and 12.5% when the secondary amine in the adduct of epoxy and APTS reacted with new epoxy. This implies that the amine in APTS reacts with two epoxy groups and forms a 1:2 adduct with epoxy; this coincides quite well with the EEW results. Consequently, the reaction mechanism of the amine in APTS with epoxy follows the generally known reaction of amine with epoxy.[24] The epoxy conversion was not affected by the vacuum process with the reaction, and its trend was almost consistent with that of the viscosity. This means that the reaction of the epoxy group with amine thoroughly determines the viscosity of the intermediate.

Reaction mechanism in the pretreatment of the silane coupling (APTS) agent on phenol

The reaction of APTS with phenol was investigated and compared with that of APTS with epoxy. The viscosity change and reaction temperature as func-

TABLE IV
Analysis of the Trapped Substance in the Reaction of APTS with Epoxy During the Vacuum Process

Process	Substance	Trapped substance (g)[a]		Conversion (%)
		Empirical	Theoretical	
Before dropping APTS	H_2O	0.16	—	—
After dropping APTS	Ethanol	0.01	3.12[b]	0.16[c]

[a] Denotes the quantity of the substance trapped per 100 g of the epoxy resin mixture of 5 wt % APTS.
[b] Denotes the maximum quantity of ethanol produced by ethoxy cleavage in APTS. It was equal to the moles of APTS in 100 g of the epoxy resin mixture of 5 wt % APTS $\times$ 3 $\times$ the molecular weight of ethanol.
[c] Denotes the value calculated from the ratio of the empirical value to the theoretical value.

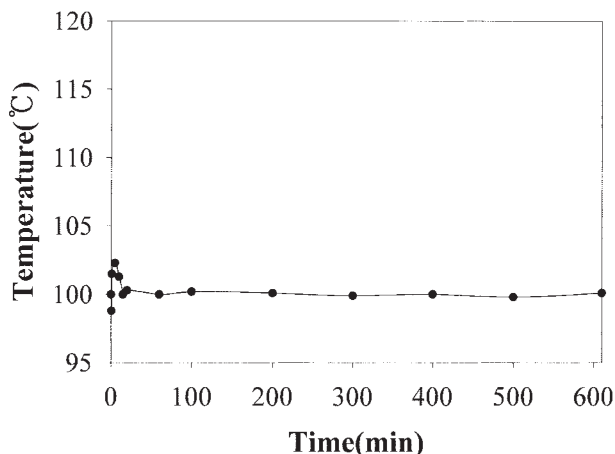

Figure 7 Reaction temperature of APTS with phenol as a function of the reaction time.

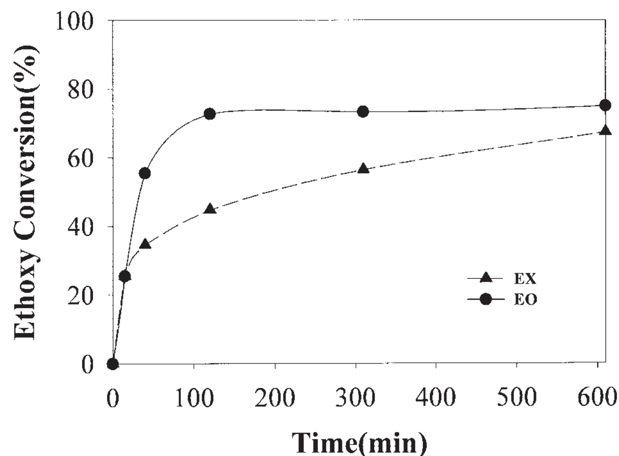

Figure 9 Conversion of ethoxy groups in the reaction of APTS with phenol as a function of the reaction time.

tions of the reaction time were monitored and are shown in Figures 7 and 8, respectively.

The temperature of the reaction increased almost instantaneously upon the dropping of APTS into phenol, with an accompanying color change from red to yellow, and then quickly leveled off. An instantaneous temperature change with the accompanying color change was assumed to be due to the neutralization reaction of amine in APTS with phenol.

The viscosity of the reacted intermediates slowly increased, and the rate of the viscosity increment was considerably accelerated by the vacuum process after the dropping of APTS because of the removal of the volatile substance made during the reaction of APTS with phenol.

H-NMR spectroscopy was used to investigate the reaction mechanism of APTS with phenol and is shown in Figure 9 and Table V. The conversion of the ethoxy groups in APTS increased up to roughly 75%, and the rate of conversion was quite accelerated by the vacuum process after the dropping of APTS. According to the analysis of the trapped substance with H-NMR, the trapped substance was identified as ethanol, and the amount of ethanol showed an empirical ethoxy conversion value of approximately 75%, which coincided well with the results from H-NMR spectroscopy.

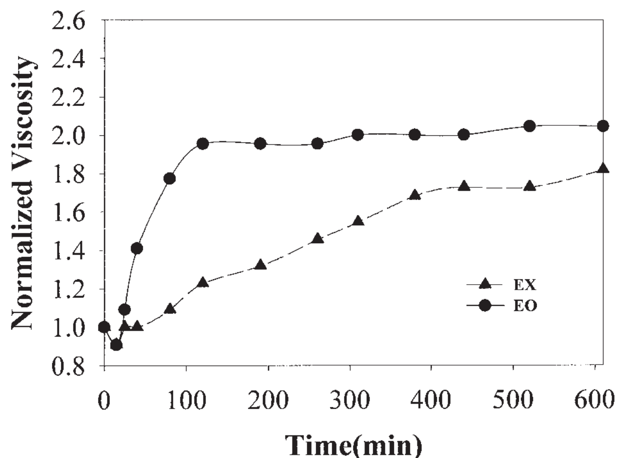

Figure 8 Viscosity change of APTS with phenol as a function of the reaction time.

These two facts, that more than 75% of the ethoxy groups in APTS disappeared in the reaction intermediates and the amount of ethanol corresponding to them was empirically trapped, implies that ethoxy groups in APTS were substituted by certain protonic nucleophiles in reaction intermediates, and a possible candidate for the protonic nucleophiles is a hydroxyl group in phenol resin. It is well known that alkoxy groups in a silane coupling agent can be easily hydrolyzed in protonic media, especially water or alcohol in the presence of an acid catalyst. Therefore, ethoxy groups in APTS were assumed to be consecutively attacked and substituted by phenol groups. Moreover, it is also assumed that because the substitution reaction of ethoxy in APTS with phenol is an equilibrium reaction, a forward reaction, that is, substitution of ethoxy by phenol, became dominant with the removal of ethanol by the application of vacuum. The degree of substitution of ethoxy groups is dependent not only on the extent of ethanol removed but also on the steric hindrance. In the case of the reaction of ethoxy in APTS with phenol, two-thirds of the ethoxy groups in APTS (75% of the ethoxy groups) were substituted.

The treatment of APTS on epoxy and phenol showed a substantial difference in the mechanism. In the case of the treatment of APTS on epoxy, amine groups in APTS consecutively attacked epoxy rings, and an adduct of one molecule of APTS with two epoxy groups was mainly formed, with ethoxy groups in APTS remaining almost not reacted. However, ethoxy substitution was the main path for the reaction of APTS with phenol, and 75% of the ethoxy groups in APTS were empirically substituted.

TABLE V
Analysis of the Trapped Substance in the Reaction of APTS with Phenol During the Vacuum Process

Process	Substance	Trapped substance (g)[a]		Conversion (%)
		Empirical	Theoretical	
Before dropping APTS	H_2O	0.47	—	—
After dropping APTS	Ethanol	2.29	3.12[b]	73.4[c]

[a] Denotes the quantity of the substance trapped per 100 g of the phenol resin mixture of 5 wt % APTS.
[b] Denotes the maximum quantity of ethanol produced by ethoxy cleavage in APTS. It was equal to the moles of APTS in 100 g of the epoxy resin mixture of 5 wt % APTS × 3 × the molecular weight of ethanol.
[c] Denotes the value calculated from the ratio of the empirical value to the theoretical value.

Application to EMC

The adhesion strength of EMC on a Cu plate and the flexural strength at 260°C, the soldering temperature of a semiconductor on PCB, were investigated with different treatment methods of APTS. Figure 10 shows the variation of the adhesion strength of EMC on a Cu plate at 260°C.

The highest and lowest adhesion strengths were observed in the specimens of integral addition and pretreatment on silica, respectively. The adhesion strengths of the specimens from the pretreatment of APTS on epoxy or phenol were similar. It is assumed that in the case of integral treatment, APTS, which is liquid and a movable molecule, especially not reacted, can easily move to the interface between the EMC and Cu plate and make chemical linkages between EMC and Cu rather than between the resin and silica. In the case of the pretreatment on silica, APTS firmly binds to silica and is hard to move to the interface of the Cu plate, so no improvement in the adhesion strength between the Cu plate and EMC was observed.

The flexural strength, one of the most important properties of EMC for estimating popcorn cracking during the soldering process, was measured with different treatment methods of APTS at 260°C. The flexural strength of the specimens from the pretreatment on epoxy showed lower values than those of the others and decreased with an increasing degree of reaction and conversion of epoxy groups. However, the flexural strength of the specimens from the pretreatment on phenol showed higher values than that from the treatment on epoxy but decreased with an increasing degree of reaction and conversion of ethoxy groups, as shown in Figure 11. The flexural strength of composites depends not only on the cohesive force between the silica and resin matrix but also on the crosslinking density of the resin matrix. To figure out the trend of the flexural strength, T_g of EMC was measured and compared with that of the neat resin.

The relationship between tan δ of dynamic mechanical thermal analysis (DMTA) and the temperature is shown in Figure 12–14, and T_g estimated from DMTA charts is shown in Tables VI and VII. T_g of EMC by the pretreatment on epoxy was lower than that by any other pretreatment method and became lower with the degree of reaction. In the case of pretreatment on phenol, T_g of EMC was higher than that by the integral method but decreased with the degree of reaction. In both cases, an increase in T_g of EMC by the pretreatment of APTS on silica could be observed. The trend of T_g according to the treatment method of APTS is nearly in accord with that of the flexural strength. Moreover, in comparison with that of the neat resin, T_g of EMC increased because of the additional constraint

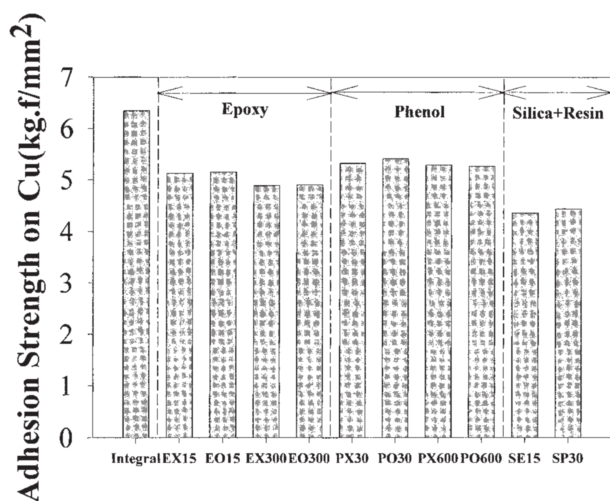

Figure 10 Adhesion strength of EMC on Cu plate at 260°C with different treatment methods of APTS.

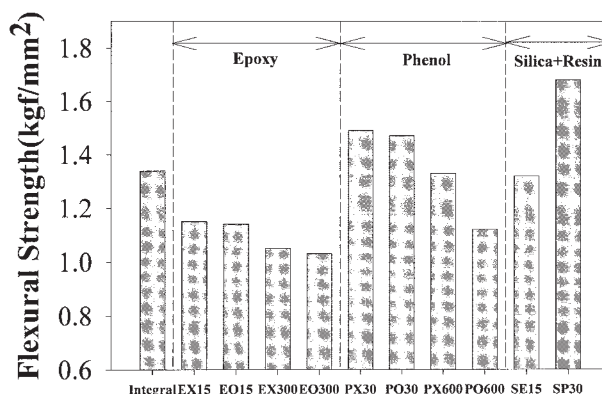

Figure 11 Flexural strength of EMC at 260°C with different treatment methods of APTS.

TABLE VI
T_g Values of EMC with Different Treatment Methods of APTS

	Treatment method										
		Epoxy resin				Phenol resin				Resin + silica	
	Integral	EX-15	EO-15	EX-300	EO-300	PX-30	PO-30	EX-600	EO-600	SE-15	SP-30
T_g (°C)	127.3	125.2	125.1	123.1	123.4	129.2	127.9	125.7	124.4	127.4	131.6

on the segmental motion of the resin. However, T_g of the neat resin system showed almost the same value, regardless of the pretreatment methods, as shown in Figure 14 and Table VII. Hence, the crosslinking density of the resin matrix should not be the major reason for the characteristic trend of the flexural strength and T_g of the EMC. It can be explained that the pretreatment of APTS on epoxy diminishes the linkage between the resin matrix and silica because APTS is confined in the resin matrix in an irreversible manner in advance, causing the reduction of the flexural strength and T_g of EMC, as shown in Figures 11 and 12, respectively. The pretreatment of APTS on phenol makes APTS effectively link to silica because of well-dispersed APTS within the resin and thus EMC in a reversible manner, and hence an increment in the flexural strength and T_g can be observed, as shown in Figures 11 and 13, respectively. However, as the number of ethoxy groups substituted in APTS increases with increasing reaction time, the flexural strength and T_g of the specimens decreases with increasing reaction time because of the excessive preoccupation of ethoxy groups by phenol groups. Therefore, in the pretreatment of APTS in the resin phase, the controlled reaction of APTS with phenol resin (a minimum degree of reaction) is the recommended method for acquiring better mechanical properties of EMC. In the case of the pretreatment on silica, the highest value of the flexural strength was observed. It is well known that the pretreatment of silane on silica makes silane effectively link between the resin matrix and silica, resulting in the higher value of the flexural strength.[18–20]

TABLE VII
T_g Values of the Neat Resin with Different Treatment Methods of APTS

	Treatment method				
		Epoxy resin		Phenol resin	
	Integral	EO-15	EO-300	PO-30	PO-600
T_g (°C)	119.0	119.3	119.0	118.9	119.2

CONCLUSIONS

The amino-functional silane coupling agent, APTS, as an important component of EMC, was pretreated on epoxy, phenol, or silica, and its reaction mechanism and effectiveness for the adhesion strength and flexural strength of EMC were closely examined. In the pretreatment on epoxy, APTS mainly formed a 1:2 adduct with epoxy groups via an epoxy ring-opening reaction without substitution of ethoxy groups, whereas the substitution reaction of ethoxy groups in APTS was the predominant route for the pretreatment on phenol.

Such a difference in the reaction mechanism had an influence on the properties of EMC manufactured by

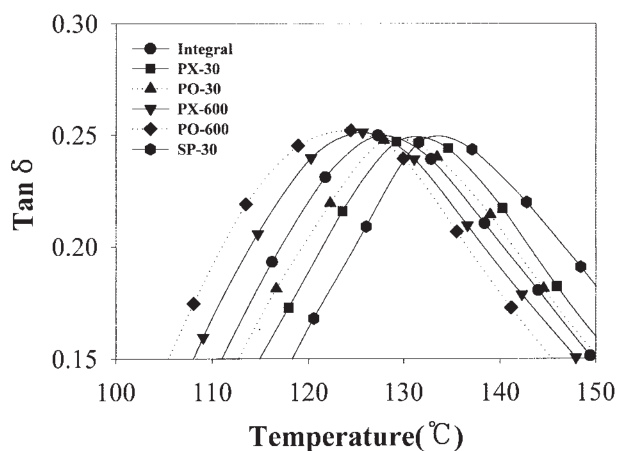

Figure 13 Analysis chart of DMTA of EMC according to the pretreatment of APTS on phenol (approximately the peak region).

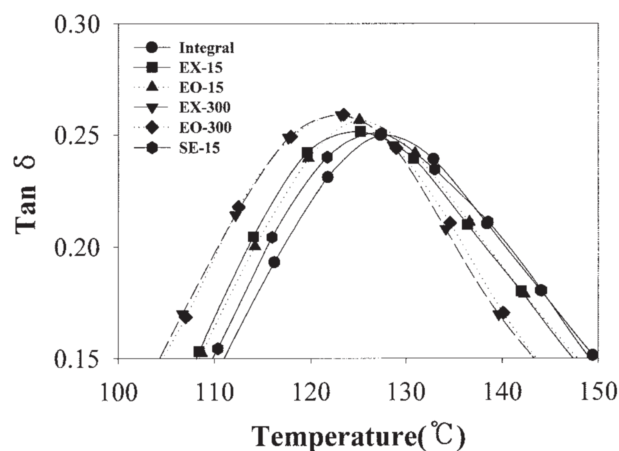

Figure 12 Analysis chart of DMTA of EMC according to the pretreatment of APTS on epoxy (approximately the peak region).

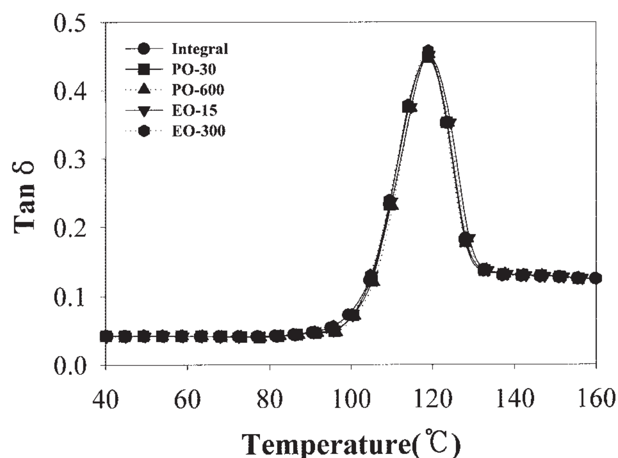

Figure 14 Analysis chart of DMTA of the neat resin according to the pretreatment of APTS on resin.

each pretreatment method. The pretreatment of APTS on epoxy was thought to diminish the linkage between the resin matrix and silica because of the confinement of APTS, which irreversibly reacted with epoxy in advance within the resin matrix, causing a decrease in the flexural strength and T_g. However, the pretreatment on phenol, a specially controlled reaction to the degree of minimum conversion of ethoxy groups, made silane more effectively link resin matrix with silica because of the better dispersion of APTS and resulted in increasing flexural strength and T_g. The pretreatment on silica enabled APTS to effectively combine silica with the organic resin and consequently resulted in the highest value of the flexural strength. In the case of the adhesion strength of EMC on the Cu plate, the highest and lowest values of the adhesion strength were observed from integral addition and pretreatment on silica, respectively.

In summary, for the pretreatment of APTS in the resin phase, a controlled pretreatment method on phenol is more desirable as an effective process, from the viewpoint of the mechanical properties of EMC, than that on epoxy. In addition, the process of the pretreatment on phenol is economical and feasible for mass production.

References

1. Wong, C. P. Adv Polym Sci 1988, 84, 65.
2. Kinjo, N.; Ogata, M.; Nishi, K.; Kaneda, A. Adv Polym Sci 1989, 88, 1.
3. Pecht, M. G.; Agarwal, R.; McCluskey, P.; Javadpour, S.; Mahajan, R. Electronic Packaging; CRC: New York, 1999.
4. Manzione, L. T. Plastic Packaging of Microelectronics Devices; Van Nostrand Reinhold: New York, 1990.
5. Omi, S.; Fujita, K.; Tsuda, T.; Maeda, T. IEEE Trans Component Hybrids Manufacturing Technol 1991, 14, 4.
6. Fukuzawa, I.; Ishiguro, S.; Nanbu, S. In Proceedings of the 23rd IEEE Int Reliability Phys Symp 1985; p 192.
7. Lin, R.; Blackshear, E.; Seriky, P. In Proceedings of the 26th IEEE Int Reliability Phys Symp 1988; p 82.
8. Nguyen, L. T. ASME Trans J Electron Packaging 1933, 165, 346.
9. Nishioka, T.; Oizumi, S.; Ikemura, K.; Igarash, K. In Proceedings of the 41st Electronic Component and Technology Conference, IEEE: New York, 1991; p 190.
10. Jung, H. Y.; Moon, K. S.; Choi, K. S.; Suh, K. S.; Yoon, H. G. J Microelectron Packaging Soc 1999, 6, 51.
11. Wong, C. P. IEEE Trans Component Packaging Manufacturing Technol Part A 1995, 18, 270.
12. Nakamura, Y.; Yamaguchi, M.; Kitayama, A.; Okubo, M.; Matsumoto, T. Polymer 1991, 32, 2221.
13. Asai, S.; Saruta, U.; Tobita, M. J Appl Polym Sci 1994, 51, 1945.
14. Kaji, M.; Nakahara, K.; Ogami, K.; Endo, T. J Polym Sci Part A: Polym Chem 1999, 37, 3687.
15. Ho, T. H.; Wang, C. S. Eur Polym J 2001, 37, 267.
16. Roh, J. H.; Lee, J. H.; Kim, N. I.; Kang, H. M.; Yoon, T. H.; Song, K. H. J Appl Polym Sci 2003, 90, 2508.
17. Yamaguchi, M.; Nakamura, Y.; Iida, T. Polym Compos 1998, 6, 85.
18. Kim, W. G.; Ryu, J. H. J Appl Polym Sci 1997, 65, 1975.
19. Hozoji, H.; Horie, O.; Ogata, M.; Numata, S.; Kinjo, N. Kobunshi Ronbunshu 1990, 47, 483.
20. Plueddemann, E. P. Silane Coupling Agents; Plenum: New York, 1982.
21. Pape, P. G.; Plueddemann, E. P. J Adhes Sci Technol 1991, 5, 831.
22. Koenig, J. L.; Emadipour, H. Polym Compos 1985, 6, 142.
23. Stafford, S. C.; Ulrich, A. D.; Canova, L. A. Plast Compd 1987, 10, 41.
24. Rozenberg, B. A. Adv Polym Sci 1986, 75, 113.