Novel Microencapsulated Curing Accelerator for Prolonging Shelf Life of Epoxy Resin Composition

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ABSTRACT: A novel micron-sized microencapsulated curing accelerator, imidazole (Im), particles, was first prepared by an ultrasound-assisted dispersing and spray-drying method and can significantly prolong the shelf life of epoxy resin-based microelectronic packaging material. The shell of the encapsulated particles was made from ladderlike copoly(phenyloctyl silsesquioxane) (Ph–Oct–T), which was synthesized by a "stepwise coupling polymerization" method. Its softening or flowing temperature can be adjusted by changing the composition. Carbon tetrachloride (CCl_4) was chosen as both a solvent of the capsular material Ph–Oct–T and a suspending/precipitating agent of the fine Im particles. Subsequently, the solution containing Ph–Oct–T and suspended Im particles was treated by a spray-drying process to produce the microencapsulated curing accelerator, Im particles, whose size and appearance was observed by scanning electronic microscopy (SEM). A greatly improved shelf life of the epoxy resin composition containing this microencapsulated curing accelerator was exhibited by curing tests and DSC measurements. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 873–878, 2002

Key words: microencapsulated; epoxy-curing accelerator; imidazole; shelf life; ladderlike copolysiloxane; curing of polymers; polysiloxanes

INTRODUCTION

Epoxy resin is one of the most important thermosetting polymers. It exhibits many outstanding properties, such as a good adhesive property, fair thermal stability, high chemical resistance, and electrical insulation.

However, an epoxy resin-based microelectronic packaging material containing a solidifying agent (usually phenolic resin) and a curing accelerator [e.g., imidazole (Im) and its derivatives] has to be stored or transported at low temperature (-20 to -10°C), because it is easily crosslinked at room temperature. To prolong its shelf life, separating the curing accelerator from the epoxy resin during storage by an encapsulation technique is an effective method.[1–3] When the temperature increases to a desired point, the capsules are broken and the curing accelerator would be liberated. The capsular materials can be hollow inorganic materials such as zeolite[1] or organic polymers.[2,3] Obviously, from a practical standpoint, the polymers used to encapsulate the curing accelerator of an

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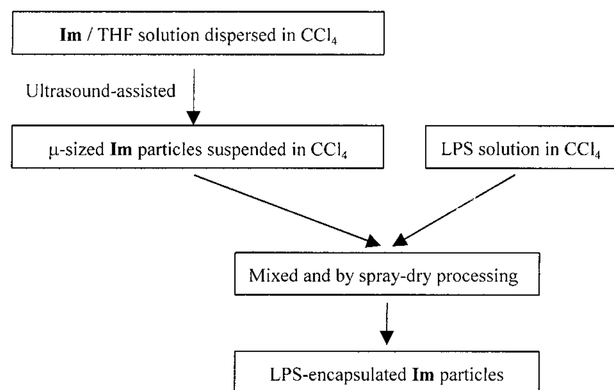


Scheme 1 Schematic process used to fabricate encapsulated Im particles.

epoxy resin microelectronic packaging material should possess controllable a softening-point or suitable decomposition temperature, besides good electric insulating resistance.

Fortunately, during the last decade, a series of novel ladderlike polysilsesquioxanes (LPSs) with different side groups, including inert[4,5] or reactive side groups,[6–9] short or longer side chains,[10,11] and their copolymers, have been synthesized by "stepwise coupling polymerization"[12,13] by our group. The inorganic and ladderlike main chain and easy modification of side groups make LPSs possess fine comprehensive properties, especially good insulating resistance, film-forming ability, and fair adhesion to different substrates. Furthermore, its physical properties, including softening or flowing temperature, can be adjusted by copolymerization. Therefore, LPS is a very hopeful candidate for capsular material of a curing accelerator in an epoxy resin composition.

The microencapsulation technique is significant and widely applied in diverse fields such as medicine, pharmaceutical, materials science, and the paint industry.[14–17] There exist a number of fabrication methods to produce nanostructured composite particles and hollow microspheres therefrom. These include nozzle-reactor systems (spray drying or pyrolysis)[14,18–22] and emulsion/phase separation techniques coupled with a sol–gel process. Scheme 1 illustrates a fabrication process to produce an LPS-capsulated curing accelerator, including an ultrasound-assisted formation of the micron-sized Im core particles and the coating of the particles with an LPS-based shell by spray-dry processing as a result of surface absorption.

EXPERIMENTAL

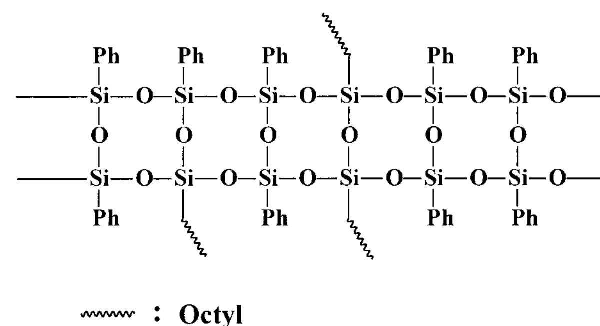
Material and Techniques

The reagents such as phenyltrichlorosilane, octyltrichlorosilane, 1,4-phenylenediamine (PDA), and triethylamine (TEA) were commercially available and purified by distillation prior to use. All solvents were dried in advance according to standard procedures.

IR measurement was carried out on a Perkin–Elmer 683 infrared spectrophotometer (USA). ^{1}H-NMR was performed with a 200 MHz, JNH-FX100 (JBOX) (USA). Molecular weights were measured with a gel permeation chromatograph (GPC), C-R2AX (Shimadzu, Japan). The flowing temperature and solidifying point were approximately determined by microscopic observation. DSC was recorded with a Perkin–Elmer DSC-4 (USA). SEM was performed on an HITACHI, S-530 (Japan).

Synthesis of Poly(phenyloctyl silsesquioxane) (Ph–Oct–T)

The structure of Ph–Oct–T is schemed as below:



The synthesis of Ph–Oct–T (molar ratio of Ph/Oct is 22/1) is referenced to early reports[4–13] and described as follows: PDA (5.4 g, 0.05 mol) was dissolved in 140 mL of dry tetrahydrofuran (THF). This solution was added dropwise to 200 mL of a dry toluene solution containing phenyltrichlorosilane ($PhSiCl_3$, 20.2 g, 0.0955 mol), octyltrichlorosilane ($octylSiCl_3$, 1.08 g, 0.0044 mol), and triethylamine (TEA, 28 mL) at −10°C. Next, the reaction mixture stirred for 30 min at −10°C. Then, H_2O (2.8 mL, 0.15 mol), dissolved in 50 mL of THF, was added dropwise to the solution at −10°C with vigorous stirring. The reaction mixture was stirred and slowly warmed to room temperature for an additional 2 h. The solid salt was filtered off and the filtrate was evaporated to re-

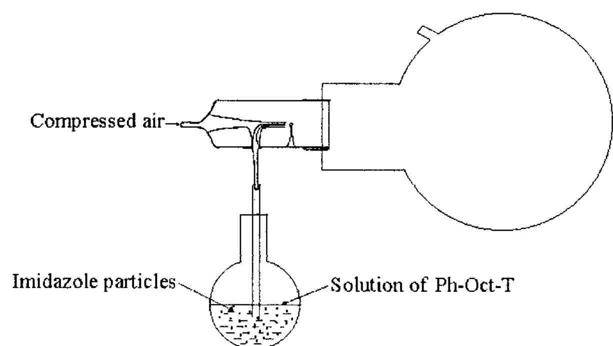


Figure 1 Apparatus for preparing microcapsulated Im by the spray-drying method.

move THF under reduced pressure to obtain a concentrated solution. After being stirred for 12 h, the solution was washed with a saturated NaCl aqueous solution to neutral and dried in a vacuum to yield 9.8 g of a white solid in an 80% yield. Extract IR (KBr, cm^{-1}): 2900–2800 (CH_3—, —CH_2—), 1600–1400 (Ph–Si), 1150–1100 (Si—O—Si); ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.9 (—CH_3); 1.1–1.3 [Si—$(CH_2)_7$—]; 6.7–7.6 (Ph–Si).

The ratio of area integration for Ph–Si and that for Si—$(CH_2)_7$—plus that for —CH_3 is 86.8:13.2, so the molar ratio of Ph and octyl groups is about 22.4:1; molecular weight (M_w) is about 1.1×10^4.

Preparation of Capsulated Imidazole Particles

The procedure for preparing micron-sized encapsulated Im particles includes two steps: First, 0.2 g Im was dissolved in a small amount of THF or acetone to form a clear saturated solution. Then, a large amount (about 10 times the original solution in volume) of cold CCl_4 was added into the Im solution under ultrasonic vibration to form a suspension solution of micro-sized Im particles. Second, 2 g of Ph–Oct–T was dissolved in CCl_4 and then mixed with the Im particle-suspended solution. The micron-sized encapsulated particles with a solid Im core were obtained by the spray-dry method as shown in Figure 1. The CCl_4 solution containing Ph–Oct–T and suspended fine Im particles was put into the round-bottom flask. The compressed air (2–4 atm) passed through the spray nozzle. The composite particles coated with the Ph–Oct–T solution were sprayed on the internal wall of the round-bottom receiver and dried rapidly. The micron-sized encapsulated Im particles were collected from the wall of the flask. Its size and appearance were observed with a scanning electronic microscope (SEM). The Im content in the fine capsules can be calculated based on the percentage of nitrogen obtained by element analysis.

Curing Tests

Curing tests of the epoxy resin were carried out at 80 and 160°C, respectively. Im, 0.6 wt % (based on the total weight of the epoxy resin and curing agent), or corresponding encapsulated particles containing the same content of Im was dispersed into the homogeneous mixture of the epoxy resin (Sumitomo ESCN-195XL) and the curing agent; phenolic resin (Bakelite, Sumitomo H-1, Japan) with a weight ratio of 100:60. After sufficient rolling, the samples were placed on a hot stage of the microscope and observed during the curing process. The thermal behavior of two kinds of samples, one containing encapsulated and another containing nonencapsulated Im, was determined by DSC analysis.

RESULTS AND DISCUSSION

Molecular Design and Preparation of Capsular Material

In previous reports, we introduced some LPSs with different side groups, such as phenyl, methyl, hydrogen, vinyl, or allyl; they are glass-like film-forming polymers. We also prepared other LPSs with longer alkyl side chains; they are a viscous liquid at room temperature. Practically, it is desired that a epoxy resin-based microelectronic packaging material has a long shelf life and can be solidified rapidly (usually 15–20 s) at 160–180°C. To prepare capsular materials with a suitable softening point or flowing temperature, copolymerization is an effective approach. The copolymer Ph–Oct–T is a noncrystalline polymer and can be softened at elevated temperature. The effect of the composition on the flowing temperatures of Ph–Oct–T is shown in Table I. When the molar ratio of Ph/Oct is about 22/1 and the molecular weight (M_w) of Ph–Oct–T (22/1) is about 1.1×10^4, the flowing temperature of Ph–Oct–T is about 165–180°C, as observed by microscopy.

Preparation of Capsulated Im Particles

To prepare capsulated Im particles by the spray-dry method, the choice of solvent is very important. It should be both a solvent of Ph–Oct–T and

Table I Effect of Composition on Flowing Temperatures of Ph–Oct–T

Sample	Feed Molar Ratio (Ph/Oct)	Flowing Temperature[a] (°C)
1	15/1	80–100
2	19/1	100–120
3	21/1	130–150
4	22/1	165–180
5	29/1	>230
6	Pure Ph–T	>300

[a] Observed by microscopy.

a suspending/precipitating agent of the fine Im particles. Besides, it should have a larger specific density so as to float the Im particles and a low boiling point (bp) for easy removal by evaporation. Obviously, CCl_4 is a favorable choice. Because its bp is only 76°C, the fine particles coated with a Ph–Oct–T solution can be dried rapidly during spray-dry processing, and, as a result, the Ph–Oct–T macromolecules adhered on the surface of the Im particles form a thin shell. An SEM image demonstrated that the diameter of the particles is about 0.2–1.0 microns.

The real content of Im in encapsulated particles is calculated from the N content determined by element analysis. To eliminate the error in the element analysis of silicon-containing compounds, accurately weighted Ph–Oct–T (0.1109 g) and Im (0.1157 g) are mixed well as a standard sample in which the content of Im is 51.1%. The determined N content of this standard sample is 24.40% and the determined N content of the spray-dried product is 15.27%. So, the content of Im is calculated to be about 32% in the spray-dried product.

Curing Testing

Microscopic observation of the samples on a hot stage at 80°C indicated that the sample containing encapsulated Im particles did not demonstrate any physical change within at least 40 min at 80°C. Compared with it, the sample containing pure Im rapidly solidified in 2 min at 80°C. On the other hand, the solidification time for both of them was almost the same at 160°C. These preliminary tests indicate that the encapsulation of the curing accelerator, Im, indeed plays a role in improving the storing stability of an epoxy resin composition at room or moderate temperatures

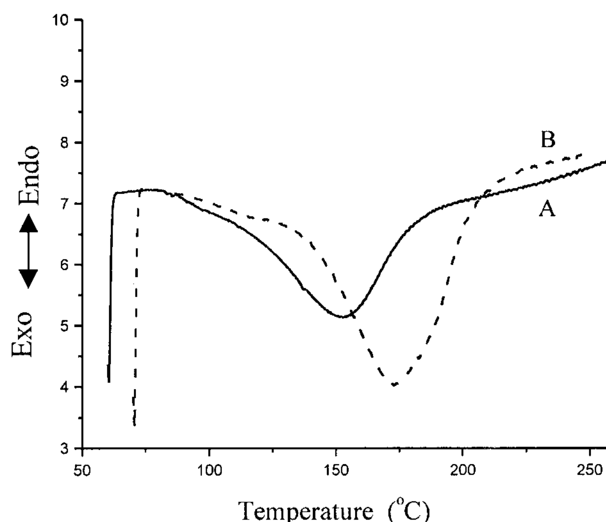


Figure 2 DSC curves of the epoxy resin composition containing (A) 0.6 wt % Im and (B) capsulated Im particles (including 0.6 wt % Im).

and, moreover, it does not inhibit solidification at expected high temperatures, which is, indeed, desirable for practical application.

Thermal Analysis

The DSC curves shown in Figure 2 indicate the difference of the thermal behavior of the epoxy resin containing capsulated or noncapsulated Im in the same stoichiometric amount. Curve A exhibits an exothermic peak centered at about

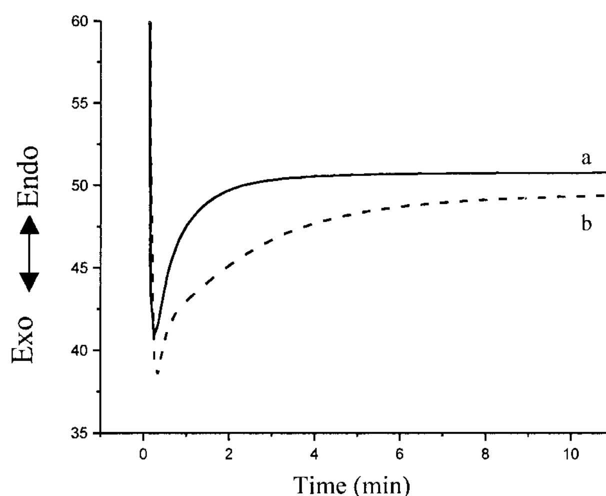
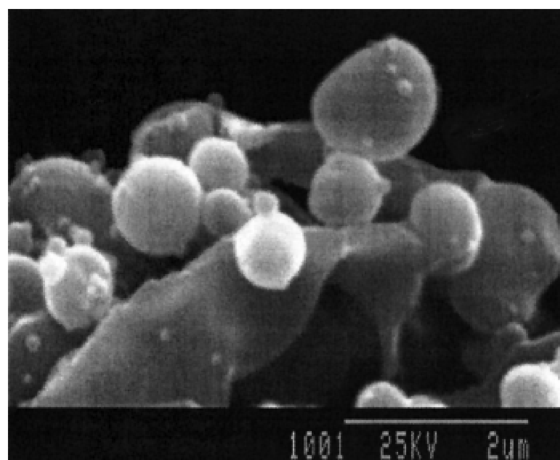
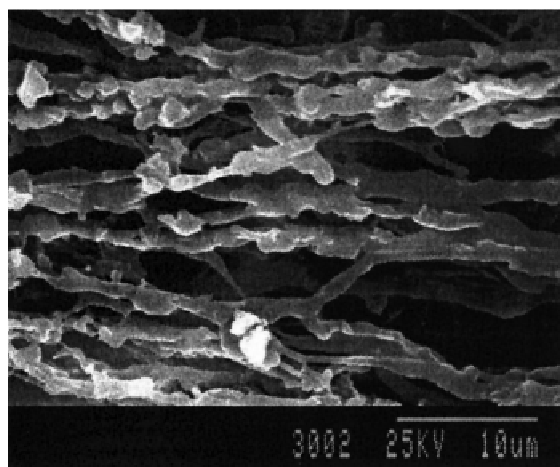


Figure 3 Isothermal DSC at 160°C of the epoxy resin composition containing (a) 0.6 wt % Im and (b) capsulated Im particles (including 0.6 wt % of Im).



a)



b)

Figure 4 SEM photographs of encapsulated Im particles: (a) ball-like capsules still intact at 80°C; (b) capsules were broken at 160°C.

152°C for the comparative sample containing 0.6 wt % Im. In comparison, curve B exhibits an exothermic peak centered at about 173°C for the sample containing encapsulated 0.6 wt % Im. The obvious exothermic process corresponding to the curing reaction starts from 70°C for sample A and 120°C for sample B, respectively, namely, the initial curing temperature of sample B is significantly increased by about 50°C. These results convincingly demonstrate the positive effect of encapsulation of the curing accelerator Im on low-temperature shelf stability.

On the other hand, the isothermal DSC curves at 160°C (Fig. 3) show that the peak time is almost the same in both cases. It is demonstrated that the encapsulation does not inhibit or retard the curing process of the epoxy resin at about 160°C.

SEM Observation of the Encapsulated Im Particles

The SEM images shown in Figure 4 were taken for the spray-dried sample, including the encapsulated Im particles, on a glass plate, which were heated to (a) 80°C and (b) 160°C, respectively, and then cooled to room temperature. Figure 4(a) illustrates that the ball-like encapsulated Im particles are still intact at 80°C, but when the temperature is increased to 160°C (b), the shell of the particles is broken. This result is fairly consistent with the DSC measurement.

CONCLUSIONS

The present work demonstrates that the encapsulated curing accelerator, Im particles, using a novel ladderlike copolymer, Ph–Oct–T, as the capsular material indeed plays role of prolonging the shelf life of epoxy resin-based microelectronic packaging material. The softening point of the copolymer as a shell material can be adjusted by changing the composition. Therefore, the capsules can be broken at the desired processing temperature. DSC measurements demonstrate that the initial curing temperature for the sample containing encapsulated Im is increased by about 50°C compared with that of the sample containing non-capsulated Im. However, encapsulation of Im does not inhibit or retard the curing process of an epoxy resin at high temperature, which is desirable for practical application.

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