Preparation and characterisation of Al-doped ZnO and PVDF composites

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Abstract: A single organic composite material having high dielectric constant is difficult to meet the needs of the market. Nowadays, polymer matrix-based composites have become a promising option that researchers are focusing on. Al-doped zinc oxide (ZnO) and composites containing ZnO as reinforcement and poly(vinylidene fluoride) (PVDF) as matrix were prepared. The microstructure of composites was analysed by scanning electron microscope and transmission electron microscope techniques. The chemical structures and crystallisation behaviour of the materials were investigated by the means of FT-IR and X-ray diffractometer. ZnO, having both rod- and sheet-shaped, was evenly distributed within the PVDF material. Additionally, the dielectric properties and breakdown field strength of composite were tested. As the content of the fillers was kept steady, the dielectric constant of the composite material increased proportionally with the Al content. Thus, a composite containing 10% ZnO with 7% Al displayed a dielectric constant of 18.5 at 100 Hz, twice when compared with the pure ZnO/PVDF composites. This phenomenon was attributed to ZnO semiconductor properties which can significantly improve the conductive nature of the materials.

1 Introduction

Recently, composites exhibiting excellent dielectric properties have attracted wide-spread concern. In various applications such as embedded capacitors [1, 2], sensors [3, 4] and electromagnetic interference (EMI) absorbers [5, 6], high dielectric materials have excellent application prospects. To obtain a polymer matrix composite with high dielectric constant, some conductive ions can be doped into the polymer as reinforcing material.

However, the literature has reported several comprehensive studies performed on materials with high dielectric properties. Chen et al. [7, 8] reported the preparation of reduced graphene oxide (RGO)/hematite core-shell nanostructure/poly(vinylidene fluoride) (PVDF) composites. They found that higher concentrations of RGO/hematite in such composites led to stronger dielectric properties. Another study conducted by Lee et al. [9, 10] reported the filing of treated BaTiO₃ with PVDF. Hence, the dielectric constant of the resulting composites was enhanced to 400.3 at 100 Hz. Devi et al. [11] employed dendrite-shaped PbS as reinforcements, and the PVDF/dendrite-shaped PbS showed large improvement in dielectric constant, nearly 1589 times greater than pure PVDF.

Zinc oxide (ZnO) is a hexagonal-type semiconductor material displaying a wide band gap of 3.37 eV, large exciton-binding energy of 60 meV and a higher optical gain of 320 cm⁻¹ at room temperature [12, 13]. In recent years, the metal-doped ZnO has become one of the hotspots in this field. Wang et al. [14, 15] synthesised Al-doped ZnO powders by a co-precipitation method. The complex permittivity of the prepared Al-doped ZnO powders have been improved in the frequency range of 8.2–12.4 GHz. Complementary, a study conducted by Zamiri et al. [16–18] has highlighted the preparation of Ag-doped ZnO nano-plates. The space charge polarisation was found to be stronger in the case of pure ZnO nano-plates, whereas orientational polarisation proved to be stronger for Ag-doped ZnO nano-plates. Besides, the above-mentioned metal-doped ZnO, Chelnikov et al. [19] have developed Mg-doped ZnO with tuning band gap and Singhali et al. [20, 21] Cu-doped ZnO nanoparticles, the electrical performance of which has been significantly improved. This has suggested that metal-doped ZnO could have great application potential in the area of high dielectric polymer-based composite materials. However, the research conducted on this particular field was relatively scarce so far, and therefore, further exploration for a comprehensive understanding of such systems is required.

In this paper, composites containing Al-doped ZnO as reinforcement and PVDF as matrix were prepared. This approach has led to remarkable enhancement of the composites’ dielectric properties compared with those of pure ZnO.

2 Experimental section

2.1 Materials

N,N-Dimethylformamide (DMF) of analytical grade was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. Polyvinylidene fluoride (PVDF) of chemical grade was supplied by Shanghai Jingdafu Co. Ltd. Industrial grade KH-570 was purchased from Yingcheng Debon New Chemical Materials Co. Ltd. Aluminium nitrate nonahydrate and zinc nitrate hexahydrate, both of analytical grade, were provided by Tianjin Zhiyuan Chemical Co. Analytical grade urea was purchased from Tianjin Tianta Chemical Plant.

2.2 Preparation of reinforcements

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O; 1.485 g) was dissolved in 50 mL deionised water and urea (CO(NH₂)₂; 1.2 g) in 100 mL deionised water. Different atomic molar ratios of Al (0, 3, 5, 7, 10%) were dissolved in 50 mL deionised water. Subsequently, Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O solutions of various concentrations were individually mixed under stirring for 10 min to obtain well-dispersed solutions. This was followed by the addition of CO(NH₂)₂ solution to the previously prepared mixtures under constant stirring to allow the formation of final suspension. Afterwards, the mixed solutions were both heated to 100°C for 1 h. The mixture was filtered and the precipitate collected and dried for 2 h at 80°C. The powder was transferred to a muffle
furnace and kept at 500°C for 2 h. The system was allowed to cool to room temperature, and then the ZnO was doped with Al.

Subsequently, ZnO was firstly surface-modified by the addition of silicon coupling agent KH-570. C₂H₅OH (20 g) and KH-570 (0.25 g) were uniformly mixed, and the pH adjusted between 4 and 5. The mixed solution was subjected to hydrolysis for 1 h. ZnO (5 g) and C₂H₅OH (20 g) underwent ultrasonic dispersion for 1 h. Then, the two solutions were mixed and stirred in a water bath at 70°C for 3 h, and finally, ZnO was filtered and dried at 80°C for 2 h.

2.3 Preparation of composites

The composites were prepared by mixing ZnO into PVDF under mechanical stirring. Various contents of ZnO were dissolved in DMF at room temperature in ultrasonic bath for 1 h. Subsequently, PVDF (10.25 g) was added into the solution and ultrasonic dispersed for 2 h. After the solution was mixed, the air bubbles forming within the mixture were drawn out by vacuum pump and cast to obtain films. The last steps in composites’ preparation consisted of films drying at 80°C for 2 h, followed by heating at 170°C for further 2 h.

2.4 Characterisation and testing of PVDF/ZnO composite

The morphology of ZnO and composites was examined using a HITACHI S-4300 scanning electron microscope (SEM) and JEM-100 transmission electron microscopy (TEM). FT-IR spectra of composites films were recorded using a BRUKER
EQUINOX55 FTIR spectrophotometer. The acquisition time was 1 min with a resolution of four wave numbers. The crystal structures corresponding to ZnO and composites were examined using an X’Pert Power X-ray diffractometer (XRD). The 2θ was collected from 20° to 80°. The dielectric properties of the composite films were examined on the BDS 4000 Broadband dielectric/impedance tester. The test frequency range was from 10<sup>3</sup> to 10<sup>7</sup> Hz. The breakdown field strength of composite films was investigated by the mean of HT-5/20 Breakdown voltage tester.

3 Results and discussion

3.1 Morphology and structure characterisation

As shown in Fig. 1, the nature of ZnO employed in this research was rod-shaped as well as sheet-shaped. When no Al was added to ZnO, the appearance of this was rod-shaped. On the other side, as the Al-doping content was increased, sheet-shaped ZnO was obtained. When the Al content reached 10%, rod-shaped ZnO disappeared from the system. A variety of ZnO in terms of diameter, length and size was involved. Sheet-shaped ZnO displayed irregular shape of about 3−4 μm. From a cross-sectional view, we observed that ZnO was arranged directionally in respect with PVDF and parallel to the film surface. Such behaviour was attributed to the external forces acting on ZnO, facilitating the arrangement along the direction of filmination.

As shown in Fig. 2, the crystal lattice of rod-shaped ZnO was neat and the arrangement direction perpendicular to its surface. As opposed to this observation, the crystal lattice of sheet-shaped ZnO exhibited an irregular arrangement. The elemental analysis showed that rod- and sheet-shaped ZnO contained different amounts of Al, under the same conditions. The Al atomic per cent of the rod-shaped ZnO was 0.3%, while for the sheet-shaped ZnO was 6.6%. During the crystallisation process, Al played the role of impurity, affecting the growth direction of the ZnO crystal lattice.

As can be seen from the XRD images collected for ZnO, the diffraction peaks of pure ZnO were clear and sharp, indicating a high degree of ZnO crystallisation. However, as the Al-doping content was enhanced, the crystallinity of ZnO decreased. The XRD images of PVDF composites showed the diffraction peaks of pure PVDF material at the crystal diffraction peak of α-phase (Figs. 3 and 4).

When ZnO was added, α-phase diffraction peaks at 17.4° and 18.4° decreased and, similarly, α-phase in PVDF crystalline dropped as well. α-Phase diffraction peak at 19.9° shifted to 20.3°, corresponding to the diffraction peak of β-phase. This suggested that the addition of ZnO affected the crystallisation behaviour of PVDF, promoting the transformation of α- to β-phase. This phenomenon can be attributed to the blocking effect induced by ZnO on the rearrangement of PVDF molecular chains, which resulted in changes within the PVDF crystallisation behaviour.

As the data collected suggested, the peaks characteristic to the PVDF α-phase were identified at 612, 766 and 795 cm<sup>−1</sup> reduced with the addition of ZnO. In pure PVDF, no characteristic peaks at 834 and 1230 cm<sup>−1</sup> were observed. However, the addition of ZnO provided the identification of PVDF β-phase characteristic peak at 834 cm<sup>−1</sup>, whereas the peak characteristic to the PVDF γ-phase appeared at 1230 cm<sup>−1</sup>. This also showed that the addition of ZnO affected the crystallisation behaviour of PVDF. Similar conclusions as for XRD data were drawn. This can be attributed to the blocking effect induced by ZnO on the rearrangement of PVDF molecular chains, resulting in changes within the PVDF crystallisation behaviour. This phenomenon is in good agreement with recent studies reported in the literature [22, 23].

3.2 Dielectric performance measurement and analysis

The dielectric constant of PVDF composites, as depicted in Fig. 5, decreased at the inception step, followed by a direct proportional increase with the amount of ZnO added. At 5 and 10% content of doping material, the dielectric constant of PVDF composites was smaller compared with the pure PVDF, while the amount of ZnO doped with 5 and 10% displayed larger dielectric constant values than the pure PVDF. When the doping amount of ZnO was 20%, the dielectric constant of PVDF composites was 27.2 at 100 Hz, three times higher than pure PVDF. The dielectric loss of PVDF composites did not change significantly, to <0.02, when the doping amount of ZnO was under 10%. Contrary to this behaviour, the dielectric loss of PVDF composites exhibited a remarkable increase when the doped ZnO was >15%. This was hypothesised to take place due to higher amount of doped ZnO, forming a conductive path within PVDF. The dielectric loss of PVDF composites was not only caused by the molecule’s polarisation but also due to the leakage current between the ZnO.
As illustrated in Fig. 6, the dielectric constant of PVDF composites raised proportionally with the increase of Al amount, while the dielectric loss was essentially unchanged. The dielectric constant of the composite exhibited a considerable expansion when the Al content changed from 5 to 7%. At 10% ZnO containing 7% Al, the dielectric constant was found to be 18.5 at 100 Hz. Therefore, we have concluded that Al-doped ZnO could not only significantly improve the dielectric constant of the

Fig. 5 Dielectric constant and dielectric loss images of PVDF composites with different content pure ZnO

Fig. 6 Dielectric constant and dielectric loss images of PVDF composites with of 10% ZnO reinforcements which contain different content Al

As illustrated in Fig. 6, the dielectric constant of PVDF composites raised proportionally with the increase of Al amount, while the dielectric loss was essentially unchanged. The dielectric constant of the composite exhibited a considerable expansion when the Al content changed from 5 to 7%. At 10% ZnO containing 7% Al, the dielectric constant was found to be 18.5 at 100 Hz. Therefore, we have concluded that Al-doped ZnO could not only significantly improve the dielectric constant of the

Fig. 7 Dielectric constant and the fitted curve of composites at 100 Hz
The addition of ZnO modified the crystallization behaviour of PVDF, promoting the transformation of α-phase to β-phase. Moreover, Al-doped ZnO can significantly improve the dielectric constant of the composite materials. When the content of the reinforcing material was kept steady, the dielectric constant of the composite increased directly proportionally with the amount of Al content.

4 Conclusion

We report herein the successful preparation of Al-doped ZnO powder and PVDF composites. SEM studies provided that the morphology of ZnO was both rod and sheet shaped. ZnO was arranged in an oriental manner within PVDF and parallel to the film surface. XRD and FTIR measurements showed that the addition of ZnO modified the crystallisation behaviour of PVDF, promoting the transformation of α-phase to β-phase. Moreover, Al-doped ZnO can significantly improve the dielectric constant of the composite materials. When the content of the reinforcing material was kept steady, the dielectric constant of the composite increased directly proportionally with the amount of Al content.

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