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Article

Effects of Coupling Agents on the Structure and Electrical Properties of PZT-Poly(vinylidene fluoride) Composites

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Abstract: PZT-Poly(vinylidene fluoride) composites were prepared by hot-pressing method. Before addition, PZT particles were firstly modified with two different coupling agents. The micromorphology, microstructure, dielectric properties, and piezoelectric properties of the composites were characterized and investigated. Results indicated that PZT particles were homogeneously dispersed in the PVDF matrix by the addition of coupling agents. The electric properties of PZT-PVDF composites with NDZ-101 were the best. Especially when the volume ratio of the titanate coupling agent NDZ-101 was 1%, the piezoelectric strain constant d33 of PZT-PVDF composites reached maximum value 19.23pC/N; its relative dielectric constant εr was 67.45; at the same time its dielectric loss tanδ was 0.0766.

Key words: PZT-PVDF; coupling agents; dielectric properties; piezoelectric properties

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1 Introduction

Hybrid organic-inorganic materials have been produced by many methods, such as sol-gel. The influence of siloxane composition on properties of ployimide-silica hybrids also has been known. The piezoelectric transducer encouraged researchers to explore the better piezoelectric materials. Then the coupling agent went into the public view. This paper carried out several researches into two kinds of coupling agents.

As an engineering material, poly (vinylidene fluoride)(PVDF) had been extensively applied in many areas such as electric industries, microelectronics, acoustic impedance with underwater, and so on [1]. During the past decade, increasing attention has been paid to the PVDF organic-inorganic composite materials, and it has been proved that the mechanical and electrical properties of PVDF hybrid films can be improved by incorporation of fillers such as carbon nanotube[2], silica [3-5], and titaniainto the pristine PVDF matrix [6,7].

Among these inorganic materials, piezoelectric ceramic transducer (PZT) power is often chosen as fillers to improve electric properties of the polymer materials due to its extremely high electric qualities [8-10]. These PZT/PVDF composites could be widely applied in microelectronics devices fields. However, due to the lack of mechanical resistance and no flexibility, the combination of PZT particles with PVDF in micro scale is

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very difficult. [11-13] One of the most important key points of PZT/PVDF hybrid composites is to improve the interface of PZT in the polymer matrix.

The coupling agents connected organic with inorganic materials and improve the compatibility between the two phases effectively [14,15]. However, little attention has been focused on the effects of different coupling agents on structure and properties of PZT/PVDF hybrid composites.

In this paper, two different coupling agents (silane coupling agent KH-570 and titanate coupling agent NDZ-101) were used to improve the surface state of the PZT particles. The PZT/PVDF composites appear as a good alternative for applications as sensors and actuators because they are capable to combine the better properties of ceramic and polymer. This work shows some results of preparation, characterizations and electric properties of composites, consisting of PVDF and PZT, with 0-3 connectivity.

2. Experimental

2.1 Materials

PVDF powders (ρ=1.77g/cm^3,T_m=167℃) with a mean particle size of about 3μm are provided by Shanghai 3F New Materials Ltd Co., China. The applied pressure is 225MPpa. PZT ceramic (ρ=7.6g/cm^3) were prepared via the conventional solid-state reaction method, which is supplied by Institute of Acoustics, Chinese Academy of Science, China. PZT powder with the average particle size of about 50~70μm was obtained from crushed PZT disks. The 3-methacryl oxypropyl-trimethoxysilane (KH-570) coupling agents were purchased from Xi'an Chemical Reagent Ltd Co., China. The isopropyl dioleic(dioctylphosphate) titanate (NDZ-101) coupling agents was purchased from Shandong Yuanhang Chemical Materials Ltd Co.,China. All other chemicals and reagents were provided by Shanghai Experiment Reagent Ltd Co., China.

2.2 Preparation of PZT-PVDF composites with coupling agents

This test prepared different concentration (0%, 0.5%, 1.0%, 1.5% and 2%) of coupling agent solution with the treatment of ultrasonic wave. The purpose of preparing coupling agent liquid is to modify the PZT power. Firstly PZT particles were dissolved in ethanol absolutely. Then the mixture was heated up in a water bath of 80℃. Then it was stirred mechanically again for 3 h and heated up at 120℃ for 12h. Finally it was abraded to use. This experiment prepared modified PZT power by mixing coupling agent solution and PZT power. Calculated quantity of modified PZT particles with two coupling agent content 0%, 0.5%, 1.0%, 1.5% and 2% were mixed with PVDF. Next this mixture was compressed into a disk of 13mm in diameter and 1mm in thickness. Next dried the disk in an oven and plated electrode on it. Then polarized it for 30 min by placing it in a constant temperature silicone oil under the condition of the polarization voltage for 3-5kV/mm, the temperature at 100℃. Finally, the samples were tested after static duration for 24h.

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2.3 Measurements

All these measurements were collected under the condition of room temperature and atmospheric pressure. The internal microstructure of PZT-PVDF composites was observed by the Scanning electron Microscopy (SEM); the dielectric constant ε_r and the dielectric loss tanδ of PZT-PVDF composites were measured by a precision LCR digital bridge under 1kHz; and the constant d_{33} of PZT-PVDF composites were measured with ZJ-3AN-type quasi-static d_{33} measuring.

3 Results and discussion

3.1 FTIR

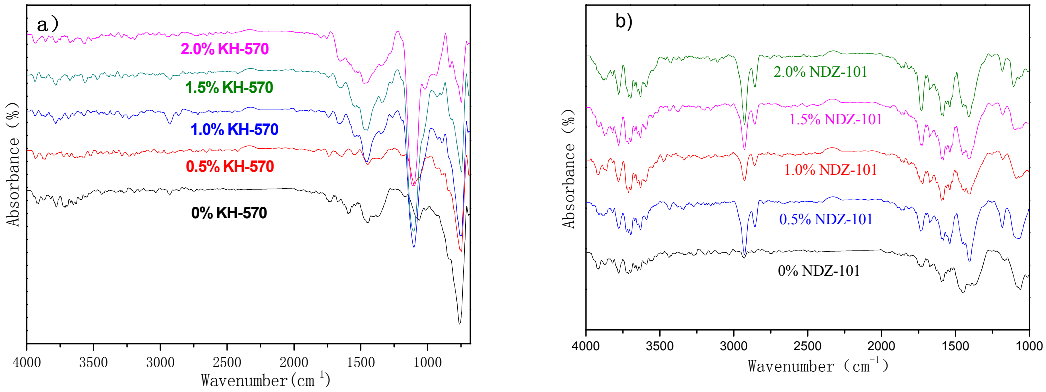

Fig.1 FT-IR spectra of PZT with surf ace treated and untreated by coupling agent

Fig.1 was the FTIR spectra of PZT particles before and after treated respectively with coupling agent contents of 0%, 0.5%, 1%, 1.5%, and 2%.As shown in Fig.1a). As shown in Fig.1, there is a stretching-vibration-absorption peak of functional groups of CH_3, CH_2, CH at 2929.7cm^{-1}. At the same time there exists a stretching vibration characteristic peak of C-O-Si at 1060.7cm^{-1}. All these peaks belonged to the characteristic peaks of KH-570. Further analysis of the results showed that the peak intensity at 761.8cm^{-1} increased, and the peak became narrowing and sharp. The appearance of such absorption peaks showed that KH-570 had an effect on the surface of PZT particles. Fig. 1b) was the FTIR spectrum PZT ceramic particles treated and untreated by the titanate coupling agent NDZ-101 respectively. It can be found that the PZT treated by NDZ-101 showed an absorption peak of CH_2 and CH_3 at 2920.07cm^{-1} evident, which was the characteristic absorption peak of

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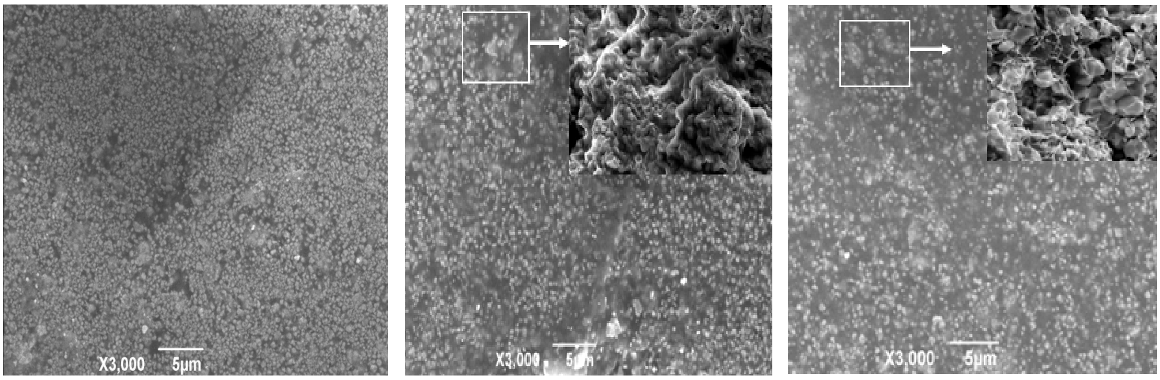
CH_2 and CH_3 functional group in NDZ-101. It showed that NDZ-101 on the surface of PZT particles. In addition, it showed an absorption peak of Ti-O bond at 1076.22cm^{-1}, which had an overlap with the absorption peak of PZT, and the peak intensity was increased that showed the chemical reaction may occur between titanate coupling agent and PZT particles.

3.2 SEM



(a) Unmodified (b) 1%KH-570 (c) 1%NDZ-101

Fig.2. SEM of PZT-PVDF composites

Fig.2 was the SEM images of PZT particles before and after 1% volume ratio coupling agent treatment in PZT-PVDF composites. Among them, Fig.2 (b) was the SEM images of PZT particles treated by KH-570 in the PZT-PVDF composites. It can be seen that the PZT particle equally distributed. Fig.2 (c) was the SEM images of PZT particles before and after 1% (volume ratio) titanate coupling agent NDZ-101 treatment in PZT-PVDF composites. From the SEM image, it can be observed that the defects of composite were greatly reduced after treatment by NDZ-101, and the microstructure was compact and dense. Compare Fig.2 (c) with the spacing between PZT particles in Fig.2 (b) became larger, and their interface faintness. It was caused by the silane coupling agent acting as the role of "molecular bridge" between ceramic phase and polymer phase, which enhanced adhesion between the two phases so as to be linked closely and weaken the traces of two phase interface.

The PZT particles were uniformly distributed in the PVDF without obvious defects. And PVDF infiltrates into the PZT ceramic material. But the effect of KH-570 treatment is not obvious, interface between PVDF and PZT are visible and clear. The results show clearly that there is not infiltration phenomenon between the PZT and PVDF. The interfacial properties in two phases were changed by NDZ-101, and the adhesion between the two phases in the PZT-PVDF composites was effectively improved.

3.3 Effects of coupling agent on the dielectric properties of PZT-PVDF

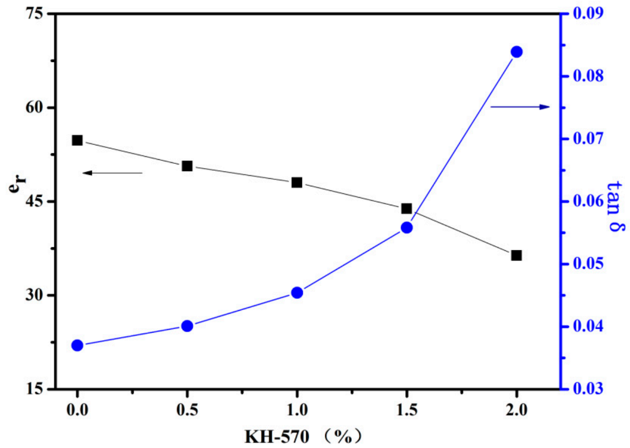


Fig.3. Effects of KH-570 on the dielectric properties of the PZT-PVDF

Fig.3 showed the dielectric properties versus volume percent of KH-570 in 0.5PZT/0.5PVDF composites. The test frequency was at 1 kHz under the condition of room temperature. As can be seen, with the content of KH-570 increased the relative dielectric constant ε_r of PZT-PVDF composites were decreased gradually. Without silane coupling agent KH-570, the relative dielectric constant ε_r of PZT-PVDF composites was 54.75. When the content of the KH-570 was 2.0%, the relative dielectric constant ε_r was reduced to 36.38, which was reduced by 33.55%. Meanwhile, the dielectric loss tanδ of the composites was increased with the increased content of KH-570. By analysis, after PZT-PVDF composites treated by KH-570 coupling agent, the infiltration effect of the ceramic phase in the polymer phase was improved, and the structures of the PZT-PVDF composites became more compact, and the porosity was decreased, all of which enhanced the dielectric constant of the PZT-PVDF composites to some extent. What cannot be overlooked was that a layer of insulation was formed on the surface of the ceramic phase which was caused by PVDF molecular chain and KH-570 wrapped. The greater the KH-570 content was, the greater the insulating layer thickness was. However, the dielectric constant of the insulating layer was smaller than the ceramic phase and polymerization phase. Therefore, the greater the content of KH-570 there was, the smaller values of the

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dielectric constant the PZT-PVDF composites had. Simultaneously, multi molecular layers which were caused by KH-570to improve the ceramic phase interface state, declined the uniformity degree of the PZT-PVDF composites interface and increased the relaxation polarization current. Finally all these lead to increase of the dielectric loss tanδ of PZT-PVDF composites.

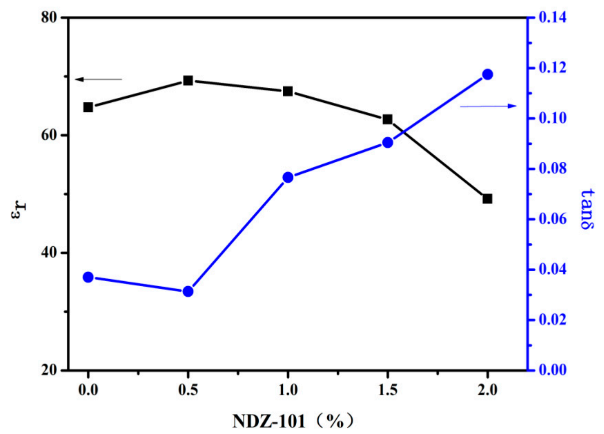

Fig.4. Effects of NDZ-101 on the dielectric properties of PZT-PVDF

Fig.4 showed the dielectric constant versus volume percent of NDZ-101 in0.5PZT/0.5PVDF composites. The test frequency was at 1 kHz under the condition of room temperature. As can be seen from the Fig.4, with the NDZ-101 content was increased, the relative dielectric constant ε_r of the PZT-PVDF was slightly increased. Especially when the content was 0.5%, the dielectric constant ε_r was increased from the initial 64.75 to maximum 69.29, increased only by 7.01%. However, with the NDZ-101 continuing to be increased, the relative dielectric constant ε_r of the PZT-PVDF composites was decreased. Simultaneously with the increase of content, the dielectric loss tanδ of the PZT-PVDF composites showed an increasing trend. When the content was 0, the dielectric loss tanδ was 0.037. When the content was 2%, the dielectric loss reached 0.1175. By analysis, during the preparation of piezoelectric composites, adding a certain amount of\ NDZ-101 improved the two-phase interface state, but the effect was not obvious. Meanwhile NDZ-101 can lower dielectric properties of PZT-PVDF. On contrast the dielectric loss tanδ

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of the PZT-PVDF composites was increased rapidly. This was because that NDZ-101 produced an accumulation phenomenon and reduced the interfacial strength greatly.

3.4 Effects of coupling agent on the piezoelectric properties of PZT-PVDF

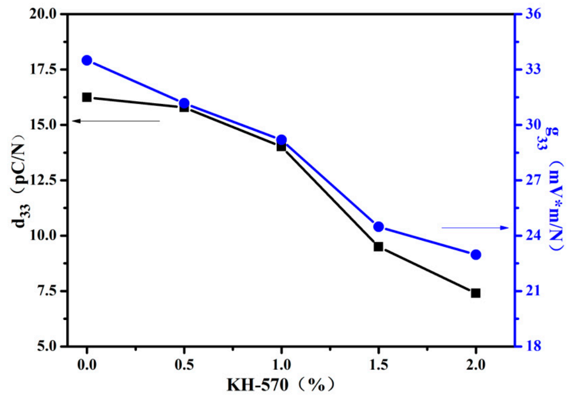

Fig.5. Effects of KH-570 on the piezoelectric properties of PZT-PVDF

Fig.5 showed the piezoelectric constant d_{33} and g_{33} versus volume percent of KH-570 in the PZT-PVDF composites. It indicated that the more contents of KH-570 was, the smaller values of the piezoelectric strain constant d_{33} and the piezoelectric voltage constant g_{33} of the PZT-PVDF composites were. According to abovementioned SEM, although KH-570 enhanced the adhesion of the two phases in the PZT-PVDF composites, it also added a layer of insulator on the surface of the ceramic, which separated the conductive path internal composites and reduced the conductivity. All these ultimately reduced the performance of the piezoelectric properties of the PZT-PVDF.

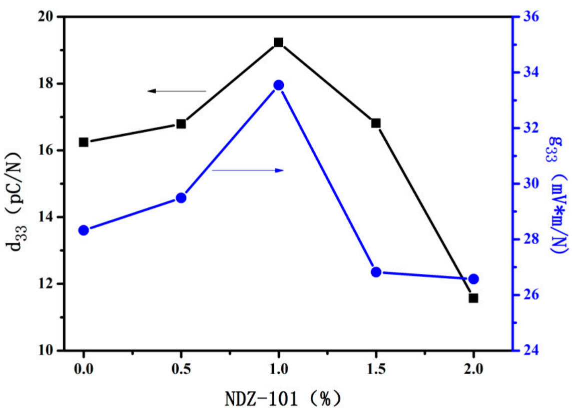

Fig.6. Effects of NDZ-101 on the piezoelectric properties of the PZT-PVDF

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Fig.6 showed the piezoelectric constant versus volume percent of NDZ-101 in PZT-PVDF composites. As shown in Fig.6, with the content of NDZ-101 increased, the piezoelectric strain constant d_{33} of the PZT-PVDF composites was firstly increased gradually and then decreased rapidly. The best content of NDZ-101 was 1%. Meanwhile the d_{33} of the PZT-PVDF composites reached the maximum 19.23pC/N. It was easy to find that with NDZ-101 coupling agent, the trends of piezoelectric voltage constant g_{33} were similar to the d_{33}. The g_{33} of the PZT-PVDF composites reached the maximum 33.54mV·m/N when the NDZ-101 was 1%.

4 Conclusions

The type and content of coupling agents had a great impact on the micro-structure and electrical properties of the PZT-PVDF composites. By the microscopic analysis, to some extent these two kinds of coupling agents both optimized the two-phase interface state of the PZT-PVDF composites. However, with the addition of KH-570, the dielectric and the piezoelectric properties of PZT-PVDF composites both were decreased, while the dielectric loss was increased. The coupling agent NDZ-101 can improve the electrical properties of the PZT-PVDF composites, and the optimal content was 1%. Under this condition, the relative dielectric constant ε_r was 67.45, the piezoelectric strain constant d_{33} was 19.23pC/N, the piezoelectric voltage constant g_{33} was 33.54mV·m/N, and the dielectric loss was 0.0766.

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Conflicts of interest

The authors declare no conflict of interest.

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