

Stretching-Induced Percolation in Polyvinylidene Fluoride and Nickel Composites

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Received 10 March 2010; accepted 23 September 2010

DOI 10.1002/app.33430

Published online 10 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: To investigate the stretching effect of polymer-based composites, the films of polyvinylidene fluoride (PVDF) and nickel (Ni) composites were stretched at 120°C. It was found there was an abrupt increase in dielectric constants and conductivities with stretching ratio (SR). In comparison to percolation effect caused by involvement of conductive particles, it was named as stretching-induced percolation here. When SR was near the threshold, dielectric

constants showed 17 times improvement and conductivities displayed four to five orders of magnitude enhancement at 100 Hz in low Ni fraction composites. And the reasons of stretching-induced percolation were analyzed here. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2368–2373, 2011

Key words: composites; polymer; dielectric properties; percolation

INTRODUCTION

Polymer-based nanocomposites with high dielectric constant and low dielectric loss have attracted significant attention because of their potential applications in capacitors, ultrasonic resonators, high-power transducer, actuators, and so on.^{1–4} Polyvinylidene fluoride (PVDF subsequently) and its copolymers are widely used as polymer matrix in the composites by virtue of excellent properties, such as piezoelectricity and ferroelectricity, high dielectric constant, wide frequency response, good mechanical characteristics, and flexibility.^{5,6} To improve the dielectric constants of these composites, currently two main methods have been employed. One is to fill high-dielectric-constant inorganic ceramic powders into the composites and the other is to fill conductive particles to induce percolation effect.^{7,8} In these composites, the electronic properties are therefore relevant to the dielectric constant of the polymer matrix, the size of the filler, the distribution of particles in host polymers, and

the interfacial interaction between the filler and polymer matrix.^{9–12} On the other hand, when the materials are stretched at 120°C, the polar β phase content of PVDF could be significantly increased, which conduces to high dielectric constant, large polarization, and good dielectric response.^{13–15} Meanwhile, the interfacial polarization was enhanced at the two-phase boundary during stretch.^{16,17} So, a greater increment in dielectric properties is anticipated when PVDF/Ni composites are stretched. Recently, Dang's group has reported the dielectric behaviors of stretched PVDF/CNT (carbon nanotube, here and subsequently) composites.^{18,19} The dielectric constant and conductivity in their composites always decreased when the main strain level of PVDF was in the plastic deformation region. But for those high aspect ratio samples, the dielectric constant exhibited a gain up to 62.5%, when the length of tensile strain was several millimeters. Unfortunately, the stretching ratio (SR, subsequently) in Dang's studies was too small to demonstrate the effect induced by stretch. As a matter of fact, the SR of PVDF can be as high as 400–500% before rupture. To fully understand the stretching effect, here were investigated the dielectric properties of stretched samples when the stretching process was carried out at higher temperature with greater tensile strains. We also reported an interesting percolation effect induced by stretch in the article.

EXPERIMENTAL

The PVDF and Ni particles (400 nm in diameter) were purchased from 3F New Materials (Shanghai, China) and Guangbo Nanomaterials (Ningbo,

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Contract grant sponsor: Natural Science Foundation of China; contract grant numbers: 11004113, 10774079.

Contract grant sponsor: Natural Science Foundation of Zhejiang Provincial; contract grant numbers: Y7080401, Y4090429.

Contract grant sponsor: Natural Science Foundation of Ningbo; contract grant numbers: 2008A610055, 2009A610056, 2009A610103, 2009A610036.

Contract grant sponsor: K.C. Wong Magna Fund, Ningbo University.

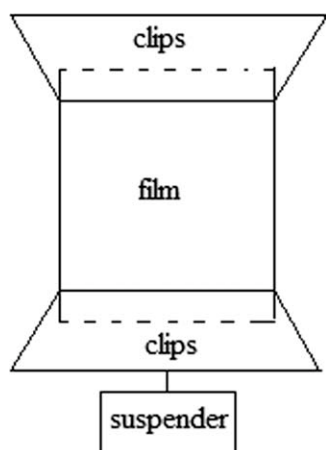


Figure 1 Schematic view of apparatus used in stretching process.

China), respectively, and used as received. The PVDF powders were dissolved in dimethylformamide and blended with Ni particles under ultrasonication for 20 min before the addition of Triton x-100, one type of emulsifiers. After another 10 min of ultrasonic dispersing, the suspension was poured onto a piece of clear glass and dried under vacuum at 135°C for 10 h, and then was allowed to cool to room temperature in 0.5 h. To explore the influence of Ni concentration, here were prepared two sets of samples whose Ni mass fractions were 10 and 20%, respectively, corresponding to the volume fractions of 5.2 and 11%, below the percolation threshold of 16%. The films were $5 \times 5 \text{ cm}^2$ in area and about 25 μm in thickness, and were divided into two identical parts before they were stretched uniaxially at 120°C till rupture on our unique stretching system, as shown in Figure 1. The length of tensile strain was controlled by the mass of the suspender and the details were illustrated in Table I. Here SR is defined as follows, $\text{SR} = (\text{length after stretch} - \text{original length}) / \text{original length}$. The electrodes were painted with silver paste to conduct electronic measurements. The dielectric properties and conductivity of the samples were measured at room temperature by use of Agilent precision impedance analyzer 4294A with fixture of 16451B. The polarization optical micrographs were observed by polarizing microscope Nikon's Eclipse e600w. X-ray diffraction was carried out using a Philips Dual X'Pert XRD system with Ni-filtered Cu K α radiation at a scanning speed

TABLE I
Dependence of Stretching Ratio on Hanged Mass Before Rupture

Mass (g)	215	230	240	250	290
SR _{PVDF/Ni(90/10)} (%)	50	100	150	200	220
Mass (g)	220	240	250	280	300
SR _{PVDF/Ni(80/20)} (%)	80	130	180	220	230

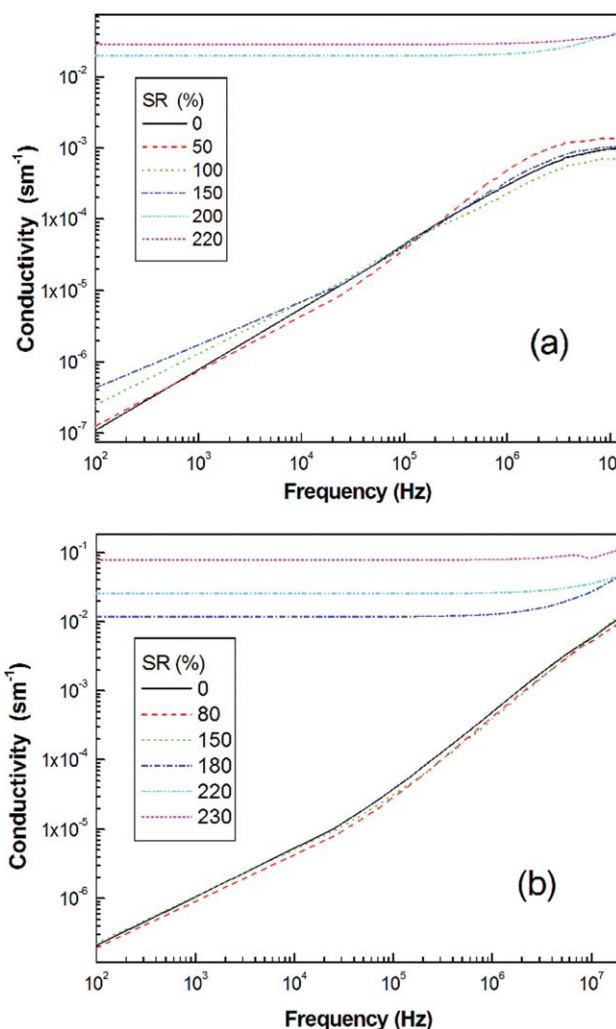


Figure 2 The conductivities of PVDF/Ni composite films on frequency after stretch. (a) 90/10; (b) 80/20. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

of $0.005^\circ \text{ 20 s}^{-1}$. The IR-ATR spectra were obtained using a Bruker Fourier transform infrared spectrophotometer (Tensor 27).

RESULTS AND DISCUSSION

The conductivities of PVDF/Ni composites under different SR are shown in Figure 2. When SR is below 150%, there is no obvious change in the conductivities of both PVDF/Ni (80/20) and (90/10) samples. When SR is above 200%, the conductivities display a remarkable increase of four to six orders of magnitude at low frequency. Similar to the percolation effect frequently observed in other polymer-based composites, the great enhancement of conductivity indicates the formation of a conductive network.^{2,20} Hence we name it as stretching-induced percolation effect for comparison.

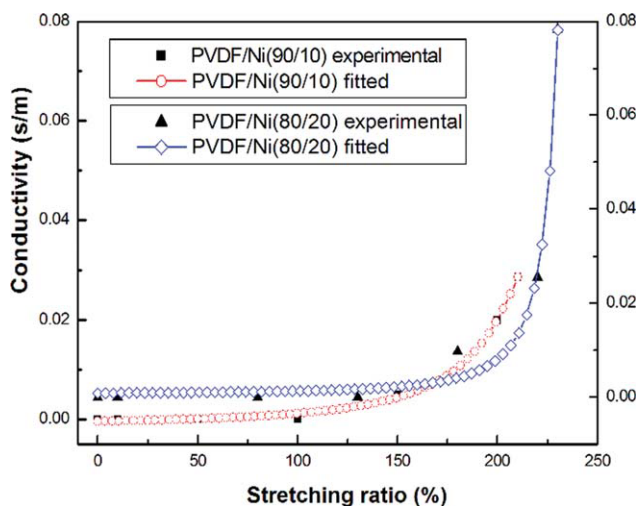


Figure 3 Dependence of conductivities of PVDF/Ni composite films with stretching ratios at 100 Hz. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

The conductivities of PVDF/Ni composite films with stretching ratios at 100 Hz are shown in Figure 3. The experimental results in Figure 3 are in good agreement with the classical percolation equation,¹

$$\sigma \propto (f_c - f)^{-s}$$

where f_c is stretching-induced percolation threshold, f is the SR and s is a critical exponent. The values of f_c and f_c here are $f_{c10} = 170$, $s_{10} = 0.58 \pm 0.11$ in 90/10 samples and $f_{c20} = 205$, $s_{20} = 0.41 \pm 0.08$ in 80/20 samples. The difference in their thresholds may be owing to the emulsifiers (Triton X-100), which can strengthen the interaction between Ni particles and polymer. Moreover, the interaction may increase along with the amount of Ni particles. So the samples with higher Ni fraction have larger rupture ratio and bigger stretching-induced percolation threshold, corresponding to $f_{c10} < f_{c20}$. The critical exponent s here is not coincident with the universal constant in other percolation systems, but in agreement with Chen's result.⁹ Here the conductivities of PVDF/Ni composites are related to the mass fraction of Ni particles and the stretching-induced percolation threshold (f_c). When $SR < f_c$, the stretching-induced percolation has not taken place, so the conductivities of PVDF/Ni composites are dependent on the amount of Ni particles, just like the typical percolation effect induced by conductive filler. Thus, when $SR < f_{c10}$, the conductivities of 90/10 composites are less than those of 80/20 ones. When $f_{c10} < SR < f_{c20}$, stretching-induced percolation does not occur in 80/20 composites, but commences in 90/10 ones, resulting in higher conductivities of 90/10 composites. When $SR > f_{c20}$, the crucial factor to influence conductivities is the stretching-induced

percolation effect rather than the amount of conductive particles. Furthermore, the samples with larger Ni fraction possess more opportunities to form a more efficient conductive network. So the 80/20 stretched samples own higher conductivities near the stretching-induced percolation threshold.

The influence of SR on the dielectric response of the PVDF/Ni composites was also investigated. As illustrated in Figure 4, there is a notable decrease with frequency in dielectric constant curves, corresponding to dielectric relaxation behavior, which indicates the existence of strong interfacial polarization and dipole polarization in PVDF/Ni composites.¹¹ After stretching, the dielectric constants have no obvious increase at low SR, but enhance greatly in the range from 100 Hz to 10 kHz when SR is more than 150%. The maximum of dielectric constant in the PVDF/Ni (80/20) composite is up to 230 when SR is 230%. This giant dielectric enhancement

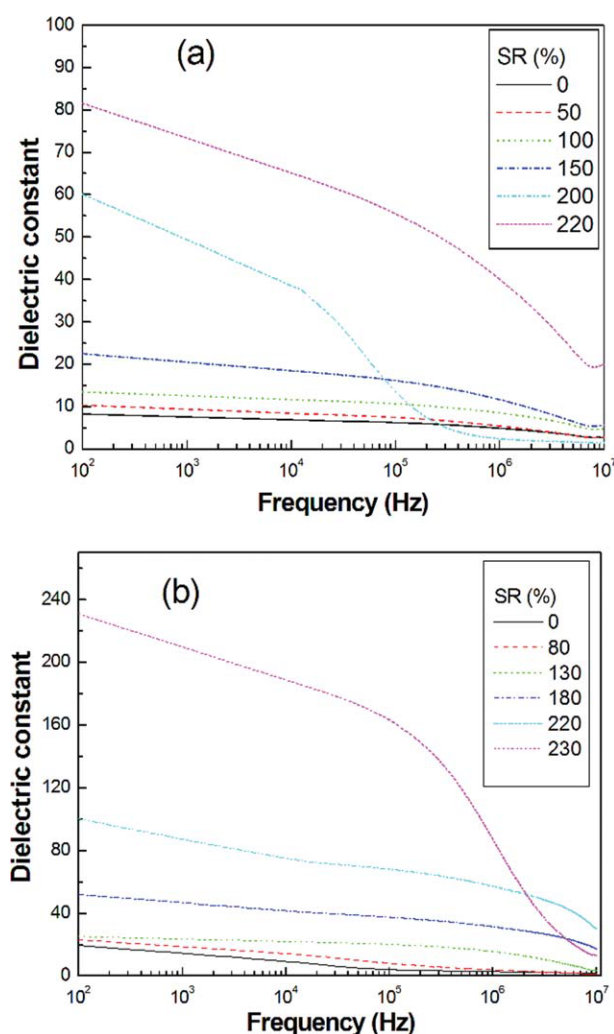


Figure 4 Dielectric constants of PVDF/Ni composite films with frequency after stretch. (a) 90/10; (b) 80/20. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

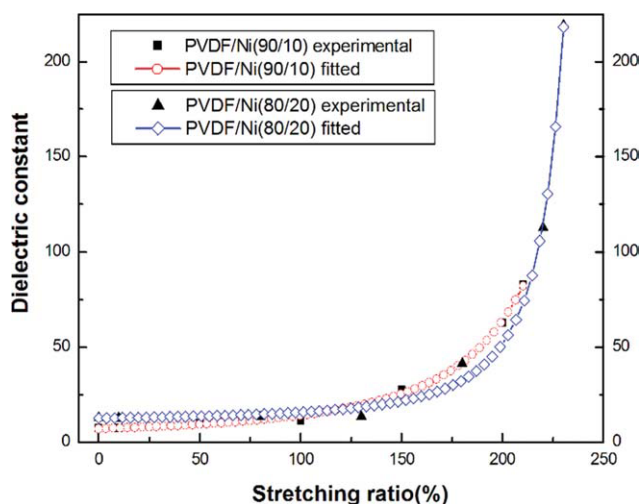


Figure 5 Dependence of dielectric constants of PVDF/Ni composite films with stretching ratios at 100 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of stretched PVDF/Ni composites may be attributable to space charge accumulation at the two-phase boundary during stretching process.

Figure 5 shows the curves of the dielectric constants of PVDF/Ni composite films versus SR at 100 Hz. The dielectric constants increased gradually after the composites were stretched. When the SR was more than 200%, the dielectric constants increased about 10 times in PVDF/Ni (80/20) samples or 17 times in PVDF/Ni (90/10) ones. Their fitted curves of dielectric constants dependent on SR also comply well with the percolation equation where $f_{c10} = 180$, $s_{10} = 0.49 \pm 0.08$, and $f_{c20} = 200$, $s_{20} = 0.53 \pm 0.04$. It is noteworthy that the percolation value of our unstretched PVDF/Ni composites is about 16% (volume fraction). Thus, to a certain extent the flexibility of polymer matrix could be maintained in our samples with a low Ni volume fraction.

Based on Dang's results, different geometric shapes of fillers exhibited different dielectric properties in stretched PVDF/CNT composites, and the CNTs in a higher aspect ratio could easily contact each other to form a percolative network.^{18,19} But our composites exhibit an amazing increase in dielectric constant when the fillers are Ni spheres. So it proves here that the way of stretching to rupture at higher temperature is a prominent approach to improve the dielectric properties of PVDF-based composites.

Dielectric loss is another important parameter of dielectricity, which is caused by conductive loss of motion of charge carrier and/or dipole loss of dipole orientation polarization.²¹ In the polar PVDF polymers, the dielectric loss is mainly from the latter. Therefore, the dielectric loss of PVDF/Ni composites was explored in this article as well. As shown in

Figure 6, there is a peak between 10^6 Hz and 10^8 Hz before the composites are stretched, which is from dipole orientation polarization.²¹ During stretching, the peaks grow with SR at the same frequency range as the polarity of polymer composites is strengthened. But when the SR exceeds the threshold, the peaks are amplified greatly and the positions of these peaks moved toward low frequency. Therefore, with the occurrence of conductive network caused by stretching-induced percolation, the conductive loss mainly contributed to the dielectric loss now with corresponding response frequency below 10^6 Hz.

To understand the stretching-induced percolation, the microstructure of our composites was studied by polarization optical microscope, X-ray diffraction, and IR-ATR spectroscopy. From Figure 7, it is observed that the Ni particles are well-distributed in matrix before stretch, but array in parallel as rod-

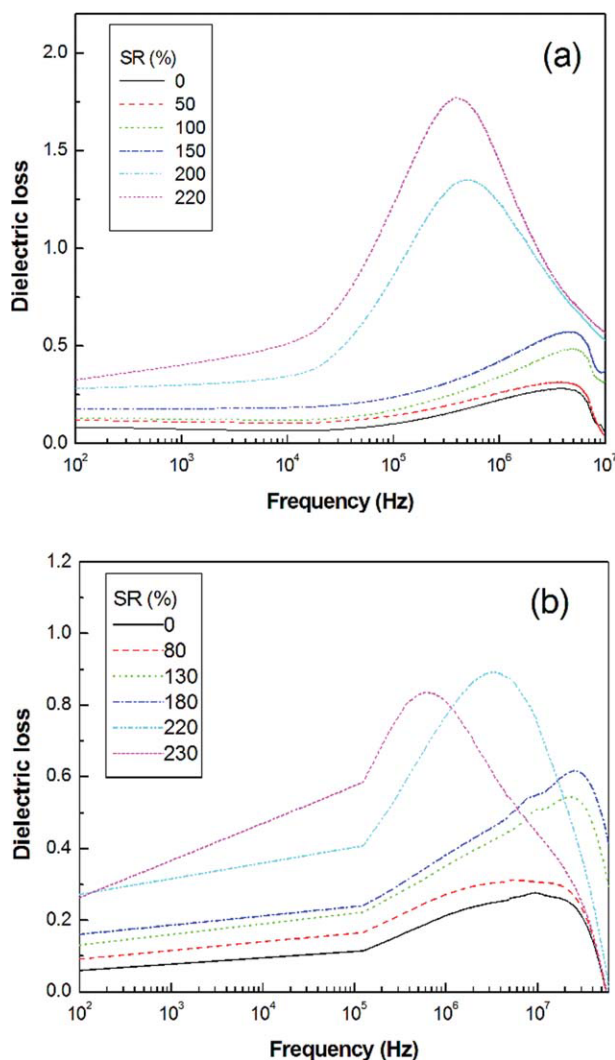


Figure 6 Dielectric loss of PVDF/Ni composite films with frequency after stretch. (a) 90/10; (b) 80/20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

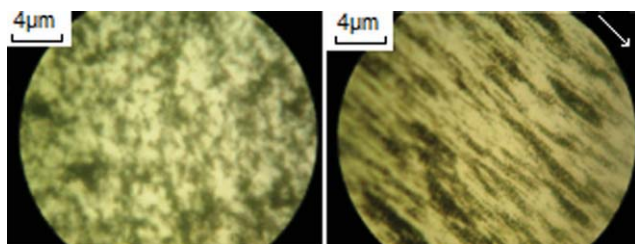


Figure 7 Polarization optical micrographs of PVDF/Ni (90/10) composite samples before and after stretch under 1000 times of magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

like clusters along with the stretch direction after drawing treatment. As illustrated in Figure 8, the reflection at $2\theta = 20.5^\circ$ gets more intense after stretch, which comes from Bragg diffraction of (110) and (200) of the polar β phase of PVDF,²² while other reflections at 44.5° and 51.9° decay greatly, corresponding to the diffraction of (111) and (200) of nickel particles, respectively.²³ It indicates that the content of polar phase increases in PVDF/Ni composites. In Figure 9, IR-ATR spectra shows obvious changes when SR is 220%, with the new peaks occurrence at 1250, 1026, and 801 cm^{-1} . The peak at 1250 cm^{-1} is the vibration of all-trans (TTTT) sequences, which is the characteristic of ferroelectric β polar phase and the peaks at 1026 and 801 cm^{-1} correspond to the sequence of TTG from the γ phase.²⁴ Thus it is suggested that the volume percent of all-trans sequences increases with stretching ratio and a phase transformation from nonpolar to polar can be induced by stretching, which is in agreement with the results of XRD.

Based on aforementioned discussions and Dang's results,¹⁹ a microscopic process can be concluded to

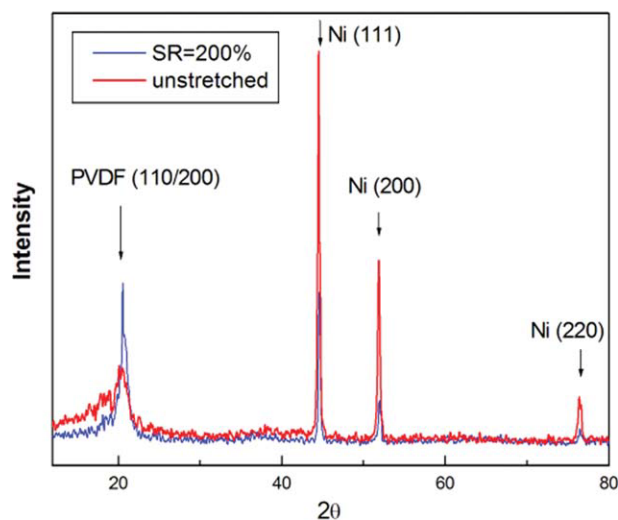


Figure 8 XRD of PVDF/Ni (90/10) composite samples before and after stretch. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

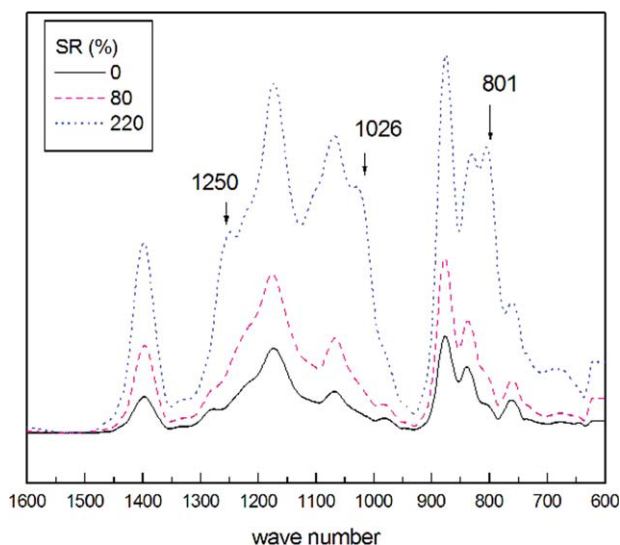


Figure 9 IR-ATR spectra of PVDF/Ni (90/10) composite samples before and after stretch. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interpret this stretching-induced percolation. As shown in Figure 10, the composite with well-distributed Ni particles exhibits low dielectric constant before stretching, because of the Ni volume fraction far below percolation value. When SR is small, the positions of those particles have not moved, resulting in no obvious change in the dielectric properties of composites. With SR increasing, some Ni particles get to touch with each other and become big clusters along the stretching direction during stretching

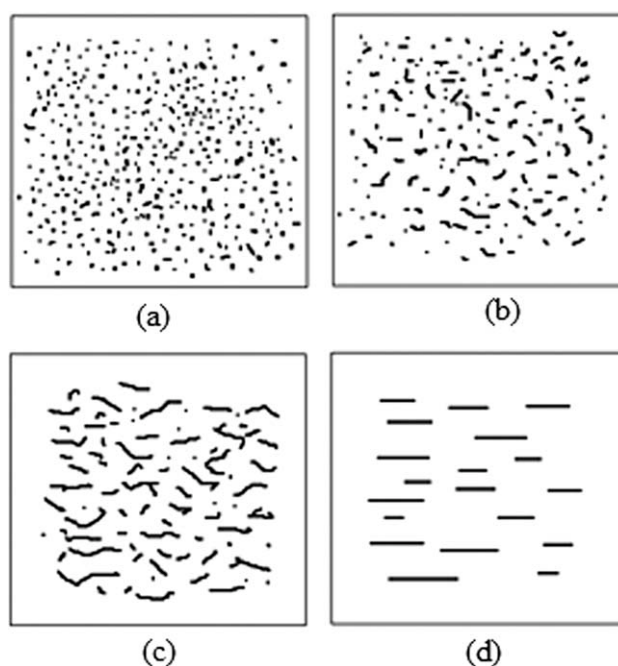


Figure 10 Schematic evolution of microstructure during stretching process.

process at high temperature, meanwhile, the volume of β phase of PVDF enhances, which brings about increase of dielectric constant and conductivity. With SR further increase, the Ni clusters get into rod-like and array in parallel along with stretching direction. The wide distribution of rod-like clusters is prone to form the conductive network, contributing to stretching-induced percolation effect. And those parallel rod-like clusters seem like a great deal mini-capitors,¹⁹ which might be the micro-mechanism of acutely increase of dielectric constants.

CONCLUSION

In summary, we have studied the stretching effect of PVDF and Ni-particles composites. It was found that the composites exhibited great enhancement in dielectric constants and altered from insulator to semiconductor after stretch. Furthermore stretching-induced percolation was proved to be an important effect to improve the dielectric properties of polymer-based composites.

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