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Electrical and dielectric sensitivities to thermal processes in carbon nanofiber/high-density polyethylene composites

Tian Liu, Weston Wood, Bin Li, Brooks Lively and Wei-Hong Zhong*

School of Mechanical and Materials Engineering,
Washington State University, Pullman, WA 99164, USA,
e-mail: katie_zhong@wsu.edu

*Corresponding author

Abstract

Owing to the huge interface region existing in a polymer nanocomposite, the effects of thermal processes on properties of nanocomposites are much more complicated than in a pure polymer. It is therefore important to determine the effects of thermal processes on nanocomposites with different interfacial interactions between the nanofillers and the polymer matrix. It is also important to explore the performance changes for nanocomposites under elevated temperatures over pure polymers. In this investigation, we examined the correlation of thermal treatment with dielectric properties of carbon nanofiber (CNF) reinforced high-density polyethylene nanocomposites. The thermal treatment of specimens was conducted for up to 120 h at 87°C and 127°C. Then, alternating current (AC) conductivity and dielectric properties were tested after definite intervals of time. Their changing rates over treatment time were analyzed. The results revealed the approximate linear relationships of AC conductivity and dielectric constant vs. heating time. Modified CNF reinforced nanocomposites had less influence by the heating treatments exhibiting better thermal resistance. The change rates of AC conductivity σ and dielectric properties have higher sensitivity to the treatment at a higher temperature. This study provides potential for further research on application of electrical and dielectric signals to detect the effects of heating process on lifetime of polymeric materials.

Keywords: alternating current conductivity; dielectric properties; nanocomposite; thermal treatment.

1. Introduction

Nanocomposites have emerged in recent years as important candidates for use as functional materials in applications of modern industries. They consist of polymer matrix and nanofiller reinforcement. It is well known that the structure and properties of polymers are affected by various environmental factors, especially temperature, because of their nature of viscoelasticity. Hence, the thermal effects from the working environment could lead to performance changes with time, i.e., ageing phenomenon, for the polymer matrix [1]. In a nanocomposite, in addition to the polymer matrix, the large interfacial areas exist between the matrix and nanofillers that are also susceptible to temperature-related changes. It has been verified that thermal effects have great influences on the fiber-matrix interface in micro- or macrocomposites [2, 3]. In this case, owing to the co-effects on both polymer matrix and interface transition region, properties of the nanocomposites can be varied under some thermal treatment although we assumed that effects on the nanofillers can be ignored. Unlike the pure polymer materials, these altering performances of polymer based composites, which are caused by imperceptible changes of internal structure, are difficult to detect before the obvious deterioration occurred in the materials. Therefore, it is important to perceive the effects of thermal processes on nanocomposites with different interfacial interactions between the nanofillers and the polymer matrix. It is also desirable to explore the performance due to changing rates under elevated temperature over the pure polymers using simple techniques.

Thus far, numerous experiments have been conducted to demonstrate the thermal related properties of polymer composites [4–14]. An abundance of different testing methods have been commonly applied, e.g., Fourier transform infrared spectroscopy [15], differential scanning calorimetry [10], X-ray diffraction [16], tensile test [17], bending test [18], etc. By examining and analyzing the variations of molecular structure and compromised performance of composites after thermal treatment, researchers could conclude the influences of thermal effects on the material properties. However, there is a deficiency in pertinent information on the rate of change in those properties during a thermal treatment process. Also, there has not been much focus on the thermal effects on nanocomposites with different fiber-matrix interfaces, although many performances of a nanocomposite are highly dependent on the interfacial interactions, in particular no studies have been reported on the time-temperature related changes for nanocomposites. It is well-known that nanoscale fillers distributed into a polymer matrix can lead to an exceptionally large interfacial surface area owing to the large specific surface areas, which will undoubtedly impact the whole performance of composites. Consequently, the stability of interfacial areas is very important to nanocomposite quality and durability. The effects caused by the interfacial changes cannot be reliably detected through the standard destructive tests and conventional thermal analysis approaches.

When compared with the testing approaches mentioned above, a dielectric method has obvious comparative advantages such as high sensitivity to polar group and non-destructive characteristics. However, for many decades of research, it has been primarily used to investigate dielectric properties of inorganic and polymeric materials [19–22], although some researchers have tried to apply dielectric testing for analyzing interfacial properties of polymer composites. Because dielectric signals are very sensitive to polar groups in materials under an external electric field, it is important to correlate the dielectric characteristics to effects on chemical structure, polarity, conformation, and interaction in interfacial areas by environmental factors, such as temperature changes, which are expected to be determined through the ability of various dipole movements to respond to the applied electric field [23, 24]. However, this possibility relies on the sensitivity of dielectric performance to thermal processes applied to the nanocomposite materials, which has never been reported.

To explore how thermal treatment processes can affect the dielectric performance of nanocomposites in ways that can reflect the contribution from the consequence of interfacial areas and thus allow determination of the dielectric sensitivity to thermal treatment, we chose high-density polyethylene (HDPE) as the polymer matrix and carbon nanofiber (CNF) as the conductive filler to make composites for the studies. As a typical hydrocarbon polymer, there is no polar group in the HDPE matrix, which implies that all the possible changes in the dielectric signal will come from interfacial interactions and/or the nanofibers. In addition, HDPE as a matrix has excellent biocompatibility along with better moldability, availability, high resistance to aging by thermal influences and relatively low cost, so that this material has been used extensively in industries [25–27]. To further extend the realm of applications for this polymer, various nanofillers have historically been involved in making such nanocomposites. Among numerous reinforcements, CNFs are attractive because of their interesting physical, thermal, and mechanical properties, as well as easy modification owing to the vast amount of edges existing on all the graphene sheets along the nanofibers [28–30]. Their high aspect ratio greatly affects thermal, dielectric/electrical applications of the composite materials [31–36]. Many studies on nanocomposites reinforced by CNFs with optimized characteristics have been carried out [37–39]. Furthermore, graphene layered structures of CNFs provide vast numbers of active edges for functionalization. Thus, not only the enhancement in performances, but also the easy treatment, makes CNFs very feasible nanofillers for the HDPE matrix.

To study the effects of thermal treatments on nanocomposites with different interfacial situations, a surface treatment approach for nanofibers was applied. It is known that appropriate treatment for nanofillers can lead to homogeneous dispersion of fibers, efficient load transfer from polymer matrices to fillers, and also strong interfacial interaction between them, which results in better thermal, physical, and mechanical performance of nanocomposites. For polar polymers, various methods for treatment of CNFs have been applied, such as oxidation, coupling agents, plasma modification, and others [40, 41]. For non-polar hydrocarbon polymers, such as HDPE, octadecyltrimethoxysilane (ODMS), which was selected for our previous study [42], has long non-polar hydrocarbon chains, so that the organosilane coupling agent can be used to modify the preoxidized carbon nanofibers (oxCNFs) to achieve preferable compatibility with HDPE. These hydrocarbon chains of the ODMS were coated onto the CNF surface by condensation reaction to form a non-polar layer, by which the improved interaction and adhesion between fiber and matrix were developed.

In this paper, we extended the previous study on sensitivity of dielectric performance with wear effects [43] by investigating the principle and mechanism of physical property changes during thermal treatment processing for the system of HDPE/CNF composites. This study monitors the sensitivity of alternating current (AC) conductivity and dielectric constant to the invariable heating temperatures with time. To make a comparative study of thermal effects on different interfaces, HDPE nanocomposites reinforced by pristine CNFs, oxidized CNFs, silanized CNFs with light coating and heavy coating were prepared. A 3 wt% concentration of CNFs was chosen for them with the aim of sensitivity to dielectric response. The experimental results revealed that an approximate linear relationship of AC conductivity and dielectric properties vs. thermal treatment time exists. The changes in these properties have sensitivity to heating time, typically at a higher temperature. Additionally, the silane coating on a CNF surface when used as a barrier improved the thermal resistance by showing less sensitivity of dielectric variations under elevated temperature.

2. Materials and methods

2.1. Sample preparation

The HDPE (HP54-60 Flake) used as a matrix in this research was supplied by Bamberger Polymers Inc. (New York, NY, USA)with density of 0.954 g cm^{-3}. The pristine CNFs (fiber type: PR-24-HHT) and pretreated oxidized CNFs (fiber type: PR-24-HHT-OX) were obtained from Applied Sciences Inc. (Detroit, MI, USA) which are approximately 60–150 nm in diameter and 30–100 μm in length. ODMS (90% technical grade) as organosilane coupling agent was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol was obtained from Decon Laboratories Inc. (King of Prussia, PA, USA).

The oxCNFs were modified under subsequent treatment in boiling ODMS (90% technical grade) ethanol solution. Then, the condensation reaction of oxCNFs and organosilane coupling agent can occur due to the reactive hydroxyl groups on the surface of organosilane after hydrolysis, forming a silane coating to cover the fiber surface. The degree of hydrolysis and the thickness of silane coating can be controlled by changing the ratio of oxCNFs, ODMS, ethanol, water, and the addition of NaOH as catalyst in this reaction. In the previous study, coating thicknesses were determined using thermogravimetric analysis data, which are approximately 46 nm for silanized CNF-h, and 2.8 nm for silanized CNF-l [42], which were chosen for this study.

The concentration of 3 wt% fibers for pristine CNFs (Comp-p), oxidized CNFs (Comp-o), and silanized CNFs (Comp-l with light coating; Comp-h with heavy coating) separately, were mixed with HDPE by a Haake Torque Rheometer (Thermo Fisher Scientific Inc., Hanover Park, IL, USA) for better dispersion. The detailed descriptions of each sample are shown in Table 1. Mixing was set at 170°C with a rotator speed of 30 rpm. The order of adding the materials was as follows: half amount of HDPE, CNFs, and then another half amount of HDPE. The speed was then raised to 70 rpm for 15 min. A neat HDPE reference was also prepared under identical conditions.

Thereafter, the processed HDPE and mixed polymeric nanocomposites were hot pressed at 180°C for 10 min via a hydraulic presser. They were allowed to cool down to room temperature naturally after turning off the heat. All samples were cut for thermal treatment and performance testing with the same size of 20 mm×20 mm and similar average thickness around 1 mm.

2.2. Thermal treatment procedure

All the samples were put into independent glass containers with plastic covers. The thermal treatment for them was carried out in a laboratory oven (non-vacuum state). To explore the influence of various thermal treatment conditions on sample properties, we chose different temperature points. Considering the melting temperature (T_m) of the HDPE matrix (137°C), two typical temperature points, 87°C of much lower than T_m and 127°C of close to T_m, were chosen. Subsequently, all samples were thermally treated at the constant temperature (87°C and 127°C, respectively) for 120 h in total. During this period, they were pulled out from the oven every 24 h for property testing after cooling down naturally.

2.3. Analysis of electrical properties

The frequency dependence of AC conductivity and dielectric properties under a constant temperature were determined by using an Alpha-N High Resolution Dielectric Analyzer (from Novocontrol, Inc., Wake Forest, NC, USA) equipped with Au parallel plate sensors, with frequencies from 10^{-3} to 10^7 Hz. The sensors and samples were cleaned by ethanol, after being dried completely, dielectric analysis testing was conducted. The changes in AC conductivity, dielectric constant, and dielectric loss were measured before and after thermal treatment (24, 48, 72, 96, and 120 h, respectively). The frequency range from 10^{-1} to 10^6 Hz and a stable frequency point of 10^3 Hz was selected for analyzing both AC conductivity and dielectric properties.

Table 1 Detailed descriptions for each HDPE nanocomposite.

Composite sample	Reinforcement	Fiber treatment	Coating thickness (nm)
Comp-p	Pristine CNFs	–	–
Comp-o	Oxidized CNFs	Oxidized	–
Comp-l	Silanized CNFs	Lightly silane treated	2.8
Comp-h	Silanized CNFs	Heavily silane treated	46

2.4. Characterizations

The microstructure features on the fracture interface of all specimens were observed by field emission scanning electron microscopy (FESEM type Quanta 200F) in order to characterize the interaction and adhesion between fibers and matrix. FESEM images for fractured surfaces were prepared by freezing in liquid nitrogen for 10 min prior to fracturing. The surfaces of all samples were sputter coated with gold for electrical conductivity. Additionally, various morphology of pre- and post-treatment with heating of pure HDPE and its nanocomposites were observed using an optical microscope (Olympus BX51TRF) equipped with a camera (Olympus U-CMAD 3, Portland, OR, USA).

3. Results and discussion

3.1. Morphology and the effects of thermal treatment

Morphology of the nanocomposites showing the dispersion and distribution of the various added CNFs (pristine, oxidized, and silanized) in the HDPE matrix were observed through field emission SEM (FESEM) with different magnifications. Figure 1A–D indicates the typical fracture surface morphology of all specimens before thermal treatment. It is clear that nanofibers were distributed uniformly and dispersed well in the silanized CNF nanocomposite specimens compared with the other two nanocomposites without treatment for CNFS. From Figure 1A and B, some obvious agglomerates can be easily seen in Comp-p and Comp-o, in which the CNFs are non-silanized. Numerous CNFs were exposed on the surface of the matrix, and many of them were pulled out. In addition, there were gaps between the nanofibers and the matrix, which revealed that adhesion was poor. In comparison, no agglomerates of CNFs can be found in Comp-l and Comp-h (Figure 1C and D), in which CNFs are silanized CNFs. Large amounts of CNFs were seen in the composite materials, and less were pulled out. These phenomena indicate the homogeneous distribution and enhanced adhesion between the silane modified CNFs and the polymer matrix. Therefore, it evidently suggests that the silane coating could induce an increased strengthening in the interfacial areas, thus attributing to the improved adhesion and interaction in the system of CNF/HDPE.

The morphology of the specimen surfaces of pure HDPE and the nanocomposites before and after 120-h thermal treatment (127°C) was examined by using optical microscopy. As shown in Figure 2, it can be observed that there were no large agglomerates in any of the samples, suggesting that the nanofibers were well dispersed in the HDPE matrix by means of the melt mixing process. Regarding the non-silanized CNFs

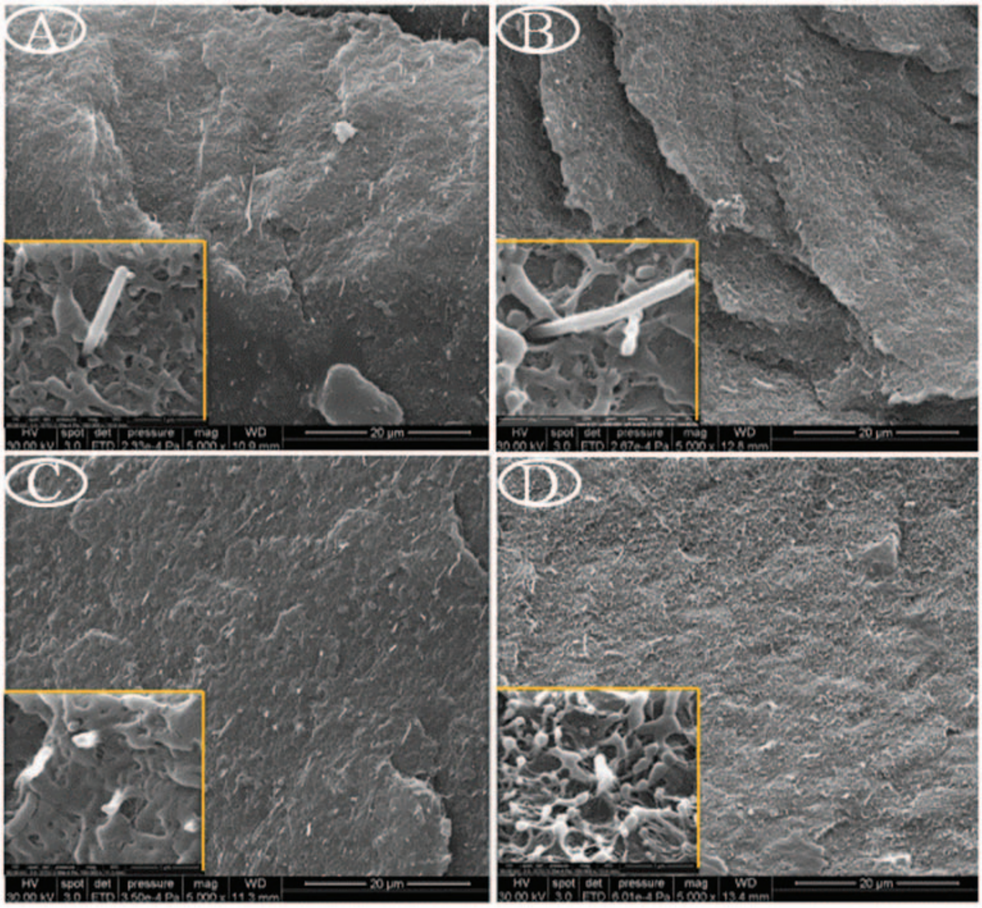

Figure 1 FESEM micrographs (scale bar: 20 μm; insert: 1 μm) of fracture surfaces of HDPE nanocomposites specimens for thermal treatment. (A) Comp-p; (B) Comp-o; (C) Comp-l; (D) Comp-h.

reinforced composites before heating treatment, there were some small CNF agglomerates (small black spots) shown in Figure 2B (Comp-p) and Figure 2C (Comp-o). However, no agglomerates can be found in the silanized CNF composites before heating treatment: Comp-l with “light” coatings on the CNF surface, which is shown in Figure 2D and Comp-h with “heavy” coatings on CNF surface, which is shown in Figure 2E. In comparison, after heating treatment, the various rumples were produced on sample surfaces (Figure 2a–e), which attributed to the thermal deformation that occurred in the materials. In particular, in Comp-p and Comp-o with untreated CNFs, more rumples can be found easily (Figure 2b and c). In addition, it should be noted that there were some circle craters in the Comp-p sample (Figure 2B) and Comp-o (Figure 2c). However, little amount of the craters existed in the composites, Comp-l and Comp-h with silane coated CNFs as shown in Figure 2d and e, respectively. Regarding the impact of silane treatment for the nanofibers, our previous studies showed that approximately a 40% increase in the storage modulus in silanized HDPE/CNF composites with the thicker coatings at a loading of only 0.4 wt% CNFs from the dynamic mechanical analysis (DMA) is found [42]. This significant enhancement is mainly due to the improved interaction and adhesion between the nanofibers and the matrix. According to the literature, the various types of fillers can make a significant impact on the mechanical properties of composite materials, which is attributed to the strengthened interfacial region [44, 45]. Hence, for Comp-p and Comp-o, there were weak interfacial strengths. For Comp-l and Comp-h, however, the strengthened interfacial zone led to less influences by thermal process. In this case, under the conditions of both thermal treatments at high temperatures (87°C and 127°C), various strengthening interfacial zones contributed from different reinforcements, we deduce that the degree of thermal deformations are primarily determined by the interfacial strength, and deformations involved the various movements of polar groups and non-polar chains, among which the movements of the polar groups can be reflected by dielectric properties of the composites.

3.2. AC conductivity with treatment time

The nanofiber content has vital influences on electrical properties of the resulting nanocomposite materials. It has been reported that AC conductivity of the percolative nanocomposites exhibits the correlation to the frequency when CNF

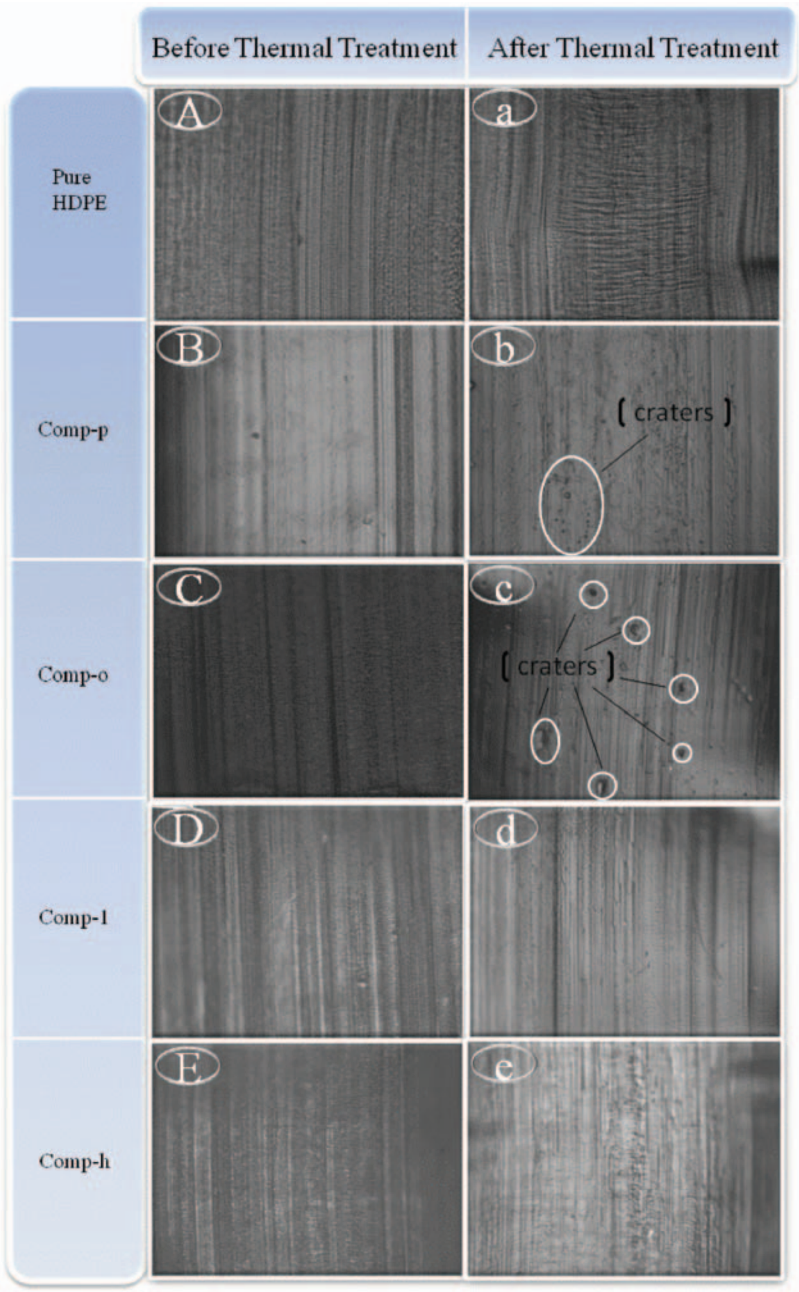

Figure 2 Optical microscopy images (magnification: 20×) for pure HDPE and its nanocomposite specimens before and after 120-h thermal treatment at 127°C.

concentration is lower than percolation threshold, and the AC conductivity displays the independence with frequency when the concentration of the CNFs is higher than the percolation threshold (46). The AC conductivity results shown in Figure 3 are consistent with previous studies, i.e., the AC conductivity (σ) of pure HDPE and the nanocomposites is a function of the frequency; in other words, the variation of σ exhibited strong correlation to the frequency for all specimens. And there was no obvious difference among the different samples. The phenomenon of frequency-dependent conductivity reveals the typical insulating behavior of these HDPE/CNF composites with the low nanofiber content (3 wt%), which is below the reported percolation threshold [47].

Subsequently, we selected a middle frequency to detect the effects of the thermal process on AC conductivity (σ) of all samples. Figure 4 displays the variations of σ at 10^3 Hz over

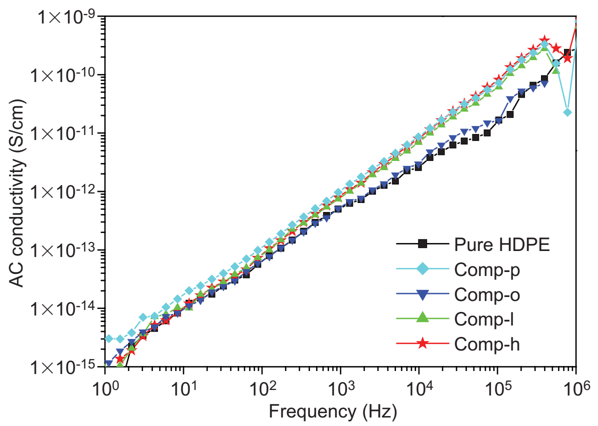

Figure 3 AC conductivity of pure HDPE and CNF/HDPE composites as a function of frequency.

thermal treatment time at constant temperatures (87°C and 127°C, respectively) for the specimens. In σ vs. heating time (*T*) plots, it can be seen that the changing in conductivity at 127°C (Figure 4B) is much more obvious than that at 87°C (Figure 4A). The tiny decreased trends in AC conductivity for all the samples after 87°C thermal treatment that can be seen from the inserted figure in Figure 4A could be attributed to the expansion of HDPE at the elevated temperature. For the composite materials, we supposed that the possible reason for this slightly decreasing trend was owing to the separation of fibers and matrix at the elevated temperature. Because of the slight thermal expansion of polymer matrix with heating time, increased gaps between conducting sites can be formed so that the free electrons cannot pass through the gaps. From Figure 4B, the thermal treatment at 127°C led to a significant increase in AC conductivity over time. The phenomenon could be due to the fact that much more formations of additional conducting pathways result from the relaxation of polymer matrix and the updated distribution of fibers nearby the melting temperature of the matrix material [48].

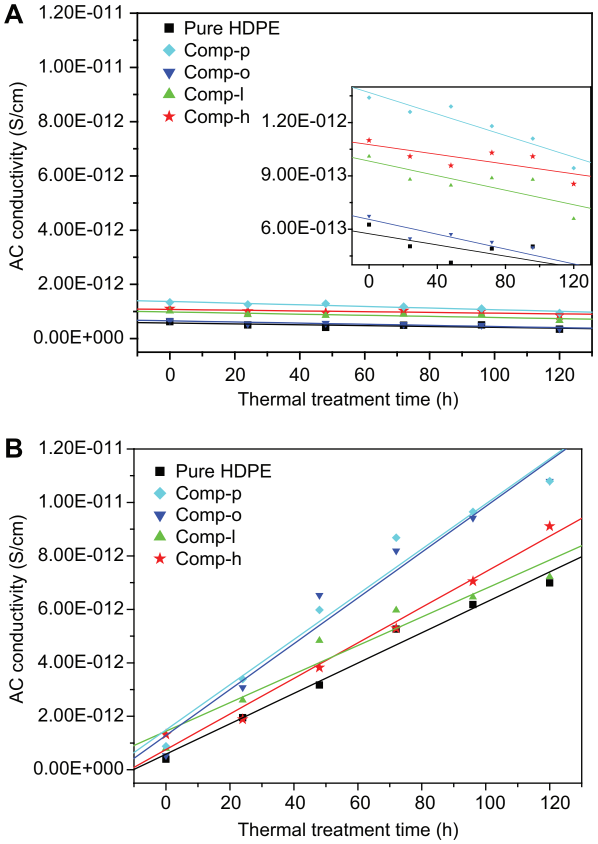

Figure 4 AC conductivity (at 10^3 Hz) changing trends vs. thermal treatment time at (A) 87°C (insert: detailed curves with different *Y* axis) and (B) 127°C.

In addition, the change rates of AC conductivity with respect to thermal treatment time (slopes of curves shown in Figure 4) at two different heating temperatures becomes clear in Table 2. Regarding the treatment temperatures, the slope values of all specimens at 127°C were 10 times higher than that at 87°C. Among four types of composite materials, the slopes of silane treated CNF composites (Comp-l and Comp-h) presented lower slopes than Comp-p and Comp-o at both temperatures 87°C and 127°C. In particular, during the 127°C thermal treatment process, the slope values of Comp-p and Comp-o (around 85) were higher than that of Comp-l and Comp-h (around 50–60). Thus, we can conclude that high slope value refers to greater sensitivity to the heating treatment and low slope means less sensitivity to the heating treatment. This conclusion indicates that the composites reinforced by silane treated CNFs minimized the effects of heat treatment, which results in better thermal resistance of the CNF/HDPE composite systems. The better thermal resistance was caused by the preferable interaction, as well as strengthened interfacial zone between fillers and matrix so that they were not easy to deform. Also, the expansion and relaxation of the polymer matrix can be constrained with the attribution of the enhanced CNF load transfer under the condition of constant heating temperature. Consequently, the results revealed the various sensitivities of AC conductivity with thermal treatment at a higher temperature based on the different strengthened interface in the composites.

3.3. Time dependence of dielectric constant

The variations of dielectric constant with the frequency over a range from 10 Hz to 10^6 Hz before thermal treatment

Table 2 Comparison of slopes of AC conductivity vs. thermal treatment time curves (Figure 4).

Samples	87°C		127°C	
	Slope	R	Slope	R
Pure HDPE	-1.6	0.84	56.8	0.99
Comp-p	-3.0	0.94	84.6	0.98
Comp-o	-2.1	0.92	85.7	0.98
Comp-l	-2.0	0.85	53.4	0.97
Comp-h	-1.4	0.87	66.5	0.99

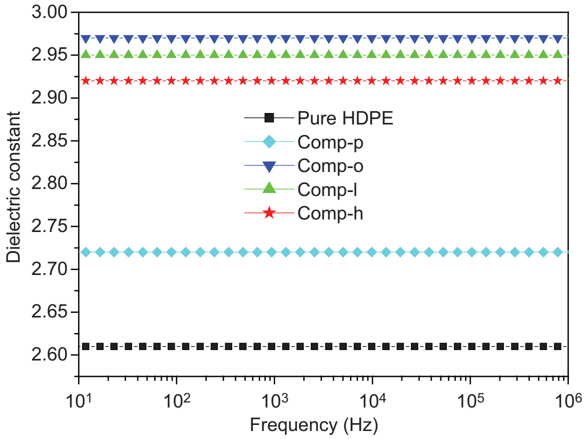

Figure 5 Frequency independent of dielectric constant before thermal treatment for pure HDPE and its nanocomposites.

for pure HDPE and the four types of nanocomposites are presented in Figure 5. Owing to the concentration of CNFs (3 wt%) in the composites being lower than the percolation threshold, the dielectric constant values of all the composite samples are independent of frequency [43]. In this case, we chose a certain frequency point to make a comparison of all samples. Figure 6 demonstrates the changes in dielectric constant (ε′) at the frequency of 1×10^3 Hz over the increasing heating time at the constant temperature. It reflected the effect of thermal treatment on dielectric constant of the HDPE/CNF systems. The tendency of all samples was increasing over time at both 87°C and 127°C, particularly at 127°C. It is true that the increased ε′ with temperature is due to the greater freedom of movement of dipoles in molecular chains in the samples at high temperature. At lower temperature, as the dipoles are rigidly fixed and the molecular motion is relatively restricted, the dipoles cannot be changed by electric field [49]. As temperature increases, however, the dipoles comparatively become more active in responding to the applied electric field. Thus, the dielectric constant of nanocomposites increases with the temperature from the polarization effect.

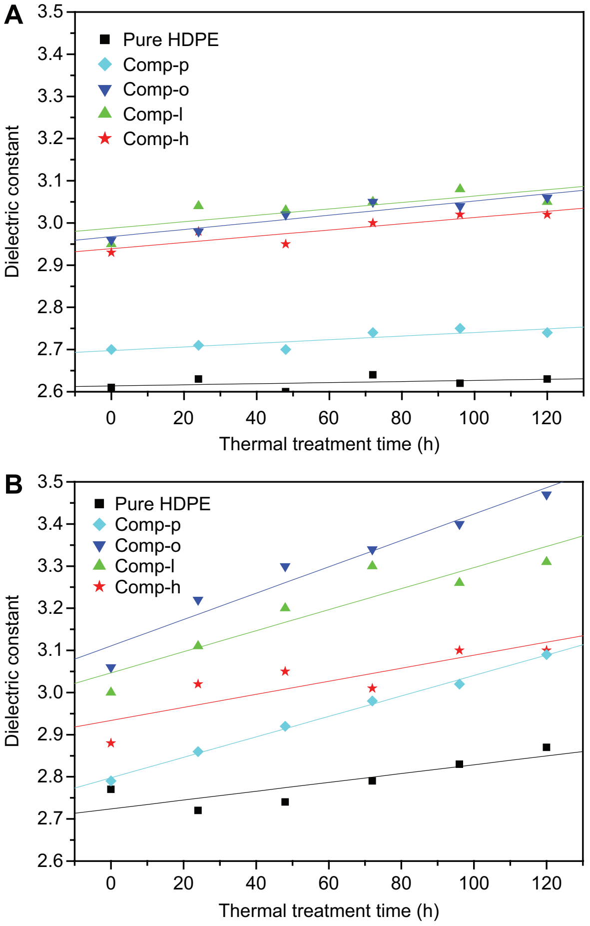

Figure 6 Dielectric constant changing trends (1×10^3 Hz) over thermal treatment time at (A) 87°C and (B) 127°C.

The summary of the changing rate of dielectric constant with respect to thermal treatment time for all samples (slope of curves in Figure 6) is shown in Table 3. In general, the slopes of the specimens treated at 127°C were several times higher than that at 87°C. For pure HDPE and Comp-p, they were performed on the relative low slope values because of their non-polar characteristics. For Comp-o, the slopes of ε′ changes at both 87°C and 127°C were the highest among pure HDPE and the other three nanocomposites at both heating temperatures due to a great deal of hydroxyl groups existing on the fiber surface. For silanized CNF composites, the trends were increasing at a lower degree because the silane coating was acting as a protective cover that leads to less polar groups in the molecular structure. In comparison, the slope of ε′ vs. temperature curve in Comp-h was even lower than that of Comp-l. It demonstrates that the heavy coating has the ability to reduce the change rate of dielectric constant vs. thermal treatment time. The reason could be that much more silanol groups react by an increased rate of hydrolysis, and thus higher density of crosslinking network of silane coating can be formed so that diminishing the hydroxyl groups on CNFs of the composites is significant. In this case, the thick silane layer acts as a shield to protect fibers, which induces less influences by the thermal treatment process in Comp-h. Based on the obtained results, we can draw the conclusion that the dielectric constant is sensitive to the thermal process, higher treatment temperature results in higher sensitivity.

Table 3 Comparison of slopes of dielectric constant vs. thermal treatment time curves (Figure 6).

Samples	87°C		127°C	
	Slope	R	Slope	R
Pure HDPE	1.7	0.77	10.5	0.86
Comp-p	4.3	0.85	24.3	1
Comp-o	8.5	0.94	31.1	0.97
Comp-l	7.6	0.83	25.0	0.93
Comp-h	7.4	0.90	15.5	0.88

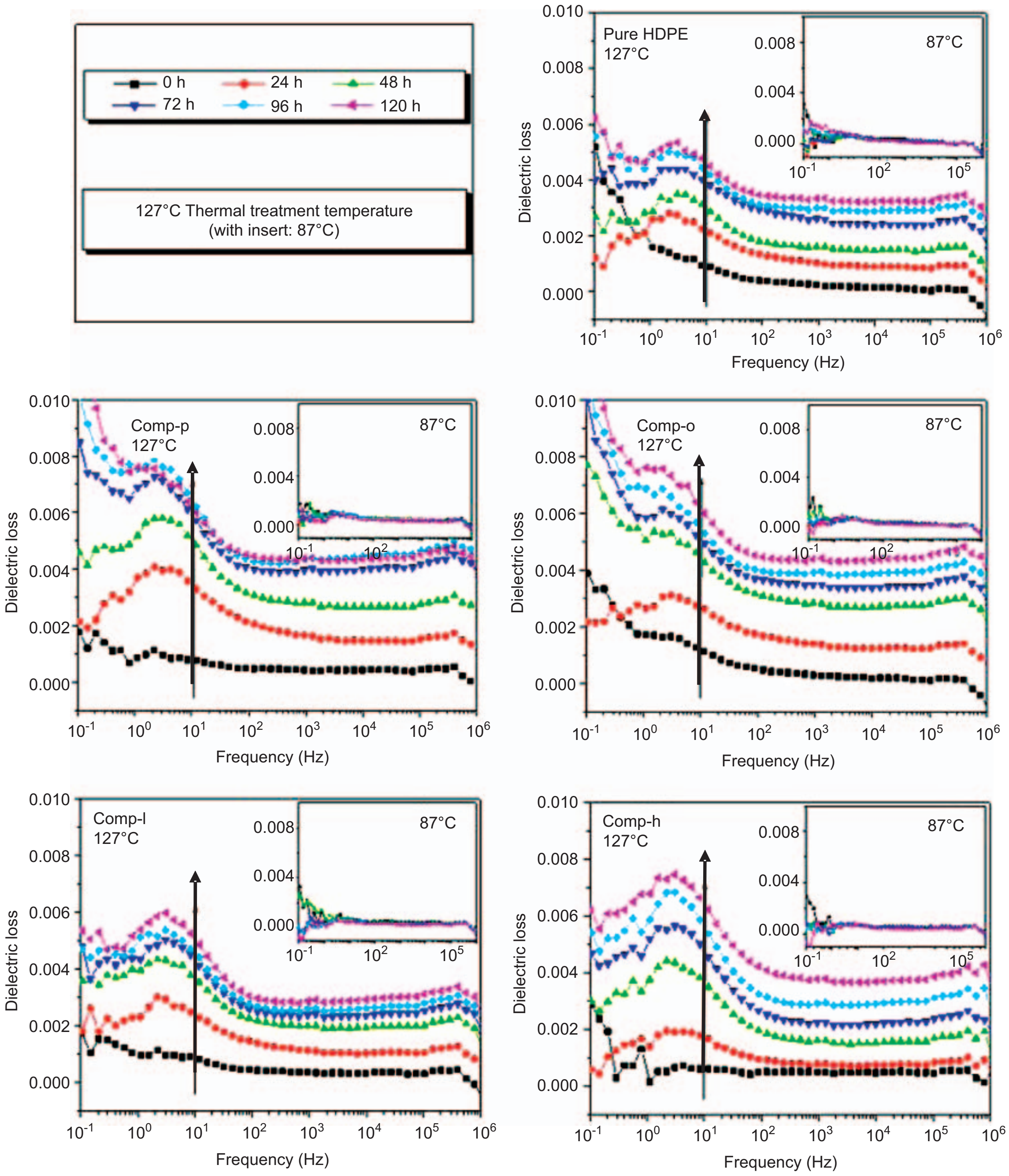

Figure 7 Frequency dependence of dielectric loss over thermal treatment time for all samples at 127°C (insert: at 87°C).

3.4. Dielectric loss analysis

Figure 7 displays the variations in dielectric loss (ε″) with frequency as heating time increases at two different temperatures, 87°C (insert) and 127°C. In comparison, it was observed that ε″ values after 127°C thermal treatment were much higher than those after 87°C for each sample. This increasing loss with thermal treatment temperature could be associated with the active molecular and chain motions of pure HDPE and the composites at higher temperature. To better analyze the effect of thermal treatment time on dielectric loss and compare the variations on different composites, we chose the curves after 127°C thermal treatment for further analysis. Pure HDPE presented little fluctuation owing to the integrated non-polar chains in the molecular structures. By contrast, all the nanocomposites showed signs of fluctuation at low frequencies under heating. For Comp-o, the main reason for the fluctuation was the large amount of hydroxyl groups on the oxidized fiber surface, being more sensitive to applied electrical field in responding to frequencies. For Comp-l and Comp-h, in which the CNFs were silane treated, in addition to the influence of residual hydroxyl groups after silane treatment, we suspect that the hydrocarbon tailed silane coatings provide additional flexible chains, which are also responses to the electric field. This is consistent in that much more additional chains existed in a thick coating layer in the Comp-h sample.

To reflect more visible effects of thermal processing on dielectric loss of these four types of nanocomposites, the comparison of loss, ε″, vs. frequencies after 120-h treatment time and the sensitivity of ε″ with treatment time, 10^3 Hz was chosen from Figure 7. In Figure 8A, the signs of fluctuations at low frequencies of Comp-p and Comp-o were shown to be greater than that of Comp-l and Comp-h after 120-h thermal treatment. Also, ε″ values of the silanized CNF composites (Comp-l and Comp-h) were lower than the other two composites. In Figure 8B, the changes of dielectric loss over thermal treatment time was exhibited. It was clear that the dielectric loss was increasing over time for all composite materials. In comparison, the changing rates of Comp-l and Comp-h were lower than Comp-p and Comp-o. Furthermore, the ε″ values of Comp-h changed slightly before 72-h heating time. After 72 h, however, the dielectric loss of Comp-l was even lower than that of Comp-h. We believe that the silane coating is beneficial to the improved interaction and adhesion between nanofibers and matrix. As a barrier, this strengthened interfacial region can protect the fillers and keeps the composites away from negative effects caused by thermal treatment, even up to the longest heating time, i.e., 120 h. In the other words, the thermal resistance of HDPE/CNF nanocomposite during a longer heating process can be realized by providing a silane coating to CNFs, and potentially the lifetime of the nanocomposites experiencing the thermal process can be extended significantly.

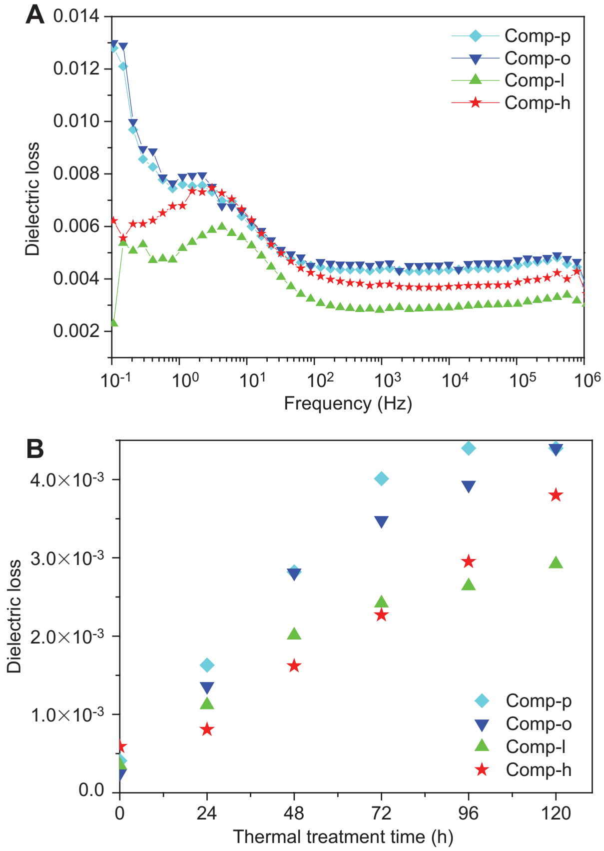

Figure 8 Dielectric loss comparison of Comp-p, Comp-o, Comp-l, and Comp-h, respectively. (A) Dielectric loss after 120-h thermal treatment vs. frequency. (B) Sensitivity of dielectric loss vs. thermal treatment time at 1×10^3 Hz.

Therefore, it can be concluded that thick silane coatings can efficiently contribute to a reduction in dielectric loss during a short thermal treatment time; and thin coatings have demonstrated more convincingly the superiority during a long heating time in such nanocomposites.

4. Conclusions

The effects of accelerated thermal treatment on electric and dielectric properties of HDPE/CNF systems were reported in this paper. The results demonstrated that the changes of AC conductivity and dielectric properties were sensitive to the increased heating treatment for the polymeric nanocomposites, typically at higher temperature. Approximately linear relationships exist between them. During thermal processing under high temperature, they were increasing over heating time. In comparison, silanized CNF composites with heavy coatings on the CNF surface displayed less sensitivity and better thermal resistance to the heating treatment. In addition, as a barrier, the silane-coating played a significant role on the reduction in dielectric loss for nanocomposites. In particular, thick silane coatings can more efficiently attribute to a reduction of dielectric loss during a short thermal treatment time; and thin coatings have demonstrated more convincingly the superiority during a long heating time. This research provides the potential for the applications of electrical and dielectric signals to detect the effects of thermal processing on lifetime of polymeric materials in many applications.

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