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Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins

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Abstract

We have developed new polymeric systems based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins. Low melt viscosity resins render void-free specimens with minimal processing steps. The material properties show a wide range of desirable reliability and processability, which are highly dependent on the composition of the monomers in the mixture. A glass transition temperature as high as 170°C and considerable thermal stability at 5% weight loss up to 370°C can be obtained from these systems. Phenolic novolac resin acts mainly as an initiator for these ternary systems while low melt viscosity, flexibility and improved crosslink density of the materials are attributed to the epoxy fraction. Polybenzoxazine imparts thermal curability, mechanical properties as well as low water uptake to the ternary systems. The materials exhibit promising characteristics suitable for application as underfilling encapsulation and other highly filled systems.

Keywords: Underfilling; Encapsulation; Electronic packaging materials

1. Introduction

Polymeric materials play a vital role in electronic packages as a result of their ease of processing, low cost, low dielectric constant, adhesive properties, etc. Moreover, many properties of polymers can be easily improved or altered by preparing polymer blends or composites [1–4]. As a result, plastic packages occupy approximately 80–90% of all integrated circuit packages [5–7]. Miniaturization with faster, denser, and more complex functionality of the packaging materials is an important trend of the present as well as future semiconductor devices. The development of the flip-chip technology is an example of such a trend [8]. Instead of using wire bonding, or tape-automated bonding, the flip-chip technology employs small solder bumps as interconnectors between a die and a substrate thus offers minimization of board area requirements in conventional low-cost assemblies as well as reduction in weight and height profile [9].

In flip-chip manufacturing, filled polymers perform a major function called underfilling [10–24]. Underfilling is the plastic encapsulant put in the gap (about 50–75 μm) between integrated circuit or die and the substrate. The encapsulant is used to mechanically couple the chip and the substrate, decreasing the residual stress in the solder joints caused by thermal expansion mismatch between the die and the substrate. The thermal fatigue property is reported to improve drastically by underfilling [10–17]. The materials for underfilling should have no void formation, good wetting characteristics, significant adhesion, low stress, and high thermal conductivity [18]. These requirements led to the development of low melt viscosity resins for high-performance electronic encapsulants since the low-viscosity resin will ensure minimal void trapping in the resin and the moldability of the encapsulant, particularly in the highly filled systems [18,25].

Recently, Ishida and Rimdusit [26] reported the use of low melt viscosity polybenzoxazine filled with boron nitride ceramics to improve the composite thermal conductivity. The resulting materials show an extraordinarily high thermal conductivity value, up to 32.5 W/mK, at the maximum filler loading of 78% by volume. Though the polybenzoxazine used showed quite low melt viscosity, the resin was still required to undergo purification and degassing processes to eliminate any unreacted residues, oligomers, or reaction by-products which may cause void formation in the curing step.

The prevention of void formation in the matrix is

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essential in the thermal management of microelectronic packaging material. Voids act as hot spots and weak points which will be subjected to thermal fatigue, thus affecting the performance and lifetime of the packaging materials [14,15,27]. Controlling material characteristics such as rheology, and filler content of the material as well as developing proper dispensing methods for the underfill encapsulants are the two main aspects of the void preventions [10,12,14,18,21].

In this study, we will examine the modification of thermally curable benzoxazine resin by partial incorporation of low-viscosity epoxy resin in order to further reduce the viscosity of as-synthesized benzoxazine resin. The need for monomer purification and degassing, which, in practice, is less cost-competitive is then eliminated. This is based on the fact that entrapped air can escape more easily from the low-viscosity liquid than from the high-viscosity material. A lower viscosity resin also allows addition of a greater amount of filler while maintaining processability of the molding compound. In addition, we will also investigate the effect of phenolic novolac on the curing of epoxy-diluted benzoxazine resin since phenolic novolac is typically used as a hardener for epoxy resin as well as an initiator for benzoxazine resin. The mixture of these three resins to form the ternary systems is believed to provide a great variety of resin properties suitable for wide applications, particularly in the microelectronic application and the highly filled systems.

2. Experimental

2.1. Materials

Benzoxazine resin used is based on bisphenol A and aniline type i.e. 2,2′-(3-phenyl-4-dihydro-1,3,2-benzoxazine)propane (designated as BA-a). The monomer synthesis is based on the patented solventless synthesis method [28]. The purification method is explained in detail by Ishida and Rodriquez [29,30]. The as-synthesized resin was used to make cured specimens while the purified material was used for curing studies. The epoxy resin, Epon 825, from Shell Chemicals, was used as-received without further purification. The resin is a clear viscous liquid at room temperature. Phenolic novolac, HRJ1166, was obtained from Schenectady International. The resin is a dark red solid at room temperature. All materials were kept in closed containers at room temperature.

2.2. Processing method

Each resin was first measured at the desirable mass fraction. The mixture was then heated to about 80°C in an aluminum pan and was mixed by hand for a few minutes until the homogeneous mixture was obtained. A part of the mixture was then taken for differential scanning calorimetry analysis. The mixture can be kept at room temperature for future use. The cured specimens were made by first liquefying the ternary system at 80°C. The liquid resin was then poured into a mold and compression molded into various dimensions, depending upon the types of experiments. All the specimens were thermally cured at 200°C with pressure of 0.1 MPa for 1 h in order to ensure the polymerization temperature is higher than the expected ultimate T_g of the ternary system. The specimens were left to cool to room temperature in the open mold for about 2 h before using.

2.3. Differential scanning calorimetry

The polymerization behavior of the samples was examined using a modulated differential scanning calorimeter (MDSC) model 2920 from TA Instruments. All samples were sealed in hermetic aluminum pans with lids. The mass of the samples are in the range of 3–5 mg. The weight of reference and sample pans with lids were within 57 ± 0.3 mg. The MDSC experiments were performed using the conditions as follows:

- isothermal equilibration for 10 min at −10°C;
- temperature amplitude ±1°C with period of 70 s;
- ramp at 5°C/min to 310°C.

The glass transition temperature was obtained by rerunning the experiment twice using the same conditions as above to ensure a complete curing reaction. In this experiment, the temperature at half extrapolated tangents of the step transition midpoint was used as the glass transition temperature.

2.4. Dynamic mechanical analysis

The dynamic mechanical spectra of the cured specimens were obtained using a dynamic mechanical spectrometer (Rheometrics, model RMS-800) which was equipped with a 2000–200 g cm dual range force rebalance tranducer. The dimensions of the specimen were about $51 \times 13 \times 2.5\ \text{mm}^3$ and the samples were tested using a rectangular torsion fixture. The strain used was 0.15% after determining the linear viscoelastic region by strain sweep. The strain was applied sinusoidally with a frequency of 1 Hz in the temperature sweep experiment. The specimens were heated at a rate of 2°C/min from 30°C to the temperature beyond the glass transition temperatures of each copolymer. A thermal soak time of 45 s was used at each measuring temperature. Steady-shear viscosity of the uncured resin was determined using a 50-cm-diameter parallel plate fixture. The experiment was performed at 100°C under steady-shear mode.

2.5. Thermogravimetric analysis

A thermogravimetric analyzer from TA Instruments (model TGA 2950) was used to study thermal stability of the cured ternary systems. The experiment was done using a heating rate of 20°C/min under nitrogen atmosphere. The

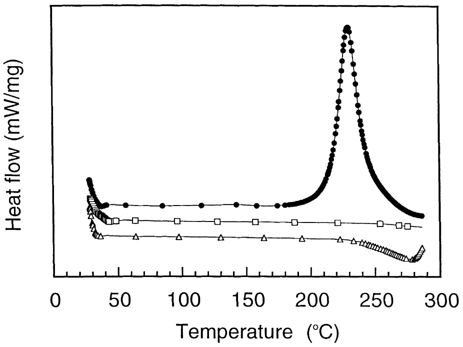

Fig. 1. DSC thermogram of the three monomers: (●) benzoxazine; (□) phenolic novolac; (△) epoxy.

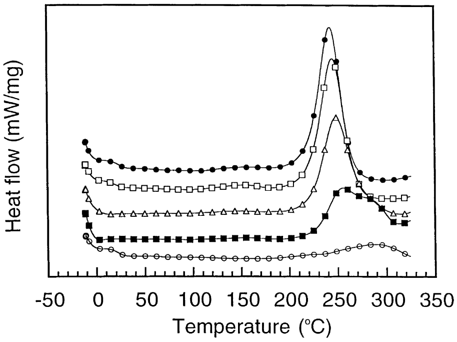

Fig. 2. DSC thermogram of binary systems between benzoxazine and epoxy: (●) EB13; (□) EB12; (△) EB11; (■) EB21; (○) EB31.

temperature was ramped from 30 to 900°C using the sample mass of about 20 mg.

2.6. Water absorption

Water absorption measurements were conducted following ASTM D570 using disk-shaped specimens having a 51 mm diameter and a 3.2 mm thickness. All specimens were conditioned, weighed, and submerged in distilled water. The specimens were occasionally removed, wiped dry, weighed, and immediately returned to the water bath. The amount of water absorbed was calculated based on the initial conditioned mass of each specimen.

3. Results and discussion

Fig. 1 shows the DSC thermograms in the temperature range of 30–300°C at the heating rate of 5°C/min of BA-a benzoxazine, epoxy, and phenolic novolac resins, respectively. The thermogram shows the curing exotherm of the benzoxazine monomer with a peak maximum of about 230°C, which is characteristic of the thermal curability of this resin [29,30]. On the contrary, the epoxy resin and phenolic novolac show no sign of a curing reaction in this temperature range without added initiators or catalysts. Amine compounds, acid anhydrides, and phenolic compounds are common curing agents for epoxy resin while acidic compounds are used to cure phenolic novolac resin. In fact, phenolic novolac is typically used as a hardner of epoxy novolac resins which have been extensively used in the electronic industry for integrated circuit encapsulation by transfer molding [31]. In the case of the epoxy resin, on the other hand, we observed the endotherm peak at about 280°C as a result of evaporation of the monomer.

In the nomenclature of binary and ternary mixtures, the letters B, E, and P stand for benzoxazine, epoxy, and phenolic resins respectively. The numbers that follow the abbreviation are the mass ratio of the resins in the same order i.e. BEP121 represents benzoxazine, epoxy, and phenolic mixture with the mass ratio of 1:2:1, respectively. The curing reaction of the binary mixture of BA-a and the epoxy resin is shown in Fig. 2. The retardation of the curing reaction of the benzoxazine resin is observed as a shift of the exotherm peaks to higher temperature. The degree of retardation increases with increasing amount of epoxy resin. The interesting feature of the curing reaction is the splitting of the curing peaks, which signifies the existence of at least two distinct reactions. The first reaction, in the temperature range about 240–250°C, can be attributed to the curing reaction among benzoxazine monomers. The reaction is predominant when the concentration of the benzoxazine monomers in the binary mixture is above 30 wt%. The second reaction can be attributed to the reaction between benzoxazine and epoxy resin which occurs at higher temperature i.e. about 290–300°C. The curing reaction among epoxy monomers is unlikely as depicted in Fig. 1.

Fig. 3 shows the curing exotherms of the mixtures between benzoxazine and phenolic novolac resin. The curing acceleration is observed from the shift of the curing exotherm peaks to lower temperature when the amount of phenolic novolac resin in the mixture increases. The relationship between the exotherm peaks and the amount of phenolic resin in the binary mixture suggests that phenolic novolac resin act as an initiator for benzoxazine resin. This is in good agreement with the past studies reported by Riess et al. [32] and Ishida and Ning [33,34].

Fig. 4 exhibits the DSC thermograms of the binary mixtures of epoxy resin and phenolic novolac resin. The thermograms show no exotherm maxima within the temperature range of 30–300°C; however, the onset of an exothermic reaction, which may be due to either the curing or degradation reactions of the mixture, was observed. This means that the reaction between these two resins can occur but at a temperature significantly higher than when one component of the binary mixture is benzoxazine resin. This is the reason that the small amount of catalyst, typically a Lewis base, is needed to accelerate the reaction between the epoxide and the hydroxyl groups [31].

From these results, we can summarize that, by adding epoxy as a reactive diluent to reduce the viscosity of benzoxazine resin, the obtained mixture appears to cure at higher temperature. On the contrary, the addition of

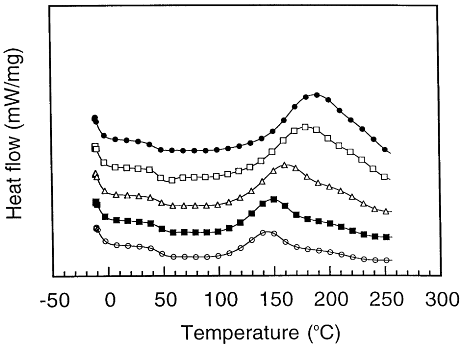

Fig. 3. DSC thermogram of binary systems between benzoxazine and phenolic novolac: (●) BP31; (□) BP21; (△) BP11; (■) BP12; (○) BP13.

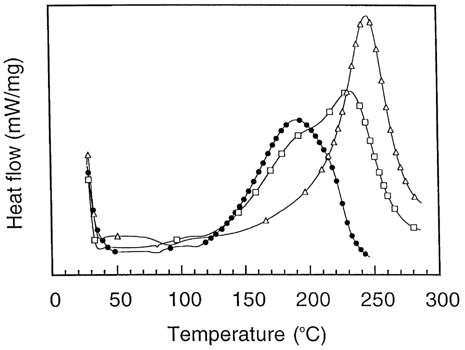

Fig. 5. DSC thermogram of ternary systems: (●) BEP111; (□) BEP121; (△) BEP131.

phenolic novolac into the benzoxazine resin results in a mixture that can be cured at lower temperature. As mentioned earlier, phenolic novolac can also act as a hardener of epoxy resin; therefore, the incorporation of phenolic novolac in the epoxy-diluted benzoxazine compound should render two-fold benefits to the polymeric composition if the homogeneous mixture is obtained.

The curing behavior of the ternary mixture is shown in Fig. 5. In this case, we fixed the composition of benzoxazine and phenolic novolac mixture at the mass fraction of 1:1 and varied the amount of epoxy diluent. From the thermograms, as expected, the lower the amount of epoxy diluent in the ternary mixture is, the lower is the onset temperature of curing reaction to occur. Epoxy, as mentioned before, acts as a diluent which retards the curing reaction. By maintaining the mass fraction of epoxy at less than 50% by weight, i.e. BEP111, BEP121, the curing reaction of the ternary mixtures can start at a relatively low temperature, near 100°C. Low curing temperature is one of the desired properties of some types of controlled collapse chip connection or C4, flip-chip, encapsulant [8,16,18,19].

The melt viscosity of these ternary mixtures is shown in Fig. 6. The measurement was performed under steady shear mode of the parallel plate fixture at 100°C. The viscosity of the ternary mixture is quite low particularly when the mass fraction of epoxy is above 50% by weight i.e. approximately 0.3 Pa s for BEP121, and BEP131. Moreover, the viscosity of BEP121 and BEP131 remains low and fairly constant up to 1000 s in the experiment which is an advantage for the compounding process. We achieved the void-free, cured polymer using compression molding as a processing technique, without degassing the resin, due to the low viscosity. In the case of BEP111, the viscosity of the resin is slightly higher than BEP121, and BEP131, i.e. about 7 Pa s compared with 0.3 Pa s of the latter two resins at 100°C. The value is even higher than the viscosity of purified benzoxazine monomer of the same type, i.e. 5 Pa s [35]. This is due to the fact that BEP111 can undergo a significant degree of curing at the experimental condition as can be seen from the rapid increase in its viscosity with time, i.e. from 7 to 70 Pa s at 100°C in 1000 s. Therefore, a resin with more than 30% by weight of epoxy is recommended to retain its low viscosity with suitable period of time at the mixing or compounding condition.

The ability to retain low viscosity at some period of time is also important in order to provide enough time for any volatile components to escape from the liquid resins. In the experiment, void-free specimens are easily obtained from BEP 121 and BEP131 compared with BEP111. The samples can be made without any purification or degassing of the precursor used, which makes the resins more cost-competitive and more desirable underfilling systems since no

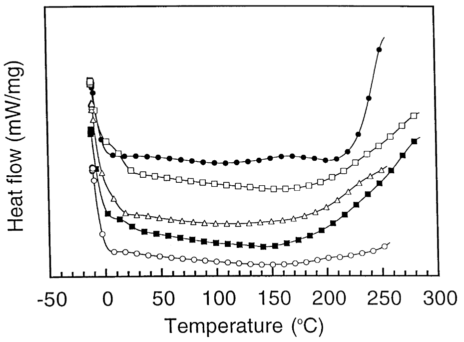

Fig. 4. DSC thermogram of binary systems between epoxy and phenolic novolac: (●) PE31; (□) PE21; (△) PE11; (■) PE12; (○) PE13.

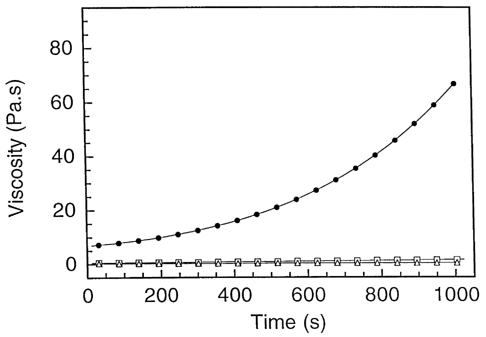

Fig. 6. Viscosity of ternary systems at 100°C: (●) BEP111; (□) BEP121; (△) BEP131.

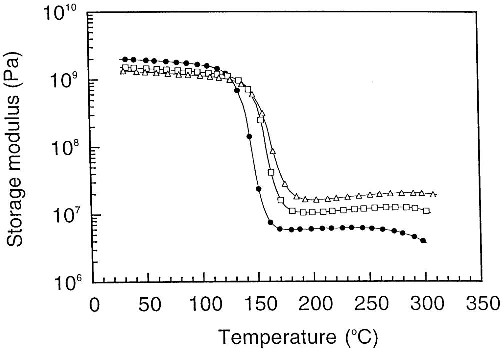

Fig. 7. Storage moduli of ternary systems: (●) BEP111; (□) BEP121; (△) BEP131.

voiding is one of the key requirements for this type of encapsulant [18]. The curing temperature and time are also significantly reduced compared with those of benzoxazine monomers alone. No sign of phase separation was observed on the ternary systems. The cured samples are transparent with light yellow to dark red in color depending on the composition of the mixture.

Fig. 7 exhibits the storage moduli of cured BEP111, BEP121, and BEP131. The moduli of the ternary systems at room temperature decrease with increasing amount of the epoxy resin in the ternary mixture, i.e. 2.1, 1.3, 1.1 GPa for BEP111, BEP121, and BEP131, respectively. This is due to the more flexibility or less stiffness of the epoxy compared with the polybenzoxazine used in the experiment [36,37]. On the contrary, the moduli of the ternary systems in the rubbery plateau increase with increasing amount of epoxy in the blends, i.e. 7, 13, and 20 MPa for BEP111, BEP121, and BEP131, respectively. The greater plateau moduli of the specimens which have higher amount of epoxy diluent is attributed to higher crosslink density in the materials.

The addition of epoxy resin provides a desirable resulting material since it renders the lower room temperature modulus of the ternary blends, thus reducing thermal stress in the materials. Thermal stress is generated by the difference in the coefficient of thermal expansion (CTE) between the chip and the encapsulant. Eq. (1) is used to roughly estimate the magnitude of the thermal stress (σ) [2,3]:

$$\sigma = \int E(T)\Delta\alpha(T)\,\mathrm{d}T \tag{1}$$

where $E(T)$ is the temperature-dependent elastic modulus of the encapsulant and $\Delta\alpha(T)$ the difference between the CTE of the encapsulating material and that of the microchip.

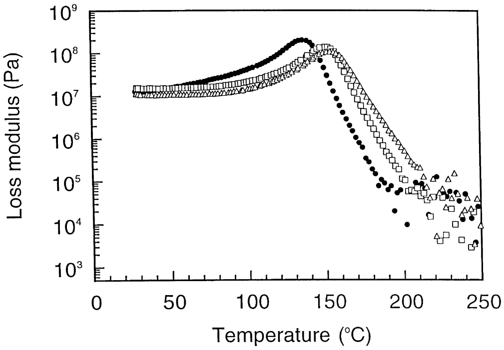

Fig. 8. Loss moduli of ternary systems: (●) BEP111; (□) BEP121; (△) BEP131.

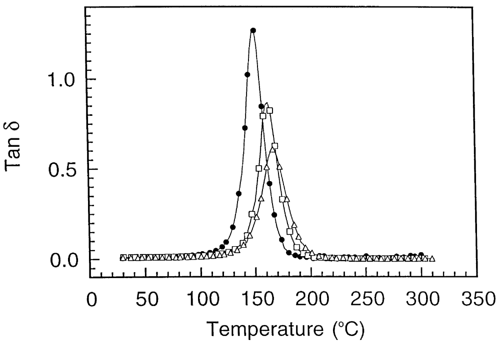

Fig. 9. Loss tangent of ternary systems: (●) BEP111; (□) BEP121; (△) BEP131.

As a consequence, thermal stress can be reduced by either lowering the CTE mismatch of the encapsulant and the die, or lowering the modulus of the encapsulant. Furthermore, the higher crosslink density, indicated by higher plateau modulus of the ternary mixture with increasing amount of epoxy resin, leads to higher glass transition temperature of the ternary systems. The glass transition temperature (T_g) is defined as the maximum value of the loss modulus of these materials as shown in Fig. 8. The T_gs of BEP111, BEP121, and BEP131 are 138, 151, and 152°C, respectively. The effect of crosslink density on T_g can be accounted for with Fox and Loshaek equation [38]:

$$T_g = T_g(\infty) - \frac{k}{M_n} + k_x\rho \tag{2}$$

where $T_g(\infty)$ is the T_g of infinite molecular weight linear polymer, k and k_x the numerical constants, M_n the number-averaged molecular weight which equals infinity in the crosslinked system, thus the second term can be neglected, and ρ is the crosslink density. From the equation, the higher the molecular weight and crosslink density are, the greater is the T_g of the polymer, which is in good agreement with the experimental results. A T_g of greater than 125°C is a minimum requirement for reliability of the underfilling encapsulants [8,16,17,19,23]. Our materials show the T_g well above the minimum requirement for underfilling materials.

Loss tangent (tan δ) of the ternary mixtures is shown in Fig. 9. The magnitude of tan δ decreases with increasing mass fraction of the epoxy resin and the maximum shifts to higher temperature. Therefore, the materials have higher crosslink density or are more elastic when the amount of the epoxy is greater in the ternary mixture. The softer or lower storage modulus at ambient temperature with increased degree of crosslinking will provide a more flexible

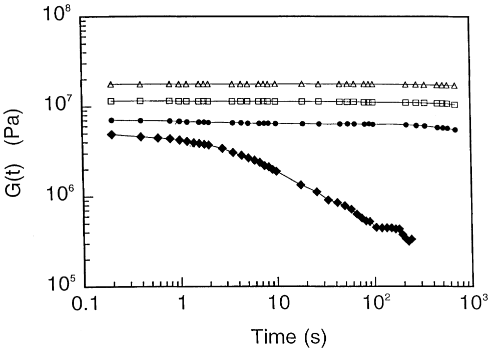

Fig. 10. Stress relaxation behavior of ternary systems at 100°C above T_gs: (●) BEP111; (□) BEP121; (△) BEP131; (◆) BA-a.

encapsulation which can reduce the number of the crack or brittle failure of the encapsulated packages during the handling process.

Fig. 10 shows the stress relaxation of BEP111, BEP121, and BEP131 at 100°C above their glass transition temperature in the time duration of about 10 min. All specimens of ternary systems showed almost negligible decay of their moduli within this time period. Furthermore, the values of the relaxation moduli increase with increasing amount of epoxy fraction in the ternary mixture. This, again, signifies the greater degree of crosslinking with increasing amount of epoxy resin in the ternary systems.

In high reliability underfilling encapsulants, a T_g of 160°C or above is desirable [11]. The enhancement of T_g of the ternary systems has also been investigated. Fig. 11 is the dynamic mechanical spectrum of the ternary mixture of bisphenol AF-type polybenzoxazine which has a reported T_g of about 200°C [39] compared with bisphenol A-type polybenzoxazine that had been used previously and has a reported T_g of about 170°C [35]. The cured specimens of the ternary mixtures with composition, 1:2:1, of benzoxazine monomers/epoxy resin/phenolic novolac resin have been made in order to compare their properties, particularly their T_gs. From Fig. 11, we can see that there is an expected increase of T_g from 150 to 157°C when the benzoxazine based on bisphenol A is substituted with bisphenol AF type. This is due to the replacement of the two methyl groups in bisphenol A with trifluoromethyl groups of bisphenol AF, increasing the steric hindrance for the flexibility of the bisphenol moiety. The rather low enhancement of T_g by this high T_g benzoxazine resin is due to the choice of the ternary mixture composition used. One purpose of this study is to demonstrate the versatility of the resin combination from these three families of resins. In this case, the use of bisphenol AF benzoxazine resin which has many fluorine atoms in the structure can be used to lower the dielectric constant of the resulting mixtures. The appropriate ternary mixture composition for high T_g is investigated in the next section.

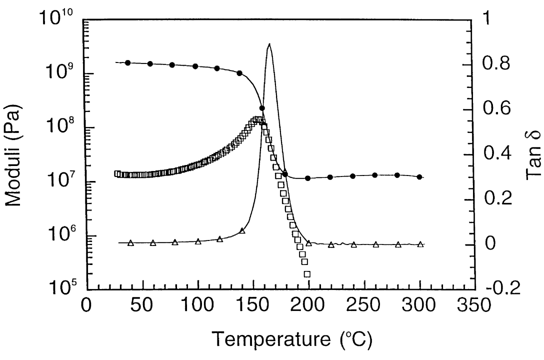

Fig. 11. Dynamic mechanical spectra of FEP121: (●) storage modulus; (□) loss modulus; (△) loss tangent.

The effect of monomer composition of these ternary systems on curing behaviors and T_g has also been studied. Fig. 12 depicts the triangular diagram of the relationship between the composition of the three resins and the corresponding curing exotherm maxima. It is evident that the ternary mixtures can be cured at lower temperature with increasing amount of phenolic novolac as described before. On the other hand, the relationship between compositions and glass transition of these ternary systems as shown in Fig. 13 indicates that the $T_{g,\mathrm{DSC}}$ of the ternary systems seems to increase with increasing amount of benzoxazine and epoxy resins in the mixture. The values of T_g obtained from the third run of the dynamic DSC experiment are about 10–20°C lower than those obtained from DMA measurement. Chartoff reviewed the discrepancies of the values of T_gs measured by DSC and DMA and pointed out that the DSC T_g value is always lower than the DMA value determined by either tan $\delta_{\max}$ or $G''_{\max}$. The frequency of 1 Hz used in DMA experiment may correspond to a DSC heating rate of about 20–40°C/min range. Dynamic mechanical analysis is approximately 1000 times more sensitive than DSC in terms of baseline deflection for detecting T_g and renders more useful mechanical property data, though larger sample size is required [40]. Another reason for the lower values of T_g in DSC experiment may be attributed to the differences in thermal curing history of the samples in both experiments. In a DSC experiment, a sample was cured in a sealed aluminum pan under a heating rate of 5°C/min while isothermal curing at 200°C in a compression molder was used to cure a sample in DMA experiment. From the high T_g region in the triangular diagram, we chose the ternary mixture with the mass ratio of 8:9:3 of benzoxazine:epoxy:phenolic novolac resin for the evaluation of its T_g. The ratio also maintains the fraction of epoxy of about 50% by weight in order to maintain the mixture at sufficiently low melt viscosity to prevent void formation.

Fig. 14 shows the dynamic mechanical spectrum of BEP893 in the temperature range of 30–300°C. The material shows significant improvement in its glass transition temperature with the obtained value of about 170°C in good agreement with the prediction by the triangular diagram which suggests higher glass transition temperature above that of BEP121 obtained with this composition.

Fig. 15 shows the TGA thermograms of BEP111,

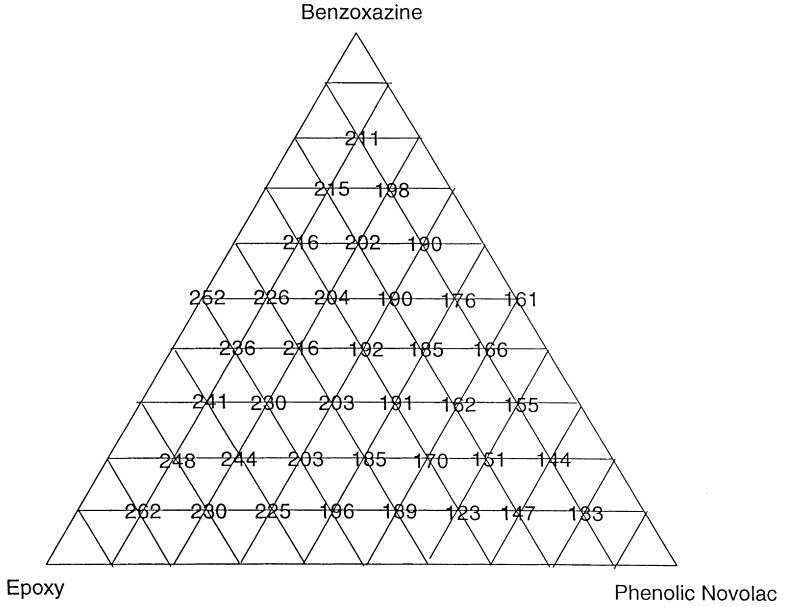

Fig. 12. Curing peak maxima from DSC as a function of composition of ternary systems.

BEP121, and BEP131 under nitrogen atmosphere. We can see that all materials show relatively high decomposition temperature reported at 5% weight loss, i.e. up to 370°C for BEP131 compared with about 350°C of the polybenzoxazine used. The materials have improved thermal stability with increasing mass fraction of epoxy in the system which may be attributed to the greater crosslink density as shown before. On the contrary, the char yield of the ternary systems increase significantly compared with the pure epoxy resin. This is due to the fact that both polybenzoxazine and phenolic novolac are known to give higher char yield compared with the epoxy resin [41].

Improving thermal stability of polymers is one of the techniques used to improve flame retardancy of the electronic packaging molding compound. Other techniques include inserting some elements having flame retardancy into polymer chains, and physically mixing flame retarding agents with polymers [2]. Non-antimony, non-halogen flame retardant systems are currently examined for high end, environmentally friendly integrated circuit packages [42,43].

Water uptake of the resin is also an important material requirement particularly for an application as electronic packaging molding compounds since moisture absorption in the molding compounds is the major cause of popcorn

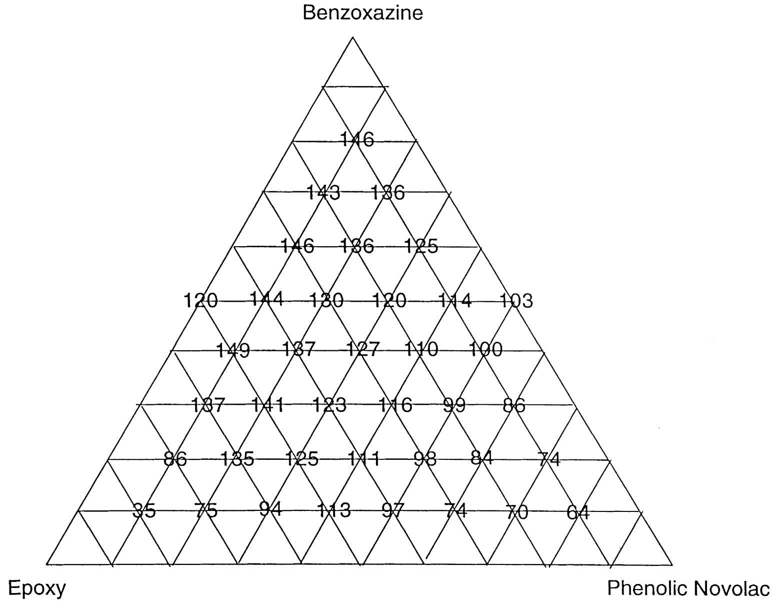

Fig. 13. Glass transition temperature from DSC as a function of composition of ternary systems.

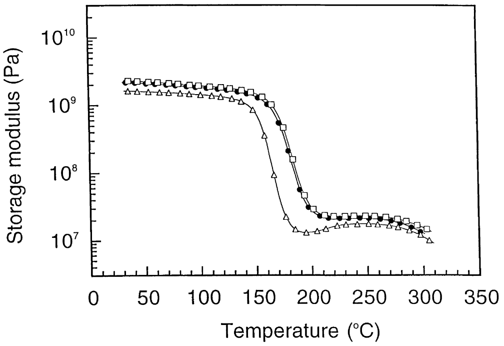

Fig. 14. Storage moduli of BEP893: (●) fully cured; (□) fully cured rerun; (△) partially cured.

Table 1
Water absorption of ternary systems compared with some thermosetting plastics

Resins	Water absorption (%)			
	24 h	7 days	120 days	Saturation
Phenolic[a]	0.23	NA	NA	NA
Epoxy[a]	0.12	0.62	1.8	NA
BA-m[b]	0.17	0.40	1.15	1.3
BA-a[b]	0.11	0.28	0.98	1.9
BEP121	0.10	0.30	1.28	1.70
BEP893	0.10	0.32	1.40	1.81

[a] Ref. [44].
[b] Ref. [37].

failure during the fabrication process. Table 1 shows the numerical comparison of the water absorption of BEP121, and BEP893 with other resins. The ternary systems show the water uptake with the values between those of polybenzoxazine and epoxy resin. In other words, the water absorption of the ternary systems is improved from their pure epoxy counterpart due to the presence of lower water uptake benzoxazine resin in the mixture.

4. Conclusions

Low-viscosity ternary mixtures of benzoxazine, epoxy, and phenolic resins have been developed. The blends render homogeneous and void-free cured specimens with a wide range of properties which are highly dependent on the composition of the starting resins in the ternary mixture. Benzoxazine resin imparts thermally curable, low water uptake, high char yield, and mechanical strength to the material while epoxy is used mainly to reduce the viscosity of the mixture for special application such as underfilling in the electronic packaging encapsulation. Melt viscosity with the value about 0.3 Pa s at 100°C can be achieved. Besides the function as a diluent, epoxy resin also gives higher crosslink density material with improved thermal stability as well as lowers the ambient temperature modulus of the ternary systems. Curing retardation and higher water absorption are the adverse effects from the use of epoxy as a diluent. Finally, phenolic novolac acts as a curing accelerator to the systems, aside from its typical function as a hardener of epoxy resin. A glass transition temperature of the ternary system as high as 170°C is also obtained. The transition temperature was found to be strongly dependent on the combined amount of benzoxazine and epoxy resins in the ternary systems.

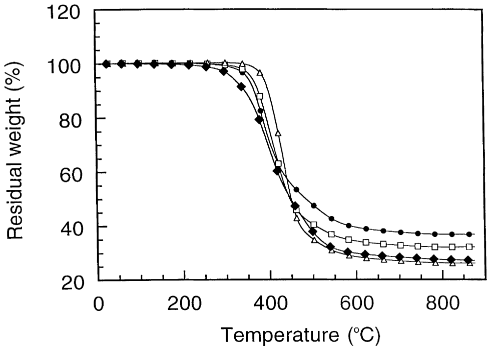

Fig. 15. TGA thermogram of ternary systems: (●) BEP111; (□) BEP121; (△) BEP131; (◆) BA-a.

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