Physical Properties of Epoxy Molding Compound for Semiconductor Encapsulation According to the Coupling Treatment Process Change of Silica

WHAN GUN KIM,[1] JE HONG RYU[2]

[1] Department of Chemistry, Seokyeong University, 16-1 Jeongneung-Dong, Seongbuk-Ku, Seoul 136-704, South Korea

[2] Chemical R&D Center, Cheil Industries Inc., 332-5 Gocheon-Dong, Euiwang-Shi, Kyungki-Do, South Korea

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ABSTRACT: The change of physical properties of an epoxy-molding compound (EMC) for semiconductor encapsulation according to the coupling treatment process change was investigated. Three different coupling treatment processes were applied in this study: the pretreatment method (PM), the internal pretreatment method (IPM), and the integral addition method (IAM). Especially, we suggested a simple and economic process, the IPM process, in which the drying and powdering process is excluded compared with the PM process. The optimum content range of the coupling agent is 1.0–2.0 wt % based on the weight of the filler, which is about a 1.3–2.5 coating layer. The flexural strength and internal stress of EMC made by the IPM process is almost equivalent to that made by the PM. We applied the model of complex layers of a silane coupling agent at the filler/matrix interface in interpretating the mechanical and thermal properties of EMC and obtaining the relationships between physical properties and the coupling process. It can be concluded that the IPM process is an effective and economic process to be able to obtain a good reliable EMC with strong mechanical strength and low internal stress. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1975–1982, 1997

Key words: epoxy molding compound; silane coupling; semiconductor encapsulation

INTRODUCTION

Silane-coupling agents are generally adsorbed on a filler surface and are most effectively used to improve the mechanical strength of composite materials. Recently, as chip sizes in semiconductors are getting larger, and the dimensions of devices are getting smaller, higher thermal resistance, moisture resistance, and lower modulus properties are needed to encapsulate materials for packaging.[1–3] Therefore, coupling studies can show the methods to improve these properties.

Generally, physical properties of polymer composite materials with a fine particle filler should be closely dependent on the surface-adhesion properties between the base resin and filler. Many studies on the analysis of surface phenomena between them have been performed in order to improve the physical properties of polymer composite materials.[4–6] Early studies on silane-coupling agents were primarily involved with glass-fiber/polymer composites. This work resulted in several theories as to how silanes provide improved mechanical strengths and hydrothermal stability. The most widely accepted was the chemical-bonding theory due to the dual functionality of the silane molecule.[7] The usual scheme of the reaction pictures was that of the silane being hydrolyzed to give an intermediate, which then will react with silanols on the surfaces of the glass fibers.

Two general methods are usually given for the

Correspondence to: W. G. Kim.
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Table I Raw Materials Used

Component	Chemical Structure /Name	Grade Name (Maker)
Epoxy resin	o-Cresol novolac epoxy: $-(C_6H_2(OCH_2CH(O)CH_2)(CH_3)-CH_2)_n-$	EOCN-1020 (Nippon Kayaku Co.)
Hardener	Phenol novolac: $-(C_6H_3(OH)-CH_2)_n-$	PSM-4261 (Gunnei Chemical Co.)
Accelerator	Triphenylphosphine	BASF AG.
Filler	Fused silica	FS-892 (Denki Kakaku Co.)
Coupling agent	$(CH_3O)_3SiCH_2CH_2CH_2OCH_2CH(O)CH_2$	TC-100 (Union Carbide Co.)
Modifier	Epoxy-terminated polydimethylsiloxane	X-22-3667 (Shinetsu Chemical Co.)

incorporation of silane-coupling agents: the dry blending-type pretreatment method (PM) or the integral addition method (IAM).[8] Reinforced plastics made with the PM often have better mechanical and physical properties than do those made with the IAM. However, few polymer composites with a fine particle filler are prepared with the PM because of the economic aspects and the difficulty and complexity of the process.

In this study, we suggested a relatively simple coupling treatment method, the internal pretreatment method (IPM), which excluded the drying and powdering process in the dry blending-type PM. Especially, the change of physical properties of the epoxy molding compound (EMC) was investigated according to the change of the coupling treatment and the content of the coupling agent. We report the optimum process and range of the coupling agent, and also the relationships between the physical properties of the EMC and the coupling process change are represented.

EXPERIMENTAL

Materials

The epoxy resin used in this study was an *o*-cresol novolac epoxy resin obtained from Nippon Kayaku Co. A phenol novolac resin as the hardener was used as received from Gunnei Chemical Co., and triphenylphosphine produced by BASF was used as an accelerator. The filler was a grind-type fused silica (mean diameter = 16 μm, specific surface area = 2.5 m^2/g) which is made by Denki Kakaku Co., and the coupling agent was 3-glycidoxypropyltrimethoxysilane (minimum surface area = 330 m^2/g) produced by Union Carbide Co. An epoxy-terminated polydimethylsiloxane polymer manufactured by Shinetsu Chemical Co. was used as a modifier to reduce internal stress. Detailed descriptions of the chemical structures and grade names are summarized in Table I.

Sample Preparation

Detailed recipes in this experiment are shown in Table II. Three different process methods were applied in this study to compare the physical properties of the EMC according to the coupling treatment change. The first method is the pretreatment method (PM) of the dry mix type which consists of dispersing silane over the filler at high shear for intimate mixing using a Henshel mixer (Mistuimike Co., Model FM 10).[9]

The silane was added neat dropwise, and then the treated filler was dried at 80°C for 1 h to liberate the hydrolysis products and powdered. Using this filler, EMC specimens were prepared through

Table II Basic Formulation of the EMC in This Study

Component	Grade Name	Parts by Weight
Epoxy resin	EOCN-1020	100
Phenol resin	PSM-4261	54.4
Triphenylphosphine		2.3
Filler	FS-892	480
Coupling agent	TC-100	Variable (0–3 wt % based on weight of filler)
Modifier	X-22-3667	10

a premixing, melt-mixing, cooling, crushing, and molding process.[10] Second is the internal pretreatment method (IPM) in which drying and powdering processes are excluded compared with the PM. Other processes of the EMC sample preparation are the same as those performed in the PM process. Third is the integral addition method (IAM) in which the coupling pretreatment should not be performed and which takes a premixing process directly. Other processes of the EMC sample are the same. The detailed processes of this experiment are summarized in Table III.

Measurements

Flexural Strength and Modulus

The specimens of 6.4 × 12.7 × 127 mm size were measured under the conditions of a span width of 100 mm and a test speed 2.8 mm/min, at room temperature using a Universal Test Machine (UTM, Zwick Co.) in accordance with ASTM D-790.

Thermal Expansion Coefficient and Temperature of Glass Transition

The specimens of 5 × 5 × 15 mm length were measured under the condition of temperature increasing at a rate of 10°C/min using a thermal mechanical analyzer (TMA, Stanton Redcroft Co., TMA 1000) from room temperature to 250°C. The coefficient of linear thermal expansion was obtained from the thermal expansion quantity. The inflection point of the TMA curve was defined as the temperature of the glass transition (T_g). All the details in the measurements were given in a preliminary note.[11]

RESULTS AND DISCUSSION

The flexural strength of the EMC prepared in three different coupling treatment processes (PM, IPM, and IAM) is represented in Figure 1. This figure shows that the PM and IPM process data are higher value in flexural strength than are those of the IAM. Generally, the adhesion between the filler and the matrix resin is not strong in the case of the IAM, i.e., as exfoliation between the filler and the matrix resin could happen before breakdown, the flexural strength of the EMC could not be improved. In the case of the PM, the breakdown of the EMC is not at the surface between the filler and the resin, but predominantly in the matrix resin, because of the strong

Table III Comparison of EMC Preparation Process in Each Coupling Treatment

Process	Pretreatment Method (PM)	Internal Pretreatment Method (IPM)	Integral Addition Method (IAM)
Coupling pretreatment	Silica + CA	Silica + CA	×
Drying	80°C/1 h	×	×
Powdering	○	×	×
Premixing	All components	All components	All components
Melt-mixing	○	○	○
Cooling	○	○	○
Crushing	○	○	○
Molding	○	○	○

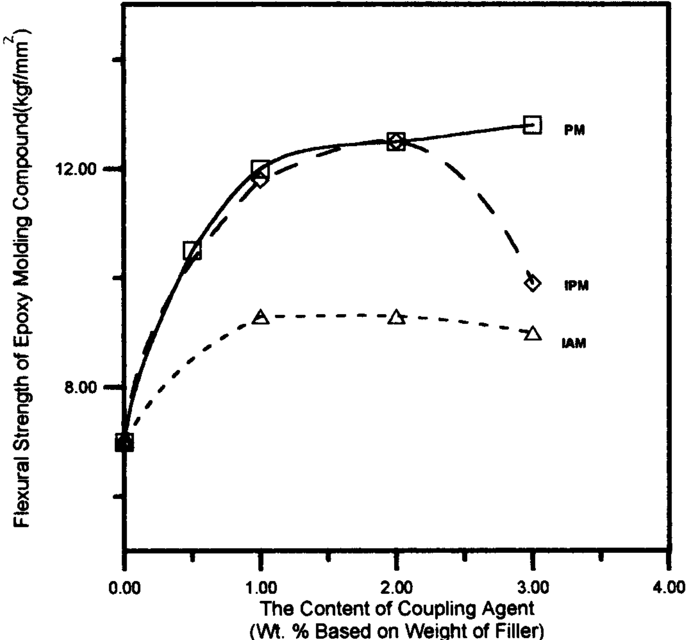

Figure 1 The change of flexural strength of the EMC according to the content of the coupling agent.

adhesion between the filler and the matrix resin.[12] Therefore, the PM process is better than is the IAM in respect of mechanical strength. The IPM process data are almost equivalent to the data of the PM up to 2.0 wt % of the coupling agent based on the weight of the filler. However, they sharply decrease with the content of the coupling agent beyond 2.0 wt %. It can be thought that this decrease is the weakening of the adhesion strength between the filler and the resin matrix due to the agglomeration of the coupling agent with a relatively high concentration of the coupling agent in the case of no drying and powdering process, because the hydrolysis product between the coupling agent and the filler cannot be removed completely.

The theoretical coating thickness (which equals 1 for the monolayer) of silane was calculated by the following equation and the results are represented in Figure 2:

$$\text{Coating thickness} = \frac{\text{weight of filler (g)} \times \text{silane coverage for monolayer (m}^2\text{/g)}}{\text{filler weight (g)} \times \text{filler surface area (m}^2\text{/g)}} \quad (1)$$

As shown in Figure 2, 2.0 wt % of the coupling agent is about a 2.5 layer coating thickness, and the relationship between the coating thickness and flexural strength is shown in Figure 3. It can be considered that a minimum 1.3 layer coating thickness is needed to achieve the effective mechanical strength of the EMC, and a maximum 2.5 layer coating thickness is effective in the IPM process.

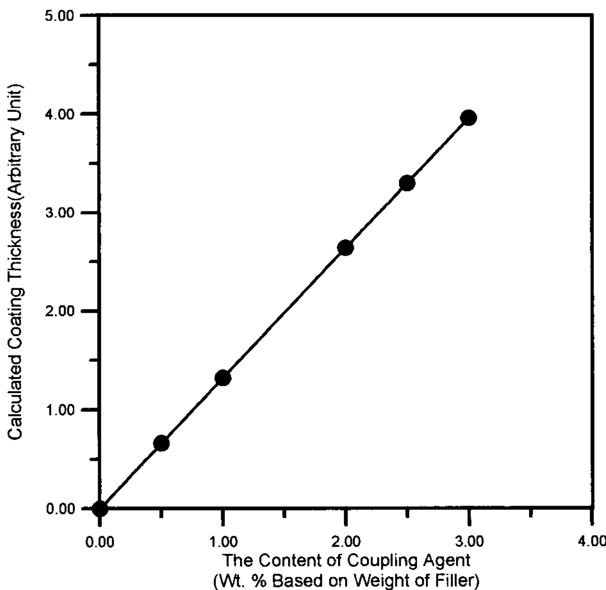

Figure 2 The change of the calculated coating thickness according to the content of the coupling agent.

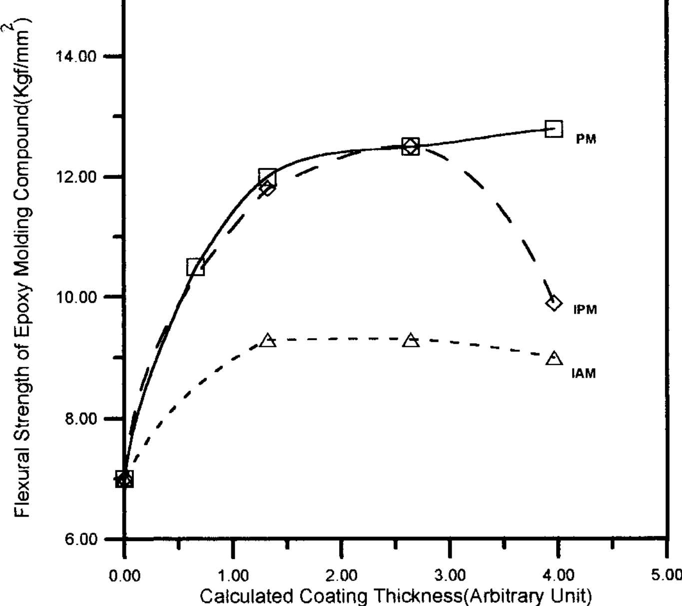

Figure 3 The relationships between the flexural strength of the EMC and the calculated coating thickness.

The modulus is one of the basic properties of the EMC; the primary intention of filler incorporation is usually to increase the stiffness of the resultant material.[13] Figure 4 shows the flexural modulus of the EMC with the content of the coupling agent, in which it can be seen that the IPM process data have a higher value than that of the PM up to 2.0 wt %. This phenomenon can be explained by the complex layers of the silane-coupling agent at the filler/matrix interface. These layers have been defined as the chemically reacted region (X region), the chemisorb region (Y

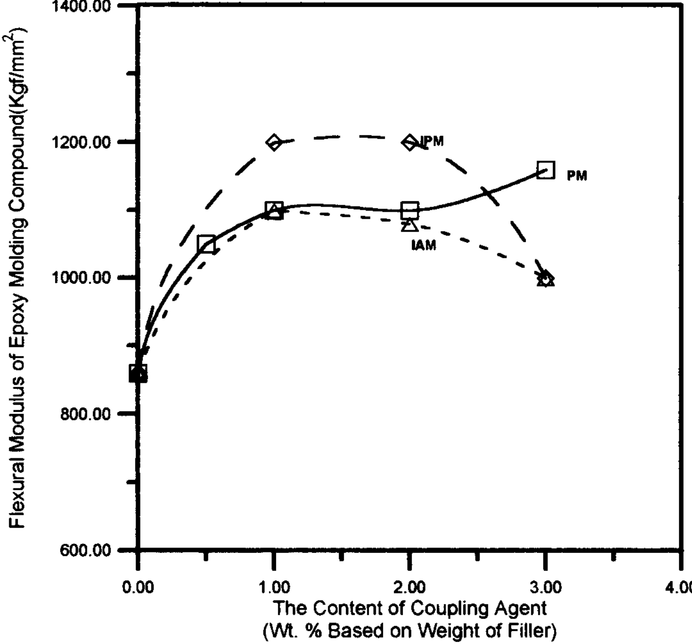

Figure 4 The change of the flexural modulus of the EMC according to the content of the coupling agent.

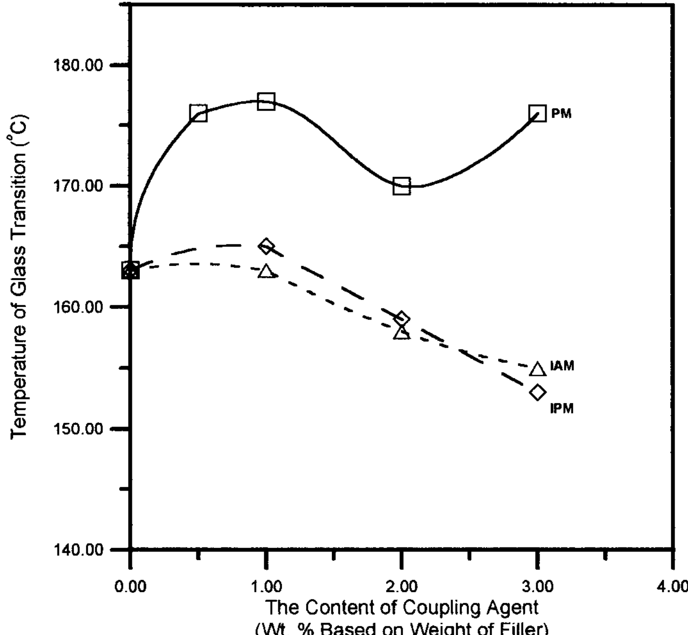

Figure 5 The change of temperature of the glass transition according to the content of the coupling agent.

region), and the physisorb region (Z region). The X region is the innermost region next to the surface of the filler and is not easily removed chemically or physically. The next layer is the Y region, which cannot be easily removed by water. The outermost layer is the Z region, which can be easily removed by water at room temperature.[14,15]

Therefore, the higher modulus value of the EMC in the IPM process indicates less X region than in the PM. Although the X region of the IPM

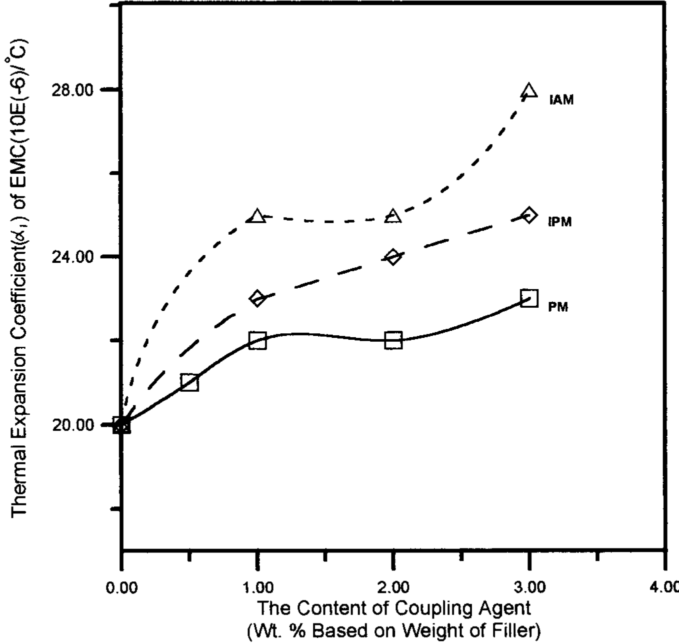

Figure 6 The change of thermal expansion coefficient of the glassy state (α_1) according to the content of the coupling agent.

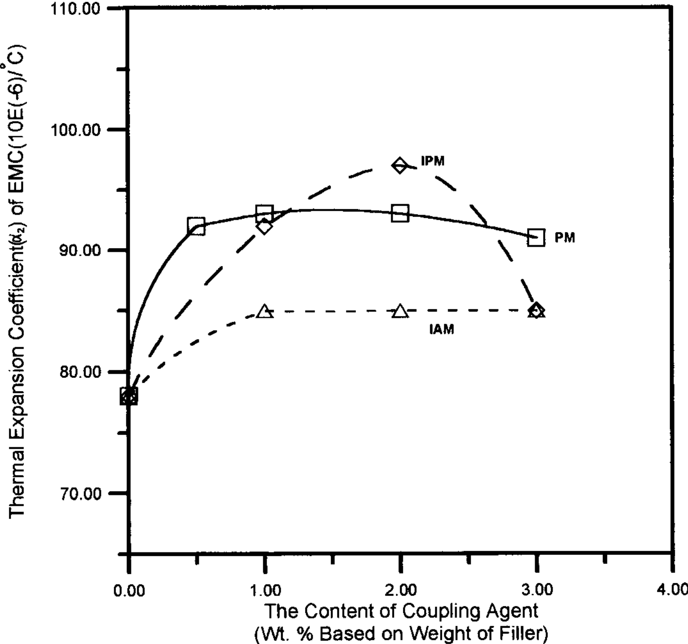

Figure 7 The change of the thermal expansion coefficient of the rubbery state (α_2) according to the content of the coupling agent.

process is less than that of the PM, an equal value of the IPM in flexural strength is due to the higher portion of the Y and Z regions, which should provide a network where the matrix resin penetrates the chemisorbed region and the physisorbed silane migrates into the matrix.[16]

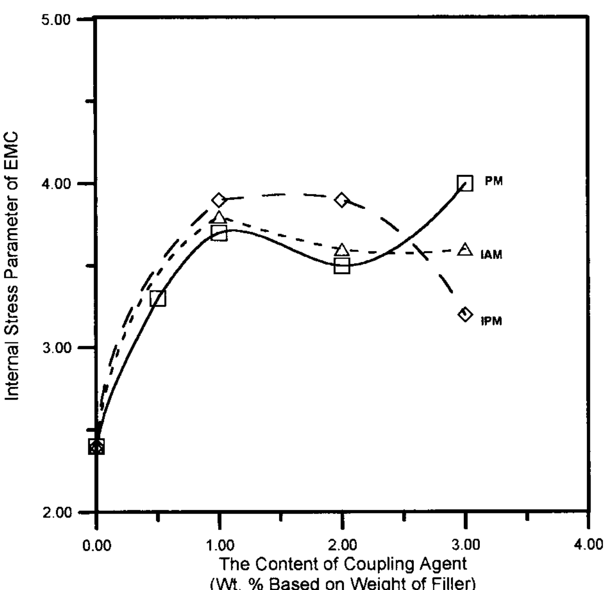

Figure 8 The change of the internal stress parameter of the EMC according to the content of the coupling agent.

Figure 5 shows the change of T_g according to the content of the coupling agent. Generally, as the crosslinking density increases, the T_g of the resin containing the same segments increases.[17] It can be seen that the PM process data are higher in value than are the other processes in this figure, which means that the PM process would have a higher crosslinking density than that of the IAM or the IPM process. It is conceivable that the higher crosslinking density of the PM process is due to the role of the crosslinking agent or of the coupling agent. As above-mentioned, the PM process may have more X region than have the others, therefore representing a higher T_g.

Many studies have been made on the relation between the crosslinking density and physical properties for the epoxy resin cured with various amine or acid anhydride hardeners, and it has been reported that the crosslinking density is the most dominant factor that determines the various physical properties of cured neat epoxy resins.[18,19] When the crosslinking density increases, the thermal expansion coefficient in the glassy region (α_1) also increases, while the thermal expansion coefficient in the rubbery region (α_2) decreases.[20]

The relationships between the thermal expansion coefficient and the content of the coupling agent are shown in Figures 6 and 7. In the case of the PM process, it can be seen that similar

relationships were observed, i.e., as the crosslinking density increases (T_g increases), α_1 also increases while α_2 decreases; however, such relationships cannot be found out in other processes: IPM and IAM. It is conceivable that this is also because of a large portion of a chemically bonded crosslinking network in the PM process which contains more X region than do the others.

As described in the Introduction, one of the most important techniques to achieve a reliable EMC for semiconductor encapsulation is the reduction of the internal stress, which is represented as the following equation[21]:

$$\sigma = \int_{T_r}^{T_g} E(\alpha_r - \alpha_s)\, dT \tag{2}$$

where σ is the internal stress, T_g is the temperature of the glass transition, T_r is the room temperature, E is the flexural modulus of the EMC, α_r is the thermal expansion coefficient of the EMC, and α_s is the thermal expansion coefficient of the chip. If α_s is constant and σ is linearly dependent on the temperature to make a relative and simple comparison, eq. (2) could be modified approximately, as follows:

$$\sigma_m = E \times \alpha_r \times T_g \tag{3}$$

The modified internal stress (σ_m) calculated by eq. (3) according to the coupling treatment process change is represented in Figure 8. It can be seen that there are no distinguishable changes between the coupling treatment process up to 2.0 wt % of the coupling agent. Therefore, it can be concluded that the IPM process is an effective and economic process to be able to obtain a reliable EMC with strong mechanical strength and low internal stress.

CONCLUSION

We investigated the physical properties of the EMC for semiconductor encapsulation according to the coupling treatment process change: PM, IPM, and IAM. In these processes, the optimum content range of the coupling agent is from 1 to 2 wt % based on the weight of the filler. The IPM process is effective in order to obtain a reliable EMC product because the process is simple and economic compared to the PM, and the flexural strength and internal stress of the EMC is almost equivalent to the PM process data. We used the complex layers' model of the silane coupling agent at the filler/matrix interface, the chemically reacted region (X region), the chemisorb region (Y region), and the physisorb region (Z region), in order to explain the relationships between the physical properties and the coupling process change of the EMC.

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