Novel High-Dielectric-Permittivity Poly(vinylidene fluoride)/Polypropylene Blend Composites: The Influence of the Poly(vinylidene fluoride) Concentration and Compatibilizer

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ABSTRACT: Novel high-dielectric-permittivity poly(vinylidene fluoride) (PVDF)/polypropylene (PP) blend composites were prepared via a blending technology, and their dielectric properties were studied over wide ranges of temperatures and frequencies. To improve the interface bonding between PVDF and PP, a suitable compatibilizer, polypropylene-*graft*-maleic anhydride (PP-*g*-MAH), was employed. The results showed that the concentration of PVDF in the composites dominated the changes in the dielectric properties and that the use of PP-*g*-MAH could improve the interface interaction between PVDF and PP, resulting in an increase in the dielectric permittivity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3649–3655, 2007

Key words: blending; compatibility; composites; dielectric properties; differential scanning calorimetry (DSC); heterogeneous polymers; interfaces; morphology

INTRODUCTION

Capacitors are important elements used extensively in electrical engineering. In the beginning, capacitors were used primarily in electrical and electronic products, but today they are used in fields ranging from industrial applications to automobiles, aircraft, space, medicine, computers, games, power supply circuits, and other power electronics.[1] They are key elements in microelectromechanical systems because the electrostatic capacitance can be controlled with high precision.[2,3] During the past years, great advances have been achieved in capacitor technology.[4] The improvements were made possible by the introduction of new dielectric materials such as polymeric films. In this field, polypropylene (PP) films have often been used as dielectric materials in engineering capacitors because of their combination of remarkable properties, such as low dielectric loss, good stability, high volume resistivity, a low water absorption rate, and a low shrinking rate. However, it is well known that the dielectric permittivity of PP is very low ($\sim$ 2.2), so it cannot satisfy the need of new capacitors with large capacitance values.

As mentioned previously, the dielectric permittivity of materials seriously affects the capacitor characteristics. Insulating materials are selected with their potential use in capacitors taken into account. Each dielectric shows a characteristic behavior as a function of the frequency and temperature and in the case of electric shocks.[4] However, the improvement of the dielectric permittivity is still a key subject in new dielectric material fields. Very recently, several methods have been used to improve the dielectric permittivity of polymers.[5–17] An electron-irradiation process can be employed to increase the dielectric permittivity of some polymers.[5] Among these methods, a great number of them are focused on mixing high-dielectric-permittivity ceramic powders into polymers; therefore, high-dielectric-constant polymer matrix composites have been achieved.[5–10] However, at a high ceramic loading for high dielectric permittivity, the flexibility of the polymer composites will decrease dramatically,

so it is very difficult to prepare thin films by a biaxial stretching process to satisfy the needs of capacitor films. On the basis of the percolation effect,[11–13] although the dielectric permittivity of polymer composites can also be improved significantly when the volume fraction of the conducting phase is close to the critical concentration, the percolation microstructure of the polymer composites is often destroyed; this gives an unstable dielectric permittivity, and large dielectric loss and conductivity exist in the percolation polymer composites.[14–17] Large dielectric loss results in great heat production when the polymer composite films are used as dielectric materials in a capacitor. Therefore, one must seek a new method to improve the dielectric permittivity of polymers used in capacitors. If the dielectric permittivity of PP were to be improved significantly, the charge-storage ability of capacitors would be subsequently increased, and the volume of capacitors could be miniaturized.

Of the presently known polymers, poly(vinylidene fluoride) (PVDF) has a relativity high dielectric permittivity value ($\sim$ 10). It is a partially crystalline, linear polymer with a carbon backbone in which each monomer [—CH_2—CF_2—] unit has two dipole moments, one associated with CF_2 and the other with CH_2 in the crystalline phase. PVDF exhibits a variety of molecular conformations and crystal structures depending on the method of preparation:[18] I(α), II(β), III(γ), IV, V, and VI. The most stable modification, I(α), is obtained upon cooling from the melting phase. However, it is seldom applied as a dielectric material because it is difficult to synthesize, and therefore the cost is high. PP films are now most often used as dielectric materials in capacitors. To improve the dielectric permittivity and to maintain the good flexibility of PP, PVDF with a high dielectric permittivity should be blended with the PP matrix. Such blend composites would display the advantage of combining the excellent dielectric properties of PVDF and the processability of conventional polymers, and they could be the new generation of dielectric films used in capacitors.

As we know that PP and PVDF are immiscible, the properties of PVDF/PP blend composites strongly depend on the interfacial interaction between PP and PVDF. Therefore, the miscibility of PP and PVDF should be improved by a mutually compatible interphase. In this study, polypropylene-*graft*-maleic anhydride (PP-*g*-MAH) was employed as a suitable compatibilizer. Here we present the effects of the PVDF volume content and compatibilizer (PP-*g*-MAH) on the morphology and dielectric properties of the PVDF/PP blend composites over wide ranges of frequencies and temperatures. Our aim is to improve the dielectric permittivity of PP by employing another polymer, without the addition of any inorganic additives, while keeping the low cost.

EXPERIMENTAL

Raw materials and preparation of the blend composites

All the polymers used were commercial products and were used as received. PVDF (type FR903, Shanghai, China), used as a dispersion phase in this study, was supplied by Shanghai 3F New Materials Co. PP (type K1300, Beijing, China), used as a continuous polymer matrix, and the compatibilizer, PP-*g*-MAH (Beijing, China) were supplied by Beijing Yanshan Petrochemical Co.

All compositions in the composites were blended in various volume ratios. The compounding of the PVDF/PP blend composites was conducted with a Haake mixer (Germany). The blending process was performed at 165°C and 60 rpm for 20 min. Then, the compounds were molded via hot pressing at about 200°C and 20 MPa. The final samples with a disc shape were 12 mm in diameter and 1 mm thick.

Dielectric measurements

The alternating-current dielectric properties of the samples were measured with an Agilent 4294A impedance analyzer (USA) over the frequency range of 10^3 Hz to 40 MHz at different temperatures and over the temperature range of −50 to 140°C at different frequencies. Before the measurements, both sides of all samples were deposited with gold for electrodes.

Thermal characteristics

Thermal analyses were performed with a DuPont TA 2010 differential scanning calorimetry (DSC, USA) instrument. The samples were heated from −70 to 190°C under dry nitrogen. The glass-transition temperature was obtained as the inflection point of the heat capacity jump recorded at a scan rate of 10°C/min.

Microstructure observations

The fractured surface microstructures of the blend composites were investigated with scanning electron microscopy (SEM). The fracture surfaces were sputter-coated with gold before the observations.
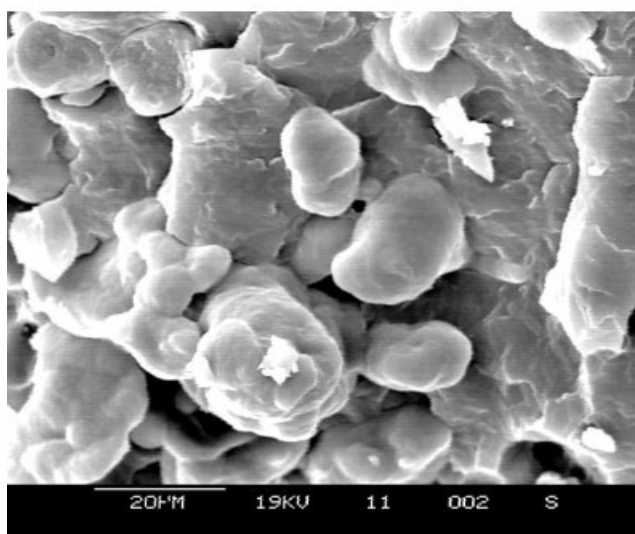
RESULTS AND DISCUSSION

Morphological characteristics of the PVDF/PP blend composites

As our samples were polymer blend composites, the miscibility between PP and PVDF was very important, and it played a crucial role in deciding the morphology, heterogeneity, and properties of the PVDF/PP blend composites. Figure 1 shows the morpholo-
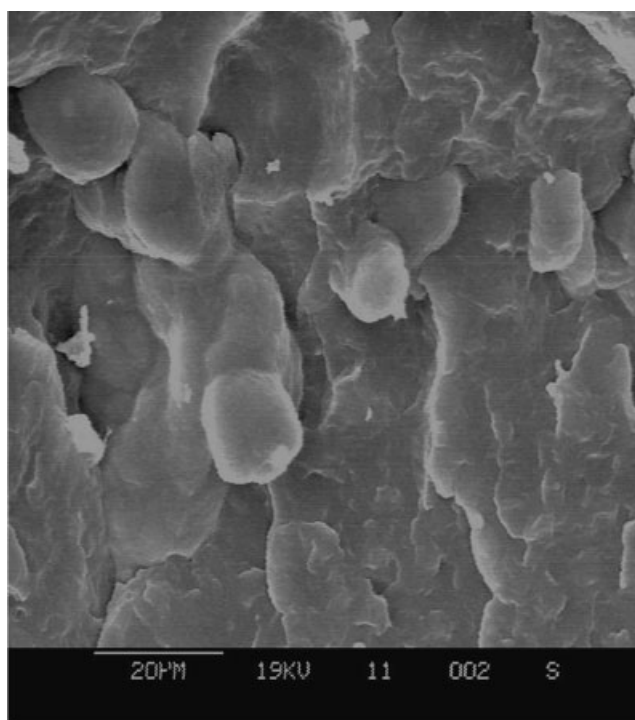
(a)

(b)

Figure 1 SEM micrographs of (a) the PVDF/PP blend composite and (b) the PVDF/PP-MAH/PP composite. The arrows point to PVDF particles.

gies of fractured surfaces of PVDF/PP blend composites. As we know, PP and PVDF are poorly miscible, although they are both thermoplastic polymers and have similar melting temperatures (~ 180°C). As shown in Figure 1(a), the PVDF phase in the PVDF/PP (20: 80) blend composite was dispersed in the PP matrix as particles 10–15 μm in diameter, and the boundaries between PP and PVDF were distinct. However, after PP-g-MAH was used as a compatibilizer, we observed a significant interface interaction

between PVDF and PP in the PVDF/PP-g-MAH/PP (20 : 10 : 70) blend composite [see Fig. 1(b)], and it was just this factor that led to the obscure boundaries in the blend composite. Figure 2 illustrates the formation process of the PVDF/PP-g-MAH/PP (20 : 10 : 70) blend composite. In the case of polymer fusion, nonpolar PP molecules interact with PP parts in PP-g-MAH, and polar PVDF molecules interact with maleic anhydride (MAH) parts in PP-g-MAH. Therefore, it could be concluded from the presented SEM micrographs that the addition of the compatibilizer decreased the heterogeneity of the mixture composite by improving the interface interaction between PP and PVDF. The good miscibility produced an important effect on the morphology and dielectric properties of the PVDF/PP blend composites. The compatibilizer existed mainly at interfaces between PP and PVDF, and perhaps some of it was dispersed in the PP phase too.

Thermal characteristics of the PVDF/PP blend composites

The DSC results for pure PVDF and PP and the PVDF/PP composites are presented in Figure 3. The corresponding temperatures of the peaks in Figure 3(b,c) are between those in Figure 3(a,d). The transition peaks of PP and PVDF are too close to distinguish two peaks in Figure 3(b,c). However, we can see that the peaks of Figure 3(b,c) are shifted to higher temperatures. A small peak is present in Figure 3(b) around −50°C, whereas the peak becomes smooth in Figure 3(c). This can be attributed to the effect of the PP-g-MAH compatibilizer. MAH forms hydrogen bonds with PVDF, and this can confirm the interaction of MAH and PVDF. In addition, the PVDF/PP blend composites present a melting peak temperature very similar to that of the PP matrix because the melting temperatures of PVDF and PP
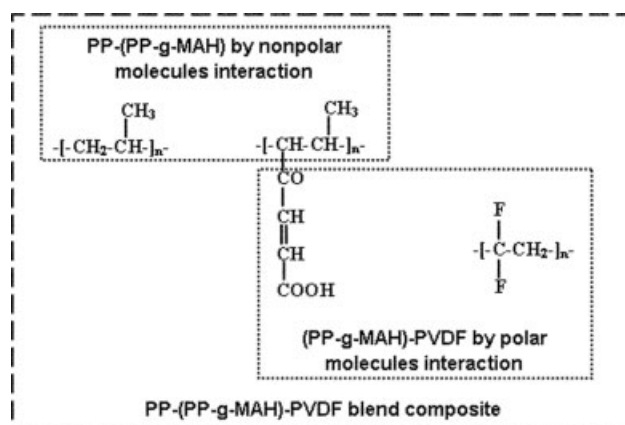

Figure 2 Schematic picture of the formation process of the PVDF/PP-MAH/PP blend composites.
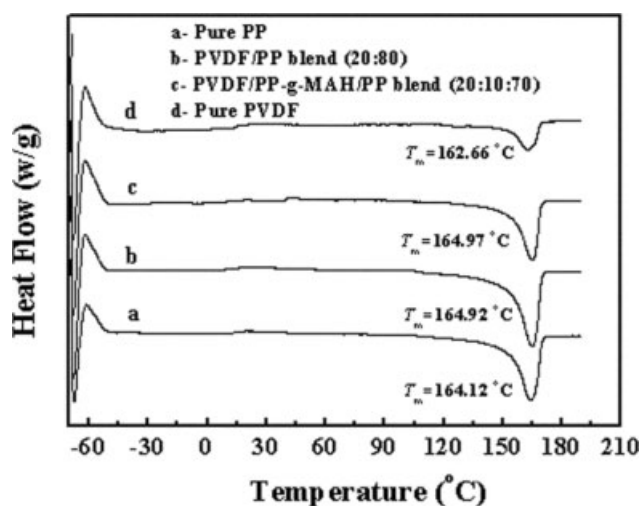
Figure 3 DSC thermograms of pure PVDF, PP and the blend composites with different volume contents of PVDF as indicated.

are very similar. This is very important for the blending and biaxial stretching processes used to fabricate PP thin films in the future.

Dielectric properties of the PVDF/PP blend composites

The temperature dependence of the dielectric permittivity of pure PVDF and the PVDF/PP (1 : 1) blend composite is shown in Figure 4. For comparison, Figure 4(a) shows that the dielectric permittivity of pure PVDF decreases with the frequency. Two relaxation peak regions can be observed, and they are denoted as α- and β-relaxation processes, respectively. They are also shifted to higher temperatures with increasing frequencies. We can see the same results in the study of Gregoria et al.[19] The low-temperature permittivity peak corresponding to the β relaxation is probably associated with the glass transition.[20,21] It has been suggested that this process is due to rotational motions of dipolar groups in the amorphous regions of the PVDF polymer. However, these rotational motions of dipolar groups are frozen at low temperature, so they cannot catch up with the frequency change of the electric field. This is in accordance with the low dielectric permittivity below the β-relaxation process. The high-temperature peak corresponding to the α relaxation has been associated with the annealing process in the crystalline regions,[22,23] which is due to molecular motions that alter the dipole direction only along the applied electrical field because the dipolar units are unfrozen at a high temperature and can move smoothly. Therefore, we can always observe the dielectric permittivity increasing with the temperature. Additionally, as shown in Figure 4(b), the dielectric behavior of the

PVDF/PP composite with 50 vol % PVDF presents two peaks. With the temperature increasing, the permittivity becomes high. In comparison with the permittivity of pure PVDF, the permittivity of the PVDF/PP (1 : 1) blend composite is always lower at the same temperature or frequency. At about 25°C and 10^3 Hz, the dielectric permittivity of pure PVDF is about 11, whereas that of the PVDF/PP composite is about 5.04.

Figure 5(a,b) shows the dependence of the dielectric permittivity and loss tangent of pure PP and the PVDF/PP composites on the frequency at different concentrations of PVDF. The dielectric permittivity and loss tangent of pure PP exhibit almost constant values over a wide frequency range (10^3 Hz → 10^6 Hz). However, the dielectric permittivity of all the studied composites decreases with increasing frequency. This can be attributed to the motion and rotation of dipoles in the PVDF phase, which is mismatched with the change in the frequency of the electrical field. In addition, as shown in Figure 5(a), the dielectric losses of all PVDF/PP composites
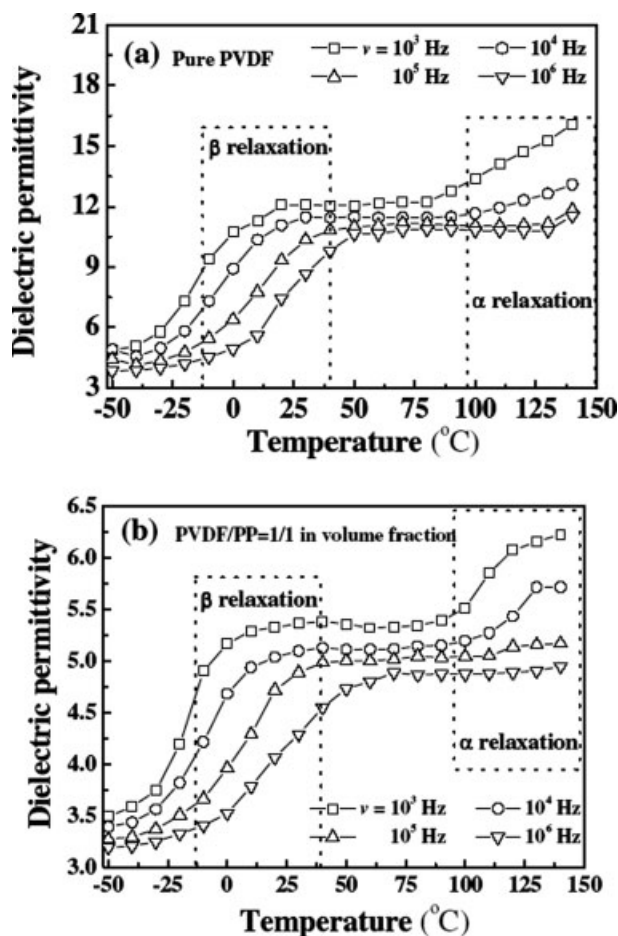

Figure 4 Temperature dependence of the dielectric permittivity of (a) pure PVDF and (b) the PVDF/PP blend composite in a 1/1 volume fraction at selected frequencies as indicated.
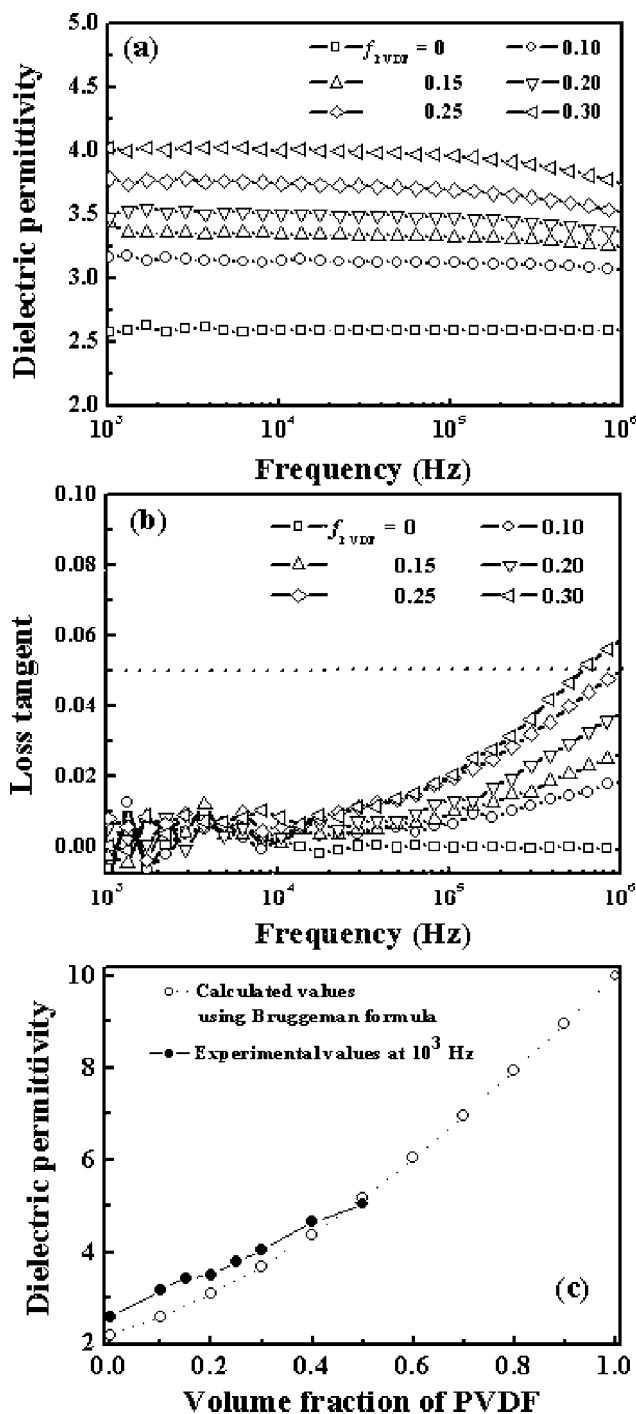
Figure 5 (a) Dependence of the dielectric permittivity and (b) dependence of the loss of the PVDF/PP blend composites on the frequency at different volume fractions of PVDF at room temperature and (c) comparison of the evaluated (with the Bruggeman formula) and measured dependences of the dielectric permittivity on the volume fraction of PVDF.

increase with the frequency. A peak of the dielectric loss appears at about 10^6 Hz for the composites with a PVDF loading. This is an obvious relaxation loss process related to the PVDF polymer. Furthermore, we observe that the loss tangent of the composites is

still at a low level (< 0.05) below 10^6 Hz, which satisfies the need for a low loss value in a practical engineering application. We can also see that the dielectric permittivity of the PVDF/PP composites increases with an increase in the PVDF concentration. This indicates that the dielectric permittivity of PP can be improved by the direct dispersion of PVDF into the PP polymer. For comparison with the experimental data, a well-known Bruggeman self-consistent effective medium approximation,[8,11,24] which is suitable for dealing with the dielectric properties of heterogeneous composite systems, has been used to estimate the dependence of the dielectric permittivity of the PVDF/PP composites on the volume fraction of PVDF:

$$f_{PVDF}\left(\frac{\varepsilon_{PVDF} - \varepsilon_C}{\varepsilon_{PVDF} + 2\varepsilon_C}\right) + f_{PP}\left(\frac{\varepsilon_{PP} - \varepsilon_C}{\varepsilon_{PP} + 2\varepsilon_C}\right) = 0$$

where ε_{PVDF}, ε_{PP}, and ε_C are the dielectric permittivities of pure PVDF, pure PP, and the measured PVDF/PP composites, respectively, and f_{PVDF} and f_{PP} are the volume fractions of PVDF and PP in the composites, respectively. Here $\varepsilon_{PVDF} = 10$ and $\varepsilon_{PP} = 2.2$ have been used to calculate the dependence of the dielectric permittivity of the composites on the concentration of PVDF. Figure 5(c) shows the calculated results and the measured ones at 10^3 Hz. It is very clear that the dielectric permittivities of the PVDF/PP composites in our experimental study are in good agreement with the values evaluated by means of the Bruggeman formula. Moreover, the very similar dielectric permittivities measured are slightly higher than the evaluated values when the volume fraction of PVDF is less than 0.5, and this can be attributed to the effect of impurity (e.g., catalyst) polarization in PP.

Figure 6 shows the dependence of the dielectric permittivity of the PVDF/PP composites on the temperature and volume content of PVDF at 10^4 Hz. We can see from Figure 6(a) clearly that the composites with low PVDF contents have two minor relaxation peaks from -40 to $30°C$ and from 100 to $140°C$, which correspond to the β and α relaxations of PVDF, respectively. With increasing PVDF content, the permittivity peak becomes obvious. It agrees with the results of Figure 4. This result can be attributed to the contribution of the polar effect of PVDF in the composites. Figure 6(b) further confirms the contribution of PVDF. With an increasing volume fraction of PVDF in the composites, the dielectric permittivity increases on the whole. We find that, at a low temperature ($-50°C$) close to the glass transition, the increase in the permittivity is slow. In this case, when the volume fraction of PVDF is 0.5, the permittivity is only about 3.1 (pure PP: 2.2). However, when the temperature is over $20°C$, the dielec-

tric permittivity increases rapidly with an increase in the volume fraction of PVDF. For a composite of the same composition, the permittivity almost keeps a constant value, and this can also be confirmed in Figure 6(a). The result suggests that all dipoles of PVDF in the composites can be polarized when the temperature is above 20°C. This is very important for the use of this kind of composite as a dielectric material in capacitors.

Dielectric properties of the PVDF/PP-*g*-MAH/PP blend composites

To study the effect of the compatibilizer (PP-*g*-MAH) on the dielectric properties, Figure 7 shows a comparison of the dielectric permittivity and loss tangent for the PVDF/PP (20 : 80) and PVDF/PP-*g*-MAH/PP (20 : 10 : 70) blend composites. The compatibilizer can improve the dielectric permittivity of the composites while still keeping a low dielectric loss below 10^6 Hz. Within all frequency ranges, the dielectric permittivity of the composites with PP-*g*-MAH is

Figure 7 Frequency dependence of the dielectric permittivity and loss tangent of the PVDF/PP (20 : 80) and PVDF/PP-MAH/PP (20 : 10 : 70) blend composites.

always larger than that of the composites without the compatibilizer. The result shows that the use of a compatibilizer can improve the dielectric permittivity of PP through an upgraded microstructure; that is, the use of PP-*g*-MAH leads to good interfacial interactions between PVDF and PP resins, as shown in Figure 1(b). This can be attributed to the polar carbonyl groups in PP-*g*-MAH because they can interact with the strong polar fluoride group in PVDF and therefore decrease the heterogeneity of composite systems. In this case, the polarization of all dipoles is effective in improving the dielectric permittivity of the PVDF/PP blend composites.

CONCLUSIONS

PVDF/PP blend composites can be prepared via a mechanical mixing method close to the melting temperature. They have high permittivity values over wide frequency regions. The permittivity increases with the temperature and amount of PVDF in the blend composites. The dielectric permittivity is about 5.4 for a composite with 50 vol % PVDF at room temperature. With respect to the cost, a composite with 30 vol % PVDF is valuable for potential practical applications. The use of PP-*g*-MAH as a compatibilizer can efficiently improve the interaction of PP and PVDF and leads to an increase in the permittivity of blend composites.
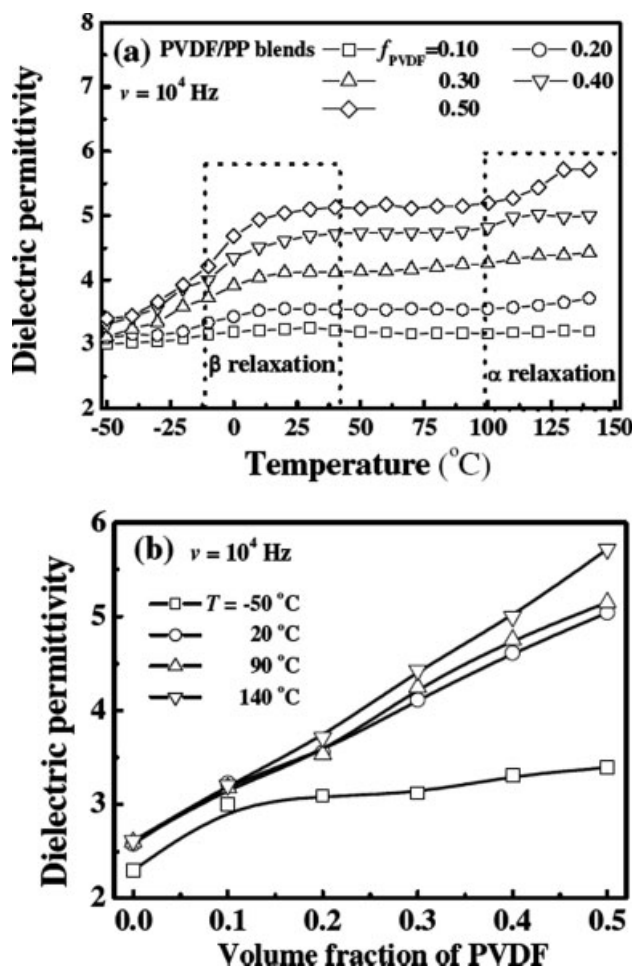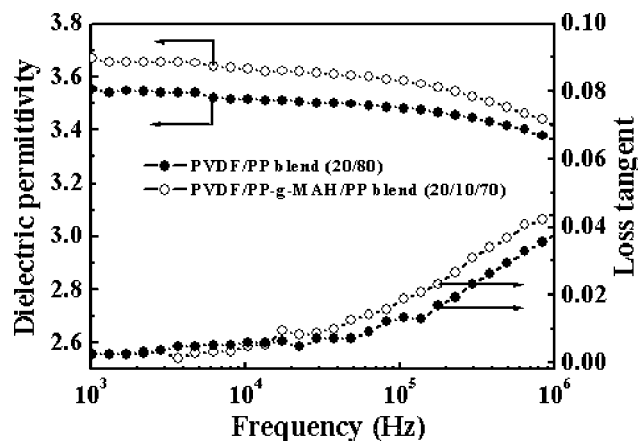

Figure 6 (a) Temperature and (b) PVDF concentration dependence of the dielectric permittivity of the PVDF/PP blend composites at selected frequencies and 10^4 Hz.

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