Improved dielectric and mechanical properties of polyolefin based laminates via surface modification silicon dioxide

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Abstract. The rapid development of 5G technique needs higher requirements for laminate under high-frequency condition. In this work, silicon dioxide (SiO$_2$) surface modified by $\gamma$-aminopropyl triethoxysilane (KH-550) was used as fillers to improve the dielectric and mechanical properties of polyolefin-based laminates. A relative low dielectric constant of 3.61 and dielectric loss of $3.69 \times 10^{-3}$ at 10 GHz is observed for the laminate with 55 wt% K-SiO$_2$. Moreover, the as-obtained laminate exhibits optimum mechanical properties. These results indicated that the SiO$_2$ (surface modified by KH-550)/polyolefin laminate is an ideal candidate for high-frequency substrate.

1. Introduction
Polyolefin has been widely used in high-frequency electronic industry due to its excellent dielectric properties, high electrical insulation and prominent structure design freedom[1-2]. However, for pure polymer systems, there are some disadvantages for their application as high-frequency laminates, such as the poor mechanical or thermal properties[3-5]. In recent years, some investigations showed that dielectric materials with good mechanical or thermal properties could be obtained by adding inorganic fillers to polymer matrix[6-7]. Silicon dioxide (SiO$_2$) has many excellent performances in high-frequency electronic industry, such as low dielectric constant at high frequency region, prominent mechanical strength, good heat resistance and low costs[8-9]. Thus, SiO$_2$ reinforced polyolefin matrix are considered to be one of the candidates for high-frequency laminates. However, it is difficult to ensure that the high content of filler can be uniformly dispersed in the polymer matrix by mechanical blending. Herein, to simultaneously enhance the mechanical and dielectric properties of the high-frequency laminates, SiO$_2$ modified by $\gamma$-aminopropyl triethoxysilane (KH-550) was incorporated into polyolefin matrix. The effect of the filler content on the laminate performances was studied in detail.

2. Experimental section
2.1. Materials
SiO$_2$ particles (Xinyi Henry Powder Co.), KH-550 (Aladdin), bis (tert-butyldioxyisopropyl) benzene (BIPB, Wengjiang Reagent Co.), xylene (ChengDu Kelong Chemicals Co.), hydrochloric acid (HCl, ChengDu Kelong Chemicals Co.), glass fibre (GF, 1080, Guangzhou Caben Composite Co.) were used as received. The information of three polyolefins used in this study are shown in table 1.
Table 1 The detail information about polyolefin.

| Product                                      | Trade name | Source              |
|----------------------------------------------|------------|---------------------|
| 1,2-Polybutadiene (PB)                       | B3000      | Nippon Soda Company |
| Ethylene-propylene-dicyclopentadiene (EPDM)  | Trilene®  65| Uniroyal Chemical Company |
| Styrene-butadiene-styrene triblock copolymer (SBS)| Kraton® D1118| Kraton Company |

2.2. Preparation of SiO2 modified by KH-550
SiO2 was added into 10% HCl and ultrasonicated for 30 min. The mixture stirred at room temperature for 2 h. The treated SiO2 was washed with distilled water and then dried at 80 °C in a vacuum. The SiO2-OH was obtained. SiO2-OH was dispersed in xylene and refluxed at 80 °C for 24 h, during excess KH-550 was slowly added. The treated particles were washed by xylene. Finally, the KH-550 modified SiO2 (K-SiO2) were dried at vacuum.

2.3. Preparation of K-SiO2/polyolefin laminates
EPDM/SBS/PB (1/2/6) were dissolved in xylene and BIPB was added into the mixture. The mixture was stirred at 60 °C for 2 h. And then the K-SiO2 was introduced into the polyolefin and the mixture was stirred. The GF was immersed into the resulting mixture. The prepreg was dried in an oven to volatilize the xylene. Finally, the 18 layers of the prepreg was pressed at 10 MPa for 180 °C/90 min and 250 °C/60 min. For convenience, the sample codes were defined according to the contents of K-SiO2, namely the K-SiO2/polyolefin laminate (25/75) was defined as L-25.

3. Characterisation
Fourier transform infrared (FTIR) spectra was recorded using a spectrophotometer (Shimadzu FTIR–8400S) at wave numbers of 4000–500 cm\(^{-1}\). Thermogravimetric analysis (TGA) was obtained using a TA instrument (TGA–Q50) at a heating rate of 20 °C/min and nitrogen flow rate of 40 mL/min. The fracture surface of K-SiO2/polyolefin laminates were examined by field emission scanning electron microscopy (FESEM) (FEI Co, USA). The flexural strength was measured on a SAN CMT6104 series desktop electromechanical universal testing machine. The impact strength was conducted with a digital display cantilever beam impact testing machine (XBL series). The dielectric properties were characterized using Agilent E8363A microwave network analyser (Agilent Technologies, USA).

4. Results and discussions
4.1. FTIR analyses of pure SiO2 and K-SiO2
The FTIR spectra from figure 1(a) suggested that the strong characteristic absorption peaks of SiO2 at 1080 cm\(^{-1}\) (Si=O-Si)[10]. Moreover, the absorbance peaks in 3450 cm\(^{-1}\) (N-H) and, 2930 cm\(^{-1}\) and 2849 cm\(^{-1}\) (-CH\(_2\)-) indicate that KH-550 has been successfully grafted onto the SiO2 surface[11].
4.2. Thermal stability analysis of K-SiO₂/polyolefin laminates

TGA was used to measure the thermal stability of materials, namely the higher decomposition temperature of 5% (T₅) demonstrates better thermal stability[12]. As can be seen in figure 1(b), the T₅ is increased with the addition of K-SiO₂. The effective contact between K-SiO₂ and polyolefin matrix gradually increases with the increase of K-SiO₂ content. Moreover, the good interfacial compatibility between K-SiO₂ and polyolefin matrix is ascribed to the filler being evenly embedded in the whole matrix. Therefore, the L-55 sample possesses higher thermal stability than those of other samples.

4.3. Mechanical properties of K-SiO₂/polyolefin laminates

Figure 2(a) and 2(b) show the flexural properties and impact strength of the K-SiO₂/polyolefin laminates. The mechanical properties of the K-SiO₂/polyolefin laminates are improved with the increase of the K-SiO₂ content. With higher filler content in inorganic-organic composite, the expansion of fillers hinder crack under the action of stress[13]. In addition, with the increase of inorganic fillers, the rigidity of the laminate also enhanced[6]. As a result, the L-55 exhibits enhanced mechanical properties in comparison with other samples.

4.4. SEM images of K-SiO₂/polyolefin laminates

The SEM microstructural of K-SiO₂/polyolefin laminates with varied filler contents is illustrated in figure 3. As shown in the images, there are fewer percentage of holes in the cross section of laminate.
All samples exhibit that the fillers and matrix were not distinguishable. This phenomenon is attributed to the SiO$_2$ modified by KH-550.

Figure 3. SEM images of different content K-SiO$_2$ in polyolefin. (a) 25 wt%. (b) 35 wt%. (c) 45 wt%. (d) 55 wt%.

4.5. Dielectric properties of K-SiO$_2$/polyolefin laminates

Figure 4 shows the dielectric properties of K-SiO$_2$/polyolefin laminates in the high frequency (10 GHz) region. The dielectric constant enhanced with the K-SiO$_2$ concentrations increase. When the filler content is low, the polyolefin matrix rather than the K-SiO$_2$ particles mainly attributed to the low dielectric constant[7]. As the concentration of K-SiO$_2$ in polyolefin matrix is increasing, the values of dielectric constant is observed to be increasing. However, the dielectric loss firstly increases and then gradually reduces with the K-SiO$_2$ concentrations increase. SiO$_2$ modified by KH-550 can restrict the movement of polymer chain and thus reduce the polarizability, which caused lower dielectric loss[7]. Hence, the L-55 sample exhibits excellent dielectric constant (3.61) and dielectric loss (3.69×10$^{-3}$) at 10 GHz, which confirms it could serve as high-frequency substrate materials.

Figure 4 Dielectric constant and dielectric loss of K-SiO$_2$/polyolefin laminates at 10 GHz.

5. Conclusions

In the present study, we reported a polyolefin-based laminate for applied in high-frequency substrate. The FTIR analysis indicates the KH-550 was successfully grafted to SiO$_2$ surface. An improvement in thermal stability by increasing K-SiO$_2$ loading was observed. The SEM images demonstrated that there are fewer voids in the as-obtained laminate. SiO$_2$ is used as a reinforcing material, and as the SiO$_2$ concentration increases, the mechanical properties of the laminate also increase. A relative low dielectric constant of 3.61 and dielectric loss of $3.69 \times 10^{-3}$ at 10 GHz is observed for the laminate with 55 wt% K-SiO$_2$, which meet the needs of high-frequency substrate applications. This work indicates the L-55 sample with excellent comprehensive performances has promising capacity in substrate materials application.
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