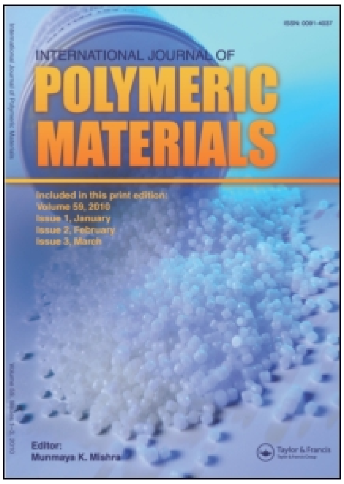

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# Electrical and Mechanical Properties of Some Composites with Polymeric Matrix

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# Electrical and Mechanical Properties of Some Composites with Polymeric Matrix

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The present study aims to investigate the dielectric properties as well as the mechanical properties of polymethyl methacrylate-carbon black and polyester-carbon black composites using semi-reinforcing furnace (SRF) and high abrasion furnace (HAF) carbon blacks.

The permittivity $\varepsilon'$ was found to increase by increasing carbon black content and showed anomalous dispersion. The absorption spectra ($\varepsilon''$ *vs.* frequency) from 100 Hz to 10 MHz were analyzed using a computer program based on Fröhlich terms. Four absorption regions were obtained for either the polymer matrix or loaded samples.

The first region in the lower frequency range could be attributed to Maxwell – Wagner effect resulting from the differences in the conductivities of the ingredients of the composite. The second and third regions in the higher frequency range could be attributed to the large and small aggregates caused by movements of the main chain. The fourth region may occur due to segmental rotation (ester group or carbonyl group) or local twisting motion of the main chain. At higher carbon black concentration, the relaxation time for different regions except that for Maxwell – Wagner effect became higher and carbon black seems to interact with the polymer matrix giving rise to large aggregates resulting high relaxation times.

The mechanical properties for the investigated samples were also examined, the results showed that the tensile strength is higher in the case of smaller particle size carbon black HAF. This could be attributed to a good incorporation of carbon black of small particle size into the polymer matrix. Also, the morphology study indicates the presence of aggregates and some arrangements on adding carbon black.

*Keywords:* Electrical properties; Mechanical properties; Composites; Polymethyl methacrylate; Carbon black

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*Corresponding author.

## INTRODUCTION

The dielectric, electrical and mechanical properties are of such obvious interest to plastic technologists, as well as chemists and physicists. The dielectric relaxation and dynamic mechanical relaxation behaviour of polymers has its origin in the various types of molecular moments undergone by the macromolecules. The motion of such species depends not only on the basic structure, steric energy barriers or inter-chain forces of each molecule, but also on inter-chain interaction energies.

Dielectric relaxation spectroscopy is in general a mean to obtain information about the spectrum of polarization fluctuations of a macroscopic sample, which of course originate in the stochastic motion of microscopic polar entities. Thus information can be yielded on microscopic dynamic process, as far as they are related to polarization fluctuations. Dielectric spectroscopy is therefore a method complementary to others, which are specifically sensitive to the fluctuation of other physical quantities, for example of compressibility as revealed in mechanical relaxation. From the combination of those methods one can hope to gain detailed information on micro-dynamics of various materials.

The electrical properties of polymer-carbon black composites have been extensively studied. Only a small part of the published works is dealing with ac properties [1] (conductivity and dielectric properties). The insulator/conductor transition in these composites is often sharp and characterized by a critical carbon black loading, called the threshold percolation concentration.

In its simplest form a filled composite consists of a continuous three dimensional structure matrix infiltrated or impregnated with a second phase filler material [2]. In effect, both the matrix and the filler exist as two separate constituents that do not alloy and (except for a bonding action) do not combine chemically to any significant extent. The matrix is the body constituent, serving to enclose the composite and give it its bulk form. The fibers, particles, laminae, flakes, and fillers are the structure constituents; they determine the internal structure of the composite. Generally, but not always they are the additive phase.

In this study two types of polymeric matrix were used namely, unsaturated polyester (UP), and poly-methyl methacrylate (PMMA), and two types of carbon black as filler were used.

The aim of the present work is to carry out a systematic study on the electrical and mechanical properties of some composites with polymer matrix. The dielectric absorption associated with the different types of molecular relaxation mechanisms is to be defined.

## MATERIALS AND EXPERIMENTAL TECHNIQUES

Polymethyl methacrylate, PMMA, is the more polar structures as a rule inferior in electrical properties. Conventional polymethyl methacrylate, is polymerized at elevated temperature by a free radical initiation. This polymer exhibits about 60% syndiotacticity, it is amorphous.

Polyester is formed by the reaction of dibasic acids saturated or unsaturated with glycols (di/tri/tetrahydric) and then it is mixed with polymerisable monomer. One of the valuable properties of polyester resins is their ability to transform readily from the liquid state to tough, hard and thermoset structure. This is achieved by the addition of a chemical compound known as "curing agent/catalyst/initiator". The function of a catalyst is activated by a compound called "accelerator/activator". In general, curing catalysts can be broadly classified as "coldsetting" and "hot-setting". There is a wide range of compounds that can be used as catalysts and accelerators. In order to obtain polyester resin having a specific characteristics, adjustment is made in the polyester/monomer ratio, inhibitor content, catalyst and accelerator percentage,..., *etc.* The mechanism of curing of polyesters is based on free radical mechanism [3–6].

Fillers are added to reduce cost and shrinkage and also, at the same time, to improve electrical and thermal conductivity properties.

The specifications of the materials used are as follows:

**Methyl methacrylate (MMA)**, $CH_2{=}C(CH_3)CO_2CH_3$, Purity: 99%, Boiling point: 100°C, Refractive index $n_D$: 1.4140, (inhibited with hydroquinone), obtained from Aldrich Chemical Co. Ltd.

**Unsaturated Polyester (UP)** (NCS 901 PA) which is obtained from NCS Resins, and styrene monomer soluble in it (in the molar proportion of 70:30), Low viscosity 300–400 mP, (sp.gr. 1.09–1.11), Geltime, using 2 phr (part per hundred parts of polymer) catalyst is 10–15 minutes.

**Cobalt (II) naphthenate (Co-Naph.)** as accelerator/activator (3% solution in methylene chloride) obtained from Serosyn web. Coating.

**Methyl Ethyl Ketone peroxide (MEK)** as catalyst/initiator (50% solution in diethyl phthalate) obtained from Aldrich Chemical Co. Ltd., sp.gr: 1.17, $n_D$: 1.488.

These were commercial chemicals and were used as received.

**Benzoyl peroxide** Ph.CO.O.O.OC.Ph as catalyst/initiator: 97%, m.p.105°C obtained from Aldrich Chemical Co. Ltd.

Benzoyl peroxide was dissolved in the least amount of chloroform and precipitated in excess methanol. It was then filtered, pressed in filter paper and dried at room temperature, it was kept in small well stoppered bottle.

**Filler** Two types of furnace carbon black were used as filler, namely; Semi-Reinforcing Furnace SRF, N770, and High Abrasion Furnace HAF, N330. They were supplied by TRINCO (Alexandria, Egypt).

The various properties of the used carbon blacks are:

| *Property* | *SRF* | *HAF* |
|---|---|---|
| Particle diameter, nm | 90 | 29 |
| BET surface, $m^2/g$ | 22 | 77 |
| Oil absorption, ml/100 g | 79 | 107 |

The preparation of the investigated samples undergoes different processes, such as pre-polymerization, mixing, curing, casting and annealing. The method of preparation is given in details elsewhere [7].

## Mechanical Tests

The capacity of a material to withstand a static load can be determined by testing that material in tension or compression [8].

Samples of diameter = 10 mm and thickness 20 mm were used all over the study. The tests were carried out using a compression load cell and Instron Universal Testing Machine. This Instron type 1128, has a self calibration done electrically daily before use. The weight of the used load cell was always balanced and also calibrated before any testing. The current or any interference were electronically canceled by zero adjustment of the instrument. The cross head speed was adjusted allover the test to be 5 mm/min with a recording speed of 5 mm/min. The results were recorded automatically as a relation between the applied load and the specimen deformation occurred to the point of specimen failure if it is traced.

### Dielectric Measurements

Measurements of the permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ for the investigated samples were carried out in the frequency range 100 Hz up to 10 MHz. For this wide range of frequency two apparatus were used. A low frequency apparatus, LCR meter, digital bridge type AG-4311 B from Ando Electric Co. Ltd. (Japan) was used for the frequency range 100 Hz to 100 kHz. A circuit magnification meter ($Q$-meter) type TF 1245A with an oscillator type TF 1246 from Marconi Instrument Co. Ltd, (England) was used for frequencies between 50 kHz and 10 MHz.

A guard ring capacitor type NFM5/T from Wissen-schaftlich-Technische-Werkstätten (WTW), Germany, was used for the dielectric measurements. All measurements were carried out at 30°C.

### Morphology Investigation

The morphology, or form and structure, of polymers or composite systems containing polymers, has been under investigation since the establishment of polymer science as distinct field around 1920 [9-13].

Scanning electron microscopy uses a focused electron beam to scan the surface of the sample. Various modes of operation can be used including an emissive and reflective mode, the latter giving a greater depth of field. As the magnification is increased, the depth of focus decreases. Nonconductive samples, which include most polymers, are coated with evaporated heavy metal to make an electrical connection between the sample and the specimen stage.

Our samples were sputtered with a gold film and investigated in a scanning electron microscope type JSMK-20 SEM from JEOL, Japan.

## RESULTS AND DISCUSSION

At first, a preliminary study was carried out to determine the proper concentration of the curing agent/catalyst/initiator that can be used in this study. Two samples with 0.5 and 1% benzoyl peroxide were prepared for PMMA, and three samples with different (Co-Naph. : MEK) ratios (0 : 2, 0.3 : 1 and 0.5 : 2) were prepared for UP.

The dielectric permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ were measured at 30°C for these samples. The results are illustrated graphically against frequency in Figure 1. From Figures 1a and c, it is clear that $\varepsilon'$, in the whole range of the tested frequencies, increases with the increase in curing agent content and shows anomalous dispersion. On the other hand, $\varepsilon''$ spectrum is slightly increased by increasing benzoyl peroxide (Fig. 1b). While for UP, Figure 1d $\varepsilon''$ decreases with the increase of frequency in the low frequency range, as Co-naphthenate content increase, whereas it increases in the higher frequency range.

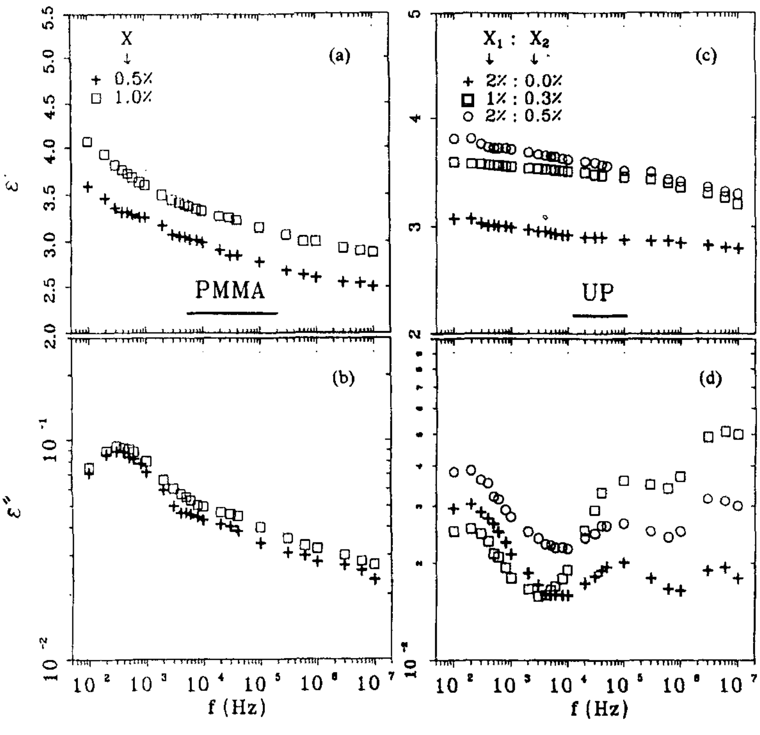

FIGURE 1 The permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ *versus* frequency for the different curing agent concentrations.

The dielectric absorption spectra $\varepsilon''$ $(\omega)$, are broader than a Debye curve, as commonly found for polymers. The data were fitted using a number of Fröhlich terms. Table I gives the analysis results using four Fröhlich terms. The obtained relaxation times $\tau_i$ and the distribution parameters $P_i$ are the same for the two samples, while the dielectric strength $S_i$ increases with the increase of benzoyl peroxide. This indicates that the presence of 1% benzoyl peroxide enhances the PMMA formation. Accordingly, 1% benzoyl peroxide concentration is selected for obtaining all PMMA samples in this study.

The relaxation parameters $\tau_i$ and $S_i$ are given in Table II for the different concentrations of the curing agent for UP. Figure 2 shows the data fitting for UP. From this figure, one can see that, the increase in the accelerator/activator content (cobalt naphthenate), with respect to the catalyst/initiator (MEK), leads to an increase in the individual dielectric loss peaks without any change in their relaxation times. This phenomena may be attributed to the increase in exothermic reactions due to the increase of cobalt naphthenate concentration.

Due to the above results, the sample having the curing agent with the ratio MEK Co Napht. = 1 : 0.3 possesses a low loss in the low frequency region. So this curing agent ratio was used for the

TABLE I Results of analyses for Poly Methyl-Meth-Acrylate [PMMA] at 30°C. $X_B$ is the concentration of benzoyl peroxide, $\tau_i$ ($i = 1$, 2, 3 and 4) the relaxation times in second, $P_i$ the Fröhlich distribution parameters and $S_i$ the relaxation strengths

| $X_B$ [%] | $P_i$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $\tau_1 \times 10^{-4}$[s] | $\tau_2 \times 10^{-5}$[s] | $\tau_3 \times 10^{-7}$[s] | $\tau_4 \times 10^{-8}$[s] |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 3 | 0.219 | 0.084 | 0.060 | 0.056 | 5.40 | 1.35 | 5.80 | 2.18 |
| 1.0 | 3 | 0.234 | 0.098 | 0.070 | 0.062 | 5.40 | 1.35 | 5.80 | 2.18 |

TABLE II Results of analyses for Unsaturated Polyester [UP] at 30°C. $X_M$ is the concentration of methyl ethyl keton peroxide, $X_C$ the concentration of cobalt naphthenate, $\tau_i$ ($i = 1$, 2, 3 and 4) the relaxation times in second, $P_i$ the Fröhlich distribution parameters and $S_i$ the relaxation strengths

| $X_M$ [%] | $X_C$ [%] | $P_i$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $\tau_1 \times 10^{-4}$[s] | $\tau_2 \times 10^{-5}$[s] | $\tau_3 \times 10^{-7}$[s] | $\tau_4 \times 10^{-8}$[s] |
|---|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 0.0 | 3 | 0.072 | 0.029 | 0.046 | 0.048 | 12.55 | 5.24 | 16.38 | 2.90 |
| 1.0 | 0.3 | 3 | 0.062 | 0.023 | 0.085 | 0.128 | 12.55 | 5.24 | 16.38 | 2.55 |
| 2.0 | 0.5 | 3 | 0.092 | 0.042 | 0.060 | 0.081 | 12.55 | 5.02 | 16.38 | 2.90 |

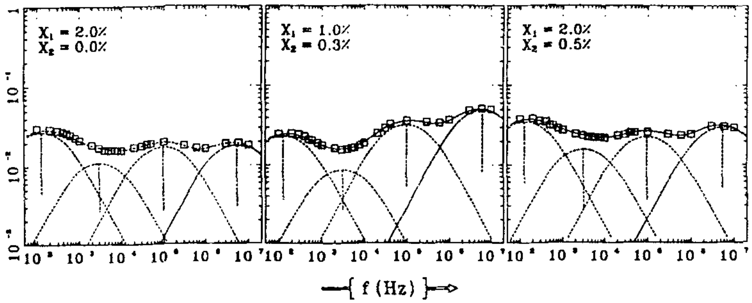

FIGURE 2 Fitting of the experimental $\varepsilon''$ values using four Fröhlich terms. $X_1$ is the concentration of methyl ethyl ketone peroxide, $X_2$ is the concentration of cobalt naphthenate.

preparation of the unsaturated polyester-carbon black composites samples.

### Polymethyl Methacrylate – Carbon Black Composite

Samples having different carbon black contents 0 – 14 phr in steps of 2 phr were prepared. Some mechanical properties as well as the dielectric properties for the samples were investigated.

#### *Mechanical Properties*

The effect of carbon black concentration on both of the tensile strength $\sigma_T$ and compression strength $\sigma_C$ is plotted graphically in Figure 3. It is clear that the tensile strength $\sigma_T$ and compression strength $\sigma_C$ of PMMA were increased by increasing carbon black content to certain concentrations. The obtained results can be separated into two stages, below and above $\cong 5$ phr carbon black content. In the first stage, a combined effect from both the surface area and pores volume is pronounced. HAF has larger surface area and lower pores volume than SRF. So, the added quantity of PMMA is effective in case of SRF which leads to higher values of the measured strengths in this region. The tensile strength is an indicative of crosslink density [14, 15].

For samples having more than 5 phr carbon black, both of the tensile strength and the compression strength are higher in the case

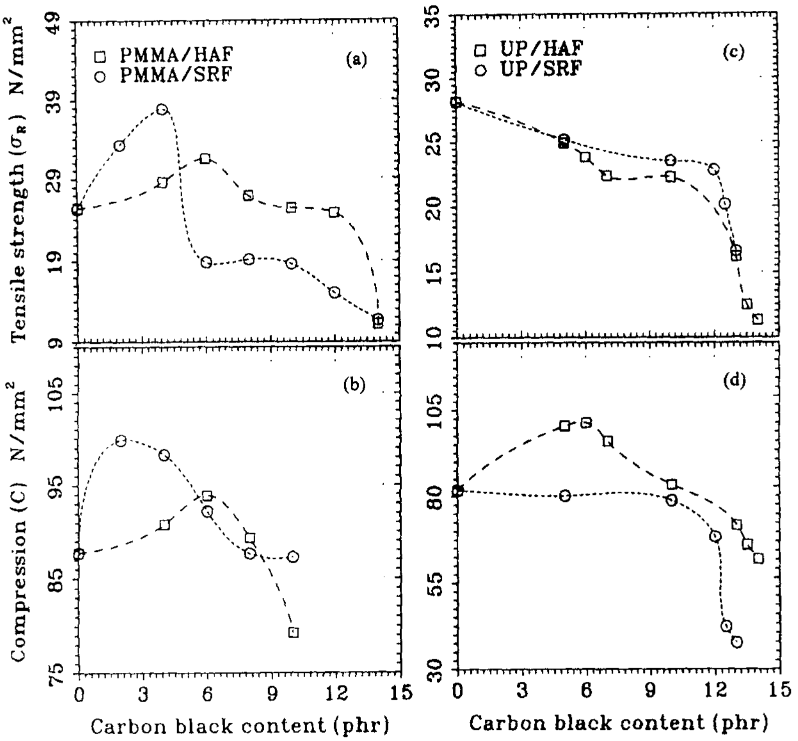

FIGURE 3 The dependence of the tensile strength $\sigma_T$ and compression strength $\sigma_C$ on carbon black content.

of smaller particle size carbon black (HAF). This could be attributed to a good incorporation of carbon black of small particle size into the PMMA matrix at these concentrations.

### Dielectric Properties

The permittivity (dielectric constant) $\varepsilon'$ and the dielectric loss $\varepsilon''$ for PMMA-carbon black samples are displayed in Figures 4a and c. The permittivity ($\varepsilon'$ *vs.* $f$) increases with the increase in carbon black content and shows anomalous dispersion. Figures 4b and d illustrate the dependence of the dielectric loss $\varepsilon''$ on the frequency. $\varepsilon''$ decreases with increasing frequency, whereas it increases as the carbon black content increases.

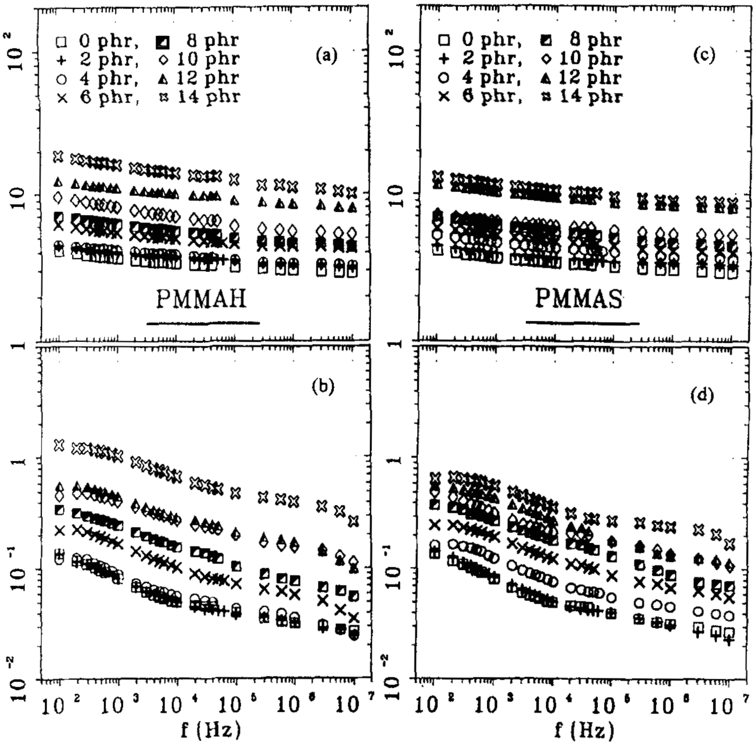

FIGURE 4 The permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ *versus* frequency for polymethyl methacrylate (PMMA) composites.

All absorption spectra $\varepsilon''(\omega)$ are broader than Debye. They were fitted using a computer program based on superimposed Fröhlich terms. The relaxation times $\tau_i$, the Fröhlich distribution parameters $P_i$ and the relaxation strengths $S_i$ obtained by fitting data are given in Table III. Examples for fitting data of the carbon free sample and those loaded with 4, 8 and 12 phr HAF carbon black are displayed in Figure 5.

The low frequency absorption that has a maximum at about 295 Hz for all the concentrations of carbon black, is particularly a Maxwell–Wagner effect ($\varepsilon''_{MW}$). This was confirmed by attempting to measure the d.c. resistance for the samples under investigation. No current was detected when a potential difference of 0–150 V was applied, indicating that there is no d.c. conductivity up to this voltage. Also

TABLE III Results of analyses for Poly Methyl–Meth–Acrylate [PMMA] loaded with two types of carbon black (HAF and SRF) at 30°C. $X$ is the concentrations of the carbon black in phr, $\tau_i$ ($i = 1, 2, 3$ and 4) the relaxation times in second, $P_i$ the Fröhlich distribution parameters and $S_i$ the relaxation strengths. The concentration of benzoial peroxide 1%

| $X$ [*phr*] | $P_i$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $\tau_1 \times 10^{-4}[s]$ | $\tau_2 \times 10^{-5}[s]$ | $\tau_3 \times 10^{-7}[s]$ | $\tau_4 \times 10^{-8}[s]$ |
|---|---|---|---|---|---|---|---|---|---|
| PMMA/HAF | | | | | | | | | |
| 0.0 | 3 | 0.234 | 0.098 | 0.070 | 0.062 | 5.40 | 1.35 | 5.80 | 2.18 |
| 2.0 | 3 | 0.234 | 0.094 | 0.073 | 0.061 | 5.40 | 1.54 | 6.06 | 2.27 |
| 4.0 | 3 | 0.250 | 0.117 | 0.086 | 0.058 | 5.40 | 1.68 | 6.32 | 2.59 |
| 6.0 | 3 | 0.490 | 0.193 | 0.129 | 0.096 | 5.41 | 1.75 | 6.89 | 3.81 |
| 8.0 | 3 | 0.687 | 0.315 | 0.192 | 0.151 | 5.41 | 1.83 | 9.31 | 3.81 |
| 10.0 | 3 | 1.089 | 0.531 | 0.343 | 0.271 | 5.41 | 1.91 | 9.31 | 3.81 |
| 12.0 | 3 | 1.623 | 0.791 | 0.528 | 0.443 | 5.41 | 2.08 | 9.31 | 4.52 |
| 14.0 | 3 | 2.735 | 1.333 | 0.863 | 0.747 | 5.41 | 2.27 | 9.31 | 4.52 |
| PMMA/SRF | | | | | | | | | |
| 0.0 | 3 | 0.234 | 0.098 | 0.070 | 0.062 | 5.40 | 1.35 | 5.80 | 2.18 |
| 2.0 | 3 | 0.239 | 0.094 | 0.073 | 0.055 | 5.41 | 1.54 | 6.60 | 2.59 |
| 4.0 | 3 | 0.357 | 0.146 | 0.102 | 0.087 | 5.41 | 1.68 | 6.89 | 2.59 |
| 6.0 | 3 | 0.540 | 0.250 | 0.158 | 0.134 | 5.41 | 1.75 | 7.19 | 2.59 |
| 8.0 | 3 | 0.781 | 0.361 | 0.229 | 0.177 | 5.40 | 1.83 | 7.51 | 2.59 |
| 10.0 | 3 | 0.883 | 0.447 | 0.331 | 0.256 | 5.40 | 1.83 | 7.51 | 2.59 |
| 12.0 | 3 | 1.237 | 0.572 | 0.437 | 0.337 | 5.40 | 1.99 | 7.51 | 2.59 |
| 14.0 | 3 | 1.488 | 0.687 | 0.558 | 0.431 | 5.41 | 2.27 | 7.51 | 2.59 |

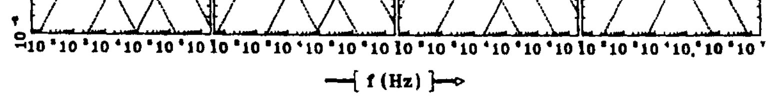

FIGURE 5 Absorption spectra for PMMA samples loaded with different carbon black at 30°C. Fitting of the experimental values using four Fröhlich terms.

good contacts between the samples and the condenser plates was achieved and confirmed. As seen from Figure 5, $\varepsilon''_{\mathrm{MW}}$ increase with increasing HAF content without any change in $f_m$, *i.e.*, no change in the relaxation time. This effect was also found in case of some rubber–carbon black mixes [16, 17].

The second absorption region in the higher frequency range whose relaxation time is found to be in the order of $10^{-5}$ s, could be attributed to the large aggregates or agglomerates due to the presence of carbon black which is a conductive filler. It was found that $\tau_2$ slightly increases with the increase of carbon black content.

The third absorption region could associated with the small aggregates due to dipole rotations caused by movements of the main chain. The higher relaxation time value estimated at high carbon black content could be due to an interaction which may takes place between poly methyl methacrylate and the carbon black.

Comparing the obtained results of the relaxation times in this region ($\tau_3$) for the two types of carbon black, it is clear that HAF carbon black creates bigger aggregates at higher concentrations than SRF carbon black.

There was a fourth absorption region whose relaxation time is found to be $2.18 \times 10^{-8}$ s for the free carbon black sample, and $2.59 \times 10^{-8}$ s for the other samples loaded with carbon black. This region could be caused by segmental rotation or local twisting motion of the main chain.

Heijboer *et al.* [18] carried out a theoretical molecular mechanisms study on rotational motions of side group in PMMA and have partly confirmed that the $\beta$-maximum is due to reorientation of the ester side group. They also revealed the existence of a significant contribution of the main chain units to the intramolecular barrier. Also, Ribes–Greus *et al.* [19] found that the apparent activation energy of $\beta$-relaxation has smooth energy distribution which may be associated with intermolecular interactions that contribute to this relaxation. Thus, the fourth absorption region may be caused by a rotational movements of the ester side chain (—$COOCH_3$—) around the C—C main chain bond. The ester group in poly methyl methacrylate, can not rotate freely in the solid about the C—C bond which links it to the main chain because of the large inter- and intra-molecular forces. As a result of this, the side group has different energies in different rotational positions.

## Unsaturated Polyester–Carbon Black Composite

Unsaturated polyester samples loaded with different concentrations of carbon black (HAF, SRF) were prepared. The carbon black content was increased from 5 up to 7 and 12.5 phr for HAF and SRF, respectively.

### Mechanical Properties

The tensile strength $\sigma_T$ as well as the compression strength $\sigma_C$ of unsaturated polyester–carbon black composite samples loaded with different carbon black concentrations was measured. The obtained data is displayed in Figure 3. It is clear that $\sigma_T$ decreases slightly at first then sharply on adding carbon black.

On the other hand, the compression strength $\sigma_C$, is higher for samples containing HAF than those with SRF. This could be attributed to the good incorporation of the smaller particle size HAF carbon black into the polymer matrix (unsaturated polyester). Also, the obtained results indicate that carbon black does not affect the cross-linking but it share as a reinforcing agent.

### Dielectric Properties

Figure 6 illustrates graphically the data obtained for the permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$, for UP-carbon black composite at different frequencies.

Figures 6a and c show that the permittivity $\varepsilon'$ in the whole frequency range increases with the increase in the carbon black content and shows anomalous dispersion. This behaviour is similar to that obtained for PMMA composite.

Figures 6b and d show the absorption curves relating $\varepsilon''$ as function of the frequency $f$. The data were fitted in the same way as in the case of PMMA–carbon black composites by a number of Fröhlich terms. The relaxation times $\tau_i$ and the corresponding distribution parameters $P_i$ are given in Table IV.

From the analysis of the curves the first absorption region which has a maximum at about 127 Hz with relaxation time $\tau_1$, is expected to be due to Maxwell–Wagner effect as no indication for the direct current was seen to flow through the samples under investigation and consequently no d.c. conductivities are present.

The second absorption region in the higher frequency range could be attributed to the large aggregates or agglomerates resulting from the addition of carbon black to the matrix of unsaturated polyester (UP).

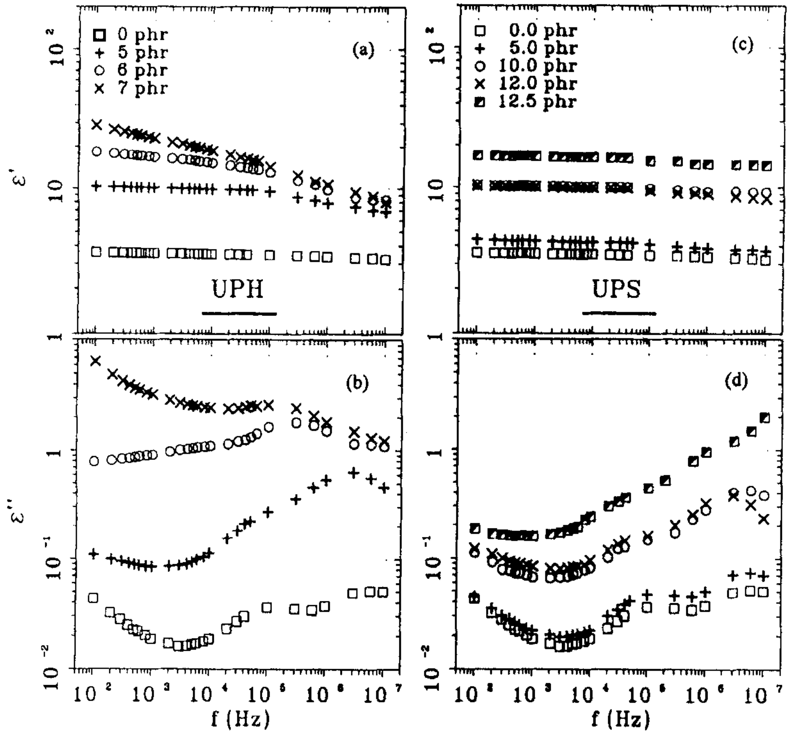

FIGURE 6 The permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ *versus* frequency for unsaturated polyester composites.

TABLE IV Results of analyses for Unsaturated Polyester [UP] loaded with two types of carbon black (HAF and SRF) at 30°C. $X$ is the concentrations of the carbon black in phr, $\tau_i$ ($i=1$, 2, 3 and 4) the relaxation times in second, $P_i$ the Fröhlich distribution parameters and $S_i$ the relaxation strengths. The concentration of methyl ethyl keton peroxide 1% and the concentration of cobalt naththenate 0.3%

| $X$ [*phr*] | $P_i$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $\tau_1 \times 10^{-4}[s]$ | $\tau_2 \times 10^{-5}[s]$ | $\tau_3 \times 10^{-7}[s]$ | $\tau_4 \times 10^{-8}[s]$ |
|---|---|---|---|---|---|---|---|---|---|
| UP/HAF | | | | | | | | | |
| 0.0 | 3 | 0.062 | 0.023 | 0.085 | 0.128 | 12.55 | 5.24 | 16.38 | 2.55 |
| 5.0 | 3 | 0.211 | 0.139 | 0.502 | 1.540 | 12.55 | 5.47 | 16.30 | 5.30 |
| 6.0 | 3 | 1.602 | 2.010 | 3.216 | 2.536 | 12.55 | 5.47 | 16.30 | 6.57 |
| 7.0 | 3 | 10.106 | 4.858 | 5.503 | 3.868 | 12.55 | 5.47 | 16.30 | 8.15 |
| UP/SRF | | | | | | | | | |
| 0.0 | 3 | 0.062 | 0.023 | 0.085 | 0.128 | 12.55 | 5.24 | 16.38 | 2.55 |
| 5.0 | 3 | 0.066 | 0.030 | 0.099 | 0.185 | 12.50 | 6.23 | 16.38 | 2.78 |
| 10.0 | 3 | 0.170 | 0.109 | 0.307 | 1.065 | 12.50 | 6.23 | 19.46 | 3.16 |
| 12.0 | 3 | 0.225 | 0.127 | 0.327 | 1.065 | 12.50 | 6.23 | 21.20 | 4.09 |
| 12.5 | 3 | 0.356 | 0.265 | 0.820 | 3.026 | 12.50 | 6.23 | 21.20 | 5.08 |

The third absorption region could be associated with the small aggregates due to dipole rotations caused by movements of the main chain. The relaxation time associated with that region is found to be increased for higher carbon black content. This result could be a good support for the interaction may take place between unsaturated polyester and carbon black.

The fourth absorption region may be due to relaxation which can occur by segmental rotation or local twisting motion of the main chain. This may be assigned to the carbonyl group ($C{=}O$) rotation hindered by the crosslinker styrene phenyl group.

It is clear that the polymer matrix, unsaturated polyester accepted higher concentrations of SRF (12.5 phr) than HAF (7phr). This may be due to the nature of the carbon black type. HAF is more conductive than SRF. Also, the surface area of HAF particles are larger than those of SRF.

To declare the role of carbon black in the dynamic properties of the investigated composite samples, the relaxation strength $S_i$ was plotted as a function of carbon content in Figure 7. It is obvious that the effect of carbon black differs from one polymer matrix to the other.

For polymethyl methacrylate matrix, carbon black is more effective in the first absorption region with relaxation strength $S_1$. The rate of effect is in the sequence $S_1 > S_2 > S_3 > S_4$. This supports the discussion suggested earlier to interpret the four relaxation processes taking place in case of PMMA–carbon black composite.

For unsaturated polyester matrix, carbon black affect the four relaxation processes in no sequence at higher concentrations. This is in agreement with the findings of Jelcic *et al.* [20] who reported that the electrical properties of unsaturated polyester resins are mainly determined by inter and intra-molecular hydrogen bonds.

Generally, it is obvious that unsaturated polyester–carbon black composite samples posses higher relaxation times than those for PMMA–carbon black composite samples. This could be due to the polymer matrix structure. PMMA has a linear structure while unsaturated polyester has a three dimensional network [2]. Thereof, it was easy to prepare and measure the mechanical and electrical properties of samples having larger carbon content for PMMA–HAF system, whereas only small amount of carbon black for UP–carbon black composite could be measurable.

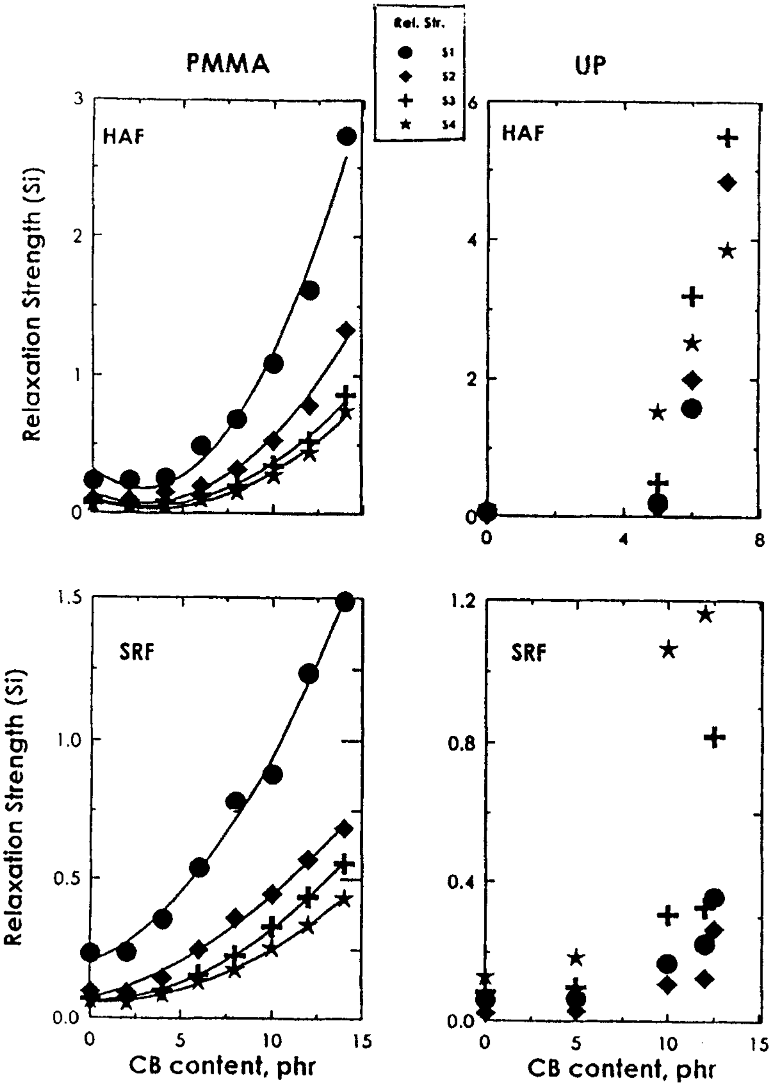

FIGURE 7 The relaxation strengths $S_i$ dependence on carbon black content.

## Morphological Study

Morphological study was carried out on the samples prepared in this work. The micro-graphs to be presented depict the effects on the resulting morphology of adding carbon black. The polymer matrices illustrated in this section include: polymethyl methacrylate and unsaturated polyester.

Figure 8 is the scanning electron micro-graph of the used polymer matrices. It shows two different structural surface arrangements. The

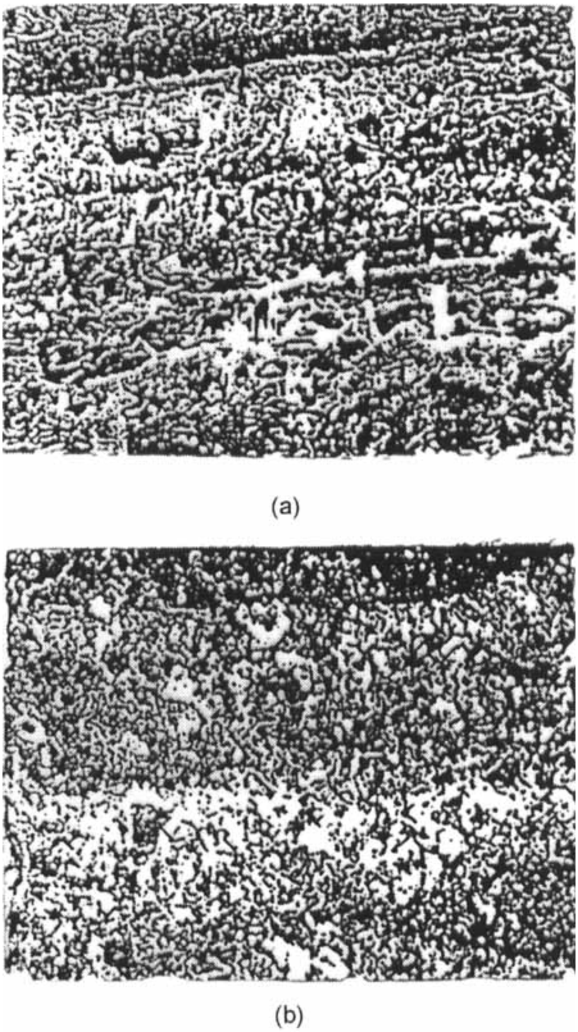

FIGURE 8 Scanning electron micrographs of polymer matrix (X500). (a) Polymethyl methacrylate, (b) Unsaturated polyester.

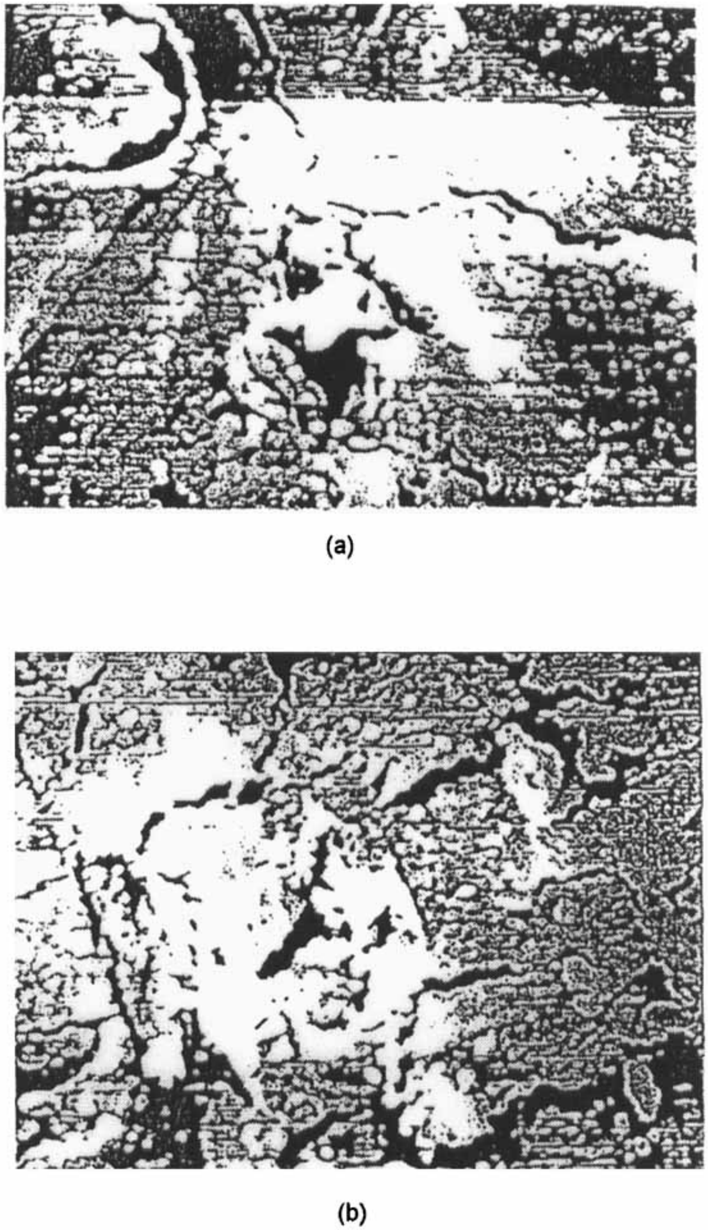

FIGURE 9 Scanning electron micrographs of polymethyl methacrylate loaded with 8 phr (a) and 14 phr, (b) HAF carbon black (X2000).

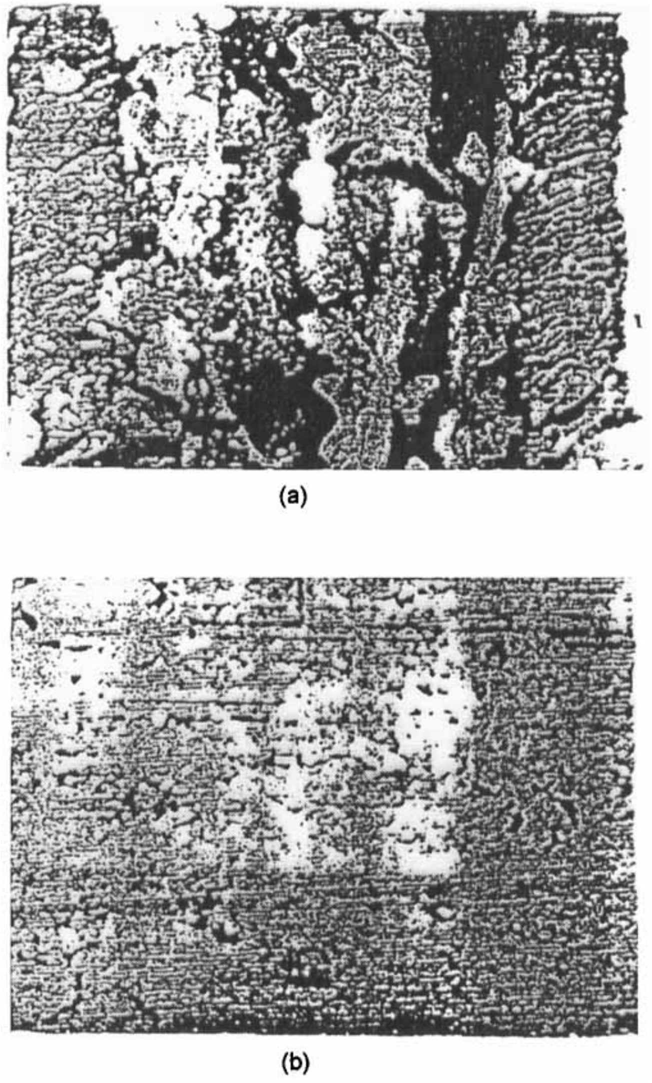

FIGURE 10 Scanning electron micrographs of polymethyl methacrylate loaded with 8 phr (a) and 14 phr, (b) SRF carbon black (X2000).

formation of aggregates was confirmed (Figs. 9 and 10). The observed change in the morphology of the micro-graphs depends on the amount and type of carbon black present.

## CONCLUSIONS

The following conclusion can be drawn from the experiments described herein:

1. The measured mechanical properties, tensile strength as well as the compression strength, reveals that the smaller particle size makes good incorporation in to the polymer matrix rather than the larger particle size one.
2. The dielectric absorption spectra analysis gives four absorption regions. The first, in the low frequency range, could be attributed to the Maxwell–Wagner effect, whereas the second and third terms, in the higher frequency range, may be due to large aggregates or agglomerates and to small aggregates due to dipole rotations caused by movements of the main chain, respectively. The fourth may be associated with the hindered rotational movements of the ester side chain, and the carbonyl group in the polymethyl methacrylate and unsaturated polyester, respectively.
3. The morphology study assure that there is relation between the direction and the degree of the observed arrangement, on one hand, and the carbon black type and content, on the other hand. Also, the formation of aggregates was explored.

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