Electrical and Thermal Studies of the Distribution of Carbon Black in a Polyester Matrix in the Presence of Aluminum Oxide

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ABSTRACT: The distribution of a filler in a polymeric matrix is one of the most important factors affecting the physical properties of the final product. For this reason, the main objective of this study was to introduce aluminum oxide (Al_2O_3), acting as a dispersing agent, to reduce the filler–filler interaction and enhance the filler–polymer interaction. To achieve this aim, the electrical behavior of a styrenated polyester resin filled with different amounts of high-abrasion furnace black in the presence of 5% Al_2O_3 was studied in the vicinity of the percolation threshold to evaluate the effect of the addition of Al_2O_3 in an attempt to reduce the filler–filler interaction through the polyester matrix. At a certain concentration of carbon black, an abrupt increase was noticed through electrical conductivity, permittivity, and dielectric loss investigations. With this increase, the tendency of conductive chain formation increased through the aggregation of a carbon black particle network. The addition of 5% Al_2O_3 improved the filler distribution by lowering the aggregate size and consequently enhanced the formation of the network. From the Arrhenius temperature dependence of the electrical conductivity, the activation energy and pre-exponential factor were obtained, and they confirmed the validity of the compensation law for the semiconducting composite systems. The composites were also analyzed by thermogravimetric analysis. Al_2O_3 improved the thermal stability of the composites in comparison with that of a sample free of Al_2O_3. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2250–2258, 2008

Key words: activation energy; dielectric properties; fillers; polyesters; thermal properties

INTRODUCTION

Conducting polymeric composites based on conductive particles in a polymer matrix are widely used because of their unique electrical and mechanical properties.[1–3] Most polymers are typical insulators, and the conductivity of their composite materials predominantly depends on the content and properties of the filler as well as the composite structure. The most general approach for the description of charge transport in conducting polymeric composites in relation to the content of conducting particles is provided by the percolation theory.

One of the important methods for forming a carrier path in an insulating polymer matrix is the incorporation of conductive additives such as carbon black, carbon fiber, and metals.[4,5] Among the large number of electrically conductive additives, carbon black is widely used because it is easily processed and also produces a reinforcing effect on polymer materials.[6–8] Recently, these conductive composite materials have become very popular because of their low cost, high flexibility, and weather and chemical resistance.

The changes in the conductivity in this type of composite have been ascribed to a percolation process because, if the filler content increases, the number of conductive paths increases, the average distance between the conducting particles becomes smaller, and, consequently, the resistivity of the composite decreases.

On the other hand, the thermal stability of polymeric materials that are affected by temperature changes plays an important role in many industrial applications. Thermogravimetric analysis (TGA) is one of the major thermal analysis techniques and has broad applications in the characterization of polymeric materials.[9–11]

It is well known that the distribution of a filler in a polymeric matrix is one of the most important factors affecting the physical properties of the final products.[12] For this reason, the objective of this study was to investigate the electrical properties of a prepared polyester resin filled with various contents of high-abrasion furnace black (HAF) before and after the addition of 5% aluminum oxide (Al_2O_3) in an

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attempt to reduce the filler–filler interaction and to provide better distribution of HAF through a styrenated polyester (SP) matrix.

EXPERIMENTAL

Materials

1,2-Propylene glycol, triethylene glycol, phthalic anhydride, maleic anhydride, fumaric acid, and styrene were obtained from Merck (Darmstadt, Germany) and used without further purification.

HAF with a specific gravity of 1.78–1.82, a pH value of 8–9.3, a particle size of 40 μm, and fine granules (HAF-N330) was supplied by Transport and Engineering Co. (Alexandria, Egypt).

Al_2O_3 powder with an average particle size of 23–46 nm was supplied by VEB Laborchemie (Apolda, Germany).

Techniques

The nuclear magnetic resonance (NMR) spectrum was taken on a JEOL (Tokyo, Japan) Ex-270 NMR spectrometer.

The molecular weight determination was performed by gel permeation chromatography. Gel permeation chromatography was carried out with an Agilent Technologies (Walden Bornn, Germany) 1100 series instrument equipped with three Styragel columns (10^2, 10^4, and 10^5 Å) and a refractive-index detector (Agilent G 1362). Tetrahydrofuran was used as an eluent at a flow rate of 1 mL/min. The columns were calibrated by means of polystyrene (an internal standard was used).

Dielectric measurements were carried out in the frequency range of 100 Hz to 100 kHz with an AG-411 B LCR meter (Ando Electric, Ltd., Tokyo, Japan). The capacitance, loss tangent, and resistance (R) were obtained directly from the bridge, from which the permittivity (ε'), dielectric loss (ε''), and conductivity (σ) were calculated according to the equation $\sigma = (1/R) \times (d/A)$, where d is the thickness of the sample (cm) and A is its area (cm^2). An NFM/5T guard ring capacitor (Wiss Technische Werkstatten GmbH, Weilheim, Germany) was used as a measuring cell. The cell was calibrated with standard materials,[13] and the experimental error in ε' and ε'' was found to be ±3 and ±5%, respectively. The temperature was controlled with an ultrathermostat, and the experimental error in temperature control was 0.1°C.

The samples were molded in the form of discs 5 cm in diameter and 3 mm thick.

TGA and derivative thermogravimetric analysis (DTA) of SP and its composites were investigated on finely powdered samples. The instrument was a PerkinElmer (United States) TGA 7 thermal analyzer. The rate of heating was 10°C/min up to 750°C under a nitrogen atmosphere.

A JEOL JXA-840A scanning electron microscope with an applied voltage of 20 kV was used. Scanning electron microscopy (SEM) was performed on fracture surfaces of samples at the temperature of liquid nitrogen. The surface of each sample was mounted on a standard specimen sub. A thin layer of gold was first deposited onto the fracture surface and attached to the stub to ensure electron conductivity between the samples and the specimen stage.

Synthesis and identification of the polyester resin

In a two-necked, round-bottom flask provided with a magnetic stirrer and a water condenser, phthalic anhydride (0.5 mol), maleic anhydride (0.25 mol), and fumaric acid (0.25 mol) were added to 1,2-propylene glycol (0.7875 mol) and triethylene glycol (0.2625 mol). The acid/glycol ratio was 1 : 1.05 mol. The reaction mixture was heated in an oil bath at 160°C for 1 h. The temperature was then increased gradually at a rate of 10°C/h up to 210°C and was maintained at that temperature until the acid value of the polyester reached 35 mg of KOH/g. The acid value was determined by titration of a solution of a weighed quantity of the resin in acetone with an approximately $0.2N$ standard alcoholic KOH solution with phenolphthalein as an indicator. A vacuum was applied for a short time before the polycondensation was stopped to assist in water removal from the reaction medium.

The specific gravity at 20°C, the number-average molecular weight, and polydispersity of the prepared polyester resin were 1.57, 1743 g/mol, and 2.2, respectively.

The structure of the prepared unsaturated polyester resin was established with the ^{1}H-NMR spectrum shown in Figure 1.

^{1}H-NMR (δ, ppm): 1.3 ($-CH_3$), 3.8–3.2 ($-CH_2-O-CH_2-$), 4.2 ($-CH_2-OH$), 4.5 ($-COO-CH_2-$), 5.3–5.1 ($-CH-$), 6.6 ($-CH=CH-$), 7.7–7.3 (ph–H).

Curing of the prepared unsaturated polyester with styrene

The prepared unsaturated polyester resin was diluted with styrene monomer (70 : 30 w/w) in the presence of 2 wt % methyl ethyl ketone peroxide as an initiator and a 0.25 wt % solution of 8% cobalt naphthenate as a promoter. The polyester/styrene mixture was left at room temperature (25°C) for 4 h, and this was followed by 2 h at 60°C in a thermostat oven until curing occurred.
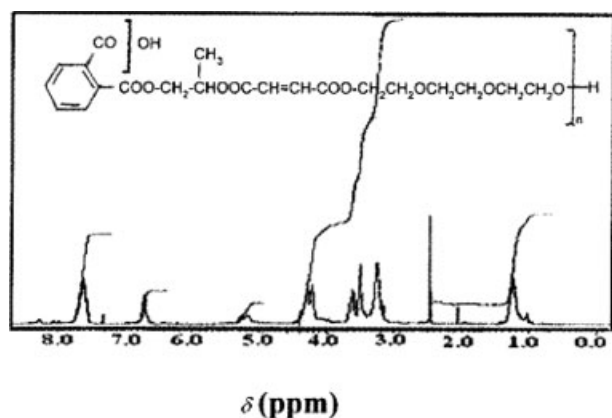
Figure 1 ^{1}H-NMR spectrum of the prepared polyester resin.

Preparation of the polymeric composites

A moldable and curable composition was prepared through the mixing of different ratios of the carbon black filler (0–40%) in the absence and presence of 5% Al_2O_3 with a polyester/styrene mixture. The prepared composites were cured under the same conditions.

RESULTS AND DISCUSSION

Electrical properties

Conductivity

Polyesters are generally insulating materials with electrical conductivity ranging from 10^{-14} to 10^{-12} Ω^{-1} cm^{-1}.[14,15] On the other hand, carbon black has electrical characteristics, in that it is semimetallic in nature and exhibits electrical conductivity varying considerably with its origin and chemical state, but it is generally never less than about 10^{-1} Ω^{-1} cm^{-1}.

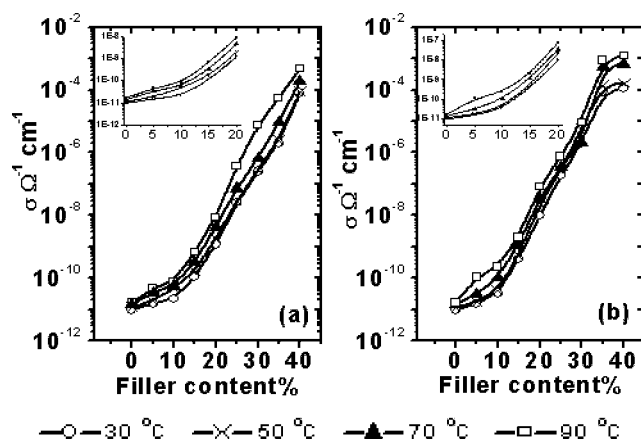Consequently, the electrical conductivity of a carbon-black-filled composite increases from that of the pure polymer to that of pure carbon. This increase does not exhibit a simple linear additive character. A percolation threshold and a drastic increase in the electrical conductivity exist at which the volume fraction of the carbon becomes sufficient to provide continuous electrical paths through the polymer matrix.[16] The conducting elements of these paths either are making physical contact between themselves or are 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. Figure 2(a,b) depicts the electrical conductivity of SP/HAF and SP/HAF/Al_2O_3 at different temperatures, respectively. Up to a certain concentration of HAF, the threshold percolation is 20% for SP/HAF and 10% for SP/HAF/Al_2O_3. The conductivity values of the composites are the same or a little higher than those of the pure polyester matrix. This finding is due to the fact that the network necessary to form a conducting path is not formed at such concentrations. Above such concentrations, the conductivity increases many orders of magnitude with very little increase in the filler content.

The formation of the network is faster in the case of SP/HAF/Al_2O_3 composites (after 10% HAF) in comparison with that of SP/HAF (20% HAF). This may be due to the uniform distribution of HAF particles in the presence of Al_2O_3, the volume effect, or both.[17,18] The presence of Al_2O_3 may improve the filler distribution by lowering the aggregate size and consequently enhance the formation of the network; in addition, Al_2O_3 is a conducting material. This finds further justification in SEM micrographs. The high surface energy of thermally conductive particles such as silver and ceramics (e.g., Al_2O_3) makes bare metal surfaces susceptible to sintering, which
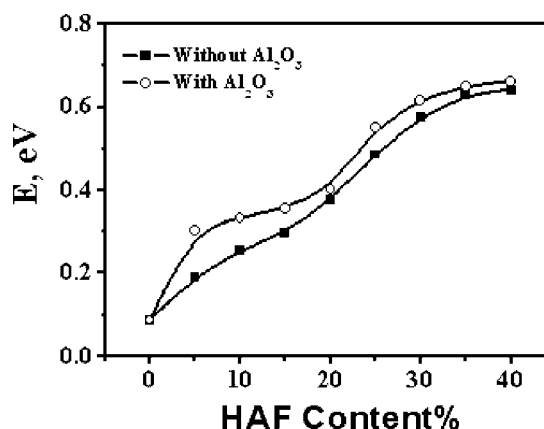

Figure 2 σ versus the HAF content: (a) SP/HAF and (b) SP/HAF/Al_2O_3.

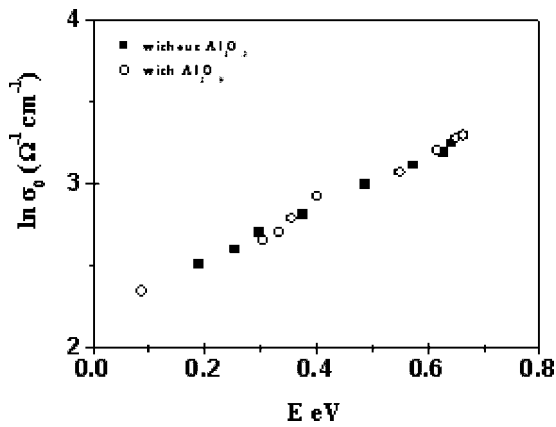**Figure 3** Relation between E and the HAF content.

Figure 4 Relation between ln σ_0 and E.

reduces the surface area and hence the net surface energy by forming necks of metallic bonds between the particles.[19,20]

It is clear from Figure 2 that a pronounced increase in the conductivity with the temperature increasing up to 90°C can be observed for both SP/HAF and SP/HAF/Al$_2$O$_3$.
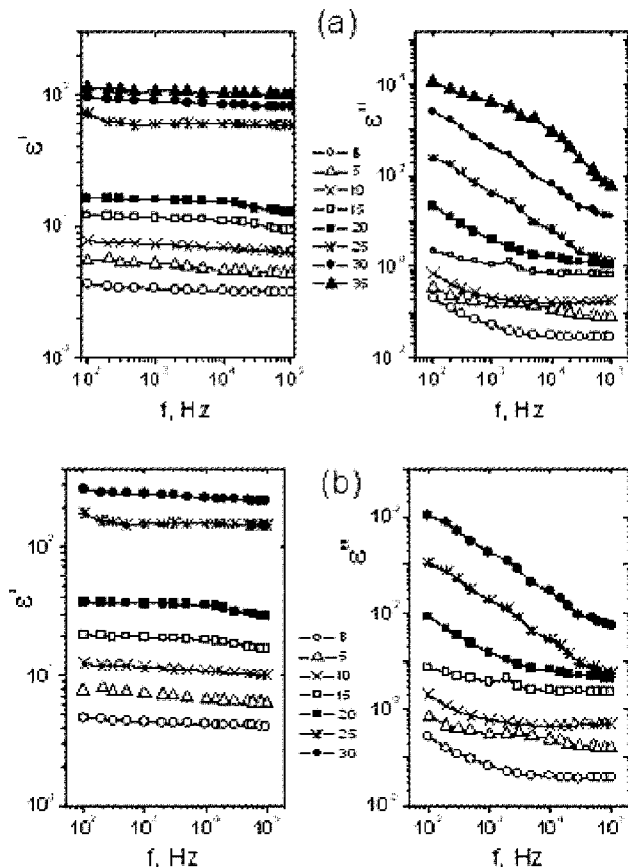

Figure 5 ε' and ε'' at different values of f for SP/HAF composites with different percentages of HAF at (a) 30 and (b) 70°C.
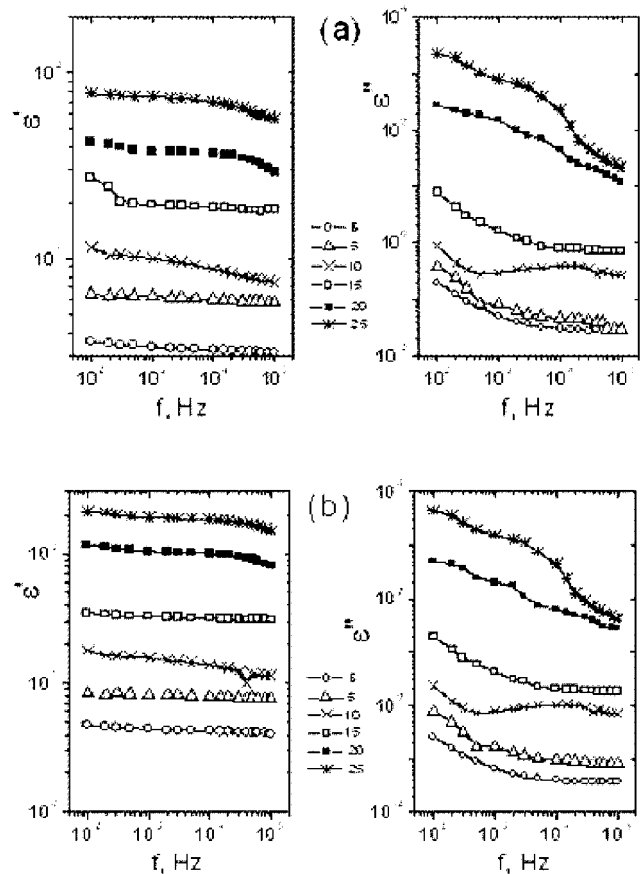

Figure 6 ε' and ε'' at different values of f for SP/HAF/Al$_2$O$_3$ composites with different percentages of HAF at (a) 30 and (b) 70°C.

The temperature dependence of the conductivity (σ) can be expressed by the Arrhenius equation $\sigma = \sigma_0 \exp(E/KT)$, where E is the activation energy, K is the Boltzmann constant, T is the absolute temperature, and σ_0 is a pre-exponential factor depending on the mobility of charge carriers. For both systems (before and after the addition of 5% Al$_2$O$_3$) with different HAF contents, ln σ_0 was plotted graphically versus $1/T$, and straight lines were obtained from which E and σ_0 were estimated. Figures 3 and 4 show that E increases with increasing HAF content, whereas the dependence of ln σ_0 on E is linear; this confirms the validity of the compensation law for the semiconducting composite system.[21]

ε' and ε''

ε' and ε'' were measured in the frequency range of 100 Hz to 100 kHz and in the temperature range of 30–90°C for SP filled with HAF (SP/HAF) and SP filled with HAF in the presence of 5% Al$_2$O$_3$ (SP/HAF/Al$_2$O$_3$). The concentration of HAF ranged from 0 to 40%. Examples of these measurements are illustrated in Figures 5 and 6 at 30 and 70°C, respectively.
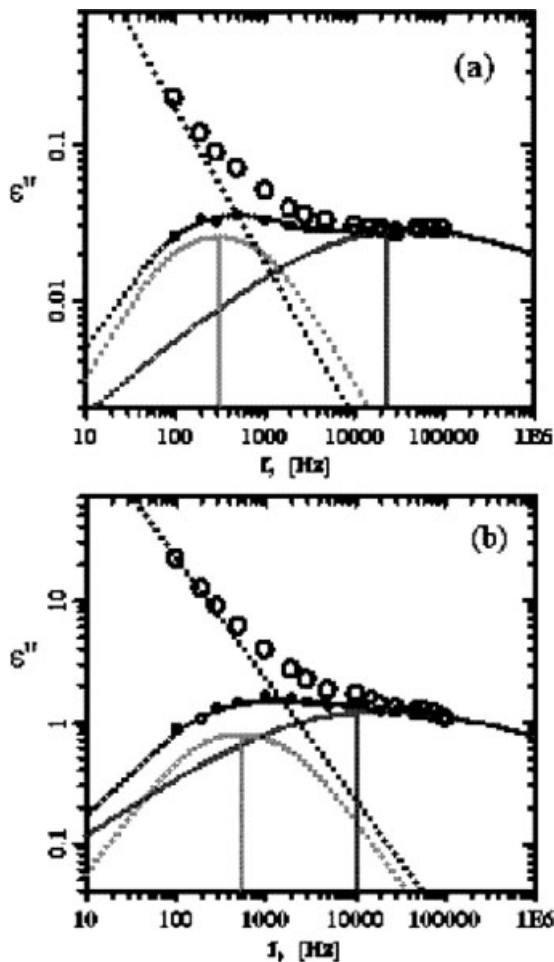
Figure 7 Example of the analyses for SP/HAF composites: (a) SP and (b) 20% HAF. The experimental data were fit after the subtraction of the losses due to direct-current conductivity with Fröhlich and Havriliak–Negami functions.

Dielectric relaxation

Absorption curves relating ε'' and $\log f$, illustrated in Figures 5 and 6, indicate that these curves are

broader than one Debye curve in which more than one relaxation process is expected. The values of ε'' at the lower frequency are high. These higher values may be due to the Maxwell–Wagner effect, direct-current conductivity, or both.[13,22]

To follow up the different relaxation mechanisms and how these mechanisms are affected by the presence of either HAF or HAF/Al$_2$O$_3$ in the polyester matrix, curves relating ε'' and f at 30°C were analyzed with Fröhlich and Havriliak–Negami functions[22] in addition to the conductivity term.

The Fröhlich function is

$$\varepsilon''(\omega) = \sum_{i=1}^{n} \frac{\varepsilon_s - \varepsilon_\infty}{P_i} \arctan\left[\frac{\sinh P_i/2}{\cosh \ln (\omega \tau_i)}\right]$$

where P_i is a parameter describing the width of the distribution of relaxation times and is equal to $\ln(\tau_1/\tau_2)$. τ_i is the mean relaxation time and is equal to $(\tau_1\tau_2)^{1/2}$, whereas ε_s and ε_∞ are the static permittivity and the permittivity at infinite frequency, respectively.

The Havriliak–Negami function is

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty) \cos(\beta \theta)}{\{(1 + 2(\omega\tau)^{1-\alpha} \sin(\pi\alpha/2) + (\omega\tau)^{2(1-\alpha)})\}^{\beta/2}}$$

where

$$\theta = \arctan \frac{(\omega \tau)^{1-\alpha} \cos \pi \alpha/2}{1 + (\omega \tau)^{1-\alpha} \sin \pi \alpha/2}$$

α and β are constants called the Cole–Cole and Cole–Davidson distribution parameters, respectively; ω is the applied frequency (i.e., $2\pi f$); and τ is the relaxation time.

An example of the analyses is given in Figure 7 for the SP free from carbon black and SP loaded
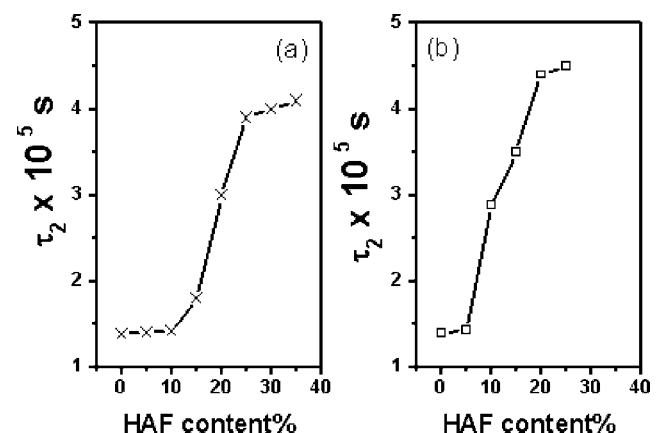
From both figures, it is clear that ε' decreases with the applied frequency (f) increasing, whereas it increases with both the temperature and HAF content increasing. Also, the increase in ε' with increasing HAF content is not systematic, but at a certain concentration at which the network is expected to be formed, an abrupt increase in ε' can be noticed. From both figures, it is clear that this increase occurs after 20% HAF for SP/HAF and after 10% HAF for SP/HAF/Al$_2$O$_3$. These critical concentrations are in good agreement with those found in the case of the conductivity measurements. This result is considered to be an indication for the formation of the network through the percolation thresholds, which are discussed briefly in the section on conductivity.

Figure 8 τ_2 versus the HAF content: (a) SP/HAF and (b) SP/HAF/Al$_2$O$_3$.
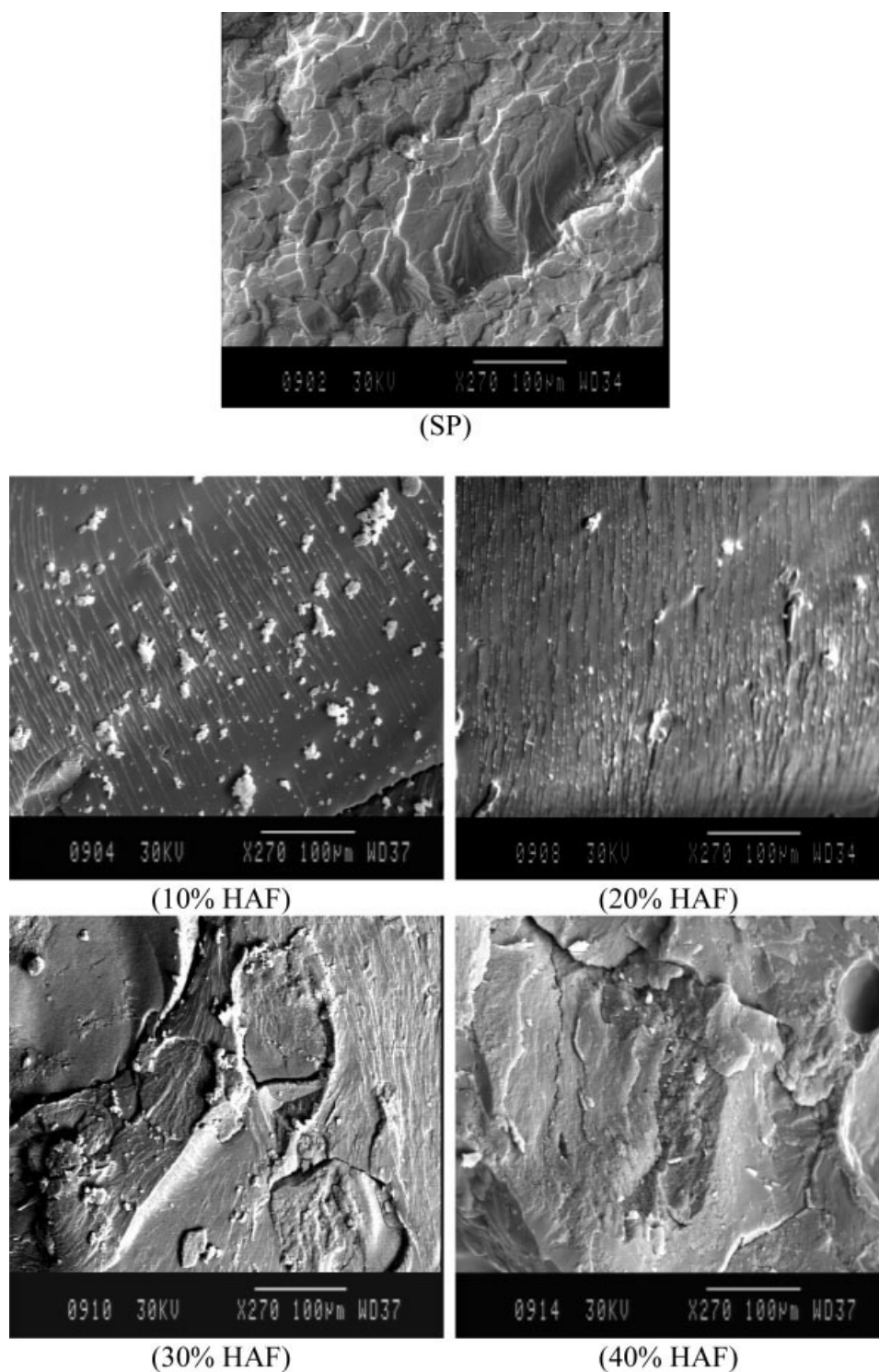
Figure 9 SEM images of fracture surfaces of SP/HAF.

with 20% HAF before the addition of Al_2O_3. An absorption region can be detected at a frequency lower than 500 Hz with τ_1 equal to 3.2×10^{-4} s. The relaxation time associated with this process is independent of the HAF content. This region could be attributed to the Maxwell–Wagner effect, as it is expected to be in the lower frequency range because of the multiple constituents of the investigated systems. In the higher frequency range, the absorption region, which has been fitted with the Havriliak–Negami function, can be associated with some local molecular motions rather than the main-chain
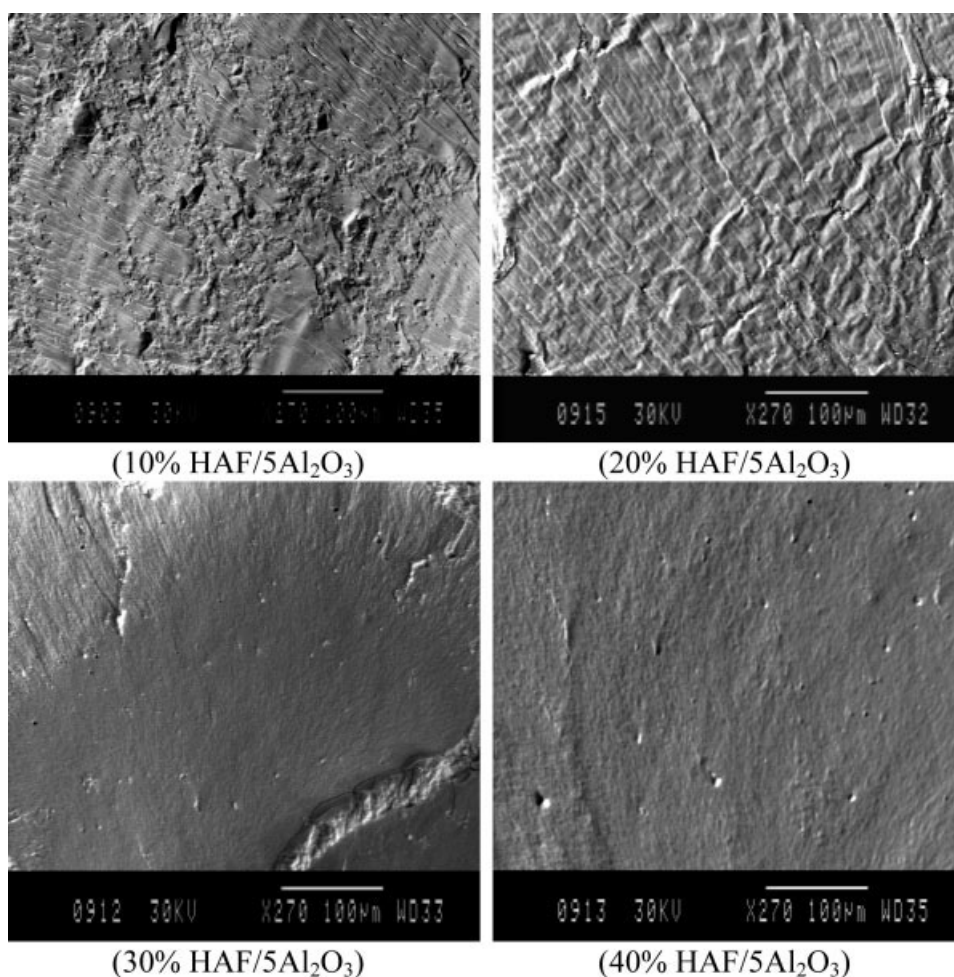
(10% HAF/5Al$_2$O$_3$) (20% HAF/5Al$_2$O$_3$)

(30% HAF/5Al$_2$O$_3$) (40% HAF/5Al$_2$O$_3$)

Figure 10 SEM images of fracture surfaces of SP/HAF/Al$_2$O$_3$.

motion as it is frozen because the measurements were carried out at 30–90°C, that is, below the glass-transition temperature of SP itself.[23]

The relaxation time associated with such a process, τ_2, is illustrated graphically versus the HAF content in Figure 8. τ_2 is nearly the same for lower concentrations of HAF up to 20% for SP/HAF and 10% for SP/HAF/Al$_2$O$_3$, after which a dramatic increase can be observed.

This finding is considered to be further justification for the formation of the network through the investigated systems observed through the ε' and conductivity measurements.

SEM

To confirm the assumption, it was reasonable to investigate the distribution of HAF on a fracture surface of the polyester before and after the addition of Al$_2$O$_3$ with SEM (Figs. 9 and 10).

Figure 9 presents an SEM photograph of SP without the filler, showing small crazes and clear river lines with a smooth surface on the fracture surface.

On the other hand, SEM images of the composites with different concentrations of carbon black (10, 20, 30, and 40%) show river lines crowded together that are comparable to those of the pure polyester resin. From Figure 9, it is apparent that at a higher concentration of carbon black, a massive new surface is created. When the amount of HAF increases from 20 to 40%, the network is formed and leads to the disappearance of the aggregation of HAF noticed at the lower concentrations.

From Figure 10, it can be deduced that the incorporation of 5% Al$_2$O$_3$ reduces the domain size of carbon black particles, and consequently, the dispersion increases.

In general, it can be said that the dispersion is improved for all carbon black composites containing 5% Al$_2$O$_3$ in comparison with those of composites without Al$_2$O$_3$.

TGA

DTA and TGA of the SP resin and the corresponding carbon black polyester composites loaded with 10

TABLE I
Thermal Degradation of SP Composites

Specimen	T_0 (°C)	T_{max} (°C)	Peak height at T_{max} (%/min)
SP	154	330	−14.4
SP/HAF (10%)	157	416	−2.6
SP/HAF (35%)	178	650	−1.5
SP/HAF/Al$_2$O$_3$ (10%)	159	428	−2.5
SP/HAF/Al$_2$O$_3$ (35%)	181	690	−1.2

T_0 = peak onset temperature of degradation; T_{max} = peak maximum temperature.

and 35% carbon black in the presence and absence of 5% Al$_2$O$_3$ were performed.

TGA is characterized by the peak maximum temperature, that is, the temperature of maximum degradation, and the peak onset temperature of degradation. The area under a DTA curve is proportional to the mass change and the height of the peak at any temperature, that is, the rate of degradation at that temperature. The characteristic degradation temperatures obtained from the thermograms are summarized in Table I.

The results indicate that the thermal stability and degradation behavior of these samples were influenced by either the variation of the content of carbon black or the addition of Al$_2$O$_3$.

Table I shows that the peak onset temperature of degradation and peak maximum temperature increase with increasing carbon black in the absence or presence of Al$_2$O$_3$.

Al$_2$O$_3$ as a dispersing agent improves the thermal stability of carbon black composite samples by delaying the onset degradation temperature and peak maximum temperature. Also, the mass degradation rate is shifted from −14.4%/min for SP to −2.5%/min for SP/HAF/Al$_2$O$_3$ (10%) and to −1.2%/min for SP/HAF/Al$_2$O$_3$ (35%).
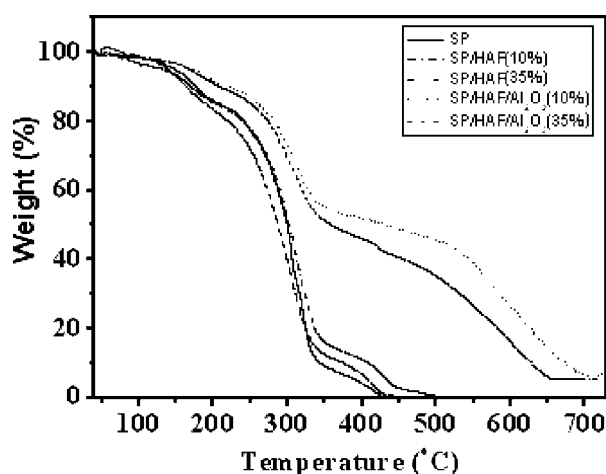
Figure 11 shows the mass retention percentage as a function of temperature for polyester composites. The TGA curves of SP show that the total weight loss of the polyester occurs at 400°C. It is obvious that the thermal stability of the carbon black composites increases with an increasing percentage of the filler, whereas the weight loss decreases. Al$_2$O$_3$ improves the thermal stability of the composites in comparison with a sample free of Al$_2$O$_3$.

CONCLUSIONS

- The electrical conductivity and dielectric measurements for SP/HAF and SP/HAF/Al$_2$O$_3$ indicate that at a certain concentration of carbon black, an abrupt increase can be observed as a result of network formation.
- These critical concentrations, which are called the percolation thresholds, are reduced from 20 to 10 phr as a result of the addition of Al$_2$O$_3$.
- The validity of the compensation law for the semiconducting composite systems has been studied through calculations of E and σ_0.
- TGA indicates that the thermal stability of carbon black composites increases with the percentage of the filler increasing and also in the presence of Al$_2$O$_3$.
- SEM micrographs indicate that the incorporation of 5% Al$_2$O$_3$ leads to an improvement in the HAF dispersion in the SP matrix.
- This investigation has led to the conclusion that the addition of Al$_2$O$_3$ as a dispersing agent solves to some extent the problem of aggregation of HAF in the polymer matrix and consequently reduces the amount of HAF necessary for network formation.

Figure 11 TGA curves of SP/HAF and SP/HAF/Al$_2$O$_3$.

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