**Benzoxazine-modified BMI Heat-resistant Resin with Low Dielectric Properties**

Pitao Kuo* and Hitoshi Habuka

1 Graduate School of Engineering Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
2 Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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**Abstract**

Benzoxazine modified BMI resin is a low dielectric curing resin obtained by synthesizing three types of benzoxazines with C36 diamine (C36DA) biomass material and reacting them with BMI having a biomass material backbone. In particular, the 2-allyl phenol/C36 diamine type benzoxazine modified C36 bismaleimid (B36-APda) resin curing compound (equivalent ratio 1:0.3) has a high 3% and 5% weight loss temperature (Td3 = 372°C/Td5 = 393°C), excellent strength (Max.stress = 1.71 kgf/mm²) and toughness (Toughness = 42.6 kgf-mm/mm³) properties, and low dielectric loss tangent, which implies the presence of the so-called ene reaction between the combined allyl and maleimide. The addition of the paraxylylene bisdiphenylphosphine oxide (PBO) phosphorus flame retardant to this resin after curing produces a flame retardancy and can further improve the heat resistance and reduce the dielectric loss tangent to 0.0015–0.0019 at 10 GHz.

**Keywords:** Benzoxazine, Bismaleimide, Biomass, Low Dielectric, Phosphorus Flame Retardant

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1. **Introduction**

In semiconductor packaging, new generation packaging, such as FOWLP (Fan-out Wafer Level Packaging), with the short distance connection of components is being actively developed together with low dielectric properties and re-routing materials[4] (Fig. 2) to shorten the line length (Fig. 1). The overall semiconductor packaging by FOWLP can be thinner since it does not require an IC carrier board. Thus, U.S. Apple, Inc., has adopted the FOWLP technology in the iPhone 7.

In recent years, rapid development electronic modules used in electric vehicles, autonomous driving and automotive electronics technologies have attracted everyone’s attention and driven the continuous growth of the semiconductor industry. Automotive electronic modules include electronic control units (ECUs), power control units and advanced driver-assistance systems (ADAS).

ADAS is the keystone of autonomous driving, which applies all kinds of sensors to collect vehicle data from its interior and exterior. These sensors include millimeter wave radar, ultrasonic radar, infrared radar, laser radar, CCD/CMOS image sensor and wheel speed sensor. In particular, millimeter wave radar is a crucial component of ADAS. The attractable FOWLP applications in the high-frequency field include millimeter wave radar and antenna packaging.

The two frequency bands commonly used in millimeter wave radars are 24 GHz and 77 GHz/79 GHz. The 24 GHz sensor radar is mainly used for short and medium range detection applications such as blind spot detection, pedestrian detection and parking assistance, while the 77 GHz/79 GHz sensor radar detects longer distances and is thus used for cruise control and collision pre-warning. They are both used in an MMIC (Monolithic microwave integrated circuit) manner. For the MMIC package of millimeter wave radar, the signal waveform becomes passivated as the dielectric loss tangent (tanδ) of the liquid packaging material increases. Therefore, the dielectric loss tangent (tanδ) of liquid packaging material is the main cause of signal transmission loss and the key to the safety of automatic driving.

The semiconductor liquid packaging materials used in millimeter-wave radars require properties not previously available and a high reliability. In particular, it is not easy to produce gas-sealed packages with good characteristics in the millimeter-wave domain, especially in the feedthrough...
portion of the signal ingress and egress.[5] (Fig. 3)

The circuit is connected between the wafer and the substrate by lead wires and TAB (Tape automated bonding), and liquid packaging material is applied to the wafer surface and the joints. Liquid sealing is performed in the gap between the wafer and the substrate when the flip chip is connected. The material after curing is known as underfill material to protect and reinforce the joint.[6] In high-frequency communications, when signals are transmitted at metal joints, the effect of the dielectric loss tangent ($\tan \delta$) on the signal transmission loss should be considered for liquid sealing materials that are metal insulators.

In this study, a new liquid packaging material based on the benzoxazine-modified BMI heat-resistant resin with low dielectric properties in the high-frequency field is discussed.
2. Experiment

2.1 Reagents

Cardanol (NX-2026, made by Cardolite; abbreviated as CP), purity 99.2%; C36 dimer diamine (Priamine 1074, made by Croda; abbreviated as C36DA), with the amine value of 205; p-tert-butylphenol (made by Sigma-Aldrich; abbreviated as PTBP), purity 99.0%; 2-allylphenol (made by Sigma-Aldrich; abbreviated as AP), purity 99.0%; maleic anhydride (made by Sigma-Aldrich; abbreviated as MA), purity 99.0%; and paraxylylene bisdiphenylphosphine oxide (made by Chin Yee Chemical; abbreviated as PBO), melting point 336°C.[7] (Scheme 1)

2.2 Synthesis of Benzoxazine

0.10 mol of C36DA, 150 g of toluene and 100 g of isobutanol were added to a 4-port reaction flask equipped with a stirrer, condenser, distillation receiver, nitrogen tube and isocratic dropping funnel. 0.40 mol of 37% formaldehyde was dropwise added to the reaction flask, the temperature was controlled at 20 to 30°C and the reaction was carried out for 5 h. 0.20 mol of PTBP was then added and the temperature was raised to 90 and 120°C. After azeotropic boiling and removal of the produced water at 120°C, the solvent was distilled under reduced pressure to obtain the benzoxazine labeled TPda (para-tert-butyl phenol/C36 dimer diamine type benzoxazine) (Scheme 2). The HPLC

![Scheme 1](image1) Structure of chemical compounds under test.

![Scheme 2](image2) Synthesis of benzoxazine and bismaleimide.
analysis showed that the residual amount of C36DA was 0.030% and the residual amount of PTBP was less than 0.022%.[8]

0.10 mol of C36DA, 200 g of toluene and 100 g of isobutanol were added to a 4-port reaction flask equipped with a stirrer, condenser, distillation receiver, nitrogen tube and isocratic dropping funnel. 0.40 mol of 37% formaldehyde was dropwise added to the reaction flask, the temperature was controlled at 20 to 30°C and the reaction was carried out for 5 h. 0.20 mol of CP was then added and the temperature was increased to 90 and 120°C. After azeotropic boiling and removal of the produced water at 120°C, the solvent was distilled under reduced pressure to obtain the benzoxazine labeled CPda (Cardanol/C36 dimer diamine type benzoxazine) (Scheme 2). The HPLC analysis showed that the residual amount of C36DA was 0.026% and the residual amount of CP was less than 0.020%.[8]

0.10 mol of C36DA, 150 g of toluene and 100 g of isobutanol were added to a 4-port reaction flask equipped with a stirrer, condenser, distillation receiver, nitrogen tube and isocratic dropping funnel. 0.40 mol of 37% formaldehyde was dropwise added to the reaction flask, the temperature was controlled at 20 to 30°C and the reaction was carried out for 5 h. 0.20 mol of AP was then added and the temperature was increased to 90 and 120°C. After azeotropic boiling and removal of the produced water at 120°C, the solvent was distilled under reduced pressure to obtain the benzoxazine labeled APda (2-Allaly phenol/C36 dimer diamine type benzoxazine) (Scheme 2). The HPLC analysis showed that the residual amount of C36DA was 0.030% and the residual amount of AP was less than 0.022%.[8]

2.3 Synthesis of BMI (Bismaleimide)

0.2 mol maleic anhydride, 150 g of xylene, 30 g of dimethylformamide 0.06 g of cupric sulfate and 0.3 g of 4-methoxyphenol were added to a 4-port reaction flask equipped with a stirrer, condenser, drying tube and distillation receiver and filled with nitrogen. An ice bath was used to lower the reaction temperature to 5–10°C. 0.099 mol of C36DA was slowly added, reacted for 1 h, 1 g of sulfuric acid added, heated to 120–150°C, removed the water by azeotropy, cool to room temperature and separated to remove the lower catalyst layer. B36 BMI was washed twice with 1% aqueous sodium carbonate and three times with distilled water, and the solvent was removed by decompression distillation at 100°C. The yield was 80% and the purity was 99.5% (by HPLC). This is achieved by (Scheme 2).[9]

2.4 Benzoxazine-Modified BMI Resin

It is generally believed that the hydroxyl group produced by the ring-opening polymerization of benzoxazine reacts with the double bond to form an ether structure.[10, 11] The thermal ring opening reaction of benzoxazine results in the formation of ionic pairs of phenoxy anions and imine cations. Among them, the phenoxy anions have strong nucleophilic properties. The phenoxy anion may also attack the electron deficient double bond and play a catalytic role in the reaction of benzoxazine with BMI, represented in Scheme 3 by the opening of the benzoxazine ring and the anionic polymerization of BMI (Scheme 3).

It is hypothesized that in addition to the general hot radi-
cal polymerization of BMI, nucleophilic attack can cause anion polymerization, which contributes to the reactivity. In particular, in the system with the benzoxazine: BMI equivalent ratio of 0.3:1, the post-hardening properties of BMI were improved by the interaction between BMI and benzoxazine. The system has been found to be excellent in terms of physical and chemical heat resistances.[12]

Therefore, in this study, the reaction behavior of a mixture of benzoxazine containing long fat chains and BMI containing long fat chains with the equivalent ratio of 0.3:1 was investigated, and the dielectric, thermal and mechanical properties of the hardened material were evaluated with the equivalent ratio of 0.3:1 as the centerpiece.

2.5 Flame Retardation of Benzoxazine-Modified BMI Resins

Automotive electronic modules are exposed to extreme environmental conditions such as high temperature and high humidity. Thus, the insulating polymers of semiconductor packaging materials in automotive electronic modules are required to have low dielectric properties and thermal resistance. The flame retardant added to the packaging material must also take into account its dielectric properties and thermal resistance.

PBO flame retardants have the high thermal decomposition temperature $T_d=359^\circ C$, melting point $m_p=336^\circ C$, and refractive index $n=1.700$. The crystallinity of their molecules is higher than that of ordinary phosphorus flame retardants, which can reduce the dielectric loss tangent because their own crystallinity inhibits molecular motion. The PBO flame retardants were added to the benzoxazine-modified BMI resins BT, BC and BA, and their effects on the dielectric and mechanical properties were investigated.

Each weight ratio was as follows:

- BT (B36:TPda = 1:0.3):PBO = 100:0,
- BT:PO = 100:20,
- BT:PO = 100:30,
- BT:PO = 100:50,
- BC (B36:CPda = 1:0.3):PBO = 100:0,
- BC:PO = 100:20,
- BC:PO = 100:30,
- BC:PO = 100:50,
- BA (B36:APda = 1:0.3):PBO = 100:0,
- BA:PO = 100:20,
- BA:PO = 100:30,
- BA:PO = 100:50,

They were then uniformly dispersed. The curing conditions were $120^\circ C/1 \text{ h} + 150^\circ C/1 \text{ h} + 180^\circ C/1 \text{ h} + 220^\circ C/1 \text{ h}$. Finally, heating to $250^\circ C/2 \text{ h}$, then the curing compounds were be obtained.

### 2.6 Measurement

#### 2.6.1 Reaction Behavior

The reaction behavior of the resins was studied using a differential scanning thermal analyzer (DSC: TA Q10). The samples mixed with benzoxazine and BMI were dried at $150^\circ C$ for 2 hours. A 40 mg sample was measured from room temperature to $300^\circ C$ at the temperature rise rate of $10^\circ C/\text{min}$ and the nitrogen flow rate of 50 ml/min.

#### 2.6.2 Thermal Decomposition Behavior

Thermal decomposition behavior of the cured materials was measured by thermogravimetric analysis (TGA: TA Instruments, Q500) at the temperature rise rate of $10^\circ C/\text{min}$ and the nitrogen flow rate of 20 ml/min. The 3 wt% and 5 wt% weight loss temperatures ($T_d=3, T_d=5$) were used as indicators of the chemical heat resistance.

#### 2.6.3 Dynamic Viscoelasticity

The glass transition temperature of the cured product was studied based on its dynamic viscoelasticity (DVA: TA Instruments, DMA-Q800). A test piece of $10 \text{ mm} \times 41.5 \text{ mm} \times 2 \text{ mm}$ was used and measured at the heating rate of $5^\circ C/\text{min}$ and the frequency of 1 Hz. In the report, the maximum temperature of the loss-positive connection ($\tan \delta = \text{loss elasticity/energy storage elasticity}$) with $\alpha$ relaxation was defined as the glass transition temperature ($T_g$).

#### 2.6.4 Thermal Expansion Coefficient

The coefficient of thermal expansion (CTE) at 50 to $300^\circ C$ was evaluated by a thermomechanical analysis (TMA: TA Instruments, TMA Q400). Test pieces of 5.0 g and up to $5 \text{ mm} \times 5 \text{ mm} \times 10 \text{ mm}$ were measured at the heating rate of $5^\circ C/\text{min}$ and the nitrogen flow rate of 20 ml/min.

#### 2.6.5 Scanning Electron Microscope

A scanning electron microscope (SEM: OXFORO Energy, JEOL 6360-LV) was used to observe the cross-section of the cured resin product.

#### 2.6.6 Relative Permittivity ($\varepsilon$) and Dielectric Loss Tangent ($\tan \delta$)

A $1 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$ sample was inserted into the cavity resonator and measured using a network analyzer (E5071C, KEYSIGHT) using the resonant cavity method (measurement frequency 10 GHz).

#### 2.6.7 Stress and Strain

Stress and strain were measured using a tensile tester (PRO, PT-1699V) and the ASTM D638 test method, 23°C and TYPE IV specimen conditions.
2.6.8 Viscosity
The viscosity measurement was done using a TOKIMEC BM2 rotary viscometer (30 rpm, 40°C).

2.6.9 HPLC Analysis
The HPLC conditions were measured in C-18 reversed-phase chromatography tubes with acetonitrile/H2O = 8/2 and the flow rate of 1.0 ml/min.

2.6.10 Water Absorption Rate
Water absorption is the rate of increase in weight of the sample measured by impregnation with distilled water at 23°C for 24 hours.

3. Results and Discussion
3.1 Reaction Behavior Investigation
The DSC measurements as shown in Fig. 4 showed that B36 and TPda each had a single exothermic peak, indicating a polymerization temperature of 293°C for B36 and 274°C for TPda. There was no original exothermic peak in the mixture of B36 and TPda, but a new exothermic peak appeared at low temperature with an exothermic temperature of 228°C, which represents a possible inter-reaction between B36 and TPda.

DSC measurements as in Fig. 5 show that B36 and CPda each have a single exothermic peak, indicating a polymerization temperature of 293°C for B36 and 262°C for CPda. The mixture CPda: B36 = 0.3:1 does not show the original exothermic peaks for B36 and CPda, but a new exothermic peak appeared at the low temperature of 218°C, indicating a possible interaction between B36 and TPda. This indicated a possible inter-reaction between B36 and TPda. The
The DSC measurements in Fig. 6 showed that ATda had two exothermic peaks at 187°C and 270°C, while B36 had an exothermic peak at 293°C. It is presumed that the exothermic peak at 270°C is the benzoxazine ring opening reaction of ATda, the exothermic peak at 187°C is the allyl polymerization reaction of ATda, and the exothermic peak at 293°C is the maleimide polymerization reaction of B36. The mixture of APda: B36 = 0.3:1 showed that the original exothermic peaks of B36 and APda disappeared and two new exothermic peaks appeared at the low temperatures of 162°C and 210°C. The 162°C exothermic peak was probably caused by the reaction between the allyl and maleimide, while the 210°C exothermic peak showed the mutual reaction between benzoxazine and maleimide. The ene reaction that usually occurs at low temperature, leads to the formation of a styrene structure intermediate which undergoes the Diels-Alder reaction with maleimide. It can be assumed that the toughness of the resulting product is higher than that of the maleimide homopolymer. (Scheme 4)

The compound has two-stage curing characteristics, so it can be cured by heating at 162°C to reach stage B and at 210°C to reach stage C. The two-stage curing characteristics are very suitable for application in interlayer insulation films.

3.2 Evaluation of Dielectric and Thermal Properties

The TP molecule has a symmetric structure, and the AP molecule and the CP molecule have an asymmetric structure. The polarity of the segment centered on TPda is lower than that of the segment centered on CPda and APda. Therefore, the dielectric constant \( \varepsilon_r \) = 2.32 and the dielectric loss tangent \( \tan \delta \) of TPda are the lowest among the cured benzoxazines. Furthermore, CPda shows the highest value of dielectric loss tangent \( \tan \delta = 0.0046 \). This may be related to the mobility of CP long aliphatic chain C15.

Figure 7 and Table 1 shows the equivalent ratios of
Among them, the specific dielectric constant ($\varepsilon_r$) and dielectric loss tangent ($\tan\delta$) are the lowest values for the equivalent ratio of 0.3:1. Table 1 and Table 2 show the equivalent ratios of TPda/B36 to dielectric properties.

| Equivalence ratio | $\varepsilon_r$ (10 G) | $\tan\delta$ (10 G) |
|-------------------|-------------------------|---------------------|
| Neat B36 = 0:1    | 2.46                    | 0.0025              |
| TPda:B36 = 0.15:1 | 2.31                    | 0.0024              |
| TPda:B36 = 0.3:1  | 2.16                    | 0.0022              |
| TPda:B36 = 0.5:1  | 2.28                    | 0.0025              |
| Neat TPda = 1:0   | 2.32                    | 0.0031              |

| Equivalence ratio | $\varepsilon_r$ (10 G) | $\tan\delta$ (10 G) |
|-------------------|-------------------------|---------------------|
| Neat B36 = 0:1    | 2.46                    | 0.0025              |
| CPda:B36 = 0.15:1 | 2.40                    | 0.0030              |
| CPda:B36 = 0.3:1  | 2.32                    | 0.0034              |
| CPda:B36 = 0.5:1  | 2.33                    | 0.0041              |
| Neat CPda = 1:0   | 2.36                    | 0.0046              |

Figure 8 and Table 2 show the equivalent ratios of CPda/B36 to dielectric properties.

Fig. 8  The equivalent ratio of CPda/B36 to dielectric properties.

TPda:B36 = 0:1, TPda:B36 = 0.15:1, TPda:B36 = 0.30:1, TPda:B36 = 0.50:1, and TPda:B36 = 1:0. Among them, the specific dielectric constant ($\varepsilon_r$) and dielectric loss tangent ($\tan\delta$) are the lowest values for the equivalent ratio of 0.3:1. Figure 8 and Table 2 show the equivalent ratios of CPda:B36 = 0:1, CPda:B36 = 0.15:1, CPda:B36 = 0.30:1, CPda:B36 = 0.50:1, and CPda:B36 = 1:0. Therefore, the dielectric constant ($\varepsilon_r$) tend to decrease for the equivalent ratio of 0.3:1.

Figure 9 and Table 3 show that the equivalent ratios of
Among them, the 0.3:1 equivalence ratio has a tendency to decrease the dielectric constant (εr) and dielectric loss tangent (tanδ).

Based on these results (Table 4), it has been shown that the εr of the hybrid system was lower than that of the single benzoxazine and BMI, especially in the benzoxazine:B36 = 0.3:1 hybrid system. In addition to the lowest εr, the water absorption also decreased, confirming the double bond of the maleimide and phenolic hydroxyl groups for producing ether bonds.

According to the dielectric theory of Clausius-Mossotti relation and Debye relaxation, it can be known. The factors affecting the dielectric loss tangent of the polymer include the size of the polymer molecule, the concentration of the polar groups, the vibration and rotation of the

Table 3  The equivalence ratio of APda/B36 to dielectric properties.

| Equivalence ratio | εr (10 G) | tanδ (10 G) |
|-------------------|-----------|-------------|
| Neat B36 = 0:1    | 2.46      | 0.0025      |
| APda:B36 = 0.15:1 | 2.26      | 0.0023      |
| APda:B36 = 0.3:1  | 2.25      | 0.0021      |
| APda:B36 = 0.5:1  | 2.32      | 0.0028      |
| Neat APda = 1:0   | 2.35      | 0.0032      |

Table 4 Benzoxazine modified bismaleimide resin characteristics.

| Equivalenc ratio Benzoxazine:B36 | Tg °C | Td3 °C | Td5 °C | εr (10 G) | tanδ (10 G) | water absorption Wt% |
|----------------------------------|------|-------|-------|-----------|------------|----------------------|
| Neat B36 = 0:1                   | 48   | 390   | 408   | 2.46      | 0.0025     | 0.32                 |
| TPda:B36 = 0.3:1                 | 25   | 349   | 375   | 2.16      | 0.0022     | 0.24                 |
| CPda:B36 = 0.3:1                 | 20   | 360   | 383   | 2.32      | 0.0034     | 0.29                 |
| APda:B36 = 0.3:1                 | 57   | 372   | 393   | 2.25      | 0.0021     | 0.28                 |
| Neat TPda = 1:0                  | 35   | 335   | 354   | 2.32      | 0.0031     | 0.50                 |
| Neat CPda = 1:0                  | 26   | 264   | 287   | 2.36      | 0.0046     | 0.39                 |
| Neat APda = 1:0                  | 20   | 332   | 358   | 2.35      | 0.0032     | 0.46                 |
polar groups or chain segments and the degree of crosslinking. Based on these points of view, the cured allyl vibration and rotation are suppressed, so APda:B36 = 0.3:1 shows the lowest dielectric loss tangent of tanδ = 0.0021.

In terms of the heat resistance properties, the heat resistance properties of the cured compounds are shown in Table 4. In the benzoxazine: B36 = 0.3:1 mixture, APda:B36 = 0.3:1 has the highest Tg = 57°C, with the highest values of Td3 = 372°C and Td5 = 393°C. It is presumed that such results are related to the ene reaction with the allyl and maleimide.

### 3.3 Mechanical Properties

Strength is the maximum stress that can withstand deformation and fracture. Toughness is obtained by integrating the stress, i.e., the area under the strain curve. The formula is

\[
\text{Toughness} = \int_{\text{s}}^{\text{e}} \frac{\text{energy}}{\text{volume}} \text{d}e
\]

s: Stress
e: Strain
ef: Fracture Strain

Looking at the area of the region below the stress-strain curve, the area of TPda:B36 = 0.3:1 is larger than of B36 and TPda, the area of CPda:B36 = 0.3:1 is larger than of B36 and CPda, and APda:B36 = 0.3:1 than for B36 and APda. Based on the ether bond, it can be seen that the cocure of the benzoxazine and B36 equivalent ratio of 0.3:1 has the tendency to be strong and tough at the same time due to the combination of the ether bond. In the benzoxazine-modified BMI resin, APda:B36 = 0.3:1, the allyl and maleimide are bonded to each other by the ene reaction. The resulting product has a significantly higher toughness, which is higher than that of the maleimide homopolymer, and the highest strength and toughness among all.

In terms of the energy storage modulus, the co-curing material with an equivalent ratio of 0.3:1 is higher than that of benzoxazine and B36. TPda, CPda, APda have a low viscosity and can be used as a diluent to reduce the viscosity of B36. In flip chip packaging, the gap between the semiconductor wafer and the substrate is protected and secured by a liquid packaging material with flow requirements by using a dispenser to connect the semiconductor wafer to the substrate. Benzoxazine-modified BMI resins with a flowability are suitable liquid packaging materials for gap seal applications (Table 5).

### 3.4 Analysis of Benzoxazine-Modified BMI Resin with Added Flame Retardant

The increasing addition of the PBO flame retardant can increase the glass transition temperature (Tg), thermal decomposition temperature (Td3) and dielectric constant (εr) of B36-TPda (B36:TPda = 1:0.3), but reduce the storage modulus, dielectric loss tangent (tanδ) and thermal expansion coefficient (CTE). When 30 phr or more of PBO is added, B36-TPda can achieve the UL-94/V-0 flame retardancy (Table 6).

The increasing addition of the PBO flame retardant can also increase the Tg, Td3, εr and storage modulus of B36-CPda (B36:CPda = 1:0.3), but reduce the tanδ and CTE. When PBO 30 phr or higher is added, B36-CPda achieves the UL-94 V-0 flame retardancy (Table 7).

The increasing addition of the PBO flame retardant can also increase the Tg, Td3, εr and storage modulus of B36-APda (B36:APda = 1:0.3), however, it reduces the tanδ, Td3 and CTE. When PBO 30 phr or higher is added, B36-CPda achieves the UL-94 V-0 flame retardancy (Table 8).

The PBO of the signal is a long strip of crystalline particles (Fig. 12A). When dissolved in chloroform and allowed to recrystallize, the elongated crystals can be clearly observed under a microscope (Fig. 12B). PBO and B36-TPda/B36-CPda/B36-APda were mixed, cured and

| Equivalence ratio | Storage Modulus (GPa) | Strain (%) | Max. stress (kgf/mm²) | Toughness (kgf-mm/mm³) | Viscosity (mPa.s) |
|-------------------|-----------------------|------------|-----------------------|------------------------|------------------|
| Neat B36 = 0:1    | 0.2                   | 4.48       | 0.82                  | 1.8                    | 1,560            |
| TPda:B36 = 0.3:1  | 0.5                   | 8.24       | 1.04                  | 4.5                    | 46,100           |
| CPda:B36 = 0.3:1  | 0.3                   | 34.24      | 0.56                  | 15.6                   | 530              |
| APda:B36 = 0.3:1  | 0.6                   | 14.63      | 1.71                  | 42.6                   | 1,618            |
| Neat TPda = 1:0   | 0.3                   | 4.99       | 0.59                  | 1.5                    | 15,100           |
| Neat CPda = 1:0   | 0.1                   | 13.00      | 0.04                  | 0.3                    | 1,250            |
| Neat APda = 1:0   | 0.3                   | 12.67      | 0.34                  | 28.4                   | 1,881            |
### Table 6  Characteristics of B36-TPda resin containing flame retardant.

| weight ratio B36-TPda:PBO | Tg °C | Td3 °C | Td5 °C | elastic modulus GPa | $\sigma$ (10 G) | tan$\delta$ (10 G) | CTE ppm/K | UL-94 |
|--------------------------|-------|--------|--------|---------------------|----------------|-----------------|-----------|-------|
| 100:0                    | 24    | 349    | 375    | 0.5                 | 2.20           | 0.0022          | 333       | NG    |
| 100:20                   | 24    | 352    | 378    | 0.32                | 2.23           | 0.0019          | 260       | V-1   |
| 100:30                   | 25    | 354    | 379    | 0.25                | 2.36           | 0.0016          | 236       | V-0   |
| 100:50                   | 25    | 355    | 380    | 0.25                | 2.41           | 0.0014          | 194       | V-0   |

### Table 7  Characteristics of BC resin containing flame retardant.

| weight ratio B36-CPda:PBO | Tg °C | Td3 °C | Td5 °C | elastic modulus GPa | $\sigma$ (10 G) | tan$\delta$ (10 G) | CTE ppm/K | UL-94 |
|--------------------------|-------|--------|--------|---------------------|----------------|-----------------|-----------|-------|
| 100:0                    | 23    | 360    | 383    | 0.20                | 2.30           | 0.0034          | 331       | NG    |
| 100:20                   | 23    | 360    | 383    | 0.23                | 2.32           | 0.0023          | 310       | V-1   |
| 100:30                   | 23    | 361    | 385    | 0.27                | 2.36           | 0.0021          | 236       | V-0   |
| 100:50                   | 25    | 363    | 386    | 0.32                | 2.38           | 0.0017          | 203       | V-0   |

### Table 8  Characteristics of BA resin containing flame retardant.

| weight ratio B36-APda:PBO | Tg °C | Td3 °C | Td5 °C | elastic modulus GPa | $\sigma$ (10 G) | tan$\delta$ (10 G) | CTE ppm/K | UL-94 |
|--------------------------|-------|--------|--------|---------------------|----------------|-----------------|-----------|-------|
| 100:0                    | 57    | 372    | 393    | 0.60                | 2.25           | 0.0021          | 267       | NG    |
| 100:20                   | 57    | 371    | 390    | 0.58                | 2.27           | 0.0023          | 242       | V-1   |
| 100:30                   | 58    | 368    | 382    | 0.55                | 2.31           | 0.0019          | 217       | V-0   |
| 100:50                   | 59    | 364    | 379    | 0.52                | 2.35           | 0.0015          | 185       | V-0   |

![Stress-strain curve B36-TPda and B36-CPda.](image)
Fig. 11  Stress-strain curve of B36-APda.

Fig. 12  SEM image of the fracture surface (CDE)/SEM image of the surface (A)/Microscope image of the Surface (B).
observed by scanning electron microscopy (SEM), and the PBO crystals could be uniformly dispersed in the resin (Fig. 9CDE). Moreover, the PBO molecular structure has a high symmetry and small dipole moment of molecules, so it is presumed to effectively inhibit the elevation of the $\varepsilon_r$ and $\tan\delta$.

In a hybrid system with the equivalent ratio of 1:0.3, B36-TPda, B36-CPda, and B36-APda are curing resins with added the PBO flame retardant, which can give the curing resin a flame retardancy, improve the heat resistance of the curing resin, and reduce the dielectric loss tangent and thermal expansion coefficient, and are expected to be used as packaging materials for high-speed and high-capacity signal transmission.

4. Conclusions

The benzoxazine-modified BMI resin, a low dielectric curing resin, in this study was obtained by synthesizing three types of benzoxazines with the C36DA biomass material and reacting them with bismaleimide with the biomass material as the backbone. In particular, the B36-APda resin curing compound (1:0.3 equivalent ratio) has a high Td3/Td5 temperature, excellent strength and toughness properties, and low dielectric loss tangent, which implies the presence of the so-called ene reaction between the combined allyl and maleimide. The addition of the PBO phosphorus flame retardant to this resin after curing provides a flame retardancy and can further improve the heat resistance and reduce the dielectric loss tangent.

By using C36DA from biomass as a raw material to synthesize benzoxazine and BMI, liquid TPda, CPda, APda and B36 resins can be obtained, which can be applied to liquid packaging materials that require a flowability.

When the equivalent ratio is 1:0.3, it can be seen that the co-curing material of the benzoxazine-modified BMI can be strengthened by ether bonding, and the co-curing can be toughened. Therefore, it is possible to use it in thin-layer packaging materials where a toughness is required.

In addition, the B36:Benzoxazine = 1:0.3 hybrid system has a new exothermic peak at low temperatures, and the dielectric properties ($\varepsilon_r/\tan\delta$) and moisture absorption tend to decrease, which implies the possibility of an interaction between B36 and TPda/CPda/APda.

For a hybrid system with an equivalent ratio of 1:0.3, the addition of the PBO flame retardant to the benzoxazine-modified BMI resin can give the cured resin a flame retardancy, improve the heat resistance of the resin, and reduce the dielectric loss tangent and thermal expansion coefficient. At the same time, it retains a flame retardancy and low dielectric properties, which makes it suitable as a packaging material for high frequency field use.

In this study, it was found that the B36 resin was modified with TPda/CPda/APda resin to give the benzoxazine-modified BMI resin a strong toughness and low dielectric properties. By reducing the number of polar groups in the molecular structure, an environmentally-friendly phosphorus-based flame retardant with a low dielectric constant and dielectric loss tangent was added to the C36DA/CP/ AP with a 1:0.3 equivalent ratio using biomass. It is expected that a halogen-free flame retardancy and low dielectric properties can be achieved for packaging materials in the high-frequency field.

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Pitao KUO
Hitoshi HABUKA