

Effect of aging time on the dielectric properties of PI/CCTO composite thin films

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Abstract. In this paper, Pyromellitic dianhydride (PMDA) and 4,4'-Oxydianiline (ODA) were selected as the monomers and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) particles were used as filler to synthesize the PI/CCTO composite film by the in situ polymerization. The phase composition and dielectric property of the composites were analyzed and tested by XRD and a broadband dielectric spectral instrument. The effects of aging time on the dielectric properties of PI and PI/CCTO composite films were researched. Results show that the aging time can improve the dielectric property of the PI composite film and the optimal aging time is 24h. The PI/CCTO composite film plays the minimum value of the loss tangent about 0.022 and the maximum value of the dielectric constant about 8.8 at 100Hz, which is 1.6 times larger than that of PI film.

1. Introduction

Polyimide (PI) is widely used in electrical and microelectronic industries due to its excellent mechanical, electrical and thermal properties [1-3]. However, this PI is difficult to dissolve or melt due to the strong interaction between the molecules and plays the low dielectric constant of 3.0~3.5, which is difficult to be used for high energy storage density film. To improve its processing and dielectric properties, the CCTO particles with a giant high dielectric constant was synthesized, and then the PI/CCTO composite thin films with different aging time was prepared by the in-situ polymerization in this paper. In addition, the phase composition and dielectric property of the PI composites were analyzed and tested. Moreover, the effects regular of aging time on its dielectric property were researched emphatically.

2. Experimental

2.1. Sample Preparation

The CCTO particles were prepared by a sol-gel combustion method. Firstly, pre-calculated amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in glycol methyl ether with a heating stirring. When the solution was cooled, tetrabutyl titanate was poured into above solution, continually stirring for 1h. And then, the resulting sol was stored for 24h and then kindled in open air to obtain CCTO sol powders. Finally, prepared powders were crystallized by sintering at 800°C for 2 h after grinded, and then re-sintering at 1050°C for 6 h in air at a heating rate of $5^\circ\text{C}/\text{min}$. The CCTO ceramic particles were obtained by ball milling crystallized powders for 4h.



The PI/CCTO composite films were prepared by in-situ polymerization. The initial suspension was prepared by adding 20vol. % CCTO particles to the mixed solution of ODA and DMAc by ultrasonic for 2h. The uniform PAA/CCTO precursor solution was synthesized by filling PMDA into ready suspension. Then the solution was aged for 6h, 12h and 24h, respectively. Finally, those solutions were casted on the glass substrates and heated by a staged warming method at 60°C, 200°C, 240°C, 260°C, 280°C, 300°C and 330°C for 1h, respectively, in order to obtain composite films with an average thickness of about 25µm, which were classed as PI/CCTO-6h, PI/CCTO-12h and PI/CCTO-24h. Meanwhile, the PI composite films with different aging time of 6h, 12h and 24h were classed as PI-6h, PI-12h and PI-24h, respectively.

2.2. Characterization

The phase compositions of these films were analyzed by X-ray diffraction. The dielectric properties of all samples were measured by a broad-band dielectric spectral instrument in the frequency range from 100Hz to 100 KHz at room temperature. Prior to the measurements, a hybrid layer of Al paste was evaporated on both surfaces of all samples.

3. Results and discussion

3.1. Phase Compositions of CCTO, PI and PI/CCTO

Figure 1 shows the XRD patterns of CCTO, PI and PI/CCTO. It can be seen that the characteristic peaks of CCTO were clearly visible and belonged to the body-centered cubic perovskite crystal structure and perfect, which demonstrated a perfect crystallinity [4]. In addition, unshaped diffraction peak of PI was seen at $2\theta \approx 20^\circ$ in Figure 1. However, it weakened in the pattern of PI/CCTO, which could be attributed to the destruction of molecular chains of PI due to the introduction of CCTO fillers [5-7]. Moreover, XRD pattern of PI/CCTO clearly demonstrated that CCTO particles filled into PI matrix to form two phases composite system.

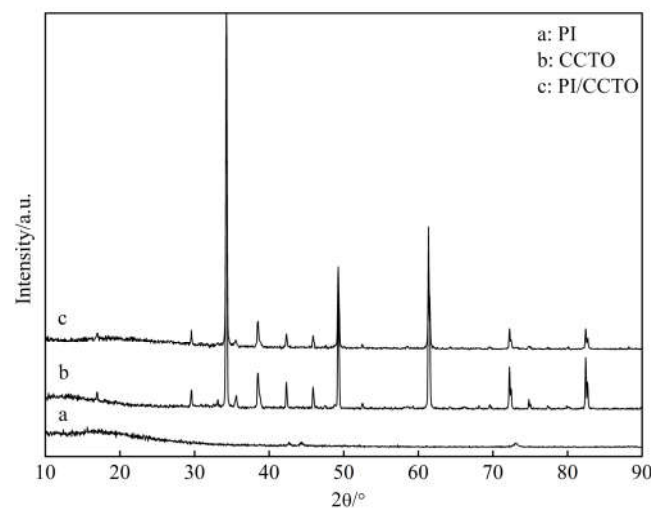


Figure 1. XRD patterns of CCTO, PI and PI/CCTO.

3.2. Dielectric properties of PI thin films

The effects of aging time on the dielectric properties of PI films are shown in Figure 2. It can be seen from Figure 2(a) that the dielectric constant of PI films with different aging times possessed frequency stability, except for decreasing slightly over 10k Hz. And the dielectric constant of PI films increased with the increase in aging time. Especially, the PI-24h film with the aging time of 24h showed the maximum of dielectric constant about 3.475 at 100Hz. This results show that the increasing aging time improves the polarization of free-radicals in the molecular chains and reduces the formation of bubbles

in PI matrix, increasing the dielectric constant of PI. In addition, the loss tangent of the PI films decreased slightly with the increase in the frequency and then increased dramatically over 10k Hz. Furthermore, the loss tangent of the PI films decreased with the increase in aging time. Especially, the PI-24h film possessed the smallest loss tangent of about 0.0017 at 100Hz. Figure 2(b) showed that the conductivity of PI films reduced slightly and increased significantly with the increase in aging times and frequency, respectively. Such as, the conductivity of the PI-24h film was about 3.12×10^{-11} S/m at 100Hz.

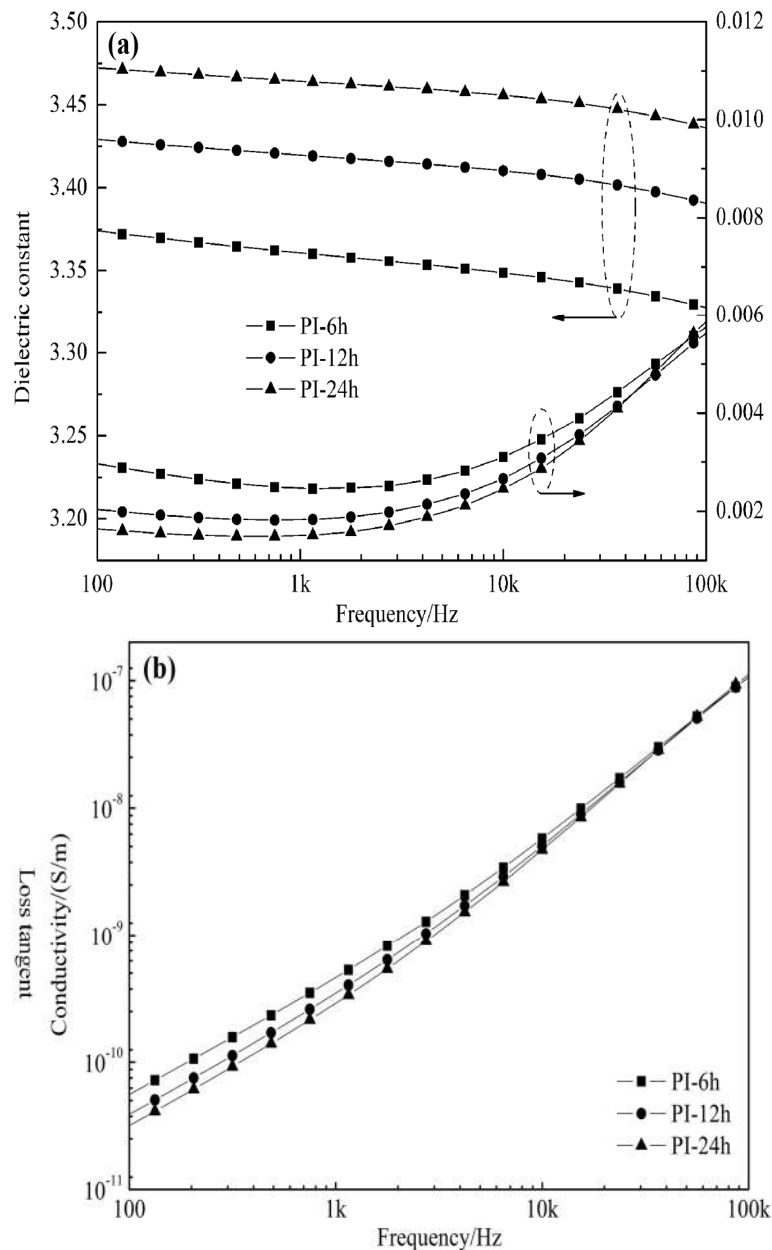


Figure 2. Dependence of (a) dielectric constant and loss tangent, and (b) conductivity on frequency for the PI film with different aging times at room temperature.

3.3. Dielectric properties of PI/CCTO thin films

The effects of aging time on the dielectric properties of PI/CCTO films are shown in Figure 3. It can be seen from Figure 3(a) that the dielectric constant and loss tangent of PI/CCTO films decreased

significantly with the increase in the frequency. In addition, the dielectric constant increased dramatically with the increase in aging time. Especially, the value of PI-24h was about 8.8 at 100Hz, which was 1.6 higher than that of PI film. Furthermore, the loss tangent of PI/CCTO films increased slightly and then reduced significantly with the increasing aging time from 6h to 24h. For an example, the loss tangent of the PI-24h film was about 0.0425 at 100Hz. Another phenomenon was that the loss tangent of the PI/CCTO films showed a perfect stability on the frequency over 10kHz and was smaller than that of PI films. Figure 3(b) showed the conductivity of the PI/CCTO films reduced with the increase in aging time and the value of the PI-24h film was 2.12×10^{-9} S/m at 100Hz, which showed a good insulation property. These results showed the increasing aging time could improve dramatically the dielectric properties of PI/CCTO. Because the increasing aging time can disperse uniformly CCTO in PI matrix and CCTO can increase the polarization effect in the PI/CCTO composites.

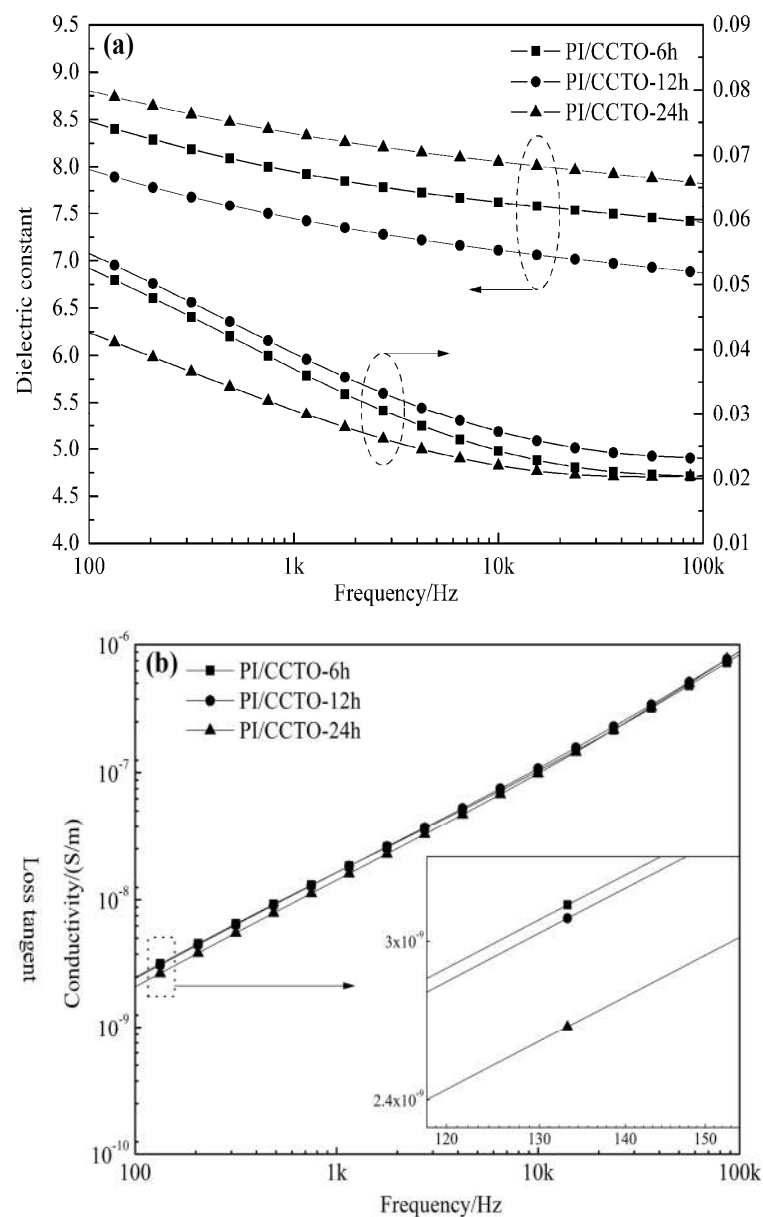


Figure 3. Dependence of (a) dielectric constant and loss tangent, and (b) conductivity on frequency for the PI film with different aging times at room temperature

4. Conclusion

The PI/CCTO composite thin films with different aging times were synthesized by the in-situ polymerization. The effects of aging time on the dielectric properties of PI and PI/CCTO composite thin films were researched by XRD and a broadband dielectric spectral instrument. The results showed that the unshaped diffraction peak of PI film was weakened due to the introduction of CCTO particles, and CCTO maintained a perfect perovskite crystal structure and crystallinity. The increasing aging time can disperse uniformly CCTO in PI matrix and CCTO can increase the polarization effect in the PI/CCTO composites, resulting in improving the dielectric properties of PI/CCTO composite thin films. When the optimal aging time was 24h, the dielectric constant of PI/CCTO thin film was maximal value of 8.8, which is 1.6 times higher than that of pure PI film, and the minimal loss tangent was 0.022.

Acknowledgments

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