

Moldability and Properties of Phenolic/Artificial Zeolite Composites

Akihiro Matsumoto,¹ Keiko Ohtsuka,¹ Hajime Kimura,¹ Shin-ich Adachi,² Minoru Takenaka²

¹Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya Joto-ku, Osaka 536-8553, Japan

²KT Material Co., Ltd., 2-8 Awajimachi 3-chome, Chuo-ku, Osaka 541-0047, Japan

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ABSTRACT: The purpose of this study is to improve the several properties of composites consisting of a phenolic and fly ash or artificial Zeolite such as sodium type Zeolite (Na—Ze) or calcium type Zeolite (Ca—Ze). And it also includes the improvement in the flowability of molding compounds. The molding compounds were prepared from a phenol novolac, a curing agent, and several fillers. The flowability of the compounds containing fly ash and artificial Zeolite as a filler, mentioned above, was superior to that of the compounds containing glass fiber (GF), calcium carbonate (CaCO₃), or talc as a filler. The phenolic composites were prepared from the above molding compounds by transfer molding. The phenolic composite containing Ca—Ze had most superior heat resistance, electrical insula-

tion, and flexural strength, though in the lastly listed property it ranked next to the GF-filled composite. The linear expansion coefficient of the composite containing Ca—Ze was as low as almost isotropic. The reasons of obtaining these excellent properties were thought to be as follows: (1) Ca—Ze could finely be dispersed in the phenolic resin to bring good impregnation. (2) The surface chemical and physical interaction between the resin and Ca—Ze was higher than that between the resin and the other fillers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3666–3673, 2007

Key words: thermosets; fillers; mechanical properties; composites; thermal properties

INTRODUCTION

Phenolic molding compounds contain several fillers to improve the properties or to endow with high functionality. It was known that smaller aspect ratio of filler was preferable to improve the flowability of molding compounds.^{1,2} And it was also known that chemical and physical interaction of interface between resin and filler was important to improve the mechanical strength and heat resistance of composites.^{3,4} In this study, spherical fly ash (aspect ratio ≈ 1) or porous artificial Zeolite which was produced from the fly ash were used by filler of novolac type phenolic resin to improve the flowability of phenolic molding compounds and the several properties such as mechanical strength and heat resistance of phenolic composites.

Artificial Zeolite has function to impregnate the substance into porous parts, or to exchange the cation for heavy metal. It has been used as the purifier of lead or the adsorbent of trimethyl amine gas which was generated from spoiled fish, and so on. It has been also contributive to promote the growth of seaweeds by purification of sea water.

It was already reported that phenolic composites containing small amounts of the artificial Zeolite were able to adsorb ammonia gas and formaldehyde generated in the course of curing reaction. And those were also able to deodorize from phenolic composites and to prevent the corrosion of insert molded composite.^{5–8} In these reports, however, the amount of the artificial Zeolite was only 20–30 wt % of phenol novolac, because the main purpose of addition of the Zeolite was deodorization of phenolic composite. There was no report which was examined the properties of molding compounds and composites consisted of phenolic resin and Zeolite of same quantity, in comparison to those consisted of phenolic resin and other general fillers. The purpose of this study is to improve the several properties of composites consisting of a phenolic and fly ash, sodium type artificial Zeolite or calcium type artificial Zeolite, and it also includes the improvement in the flowability of molding compounds.

EXPERIMENTAL

Materials

Fly ash, sodium type artificial Zeolite (Na—Ze), and calcium type artificial Zeolite (Ca—Ze) were obtained from Chubu Electric Power Co., Inc. Fly ash was collected in coal stream-power station. The

Correspondence to: A. Matsumoto (akihirom@omtri.city.osaka.jp).

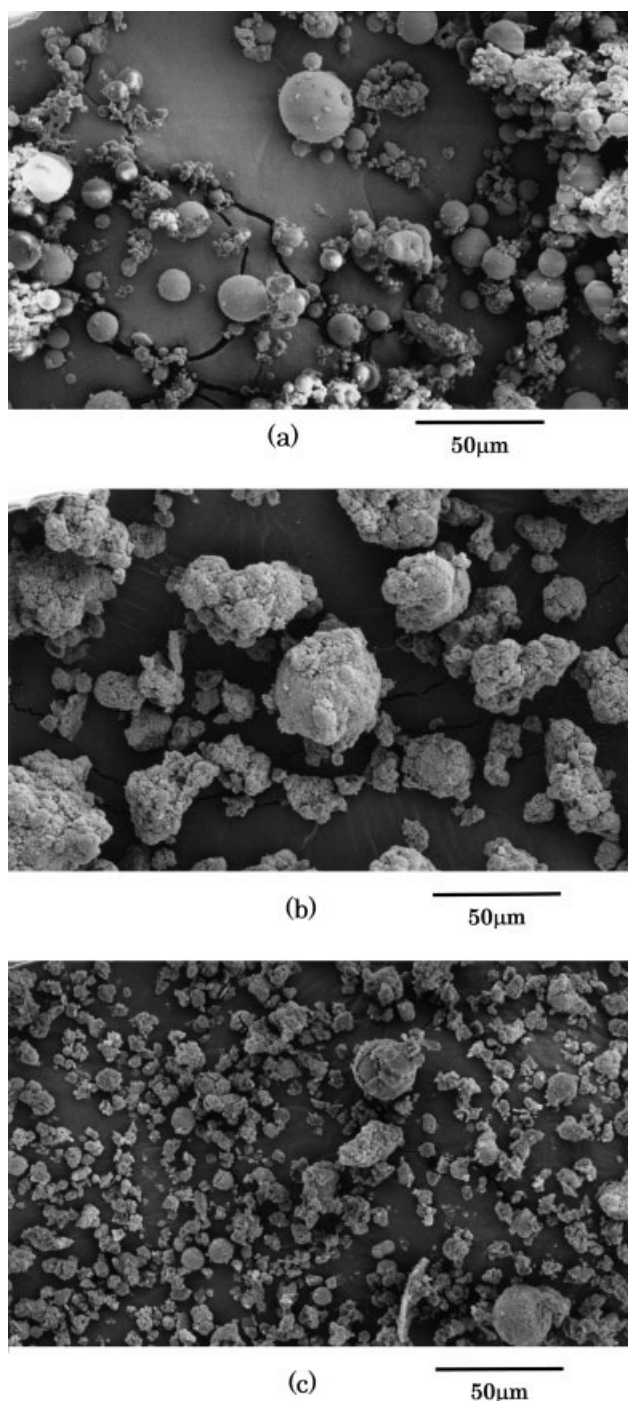


Figure 1 Morphology of fly ash (a), Na-Ze (b), and Ca-Ze (c) by SEM.

morphology of fly ash by SEM was shown in Figure 1(a). The average diameter of the particle of fly ash was about 20 μm and maximum diameter of those was about 30 μm . Maximum particle size of condensed fly ash was 70 μm . According to the elemental analysis, the principal constituents of fly ash were SiO_2 and Al_2O_3 , and small amount of Fe ion was also recognized. Na-Ze was obtained from the reaction of the fly ash with NaOH aqueous solution.

The morphology of Na-Ze by SEM was shown in Figure 1(b). The surface of spherical Na-Ze was rough. And the diameter of many Na-Ze was 20–30 μm and the diameter of some Na-Ze was less than 10 μm . According to the elemental analysis of Na-Ze, the principal constituents were Si, Al, O, and Na. Ca-Ze was obtained from the reaction of Na-Ze with $\text{Ca}(\text{OH})_2$ aqueous solution by cation exchange. The morphology of Ca-Ze by SEM was shown in Figure 1(c). The surface of spherical Ca-Ze was also rough. And the diameter of much Ca-Ze was less than 10 μm . The true specific gravity, average particle size and particle size distribution of fly ash, Na-Ze, and Ca-Ze were shown in Table I.

As a reference of the artificial Zeolite, commodity CaCO_3 as a grinding filler, talc as a flat filler, and chopped strand of glass fiber were used. These morphology by SEM was shown in Figure 2. The character of those was also shown in Table I. The true specific gravity of commodity filler as CaCO_3 or talc was a little bit higher than that of artificial Zeolite. But it is difficult to adjust the volume ratio of each filler in the phenolic composite, because artificial Zeolite is porous and it has potential to impregnate phenolic resin. Consequently, in this study the content of the each filler was adjusted by the weight ratio of phenol novolac.

Phenol novolac was general industrial grade ($M_n = 800$, $M_w = 2000$) obtained from Asahi Organic Chemicals Industry Co., Ltd.

Preparation of molding compounds and evaluation of flowability

The molding compounds of phenolic resin were prepared from novolac(100 phr), hexamethylenetetramine as a curing agent(12 phr), zinc stearate as a lubricant(1 phr), and several fillers(100 phr) by hot roll-kneading (front roll : 100°C, 20 rpm, rear roll: 110°C, 24 rpm). Flowability of the molding compounds was examined by the disk cure test.⁹ Curing behavior was examined by compact rheometer.

Molding of composites and evaluation of properties

Phenolic composites were prepared by transfer molding from the molding compounds preheated by

TABLE I
True Specific Gravity (SG) and Particle Size of Fillers

	Fly ash	Na-Ze	Ca-Ze	CaCO_3	Talc	GF
SG	2.2	2.3	2.3	2.8	2.8	2.5
Average diameter (μm)	20	42	25	1.4	21	–
Distribution (μm)	3–70	5–74	5–67	0.3–13	1–93	–

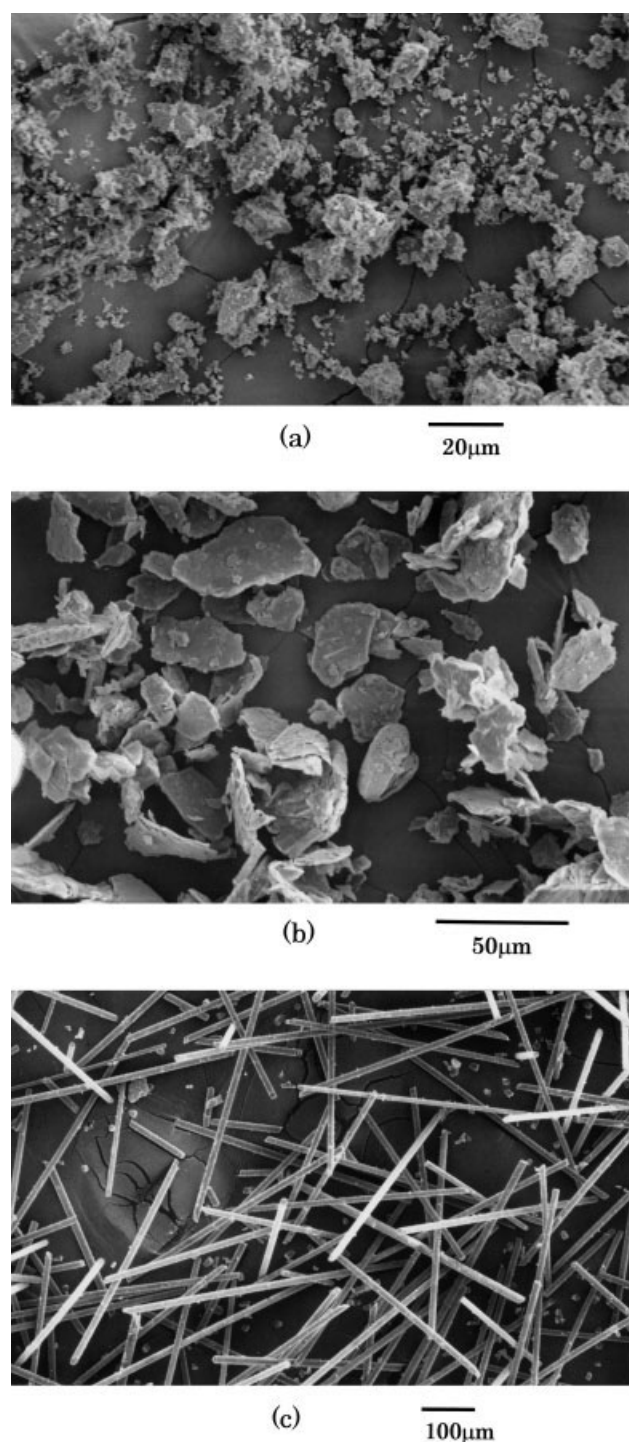


Figure 2 Morphology of CaCO_3 (a), Talc (b), and GF (c) by SEM.

high-frequency dielectric heating. Conditions of the transfer molding were 180°C and 15 min. Injection pressure of plunger was controlled 3–6 MPa according to the flowability of the molding compounds. Flexural strength, deflection temperature under load, volume resistivity, and coefficient of linear expansion were measured according to JIS K 6911.

RESULTS AND DISCUSSION

Flowability of molding compounds

Results of the disk cure test of the molding compounds containing fly ash, Na–Ze, or Ca–Ze as a filler were shown in Figure 3. Original flowability, indicated at intercept value of vertical line corresponding to JIS Disk Flow, of the compound containing fly ash was higher than that of others. The reasons for this phenomenon were considered by the sectional SEM morphology of these composites (Fig. 4). Spherical fly ash was dispersed in phenolic matrix and the diameter was 1–15 μm and the surface of the fly ash was smooth. The morphology of fly ash in the molding compound scarcely changed under the process of roll-kneading. On the other hand, in the composites containing Na–Ze or Ca–Ze, uneven fillers which were divided finely under the process of roll-kneading were dispersed in phenolic matrix. These fillers were divided less than 1 μm under and phenolic resin was impregnated into these fillers which maintained about 10 μm diameter. It was considered that the morphology of Na–Ze and Ca–Ze in the molding compound was almost same as those in the composite as shown in Figure 4, because the shear stress to the molding compound under the process of transfer molding was less than that under the process of roll-kneading. Generally speaking, the melt viscosity of the molding compound was lowered and the flowability of those was increased, when the shape of filler was spherical and the distribution of particle size of filler was wide.^{10,11} And the viscosity of the molding compound was increased and the flowability of them was lowered, when the diameter of filler in the compound was fine.¹ It was found that the results of

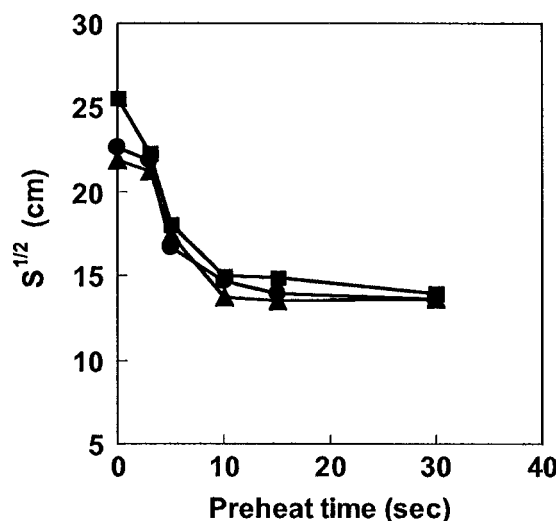


Figure 3 Flowability of molding compounds at 180°C by Disk cure test. ●: Ca–Ze, ▲: Na–Ze, ■: Fly ash.

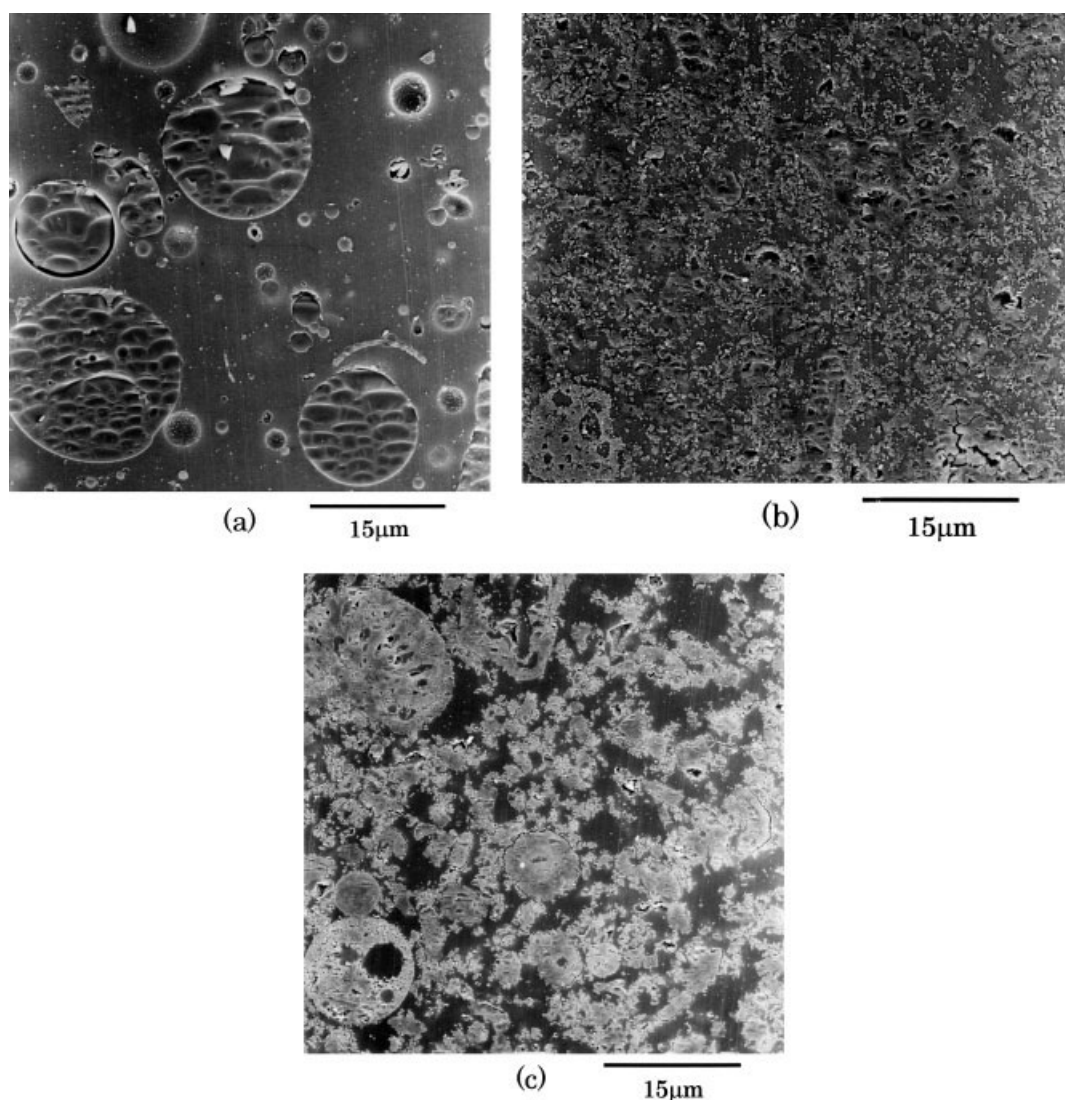


Figure 4 Sectional morphology of phenolic composites by SEM. (a) Fly ash, (b) Na-Ze, (c) Ca-Ze.

Figure 3 corresponded to these phenomena. It was not possible to extract the filler from the molding compound to measure the particle size distribution data and surface area of fillers. The reasons were as follows: (1) The gelation reaction of the molding compound began in limited amounts under the process of roll-kneading, (2) it was not possible to separate the fillers from the molding compound by solvent extraction or thermal decomposition and so on. So the particle size distribution and interface area between phenolic matrix and filler of each molding compounds were compared relatively by morphology of SEM as shown in Figure 4.

Results of the disk cure test of molding compounds containing commodity filler were shown in Figure 5. Original flowability of the molding compound containing CaCO_3 was superior to those containing Ca-Ze. The reason was considered that the volume ratio of CaCO_3 in the compound was lower

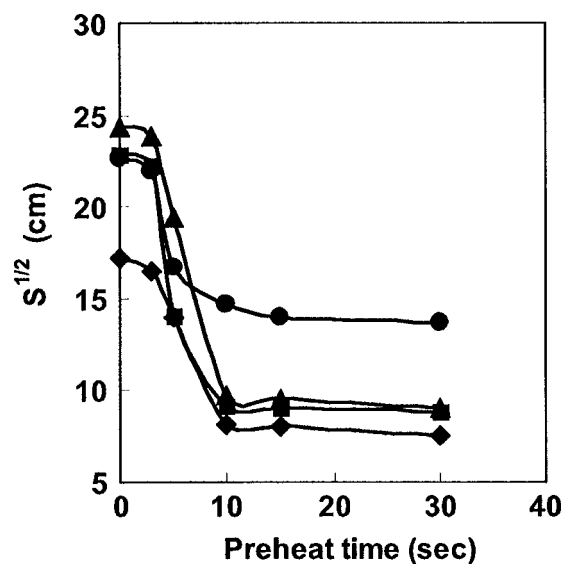


Figure 5 Flowability of molding compounds at 180°C by Disk cure test. ●: Ca-Ze, ◆: Glass fiber, ▲: CaCO_3 , ■: Talc.

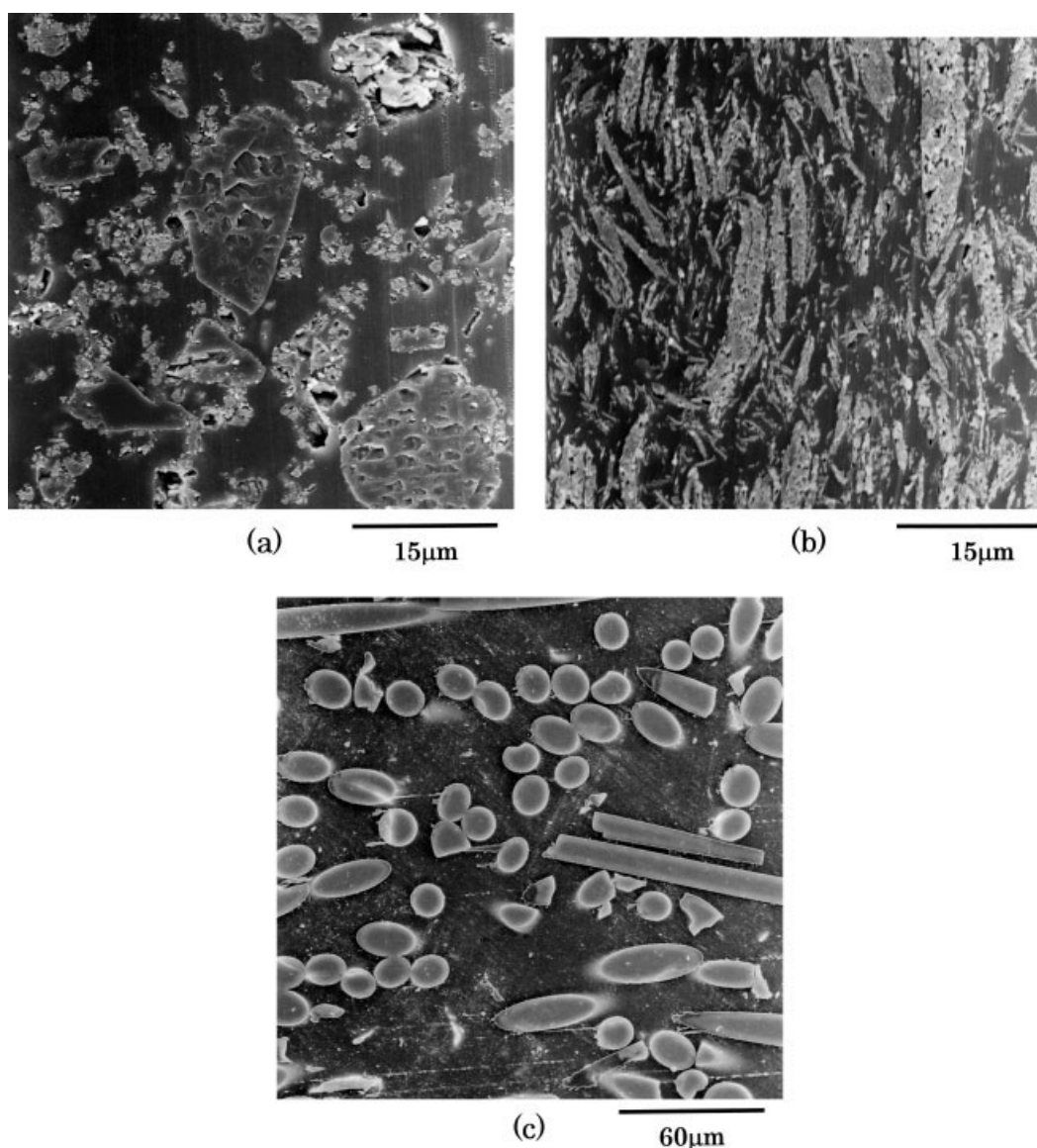


Figure 6 Sectional morphology of phenolic composites by SEM. (a) CaCO_3 , (b) Talc, (c) GF.

than that of Ca—Ze in the compound, because the true specific gravity of CaCO_3 was higher than that of Ca—Ze. But after gelation reaction began, that is, at solidifying point, the flowability of the molding compound containing CaCO_3 was inferior to those containing Ca—Ze. The reasons were considered as follows: (1) uneven CaCO_3 or talc which had above 10 μm diameter was dispersed in the phenolic matrix, because CaCO_3 or talc in the molding compound was not divided finely under the process of roll-kneading like Ca—Ze in the compound (Fig. 6).(2) It was possible that Ca^{2+} of CaCO_3 interacted with OH^- of phenolic resin and gelation reaction was accelerated, because $\text{Ca}(\text{OH})_2$ was used as curing accelerator of novolac cured with hexamethylenetetramine.¹²

Acceleration of the curing reaction by CaCO_3 was also suggested by viscosity curve of compact rheom-

eter (Fig. 7). The viscosity curve of the molding compounds was examined under the follow conditions; the molding compound containing Ca—Ze or CaCO_3 was inserted between two parallel plates at 100°C. The thickness of the molding compound was about 1 mm. And the temperature of those was raised to 180°C corresponding to the molding temperature rapidly vibrating at 1 Hz. As a result, at first the complex viscosity of both was lowered and that of the molding compound containing CaCO_3 was a little bit lower than those containing Ca—Ze at below about 4 min. This result corresponded to the result that the original flowability of the molding compound containing CaCO_3 was superior to those containing Ca—Ze by disk cure test (Fig. 3). Second, after 4–5 min the complex viscosity of both began to rise because the gelation reaction started. At this stage the complex viscosity of the molding com-

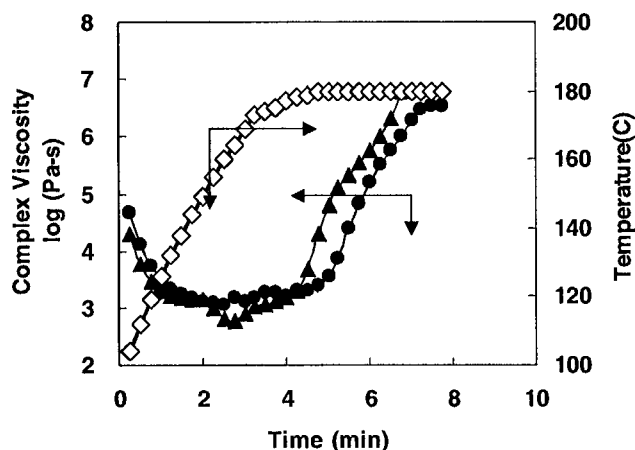


Figure 7 Curing behavior of phenolic compounds by DMA. ●: Ca-Ze. ▲: CaCO₃.

pound containing CaCO₃ was higher than those containing Ca-Ze. This result corresponded to the result that after gelation reaction began, the flowability of the molding compound containing CaCO₃ was inferior to those containing Ca-Ze by disk cure test (Fig. 3).

These results suggested that the phenolic composites from the molding compounds containing fly ash or the artificial Zeolite were able to prepared by transfer molding at low injection pressure of plunger, because the flowability of these compounds in hot cavity of mold was superior to those of the compounds containing commodity filler. It was expected that the properties of the phenolic composite were improved and the anisotropy of those decreased owing to decrease the residual stress in the composite when the composite was prepared at lower injection pressure of plunger. In this study, the injection pressure of plunger of the molding compounds containing fly ash or the artificial Zeolite, CaCO₃ or talc, and chopped strand of glass fiber were 3, 4, and 6 MPa, respectively.

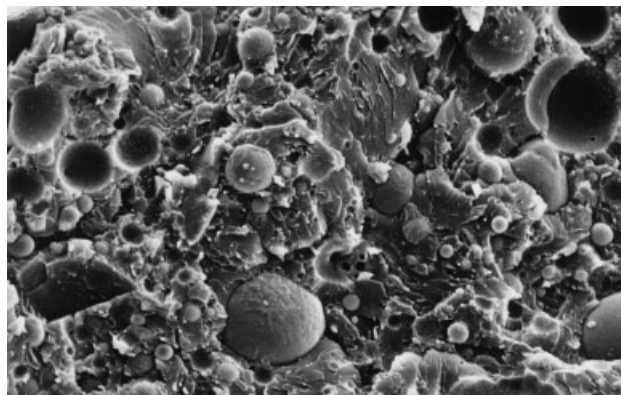
Properties of phenolic composite

Flexural strength, deflection temperature under load, and volume resistivity of phenolic composites con-

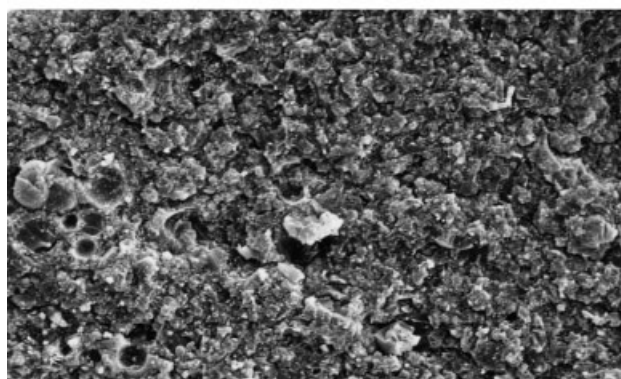
TABLE II
Properties of Phenolic Composites

	Filler		
	Fly ash	Na-Ze	Ca-Ze
Flexural strength (MPa)	110	90	105
Deflection temp. under load (°C)	166	188	186
Volume resistivity (Ω-cm)	8.8 × 10 ¹¹	3.4 × 10 ¹⁰	4.4 × 10 ¹²

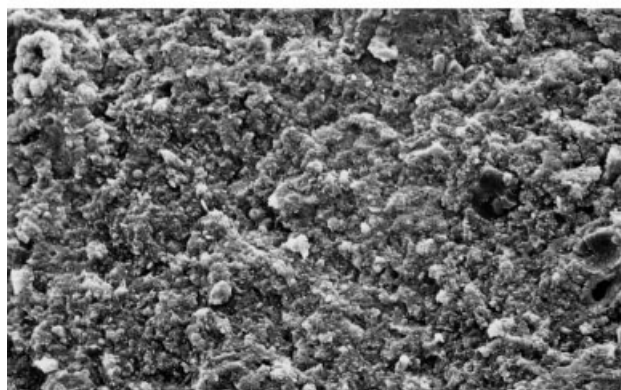
taining fly ash, Na-Ze, or Ca-Ze as filler were shown in Table II. The phenolic composite containing fly ash had most superior flexural strength (110 MPa). The flexural strength of phenolic composite containing Ca-Ze was 105 MPa and those containing Na-Ze was 90 MPa which was about 85% value of those containing Ca-Ze. On the other hand, the heat resistance of the composite containing Na-Ze was almost same as those containing Ca-Ze. But



(a) 10µm



(b) 10µm



(c) 10µm

Figure 8 Morphology of fracture surface of phenolic composites by SEM. (a) phenolic/Fly ash, (b) phenolic/Na-Ze, (c) phenolic/Ca-Ze.

TABLE III
Thermal Expansion Coefficient of Phenolic Composites

	Filler		
	Fly ash	Na—Ze	Ca—Ze
Coefficient of linear expansion (MD)			
25°C	2.4×10^{-5}	3.1×10^{-5}	2.4×10^{-5}
50°C	2.5×10^{-5}	3.6×10^{-5}	2.7×10^{-5}
100°C	2.9×10^{-5}	2.9×10^{-5}	3.0×10^{-5}
Ratio of MD to TD of Coefficient of expansion			
25°C	1.20	1.03	1.06
50°C	0.94	1.03	1.04
100°C	1.03	0.96	1.03

the composite containing fly ash had most inferior heat resistance, that is, the value of deflection temperature under load of the composite containing fly ash was about 20°C lower than those containing Na—Ze or Ca—Ze.

The reasons of those results were examined from morphology by SEM of fracture surface of test piece after flexural test (Fig. 8). It was considered that the fracture of the phenolic composite containing fly ash progressed along the interface between the phenolic matrix and fly ash, because many spherical fly ash were dispersed in the fracture surface. On the other hand, the fracture surface of the composite containing Na—Ze or Ca—Ze was uneven and the interface between the phenolic matrix and filler was not clear-cut. These results were corresponded to the sectional morphology of these composites by SEM shown in Figure 4. That is to say, the spherical fly ash was dispersed in phenolic matrix maintaining the shape of filler before hot roll-kneading. On the other hand, Na—Ze or Ca—Ze which was divided less than 1 μm under the process of roll-kneading was dispersed in phenolic matrix and phenolic resin was impregnated into these fillers which maintained about 10 μm diameter. Generally speaking, the tensile strength of composite increases as the particle size of filler in matrix becomes small and surface area of filler becomes wide.^{3,13} However, in this study, the flexural strength of phenolic composite containing fly ash was superior to those containing Na—Ze or Ca—Ze, though particle size of fly ash in the phenolic composite was bigger than those of Na—Ze or Ca—Ze in the phenolic composite. The reasons for this phenomenon were considered as follows: (1) Fly ash had wide distribution of particle size from above 10 μm to about 1 μm , (2) Fly ash was very tough because it was scarcely divided under the process of roll-kneading, and (3) the artificial zeolite was brittle, though interface area between phenolic matrix and the artificial zeolite was wider than those between phenolic matrix and fly ash, and though there was anchor effect between phenolic

resin and the artificial zeolite. The flexural strength of phenolic composite containing Ca—Ze was superior to those containing Na—Ze. The reasons were considered as follows: (1) the chemical interaction between Ca^{2+} in Ca—Ze and OH^- in phenolic resin was stronger than those between Na^+ in Na—Ze and OH^- in phenolic resin, and (2) the physical interaction between Ca—Ze and phenolic matrix was stronger than those between Na—Ze and the matrix owing to the anchor effect derived from impregnation of phenolic resin into Ca—Ze.

Heat resistance of phenolic composite containing Ca—Ze or Na—Ze was superior to those containing fly ash. The reasons were considered as follows: (1) the artificial zeolite was divided and dispersed finely in the phenolic matrix and phenolic resin was impregnated into the artificial zeolite, and (2) ratio of continuous phenolic phase in the composite containing fly ash was more than those in the composite containing the artificial zeolite, and phenolic resin was scarcely impregnated into fly ash (Fig. 4).

Electrical insulation of the phenolic composite containing Ca—Ze was most superior and those containing Na—Ze was inferior (Table II). The reasons were presumed as follows: (1) Na^+ in Na—Ze and Fe^{2+} in fly ash had bad influence upon the electrical insulation of the composite, and (2) Ca^{2+} in Ca—Ze did not have a bad influence upon the electrical insulation of the composite, owing to the strong interaction between Ca^{2+} in Ca—Ze and OH^- in phenolic resin.

Thermal expansion coefficient of the phenolic composites containing fly ash, Na—Ze, or Ca—Ze as a filler were shown in Table III. Ratio of machine direction (MD) to traverse direction (TD) of coefficient of linear expansion of the composite containing Na—Ze or Ca—Ze was almost 1. The result suggested that these composites were almost isotropic. The reasons were considered as follows: (1) aspect

TABLE IV
Properties of Phenolic Composites

	Filler		
	GF	CaCO_3	Talc
Flexural strength (MPa)	190	90	78
Deflection temp. under load (°C)	183	165	167
Volume resistivity ($\Omega\text{-cm}$)	1.4×10^{12}	1.9×10^{12}	2.4×10^{12}
Coefficient of linear expansion (MD)			
25°C	3.2×10^{-5}	2.2×10^{-5}	1.8×10^{-5}
50°C	2.4×10^{-5}	2.7×10^{-5}	2.1×10^{-5}
100°C	2.5×10^{-5}	3.0×10^{-5}	2.4×10^{-5}
Ratio of MD to TD of Coefficient of expansion			
25°C	0.76	0.85	0.85
50°C	0.70	0.90	0.91
100°C	0.69	0.88	0.83

ratio of these fillers was almost 1, (2) these fillers were dispersed finely in the phenolic matrix, and (3) ratio of continuous phenolic phase in the composite containing Na—Ze or Ca—Ze is less than those in the composite containing fly ash.

Next, the several properties of the phenolic composites containing glass fiber (GF), calcium carbonate (CaCO_3), or talc as a filler were shown in Table IV to compare with those of the phenolic composite containing Ca—Ze. The phenolic composite containing GF had most superior flexural strength (190 MPa). But the flexural strength of the composite containing CaCO_3 was about 90% value of those containing Ca—Ze and those containing talc was about 75% value of those containing Ca—Ze. Heat resistance of the phenolic composite containing Ca—Ze was almost same as those containing GF and was very superior to others. Electrical insulation of the composite containing Ca—Ze was the most superior. Coefficient of the phenolic composites containing GF, CaCO_3 , or talc was almost same level as those containing Ca—Ze. However, Ratio of MD to TD of coefficient of linear expansion of the composite containing GF, CaCO_3 , or talc was less than 1, though those containing Ca—Ze was almost 1. Especially the composite containing GF was anisotropic.

CONCLUSIONS

To improve the flowability of phenolic molding compounds and the several properties of phenolic composites, spherical fly ash or artificial Zeolite such as sodium type Zeolite (Na—Ze) or calcium type Zeolite (Ca—Ze) were used as fillers of phenolic resin. As a result, the molding compounds containing fly

ash and artificial Zeolite as a filler was superior to that of the compounds containing glass fiber (GF), calcium carbonate (CaCO_3), or talc as a filler. And the phenolic composite containing Ca—Ze had most superior heat resistance, electrical insulation, and flexural strength, though in the lastly listed property it ranked next to the GF-filled composite. The linear expansion coefficient of the composite containing Ca—Ze was as low as almost isotropic. The reasons of obtaining these excellent properties were thought to be as follows: (1) Ca—Ze which was divided less than 1 μm under the process of roll-kneading was dispersed in phenolic matrix and phenolic resin was impregnated into these fillers which maintained about 10 μm diameter. (2) The surface chemical and physical interaction between the resin and Ca—Ze was higher than that between the resin and the other fillers.

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