

Piezoelectric properties of hot compression molded PVDF/SiC nanocomposites

*Mina Rasoolzadeh, Zahra Sherafat**

Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran.

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**Corresponding author email: zsharafat@shirazu.ac.ir*

ABSTRACT

Poly(vinylidene fluoride), PVDF, has been studied extensively because of its outstanding piezoelectric properties. PVDF shows five crystalline polymorphs known as α , β , γ , δ , and ϵ phases. Among them, the β phase exhibits piezoelectric properties, but the α phase is thermodynamically more stable. The incorporation of additives into PVDF can promote β phase formation. In this study, PVDF-nano SiC composites with different SiC contents were fabricated through hot compression molding and the effects of SiC on the crystal structure, crystallinity and piezoelectric properties of PVDF were studied. The microstructure of the composite samples was investigated by SEM. The prepared samples were perfectly dense with a density more than 97% of the theoretical density. The amount of β phase was determined by FTIR analysis and the crystallinity of the PVDF was deduced from DSC analysis. Finally the piezoelectric properties of the samples were measured by a piezotester. The results showed that by increasing SiC content up to 1 wt%, the amount of β phase, crystallinity and sensitivity of the samples increased and then decreased afterwards.

Keywords: *Piezoelectric Polymer, Polyvinylidene Fluoride, Silicon carbide, Hot Compression Molding, Beta phase*

1. Introduction

Polyvinylidene fluoride has been paid much attention by many researchers owing to its mechanical properties, chemical stability, and excellent ferroelectric and piezoelectric properties. This polymer has a simple chemical structure and exhibits five crystalline polymorphs, i.e., α , β , γ , δ , ϵ . The α -phase is thermodynamically the most stable crystalline phase of PVDF; however, the electrical properties of PVDF are affected by the presence of the β -phase, which has the highest dipole moment among the five polymorphs of PVDF. This phase enhances the piezoelectric and dielectric properties, and the presence of this phase in the structure induces polarity [1]. Although this polymer has less piezoelectric properties than ceramic materials, due to its desirable properties such as reasonable

price, flexibility, and biocompatibility, it is superior to piezoelectric ceramics and has found a wide range of applications in various fields, including sensors, transducers, and biomaterials [2].

In order to enhance the piezoelectric properties of PVDF, various methods have been investigated to create and increase the β -phase, including mechanical stretching, applying high pressures, the use of polar solvents, melt injection, the addition of additives, polarization under high electric field, the use of copolymers, the addition of nanoparticles, solvent casting, and electrospinning [3].

The addition of additives including RGO [4], CNT [5], ZnO [6], BaTiO₃ [7], and SiC [8] is also one of the ways to increase the β -phase in PVDF.

Silicon carbide (SiC) is a very hard ceramic material with a hexagonal or cubic crystal

structure [9]. The density of this material is 3.21 g/cm³. Chemical resistance at high temperatures, semiconducting properties, high thermal stability, and thermal conductivity have made this ceramic an applicable material for electrical equipment used at high temperatures [10,11]. The semiconducting properties of SiC can improve the electrical properties of the polymer matrix in polymer-ceramic composites. Research in this field has shown that the presence of SiC nanoparticles in the PVDF polymer causes an increase in the dielectric constant of the composite [12-14]. The addition of SiC to PVDF also increases the hydrophilicity of the composite, enhances the tensile modulus, and increases the β -phase in PVDF, which leads to improved piezoelectric properties [15].

In most studies, casting, as an appropriate method for the production of sheets and thick films, have been selected to investigate the effect of SiC on the piezoelectric properties of the PVDF-SiC composites. However, casting is not suitable for producing thick components, and the hot compression molding method can be alternatively used for this purpose. In this study, by adding SiC nanoparticles to polyvinylidene fluoride and fabricating the composite using hot compression molding, the effect of SiC on the formation of the β -phase in PVDF and the piezoelectric properties of the composite has been investigated.

2. Experimental details

PVDF (manufactured by Kynar company) and silicon carbide (beta) with a purity of 97.5% with a particle size range of 45 to 55 nm (manufactured by Arman Conda company) were used to fabricate PVDF-SiC composite samples. Ethanol (96%-manufactured by Zakaria Jahrom Company) was used to mix the primary powders.

In order to fabricate the PVDF-SiC composite by hot compression molding, first polyvinylidene fluoride and silicon carbide powders with different SiC contents (0, 1, 2.5, and 4 wt%) were mixed in ethanol by using a magnetic stirrer to form a homogeneous mixture. The resulting mixture was dried in an oven at 90 °C. Then, the powder was passed through a 60-mesh sieve to obtain a uniform powder. The composite powder was formed into 1 cm disks using hot pressure molding, at 200°C, under a pressure of 150 MPa, for 40 minutes. The density of the molded composite samples was measured by the Archimedes method. Scanning electron microscopy (SEM) was used

to investigate the morphology and quality of composite specimens. FTIR and DSC tests were used to determine the phases in PVDF and the percentage of crystallinity. Finally, piezoelectric properties were investigated by the PiezoTester device. To prevent the effect of sample dimensions on piezoelectric properties, samples with the same thickness were prepared for testing.

3. Results and discussion

3.1. Density measurements

The Archimedes method was used to determine the density of the samples fabricated by the hot compression molding method and the results are presented in Table 1. As shown in this table, the relative density of the samples is higher than 97% of the theoretical density. Thus, it is possible to fabricate high-density samples using hot compression molding.

3.2. Investigation of microstructure

To further confirm the dense structure of the composite samples, the SEM images of the fracture surfaces of the composite samples with different amounts of SiC (0, 1, 2.5, and 4 wt%) are shown in Figure 1. As can be seen, all the samples are completely dense and almost free of pores, which is consistent with the density results of the samples.

3.3. Investigation of FTIR test results

FTIR analysis was used to detect the phases present in PVDF and also to obtain their values. This analysis was performed on the composite samples fabricated by hot compression molding with different weight percentages of SiC, and the resultant FTIR spectra are shown in Figure 2. The peak at 530 cm⁻¹ can be assigned to CF₂ bending, the peaks at 615 cm⁻¹ and 765 cm⁻¹ are related to CF₂ bending and skeletal bending, and the peak at 795 cm⁻¹ is attributed to CH₂ rocking. These peaks are the characteristic peaks of α -phase. The peaks at 510 cm⁻¹ and 840 cm⁻¹ are characteristic peaks of β phase and related to the CF₂ bending and CH₂ rocking, respectively [16,17].

Table 1- The density of the composite samples fabricated by hot compression molding

Sample	SiC (wt%)	ρ (g/cm ³)	ρ_{th} (g/cm ³)	ρ/ρ_{th} (%)
1	0	1.732	1.780	97.30
2	1	1.742	1.788	97.42
3	2.5	1.791	1.800	99.49
4	4	1.758	1.812	97

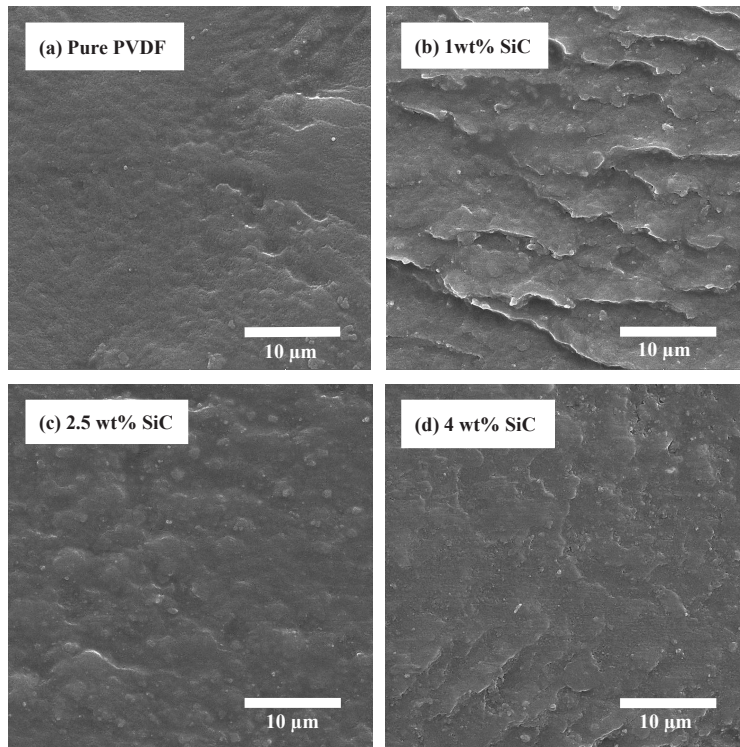


Fig. 1- SEM images of the fracture surfaces of composite samples fabricated by hot compression molding with different percentages of SiC: a) Pure PVDF, b) 1 wt% SiC, c) 2.5 wt% SiC, and d) 4 wt% SiC.

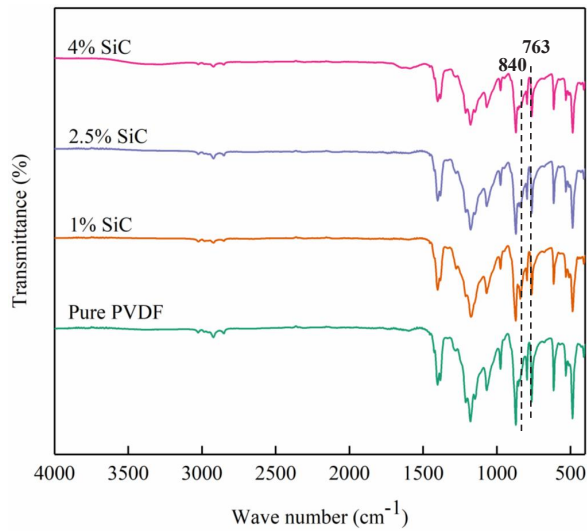


Fig. 2- FTIR spectra of the composite samples fabricated by hot compression molding.

As was mentioned earlier, the absorbances at 763 cm^{-1} and 840 cm^{-1} characterize the α and β phases, respectively [18]. The fraction of β -phase in PVDF samples containing α and β phases can be calculated using (eq. 1 and 2). In these equations, A_α and A_β represent the absorption bands at 763 and 840 cm^{-1} , respectively; $I_{\alpha,\beta}^0$ and $I_{\alpha,\beta}$ are the incident and

transmitted intensities of the radiation, respectively [19].

$$F_{(\beta)} = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (1)$$

$$A_{\alpha,\beta} = \log \left(\frac{I_{\alpha,\beta}^0}{I_{\alpha,\beta}} \right) \quad (2)$$

As can be seen in Figure 2, there are two peaks in all the composite samples, indicating the presence of both α and β phases. Fraction of the β -phase was calculated using (eq. 1 and 2) and its values are presented in Table 2.

As can be seen, with increasing the weight percentage of SiC, the amount of the β -phase increased and then decreased afterward. This can be attributed to the increased probability of the agglomeration of SiC particles with increasing the SiC content. Agglomeration reduces the effective surface area of the SiC particles and reduces the PVDF-SiC interaction. On the other hand, SiC agglomerates can prevent the movement of polymer chains and change the arrangement from the alpha to beta phase. Therefore, the highest amount of the β -phase was obtained in the sample containing 1 wt% SiC.

3.4. Investigation of DSC test results

In order to evaluate the percentage of crystallinity and melting temperature, DSC tests were performed on the composite samples fabricated by hot compression molding. By using the results of the DSC test and (eq. 3), the degree of crystallinity (ΔX_c) can be calculated [20]. ΔH_m is the melting

enthalpy of the samples and $\Delta H_{100\%, crystalline}$ is the melting enthalpy for a 100% crystallized sample of pure PVDF, which was reported to be 104.6 J/gr.

$$\Delta X_c = \frac{\Delta H_m}{\Delta H_{100\%, crystalline}} \quad (3)$$

Figure 3 displays the results obtained from the DSC test, and Table 3 shows the percentage of crystallinity and melting temperatures of the samples. As can be observed, as the weight percentage of SiC increases to 1 wt%, the degree of crystallinity increases and then decreases afterward. As the weight percentage of SiC increases, the agglomeration of SiC particles will be possible. SiC agglomerates can inhibit the movement of polymer chains and change the arrangement from α -phase to β -phase [20].

3.5. Investigation of piezoelectric properties

The composites with different weight percentages of SiC (0, 1, 2.5, and 4 wt%) were fabricated by hot compression molding and the effect of SiC on piezoelectric properties was investigated. In order to measure the piezoelectric properties, a specific force (2.66 or 3.45 N) with a frequency of 5 Hz (the period is 0.2 seconds) in a

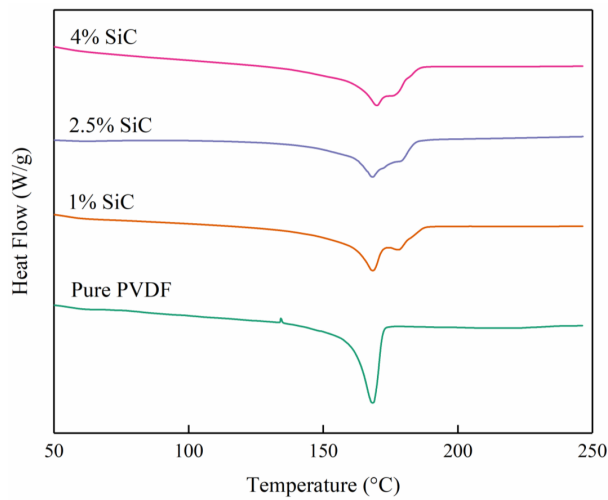


Fig. 3- DSC profiles of the composite samples fabricated by hot compression molding.

Table 2- The fraction of the β -phase of the composite samples fabricated by hot compression molding

Sample	SiC (wt%)	Beta fraction
1	Pure PVDF	0.33
2	1% SiC	0.47
3	2.5% SiC	0.4
4	4% SiC	0.37

Table 3- Melting temperature, melting enthalpy and the degree of crystallinity of the composite samples

Sample	SiC (wt%)	T_m (°C)	ΔH_m (J/gr)	ΔX_c (%)
1	Pure PVDF	168.45	40.34	38.56
2	1% SiC	168.51	43.38	41.47
3	2.5% SiC	168.26	41.70	39.86
4	4% SiC	170.02	39.51	37.77

time of one second was applied to the composite samples and the output voltage in each time of force application was measured and their average was recorded as the sample piezoelectric voltage. By dividing the piezoelectric voltage by the applied force, the sensitivity of the sample was obtained, which indicates the piezoelectric behavior of the sample [21]. Figure 4 shows the sensitivity of the composites versus the weight percentage of SiC. As can be seen, the sensitivity has increased up to 1wt% SiC but has not changed much after that. SiC can affect the piezoelectric behavior of composite samples in two ways. SiC particles can increase the amount of the β -phase and thus enhance the piezoelectric properties. In addition, since SiC is a semiconducting material, it can contribute to the charge transfer within the material and improves the piezoelectric properties. As mentioned earlier, the probability of agglomeration of SiC particles increases, exceeding the 1wt% SiC limit. As a result, both the amount of the β -phase and, consequently, the sensitivity of the samples decreases. But since increasing SiC helps charge transfer within the material and improves piezoelectric properties, the sensitivity of the samples has not changed much beyond 1wt.% SiC.

4. Conclusions

The presence of SiC additive increases the β -phase in PVDF only if there is a uniform distribution of SiC in the polymer phase. The results show that the addition of SiC up to 1 wt% increases the β -phase. Further increase in the amount of SiC, due to the agglomeration of particles, decreases the amount of the β -phase. The SEM images and the density of the composite samples fabricated by hot compression molding indicate that this method is appropriate for producing dense and pore-free components. The results of the DSC test show that the highest percentage of crystallinity is obtained in the sample containing 1 wt% SiC. In addition, the results of the piezoelectric behavior show that with increasing the amount of SiC up to 1 wt%, the piezoelectric property of the sample enhances while no significant changes were noticed beyond 1 wt% SiC.

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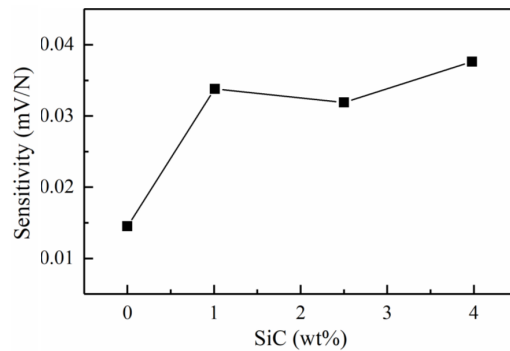


Fig. 4- The variations of sensitivity with SiC content.

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