



Electrical and Mechanical investigations on polyvinyl chloride filled with HAF black

By

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Abstract

Polyvinyl chloride (PVC) was chosen to be loaded with various amount of high abrasion furnace black (HAF). The mechanical as well as electrical properties of the prepared composites were investigated. The Dielectric properties of these composites were investigated in the frequency range $10^2 - 10^5$ Hz at temperature range from 30 to 120 °C . In addition to the conductivity term, the experimental data of the dielectric losses ϵ'' were analyzed using a computer program based on both Havriliak-Nagami and Fröhlich equations into two relaxation processes. The first relaxation process in the lower frequency range could be attributed to Maxwell Wagner effect. The second relaxation could be attributed to the combination of the large scale mobilization of the chains i.e. the glass rubber relaxation process in addition to a contribution of the motion of the large aggregates caused by the movement of the main chain, which are expected to be formed by the addition of different ingredients to PVC such as plasticizer.

The percolation threshold concentration, which is the concentration after which the conductivity increases many orders of magnitude with very little increase in the filler amount for PVC/HAF composites depends upon the measuring temperature, whether it is below or above the glass transition of the polymer matrix.

Stress-strain plot, hardness, and other mechanical properties such as stress at yield, stress at rupture, strain at yield, strain at rupture and Young's Modulus were investigated at room temperature. This investigation led to the conclusion that all the mechanical properties are improved by increasing HAF content and reaches its optimum values at about 30 phr HAF loading. On the other hand, The addition of HAF black by concentration up to 40 phr increase the electrical conductivity to be in the order of 10^{-10} Sm^{-1} at 30 °C and 10^{-9} Sm^{-1} at 120 °C which highly recommend such composites to be used in antistatic applications as the suitable range of electrical conductivity for such application is $10^{-9} - 10^{-14} \text{ S m}^{-1}$.



Introduction

Conducting polymeric composites (CPCs) are traditionally prepared by the blending of conventional polymers with electrically conductive fillers, and they have important applications in antistatic materials, low-temperature heaters, electromagnetic radiation shielding, and electric field grading [1]. Among the available fillers, carbon black (CB) has been extensively employed because of its ability to impart high electrical conductivity to an insulating polymer at a relatively low filler content.[2]. These systems usually present a sharp insulator– conductor transition characterized by a critical CB loading, that is, the percolation threshold concentration. This behavior is principally due to the unique elongated aggregate structure and the tendency to agglomerate [1].

An important aspect in the production of these composites is the filler content, which should be as low as possible and still allow the composite to fulfill its electrical requirements, otherwise the mixture processing become difficult, the mechanical properties of the composite is poor and the final cost is high. [3].

The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. At low filler loading, the conductivity of the composite is still very close to that of the pure, electrically insulating polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases many orders of magnitude with very little increase in the filler amount. After this region of drastic increase, the conductivity levels off and approaches that of the filler material. At the percolation threshold the filler begins to form a continuous conductive network through the composite [4].

The aim of the present work is to investigate the dependence of the percolation threshold upon the temperature below and higher than the glass transition. Poly vinyl chloride PVC with $T_g = 87^\circ\text{C}$ [5] was chosen to be loaded with various amount of HAF black and the dielectric properties as well as electrical conductivity will be measured with the aim to investigate the percolation threshold over a wide range of temperature 30 up to 120°C . The mechanical properties of the composites will be also investigated.

Experimental



Table (1): The concentrations of all samples under investigations

PVC,phr	100	100	100	100	100	100	100	100	100	100
HAF,phr	0	0	7.5	10	12.5	15	20	25	30	40

The general formulations for PVC and HAF used in this study are given in Table (1). 5 phr, parts per hundred part of the thermal stabilizer (Akedenz) and the plasticizer (DINP) 5 phr were added to all formulations. The mixing was carried out in a Brabender (C.W.Pra, instrument, INC. 50 Hackensack NJ 230 volt, 40 AMP). The PVC, DINP and thermal stabilizer were mixing at 200 °C, 35 rpm and for 7 min., then increased the velocity to 80 rpm and added the HAF for 4 min., all batches were mixed on a two roll laboratory mill of outside diameter 470 mm and working distance 30mm, with a speed of slow roll at 24 rpm and a gear ratio 1:1.4. The mixing was completed within 5 min. The samples were compressed in clean polished molds at 180°C for 5 min. with a thickness about 2.3 mm.

Materials

PVC resin used in this study was a white powder made by suspension polymerization with a k value of 70 with $T_g = 87$ °C.

Plasticizers used were di-isononyl phthalate (DINP) and epoxidized fatty acid soya oil.

Akedenz, 1,3bis- (isopropyl) benzene peroxide on calcium carbonate (IPBP) commercially known as perkadox 1410 were used as the thermal stabilizing and the curing agent, respectively.

High abrasion furnace black (HAF) with specific gravity = 1.78 – 1.82, pH value = 8 – 9.3 and fine granules with particle size = 40 nm was supplied by Transport and Engineering Company, Alexandria, Egypt.

Techniques

Stress and strain at yield and rupture were carried out at room temperature on a tensile testing machine, Zwick 1425, according to ASTM-D 412-98a, 1998.

The hardness of the samples were carried out according to ASTM- D 2240-97, 1998.



Dielectric measurements, were carried out in the frequency range 100 Hz to 100 kHz by using an LCR meter type AG-411 B (Ando electric Ltd. Japan). The capacitance C , the loss tangent $\tan \delta$ and the resistance R were obtained directly from the bridge from which the permittivity ϵ' , dielectric loss ϵ'' and conductivity σ were calculated. A guard ring capacitor type NFM/5T Wiss Tech. Werkstätten (WTW) GMBH Germany was used as a measuring cell. The cell was calibrated by using standard materials [6] and the experimental error in ϵ' and ϵ'' was found to be $\pm 3\%$ and $\pm 5\%$ respectively. The temperature was controlled using an ultra-thermostat. The experimental error in temperature controlling was 0.1°C .

Results and discussion:

Electrical Properties

The permittivity ϵ' and the dielectric loss ϵ'' were measured in the frequency range 100 Hz up to 100 kHz at wide range of temperature 30 up to 120°C for PVC filled with different concentrations of HAF black ranging from 2.5 up to 40 phr. The obtained data are illustrated graphically in Figure (1a). From this figure it is clear that ϵ' increases by increasing HAF content, while it decreases by increasing the applied frequency, which shows anomalous dispersion. Also it is found that the value of ϵ' increases by increasing temperature. To discuss the relaxation mechanisms associated with such dispersion, the dielectric loss values ϵ'' are plotted graphically versus the applied frequency, f , as shown in Fig (1b). From this Figure it is clear that the values of ϵ'' increase by

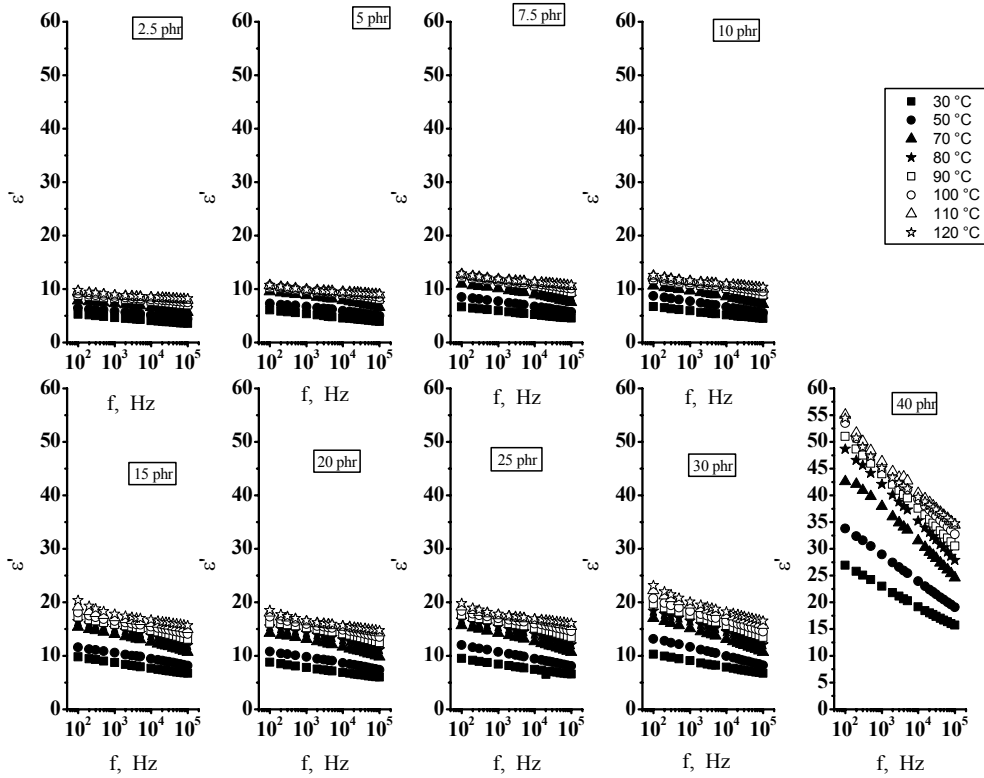


Figure (1a) The permittivity versus the applied frequency at different temperatures for PVC/HAF Composites with various HAF Content

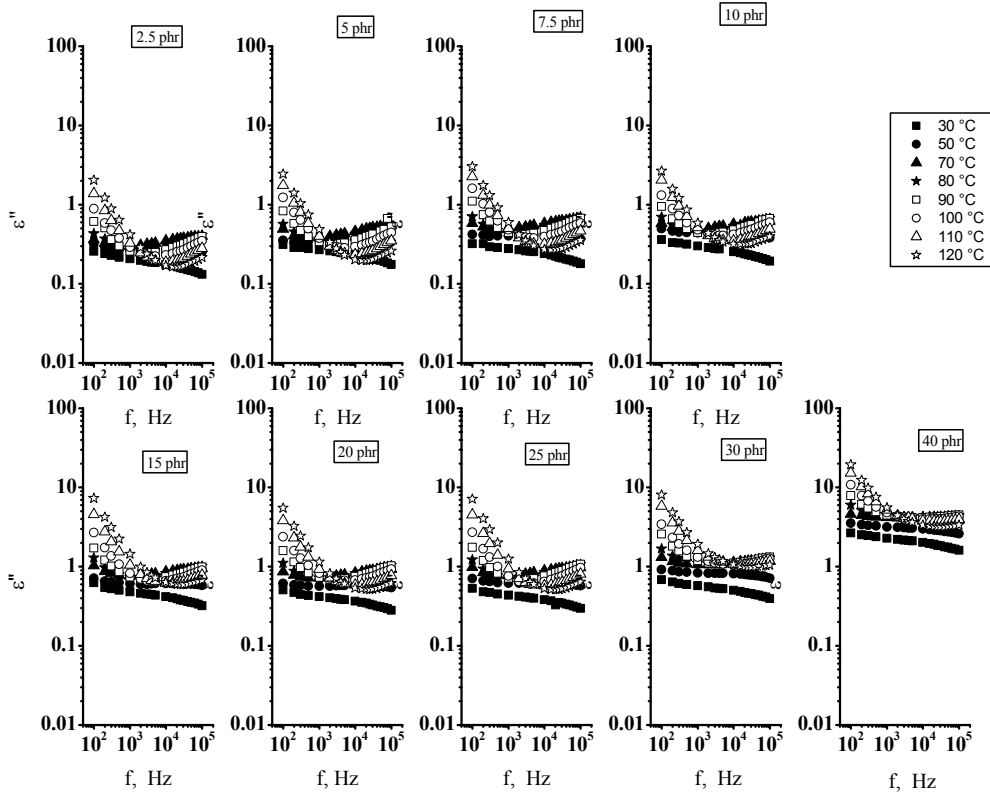


Figure (1b) The dielectric loss versus the applied frequency at different temperatures for PVC/HAF Composites with various HAF Content

increasing HAF content. This increase is found to be much more pronounced at certain concentration that may ascribe the network formation after the percolation threshold, which will be discussed later. From Figure (1b) one can notice that the dc conductivity makes a significant contribution to the apparent dielectric loss measured. The instrument cannot distinguish between the true dielectric loss and the loss due to dc transport processes. However, this distinction is vital for the interpretation of the physical processes involved [7,8], particularly in the cases, where the concentration of conducting particles is high. For such reason the obtained data was done in terms of superposition of a Fröhlich term and a Havriliak-Nagami function in addition to the conductivity term [9].

I) Conductivity term,

The dielectric loss due to dc conductivity, ϵ''_{σ} , at the different frequencies ω were calculated using the equation: [9]



$$\varepsilon''_{\sigma} = \frac{9 \times 10^{11} \times 4 \pi \sigma}{\omega}$$

II) Fröhlich equation

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

Where P_i is a parameter describing the width of distribution of relaxation times and equals $\ln(\tau_1 / \tau_2)$. $\bar{\tau}$ is the mean relaxation time and equals $(\tau_1 \tau_2)^{1/2}$. ε'' is the dielectric loss, while ε_s and ε_{∞} are the static permittivity and the permittivity at infinite frequency, respectively.

III) Havriliak-Nagami function

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

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 (which are found to be constants for these samples and equals to 0.35 and 0.70 respectively). ε_s and ε_{∞} are the static permittivity and the permittivity at infinite frequency, ω is the applied frequency = $2 \pi f$, while τ is the relaxation time. An example of analyses was given in Figure (2).

The low frequency region is detected with relaxation time τ_1 in the range $4-6.5 \times 10^{-4}$ s. This region is found to be unaffected by either temperature or filler content. This region could be attributed to Maxwell-Wagner effect [10] that is expected to be at a lower frequency range due to the multi-constituents of the investigated systems. The second absorption region with relaxation time in the order of 10^{-5} s, which is fitted by Havriliak-Nagami function with $\alpha = 0.5$ and $\beta = 0.5$ could be attributed to the combination of the large scale mobilization of the chains i.e the glass rubber relaxation process in addition to a contribution of the motion of the large aggregates caused by the movement of the main chain, which are expected to be formed by the addition of different ingredients to PVC such as plasticizer,....etc. The obtained relaxation time τ_2 associated with this region was illustrated graphically in Figure (3) versus HAF content at different temperatures.

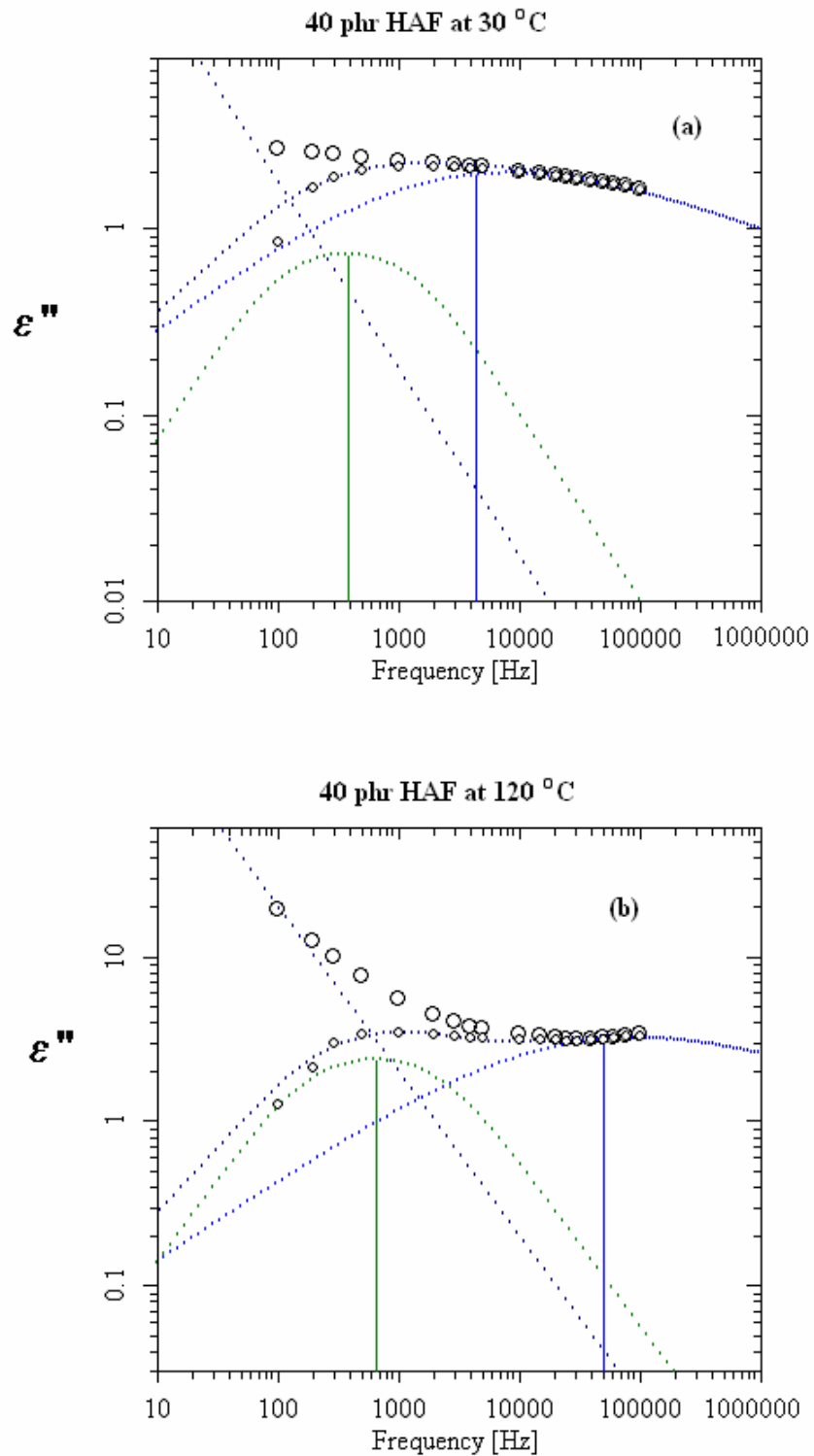


Figure (2) Example of the analyses for PVC / HAF composites with 40 phr HAF at (a) 30 °C and (b) 120 °C. Fitting the experimental data after subtraction of the losses due to dc conductivity with Froehlich term and a Havriliak Nagami function.

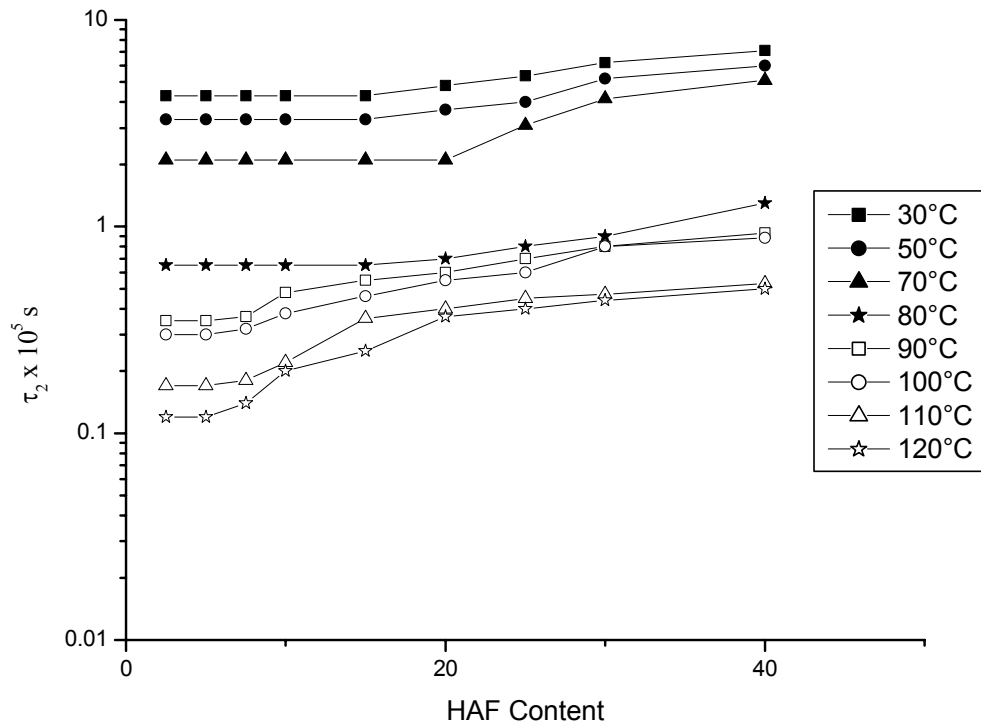


Figure (3) The obtained relaxation time τ_2 vs. HAF content at different temperatures.

From this Figure one can observe that at temperatures below the glass temperature T_g , the relaxation time τ_2 is found to be unaffected by increasing the filler loading upto 20 phr after which it begin to increase dramatically. For temperatures higher than T_g , the abrupt increase is noticed after 15 phr HAF.

The variation of ϵ'' versus the temperature, the isochrones temperature scans, were illustrated graphically at two fixed frequency 100 Hz and 50 kHz in Figure (4). From this figure on can see that ϵ'' increases by increasing temperature at 100 Hz. This increase may be due to the highly dc conductivity in the dielectric loss values. On the other hand the variation of ϵ'' with temperature at $f = 50$ kHz shows a broad peak. This result is considered to be a good evidence for the presence of superimposed processes due to the orientation of the main chain and its related motions which may be attributed to the large scale mobilization of the chains i.e. the glass rubber relaxation which expected to appear at ($\approx 87^\circ\text{C}$) [5]. In addition to the glass rubber relaxation process, a

contribution of the side chain motion may be present as the spectra are broad.

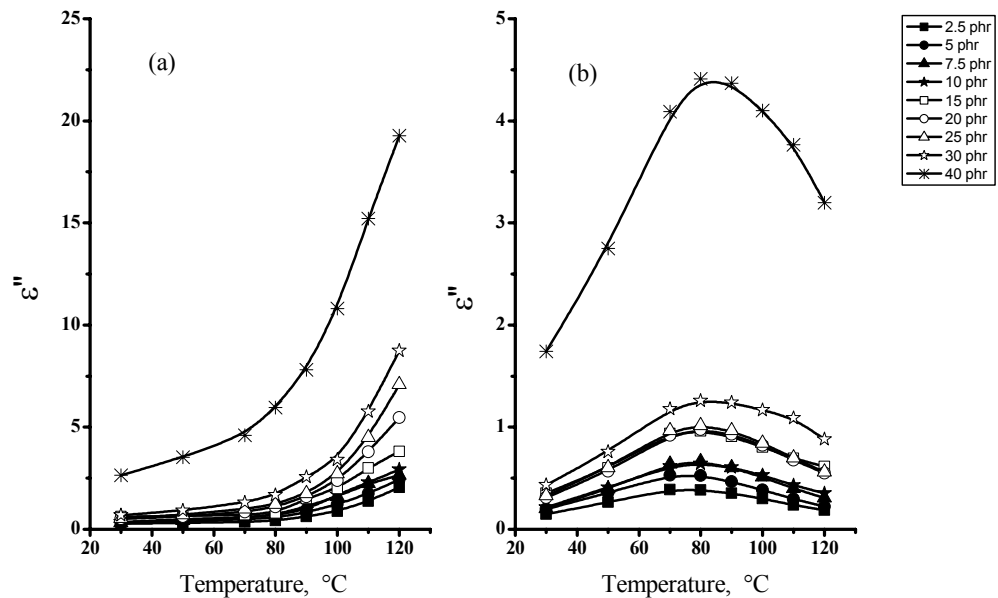


Figure (4) The dielectric loss ϵ'' versus temperature at two fixed frequencies (a) 100 Hz and (b) 50 kHz for PVC/HAF composites with various HAF contents.

The variation of the electrical conductivity σ_{dc} , with filler content is illustrated graphically in Figure (5) at different temperatures. It was observed that, when the quantity of filler was less than 25 phr for temperatures lower than 90 °C and 15 phr for temperatures higher than 90 °C, the conductivity of the composites was slightly increase by increasing filler content. However, beyond the certain critical filler loading a significant increase in conductivity was observed. In this region a relatively small increase in filler loading produced a large increase in conductivity. This region of rapid conductivity increase is called the percolation region.

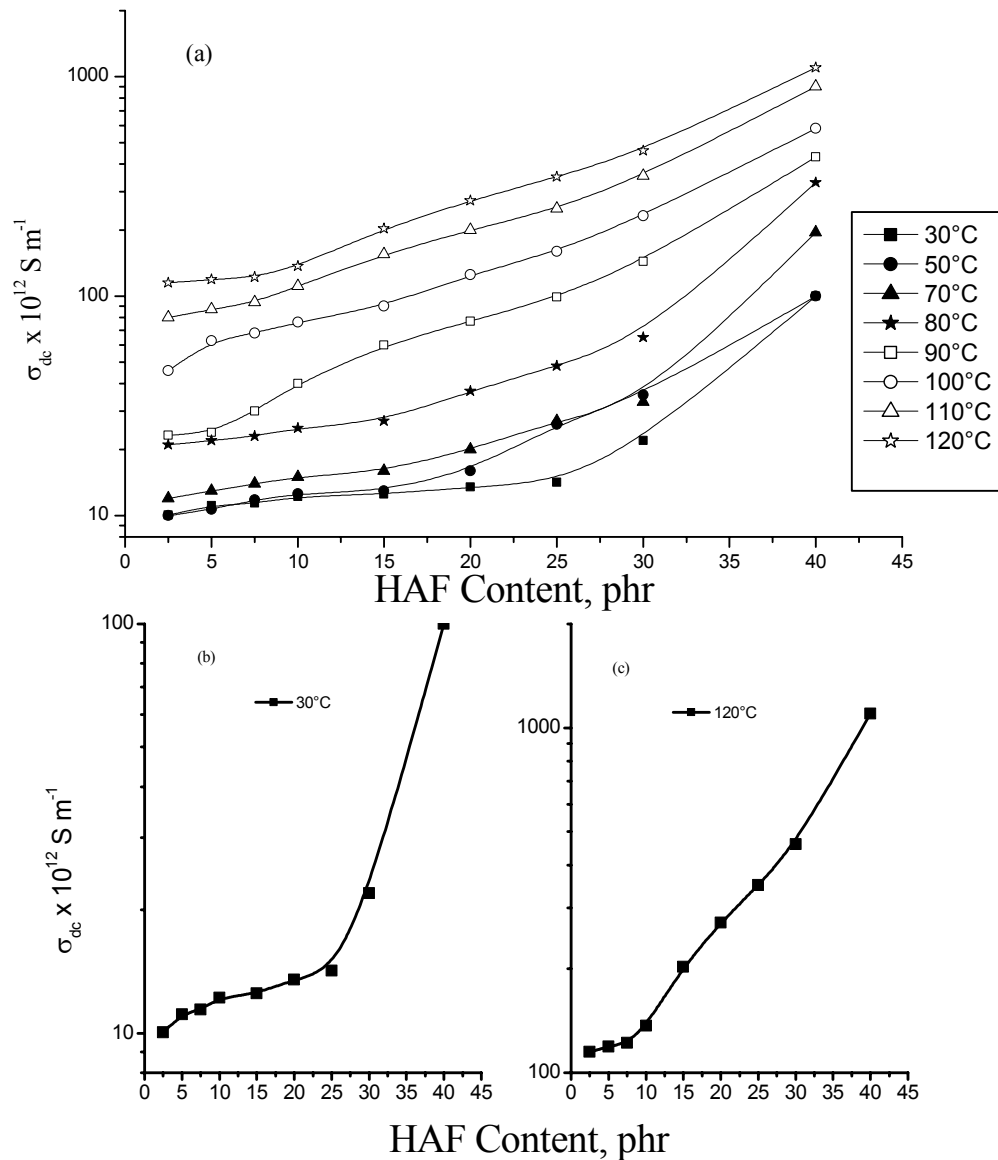


Figure (5) The variation of dc conductivity σ_{dc} versus HAF content (a) at different temperatures, (b) at 30 °C and (c) at 120 °C.

Physico-mechanical characteristics

The mechanical properties of PVC/HAF composites at room temperature $25 \approx ^\circ\text{C}$ were studied in terms of stress at yield, stress at rupture, and strain at yield and strain at rupture. The obtained data are illustrated graphically in Figure (6) versus HAF content. PVC is considered to be non-self-reinforcing polymer and HAF is regarded as reinforcing filler. From this figure it is clear that there is no noticeable

change in the mechanical properties by the addition of HAF up to a concentration of 10 phr after that the values of mechanical parameters begin to increase rapidly uptill 30 phr, after which leveling off (one can see no significant increase in the mechanical properties).

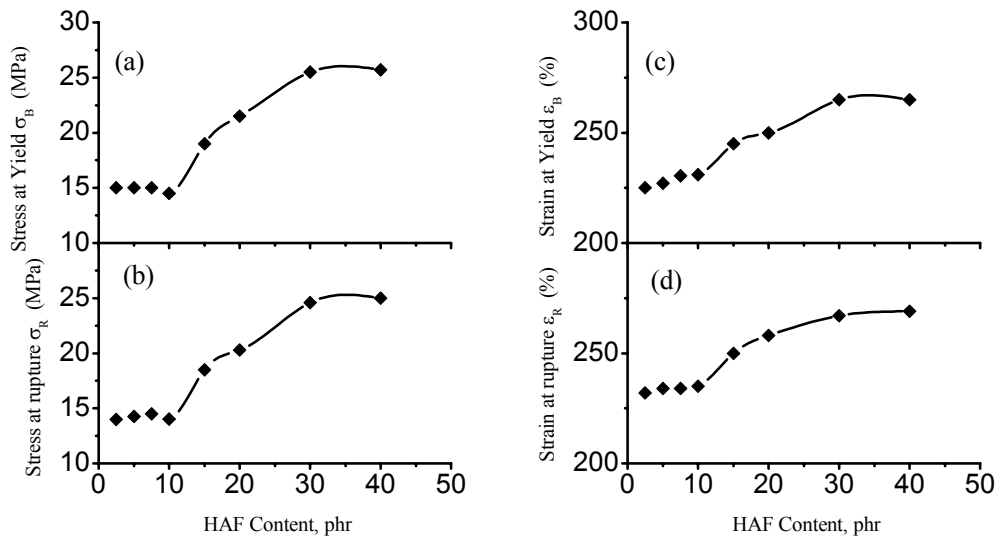


Figure (6) Mechanical properties versus HAF content at room temperature.

(a) stress at yield σ_B ,

(b) stress at rupture σ_R ,

(c) strain at yield ϵ_B ,

(d) strain at rupture ϵ_R .

The increase in such properties may be due to the reinforcement efficiency of HAF beside the formation of physical bonds between PVC chain and HAF particles.

Stress is related to the energy required to deform and fracture the polymer chains. The effect of crosslinking density of the composites increases with increase of polymer filler interaction with addition of filler [11]. Thus at low filler loading, the energy required to deform and fracture the polymer chain is less because of lower crosslinking density, whereas at higher filler loading, the energy required to deform and fracture the chain is high. This results in the increase in the mechanical properties with increasing filler loading.

The strain at rupture increase with increase filler loading this increase can be explained by the following mechanisms: at low filler loading; the rubber chains are entrapped in the pores of the HAF, a phenomenon termed polymer occlusion, which increases the effective volume fraction of filler. With further increase in the filler loading other than occlusion, the polymer chains form a thin immobilized layer, called



polymer shell, around the filler aggregates, which is responsible for the further increase in strain at rupture.

Figure (7) represents the variation of Young's modulus and Shore A hardness versus HAF content at room temperature $\approx 25^\circ\text{C}$. From this figure it is clear that the two properties follows the same trend as the other mechanical properties.

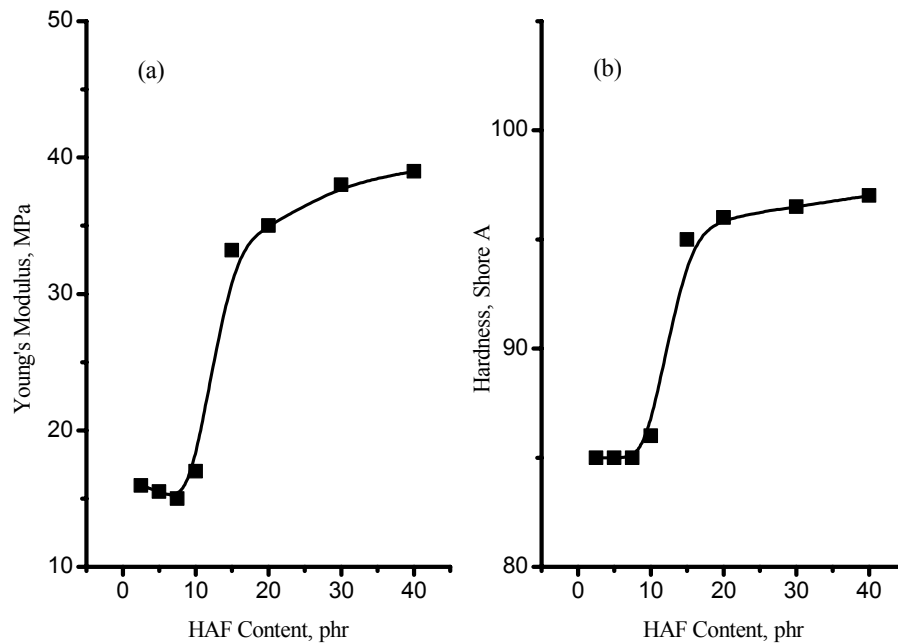


Figure (7) The variation of (a) Young's Modulus and (b) Shore A hardness versus HAF content at room temperature.

The stress-strain plots of different PVC/HAF composites at room temperature $25 \approx ^\circ\text{C}$ are plotted in figure (8). From this figure one can see that stress increases by increasing strain in all the investigated composites; this increase is highly pronounced after 10 phr filler loading. Also it is clear that after 30 phr no significant change was noticed by increasing filler content. This behavior may be due to the reinforcing effect of HAF for PVC matrix.

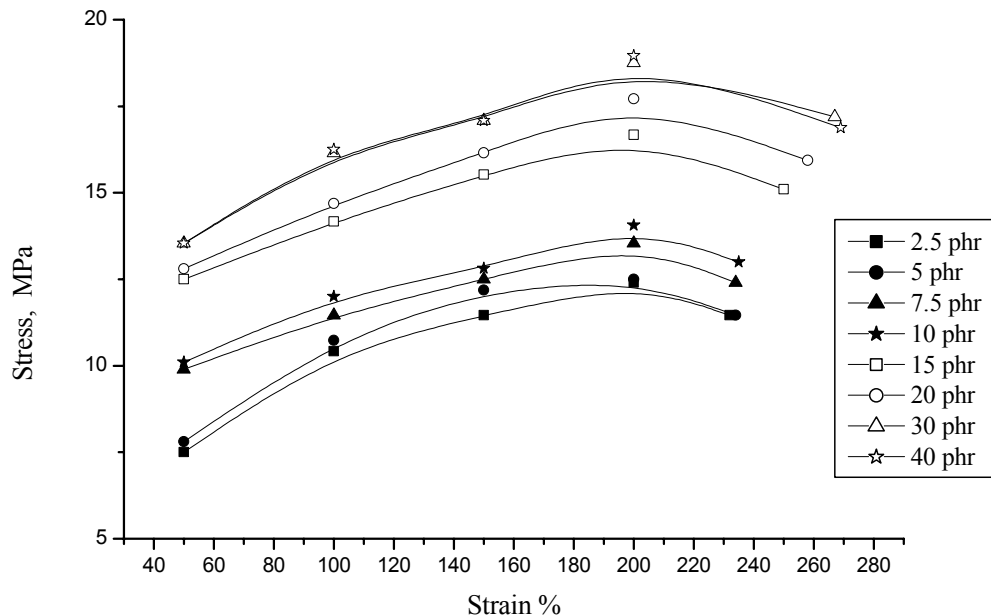


Figure (8) The stress-strain plots of different PVC/HAF composites at room temperature.

Conclusion

From the above study it could be concluded that:

- The percolation threshold concentration which is the concentration after which the conductivity increases many orders of magnitude with very little increase in the filler amount PVC/HAF composites depends upon the measuring temperature whether it is below or above the glass transition of the polymer matrix.
- The addition of HAF black by concentration up to 40 phr rise up the electrical conductivity to be in the order of $10^{-10} \text{ S m}^{-1}$ at 30°C and 10^{-9} S m^{-1} at 120°C which highly recommend such composites to be use in antistatic applications as suitable range of electrical conductivity for such application is $10^{-9} - 10^{-14} \text{ S m}^{-1}$.
- Stress-Strain plot, hardness, other mechanical properties such as stress at yield, stress at rupture, and strain at yield and strain at rupture was also investigated at room temperature. This investigation led to the conclusion that all the mechanical



properties are improved by increasing HAF content and reaches its optimum values at about 30 phr HAF loading.

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