Electrical Properties of Composites in the Vicinity of the Percolation Threshold

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ABSTRACT: The electrical response of thermoplastic composites composed of carbon black and high-density polyethylene near the electrical percolation threshold (p_c) has been investigated through the study of the volume resistivity and complex permittivity. The change in conductivity beyond p_c exhibited a critical exponent that was greater than predicted from percolation theory. Composites with carbon black contents slightly larger than p_c exhibited the greatest sensitivity in volume resistivity with temperature variations under the melting point of polyethylene. In addition, percolating composites with low carbon black contents exhibited significant "negative temperature coefficient" (NTC) effects and improvements in conductivity with annealing. Maxwell–Wagner interfacial polarization resulted in moderate increases in both the permittivity (ϵ') and dielectric loss factor (ϵ'') below p_c , while at percolation, an abrupt and dramatic increase was observed for both components of the complex permittivity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1573–1582, 1999

Key words: electrical properties; polyethylene–carbon black composites; percolation threshold; volume resistivity; complex permittivity

INTRODUCTION

The ability of polymers to act as electrical insulators is the basis for their widespread use in the electrical and electronic fields. However, material designers have sought to combine the fabrication versatility of polymers with many of the electrical properties of metals. There are instances when an increased conductivity or permittivity of the polymer is warranted, such as in applications that require antistatic materials, low-temperature heaters, electromagnetic radiation shielding, and electric field grading. The method most often employed to significantly alter the electrical properties of a polymer is an extrinsic approach whereby the insulating polymer is combined with a conductive additive. The conducting additive is incorporated into polymers at levels that allow the

composite to maintain its electrically insulative qualities, as well as at higher levels, which allow the composite to become electrically (semi)conductive. Due to the ease of fabrication and low cost, there has been a high level of utilization of conductive carbon-black-filled polyethylene and polyethylene copolymer blends. The influence on conductivity of temperature,¹⁻⁴ blend morphology,^{5,6} crosslinking,⁷⁻⁹ and the addition of immiscible polymers to the blend^{10,11} have been the focus of a number of researchers, while the dielectric behavior has not been extensively reviewed.¹² In addition, theoretical analyses on the conductivity of heterogeneous mixtures have been presented.¹³⁻¹⁵

A crucial aspect in the production of conducting composites is the filler content, which must be as low as possible and still allow the composite to fulfill its electrical requirements; otherwise, the mixture processing becomes difficult, the mechanical properties of the composite are poor, and the final cost is high. The present study reported

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herein focuses on the conductivity and dielectric behavior of high-density polyethylene composites with conductive carbon black concentrations in the vicinity of the insulator-conductor transition.

EXPERIMENTAL METHOD

A commercial grade of high-density polyethylene, listed as Petrothene LS 6081-00 ($\rho_{\text{density}} = 0.963$ g cm³; MFI = 8.4 g/10 min; $M_n = 17,000$; $M_w = 77,300$), was used throughout this study and was supplied by Equistar Chemical Co., Houston, TX. The chosen carbon black was Vulcan XC-72 (N₂ surface area = 254 m²/g; DBP oil absorption = 174 cm³ 100 g; mean particle diameter = 300 Å) produced by the Cabot Corporation, Boston, MA. This carbon black is a high structure, relatively porous material characterized by highly extended aggregates and by an exceptionally broad particle and aggregate size distribution assisting in the formation of a strong network and enhanced conductivities.

All compounds were mixed at 170° C in a Brabender internal mixer with a 300-cm^3 cavity using a 40-rpm mixing rate, resulting in an average shear rate of approximately 110 s^{-1} . The mixing procedure involved adding the polyethylene into the preheated rotating mixer and allowing the polymer to mix for 6 min prior to the addition of the carbon black, after which the compound was allowed to mix for an additional 9 min. This procedure insured a uniform distribution of carbon black within the base polymer. The final compound was then molded at a pressure of approximately 6 MPa for 12 min at 170°C into approximately 0.75-mm-thick plaques.

The level of electrical conductivity of the composite dictated the experimental set-up for measuring both the volume resistivity (ρ) and the dielectric characteristics. For measuring the volume resistivity of electrically insulative composites, samples were in the form of 88.9-mm-diameter disks cut from the plaques. Current-time curves were generated using a Kiethley Model 6517A Electrometer and Model 8009 Resistivity Test Fixture, all coupled to a personal computer for data acquisition. The volume resistivity is based on the current flow in the sample after 20 s had elapsed from the application of a 1000 dc voltage. This procedure was repeated eight consecutive times on a sample with alternating polarity to arrive at an average volume resistivity.

For samples exhibiting (semi)conductive characteristics (i.e., $\rho < 10^8 \ \Omega \ cm$), $101.6 \times 6.35 \times 1.8$ mm strips were cut from plaques, and colloidal silver paint was used to fabricate electrodes 50 mm apart along the strips in order to remove the contact resistance. A Fluke 75 Series II digital multimeter and a two-point technique was used to measure the electrical resistance of the strips.

A number of different equipment were utilized to perform dielectric measurements. For electrically insulative materials, the signal was generated by a Hewlett Packard 651B Test Oscillator, which was passed through a General Radio Model 1615-A Capacitance Bridge in conjunction with a Balsbaugh Laboratories Model LD-3 Three-Terminal Sample Holder. For null signal detection, a General Radio Type 1232-A Tuned Amplifier was used. In addition, a TA Instruments Dielectric Analyzer (DEA) Model 2970 was used with a guarded parallel plate electrode system to study the dielectric response of insulating composites at frequencies from 10^{-3} to 10^{5} Hz. For dielectric measurements of semiconductive materials, a General Radio 1650-B Impedance Bridge was used in conjunction with a Rhodes and Schwartz parallel plate capacitor Model FNR.KL 1102/17. Semiconductive samples had a conductive silver paint applied as the electrodes to counteract the creation of a high impedance layer, which could result in electrode polarization.¹⁶ All dielectric measurements were taken at a temperature of 23°C unless otherwise indicated.

RESULTS AND DISCUSSION

Electrical Resistance

Compositional Dependence

The electrical conductivity of carbon-filled polyethylene is reasonably well established.^{1-4,6-9,11,12,15,17} Polyethylene is an insulator with a volume resistivity on the order of 10^{16} – 10^{18} Ω cm, while carbon black has electrical characteristics that are semimetallic in nature and exhibit a volume resistivity that varies considerably with its origin and chemical state, but is generally never less than about $10^{-1} \Omega$ cm. Consequently, the volume resistivity of a carbon-black-filled polyethylene composite varies as the carbon content is increased from that of pure polyethylene to that of pure carbon, though the change in volume resistivity with composition does not exhibit a simple linear additive characteristic. A percolation threshold and drastic decrease in vol-



Figure 1 Volume resistivity of high-density polyethylene-carbon black composites.

ume resistivity exists where the volume fraction of the carbon becomes sufficient to provide continuous electrical paths through the polyethylene.¹⁵ The conducting elements of these paths are either making physical contact between themselves or separated by very small distances across which electrons can tunnel. The percolation threshold varies considerably with the shape and agglomeration of the carbon black as well as the type of polymer used,¹ with the threshold occurring at higher volume fractions for carbon particles that have a low surfaceto-volume ratios and low agglomeration. Figure 1 depicts the volume resistivity-carbon black concentration curve for the current composites and identifies the percolation threshold at a loading of 6 wt %of carbon black. Numerous theoretical attempts to predict the exact shape of the volume resistivity concentration curve have been undertaken, but unfortunately, the detailed prediction seems far remote at the present time due to many factors that need to be accounted for. $^{13-15}$

In Figure 1, composites under the percolation threshold exhibit a gradual increase in conductivity with increasing carbon black content. For these nonpercolating compositions, a non-ohmic tunneling mechanism is speculated to be the dominate conduction process,¹⁸ and an elevated propensity of electrons to effectively tunnel between isolated carbon black domains with diminishing separation distances results in the enhanced conductivities. For composites greater than the threshold, a significant decrease in volume resistivity with increasing levels of carbon black is exhibited. The change in conductivity (σ) beyond the threshold can be expressed using percolation theory as

$$\sigma \propto (p - p_c)^t \tag{1}$$

where p_c represents the volume fraction of carbon black at the percolation threshold, and the critical exponent t governs the scaling behavior in the region of p_c . The experimentally determined percolation threshold is approximately 3.3 vol% and is significantly less than the theoretically predicted threshold of 16.4 vol% for a composite system consisting of conductive hard spheres dispersed within an insulating matrix.¹⁹ This theoretically predicted value is largely dependent on the shape of the dispersed conducting phase and can be extremely low in composites consisting of a highly anisotropic filler, for example, thin cylinders, because the critical volume fraction in this case is determined by the excluded volume per cvlinder.²⁰

For single percolation, the critical exponent depends solely on the dimensionality of the system and follows a power-law dependence of approximately 2 in three dimensions.²¹ In Figure 2, the change in conductivity is presented as a function of $p - p_c$ where the density of carbon black has



Figure 2 Conductivity of high-density polyethylene– carbon black composites as a function of $p - p_c$.

been estimated to be 1.8 g/cm³. The slope of the experimental data is 3.1, larger than the value predicted from percolation theory. The source of this greater power-law dependence is unclear, though possible sources include an additional conduction mechanism (e.g., electron tunneling) in combination with the percolative process. In addition, the current system could be exhibiting multiple percolation characteristics. Conducting composites utilizing a multiple percolation or "percolation-within-percolation" approach to achieve conductivity have been suggested to exhibit critical exponents that are greater than in single percolation systems.²² In the present highdensity polyethylene and carbon black composite, the separation of the crystalline and amorphous regions of the polyethylene, coupled with the affinity of the carbon black to be preferentially located in the amorphous phase, could result in the composite exhibiting multiple percolation characteristics.

Temperature Dependence

The volume resistivity of carbon-black-filled polyethylene exhibits unusual changes with temperature variations that have been utilized to design electrically self-regulating materials. Composites with levels of carbon black just above the percolation threshold may increase their volume resistivity by orders of magnitude if the interaggregate distances between carbon black particles increases by external means, such as thermal expansion or mechanical stressing.⁶ The temperature response can be exaggerated through the incorporation of a polymeric phase that is highly crystalline. A sharp resistivity increase is generally seen in the vicinity of the polymer melting point and has been termed the positive temperature coefficient (PTC) effect of resistivity.^{8,23} The PTC effect is most often explained in terms of a reduction in intergranular electron transport that accompanies a change in the tunneling length at the melting transition.²⁴ This effect can be seen in Figure 3, which presents the volume resistivity of the percolating composites between the temperatures of 50 and 140°C on the first heating cycle after molding. At approximately 120°C, the volume resistivity of the composites begin to increase dramatically with temperature; this temperature corresponds to the onset to melting of the unfilled polyethylene as determined by differential scanning calorimetry (DSC). In a thermoplastic material destined to be used as an electri-



Figure 3 Volume resistivity as a function of temperature for high-density polyethylene–carbon black composites. Number to left of curves corresponds to weight percent of incorporated carbon black. Data were obtained on the first heating cycle after molding.

cally self-regulating device, it is advantageous to have a significant volume resistivity rise with elevated temperatures under the polymer melting point in order to maintain the dimensional characteristics of the material. Modeling the rise in volume resistivity between 50-120°C as a powerlaw dependence of the form $\rho \propto T^m$ results in Figure 4, which presents the temperature exponent (m) of the composites. The composites have two distinct regions of temperature sensitivity that flank either side of the composite with 10 wt % of incorporated carbon black. Composites with carbon black contents under this amount exhibit the largest sensitivity to temperature variations and the greatest relative differences between loadings of carbon black, while composites with levels above 10 wt % of carbon black exhibit significantly reduced temperature responses. Nonpercolating systems are not presented in Figures 3-4 due to a relative lack of temperature sensitivity.

It is with compounds that exhibit a positive volume resistivity increase with temperature and a significant PTC effect at the polymer melting point that the thermoelectric switching behavior may be utilized in practice. Unfortunately, this resistivity increase is often followed by a rapid resistivity decrease termed the negative temper-





Figure 4 Temperature exponent (m) of volume resistivity for high-density polyethylene-carbon black composites.

ature coefficient (NTC) effect and is clearly seen in Figure 3 in the temperature range of 130-140°C. The NTC effect becomes more pronounced as the level of carbon black in the composite is decreased; the composite at the threshold exhibits a drop in volume resistivity of approximately two orders of magnitude (i.e., 3.4×10^5 to $3.0 \times 10^3 \Omega$ cm) between 130-140°C, while the composite with three times the critical carbon concentration (18 wt %) exhibits a 39% increase in volume resistivity in the same temperature interval. In this regard, the NTC phenomenon is a serious drawback since the switching properties imparted to a system by the positive increase in volume resistivity with temperature and PTC effect may lose their significance once followed by a distinguished NTC behavior. Figure 5 presents the ratio of volume resistivity at 140°C to the volume resistivity at 50°C ($\rho_{140^{\circ}C}/\rho_{50^{\circ}C}$) for the composites. This ratio defines the NTC character of the composites, with ratios less than unity indicative of composites that will ultimately lose all self-regulating qualities if the temperature is raised sufficiently high. The composite with 10 wt % of carbon black has a ratio of unity and is the crossover point from composites with large NTC behavior to small NTC behavior. The NTC effect can be reduced in practice by crosslinking of carbon black loaded polyethylene³; and although the NTC phenomenon is not well understood, its absence in



Figure 5 Ratio of $\rho_{140^{\circ}C}/\rho_{50^{\circ}C}$ for high-density polyethylene–carbon black composites.

crosslinked systems suggests that its associated with movement of particles in the polymer. Unfortunately, crosslinking can increase the percolation threshold by reducing the level of crystalline phase of material. Figure 6 presents the volume resistivity-carbon black concentration curve for the thermoplastic composites and an equiva-



Figure 6 Volume resistivity of thermoplastic (—) and thermoset (---) high-density polyethylene–carbon black composites.



Figure 7 Reproducibility of volume resistivity with first (\bigcirc) and second (O) thermal treatment of high-density polyethylene with 12 wt % of carbon black during the heating (-) and cooling (- -) cycle.

lent system where 1.5 wt % of dicumyl peroxide has been used to crosslink the composites. The thermoset composites exhibits a percolation threshold at a level of 16 wt % of incorporated carbon black, a significantly higher amount than the 6 wt % required for percolation in the thermoplastic system. DSC studies indicated that the crosslinked composites had been reduced in total fusionable material by approximately 20% relative to the thermoplastic versions. In semicrystalline polymers, the fine carbon blacks aggregates tend to concentrate in amorphous regions. During the crystallization process, a major part of the carbon black aggregates is rejected into interspherulitic boundaries, and the rest may be located in amorphous regions within the spherulites. As a result, the percolation threshold concentration in semicrystalline systems is lower than in structurally similar amorphous polymers. Annealing of a carbon black composite that incorporates a semicrystalline polymer can refine and increase the crystalline phase resulting in an improvement of the conductive network. Figure 7 is a typical example of the reproducibility of the volume resistivity curve of a percolating system with temperature cycling. During the heating and cooling cycles, the samples were allowed to equilibrate for 15 min at each temperature prior to taking a measurement. A slight improvement in

the conductivity could be achieved in the second thermal cycle, although additional thermal cycling did not promote any further improvements in the conductivity of the composite. The reduction in the volume resistivity (presented as an absolute change) at 23°C for the percolating compounds after a thermal treatment of 110°C for 24 h is presented in Figure 8. The reduction in the volume resistivity for the composites predicts a relationship of the form $|\Delta \rho| \propto (p - p_c)^{-5.6}$ and indicates that compounds that are near p_c benefit the most from the annealing process. DSC analysis of the composites before and after the annealing process indicated an approximately constant increase in the quantity of the total fusionable phase of 25 J/g HDPE for all concentrations, indicative of a higher quantity of an ordered phase. Unfortunately, for highly filled composites, the network is so sufficiently established after the initial molding that the refinement of the continuous network after annealing does little to improve the conductivity of the composite.

Dielectric Properties

The dielectric properties of a polymer composite depend on the following three major factors: (1) the properties of the constituent phases, specifically their permittivity and conductivity; (2) their relative volume fractions; and (3) the morphology



Figure 8 Absolute change in volume resistivity of high-density polyethylene–carbon black composites after annealing for 24 h at 110°C. See text for details.

in which the different phases are connected in three dimensions. The total complex permittivity (ϵ^*) can be represented as

$$\boldsymbol{\epsilon}^*(\boldsymbol{\omega}) = \boldsymbol{\epsilon}'(\boldsymbol{\omega}) - i\boldsymbol{\epsilon}''(\boldsymbol{\omega}) \tag{2}$$

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the observed relative permittivity and dielectric loss factor, respectively, and $\omega = 2\pi f$ is the angular frequency of the measuring electric field. The observed dielectric loss factor can be divided into

$$\epsilon''(\omega) = \epsilon''_{dp}(\omega) - \epsilon''_{dc}(\omega) + \epsilon''_{mw}(\omega)$$
(3)

where $\epsilon_{dp}^{"}$, $\epsilon_{dc}^{"}$, and $\epsilon_{mw}^{"}$ are the losses associated with dipole orientation, dc conductance, and Maxwell–Wagner interfacial polarization, respectively.²⁵ Maxwell–Wagner (MW) interfacial polarization occurs in heterogeneous systems where the conductivity and permittivity of the constituent phases differ. The dc conductance loss can be represented as

$$\epsilon_{dc}^{\prime\prime}(\omega) = \frac{\sigma}{\epsilon_o \omega} \tag{4}$$

where ϵ_o is the vacuum permittivity, and σ is the frequency independent dc conductivity of the sample that arises from the motion of charge carriers through the polymer.²⁶ The conductance loss can be particularly strong at the high-temperature–low-frequency limits, where the charge carriers exhibit enhanced mobilities. In high-density polyethylene, polarization effects due to dipole reorientations are minimal due to a lack of structural components in the repeat unit that can couple to the electric field at radio frequencies; the observed ϵ' and ϵ'' of the unfilled polymer exhibit relatively constant values of approximately 2.39 and 4×10^{-5} , respectively, up to the melting point.

The variation of the relative permittivity with carbon black concentration in high-density polyethylene is presented in Figure 9; these measurements were taken at a frequency of 1 kHz on unannealed samples. The permittivity increases moderately below the threshold and then exhibits an abrupt increase at percolation. At the percolation threshold, ϵ' is approximately six times larger than the next lower concentration. Calculations on conducting spheres treated as a mixture of randomly intermingled insulative and metallized regions attributed permittivity en-



Figure 9 Relative permittivity (ϵ') of high-density polyethylene–carbon black composites at a frequency of 1 kHz.

hancements to higher multipole interactions localized in particle clusters and predicted a singularity to coincide with the percolation threshold.²⁷ Percolating composites with increasing levels of carbon black exhibit significantly greater permittivity values, with the composite containing 9 wt % of carbon black having a value of approximately 1×10^{5} . Particle multipole interactions stemming both from the heterogeneous nature of carbon black and high-density polyethylene, as well as the amorphous and crystalline regions in the polymer, results in large capacitances and permittivity values that are not observed in homogeneous materials that have values that generally range between 2-150.^{26,28} The relative mobility of charge carriers in the differing phases of the composite results in the carriers being absorbed in the dielectric through entrapment at interfaces of separation within the dielectric or at an electrode. By being unable to discharge freely or be replaced from an electrode, an overall field distortion appears, which gives rise to an increase in the system capacitance. Figure 10 presents the corresponding dielectric loss factor of the composites. The response appears to increase with elevated carbon black concentrations in a manner similarly observed with the permittivity values of Figure 9, though the change in the losses in the nonpercolating composites is more dramatic than in their corresponding permittivity values. In



Figure 10 Dielectric loss factor (ϵ'') of high-density polyethylene–carbon black composites at a frequency of 1 kHz.

both the ϵ' and ϵ'' curves, the percolation threshold is clearly discernible. Figure 11 presents the results of Figures 9–10 in a format that highlights the dramatic changes that take place in the complex permittivity at percolation. The changes in the complex permittivity for compounds under the percolation threshold are relatively localized in the dielectric loss factor, with ϵ'' increasing three orders of magnitude from the unfilled polymer up to a composite with 5 wt % of carbon black. This response is contrasted to the significant changes in both components of the complex permittivity with composites above the threshold. In the percolating composites, ϵ' and ϵ'' increase four and seven orders of magnitude, respectively, from passing from a composite with 6 wt % of incorporated carbon black to a composite with 9 wt %. Unfortunately, the disparity in the electrical characteristics of the constituents of the current system of interest, coupled with the complex aggregate structure of carbon black and its affinity to develop networks throughout the base polymer, imparts to the filled polyethylene system a concentration behavior that theoretical and empirical mixing equations developed for calculating the complex permittivity of heterogeneous systems are unsuccessful in predicting.¹² In addition, annealing the percolating composites did not result in drastic alterations in the complex permittivity similar to those changes seen in the volume resistivity (see Fig. 7). Its speculated that the minor molecular rearrangements necessary to transform a network dead end into a branch with an infinite cluster size does not significantly alter the complex permittivity. When MW effects are the dominate polarization phenomena, the dielectric properties are sensitive to larger-scale surface area and volumetric modifications between dissimilar phases.

MW polarization requires an interfacial charge accumulation that is supplied by a flow of charge through the dielectric phases, a process which may span orders of magnitude in time, depending on the relative conductivity of the dissimilar phases. Figure 12 presents the permittivity of the unfilled polyethylene and a composite with 5 wt % of incorporated carbon black at 70°C within the frequency range of $1 \times 10^{-3} - 1 \times 10^{5}$ Hz, while the corresponding dielectric loss factor for the filled composite is presented in Figure 13. The permittivity of the unfilled and filled system are relatively constant from 1×10^5 Hz down to 3 \times 10⁻² Hz, at which point both systems exhibit a rise in ϵ' with decreasing frequency. The occurrence of the steep rise of both systems at a similar frequency raises the speculation that electrode polarization or MW polarization between amorphous and crystalline polyethylene phase is responsible for the response, rather than the MW



Figure 11 Plot constructed from results presented in Figures 9 and 10. Percolation threshold (p_c) is indicated.



Figure 12 Relative permittivity (ϵ') of high-density polyethylene (—) and high-density polyethylene with 5 wt % of carbon black (- - -) at a temperature of 70°C.

polarization between the polyethylene and carbon black. The Wagner analysis²⁹ of a dielectric composite, modeled as dispersed conducting spheres in an insulating matrix, predicts the frequency of the MW polarization relaxation and maximum loss to be proportional to the conductance of the dispersed spheres, that is, $f_{\rm max} \propto \sigma_{\rm sphere}$. The minor difference in conductivity between amorphous and crystalline polyethylene phases, relative to the polyethylene and carbon black, may require seconds or min to allow for charge accumulation at interfaces so that the polarization response may observed only at lower frequencies. The dielectric loss factor is presented in Figure 13 for the filled composite at a shortened frequency range of 1×10^{-1} – 1×10^{5} Hz. The dielectric loss factor exhibits a gradual drop with decreasing frequency, falling below the resolution of the equipment at 1×10^{-1} Hz and does not show the characteristic dc conductance loss with frequency [see eq. (4)] often observed in polymers with mobile ionic impurities.^{30,31} The lack of an observable ionic dc conductance loss supports the speculation that the reduction in volume resistivity seen for the composites under the percolation threshold (see Fig. 1) stems from electron tunneling effects and not mobile ionic impurities. In addition, the absence of a polarization relaxation or maximum in the dielectric loss factor for the

filled system suggests that the frequency of maximum loss due to the MW polarization for the high-density polyethylene–carbon black phases is greater than 10^5 Hz.²⁵

CONCLUSION

The electrical response of thermoplastic composites composed of carbon black and high-density polyethylene near the electrical percolation threshold (p_c) , identified at 6 wt % of incorporated carbon black (ca 3.3 vol%), has been investigated through the study of the volume resistivity and complex permittivity. The change in conductivity beyond p_c exhibited a critical exponent of 3.1, which was greater than the power-law dependence of approximately 2 predicted from percolation theory. Composites with carbon black contents slightly larger than p_c exhibited the greatest sensitivity in volume resistivity with temperature variations under the melting point of polyethylene. In addition, percolating composites with low carbon black contents exhibited significant negative temperature coefficient (NTC) effects and improvements in conductivity with annealing. Maxwell–Wagner interfacial polarization resulted in moderate increases in ϵ' and ϵ'' below p_c . At percolation, an abrupt and dramatic



Figure 13 Dielectric loss factor (ϵ ") of high-density polyethylene with 5 wt % of carbon black at a temperature of 70°C.

increase was observed for the complex permittivities, resulting in a composite with 9 wt % of carbon black exhibiting an ϵ' and ϵ'' of approximately 1×10^5 and approximately 5×10^5 , respectively.

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