Thermally Stable Siloxane Hybrid Matrix with Low Dielectric Loss for Copper-Clad Laminates for High-Frequency Applications

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ABSTRACT: We report vinyl-phenyl siloxane hybrid material (VPH) that can be used as a matrix for copper-clad laminates (CCLs) for high-frequency applications. The CCLs, with a VPH matrix fabricated via radical polymerization of resin blend consisting of sol–gel-derived linear vinyl oligosiloxane and bulky siloxane monomer, phenyltris-(trimethylsiloxy)silane, achieve low dielectric constant (Dk) and dissipation factor (Df). The CCLs with the VPH matrix exhibit excellent dielectric performance (Dk = 2.75, Df = 0.0015 at 1 GHz) with stability in wide frequency range (1 MHz to 10 GHz) and at high temperature (up to 275 °C). Also, the VPH shows good flame resistance without any additives. These results suggest the potential of the VPH for use in high-speed IC boards.

KEYWORDS: copper clad laminates, low dielectric loss, low dielectric constant, siloxane hybrid material, thermal stability

The integrated circuit (IC) board is one of the greatest inventions in the electrical industry during the past century and is a crucial component of most electrical devices in the current era.1–4 The IC board, which is fabricated with copper clad laminates (CCLs) and electronic components, plays critical roles in serving as a structural basis and performing electrical functions for electrical devices by interconnecting the electronic components. CCLs are key base materials to fabricate IC boards; CCLs consist of a polymeric matrix reinforced with glass fabric and copper layers. Among these components, the polymeric matrices mainly determine the dielectric, thermal, and mechanical properties of CCLs.2,3 Because of their acceptable dielectric properties, thermal stability, and good processability, the polymeric matrices conventionally used for CCLs are epoxy resins.5–7 However, modern electronic devices such as mobile phones, computers, network routers, etc., are more integrated and require high-speed information transfer in a high-frequency range, so there has been increasing demand for high performance CCLs (HPCCLs) that have lower dielectric constants (Dk) and dissipation factors (Df) and higher thermal stability that can be maintained in high frequency range; these factors are not achievable by conventional epoxy resins.8–10 It should be noted that the signal propagation speed in IC boards is inversely proportional to the square root of Dk; the signal propagation loss is proportional to frequency, Df, and the square root of Dk.8–10

Modified epoxy resins (e.g., dicyclopentadiene epoxy), because of their enhanced thermal and dielectric properties with good process ability by introducing dicyclopentadiene (DCPD) groups that have excellent dielectric properties and thermal stability, are currently used as alternatives to conventional epoxy resins.10,11 Furthermore, epoxy based nanocomposite and modified glass fabric that can enhance the performances of CCLs have been reported.12,13 Despite such efforts, the dielectric properties of such epoxy resins are not greatly improved because of the presence of polar hydroxyl groups, which drastically increase the values of Dk and Df in polymeric dielectrics via the curing of the epoxy resins.14–16

To address this issue, researchers use engineering plastics (e.g., polyimide, poly(p-phenylene ether), bismaleimide, and polytetrafluoroethylene) for HPCCLs.1–4 Despite their high thermal stability and excellent dielectric properties, such engineering plastics generally have poor processability. In an attempt to improve their processing ability, engineering plastics blended with other kinds of thermoplastic or thermoset polymers have been reported. However, such polymer composites lose their own excellent dielectric and thermal stability because of the decreased cross-linking density of the original polymer matrix.2,3

In this paper, we report, to the best our knowledge, the first siloxane based matrix for CCLs to exhibit excellent dielectric properties (low Dk ≈ 2.75, low Df ≈ 0.0013 @ 1 GHz) that are maintained at high temperature (~275 °C) and in a high frequency range (up to 10 GHz), allowing the fabrication of HPCCLs based on vinyl-phenyl siloxane hybrid material (VPH). In VPH, in order to decrease Dk and Df, a high...
The amount of rigid aromatic moiety is introduced, along with bulky siloxane monomer, which can increase the free volume.

As illustrated in Scheme 1, CCLs with the VPH matrix were fabricated by impregnation and lamination of glass fabrics with thermally curable resin blend consisting of linear vinyl-phenyl oligosiloxane (LVPO) and phenyltris(trimethylsiloxy)silane (PTTMSS) between two copper layers; this is the conventional fabrication method of CCLs. The LVPO resin was synthesized by mild nonhydrolytic sol–gel condensation between vinyl-methyldimethoxysilane (VMDMS) and diphenylsilanediol (DPSD) (Scheme 1a). The detailed synthesis method and the expected structures of LVPO were previously reported (see the Figures S1 and S2 for the FT-IR and 29Si NMR spectra). To decrease Dk and Df of VPH, we blended a bulky methyl monomer, phenyltris(trimethylsiloxy)silane (PTTMSS), with LVPO at a certain amount for increasing free volume of the VPH (Figure 1b). 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane was used as an initiator for the radical polymerization of the LVPO/PTTMSS resin blend (see the Figures S3 and S4 for the structure and mechanisms of the radical polymerization). 7628 woven E-glass fabric (a kind of standard woven fabric developed by IPC), which is commercially available and commonly used for printed circuit board, was used for mechanical enhancement of the final product. First, four sheets of woven glass fabrics were impregnated with the LVPO/PTTMSS resin blend, which is a viscous, clear, and thermally curable resin blend. The four drenched sheets were then stacked on a copper layer perpendicular to each other (across or along the fiber orientation). After the sample was covered with another copper layer, the laminating process was conducted in vacuum hot pressing, which is a typical fabrication method of CCLs; subsequently the LVPO/PTTMSS resin blend was cured via radical polymerization to form VPH-based CCLs.

To optimize the dielectric properties of VPH, we compared properties of various linear vinyl-phenyl siloxane hybrid materials (LVPH, i.e., a PTTMSS-free version of VPH) with varying Ph/Si ratios (Figure 1a). The assessment of the
dielectric properties was conducted using pure bulk samples in order to exclude the effects of the other components of the CCLs such as glass fabric or copper layers. Interestingly, at higher amounts of phenyl groups, both the dielectric constant and dissipation factor decreased. From point of view in polymer dielectric, the phenyl groups are like a double-edged sword because introducing phenyl groups can increase the dielectric constant because of their high polarizability but can also decrease the dielectric constant because of their high rigidity. According to the Debye relaxation model, the real and imaginary parts of the dielectric constant can be expressed by the following equation

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]

\[ \varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]

where \( \varepsilon_\infty \) is the dielectric constant of infinite frequency, \( \varepsilon_0 \) is the static dielectric constant, \( \omega \) is the angular frequency, and \( \tau \) is the relaxation time. The high rigidity leads to high relaxation time, resulting in a decrease in the dielectric constant. These results suggest that introducing phenyl groups in the LVPH can have a greater contribution to increasing the rigidity than to increasing polarizability. The increased rigidity of the LVPH with higher amount of phenyl groups can be confirmed by the low tan \( \delta \) peak value in the DMA measurements (Figure 1b). The LVPO with Ph/Si ratio higher than 1 might have better dielectric properties; however, they have poor storage stability resulting in precipitation (see Figure S5).

Generating free volume is the one effective way to decrease the dielectric constant and the dielectric loss. PTTMSS, a siloxane monomer with methyl groups, was introduced in an

![Figure 1. Optimization of dielectric properties of the LVPH. (a) Dielectric properties of the LVPH depending on varying Ph/Si ratio. (b) The peak value of the tan \( \delta \) of the LVPH in DMA measurement. Note that the greater damping peak reflects the lower rigidity of the materials. (c) Dielectric properties of VPH depending on varying amounts of PTTMSS. (d) Density of VPH depending on varying amounts of PTTMSS.](image1)

![Figure 2. (a) Dielectric constant and (b) dissipation factor of VPH and DCPD epoxy according to 1 MHz to 10 GHz frequency range at room temperature. VPH exhibits superior dielectric properties in the entire measured frequency range. In particular, the dissipation factor of VPH maintains its superiority up to the 10 GHz range. The inset photograph shows a disk-like bulk sample of VPH (left) and the DCPD epoxy (right) with 2.5 cm diameter and 2 mm thickness.](image2)
attempt to increase the free volume of the VPH. As illustrated in Scheme 1b, VPH with PTTMSS could have higher free volume because of its steric hindrance, which originates from its bulky structure, as evidenced by the lower density of the VPH compared to its PTTMSS-free version (Figure 1d); 4.85 wt % PTTMSS is the most effective amount for decreasing the values of Dk and Df (Figure 1c, d). Above 4.85 wt % PTTMSS, the decreasing rate of the density was gradually dropped and the values of Dk and Df increased. This is thought to be due to the excess amount of the PTTMSS filling the free volume in the VPH rather effectively increasing the free volume of VPH. To determine the best dielectric performance of VPH as a matrix for CCLs, we blended LVPO, whose Ph/Si ratio is 1, with 4.85 wt % PTTMSS because that resin blend exhibits the best dielectric properties.

To evaluate the dielectric performance reliability in terms of the stability over a wide frequency range, we compared the dielectric properties of the VPH and DCPD epoxy (a commercial high performance epoxy) at 1 MHz, 1 GHz, and 10 GHz (Figure 2). The DCPD epoxy was used as reference for comparison. The dielectric properties of the VPH (Dk = 2.75 and Df = 0.0015 at 1 GHz) are superior to those of DCPD epoxy (Dk = 3.08 and Df = 0.0167 at 1 GHz) in the 1 MHz to 10 GHz frequency range. In particular, the Df of the VPH shows stable performance up to 10 GHz (Df = 0.0033 @ 10 GHz). This result confirms the excellent dielectric performance stability of the VPH over a wide frequency range.

Because the fabrication process of electronic devices applies heat during soldering and because the operation of electronic devices inevitably generates heat, thermal resistance is another important factor for CCLs in terms of both thermal decomposition and dielectric properties. Because of the degradation of dielectric properties and the drastic dimensional change of the epoxy matrix at the glass transition temperature (Tg), followed by subsequent delamination of the copper layer, which can be confirmed by the peak temperature of tan δ in DMA measurement,23 Tg is generally considered an indicator of the thermal resistance of epoxy-based CCLs.24 Tg, however, is not an appropriate indicator for comparing the thermal resistance between DCPD epoxy and VPH, as evidenced by the TGA measurement (Figure 3a, b). It should be noted that VPH, which has a lower Tg value than that of the DCPD epoxy, has higher thermal decomposition temperature than DCPD epoxy, which confirms the higher thermal resistance of VPH (Figure 3b).

To evaluate the thermal stability in terms of the dielectric properties of the VPH, we assessed the dielectric properties in a temperature range of 25 to 275 °C at intervals of 50 °C at 10 GHz frequency (Figure 3c, d). As the temperature increases, the values of Dk of both VPH and DCPD epoxy increase because of the reduced relaxation time that result from thermal agitation.18 Above the Tg value of the DCPD epoxy, significant increases of Dk and Df were observed, whereas VPH maintains its excellent dielectric properties (Dk = 2.73, Df = 0.0039 at 275 °C) up to 275 °C (Figure 3a, c, d). These results suggest that VPH maintains its structural rigidity at high temperature, suppressing the chain mobility, as further evidenced by the small value of the maximum peak of tan δ.

The properties of the VPH were further confirmed by assessing the dielectric properties and SEM analysis of the interfaces of the CCLs fabricated with the VPH matrix (Figure 4a and Table 1, see the Figure S6 for the SEM image of the
consistent with that demonstrated by the TGA measurement delamination after 30 min, which indicates a tendency whereas the CCLs with the DCPD epoxy matrix shows an hour of thermal aging at 260 °C, even in a bended state, whereas the CCLs with the VPH matrix maintains their laminated state after time to delamination of the layers, is considered as a useful not ignitable. The CCLs with the VPH matrix display good resistance without any additives; on these substances, a does not self-propagate (Table 1 and Video S1).

Table 1. Comparison of Properties of CCLs with Varying Matrices

<table>
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<tr>
<th></th>
<th>VPH</th>
<th>DCPD epoxy</th>
<th>FR-4*</th>
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<tbody>
<tr>
<td>dielectric constant</td>
<td>3.56</td>
<td>4.0</td>
<td>4.0-4.5</td>
</tr>
<tr>
<td>dissipation factor</td>
<td>0.002</td>
<td>0.012</td>
<td>~0.02</td>
</tr>
<tr>
<td>( T_{260} )</td>
<td>&gt; 60 min</td>
<td>~30 min</td>
<td>X</td>
</tr>
<tr>
<td>flame resistance</td>
<td>V-0</td>
<td>X</td>
<td>V-0</td>
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"Dielectric properties measured at 1 GHz frequency. *From ref 25.

cross-section of the CCLs). The fabrication procedure of the CCLs with the VPH matrix was conducted almost same condition with the procedure for the fabrication of the CCLS with epoxy matrix except for curing temperature, pressure and time, which confirms high processability of the VPH matrix (see the Supporting Information for the experiment details). The CCLs with the VPH matrix still exhibit superior dielectric properties compared to those of DCPD epoxy or the conventional FR-4 CCLs (Table 1). \( T_{260} \) which specifies the time to delamination of the layers, is considered as a useful indicator for comparing the maximum service temperature. The CCLs with the VPH matrix maintains their laminated state after an hour of thermal aging at 260 °C, even in a bended state, whereas the CCLs with the DCPD epoxy matrix shows delamination after 30 min, which indicates a tendency consistent with that demonstrated by the TGA measurement (Figure 4b).

Flame resistance is another important issue for CCLs; however, petroleum-based polymers such as epoxy resins are easily ignitable.20 To achieve flame resistance, halogenated or phosphorus compounds are generally added to epoxy resins, but the additives can lead to negative health or environmental issues.27 On the other hand, VPH, a siloxane-based material, is not ignitable. The CCLs with the VPH matrix display good fire resistance without any additives; on these substances, a flame does not self-propagate (Table 1 and Video S1).

In summary, we report a low dielectric constant (Dk = 2.75 at 1 GHz), low dissipation factor (DF = 0.0013 at 1 GHz) siloxane matrix for CCLs using vinyl-phenyl siloxane hybrid material (VPH). CCLs with VPH matrix were fabricated via radical polymerization of a resin blend consisting of sol−gel derived linear vinyl-phenyl oligosiloxane and bulky monomer, phenyltris(trimethylsiloxy)silane. The addition of the bulky monomer effectively enhances the dielectric properties by generating free volume in the VPH. The dielectric properties of the CCLs with the VPH matrix were maintained in a wide frequency range (up to 10 GHz) and in a wide temperature range (up to 275 °C); they exhibited excellent and stable dielectric performance. The CCLs with the VPH matrix also shows good thermal decomposition and flame resistance without any additives.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b01497.

Experimental section, FT-IR and 29Si NMR spectra of LVPO resin, structure of 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, mechanisms for radical polymerization between vinyl-functionalized and methyl-functionalized siloxane resin, a photograph of precipitated LVPO resin with 1.5 Ph/Si ratio, and SEM image of the cross-section of the fabricated CCLs (PDF)

Video of the simple flame resistance test with conventional lighter (AVI)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


