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Study of the Preparation and Dielectric Property of PP/SMA/PVDF Blend Material

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Abstract: Polypropylene (PP) and polyvinylidene fluoride (PVDF) polymer materials have been widely used because PP has excellent piezoelectricity and PVDF has a robust tensile strength. However, few studies have been reported about PP/PVDF blends, and the main issue has proven to be the interfacial compatibility of blends. This research investigated the microstructure of blends to characterize their compatibility. X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis showed the poor interactions between PP and PVDF interface, and thus this study adopted styrene maleic anhydride (SMA) copolymer as compatibilizer to modify the properties of blends. The XRD and SEM investigations showed an enhancement in the interactions between PP and PVDF after the addition of SMA. The dielectric properties of PP/SMA/PVDF blends showed a significant increase when PP content was 40%–60% and the dielectric constant (ϵ) was up to 13; meanwhile, the dielectric loss ($\tan\delta$) of PP/SMA/PVDF was lower than PP/PVDF blends.

Keywords: polymer blends; PP/PVDF; compatibilizer; dielectric property; microstructure

1. Introduction

Requirements for polymer materials have gradually increased with the development of technology [1,2]. However, there are many limitations, such as source of raw material, synthesis technology, and cost of production, to the development of a new kind of polymer [3]. Therefore, researches focus on the study of polymer blends which combine the performances of the blended polymers. Polymer blends are easy to process and shape, and have great flexibility [4,5]. Meanwhile, the application prospects of polymer blends is extensive, and they can typically be adopted by the modern electronic industry [6,7]. In our previous study, polyamide (PA) 11/PVDF and PA66/PVDF blends were reported as novel blends for capacitors [8–10]. Polyvinylidene fluoride (PVDF) is known as the polymer with the best dielectric properties, and has stable chemical and mechanical performance. The blends comprised of PVDF and other organic materials have also demonstrated that the organic–polymer composites possess very distinct dielectric properties that can be applied in electrics, such as hydroacoustic sensors and medical applications [8–11]. Nevertheless, most of the high-molecular weight polymers are incompatible due to the lack of effective interactions with each other between mixed phases and the strong surface tension when melting [12]. Consequently, a compatibilizer is introduced in this research to promote the compatibility between polymers.

Because of the excellent piezoelectricity and robust tensile strength of PVDF and polypropylene (PP), respectively [13,14], this research prepared PP/PVDF through machinery blending. Then, styrene maleic anhydride copolymer (SMA) was adopted as compatibilizer and added into PP/PVDF blends. SMA has been widely applied as a compatibilizer since it has grafting reactions with some polymers. There are anhydride groups on the backbone structure of SMA which result in various reactions with other groups and produce derivatives that enhance the interactions between two polymers [8]. As a

result, the mechanical and dielectric properties of the blends are significantly improved. Although there are some studies about the dielectric properties of PP/PVDF blends [15,16], few correlate the results with the microstructures of blends. Thus, this research studies the correlation between blend microstructures and dielectric properties. Besides, PP/SMA/PVDF blends are investigated to verify the compatibilization of PP/PVDF blends by SMA. The paper proceeds as follows: firstly, the preparation method of PP/PVDF and PP/SMA/PVDF blends is introduced. Then, a description of the structural analyses of these blends as conducted based on XRD and SEM is provided. Next, we present the results of the evaluation of the dielectric properties of blends tested by the dielectric spectrum tester. Finally, some discussions about the relationships between microstructures and dielectric properties of blends are presented and are then followed by conclusions of the research.

2. Experimental

2.1. Materials

PVDF powders were produced by the Shanghai organic fluoride research institution (Shanghai, China) and PP powders were provided by the Yanshan Petrochemical (Beijing, China). SMA (MA content 18 wt %) and acetone were purchased from Tianjin Chemical reagent Co., Ltd. (Tianjin, China).

2.2. Preparation of PP/PVDF and PP/SMA/PVDF Multiple Blends of Each Composition

PVDF and PP were mixed for 5 min by the XSS-300 torque rheometer (Shanghai Kechuang Rubber Plastic Machinery Co., Ltd., Shanghai, China) at 190 °C, and then the mixture was placed on the press vulcanizer under 25 MPa thermocompression at 195 °C for 10 min. Next, the mixture was cooled to the room temperature and was taken out after 3 min of pressure holding. A circular sheet of PP/PVDF with 12 mm diameter and 1 mm thickness was made after these procedures, and the sheet was polished and silvered with silver paint.

The optimum volume of PVDF, PP, and SMA were mixed by the torque rheometer. We then put each blend into the internal mixer and kept the temperature between 180–185 °C at the rotating speed of 40 rpm for 5 min. A press vulcanizer was then used to press the PP/SMA/PVDF blends under 10 MPa compression at the temperature between 180–185 °C for 5 min to get 2 mm-thick sheets. Finally, the sheets were washed with distilled water to remove the residues on the surface and dried at room temperature.

2.3. Instrumental Analysis

The dielectric spectrum tester HIOKI3532-50 LCR (HIKO Company, Nagano-ken, Japan) was adopted to test the dielectric properties of the samples at frequencies ranging from 10^2 to 10^6 Hz at room temperature. The crystal phase compositions of the samples were determined and identified by XRD analysis, and were carried out on a D/MAX-III-type XRD instrument (Japanese Rigaku Company, Tokyo, Japan). The experimental conditions were as follows: Cu K α radiation; wavelength 1.5406 Å; graphite monochromator 40 kV, 30 mA; scan rate 10 °/min. A JM5610LV-type SEM (Japanese Electronics Corporation, Tokyo, Japan) instrument was used for the microstructural analysis of the samples. The acceleration voltage was 20 kV in a low vacuum mode of 1–270 Pa.

3. Result and Discussion

3.1. Structure Analysis

Figure 1 shows the XRD pattern of PP/PVDF blends. The diffraction peaks of pure PVDF are at $2\theta = 18.3^\circ$, 19.9° , and 26.5° , respectively, while that of PP are at $2\theta = 14^\circ$, 19.9° , and 18.5° , respectively [8,17]. It can be seen from Figure 1 that the diffraction peaks of PP and PVDF coexist after their blending. The diffraction peak of PP was enhanced with the increase of PP, and the β -crystal form diffraction peak of PVDF gradually weakened. The diffraction peak of PP started to emerge

since PP/PVDF blends contained 40% PP. New phases did not appear among the above blending proportions (20/80, 40/60, 60/40, 80/20), which means that the crystal structure remained constant.

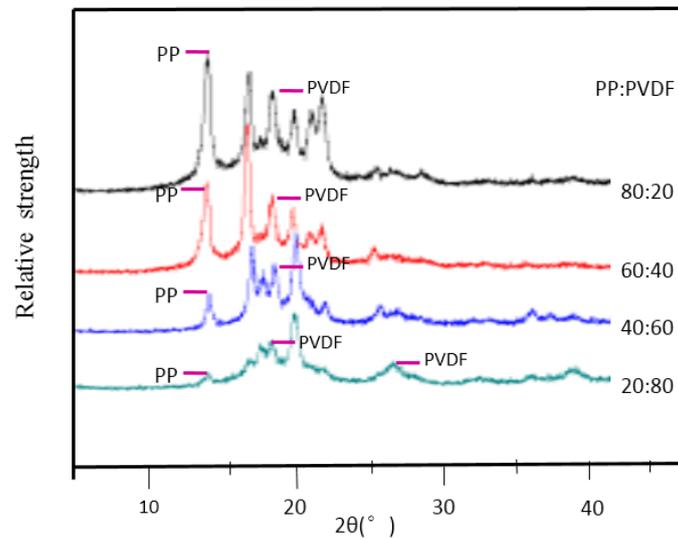


Figure 1. X-ray diffraction (XRD) pattern of polypropylene/polyvinylidene fluoride (PP/PVDF) blends.

Figure 2 shows the XRD pattern when PVDF and PP are mixed at same volume proportion and the SMA content is 0%, 3%, and 5%. It can be seen from the figure that adding a small amount of SMA compatibilizer increases the voltage of PVDF applied to blends, facilitates the electric domain diversion of PP, and thus improves the polarizability of PVDF in blend material and finally achieves a good polarization effect under the condition of low polarized voltage. With the continuous addition of SMA, it can be observed that when the content was 5%, the composite material could hardly apply voltage and the leak current showed excellent polarizability.

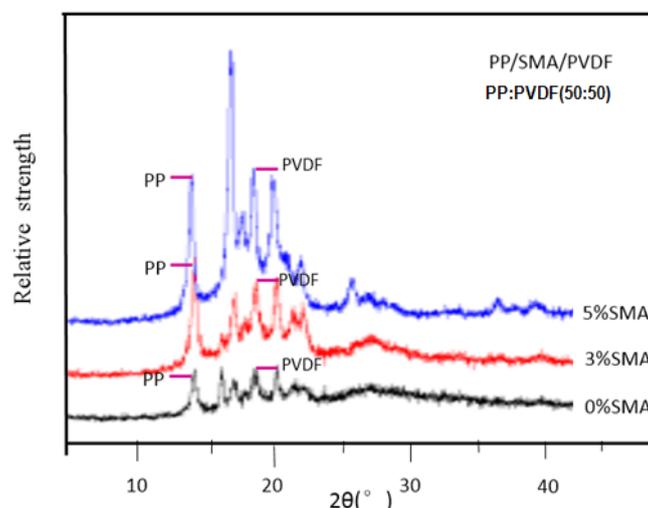


Figure 2. XRD pattern of PP/SMA/PVDF blends. SMA: styrene maleic anhydride copolymer.

Figure 3 is the SEM image of PP/PVDF blends. It can be seen from the figure that the PP particles are uniformly distributed in PVDF, and the structure of the blends is relatively compact. When PP content was relatively high, PVDF particles were completely wrapped by PP. However, the distinction between PP and PVDF was obvious.

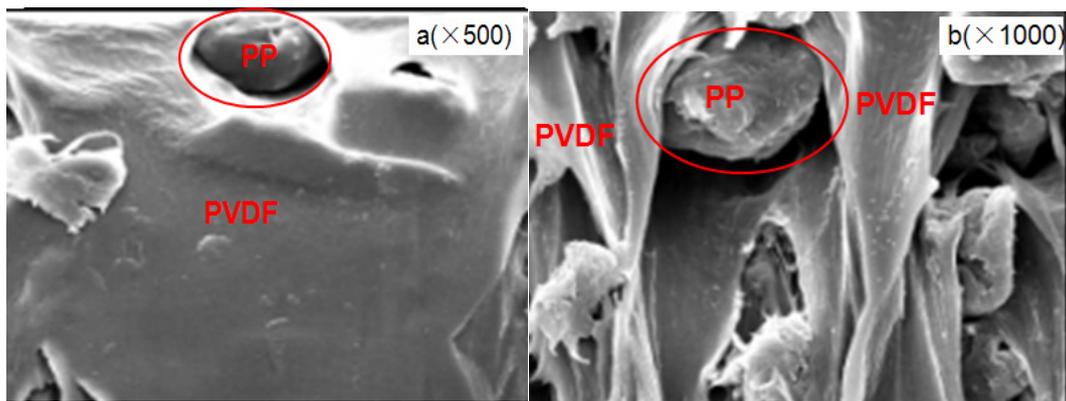


Figure 3. Scanning electron microscope (SEM) micrographs of PP/PVDF blends in different magnification. (a) PP/PVDF (40:60); (b) PP/PVDF (80:20).

Figure 4 is the SEM image of PP/SMA/PVDF blends with 3 wt % SMA. As indicated in Figure 4, the interface of the blend systems is not visible. This can be explained by the in situ reaction at the interface between PP and PVDF phases, and this reaction creates PP-g-SMA, which reduces the interfacial tension and the size of dispersed phase, facilitates diffusion, promotes the interaction and permeation between phases, and improves the structure form. Meanwhile, PP-g-SMA improves the interface bonding between components.

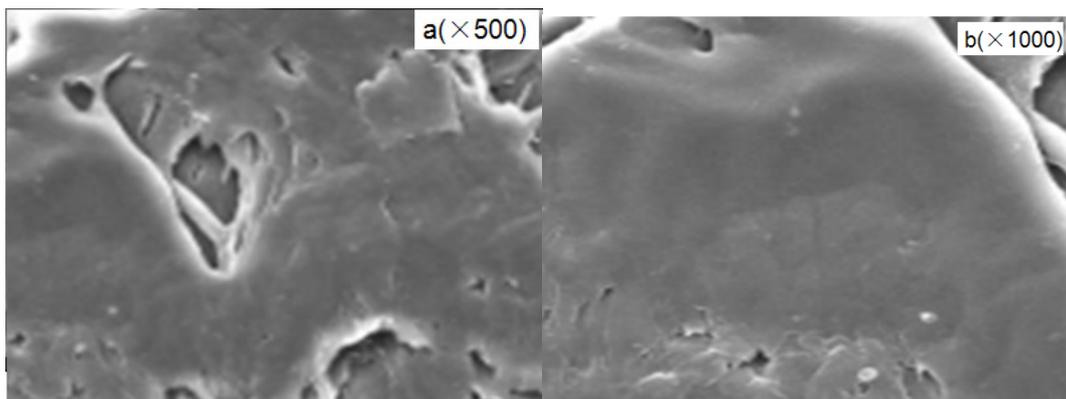


Figure 4. SEM micrographs of PP/SMA/PVDF blends in different magnification. (a) PP/PVDF (20:80); (b) PP/PVDF (50:50).

3.2. Dielectric Properties

The relationship of the dielectric constant (ϵ) of PP/PVDF blends to frequency is shown in Figure 5a. It can be seen from the figure that ϵ became greater with the increasing addition of PVDF, which can be explained by the influence of high dielectric properties of PVDF. There is an exception in PP/PVDF (60/40), due to the poorest interactions between two polymers according to our previous study [8–10]. A PVDF molecule contains two fluorine groups (-F) which show an intense polarity and have an orientation under the effect of external electric field, and the relaxation of the fluorine groups happens during the electric cycle. The orientation speed of fluorine groups (-F) is in line with the variations of the electric field at low frequency, and thus the ϵ curve was flat at the beginning. However, as the frequency increases, those movements are prevented. The orientation speed of polarity groups of PVDF was less than the variations of electric field, which led to a steep fall of the ϵ curve. Although the dielectric constant ranges of PP and PVDF are 2.2–3 and 8.4–13.5, respectively, PP/PVDF blends have poor dielectric properties, as their dielectric constant has a maximum value of 3, which is lower than that of pure PVDF [16,17].

Figure 5b shows the relationship of ϵ of PP/SMA/PVDF blends to frequency. It can be observed that the dielectric constant ϵ became greater with the increasing addition of PVDF, which is consistent with that of PP/PVDF blends. Besides, compared with PP/PVDF blends, the dielectric constant ϵ of PP/SMA/PVDF blends improved significantly, which proved that the polarization degree of PP was promoted through only a small amount of SMA addition in PP/PVDF blends, and thus the dielectric property improved and the dielectric constant ϵ increased as well.

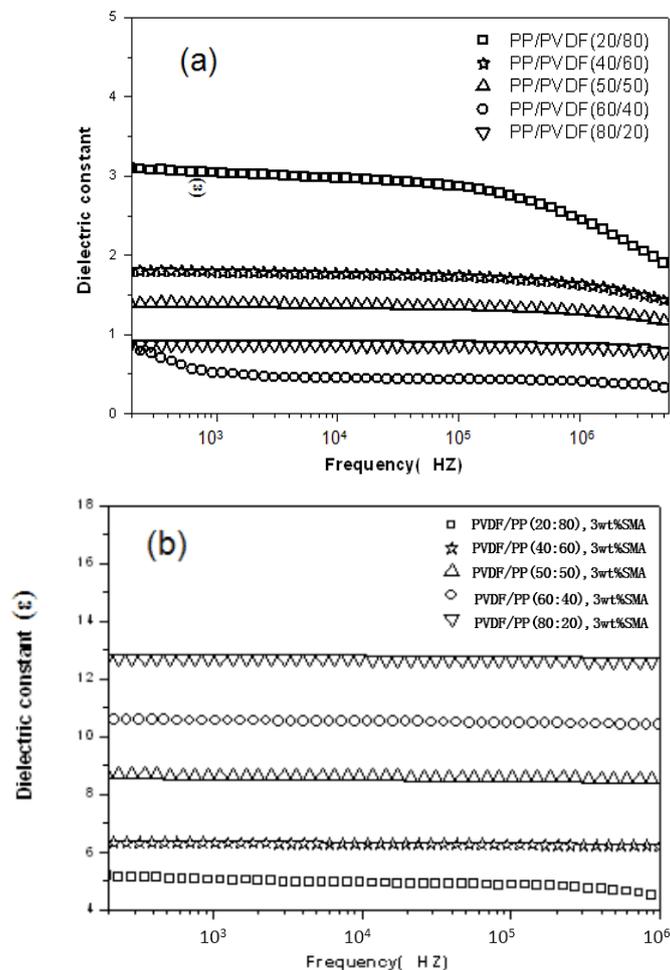


Figure 5. Frequency dependence of ϵ for (a) PP/PVDF and (b) PP/SMA/PVDF.

Figure 6a shows the relationship of the dielectric loss ($\tan\delta$) of PP/PVDF blends to frequency. $\tan\delta$ of PP/PVDF blends increased gradually with frequency, and this tendency became more obvious with the increase of PVDF. An exception was seen in PP/PVDF (60/40), which can be explained by the reason discussed previously. The curve of dielectric loss is flat at low frequency, but it increased drastically starting at a frequency of 10^5 Hz and resulted in a significant inflection point in the graph. In addition, the inflection point appeared at approximately the same frequency for all compositions although the content of PVDF kept increasing, which suggested that the inflection point correlated to the basic property of the blends rather than PVDF.

The relationship of the $\tan\delta$ of PP/SMA/PVDF blends to frequency is shown in Figure 6b. At small frequency, $\tan\delta$ showed the tendency to decrease with frequency. Meanwhile, with the decrease of PP amount, this tendency became more significant. In addition, with the increase of frequency, $\tan\delta$ of PP/SMA/PVDF blends remained almost constant, independent of frequency. Although there was a rising trend at large frequency, the $\tan\delta$ of PP/SMA/PVDF blends was relatively small, and it was below 0.03 with 3% SMA addition.

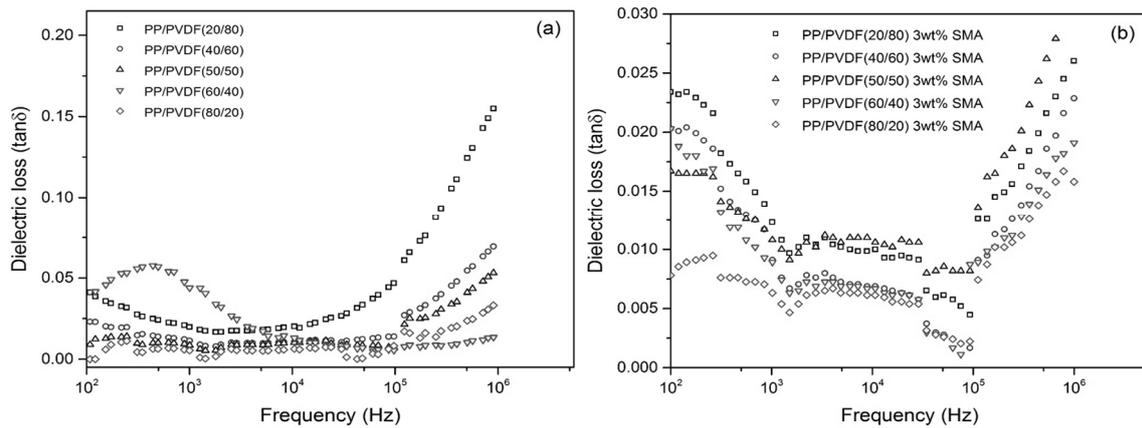


Figure 6. Frequency dependence of $\tan\delta$ for (a) PP/PVDF and (b) PP/SMA/PVDF.

The dielectric constant of PP/PVDF blends and PP/SMA/PVDF blends with 3% SMA addition were tested at room temperature and at a frequency of 10^6 Hz. In Figure 7a, the dielectric constant ϵ of PP/SMA/PVDF blends decreased with the increase of PP content. In addition, it can also be seen from the figure that the dielectric constant of blends with added SMA was greater than that of PP/PVDF blends. This is attributed to the addition of SMA, which improved the compatibility of the polymer matrix, then made electrons migrate between conductive particles, and thus increased electric field intensity of PVDF, promoted polarization degree, and finally resulted in the increase of the dielectric constant of blends.

The dielectric loss of PP/PVDF blends and PP/SMA/PVDF blends with 3% SMA addition were tested under the same condition as Figure 7a, and the results are shown in Figure 7b. It can be found that the dielectric loss of both blends decreased with the increase of PP, while that of the blends with SMA addition was less than that of PP/PVDF blends. Although there was a slight increase when PP content was 50%, the general trend decreased gradually and stayed at around 0.01.

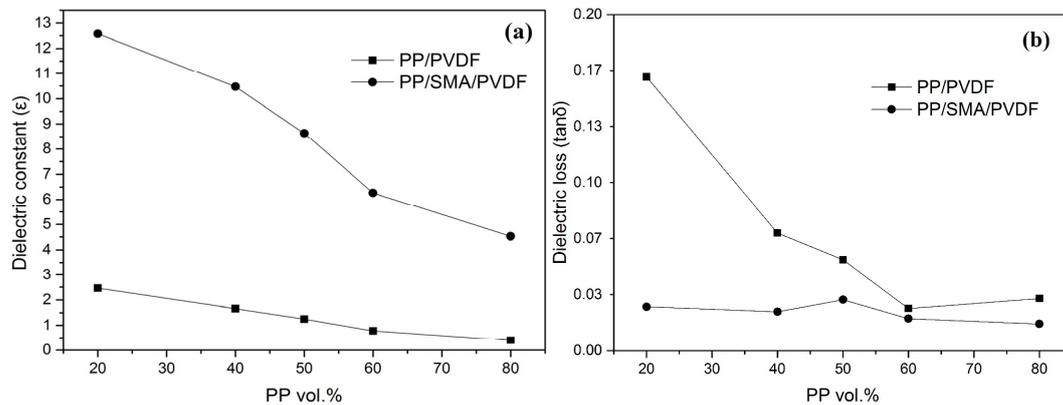


Figure 7. Variation of (a) ϵ and (b) $\tan\delta$ versus PP content of PP/PVDF and PP/SMA/PVDF blends.

4. Conclusions

In this work, the microstructures and dielectric properties of PP/PVDF and PP/SMA/PVDF blends were studied. As indicated by the results of XRD pattern and SEM images, the blend system of PP/PVDF is a two phase structure without the presence of a new phase or the change of crystal structure. PP phase was uniformly distributed in the continuous PVDF phase. SMA can be used as compatibilizer in PP/PVDF blends to modify the properties of blends. The interface between PP and PVDF was absent after the addition of SMA. Additionally, SMA triggered the in-situ reactions at the PP/PVDF interface and produced PP-g-SMA, which decreased the interfacial tension and

promoted the interactions between interfaces, thus realizing the good dielectric frequency stability of PP/PVDF blends. The dielectric constant of PP/SMA/PVDF blends increased with the growing content of PVDF, and it was much greater than that of PP/PVDF blends; meanwhile, the dielectric loss of PP/SMA/PVDF changed slightly with frequency and decreased with PP content, with the value finally stabilizing at around 0.01.

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Author Contributions: Rui Li and Zixuan Chen conceived and designed the experiments; Zixuan Chen performed the experiments; Zixuan Chen and Jianzhong Pei analyzed the data; Rui Li contributed reagents/materials/analysis tools; Rui Li and Zixuan Chen wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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