High-Frequency Dielectric Characterization for Liquid Crystalline Polyimide/SiO_2 Nanocomposites

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ABSTRACT: In this study, we investigated the influence of frequency, film thickness, and SiO_2 content on the dielectric constant (K) and loss tangent (tan δ) of liquid crystalline polyimide (LCPi) and liquid crystalline polyimide/SiO_2 (LCPi/SiO_2) nanocomposites in a high frequency environment. We tested the loss tangent of the LCPi and LCPi/SiO_2 nanocomposites within the high frequency 1 MHz to 3 GHz range, and determined its value to be between 0.01 and 0.001. In addition, we found a formant for frequencies ranging from 0.5 GHz to 1 GHz. We also inferred from the dielectric loss graphs of films with different thicknesses that the formants of the loss tangent shifted toward higher frequencies with increasing thicknesses. When measuring the dielectric constant at high frequencies, we found that the dielectric constant decreased markedly with increased SiO_2 contents. Using the dielectric constant of high-frequency circuit board materials as the standard, the dielectric constant of the LCPi/SiO_2 nanocomposites at the frequency range from 1 MHz to 3 GHz was found to be as high as 2.2–3.4, thereby confirming the viability of LCPi/SiO_2 nanocomposites as candidate materials for high-frequency circuit board. In addition, the volume resistivity (ρ_V) of the LCPi and LCPi/SiO_2 nanocomposites also increased with increased SiO_2 contents. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3454–3459, 2010

Key words: polyimide; film; nanocomposites; dielectric constant; high frequency

INTRODUCTION

Polyimide (PI) is a high polymer material with several highly desirable characteristics. Because its discovery by the DuPont Co. in 1955 and subsequent commercialization in the 1960's, it has found widespread applications in several fields, mainly due to its superior heat and chemical resistance, high mechanical strength, low dielectric constant, ability to form ultra-thin film, high gas permeability, etc. However, drawbacks of PI include high moisture absorption (~ 4 wt %) and coefficient of thermal expansion (~ 50 ppm/K), shortcomings that are preventing its widespread use as an electronic material. One proposed approach to address these deficiencies is the addition of inorganic filling material such as SiO_2.[1–3]

SiO_2 has very low moisture absorption (~ 0 wt %) and coefficient of thermal expansion (~ 0.5 ppm/K), but its dielectric properties and dimensional stability are far inferior to those of PI. Therefore, by mixing materials with the right proportion of PI and SiO_2, one can complement the respective strengths and drawbacks of the latter two so as to markedly improve their versatility and utility in material applications.[4–6] In a previously reported experiment,[6] we first dispersed SiO_2 nanoparticles in the liquid crystalline polyimide (LCPi) base material via the sol–gel method, and then studied the heat resistance, mechanical properties, electrical properties, etc.

The most commonly used PI dielectric insulating material in the general market is the non-LC type polymer. Although PI is the most cost-effective low dielectric constant (low-K) material used in ultra large scale integrated circuit (ULSI) multilevel metal interconnect, the rapid increase in the semiconductor device packing density means that the dimensions of the devices have gradually decreased, leading to greater capacity per unit wafer area while simultaneously enhancing the operating speeds and thus performance of the devices. As the process technology dips below 0.25 μm, the RC time delay due to the interconnects[7–9] will adversely affect the operating speed, response time, etc. of the devices, resulting in delays caused by the propagation of electronic signals between the metal wires. When the wafer surface becomes unable to provide sufficient area for the metal interconnect required, the need therefore arises to vertically develop the connection

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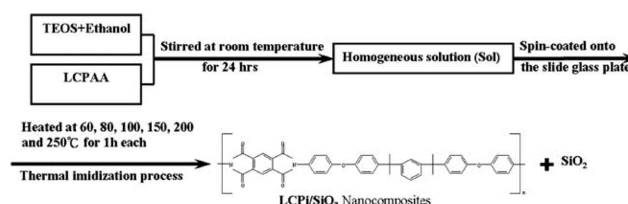
architecture upward during the process design, which leads to the emergence of multilevel metal interconnect architecture.

As such, the development of next generation electronics production necessitates research on low dielectric constant ($K < 3$) thin film materials[10] to reduce the incidence of problems such as RC time delay due to the shrinking of the IC line width, increasing interconnect capacitance, power consumption, crosstalk noise, etc.[11] Therefore, with shrinking IC line width within the multilevel metal interconnect, the development of low dielectric constant materials has taken on increasing importance in recent years. The dielectric constants for general PI range between 3.1 and 3.4, and because one of the methods for reducing the material dielectric constant is to "loosen" the material structure, we have attempted to synthesize in a previous study PI possessing the LC phase[6] and to further create a mixture complex with SiO_2. From XRD experiments, we deduced that the overall molecular arrangement regularity of the LCPi synthesized was poor and characteristic of amorphous liquid crystalline polymer.[6]

The molecular structure of the crystalline polymer is highly ordered and tightly packed, and therefore, conducive for the transfer of electric charges among molecules.[6,12] However, in the LCPi/SiO_2 mixture systems, because the SiO_2 nanoparticles would damage the ordering of the polymer molecular structure and impede the transfer of electric charges among the molecules, the molecular arrangement of the LCPi became more "loose," which effectively reduced the dielectric constant of the material itself to the levels required for applications nowadays.[6] It is apparent that the trend of future electronics production would be toward the development of higher packing density, with enhancement in the application frequency and bandwidth.

In recent years, dielectric materials are increasingly finding applications in high-frequency circuit boards and high frequency environments. For example, the receive frequencies of pagers and mobile phones in general range from 1 GHz to 3 GHz. For TV satellite frequency demultipliers (LNB/LNA) and global positioning system (GPS) satellite applications, the range is 2–3 GHz and 1.575–2.4 GHz, respectively. In other words, high-frequency circuit boards are ubiquitous in daily communication products. Within the next few years, it is certain that developments of high-frequency circuit boards will continue apace and that huge demands will arise in the market.[13–19] Therefore, in this study, we investigated the dielectric properties of LCPi/SiO_2 nanocomposites within the high frequency range from 1 MHz to 3 GHz to observe changes in their dielectric properties.



Scheme 1 Preparation of the LCPi/SiO_2 nanocomposites via the sol–gel process.

EXPERIMENTAL

Materials

1,3-Bis(4-hydroxy-α,α-dimethylbenzyl)benzene (99%, Aldrich), ethanol(ethyl alcohol) (99.8%, Fluka) and tetraethoxysilane (TEOS) (≧99%, Fluka) were purchased from Uni-Onward Co. (Taipei, Taiwan). 1-Chloro-4-nitrobenzene (98+%, Lancaster), potassium carbonate (99.9%, Scharian), ethanol(ethyl alcohol) (99.5%, made in Japan), palladium on activated carbon (5% Pd, Acros), and potassium bromide (IR grade 99+%, Acros) were purchased from Dinhaw Enterprise Co. (Taipei, Taiwan). *N,N*-dimethylformamide (DMF) (99.98%, Tedia), *N,N*-dimethylacetamide (DMAC) (Tedia), *d*-chloroform (99.8 Atom % D, Acros) and hydrazine monohydrate (98+%, TCI) were purchased from Echo Chemical Co. (Taipei, Taiwan). Pyromellitic dianhydride (PMDA) (99%) was obtained from Tai-Flex Scientific Co. (Kaohsjung, Taiwan).[6]

Preparation of the LCPi/SiO_2 nanocomposites

For more information on the composite system, please refer to the literature[6]; the relatively straightforward preparation method is outlined as follows. At room temperature, the precursor solution of liquid crystalline polyamic acid/silanol (LCPAA/silanol) was removed from cold storage and stirred for ~ 20–30 min and warmed to room temperature. An appropriate amount of the solution was then coated evenly on a piece of glass measuring 5 cm × 5 cm, with the necessary steps taken to ensure that the area of glass and amount of solution used were fixed, so as to yield three different thicknesses to be used as variables. The coated glass was subsequently placed in a hot air circulation oven for baking. After thermal imidization process, we obtained the LCPi/SiO_2 nanocomposites. The synthesis process of the LCPAA solution and preparation of the LCPi/SiO_2 nanocomposites via the sol–gel process are illustrated in Scheme 1 (T_m: 350–360°C).

Measurements

To test the high-frequency dielectric properties of the LCPi/SiO_2 nanocomposites, we utilized a high-

Figure 1 The dielectric material test fixtures with high-frequency impedance analyzer E4991A and clamping apparatus 16453A.

frequency impedance analyzer E4991A (Agilent Technologies, Santa Clara, CA) and clamping apparatus 16453A (Agilent Technologies), as shown in Figure 1. We first cut the test films into rectangles measuring 3.0 cm × 1.5 cm, with coat thicknesses of 50, 100, and 200 μm, respectively, with the amount of SiO_2 mixed being 1.5, 3.0, 5.0, and 6.5 wt % respectively.[6] For the E4991A, the clamping apparatus electrode took on the shape of a circle with a diameter of 0.6 cm. The testing frequency ranged from 1 MHz to 3 GHz and the applied voltage was 1 kV. We then measured the loss tangent and dielectric constant at room temperature and a humidity of 55%. The volume resistivity of the LCPi and LCPi/SiO_2 nanocomposites were measured at room temperature with high resistance analysis.

RESULTS AND DISCUSSION

Electrical analysis of the LCPi and LCPi/SiO_2 nanocomposites

High-frequency loss tangent analysis of the LCPi and LCPi/SiO_2 nanocomposites

The loss tangents of the LCPi/SiO_2 nanocomposites with different thicknesses within the frequency range 1 MHz to 3 GHz are shown in Figure 2. As can be seen from Figure 2(a), the formant frequency of the LCPi appeared at ~ 0.5, 0.75, and 0.85 GHz for film thickness of 50, 100, and 200 μm, respectively. This result indicated that the formants of the loss tangent were shifted toward higher frequencies as the thickness increased. The same trend was observed in films with 5.0 wt % SiO_2 content, as shown in Figure 2(b).

The phenomenon of resonance frequency occurs when the frequency of the applied electric field is identical with the natural frequency of the atoms or electrons in the material, leading to resonance absorption. In this case, the electrical energy will be largely dissipated in overcoming the dielectric inner viscosity and converted to heat. At this point, the field energy dissipation is at its maximum.[20–25]

Because no conductor and dielectric can be perfectly combined, when a current is flowing or an electromagnetic-wave signal is transmitted in a material, the atoms in the vicinity will also be polarized by the electric field and exhibit electric conduction and electric leakage. As the thickness increases, the number of dipoles in a unit electrode area will increase, rendering the overall dipole orientation difficult and thereby increasing the resonance frequency.

When comparing the results of Figure 2(a,b), we found that the formants of the loss tangent shifted toward higher frequencies with higher SiO_2 contents. In addition, as can be inferred from Figure 3(a,b) [partial blowups of Fig. 2(a,b) respectively], except for the resonance frequency range, the range of low and high frequency applications was ~ 1–300 MHz

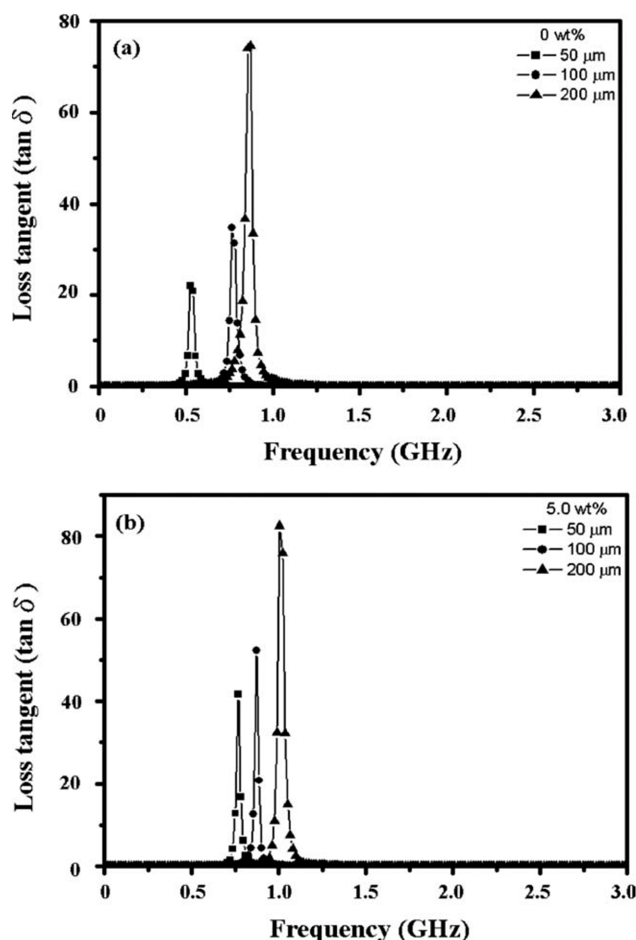


Figure 2 The variation of the loss tangent with LCPi and LCPi/SiO_2 nanocomposites with different thicknesses. The LCPi films contained (a) 0 and (b) 5 wt % of SiO_2 (at 1 MHz to 3 GHz).

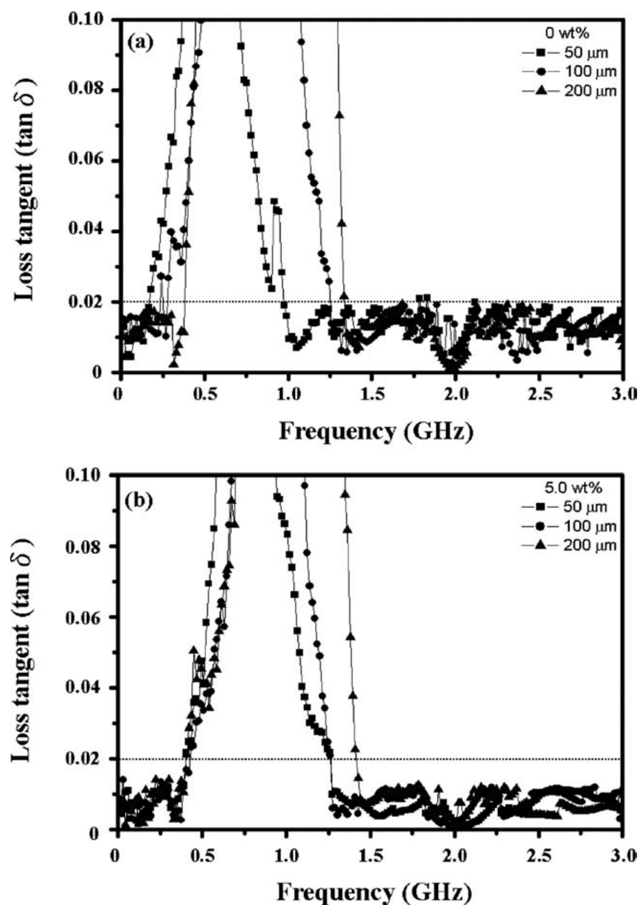


Figure 3 Partial blowup of Figure 2.

and 1.5–3 GHz, respectively. As for films with 5.0 wt % SiO_2 content, the maximum loss tangent value was 0.014, significantly lower than that of LCPi at 0.021. Apparently, the loss tangent value was more stable at high frequency.

The molecular structure of crystalline polymer is highly ordered and tightly packed, conducive for the transfer of electric charges among molecules. However, in the LCPi/SiO_2 nanocomposites, the SiO_2 nanoparticles serve as obstacles for the orderly orientation of molecules, thereby decreasing the order of the polymer molecular structure and impeding the transfer of electric charges among the molecules.[6,12] In the X-ray diffractometer analysis of the LCPi/SiO_2 nanocomposites,[6] the diffraction peaks broadened as the SiO_2 content increased, proving that the SiO_2 did impede the orderly orientation of the polymer molecular structure. Therefore, as the SiO_2 content increased, the insulation became better and the loss tangent tended to decrease. The increase in insulation made it harder for dipoles to move about and for molecules to become polarized, resulting in a shift of the formant toward higher frequencies. The increase in the SiO_2 particle size clearly resulted in an increase in the aggregation tendency and phase separation as the SiO_2 content was increased (FESEM analysis of the LCPi and LCPi/SiO_2 nanocomposites).[6]

Dielectric constant analysis of the LCPi and LCPi/SiO_2 nanocomposites

The dielectric constants of the LCPi/SiO_2 nanocomposites with different SiO_2 contents within the frequency range from 1 MHz to 3 GHz are shown in Figure 4. As can be seen from Figure 4(a), when the film thickness was 50 μm, the dielectric constant of the LCPi exhibited little changes in the low frequency range from 1 MHz to 3 GHz, with a formant appearing at the low frequency of 1.5–2 GHz. Beyond the formant, the dielectric constant began to drop. The same trends were observed in films with 1.5 wt %, 3.0 wt %, 5.0 wt %, and 6.5 wt % SiO_2 contents, as shown in Figure 4(a). The phenomenon can be explained according to the following theories.

There are three stages where the dipoles dictate the frequency[20–25]: (1) During the polarization of a dielectric material and at low-field frequency, the transfer of dipoles are completely capable of keeping up with the variations in the electric field. Within the cycle of the electric field, the distances among dipoles are invariant, with essentially no dissipation of the field energy. (2) When the field frequency increases past a certain point, the transfer of the dipoles will not be able to keep up with the variations in the electric field because the dielectric inner viscosity will affect the transfer of dipoles by means of a frictional resistance. The dipoles are forced to move about through the effect of the electric field, leading to extensive dissipation of the field energy which results in the creation of the formant. (3) If the frequency of alternating-electric field continues increasing, the dipoles will be completely incapable of keeping up with the variations in the electric field. Polarization will almost certainly not occur, and the dissipation of field energy will decrease.

After comparing Figure 4(a,c), we can conclude that the formant will shift toward higher frequencies and that the dielectric constant will also increase as the thickness increases.

Because the increase in thickness resulted in an increase in the number of dipoles per unit electrode area, the overall dipole orientation became difficult, and the resonance frequency increased. The dielectric constant is a measure of how well insulators store electrical energy. The increase in thickness increased the electric energy in a unit electrode area, thereby increasing the dielectric constant. The dielectric constant can be calculated from the following equation.

$$K = \frac{C_p \times t_0}{A \times \varepsilon_0} \quad (1)$$

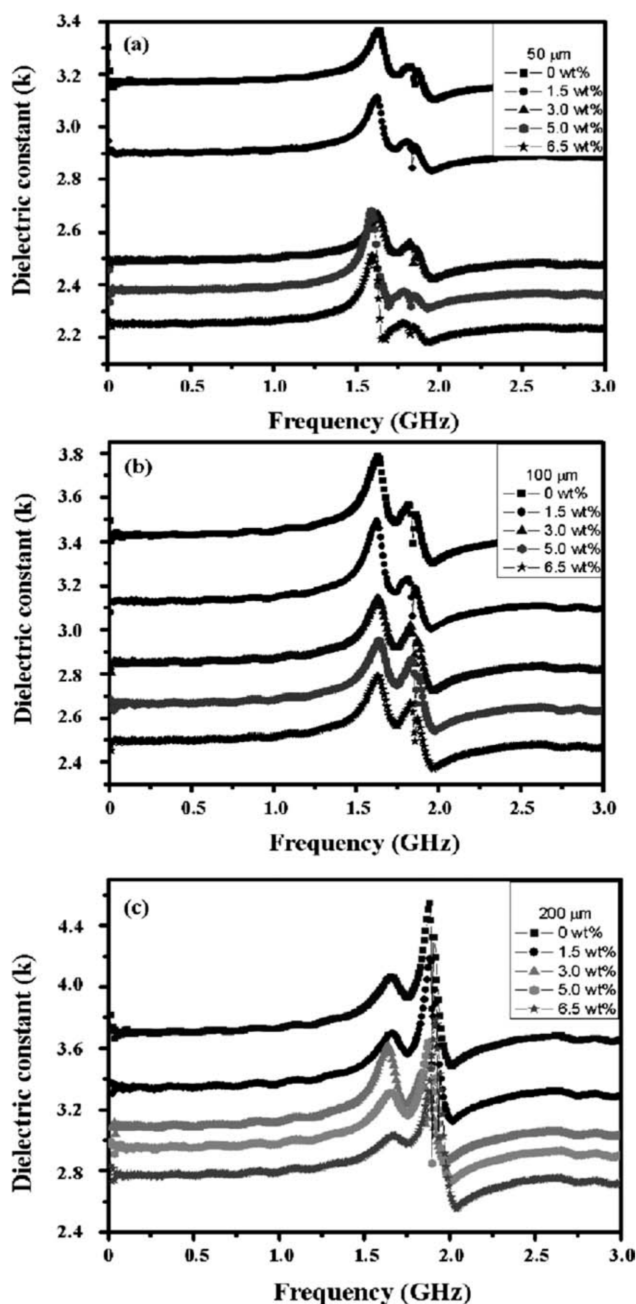


Figure 4 The dielectric constants of LCPi and LCPi/SiO_2 nanocomposites with different SiO_2 contents. The thickness of films were (a) 50 μm, (b) 100 μm, and (c) 200 μm (at 1 MHz to 3 GHz).

where K is the dielectric constant, C_p is the parallel capacity (pF), t_0 is the film thickness (μm), A is the parallel pole area (m^2), and ε_0 is the vacuum permittivity [8.854×10^{-12} (F/m)]. In addition, after inspecting Figure 4(a,c), we found that as the SiO_2 content increased, the dielectric constant decreased, and the formant shifted toward higher frequencies. From the X-ray diffractometer pattern analysis, we deduced that the filling of SiO_2 nanoparticle resulted in a loose inner molecular structure. Therefore, we can conclude that the loose structure increased air porosity (the air content increased), a major contribution to the decrease of the dielectric constant.[6]

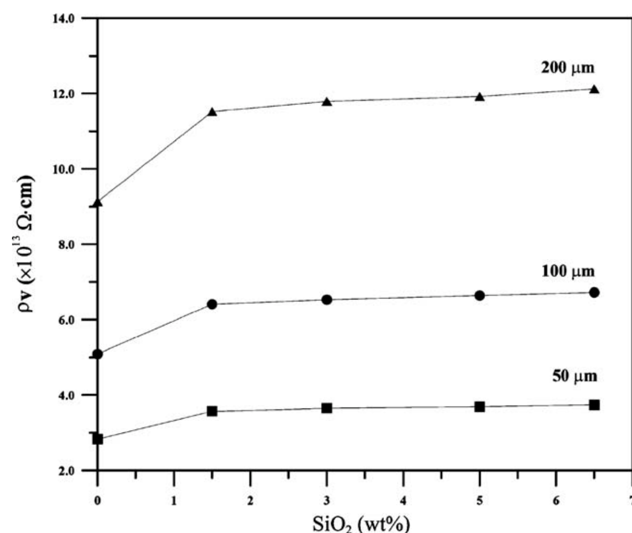


Figure 5 The volume resistivity of the LCPi and LCPi/SiO_2 nanocomposites with different film thicknesses.

Volume resistivity analysis of the LCPi and LCPi/SiO_2 nanocomposites

The effect of the SiO_2 contents on the volume resistivity of the LCPi and LCPi/SiO_2 nanocomposites is shown in Figure 5 and Table I. As the film thickness and SiO_2 content of the LCPi/SiO_2 nanocomposites increased, the volume resistivity increased.

Dense packing is necessary for the formation of the ordered structures required for intermolecular charge transfer. Therefore, in the LCPi/SiO_2 nanocomposites, the SiO_2 acted as a hindrance, reducing the likelihood for the liquid crystalline polymer chain to form well-packed donor/acceptor pairs.[6,12] Therefore, the increase in the volume resistivity was likely caused by the inhibition of electrical treeing by the SiO_2 particles. However, the LCPi synthesized in this study can be considered an amorphous liquid crystalline polymer. Consequently, the LCPi and

TABLE I
The Volume Resistivity of the LCPi and LCPi/SiO_2 Nanocomposites with Different Film Thicknesses

LCPi/SiO_2 nanocomposites (SiO_2 content, wt %)	Film thickness (μm)		
	50	100	200
	Volume resistivity ρ_V (Ω cm)		
0	2.83×10^{13}	5.09×10^{13}	9.13×10^{13}
1.5	3.57×10^{13}	6.41×10^{13}	11.52×10^{13}
3.0	3.65×10^{13}	6.53×10^{13}	11.79×10^{13}
5.0	3.69×10^{13}	6.64×10^{13}	11.92×10^{13}
6.5	3.74×10^{13}	6.72×10^{13}	12.12×10^{13}

LCPi/SiO_2 nanocomposites all have lower dielectric constants.

CONCLUSIONS

The loss tangents of the LCPi/SiO_2 nanocomposites exhibited a formant within the frequency range from 0.5 to 1 GHz, whereas the dielectric constant exhibited a formant within the frequency range from 1.5 to 2 GHz. Beyond the formant, the dielectric constant began to decrease. At high frequencies, the dielectric constants of the LCPi/SiO_2 nanocomposites varied inversely with the SiO_2 contents. The higher the SiO_2 content, the more pronounced the shift of the formant of the dielectric constant toward higher frequencies. As the film thickness of the LCPi/SiO_2 nanocomposites increased, so did the dielectric constant, with the formants of the loss tangent and dielectric constant shifting toward higher frequencies. Generally speaking, the dielectric materials used in 1–10 GHz high-frequency circuit boards have a dielectric constant of lower than 3.5, and a loss tangent of lower than 0.02.[4,5] In this experiment, the LCPi/SiO_2 nanocomposites satisfied the requirement with different film thicknesses and SiO_2 contents at high frequencies. When the SiO_2 content was 5.0 wt %, the loss tangent was lower than $\sim$ 0.014, which was still lower than the standard values. However, attention should be paid to the resonance frequency; the dielectric properties near the resonance frequency may be significantly impacted. Therefore, when using the nanocomposites, it is advisable to veer clear of the range of formant with resonance frequency. The volume resistivity of the LCPi and LCPi/SiO_2 nanocomposites also increased with increasing film thickness and SiO_2 content.

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