

Suppression of AC conductivity by crystalline transformation in poly(vinylidene fluoride)/carbon nanofiber composites

Li-Li Sun^{a,b}, Bin Li^b, Yan Zhao^a, Wei-Hong Zhong^{b,*}

^aSchool of Materials Science and Engineering, Beihang University, Beijing 100191, China

^bSchool of Mechanical and Materials Engineering, Washington State University, Pullman WA 99164, USA

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) is an important ferroelectric semi-crystalline polymer with multiple-phase behavior. In this study, remarkable effects of the various crystalline structures of PVDF nanocomposites on alternating current (AC) conductivity were discovered using carbon nanofibers (CNF). It was found that the transformation from α -phase to β -phase in PVDF, induced by the addition of CNFs, had a surprisingly suppressive effect on the AC conductivity of the nanocomposites. These unexpected results indicate that the decline in conductivity occurs after re-crystallization treatment (annealing) of the nanocomposites, and the reduction levels increase with increasing amounts of CNFs. Interestingly, the AC conductivity of annealed 5 wt% CNF/PVDF composites becomes even lower than that of re-crystallized nanocomposites with 3 wt% CNFs. These findings are believed to be very significant for fabrication and long-term service of PVDF composites in industry, which often involves exposure to repeated thermal cycling.

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1. Introduction

As is well known, thermal variation and/or long-term service have significant effects on the properties of polymers, e.g., for all polymers there will be aging considerations during long-term usage; for some crystalline polymers, property changes can be apparent even within short-term usage since the crystalline phases are sensitive to thermal history. For polymer nanocomposites, more complicated effects can be exerted on both structures and properties during the service period under certain application environments, in particular for crystalline polymer nanocomposites. Due to the addition of nanofillers, thermal effects on polymer crystalline structures in nanocomposites will not be the same as that in the pure polymers, and the performance benefits from the nanofillers to the polymers may also be changed. Therefore, it is critical to carry out studies on the relationship thermal effect-crystalline structure-property stability for nanocomposites for their successful applications in long-term service.

Poly(vinylidene fluoride) (PVDF) is an important ferroelectric semi-crystalline polymer. It has high permittivity, extraordinary pyro- and piezoelectric properties and other excellent physical properties [1–5], which can be significantly affected by its

crystalline structures. PVDF is characterized in a multiple-phase behavior that exhibits at least five crystalline phases (α , β , γ , δ and ϵ). These possible crystal phases can exist singly or as mixed phases in PVDF [6]. The combinations of the crystalline structures can be very complicated [7], but the most important crystalline phases in PVDF are α - and β -phase. α -phase is the most common one with the alternating trans and gauche stereochemical conformation [8,9], while the β -polarized PVDF phase is characterized by all-trans planar zigzag conformation with all the fluorine atoms located on the same side of the polymer chains [10]. PVDF formed in β -phase has higher polarity compared with other types of phases due to the net dipole moment [10], which is related to the attractive piezo- and pyroelectric properties and ferroelectric activity as well as ionic conduction behaviors of PVDF [7,8,11,12]. All these results indicated that the crystalline structures have remarkable influence on the physical properties of PVDF.

Due to the excellent and versatile properties, PVDFs are widely used as protective coatings, detectors, ferroelectric memories, biomedicine, etc [13]. However, for the applications as functional materials, especially as dielectrics, electrolytes and capacitors, adding nanofillers into the polymer has been shown to be a good approach to making improvements. In order to further improve the electrical properties of PVDF, various conductive particles are introduced into PVDF, such as carbon black (CB) [14,15], metal particles [16,17], carbon nanotubes (CNT)[18–22] and carbon nanofibers (CNF) [12]. The introduction of these additives intensively increased

* Corresponding author. Tel.: +1 509 335 7658; fax: +1 509 335 4662.

E-mail address: katie_zhong@wsu.edu (W.-H. Zhong).

the conductivity of the polymer by several orders of magnitude when the filler concentration reaches the percolation threshold. For example, the direct current (DC) conductivity of CNF/PVDF composites increased 4 orders of magnitude with 0.1 wt% CNFs [12]. In another example the addition of 2 vol% CNTs caused a nearly 6 orders of magnitude increase in alternating current (AC) conductivity in PVDF nanocomposites [21]. AC conductivity is a property of spiraling significance, critical to a growing number of applications that require the flexibility of AC power and the further progress in energy efficient power generation, in which PVDF may have important applications. Therefore, AC conductivity is the focus of our study.

Besides the effects on the physical properties of nanocomposites, the additives also significantly affect the crystallization of the polymer matrix, including the crystallinity, the crystalline melting temperature (T_m), the crystal size, the transformation of crystal phases, etc. For instance, loading graphite into PVDF matrix increased the crystallinity and T_m of PVDF [10]. Addition of carbon black and other nanoparticles has shown effects on the crystallinity and the crystal perfection of PVDF [16,23,24]. Besides the influence on the above aspects of crystallization, the formation of phases in PVDF is also affected by the addition of nanofillers, which is closely related to the electrical properties. It has also been reported that β -phase PVDF was induced by the introduction of nanoclay and CNTs [9,25–32].

On the other hand, even though the effects of nanofillers on either the electrical properties of PVDF nanocomposites or the crystallization of PVDF matrix were reported as summarized above, the relationships among the conductive nanofillers, electrical conductivity and crystalline structures for the nanocomposites have rarely been studied. Our previous studies already have indicated that the addition of nanofillers not only affected the physical properties of crystalline polymers directly, but also caused indirect effects through influencing the crystalline structures of the thermoplastic [33]. For PVDF nanocomposites, the variation of the electrical properties cannot solely be directly caused by the addition of conductive nanofillers, but also can be affected by the complex crystallization of PVDF matrix that can be indirectly induced by the additives. The investigation on the combination of the direct and indirect effects is therefore crucial for the continued expansion of applications of PVDF nanocomposites.

A reported study on PVDF nanocomposites [12] showed that DC conductivity of CNF/ β -PVDF composites was lower than that of CNF/ α -PVDF composites. However, in that study, β -crystal was formed by stretching, which implied that not only the crystal structure changed, but also the dispersion of CNFs and thus the conductive network likely was changed as a result of the stretching process. It is difficult to tell which factor(s), the crystalline structure and/or the stretching induced separation of CNFs, is/are responsible for this conductivity reduction.

CNFs are an important type of high performance and low-cost nano-scale additives. High volume nanocomposite production is demanding low-cost, high quality stable nanofillers. Commercialized CNFs, such as Pyrograf[®] have very high purity levels, above 98%. The benefits that these nanofillers can offer include (1) no need for purification due to the high purity levels, and (2) easy chemical treatments due to the abundant active edges (along the fiber directions). CNFs may have great potential for development of useful nanocomposites for industrial applications; hence there is great value to studying this aspect. However, the effects of CNFs on the crystallization of PVDF have thus far been rarely reported, and it clearly justifies our interest in this field.

In this paper, CNFs are chosen as the nanofillers for preparing the PVDF nanocomposite thin films with 1, 3, and 5 wt% CNF loading levels via a solution casting method. Differing from the traditional stretching method to change the crystallization of the

PVDF matrix, we alter the crystalline structures of PVDF in the nanocomposites by isothermally crystallizing samples at high temperature (165 °C) while keeping the same dispersion of CNFs in the nanocomposites as in that without isothermal crystallization. The crystallization behaviors of PVDF influenced by the addition of CNFs and then by the crystallizing processing are analyzed first. It is found that the transformation from α -phase to β -phase in PVDF induced by the addition of CNFs has a surprising suppressing effect on the AC conductivity of nanocomposites. The results indicate that a decline in AC conductivity occurs in the nanocomposites after re-treatment (isothermal crystallization). A more interesting result is that the AC conductivity of 5 wt% CNF/PVDF composites surprisingly becomes even lower than that of nanocomposites with 3 wt% CNFs after isothermal crystallization.

2. Experiment

2.1. Materials

The PVDF with average molecular weight (M_w) of 534,000 was supplied by Aldrich, USA, under the trade name 182702, and has a density of 1.74 kg m⁻³. CNFs used for nanocomposites preparation were graphene cup-stacked CNFs as indicated in Fig. 1, supplied by Pyrograf[®] Products, Inc., OH, USA, under the trade name Pyrograf III[®] Carbon fiber, which are characterized with a hollow core and a great portion of open edges at the ends of each graphene sheets. Many layers of truncated conical graphene sheets are stacked under van der Waals force, which shows an angle (10–30°) to the fiber axis. The average fiber diameters and lengths vary from 60 nm to 150 nm and 30–150 μ m, respectively, and the CNFs content is >98%. CNFs were used as received in this paper. The *N,N*-dimethylformamide (DMF) used as solvent was supplied by J. T. Baker, Inc., USA, under the trade name 9222-01 PHOTREX[®] Reagent and has a density of 0.944 g ml⁻¹ at 25 °C. The acetone as another component of solvent was purchased from Emd chemicals, USA, under the trade name AX0120-8.

2.2. Preparation of the CNF/PVDF composite samples

The nanocomposites studied here were prepared as films via a solution casting method. An appropriate amount of PVDF

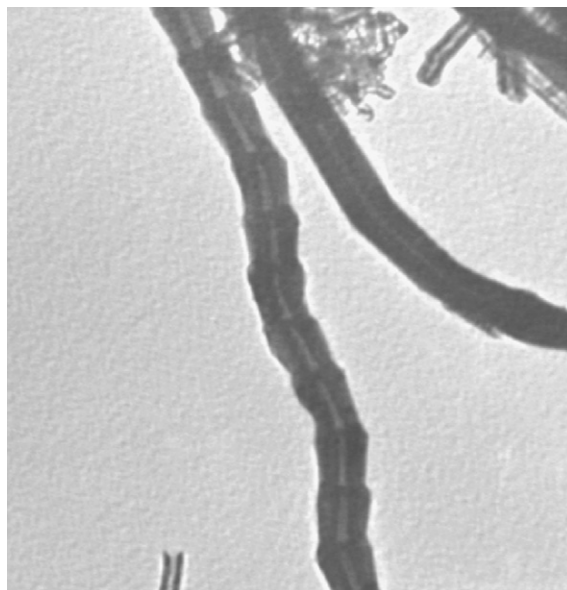


Fig. 1. TEM images showing the cup-stacked structures of CNFs.

powders were dissolved in the solvent composed of DMF and acetone with a volume proportion of 60/40. Simultaneously as-received CNFs with different amount were also dissolved in this solvent. The mixture was magnetically agitated in a 70 °C water bath for 1 h. Then it was put into a bath-type sonicator for 1 h to improve the dispersion of CNFs and eliminate the air bubbles. The mixture was cast on a smooth glass dish and kept in oven at 70 °C for 15 min to ensure the removal of solvent traces. The same procedure was executed to prepare pure PVDF film as a reference. The thicknesses of the films were in the range of 0.05–0.10 mm measured with a digital vernier caliper, dependent on the concentration levels of CNFs, which in this study were 0 wt%, 1 wt%, 3 wt% and 5 wt% respectively. In order to study the influence of CNFs on the crystallization of PVDF, as well as the influence of which on the electrical properties of nanocomposites, isothermal crystallization was performed on the samples prepared above. All the samples were reheated at 200 °C for 2 h and kept at 165 °C for 5 h. The information of the molecular or meso-scale structures of samples is provided in Figs. 2–4.

2.3. Characterizations and observation of the materials

Differential Scanning Calorimetry (DSC) analysis was performed using a TA Instruments DSC 2920 Modulated DSC in a nitrogen atmosphere. The specimens were maintained at 25 °C for 2 min and heated at a rate of 10 °C min⁻¹ from 25 °C to 250 °C. The specimens

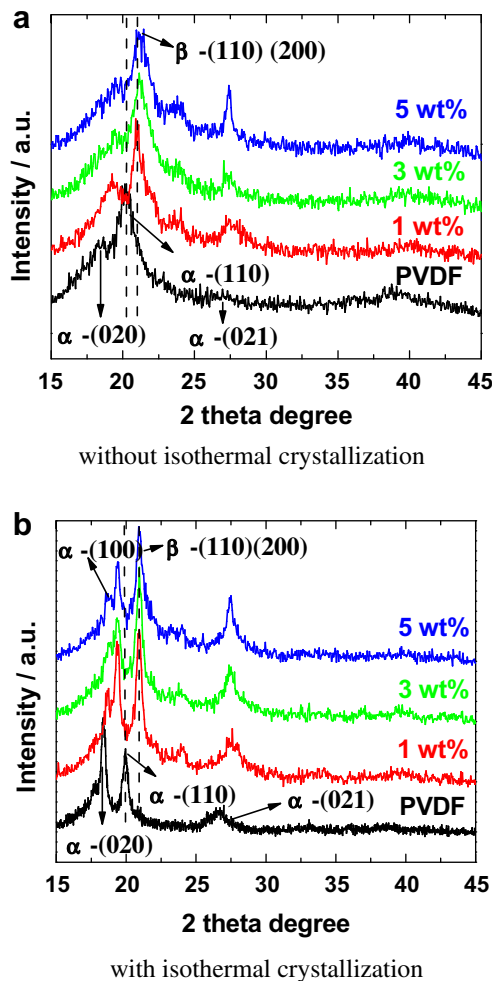


Fig. 2. XRD patterns of pure PVDF and CNF/PVDF.

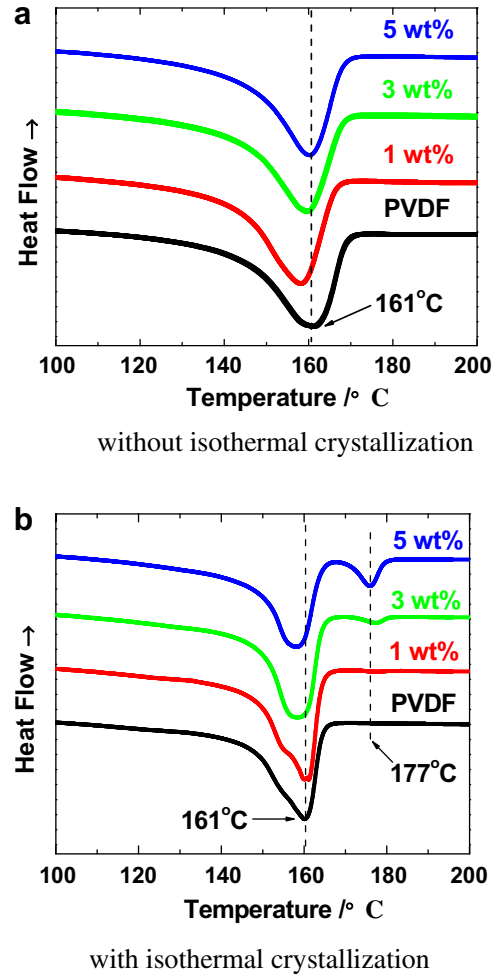


Fig. 3. DSC curves of CNF/PVDF composites with different CNF contents.

were weighed accurately at 9 mg. X-Ray Diffraction (XRD) experiments were performed at room temperature with Cu target $K\alpha$ radiation using a Siemens D-500 X-Ray Diffractometer system. The wave length of the X-ray was 0.154059 nm. All XRD data were collected from $2\theta = 10$ – 45° with a step interval of 0.05° and the test was repeated three times. The samples were the films with the thickness of 0.05–0.10 mm and the data was collected by scanning the top surface of the corresponding films. The AC conductivity of samples was measured at room temperature using a Novocontrol Technologies Alpha-N high-resolution Dielectric Analyzer made in Germany, which was performed at least 5 times for each type of materials. An Olympus BX51 Polarized Optical light Microscopy (POM) was adopted to observe the crystalline structures of the polymer.

3. Results and discussion

3.1. Crystal structures of PVDF and PVDF/CNF composites

3.1.1. XRD analysis

3.1.1.1. Without isothermal crystallization. According to reported studies [13,34–36], the crystalline phase structures of PVDF films prepared by solution cast method strongly depended on the solvent evaporation temperature. Close to the evaporation temperature of ca. 70 °C – the temperature applied in our study,

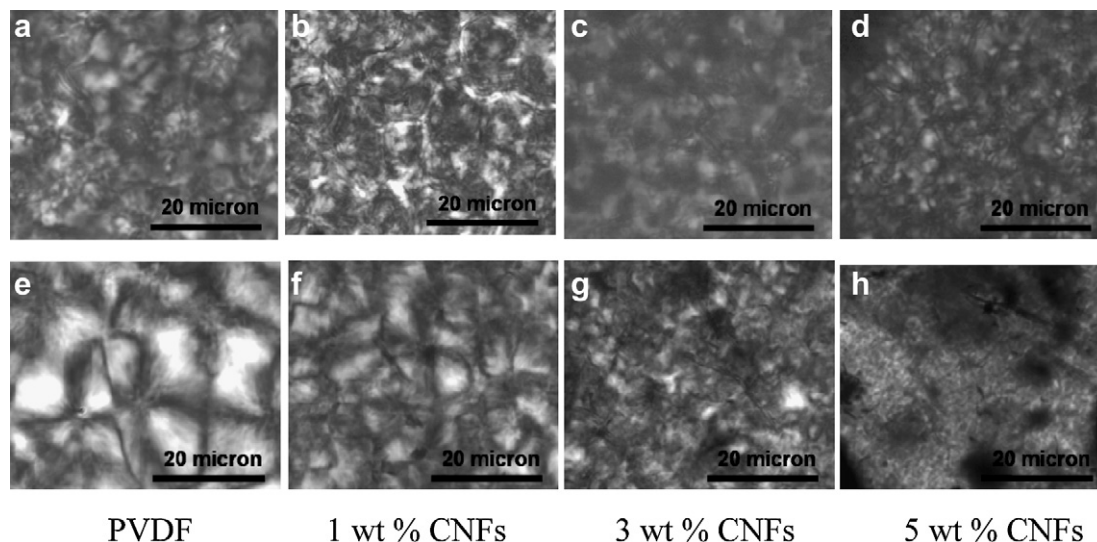


Fig. 4. Polar microscopy images of pure PVDF and CNF/PVDF composites with different CNF contents before and after isothermal crystallization (scale bar: 20 μm ; (a)–(d) represent the samples before isothermal crystallization; (e)–(h) represent the samples after isothermal crystallization).

both α -crystal and β -crystal can form in PVDF films. However, the XRD spectrum of pure PVDF only shows (Fig. 2(a)) peaks around, $2\theta = 18.7^\circ$, 20.0° , 26.4° , which can be assigned to the (020), (110) and (021) reflections of α -crystal [9,30,31,37]. The blurring peaks are probably owing to the very short drying time (15 min, i.e., crystallization time), which led to the imperfect crystal structures. This is also why another characteristic peak of α -crystal, (100) at $2\theta = 17.9^\circ$ cannot be distinguished clearly in Fig. 2(a). The absence of characteristic peak of β -crystal around 20.6° [9,29,37] indicates that there is no β -crystal forming during drying of PVDF solution. The addition of CNFs in PVDF seems to affect the crystal structures of PVDF in the following two ways: (1) induce the formation of β -crystal; (2) improve the α -crystal phase in some specific crystallographic planes.

Specifically, the emergence of a peak at $2\theta = 20.9^\circ$ indicates the formation of β -crystal, corresponding to the (110) and (200) reflections of β -crystal. Combined with the XRD spectrum of pure PVDF, it is believed that β -crystal was induced by the addition of CNFs. It was reported that CNTs could induce the formation of β -crystal PVDF without stretching the samples [9,31,32]. In our study, the CNF we used is a type of cup-shaped CNF consisting of cup shaped graphene layers with circular cross section and hollow core (Fig. 1). The results suggest that the CNFs have the similar effect as CNT on β -crystal of PVDF. However, the formation mechanisms of β -crystal in non-stretching PVDF samples are still unclear. Some alternative mechanisms have been proposed by different groups. For example, it was reported probably the zigzag carbon atoms on CNT induced the β -crystal of PVDF [32], whereas another research revealed that the β -crystal was related to ultrasonication cavitations and independent of zigzag carbon atoms [9].

On the other hand, the CNFs also enhance the arrangement of PVDF chains in α -crystal cells, which is demonstrated by two strengthened peaks of $2\theta = 18.7^\circ$, 27.3° in CNF/PVDF composite films (Fig. 2(a)). Undoubtedly, the more distinct peak at 27.3° indicates that the CNFs promote the crystallization in the crystallographic planes (021) in α -crystal. Here, $2\theta = 27.3^\circ$ in PVDF/CNF composites is also assigned to the (021) reflection of α -crystal, equivalent to $2\theta = 26.4^\circ$ in pure PVDF.

3.1.1.2. Effect of Isothermal crystallization. Before crystallization at 165°C , the films were heated up to 200°C for 2 h in order to completely remove the thermal history of PVDF, and then cooled

down to 165°C and kept the crystallization at this temperature for 5 h. In general, the isothermal crystallization of semi-crystalline polymers can make their crystal structures more perfect, which can be reflected from the explicit characteristic peaks in Fig. 2(b) and the more distinguished crystal peak at 17.9° . The re-treated PVDF also shows the same characteristic peaks of α -crystal as the PVDF without isothermal crystallization in Fig. 2(a). Particularly, the peaks at $2\theta = 18.7^\circ$ and 26.4° become much stronger, owing to the perfection of the crystal structures. Also, no β -crystal was observed in this re-treated PVDF film, consistent with some reported work showing that β -crystal cannot form in PVDF melt because of the high energy barriers of all – trans conformation [7,38,39]. However, with the addition of CNFs, the same peak at $2\theta = 20.9^\circ$ representing the β -crystal of PVDF appear as indicated in the samples without isothermal crystallization. This phenomenon further indicates in our study, the formation of β -crystal of CNF/PVDF composites is mainly determined by CNFs, and almost independent of temperature and composite processing methods, in contrast to the crystal structures of pure PVDF showing intense dependence on the processing parameters [13]. In addition to the above, the CNFs also improve the formation of α -crystal during isothermal crystallization as indicated by the enhanced peak at 27.3° with increasing CNF loading.

Furthermore, under the crystallization temperature of 165°C , which is close to the melting temperature of α -PVDF, the γ -crystal can be formed in PVDF melt, due to the crystallization from melt and α - γ solid state phase transformation [36,40–42]. However, it is hard to tell the γ -crystal from XRD pattern, since the characteristic peaks of γ -crystal in PVDF are still unclear [13]. It was studied by DSC shown in next section.

The crystal structures can be further understood through crystallinity analysis, as shown in Table 1. The crystallinity, X_c , can be calculated according to the following equation (1):

$$X_c = \frac{\text{area of crystal diffraction peaks}}{\text{total diffraction area}} \times 100\% \quad (1)$$

Obviously, the crystallinity of the film samples decreases after isothermal crystallization, which further demonstrates the distinct peaks derived from the perfection of crystal structures by re-treatment. It is believed that the lowered crystallinity of PVDF after isothermal crystallization may be related to the deconstruction of flawed crystals that were formed in unannealed samples.

Table 1
Degrees of crystallinity for pure PVDF and CNF/PVDF composites.

The CNF content [wt.%]	X_c [%]		ΔX_c
	Un-treated	Re-treated	
0	54.02	43.49	10.53
1	54.90	54.47	0.43
3	55.51	51.41	4.1
5	57.47	50.13	7.34

Basically, the CNFs can act as the nuclei in PVDF matrix [30] and improve the crystallization and increase the crystallinity as in un-treated sample. However, although the addition of 1 wt% CNFs increases the crystallinity of the isothermal crystallized composites compared with isothermal crystallized PVDF, with the further addition of CNFs, the crystallinity of PVDF does not increase further, but actually decreases. This should be owing to the enhanced transformation of α -phase to β -phase induced by CNFs, indicating the more improved β -crystallization of CNF/PVDF composites during isothermal crystallization. It was also observed in other PVDF nanocomposites that the crystallinity decreased when the transformation from α - to β -phase occurred [12,28,43].

3.1.2. DSC analysis

Although we can easily determine the α - and β -crystals in XRD patterns, in the un-treated samples, it is difficult to find out two separate melting peaks in DSC thermogram as shown in Fig. 3(a),

owing to their almost coincident melting temperature T_m [13]. In our study, the T_m of both crystal structures in the un-treated composites corresponds to ca. 161 °C. However, for the isothermal crystallized composites (Fig. 3(b)), the melting peaks for α - and β -crystals are a little broadening and blunting, compared with Fig. 3 (a), similar results being observed as the portion of β -crystals in PVDF crystal phase increasing [13,28]. Thus, it indicates that the isothermal crystallization process in our study could help CNFs induce more β -crystals in PVDF melt.

On the other hand, it is interesting to find a melting peak at ca. 177 °C in 3 wt% CNF/PVDF and 5 wt% CNF/PVDF composites, which represents the fusion of γ -crystal formed directly from the melt at 161 °C [13], while the similar peak is not found in pure PVDF and 1 wt% CNF/PVDF composites. In combination with the fact of the stronger endothermic peak of 5 wt% CNF/PVDF composites at 177 °C, the contribution of CNFs to the formation of γ -crystal from PVDF melt is revealed. However, this γ -phase structure is not supposed to be a structure feature of the isothermal crystallized samples, and in our study it is just a resulting structure of CNFs induced re-crystallization of PVDF melt at a higher temperature. Also, if taking into consideration the absence of this endothermic peak in un-treated samples (Fig. 3(a)), the highly ordered structures in the isothermal crystallized samples may also facilitate the appearance of the peak at 177 °C. Furthermore, γ -phase obtained from α - γ solid state phase transformation is not found above 180 °C in DSC thermogram [13]. Hence, the isothermal crystallized samples, both PVDF and the CNF/PVDF composites, still contain only α - and β -crystals of PVDF, like the un-treated samples.

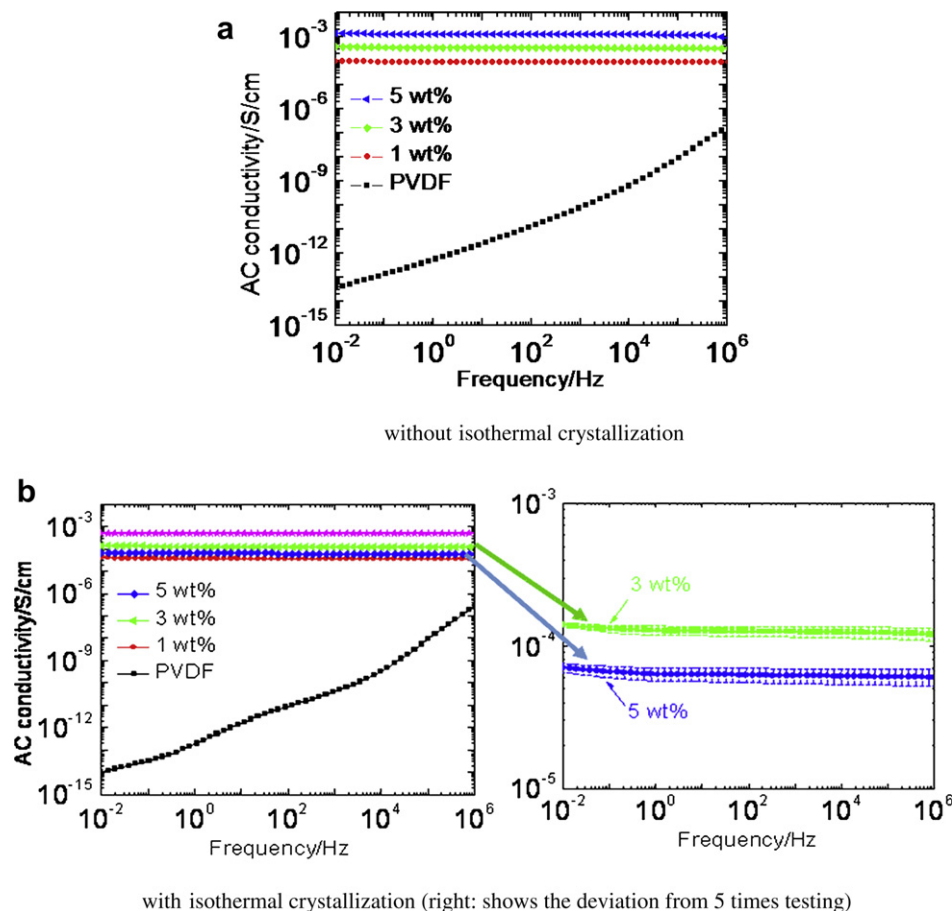


Fig. 5. Frequency dependence of AC conductivity.

However, both the perfection of crystal structure and the portion of β -crystal in PVDF are improved by isothermal crystallization.

3.1.3. Morphological analysis

Besides the crystal phase transformation and the crystallinity, the loading of CNFs and the isothermal crystallization process also affects the crystal grains of PVDF in the nanocomposites. The POM images of specimens before and after isothermal crystallization are shown in Fig. 4.

Basically, CNFs in PVDF matrix act as nuclei decreasing the size of crystal grains due to the heterogeneous nucleation effects [30]. However, a less obvious difference of the crystal sizes is observed in the samples before isothermal crystallization (Fig. 4(a)–(d)) than the isothermal crystallized samples (Fig. 4(e)–(h)). It is believed that for the samples without isothermal crystallization, the short crystallization time (15 min) is responsible for this phenomenon, which is not enough for the crystal grains to mature. After isothermal crystallization, the crystal grains in specimens grow to a larger size, especially for pure PVDF and nanocomposites with 1 wt% CNFs (Fig. 4(e) and (f)). However, for CNF/PVDF composites with 3 wt% and 5 wt% CNFs, less obvious differences in the crystal sizes can be seen (Fig. 4(g) and (h)). This is attributed to the abundant nuclei induced by high CNF content leading to insufficient space for crystal growth. These results are similar to the studies on the effects of nanoclay or CNTs on crystalline structures of PVDF [25,30,44]. On the other hand, isothermal crystallization also makes the crystal grains more perfect. Generally, PVDF reveals spherulitic crystal structures. Here, the spherulitic crystal grains are observed more clearly in specimens after isothermal crystallization. It indicates that the crystals perfection of PVDF is improved by isothermal crystallization process, which is consistent with the results obtained from XRD spectrum.

3.2. AC conductivity study

3.2.1. Concentration dependence of AC conductivity

The AC conductivity of pure PVDF and PVDF/CNF composites in the frequency range of 10^{-2} – 10^6 Hz are presented in Fig. 5. The pure PVDF films show a typical frequency dependent AC conductivity owing to its insulating nature. With only 1 wt% loading of CNFs, the AC conductivity has a significant change, showing frequency independent AC conductivity of $ca. 8.84 \times 10^{-5}$ S/cm. This dramatic increment in conductivity indicates the effective conductive network has already been formed at this loading level [16–18,20]. It is expected that the percolation threshold of this composite system should be below 1 wt%. With the further loading of CNFs, the AC conductivity is expected to increase, which is observed in the un-treated samples (Fig. 5(a)). However, differing from the AC conductivity of un-treated samples, the concentration dependence is changed: the AC conductivity in the isothermal crystallized samples (Fig. 5(b)) does not increase with the CNF loadings as seen in the samples without isothermal crystallization process. It is exhibited that the AC conductivity of re-treated 5 wt% CNF/PVDF becomes lower than that of 3 wt% CNF/PVDF composites after isothermal crystallization as indicated in Fig. 5(b), which was repeated for 5 times (the curves shown in the right figure show the deviation). It is probably owing to the changes of crystal structure caused by isothermal crystallization and will be discussed in the following sections.

3.2.2. Influences of crystal structures on AC conductivity

The influences of PVDF crystal structures on the AC conductivity of PVDF and CNF/PVDF composite films are summarized in Fig. 6. Basically, the isothermal crystallization leads to the reduction in AC conductivity, i.e., the AC conductivity of PVDF and CNF/PVDF nanocomposite films are all accordingly decreased compared with

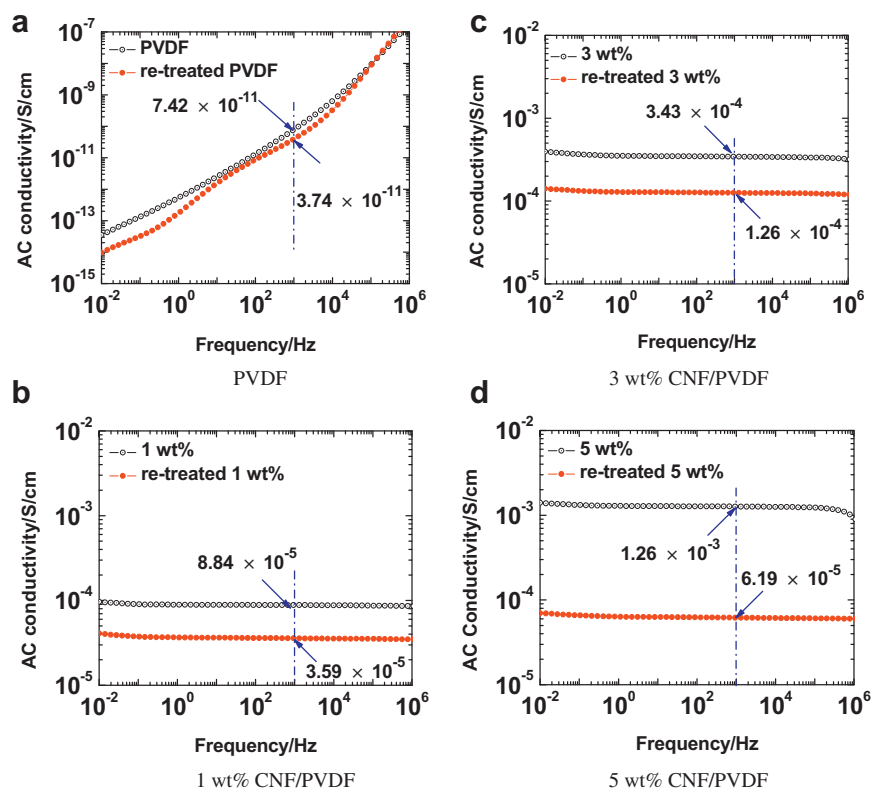


Fig. 6. Comparison of AC conductivity of CNF/PVDF composites with and without isothermal crystallization (re-treatment).

that of samples before re-treatment. The AC conductivity of 5 wt% CNF/PVDF (6.19×10^{-5} S/cm) is even lower than that of 3 wt% CNF/PVDF composites (1.26×10^{-4} S/cm) in the whole measured frequency range as indicated in Fig. 6(c) and (d). Recall that the main effect of isothermal crystallization on crystal structures in PVDF includes: (1) improve the perfection of the α -crystal; (2) facilitate the formation of CNF induced β -crystal; and (3) decrease the crystallinity of PVDF. Some of these three aspects are considered to be the main reasons for the reduced AC conductivity.

For pure PVDF, the slightly decreased AC conductivity (Fig. 6(a)) can be mainly attributed to the effects of the crystallization of the polymer from the decreased degree of crystallinity. This can be viewed in terms of the conductivity of a polymer as derived from the concept of polarons, the presence of which in PVDF was already demonstrated by other researchers [2]. When a polymer is exposed to an electric field, the polarons move up and down to overcome the energy barriers so that the polymer exhibits some electrically conductive characteristics. As a result, factors that facilitate the polarons in overcoming the energy barriers can improve the conductivity, and vice versa. The data in Table 1 show that the degree of crystallinity is reduced after isothermal crystallization by 19.5% (from 54.02% to 43.49%), which indicates that the amorphous phase increases for the specimens after isothermal crystallization. It presents more free space to the polarons, which enhances the energy barriers, thus contributing to the lowered AC conductivity of annealed PVDF.

For the CNF/PVDF composite films, the crystallinity also plays a significant role in AC conductivity. According to Table 1, the isothermal crystallization led to the decreased crystallinity which is assumed to be the main reason for this phenomenon. The variation of crystallinity (ΔX_c) (Table 1) is exactly consistent with the reduction of AC conductivity (Fig. 6). Specifically, the reduction level of AC conductivity increases with the higher concentration of CNFs, which can be seen more clearly in Fig. 7, the largest reduction level occurred in 5 wt% CNF/PVDF is as high as 95.1%, while the reduction in crystallinity by isothermal crystallization also becoming more significant with increasing CNFs loading.

As well known, in semi-crystalline polymers, conductive fillers only reside in the amorphous phase, thus the structure of an amorphous phase is crucial to the formation of conductive network within the polymer matrix. The decreased crystallinity corresponds to the increased portion of amorphous phase. In this case, the density of conductivity fillers in amorphous phase will become smaller, i.e., the conductive network is to some degree fragmented, and consequently results in the lowered conductivity. That is also

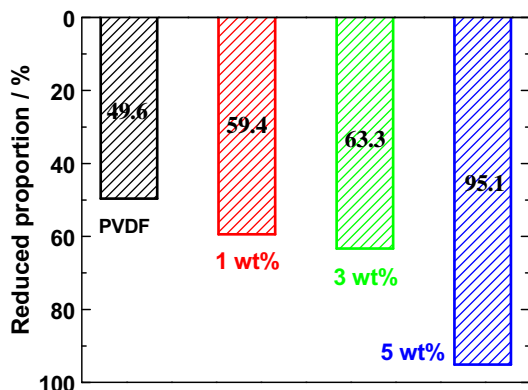


Fig. 7. Reduced levels of AC conductivity for CNF/PVDF composites as a result of isothermal crystallization.

a further explanation for the lower AC conductivity of isothermal crystallized 5 wt% CNF/PVDF composite films.

As discussed above, the decreased crystallinity of the composites is mainly caused by α - to β -crystal transformation induced by CNFs. Although the portion of β -crystal is increasing with more CNFs, the total crystal phases are getting smaller (i.e., the crystallinity is decreased). It is reasonable to conclude that the lower AC conductivity of the annealed CNF/PVDF composites as well as the largest AC conductivity reduction in 5 wt% CNF/PVDF composites is the result of the improved formation of β -crystal in PVDF induced by the increasing loading of CNFs.

4. Conclusions

The effect on the AC conductivity of the nanocomposites due to the crystallization of PVDF matrix in CNF/PVDF composites with different CNF loadings through isothermal crystallization (i.e., re-treatment), is investigated in this study. A surprising decline of AC conductivity happens after isothermal crystallization treatment, compared with the samples before isothermal crystallization, and the reduction levels increase remarkably as the CNF content increases. After isothermal crystallization, the AC conductivity of nanocomposite films with 5 wt% CNFs in the PVDF is even lower than that of 3 wt% CNF/PVDF composites owing to the different crystalline structures induced by CNFs. It is revealed that the phase transformation from α -phase to β -phase occurring in the PVDF, which is facilitated by the addition of more CNFs, is mainly responsible for the decrement of AC conductivity in the nanocomposites after isothermal crystallization.

The findings in this study are believed to be very significant for fabrication of PVDF composites in industry and for long-term service, which often involves repeated thermal cycling. Further in-depth studies in this field are expected to be very fruitful for the development of PVDF nanocomposites with well designed and appropriately controlled structures.

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