Effects of Curing Accelerators on Physical Properties of Epoxy Molding Compound (EMC)

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SYNOPSIS

The effects of various curing accelerators on the physical properties of epoxy molding compounds (EMCs) were investigated. Such properties as elasticities in rubbery and glassy regions, glass transition temperature, thermal expansion coefficient, and water absorption at 60°C of neat epoxy resins using various curing accelerators were found to be directly reflected in the properties of the EMCs that were prepared by using each resin system. However, volume resistivity and saturated water absorption at 120°C were not reflected. This was attributed to differences in the catalytic reactivity of accelerators causing different melt viscosity for the EMC, which resulted in different densities (packing degrees) and affected physical properties of molded EMC. On the other hand, it was found that the density of molded EMC was also affected by the molding conditions. To improve the physical properties of the molded EMC, in addition to proper selection of accelerators, it was very important to set the melt viscosity of the EMC as high as possible within the moldable range and to select suitable molding conditions.

1. INTRODUCTION

Epoxy resin is extensively used as bonding, insulating, or structural materials in a wide variety of industrial fields, including electronics and electrical industries. Especially in the former, the resin is widely used as an encapsulating material for semiconductors. In recent years, approximately 90% of all semiconductors were encapsulated with low-pressure transfer molding compounds made of phenolic–novolac-cured epoxy resin.[1-3] Such epoxy molding compounds (EMCs) usually involve a curing accelerator to accelerate the curing reaction of resin and to increase the molding cycle for large mass production. The reliabilities of the encapsulated semiconductors, however, differ largely, according to the kind of curing accelerator used. It is therefore important to select an adequate curing accelerator for enhancing the reliability of the encapsulated semiconductors.[4,5]

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Journal of Applied Polymer Science, Vol. 44, 1795–1805 (1992)
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Many studies have been made to clarify the relationship among the chemical structures of epoxy resin and hardener, curing reaction mechanism, and properties of the cured substance.[6-13] These studies, however, were made mainly on amine- or anhydride-cured epoxy resin systems, and very little was done on the phenolic–novolac-cured epoxy resin system. Furthermore, with regard to curing accelerators, there have been many studies related to acceleration of the curing reaction or the accelerating mechanism itself, but little has been found out about the effects exerted on the physical properties of the final cured substances.[14-16] There have also been very few studies on the relationship of characteristics between base epoxy resin and composite material.

In this respect, we have heretofore conducted a variety of studies on the effects of curing accelerators on the various properties of phenolic–novolac-cured epoxy resin that is extensively used as a base resin in EMCs for semiconductor encapsulation.[17-20] As a result, it was clarified that the cross-linking density varies with the kind of curing accelerator, causing a difference in dynamic viscoelasticity, specific volume (density), thermal expansion coefficient, water absorption, and so on of the cured resin.

Table I Formulation of Epoxy Molding Compounds (EMCs)

	Raw Materials	Parts by Weight
Epoxy resin	Polyglycidyl ether of *o*-cresol–formaldehyde novolac	90
	Diglycidyl ether of brominated bisphenol A	10
Hardener	Phenol–formaldehyde novolac resin	52
Accelerator	Table II	0.4–2.5
Filler	Fused silica	450
Flame retardant	Antimony trioxide	4
Coupling agent	Glycidoxypropyl trimethoxysilane	2
Release agent	Ethyleneglycol ester of montanic acid	1
Colorant	Carbon black	1

The purpose of this paper is to elucidate the relationship between the characteristics of neat epoxy resins and the various properties of EMCs that combine filler and various additives. Attention is focused on the following points: how the characteristics of neat epoxy resin are reflected in the composite material and how the accelerator affects the properties of the composite materials.

2. EXPERIMENTAL

2.1. Samples

Table I shows the formulation of EMCs used in the experiments. The epoxy resins used were polyglycidyl ether of *o*-cresol–formaldehyde novolac ESCN 195-6 and diglycidyl ether of brominated bisphenol A ESB 400 (both made by Sumitomo Chemical Co.), while the hardener was phenol–formaldehyde novolac resin PN (Nippon Kayaku Co.). Used as curing accelerators (Table II) were various bases and those borate compounds known to be effective for phenolic-cured epoxy resin.[4,5] The filler was fused silica with an average particle size of 8 μm (Tatsumori), the flame retardant was antimony trioxide with an average particle size of 0.02 μm (Nihon Seiko Co.), the coupling agent was glycidoxypropyl trimethoxysilane (Shin-etsu Chemical Co.), the release agent was ethyleneglycol ester of montanic acid (Hoechst Japan), and the colorant was carbon black CM 800 (Cabot Corp.).

2.2. Preparation of Cured Neat Epoxy Resin

The epoxy resin, hardener, and accelerators were rapidly mixed at 130–140°C and deaerated at reduced pressure, then subjected to curing at 150°C for 2 h and at 180°C for 6 h. In this study, epoxy resin and phenolic–novolac hardener were stoichiometrically mixed, and the added amount of accelerators was determined so that the gelation time of resin at 180°C would be around 35 s.

2.3. Preparation of EMCs and Molded Substance

The materials weighed out in the ratio given in Table I were kneaded for about 15 min by a double-shaft roll heated at 70–80°C, then cooled and pulverized. This compound was tableted and transfer-molded in a transfer machine at a molding temperature of 180°C, transfer pressure of 7 MPa, and molding time of 1.5 min to form each test specimen. The molded substance was taken out from the mold and cured fully at 180°C for 6 h.

2.4. Measuring Method

(1) Gelation Time

The prescribed amounts of epoxy resins, hardener, and accelerators were thoroughly mixed in a mortar and used as a neat resin sample. This was subjected to measurement according to JIS-K-5909 (hot plate method). The EMC was measured by means of a JSR-type curelastometer (Imanaka Kikai).

(2) Melt Viscosity

This was calculated from the maximum flow velocity when forcing out (0.98 MPa pressure) 2 g of EMC from the metal nozzle (1 mm i.d., 10 mm long) of a 301-type flow tester (Shimadzu Seisakusho) heated at 180°C.

Table II Accelerators

No.	Name	Structure
1	2-Ethyl-4-methyl imidazole (EMI)	Imidazole ring with CH_3, HN, N, C_2H_5
2	1.8-Diazabicyclo (5.4.0)-7-undecene (DBU)	Bicyclic ring, N, N
3	*N*-Methyl piperazine (MP)	HN ring N—CH_3
4	Triphenylphosphine (TPP)	$P(C_6H_5)_3$
5	2-Ethyl-4-methylimidazolium tetraphenylborate (EMI-TPB)	Imidazolium ring with CH_3, HN, NH, C_2H_5 · $B(C_6H_5)_4$
6	1.8-Diazabicyclo (5.4.0)-7-undecenium tetraphenylborate (DBU–TPB)	Bicyclic ring, N, NH · $B(C_6H_5)_4$
7	Tetraphenylphosphonium tetraphenylborate (TPP–TPB)	$(C_6H_5)_4P \cdot B(C_6H_5)_4$
8	Butyltriphenylphosponium tetraphenylborate (BTPP–TPB)	$(C_4H_9)(C_6H_5)_3P \cdot B(C_6H_5)_4$
9	Tetrabutylphosphonium tetraphenylborate (TBP–TPB)	$(C_4H_9)_4P \cdot B(C_6H_5)_4$
10	Tetraphenylphosphonium butyltriphenylborate (TPP–BTPB)	$(C_6H_5)_4P \cdot B(C_6H_5)_3(C_4H_9)$
11	Tetraphenylphosphonium tetrabutylborate (TPP–TBB)	$(C_6H_5)_4P \cdot B(C_4H_9)_4$
12	Tetrabutylphosphonium tetrabutylborate (TBP–TBB)	$(C_4H_9)_4P \cdot B(C_4H_9)_4$

(3) Dynamic Viscoelasticity

A sample of 1 × 4 × 40 mm was used to measure viscoelasticity at a frequency of 10 Hz, heating rate of 3°C/min, and chuck interval of 30 mm using a viscoelasticity spectrometer PRX-706 (Iwamoto Seisakusyo). In this report, the tan δ peak temperature was assumed to be the glass transition temperature and expressed as $T_{g(\mathrm{VES})}$.

(4) Thermal Expansion Coefficient

The thermal expansion of a 5 × 5 × 15 mm sample was measured from room temperature up to 250°C at a heating rate of 2°C/min using a thermomechanical analyzer TMA1500 (Shinku Riko). Before measurement, the sample was attached to the instrument and preheated up to nearly T_g in order to eliminate moisture and strain.[21]

(5) Water Absorption

Samples of cured neat resin (5 × 5 × 30 mm) and molded EMC (90 mm o.d. × 2 mm thick) were left in an environment of 60°C and 100% RH, and the saturated absorption rate, diffusion coefficient, and permeability of water vapor were determined from the change in weight.

Table III Curability of Neat Epoxy Resins with Various Added Accelerators

Sample No.	Accelerator	Added Amount (mmol)	Gel Time (s)			Activation Energy (kcal/mol)
			180°C	165°C	150°C	
1	EMI	3.5	33	62	115	15.8
2	DBU	7.5	32	59	112	15.9
3	MP	5.0	34	66	138	17.7
4	TPP	3.0	32	58	115	16.2
5	EMI–TPB	5.0	35	70	137	17.3
6	DBU–TPB	4.5	35	70	135	17.1
7	TPP–TPB	3.0	34	65	132	18.1
8	BTPP–TPB	3.0	33	69	143	18.6
9	TBP–TPB	5.0	30	66	129	18.5
10	TPP–BTPB	3.0	31	66	142	19.3
11	TPP–TBB	3.0	33	67	146	18.8
12	TBP–TBB	5.0	34	71	144	18.3

(6) Density

The density of a sample (10 mm o.d. × 15 mm long) was determined by a sink-and-float method using a precision balance. The reciprocal of density was assumed to be the specific volume.

(7) Volume Resistivity

The volume resistivity of a sample (90 mm o.d. × 2 mm thick) at 220°C was measured in accordance with JIS-K-6910.

(8) Flexural Characteristics

The flexural strength, modulus, and elongation of a sample (5 × 12.7 × 60 mm) were measured at room temperature, with a span interval of 40 mm and bending speed of 1 mm/min in accordance with ASTM-D-790-66.

3. RESULTS AND DISCUSSION

3.1. Acceleration of Curing Accelerators

Since the curing reaction of phenolic–novolac-cured epoxy resin is relatively slow, it is usually combined with curing accelerators to shorten the curing time.[4–5] But the curability of resin combined with various accelerators differs considerably depending not only on the characteristics of the accelerators such as the basicity and solubility, but also on their mixing ratio. To examine the effect of the accelerators on the physical properties of cured neat epoxy resin, the curing rate of the resin should be kept nearly the same for all samples. Therefore, first, we studied the relation between the mixing ratio and gelation time for various accelerators and determined the mixing ratio of accelerators so that the gelation times of the resins at the curing temperature of 180°C would be nearly the same. Table III shows the added amount of various accelerators used in the study, together with the gelation time at three curing temperatures (150, 165, and 180°C) and the activation energy of the gel reaction. The TPP, TPP–TPB, BTPP–TPB, TPP–BTPB, and TPP–TBB have nearly the same gelation time as the other acceler-

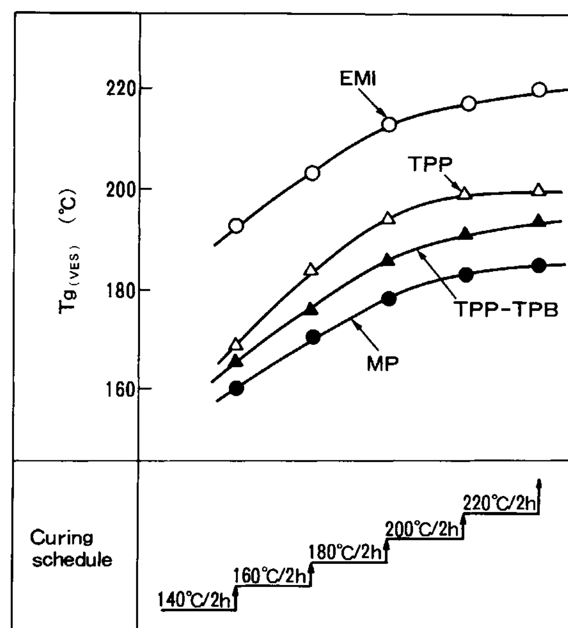

Figure 1 Effect of curing schedule on T_g.

Table IV Viscoelastic Properties of Cured Neat Epoxy Resins

Accelerator	$T_{g(\mathrm{VES})}$ (°C)	E' (dyn/cm^2) 25°C	E' (dyn/cm^2) $T_{g(\mathrm{VES})}$ + 40°C	$\rho_{(E')}$ (10^{-3} mol/cm^3)
EMI	215	2.6×10^{11}	1.4×10^{9}	10.4
DBU	201	2.5×10^{11}	1.0×10^{9}	7.9
MP	178	3.2×10^{11}	6.3×10^{8}	5.2
TPP	195	2.9×10^{11}	9.1×10^{8}	7.2
EMI–TPB	208	2.5×10^{11}	1.3×10^{9}	10.2
DBU–TPB	184	3.6×10^{11}	8.1×10^{8}	6.6
TPP–TPB	184	3.2×10^{11}	8.0×10^{8}	6.5
BTPP–TPB	193	3.4×10^{11}	9.4×10^{8}	7.4
TBP–TPB	193	2.6×10^{11}	1.0×10^{9}	8.2
TPP–BTPB	205	2.5×10^{11}	1.3×10^{9}	10.1
TPP–TBB	194	2.7×10^{11}	9.6×10^{8}	7.2
TBP–TBB	205	2.4×10^{11}	1.3×10^{9}	10.1

$T_{g(\mathrm{VES})}$: tan σ peak temperature; E': storage modulus. $\rho_{(E')}$: cross-linking density.

ators despite a relatively low mixing ratio, which means they strongly accelerate the gel reaction. The activation energy of the gel reaction with quaternary phosphonium salts such as TPP–BTPB, TPP–TBB, etc., are relatively large. This means that acceleration of the curing reaction is weak at lower temperatures and strong at higher ones, which implies that they have a latent acceleration of the curing reaction.

Next we studied the conditions for achieving sufficient curing of the resin. Figure 1 shows the relation between the $T_{g(\mathrm{VES})}$ of the cured resins and the curing conditions when, stepwisely, heating the resins combined with typical accelerators. With any of the accelerators, the $T_{g(\mathrm{VES})}$ nearly levels off when heated at 200°C or higher for 2 h, which means that the curing is almost finished. But a cured resin that has been heated at temperatures above 200°C has considerable darkening, which indicates resin deterioration. Based upon studies on the curing conditions that provide a high T_g so as to prevent deterioration of the resin, curing conditions are determined to be 150°C/2 h plus 180°C/6 h.

3.2. Cross-linking Density and Physical Properties of Cured Neat Epoxy Resin

The dynamic viscoelastic properties were measured for the finally cured neat epoxy resin that was cured using various accelerators. All the samples show a glassy region, transition region, and rubbery region characteristic of a highly cross-linked thermosetting resin. But there is a considerable difference in glass transition temperature and elasticity in the rubbery region according to the kind of accelerator. The cross-linking density of each cured resin is determined from the rubbery elastic modulus by using the statistical theory of rubber elasticity[22]:

$$\rho_{(E')} = E'/3\phi RT$$

where E' is the storage modulus of cured neat resin at $T_{g(\mathrm{VES})}$ + 40°C, ϕ is the front factor (ϕ = 1 assumed here), R is the gas constant, and T is the absolute temperature.

As shown in Table IV, there is a considerable

Table V Relationships between Cross-linking Density and Physical Properties of Cured Neat Epoxy Resins

Property	Condition	Trend
Crossing-linking density ($\rho_{(E')}$)		↗
Glass transition temperature (T_g)		↗
Thermal expansion coefficient (α)	Above T_g	↘
	Below T_g	↗
Elasticity (E')	$T_{g(\mathrm{ves})}$–60°C	↘
Water absorption (Q_S)	60°C/100% RH	↗
Diffusion coefficient of water vapor (D)	60°C/100% RH	↗
Permeability of water vapor (P)	60°C/100% RH	↗

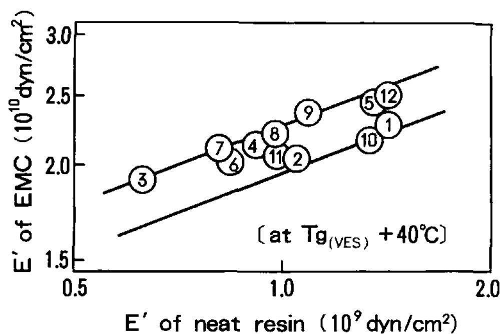

Figure 2 Comparison of elasticity in the rubbery state of molded EMC with that of cured neat epoxy resin.

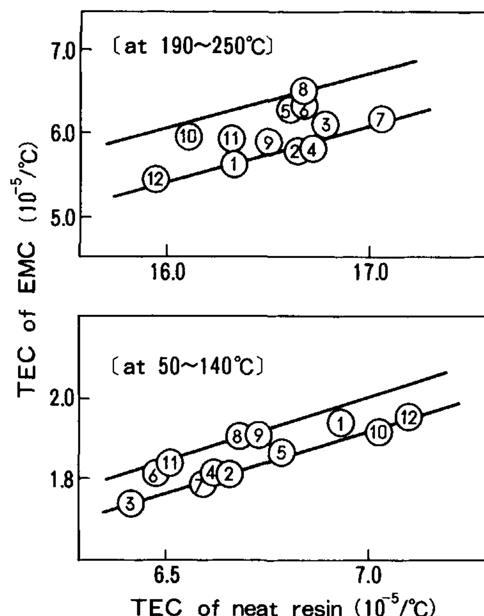

Figure 4 Comparison of thermal expansion coefficient (TEC) of molded EMC with that of cured neat epoxy resin.

difference in cross-linking density among cured resins that were prepared by using different accelerators. The resin using accelerator EMI has the highest cross-linking density, while that using MP has the lowest cross-linking density. It is conceivable that the large difference in this cross-linking density due to the kind of accelerator is because of a difference in the resin's curing reaction mechanism or curing degree with the kind of accelerator.[4,9,12,13] The most important point in Table IV is that there is a close relationship between T_g and cross-linking density: The higher the cross-linking density, the higher the T_g.

Many studies have been made on the relation between cross-linking density and physical properties for epoxy resins cured with various amine or acid anhydride hardeners, and it has been reported that similar relationships were observed for these epoxy resins.[6-8,23-27] We concluded in a previous paper[17-20] that the cross-linking density is the most dominant factor that determines the various physical properties of cured neat epoxy resins. The results show that there are relationships, given in Table V, between cross-linking density and physical properties of the cured resin; i.e., when the cross-linking density increases, the glass transition temperature also increases while the thermal expansion coefficient (TEC) in the rubbery region and elasticity in the glassy region decrease. The thermal expansion coefficient in the glassy region and saturated absorption rate, diffusion coefficient, and permeability of water

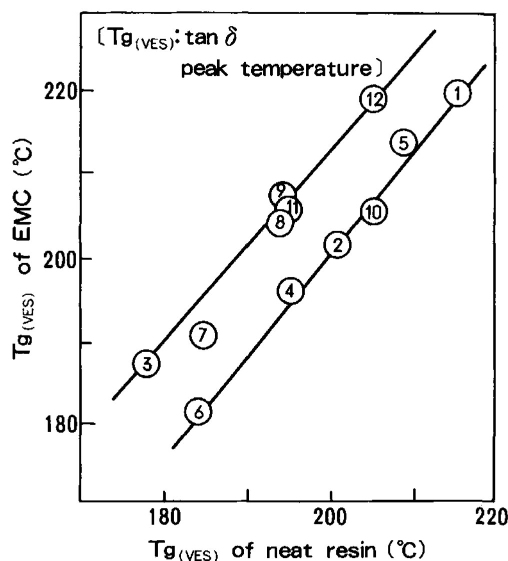

Figure 3 Comparison of $T_{g(\mathrm{VES})}$ of molded EMC with that of cured neat epoxy resin.

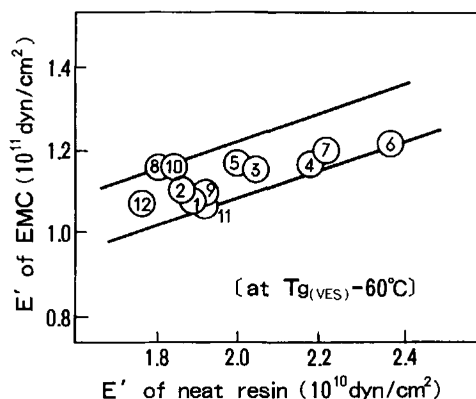

Figure 5 Comparison of elasticity at glassy state of molded EMC with that of cured neat epoxy resin.

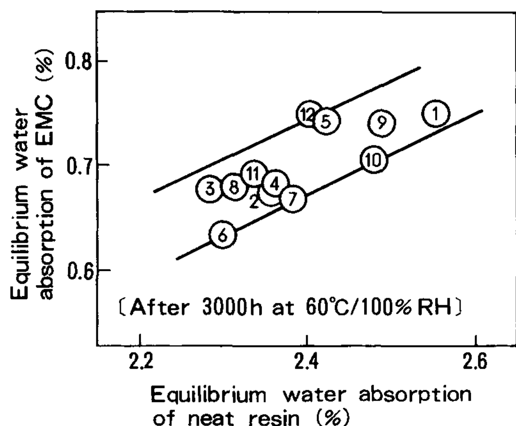

Figure 6 Comparison of equilibrium water absorption of molded EMC with that of cured neat epoxy resin.

vapor at 60°C and 100% RH also show an increase. The reason for this difference in properties of cured resins due to cross-linking density can be explained by taking into account the free volume in cured resins.[17-20]

Interest in this paper is focused on the following two questions: How are the characteristics of neat epoxy resin reflected in the various properties of a composite material like EMC that contains various additives such as filler and flame retardant and does the accelerator have any effect on the properties of the EMC besides the effect on the cross-linking density of the base resin?

3.3. Correlation of Neat Resin and Molding Compound Properties

The above questions should be answered in order to heighten the performance of a composite material like EMC and increase the reliability of the applied products. Therefore, we studied the physical properties of EMCs consisting of phenolic–novolac-cured epoxy resin using various accelerators.

The added amount of accelerators for each EMC were adjusted so that the gelation time at the molding temperature (180°C) would be nearly the same. The added amount of accelerators were the same as shown in Table III in the case of neat epoxy resins. However, there was a considerable difference in the spiral flow[28] and minimum melt viscosity that is a measure for moldability of each EMC. These differences, which are described later, were caused by a difference in the acceleration of the curing reaction of each accelerator.

The results show that the physical properties of the molded EMC vary greatly depending on accelerator species. Figures 2–6 show a comparison between the properties of cured neat resin and molded EMC. (The encircled numbers in the figures correspond to the accelerator number given in Table II; this applies to subsequent figures as well.) Because a rather large amount of hard filler is mixed in the EMC, the cross-linking density of molded EMC cannot be determined directly from the elasticity (E') in the rubbery region. Therefore, elasticity in the rubbery region ($T_{g(\mathrm{VES})}$ + 40°C) of both cured substances is indicated in Figure 2 as a measure for the cross-linking density of the resin. Although the elasticity of the molded EMC shows a value about 10 times higher than the neat resin due to the effect of filler, there is a good correlation between the two substances. It is conceivable that the properties of base resin are directly reflected in the $T_{g(\mathrm{VES})}$ of the molded EMC, as there is also a clear correlation in $T_{g(\mathrm{VES})}$ values between the two substances according to Figure 3. Therefore, it is clear that the effect of various accelerators on cross-linking density or $T_{g(\mathrm{VES})}$ of neat resins is reflected in the same way in molded EMCs. Also, there is considerable correlation in the thermal expansion coefficient, elasticity in the glassy region ($T_{g(\mathrm{VES})}$ − 60°C), and saturated water absorption at 60°C/100% RH shown in Figures 4–6. But no correlation is found with regard to volume resistivity or saturated water absorption at 120°C.

In any case, composite materials like EMCs that are composed of various additives are generally cured

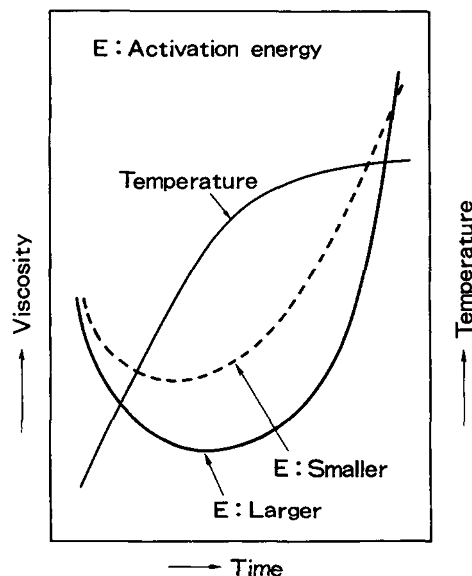

Figure 7 Schematic representation of viscosity change of EMC at molding.

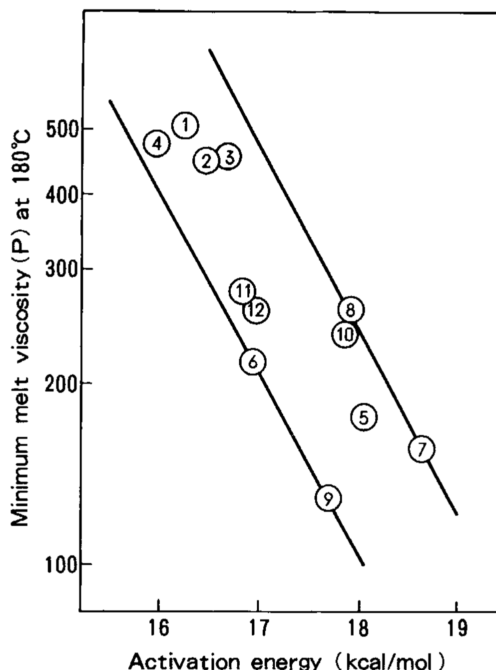

Figure 8 Minimum melt viscosity of EMCs at molding plotted against their activation energy at curing.

under a pressurized condition such as a transfer molding method. It is therefore conceivable that the fluidity and/or curability of compounds, a mutual interaction between base resin and filler/additives, will affect the physical properties of a molded substance.[29,30] Next is a study of the relation between moldability of EMCs using various accelerators and the physical properties of the molded EMCs.

3.4. Effects of Moldability on Physical Properties of Molded EMCs

The EMCs used as encapsulating materials for semiconductors are usually molded by a transfer molding machine. The EMC is transferred under pressure into a metal cavity heated at certain temperatures. The temperature of the EMC gradually increases during this process. Therefore, the EMC viscosity changes during molding. This is shown schematically in Figure 7. The EMC is melted via heating in the mold, and the viscosity decreases with the rise of temperature. The curing reaction also proceeds with the temperature rise, and upon reaching a certain temperature, the curing reaction of resin advances rapidly, which causes an abrupt increase in viscosity.[2,28] The minimum viscosity and the time period corresponding to the bottom of the u-curve in Figure 7 are very important parameters showing moldability and are called a "process window." Such melt viscosity behavior of EMC is greatly affected by the curing acceleration of the accelerator, which is expressed by activation energy E_a. Two typical EMC melt viscosity curves are compared, one having a higher E_a value, and the other, a lower E_a value. It is assumed that the physical properties of the molded EMC are also affected by the melt viscosity behavior. When EMCs showing a different melt viscosity behavior are molded under a given set of conditions, the amount of air sucked into them during injecting should differ because the pressure applied to them also differs depending on their melt viscosity. This causes a difference in the amount of air excluded from the EMCs and in how well volatile components are excluded from the equipment; it is thought that this affects the amount of voids and interstices in molded EMCs, which necessarily causes changes in density and other properties.[29]

Figure 8 shows minimum melt viscosity (η_{min}) as a function of activation energy E_a of the gel reaction. The minimum melt viscosities (η_{min}) of each EMC were determined by using a flow tester under gradual heating, simulating the actual molding procedure. Compounds having a low activation energy (E_a) for the gel reaction shows a higher melt viscosity, while compounds with a high E_a show a lower melt vis-

Accelerator	Molecular weight		
	Mn	Mw	Mw/Mn
None	810	1570	1.9
EMI	1050	4590	4.4
TPP	1060	4040	3.8
MP	960	2880	3.0
TPP-TPB	930	2620	2.8

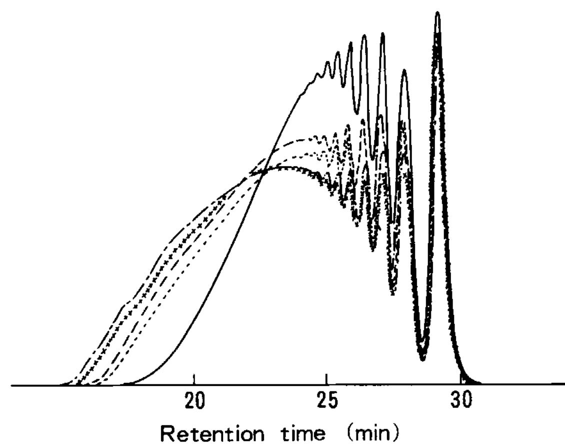

Figure 9 Molecular weight distribution of base resins after kneading [accelerator: none (——); EMI (— • —); MP (- - - -); TPP (XXXXXX); TPP-TPB (··········)].

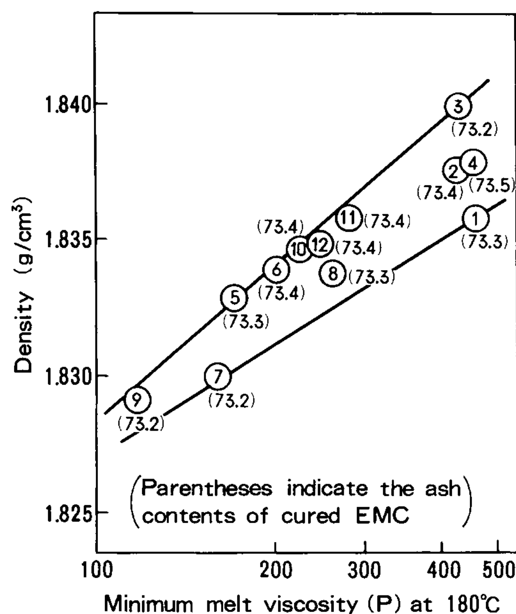

Figure 10 Density of molded EMCs plotted against their minimum melt viscosity at molding.

cosity. Even though the E_a of EMC in Figure 8 differs slightly from the E_a of neat resin given in Table III, the difference is very small. This may be because the additives affect the reactivity of resins in the EMC.

The following is thought to be the reason why minimum melt viscosity varies with E_a. Since the curing reaction of an EMC with small E_a proceeds even at a relatively low temperature, the B stage (polymerization of base resin) advances during kneading in the rolling machine for preparation of the EMC. Also, when measuring the melt viscosity of an EMC with a small E_a, since the curing reaction of base resin proceeds from a relatively low temperature, an increase in viscosity occurs due to the reaction before the melt viscosity has had a chance to decrease much. By contrast, the curing reaction of an EMC with a large E_a does not advance much at low temperature, so the B stage does not proceed during kneading in the rolling machine and there is a large decrease in melt viscosity due to the temperature rise of the EMC. Figure 9 shows gel permeation chromatograms for base resins of EMC just after kneading in the rolling machine. Upon comparing the EMC having a large E_a in which TPP–TPB is used as accelerator with the EMC having a small E_a in which EMI is used as the accelerator, the average molecular weight of base resins with the former is smaller, which indicates that the B stage does not advance much during kneading in the rolling machine.

The relation between minimum melt viscosity of the EMC and density of molded substance were examined and the results are shown in Figure 10. The lower the melt viscosity is, the lower the density. The parenthesized values in the figure indicate the ash content of the molded EMC, and as shown, there is little difference between them. The relationship in Figure 10 cannot be explained by considering the difference in neat resin density due to a difference in cross-linking densities. It is improbable that the density of the base resin changes due to mold pressure, judging from its bulk modulus. Therefore, it is thought that the difference in density of molded EMC is attributable to the difference in the packing degree of various components included in an EMC; that is, the lower the melt viscosity of the EMC, the greater the number of defects such as microvoids or interstices in the interface between resin and filler of the molded substance, which should result in lower density.

The difference in density of the molded EMC would necessarily reflect various properties. As shown in Figure 11, there is a good correlation between density and volume resistivity at 220°C and water absorption at 120°C/100% RH, indicating that internal defects in the composite material are reflected in these properties. However, other properties such as elasticity, T_g, and thermal expansion coefficient are not influenced by this difference in density of the molded substance.

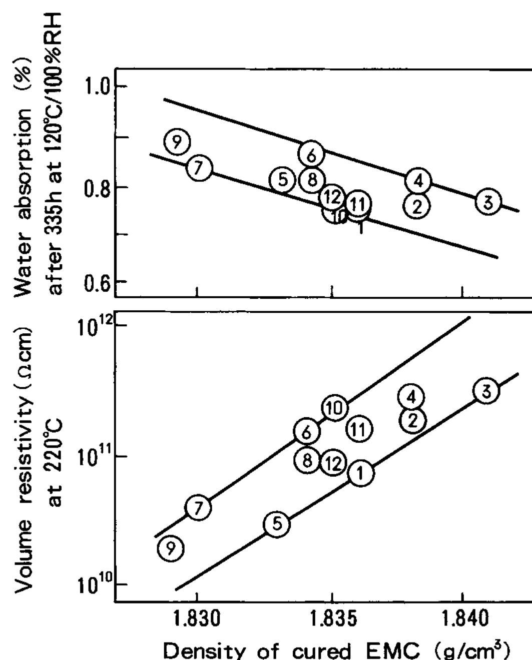

Figure 11 Water absorption and volume resistivity vs. density of molded EMCs.

Table VI Relationship Between Mold Pressure and Physical Properties of Molded EMC

	Accelerator											
	EMI			MP			TPP			TPP–TPB		
Mold pressure (MPa)	3	7	11	3	7	11	3	7	11	3	7	11
Density at 20°C (g/cm^3)	1.798	1.840	1.843	1.796	1.837	1.840	1.773	1.843	1.843	1.759	1.837	1.838
Viscoelastic properties												
Storage modulus (GPa) at 20°C	11.5	13.4	16.0	10.7	12.8	15.3	11.4	15.0	14.8	11.1	15.0	16.1
T_g (tan δ peak temp) (°C)	212	213	215	185	186	186	198	196	198	191	192	192
Flexural properties at 20°C												
Strength (MPa)	133	134	156	125	157	171	137	154	169	105	169	164
Modulus (GPa)	9.8	10.5	10.5	9.8	10.6	10.6	10.1	10.7	10.8	9.4	10.4	10.5
Elongation (%)	1.4	1.5	1.6	1.4	1.6	1.8	1.5	1.6	1.7	1.3	1.7	1.7
Volume resistivity at 220°C (10^{10} Ω cm)	5.6	8.3	8.0	62	68	82	22	32	33	16	22	23
Moisture absorption properties at 60°C/100% RH												
Q^a (wt %)	0.869	0.852	0.843	0.812	0.768	0.765	0.741	0.731	0.720	0.825	0.798	0.785
D^a (10^{-4} cm^2/h)	1.93	1.76	1.73	2.50	1.90	1.85	2.19	1.94	1.90	2.31	1.94	1.95
P^a (10^{-6} g cm/cm^2 h)	3.01	2.76	2.69	3.65	2.68	2.60	2.81	2.61	2.52	3.35	2.84	2.81

[a] *Q*: Saturated water content; *D*: diffusion coefficient; *P*: permeability.

3.5. Molding Pressure and Physical Properties of Molded EMCs

Internal defects in cured fiber reinforced plastics (FRP) are also greatly dependent on the curing pressure and this affects physical properties of cured FRP.[30] In other words, amounts of internal defects are changed by controlling the curing pressure. We then studied the effect of molding pressure on physical properties of molded EMC when using four typical accelerators, which can provide considerably different cross-linking densities of neat epoxy resins. The molding pressures were widely changed from 3 to 11 MPa in order to clarify this effect. The results are given in Table VI. There is very little change in $T_{g(\mathrm{VES})}$ of the molded EMCs upon varying the molding pressure with each accelerator, which indicates that the cross-linking density of the neat epoxy resin is hardly affected by the molding pressure. But with each type of accelerator, the density, elasticity, mechanical properties, volume resistivity at 220°C, and water absorption properties of the molded EMCs differ with the molding pressure; the lower the molding pressure, the lower the density, elasticity, flexural strength, and volume resistivity and the higher the water absorption of the molded EMCs. The reason for this is that when the molding pressure is low, defects such as microvoids or interstices in the interface between resin and filler occur easily in the molded EMCs. Therefore, in order to improve their physical properties, in addition to proper selection of accelerators and setting of melt viscosity, it is very important to set the molding pressure as high as possible.

4. CONCLUSION

The effects of various curing accelerators on the physical properties of epoxy molding compounds (EMCs) were investigated. It was clarified that several properties of cured neat epoxy resins were directly reflected in those of the molded EMCs that were prepared, but a few properties were not. The former included elasticity in the rubbery and glassy regions, glass transition temperature, thermal expansion coefficient, and water absorption at 60°C, while the latter were volume resistivity and saturated water absorption at 120°C. The reasons why a few properties of the neat epoxy resin were not reflected in the EMCs were considered to be differences in catalytic reactivity of each accelerator causing different melt viscosity for the EMC, which led to different densities (packing degrees) and physical properties of molded EMC.

Consequently, it was confirmed that the physical properties of cured composite material such as epoxy molding compounds must be considered from the following two standpoints. One was that features of

the neat epoxy resin reflected the properties of the composites directly. The other was that defects in composite materials such as microvoids or adhesiveness between resin and filler became a dominant factor determining the properties. The latter were especially susceptible to the effects of reactive acceleration of accelerators and the molding conditions. Therefore, in order to improve the properties of the EMCs, in addition to proper selection of accelerators, it was seen to be very important to set the melt viscosity as high as possible within the moldable range and to select suitable molding conditions.

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Received April 1, 1991
Accepted June 17, 1991