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Effect of microwave irradiation on crystalline structure and dielectric property of PVDF/PZT composite

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Abstract The crystalline structure change and dielectric performance of microwave-irradiated PVDF/PZT composites were studied by FTIR, DSC, DMTA, and DEA. The dielectric analysis suggests that the dielectric permissivity and loss reduce, which is useful for improving the sensitivity of composites used in passive transducers. The structure analysis results show that the microwave irradiation promotes crystalline transformation of PVDF from α to β; The crystallinity of PVDF in PVDF/PZT composites increases and ΔT decreases; the DMTA measurements illustrate that the value of E′ and tanδ peak increases after irradiation.

Introduction

Ferroelectric ceramic lead zirconium titanate (PZT) has very high pyroelectric and piezoelectric constants. However, the fragility, inflexibility, and poor processibility of ceramics limit its applications [1]. Ferroelectric polymers, such as poly(vinyidene) (PVDF) and its copolymers are flexible, easy to process, and present low mechanical impedance [1]. However, the low pyroelectric and piezoelectric constant of these materials together with the difficulty of polarizing thick films also limits their application [1]. In1978, R.E.Newnham [2] first designed a composite to combine the superior electro-active properties of the ceramics and the mechanical properties of polymers. Composites made of electroactive ceramics and ferroelectric polymer are very attractive for much application field since they exhibit high piezoelectric and pyroelectric response, low acoustic impedance matching with water and human skin and moreover, their properties can be tailored to various requirements [2]. The studies on the structure and property of PVDF/PZT composite have taken by many researchers [1–8]. Much research work has been done about the dielectric and piezoelectric behavior of piezoelectric composites, few researchers have concerned about the structure change of these composites.

Microwave irradiation (2.45 GHz) can markedly change the interface compatibility of the composite and decrease the dielectric loss [9]. Up to now, there is little study on the structure change in PVDF/PZT composites in presence of microwave irradiation. In this article the effect of microwave irradiation on the crystalline structure, interface interaction, and dielectric property of PVDF/PZT composites were demonstrated.

Experiment

PVDF and PZT are provided by Chengguang Chemical Academe of China. The PVDF/PZT composites are made by the hot compression of a mixture of PZT powder and PVDF powder. The composites were annealed at 80 °C for 24 h to dispel residual stress.

The experimental microwave reactor is a continuous microwave irradiation device, which can overcome the system error generated from the periodic microwave irradiation.

FTIR measurement is carried out with NICOLET 560 FTIR instrument. The composite is researched by normal FTIR. The measurement was taken by 2 cm^{-1} resolution and 40 scans.

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DSC analysis is taken on NEZSCH 204 DSC instrument by 10 °C/min. N_2 was 40 mL/min. Degree of crystallinity (Xc) of the present sample was determined from its DSC curve using the following equation [10]:

$$\mathrm{Xc} = \Delta H/\Delta H_c \times 100\% \quad (1)$$

where ΔH and ΔH_c are the heats of the fusion of the present PVDF sample and of '100%' crystalline PVDF, respectively. A value of 104.7 $\mathrm{Jg^{-1}}$ was used for ΔH_c, which was reported by Rosenberg and associates [10].

DMTA measurement is carried out with PL-DMTA $\mathrm{M_K}$III DMTA instrument, Rheometic Scientific Co., at a heating rate of 2 °C/min.

The dielectric permittivity (ε') and the dielectric loss (ε'') were measured by DEA 2970 instrument, DuPont Co., at a heating rate of 3 °C/min.

Results and discussion

DEA analysis

Figure 1 shows the temperature dependence of ε' and ε'' at a constant frequency 10^4 Hz for irradiated 100/50 PVDF/PZT composites. Three relaxations were reported in crystalline PVDF [7]: α_a, associated with segmental motions in the amorphous phase; α_c, related to the amorphous portions within the crystalline phase; and β, caused by weak local motions in the glassy state. As shown in Fig. 1(a), the dielectric constant ε' of PVDF/PZT composite decreases during the microwave irradiation. The increase in crystallinity of PVDF measured by DSC may influence the dielectric constant [11, 12]. This change is helpful to improve the sensitivity of PVDF/PZT composites used as passive transducers.

The dielectric loss ε'' of α_c-relaxation can be seen in Fig. 1(b). The magnitude of α_c-relaxation peak drops down with increasing the irradiation time. And the peaks shift to lower temperature. It is because that the microwave irradiation reduces the interface interaction, and lets the resistivity of the composites improve, then the peak value of the dielectric loss curves decreases [6].

FTIR analysis

It is known that PVDF can exist in three main crystalline modifications denoted as β(I) (orthorombic), α(II) (pseudo-orthorombic), and γ(III) (monoclinic) in which the chains assume the conformations *TTTT*, *TGTGT'*, and *TTTGTTTG'*, respectively. The CF_2 bending at 530 $\mathrm{cm^{-1}}$, the CF_2 bending and skeletal bending at 615 and 764 $\mathrm{cm^{-1}}$, the CH_2 rocking at 796 $\mathrm{cm^{-1}}$, the CH_2 twisting at 976 $\mathrm{cm^{-1}}$ have been widely used to confirm the αphase. The bands, such as 510 $\mathrm{cm^{-1}}$ (CH_2 bending) and 810 $\mathrm{cm^{-1}}$ (CH_2 rocking) are considered as the β phase. The dielectric constant of β phase PVDF is larger than of αphase. So, increasing the content of is helpful to the improvement of the dielectric and piezoelectric property of PVDF/PZT composites. The area ratio of IR bands at 510 $\mathrm{cm^{-1}}$ (characteristic of the β phase) and 530 $\mathrm{cm^{-1}}$ (characteristic of the α phase) were used to determine amounts of the βcrystalline structure under the microwave irradiation [13–15].

Figure 2 shows the IR spectrum of irradiated PVDF film. With the increasing of the irradiation time, the intensity of 510 $\mathrm{cm^{-1}}$ band is improved.

Figure 3 shows the area ratio A_{510}/A_{530} of the IR spectra of PVDF film. With the irradiation time increasing, A_{510}/A_{530} becomes larger. Figures 2 and 3 demonstrate that there is transformation from α to β in PVDF film. It is known that the phase transformation from α to β of PVDF can take place through the electrostatic force. The microwave field is the high speed alternating electromagnetic field. The change of C-F dipole orientation under the high speed alternating electromagnetic field may be the reason of the phase transformation. The related theory research work is still in process.

Figure 4 illuminates the area ratio A_{510}/A_{530} of 100/10 PVDF/PZT composite. With the increment of the irradiation time and power, the exchange degree of $\alpha\rightarrow\beta$ transformation of PVDF is enhanced. That means that the addition of PZT into the composite does not counteract the PVDF crystalline transformation and the microwave irradiation is also in favor of crystalline transformation of PVDF from α to β.

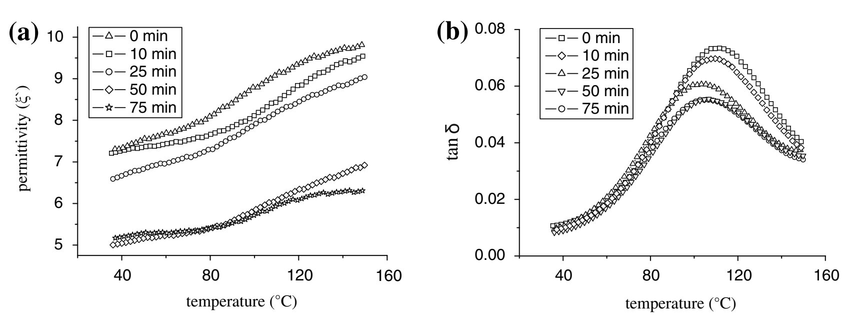

Fig. 1 Dielectric property of microwave irradiated 100/50 PVDF/PZT composites at 975 W ($f = 10^4$ Hz)

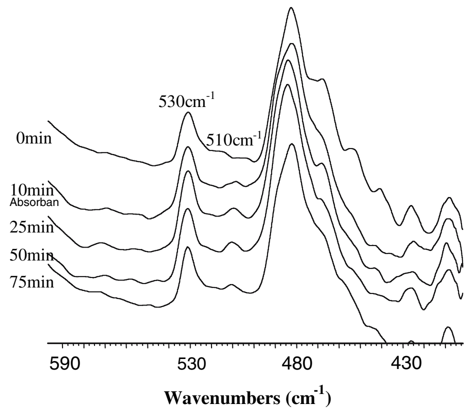

Fig. 2 IR spectra of microwave irradiated PVDF films at 975 W

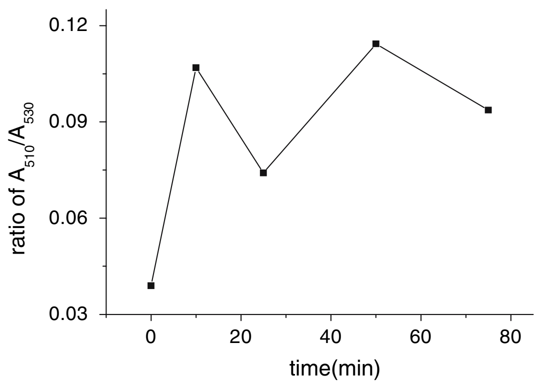

Fig. 3 A_{510}/A_{530} ratio of microwave irradiated PVDF film at 975 W

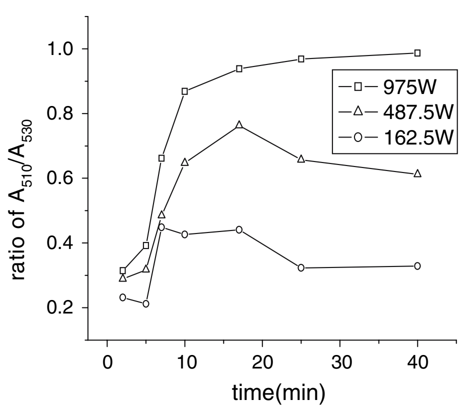

Fig. 4 A_{510}/A_{530} ratio of 100/10 microwave irradiated PVDF/PZT composites at 162.5, 487.5, and 975 W

DSC analysis

The DSC melting thermograms of the irradiated PVDF films are reported in Fig. 5. The values of the melting parameters of PVDF film are listed in Table 1. These values indicate that the crystallinity rises up with extending the irradiation time; ΔT is slightly reduced. Moreover, T_m keeps almost unchanged. That means that after microwave irradiation, the lamellar thickness remains as a constant.

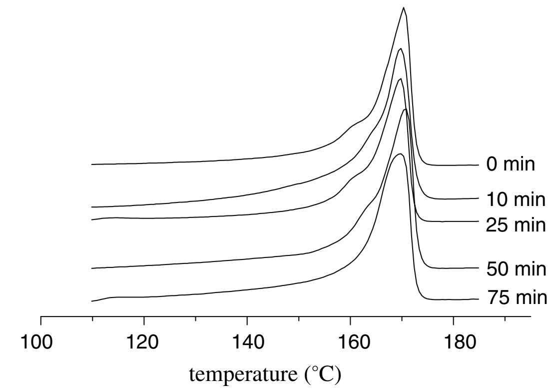

Fig. 5 DSC curves of microwave irradiated PVDF films at 975 W

Table 1 DSC results of microwave irradiated PVDF films at 975 W

Irradiation time (min)	Xc (%)	T_m (°C)	T_{onset} (°C)	T_{end} (°C)	$\Delta T = T_{end}-T_{onset}$ (°C)
0	42.3	170.8	163.6	173.1	9.5
10	45.1	169.7	163.3	172.5	9.2
25	51.5	170.0	163.7	172.8	9.1
50	54.1	169.8	163.8	172.1	8.3
75	59.1	169.5	163.9	172.5	8.6

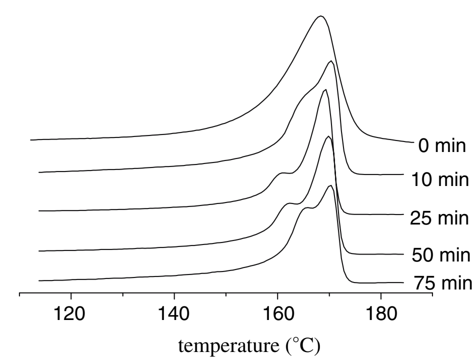

Fig. 6 DSC curves of microwave irradiated 100/50 PVDF/PZT composites at 975 W

Table 2 DSC results of microwave irradiated 100/50 PVDF/PZT composites at 975 W

Irradiation time (min)	Xc (%)	T_m (°C)	T_{onset} (°C)	T_{end} (°C)	$\Delta T = T_{end}-T_{onset}$ (°C)
0	27.9	169.8	162.8	172.8	10.0
10	31.2	169.3	162.8	172.3	9.5
25	32.5	169.9	163.2	172.8	9.6
50	31.4	170.3	163.7	171.9	8.2
75	32.5	170.4	163.6	171.8	8.2

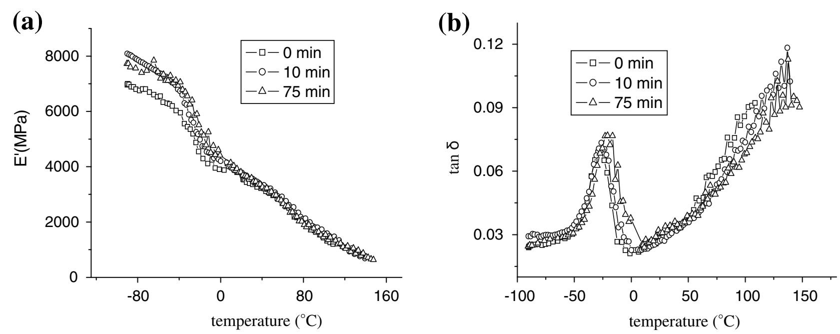

Fig. 7 Dynamic mechanical properties of microwave irradiated 100/50 PVDF/PZT composites at 975 W

Figure 6 shows DSC thermograms for the irradiated 100/50 PVDF/PZT composites. The DSC traces exhibit a shoulder peak on the low temperature side of the main melting peak. And the shoulder peak that is corresponding to β-crystal melting [13] that becomes larger with the irradiation time increasing. The results indicate that the microwave irradiation improves the amount of β-crystal in PVDF, as observed in the FTIR spectra analysis. Table 2 shows the values of the melting parameters of the irradiated 100/50 PVDF/PZT composite. The results illustrate that the crystallinity of PVDF is gradually enhanced; ΔT a little decreases. The microwave irradiation mainly has the 'thermal' influence on PVDF film and PVDF/PZT composites. The 'thermal' effect improves the development of the crystalline phase in PVDF and reduces the imperfections of the crystalline region.

DMTA analysis

Figure 7 shows dynamic mechanical properties of 100/50 PVDF/PZT composite. Lovinger and Wang [16] have reported that PVDF exhibits two distinct relaxation, namely the α-relaxation at around 80 °C related to chain vibration in the crystalline phase, and the β-relaxation related to glass transition at about –30 °C. Our results show one relaxation peak around –30 °C (β), and shifts toward higher temperature with increasing the irradiation time, the peak value of tanδ raises up in Fig. 7(b). This means that increasing the irradiation time decreases the interface interaction in PVDF/PZT composites [17].

E′ becomes larger below 0 °C with the irradiation time increasing in Fig. 7(a). It is because that after microwave irradiation, the crystallinity of PVDF/PZT composite becomes larger, E′ increases.

Conclusions

The following is a summarization of the results presented on the structure changes of PVDF/PZT composites under the microwave irradiation. With the irradiation power and time increasing, the transformation from α to $\beta$of PVDF is enhanced. The crystallinity of PVDF in polymer composites increases and ΔT decreases. The value of E′ and tanδ increases with the irradiation time. Both the dielectric permittivity and the dielectric loss reduce, which is useful for improving the sensitivity of PVDF/PZT composites used as the passive transducers.

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