B-Stage Characterization of o-Cresol Novolac Epoxy Resin System Using Raman Spectroscopy and Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

WHAN GUN KIM,[1] HYUN SIK KIM[2]

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

[2] Analytical R&D Center, LG Chemical Ltd. Research Park, P. O. Box 61 Yu Song, Science Town, Taejon 305-380, Korea

ABSTRACT: The B-stage of the o-cresol novolac epoxy resin–phenol novolac hardener–triphenylphosphine (TPP) catalyst system was characterized using Raman spectroscopy and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. The consistent decreasing intensities of characteristic epoxy resin peaks in MALDI mass and Raman spectra according to the melt mixing time were observed, which is due to the formation of the epoxy–phenol–TPP complex and the propagation reaction between them and with another epoxy resin. Our microscopic analysis method will provide a useful tool to control the optimum condition of the melt mixing process in the B-stage. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1940–1946, 2000

Key words: Raman spectroscopy; matrix-assisted laser desorption/ionization mass spectrometry; o-cresol novolac epoxy resin; phenol novolac resin; B-stage

INTRODUCTION

It is important to improve the integration density and performance of semiconductor chip according to the multifunction and small size of electronic products, so that higher thermal resistance, higher moisture resistance, lower thermal expansion coefficient, and lower modulus properties are needed to encapsulation materials for semiconductor.[1–3] However, it is also important to improve the moldability of packaging materials in order to increase the productivity of semiconductor. Recently, as the cost of semiconductor goes down, the efforts to improve the moldability of epoxy molding compound (EMC) for encapsulation materials have been taken notice of in EMC makers.

The moldability of EMC depends on its B-stage properties; therefore, its B-stage characteristics should be investigated. However, these characteristics have been studied mainly in respect to macroscopic physical properties: gel time, resin bleed, spiral flow, and melt viscosity.[4–6] The problems in the packaging process could not be explained exactly using these properties; therefore, the development of microscopic evaluation methods have been required in this field.

In this study, the B-stage characterization of epoxy resin system, which is composed of o-cresol novolac epoxy resin and phenol novolac hardeners mainly used for semiconductor packaging, has been performed using Raman spectroscopy, which has been applied to the investigation of fully cured resin system,[7–9] and matrix-assisted laser desorption ionization (MALDI) mass spectrometry, which is a recently introduced soft ionization technique that allows desorption and ionization of very large molecules without fragmentations.[10,11]

Table I   Descripton of Raw Materials Used in This Study

Materials (Grade Name)	Structure	Epoxy/Hydroxy Equivalent (g/eq)	Maker
o-Cresol Novolac Epoxy Resin (EOCN-1020)		202	Nippon Kayaku
Phenol novolac (PSM-4261)		106	Gunnei Chemical
Triphenylphosphine (TPP)		—	BASF AG.

EXPERIMENTAL

Materials and Sample Preparation

The epoxy resin used in this study was commercially available o-cresol novolac epoxy resin obtained from Nippon Kayaku Co. The hardener, phenol novolac, was received from Gunnei Chemical. Detailed descriptions of chemical properties are summarized in Table I. Triphenylphosphine as catalyst was used as received from BASF AG. For the MALDI experiment, dithranol (1,8-dihydroxy-9[10H]-anthracenone), was purchased from Sigma Chemical Co. (St. Louis, MO). Silver trifluoroacetate was from Aldrich Chemical Co (Milwaukee, WI) and analytical grade tetrahydrofuran (THF) from J. T. Baker (Phillipsburg, NJ).

The epoxy resin composition in this study is composed of the same equivalent weight ratio (1 : 1) of epoxy and hydroxyl group, and the content of triphenylphosphine as catalyst is 1 phr (part per hundred epoxy resin). These materials were well mixed using a two-roll mill at optimum temperature.[12,13] Each sample was prepared according to the melt mixing time change in order to investigate B-stage characterization of epoxy resin system, and it was stored in the dark at 4°C.

MALDI samples were prepared by applying dithranol (10 mg/mL in THF), the epoxy resin system (2 mg/mL in THF), and silver trifluoroacetate (2 mg/mL in THF) with the same volume (0.2 μL) on the same spot of stainless steel target plate one by one. Samples were allowed to air dry before moving into vacuum chamber of mass spectrometer.

Measurements

The Raman measurements were performed on a Perkin Elmer FT-Raman System 2000 spectrometer with the spectral resolution of 4 cm^{-1} using a 1064 nm line of Nd-YAG laser at 500 mW. In order to obtain a good signal-to-noise ratio, typically 100 scans were coadded for the spectra. To investigate the B-stage characteristics of this epoxy system, we selected four significant peaks: first at 1438 cm^{-1} which is the C—H stretching of epoxide; second at 1256 cm^{-1}, which represents the C—O—C stretching of epoxide; 1086 and 914 cm^{-1}, which are the epoxide C—O—C vibration modes.[14–17] We measured the relative residual functional peak ratio (R_p) to compare the B-stage characteristics of this resin system according to the change of melt mixing time, as follows:

$$R_p = \frac{(A_f/A_r)_t}{(A_f/A_r)_s} \tag{1}$$

where A_f is absorption peak height of the epoxide functional groups above mentioned; A_r is absorption peak height of the reference group, which is
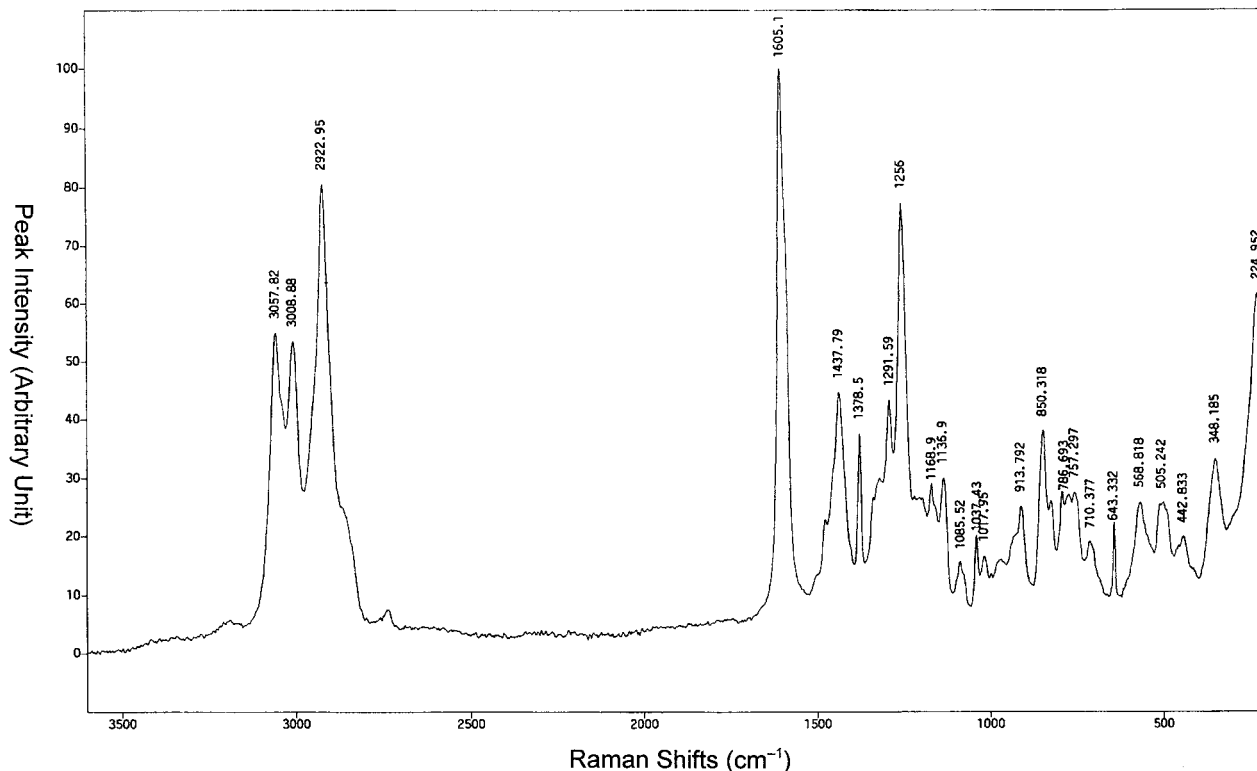
Figure 1 A typical Raman spectrum of the o-cresol novolac epoxy–phenol novolac resin system.

not changed during the melt mixing time (1605 cm^{-1}, which represents aromatic skeletal ring breathing vibration mode); and subscript t and s mean melt mixing time after t minutes and reference melt mixing time of epoxy resin system (where s = 2 min), respectively. All the values of these data were obtained using computer software and show a good reproducibility with a standard deviation of 6–10%. A typical Raman spectrum of this epoxy resin system is shown in Figure 1.

Mass measurements using matrix-assisted laser desorption ionization time-of-flight (MALDI/TOF) method were performed on TofSpec mass spectrometer (Micromass, Manchester, UK), operated in linear mode at an accelerating voltage of 25 kV. A microchannel plate-electron multiplier detector was used and was sampled at 500 MHz. A VSL-337I nitrogen laser (Laser Science Inc., Newton, MA) was employed, operating at 337nm. One hundred spectra were coadded and smoothed to improve visual interpretation. MALDI/TOF mass spectra of o-cresol novolac epoxy resin, phenol novolac, and the epoxy resin systems with different melt mixing times are shown in Figure 3, 4, and 5.

RESULTS AND DISCUSSION

As shown in Figure 1, the Raman spectrum of this epoxy resin system represents very strong peaks of the aromatic skeletal ring breathing vibration at 1605 cm^{-1}, C—O—C stretching of epoxide at 1256 cm^{-1}, a strong peak of the C—H stretching of epoxide at 1438 cm^{-1}, and the weak peaks of the epoxide C—O—C vibration mode at 1086 and 914 cm^{-1}compared with the system's infrared spectrum.[15]

Figure 2(A) shows the change of relative functional peak ratio (R_p) at 1438 cm^{-1} described in eq. (1) according to the change of melt mixing time. It can be seen that the value of R_p decreases with the increase of melt mixing time. Decreasing R_p indicates that the number of epoxide group in this epoxy resin decreases as the time of melt mixing increases. Similar decreasing R_p values can be found in all epoxy-related peaks as in Figure 2(B) at 1256 cm^{-1}, Figure 2(C) at 1086 cm^{-1}, and Figure 2(D) at 914 cm^{-1}, respectively. It can be found that the relative functional peak ratio (R_p) at 1256 cm^{-1} represent the most linear dependency with melt mixing time among these values.
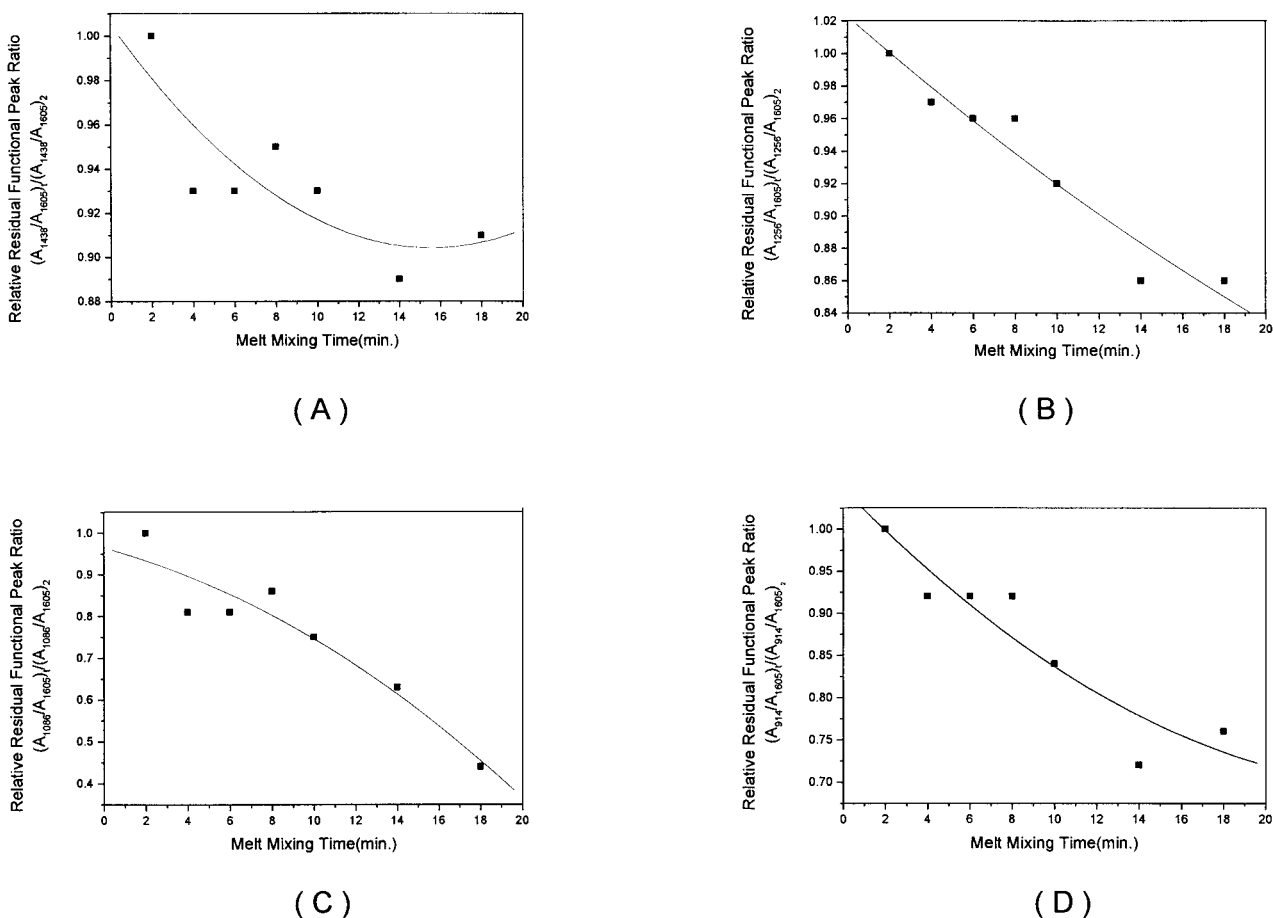
Figure 2   Relative functional peak ratio (R_p) according to the melt mixing time. (A) R_p at 1438 cm^{-1}, (B) R_p at 1256 cm^{-1}, (C) R_p at 1086 cm^{-1}, and (D) R_p at 914 cm^{-1}.

From the mass spectrum of o-cresol novolac epoxy resin (OCNE) (Fig. 3), we found silver cation attached OCNE as dimer to an 11-mer with maximum intensity at a tetramer. The OCNE was identified by its mass of repeating unit, 177 u, calculated from mass difference between peak series of the mass spectrum. In Figure 4, we can find the wide molecular weight distribution of phenol novolac (PN) between a dimer and 20-mer and a repeating mass unit of 106 u. The epoxy resin system in the B-stage was detected as the complex between OCNE and PN dimer with triphenylphosphine (TPP), as in Figure 5. After 2 min of melt mixing time [Fig. 5(A)], we found a distinct series of OCNE resin that was attached to the dimer of PN, but after 18 min, we found a rapid decrease in the signal of mixing products. With longer melt-mixing time, we found decreased peak intensities of mixing products in the spectrum normalized by matrix peak. Smaller molecular weight epoxy resins systems with TPP including phenol novolac dimer could be observed; however, larger systems were not observed, probably due to the low solubility of epoxy resin system, including larger PN resin in THF.

It was suggested for the cure mechanism of this epoxy resin system to create the initiation step as represented in Scheme 1, which is the equilibrium reaction between alcoxide ion produced by reaction of epoxy resin with TPP and phenol resin, to create the propagation step as shown in Scheme 2, which is the primary epoxy reaction between this alcoxide–phenol complex and other epoxy resin, and to create the branching reaction step, as represented in Scheme 3, which is the secondary epoxy reaction with them.[18]

As seen in the MALDI mass spectrum of B-stage of this resin system (Fig. 5), it can be considered that this B-stage resin system at initial melt mixing stage is the complex of o-cresol novolac epoxy resin opened by TPP and phenol resin, as shown in initiation reaction step (Scheme 1). The propagation
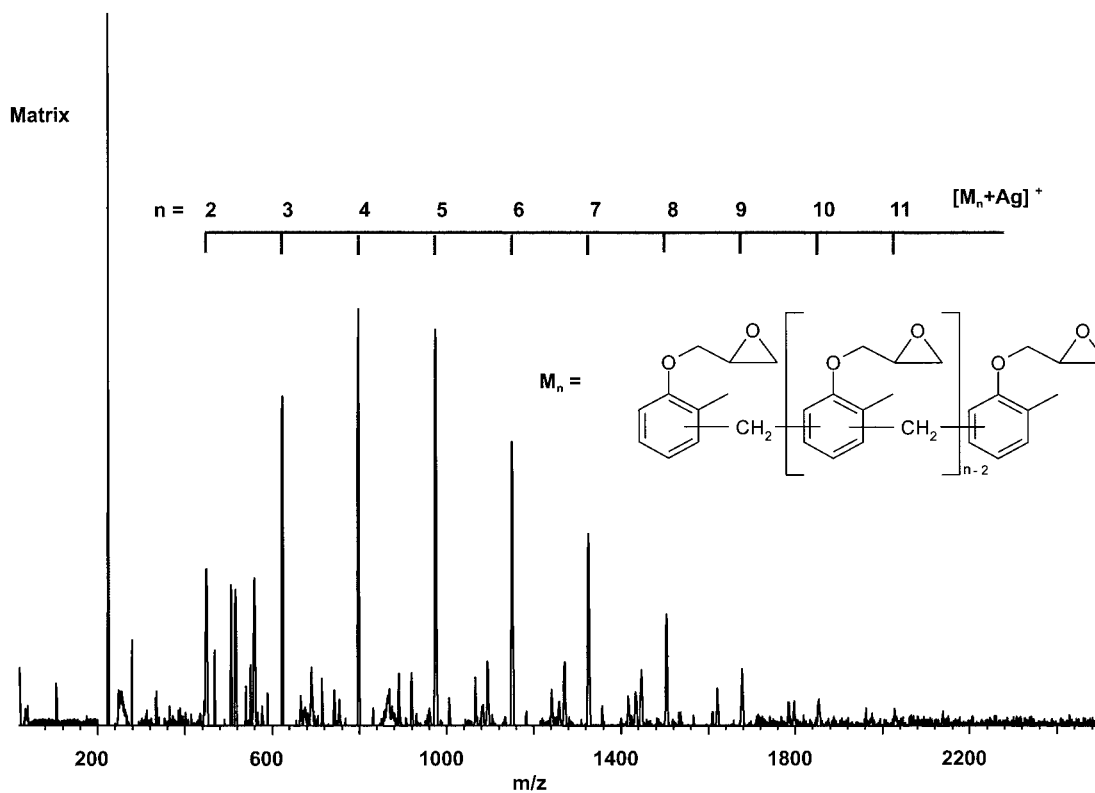
Figure 3   Positive ion MALDI-TOF mass spectrum of o-cresol novolac epoxy resin.
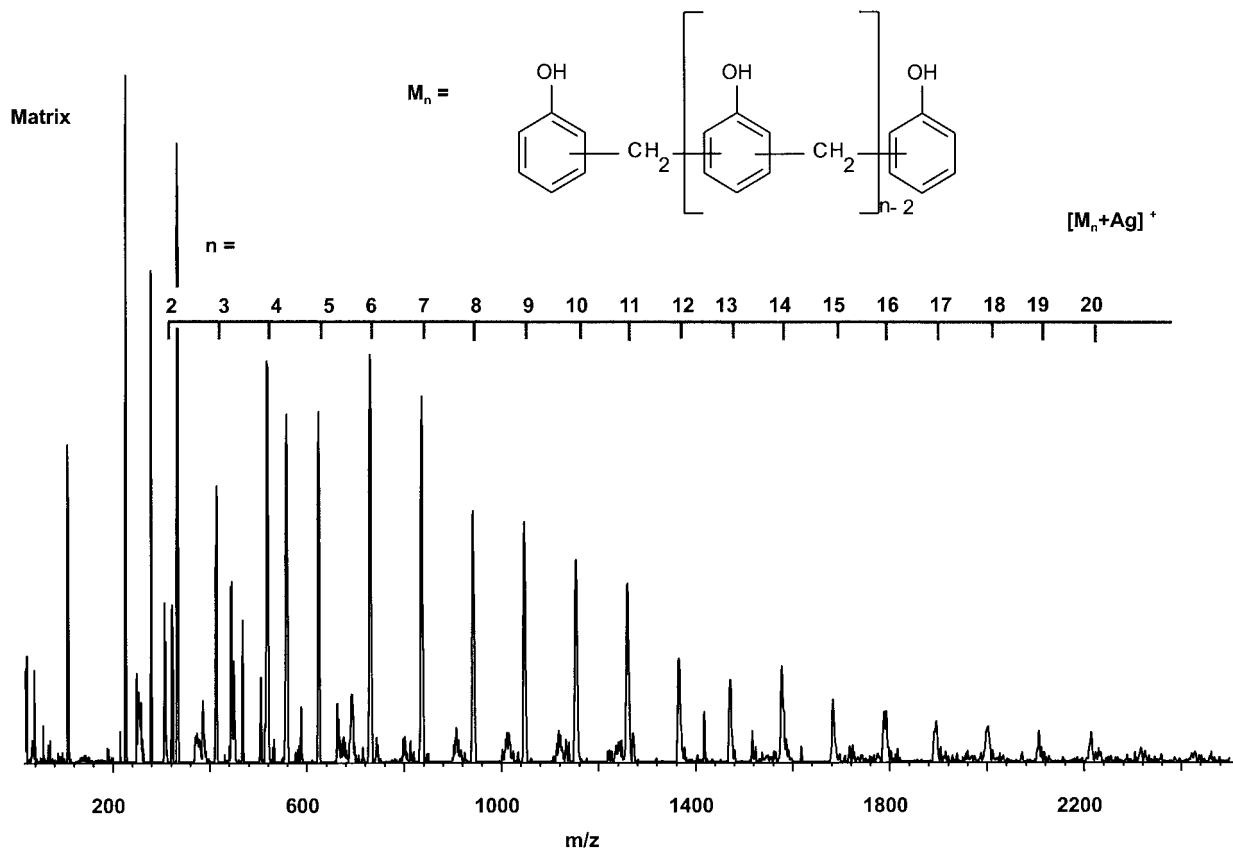

Figure 4   Positive ion MALDI-TOF mass spectrum of phenol novolac resin.
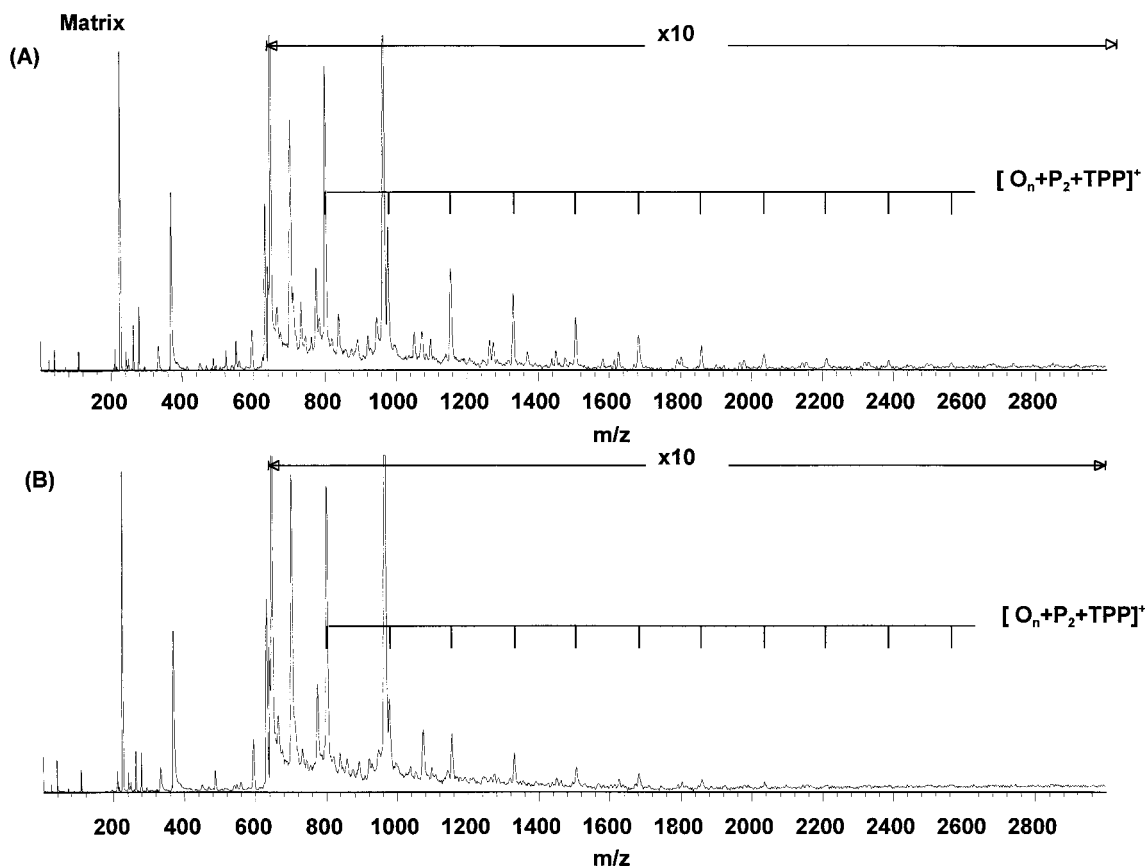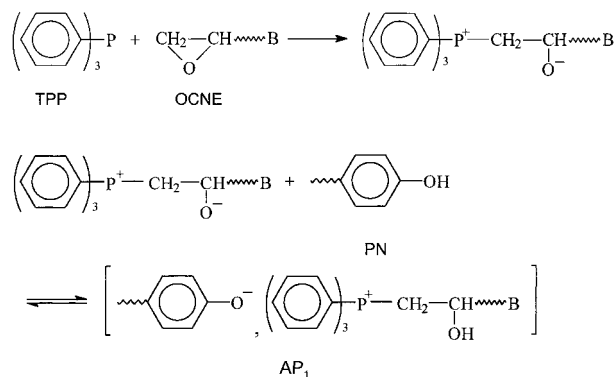
Figure 5 Positive ion MALDI-TOF mass spectrum of o-cresol novolac epoxy–phenol novolac resin system after the melt mixing time of 2 min (A) and 18 min (B). Within spectrum annotations, O represents the unit of o-cresol novolac epoxy resin, P_2 ; dimer of phenol novolac resin and TPP; triphenylphosphine.

reaction as shown in Scheme 2 proceeds with increasing the melt mixing time, so that the number of epoxy groups should decrease with melt mixing time as represented in Raman spectra. As the molecule weight of B-stage system increases with melt mixing time, the solubility of this resin system decreases, so that the MALDI mass spectra of this B-stage resin system in high mass region could not be obtained. However, the decrease of MALDI mass intensity in Figure 5(B) and the epoxy group intensity in the Raman spectra according to the melt mixing time can be thought due to the propagation
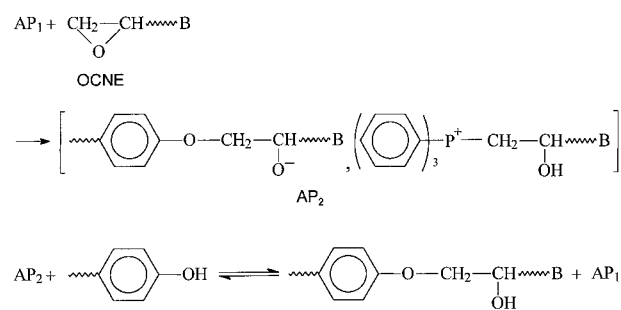
Scheme 1
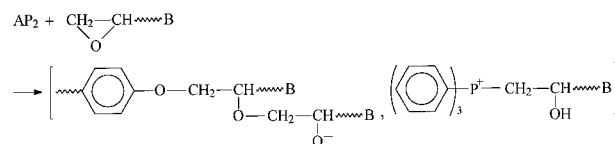
Scheme 2

Scheme 3

reaction of the epoxy–phenol–TPP complex and another epoxy resin.

CONCLUSIONS

The B-stage characterization of EMC for semiconductor encapsulation is very important to improve the moldability of the packaging process. In this study, the microscopic analysis methods; Raman spectroscopy, and MALDI mass spectrometry, were applied to characterize them using model system as o-cresol novolac epoxy resin–phenol novolac hardener–TPP catalyst. The epoxy group in o-cresol novolac epoxy resin decreases with melt mixing time, and the complex of o-cresol novolac epoxy–phenol novolac–TPP was observed at initial stage of melt mixing process. The reactions between high molecular weight epoxy resin and phenol novolac resin, and propagation reaction of complex produced in initial reaction step should make progress as the melt mixing time increases. If these microscopic analysis methods were used, therefore, the optimum control solution of melt mixing process could be obtained as compared with macroscopic physical properties; gel time, resin bleed, spiral flow, and so on.

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