Effect of Glycol and Filler Types on Some Polymeric Composite Properties

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ABSTRACT: Two unsaturated polyesters based on maleic anhydride, phthalic anhydride, and sebasic acid with each of linear 1,6-hexanediol (PE_L) and cyclic 1,4-cyclohexanediol (PE_C) were prepared. Their structures were characterized by IR and ^1H NMR spectra. Their composites were prepared by mixing different ratios (60, 70, and 80%) with talc and kaolin with polyester/styrene mixture. The effect of linear and cyclic glycols and the effect of filler type and concentration of these composites were studied in terms of their electrical properties and the hardness before and after aging. The thermal behavior of styrenated polyesters and their composites was studied using thermogravimetric analysis. It has been found that both fillers increase the thermal stability and decrease the weight loss. The permittivity ε' and the dielectric loss ε'' were measured in the frequency range 100 Hz up to 100 kHz at room temperature $25^\circ C \pm 1$. The polyester composite samples containing 70% filler lead to good electrical properties in addition to its resistance to thermal aging. The hardness value was increased by increasing the filler content before and after aging. The polyester composites based on cyclic glycol and loaded with 80% kaolin gave the highest hardness values. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1916–1924, 2008

Key words: polyester composites; fillers; glycol type; aging; TGA; electrical properties

INTRODUCTION

Unsaturated polyesters are widely used because of their low cost, easy processing, low densities, good corrosion resistance, and high strength.[1] They are used in composites for the building industry (e.g., for facade elements, dome light crowns, in the transportation sector) and the electrical industry (e.g., for cable distribution cupboards, for boats and ship building, tanks, tubes, vessels, and others). The effect of the glycol components on the physical and chemical properties of unsaturated polyester castings is as important as that of the other basic constituents, such as dibasic acid and unsaturated monomer.[2,3] The choice of glycols offers great latitude in the design of polymer backbones. Great varieties of glycols are available and are often used in combination. It is important to note that the use of glycols in any application is greatly dependent on the level of crosslinking density of unsaturated polyester styrene mixtures.[4]

However, the typical unsaturated polyester resins are not tough enough, and their impact strength is lower than that of other thermoset polymers like epoxy. Moreover, during the crosslinking process of unsaturated polyesters with vinyl monomers,[5,6] shrin-kage and cracking represent major problems. Therefore, the use of many types of filler comes as essential solution to overcome these problems and also to improve and enhance some characteristics such as electrical and thermal properties and reduce costs. A variety of fillers such as calcium carbonate, silica alumina trihydrate, clay, feldspar mica, etc. were used.[7–11] The various applications of filled polymers are a consequence of the ability of filler to change the structural and technological properties of polymers in a desired way.

The aim of this work is to investigate the electrical, hardness, and thermal properties of the polyester composites in terms of the glycol (linear and cyclic) and filler types and concentrations.

EXPERIMENTAL

Materials

The pure grade of 1,4-cyclohexanediol, 1,6-hexanediol, phthalic anhydride, maleic anhydride, and sebasic acid were obtained from Merck Co (Germany). Also styrene monomer was reagent grade from Merck, Darmstadt, Germany and used as received without further purification.

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The fine grade ($\approx$ 0.5 mm) of talc and kaolin were obtained from El-Nasr Phosphate Co., Egypt with the following specification:

	Components	
	Talc	Kaolin
Loss of ignition	5%	9–13%
SiO_2	60–63%	45–55%
Al_2O_3	Not more than 1.5%	30–36 36%
Fe_2O_3	Not more than 1%	0.5–1.5%
CaO	Not more than 1.5%	0.2–1%
MgO	30–32%	0.2–0.4%

Synthesis of polyester resins

The unsaturated polyester resins based on the reaction of maleic anhydride (0.5 mole), phthalic anhydride (0.25 mole), and sebasic acid (0.25 mole) with each of 1,6-hexanediol (PE_L, 1.05 mole) and with 1,4-cyclohexanediol (PE_C) were prepared by melt condensation method.[12]

The acid/glycol ratio was 1 : 1.05 mole. The reaction mixture was heated in an oil bath at 160–200°C until the acid number reached 33 and 45 mg KOH/g for PE_L and PE_C, respectively. The prepared polyesters resins were heated under vacuum for 30 min to remove water and unreacted monomers.

The physical properties of the prepared polyester resins PE_L and PE_C are listed in Table I.

Curing of the prepared unsaturated polyesters with styrene

The prepared unsaturated polyester resins were diluted with styrene monomer (60 : 40 wt %) in the presence of 1.5% by weight of methyl ethyl ketone peroxide as initiator and 0.5% by weight a solution of 8% cobalt naphthenate in styrene as promoter in all cases. The polyester/styrene mixtures were left at room temperature (25°C) and then at 80°C for 2 h in thermostat oven until curing occurred.

TABLE I
Physical Properties of PE_L and PE_C

Property	PE_L	PE_C
Appearance	White yellow	Pale yellow
Acid value mg KOH/g	33	45
Number average molecular weight (M_n)	1700	1300
Styrene monomer content in resin (by weight)	40%	40%

Preparation of polymeric composites

Polymer composites were prepared by mixing different ratios (wt/wt) of each filler, talc and kaolin (60, 70, and 80%) with polyester/styrene mixture. The prepared samples of appropriate shapes for various measurements were molded in a round glass mold of diameter 55 mm and thickness in the range of 3–3.5 mm, and cured at the same conditions as styrenated polyesters. The tests were carried out for both aged and unaged ones.

Techniques

The infrared spectra were recorded on a JASCOFT/IR 300 E Fourier Transform Infrared Spectrometer (Japan).

The nuclear magnetic resonance (^{1}H NMR) spectrum was run at 260 MCPS on a Jeol-Ex-270 NMR Spectrometer.

Molecular weight determination was done by gel permeation chromatography (GPC). This was carried out using Agilent Technologies Walden Bornn, Germany 1100 series equipped with three Styragel columns (10^2, 10^4, and 10^5 Å) and Refractive Index detector (Agilent G 1362). Tetrahydrofuran was used as an eluent of flow rate of 1 ml min^{-1}. The columns were calibrated by means of polystyrene (an internal standard was used).

Thermogravimetric analysis (TGA) was performed using Shimadzu-TGA-50H analyzer. The samples were heated from 25 to 800°C at a heating rate of 10°C min^{-1}.

Hardness measurements were determined using Wolpert Hardness Tester HT2004, manufactured by Otto Wolpert-Wake GMBH, 1978, Germany, explained in DIN 53456. Average of five samples was taken for the measurements.

Dielectric measurements were carried out at room temperature 25°C $\pm$ 1 and in the frequency range of 100 Hz up to 100 kHz by using an LCR meter type AG-411 B (Ando electric, Japan). The capacitance C and the loss tangent, tan δ, were obtained directly from the bridge from which the permittivity ε' and dielectric loss ε'' were calculated. A guard ring capacitor type NFM/5T Wiss Tech. Werkstatten GMBH Germany was used as a measuring cell. The cell was calibrated by using standard materials[13] and the experimental error in ε' and ε'' was found to be $\pm$3% and $\pm$5%, respectively.

To study the aging properties of the styrenated polyester and their composites, samples were aged in an air oven at 90°C for 7 days, and then were conditioned at ambient temperature for at least 16 h before hardness and electrical tests.
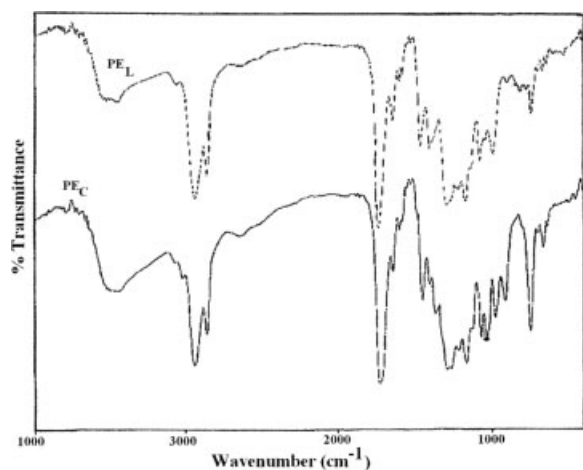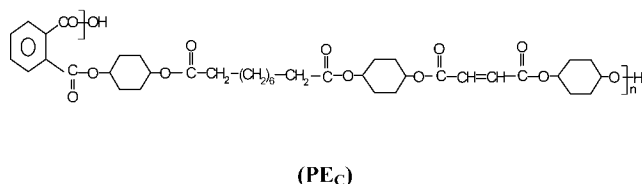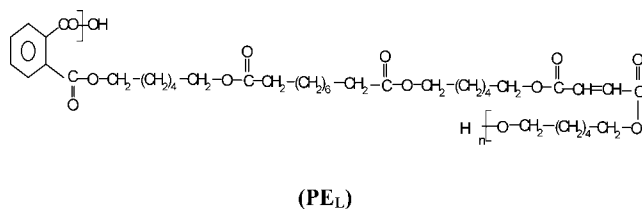
Figure 1 The IR spectra of polyesters PE$_L$ and PE$_C$.

RESULTS AND DISCUSSION

Identification of PE$_L$ and PE$_C$

The structure of the prepared unsaturated polyester resins (PE$_L$ and PE$_C$) was established via IR and ^{1}HNMR spectra.

(PE$_L$)

(PE$_C$)

The important bands in their IR spectra were detected from Figure 1 and listed in Table II. It was shown that the spectra of PE$_L$ and PE$_C$ are quite similar to each other.

TABLE II
The Main Absorption Bands Detected From IR Spectra

| Assignment	Absorption (cm^{-1})	
	PE$_L$	PE$_C$
Stretching OH terminal hydroxyl and stretching OH terminal carboxyl	3448	3787–3433.8
Stretching CH aromatic and olefinic	2935, 2859	2943, 2863
Stretching C=O ester	1728 strong	1724
Stretching C=C olefinic	1643, 1601, 1581	1643, 1603
Stretching C—O=C= ether	1165	1165
Trans-=CH=CH bending	986	980
Cis-olefnic & aromatic residues	647, 674, 745	672, 754
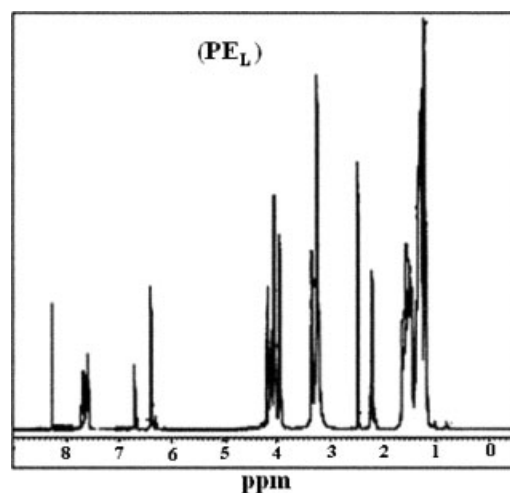
Figure 2 The ^{1}H NMR spectrum of polyester PE$_L$.

The ^{1}H NMR spectra of PE$_L$ and PE$_C$ shown in Figures 2 and 3, respectively, indicate the presence of similar bands. A multiplet between δ 7.3 and 7.6 ppm corresponding to four aromatic protons of phthalic anhydride in the acid backbone. The unsymmetrical signals at δ 6.5–6.7 seem to be two ill-defined doublet for the olefinic proton —CH=CH— in the maleic–fumaric acid residue.[14] The multiplet between δ 3.1 and 3.3 ppm indicates the presence of four terminal protons of sebasic acid residue those adjacent to carbonyl group O=C—CH$_2$- - - -CH$_2$—C=O. Two groups of bands between δ 1 and 2.4 ppm are due to internal methylene protons of the four of 1,6-hexanediol and four 1,4-cyclohexanediol —(CH$_2$)$_4$— and four of sebasic acid —(CH$_2$)$_6$—. The figure also indicates the presence of two multiplets between δ 3.9 and 4.3 due to the two methylene protons —O—CH$_2$- - - CH$_2$—O— of hexane diol residue.
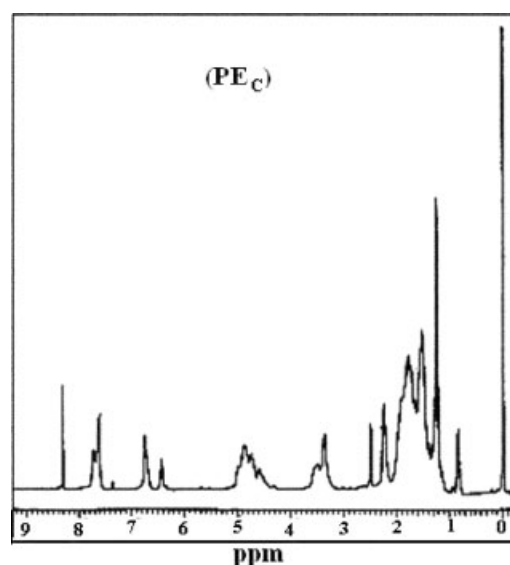

Figure 3 The ^{1}H NMR spectrum of polyester PE$_C$.
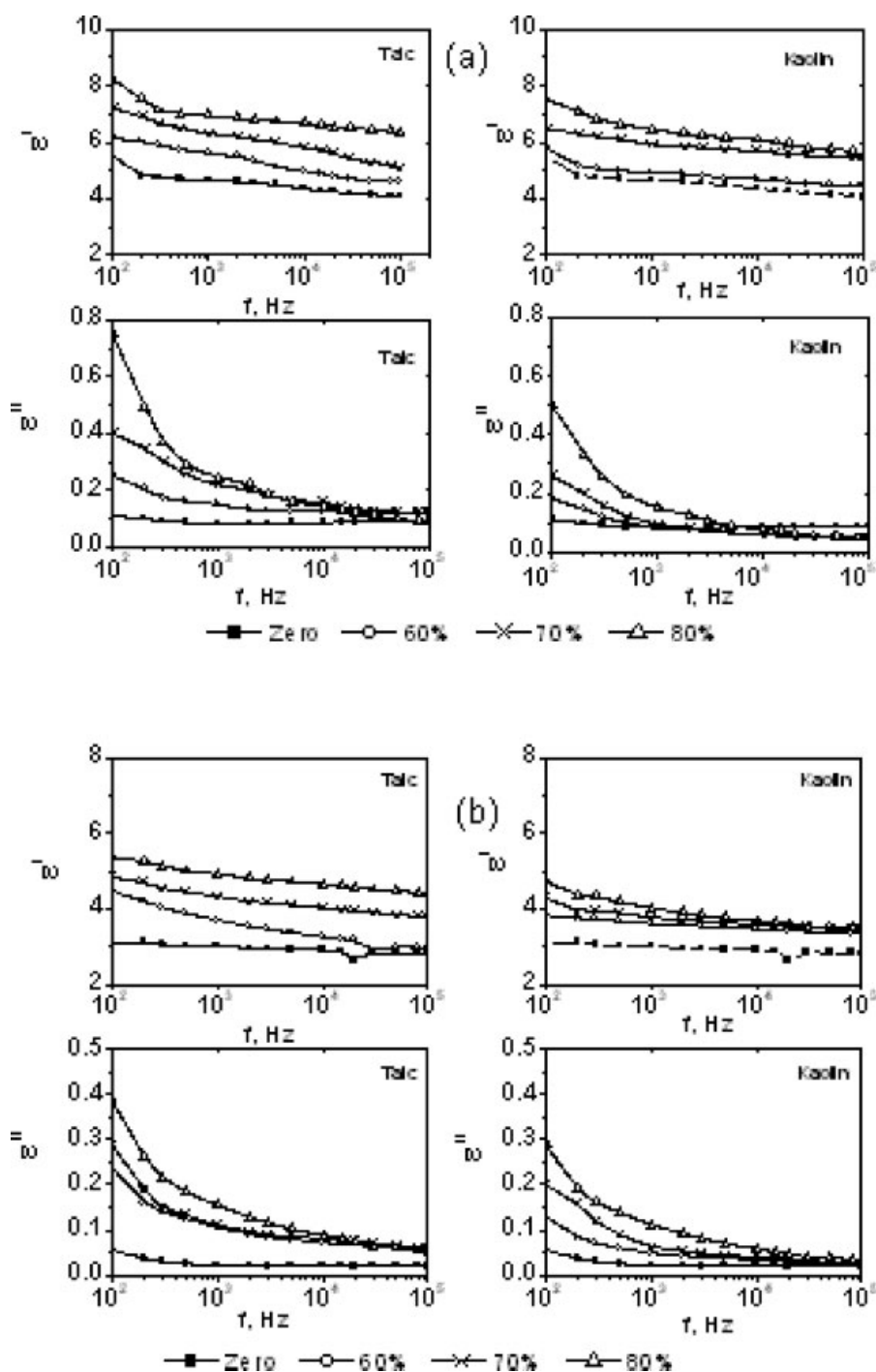
Figure 4 Permittivity ε' and dielectric loss ε'' at different frequencies for styrenated polyester [(a) PE_L and (b) PE_C] loaded with different percentages of filler before aging.

The exceptional band found at 4.9 ppm represented in Figure 3 is due to two methine protons of 1,4-cyclohexanediol —CH—.

Electrical properties

The permittivity ε' and the dielectric loss ε'' were measured in the frequency range of 100 Hz to 100 kHz at room temperature 25°C $\pm$ 1 for PE_L and PE_C

loaded with talc or kaolin with concentrations ranging from 60 to 80%. The data obtained were illustrated graphically in Figure 4. The figure shows that ε' increases by increasing the filler content whereas it decreases by increasing the applied frequency showing anomalous dispersion.

It was also noticed that the values of ε'' increased by increasing filler content for both PE_L and PE_C. Also the values of ε'' in the lower frequency range

are higher. These higher values may be due to either d.c. conductivity δ[15] resulting from the increase in ion mobility or Maxwell Wagner effect as an a.c. current is in phase with the applied potential or both.

To discuss the relaxation mechanism associated with such dispersion, the dielectric loss values ε'' are plotted graphically versus the applied frequency (f), as shown in Figure 4.

It is noticeable that the curves relating ε' and ε'' and the applied frequency (Fig. 4) are broader than one Debye curve indicating more than one relaxation mechanism. These mechanisms ascribe the rotation of the main chain and its related motions.[16] In addition to the conductivity term, the analysis of the absorption curves relating ε'' and the applied frequency after subtracting the conductivity term was done in terms of superposition of one Fröhlich and a Havriliak–Negami functions according to the equations:

d.c. conductivity ε''_σ:

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

Fröhlich function:

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

P_i is a parameter describing the width of distribution of relaxation times and equals $\ln(\tau_1/\tau_2)$. τ_i 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.

Havriliak–Negami function:

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

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. ε_s and ε_∞ are the static permittivity and the permittivity at infinite frequency, ω is the applied frequency $= 2\pi f$, and τ is the relaxation time.

Example of the analyses for styrenated PE_C before and after aging is given in Figure 5. The first absorption region that lies in the lower frequency range and fitted by Fröhlich function gives a relaxation time about 2.8–3.2×10^{-4} s may be attributed to Maxwell Wagner effect, which always appears in such range of frequency due to the multiconstituents of the sample. This region is found to be unaffected by the filler content. The second absorption region at the higher frequency range with relaxation time τ_2 is

found to be in the order of 10^{-5} s, which is fitted by Havriliak–Negami function and could be attributed to the orientation of the large aggregates caused by the movement of the main chain.

To compare between the styrenated polyesters (PE_L and PE_C) loaded with either talc or kaolin, the permittivity ε' and the dielectric loss ε'' at constant frequency $f = 100$ Hz were plotted as a function of filler content before aging (Fig. 6). From this figure it was noticed that both ε' and ε'':

• Increase by increasing filler content.
• Are higher for PE_L when compared with those for PE_C, which is an expected result as the dipole moment of the linear diol is higher than that of cyclic one.
• Are higher in the case of talc when compared with those for kaolin, which may be attributed to the difference in constituents and nature of both fillers.
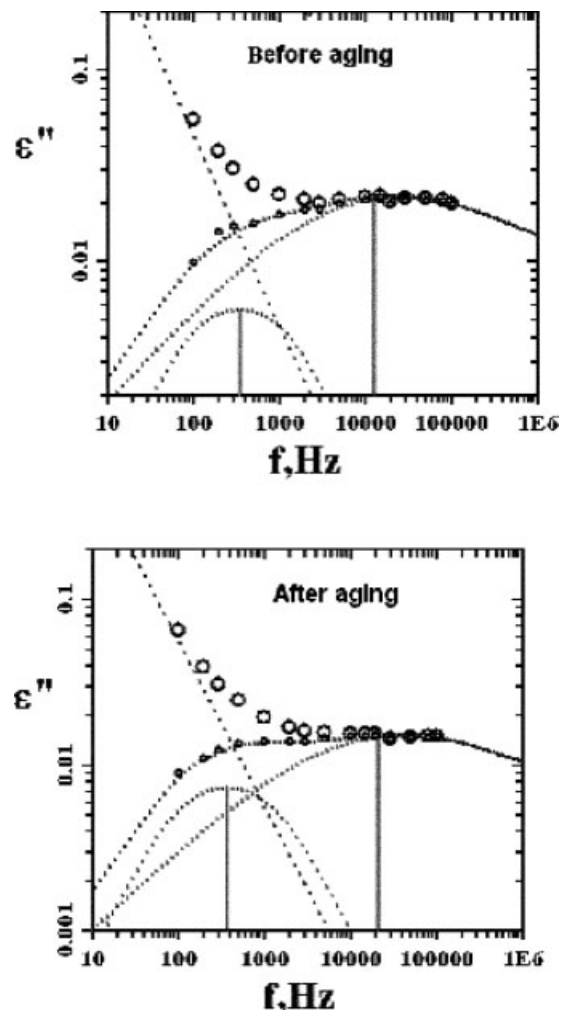

Figure 5 Example of the analyses for styrenated polyester (PE_C) before and after aging. Fitting the experimental data after subtraction of the losses due to d.c. conductivity with Fröhlich term and a Havriliak Nagemi function.
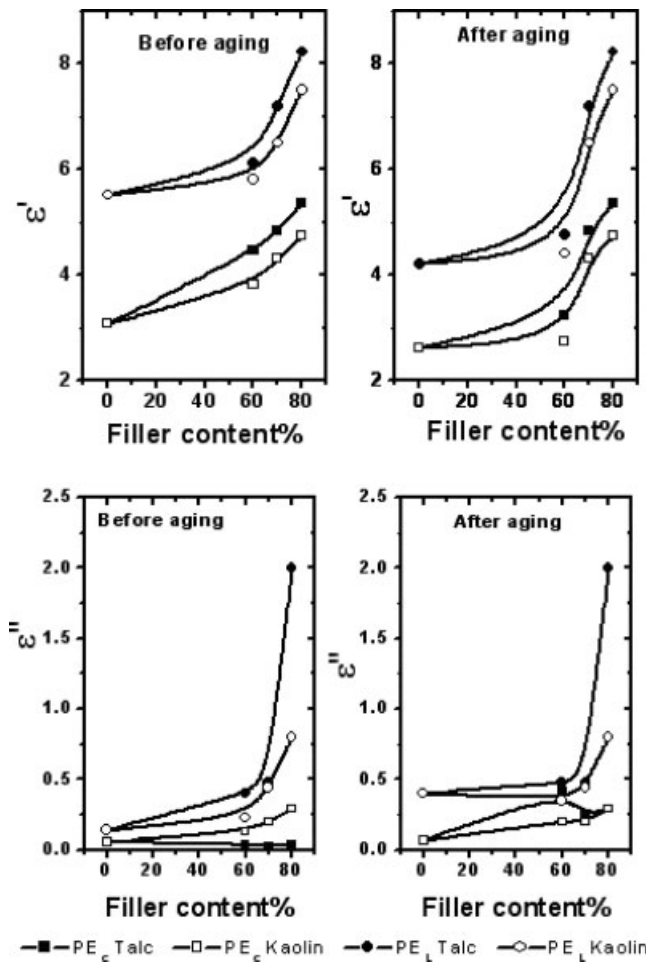
Figure 6 Variation of the permittivity ε' and dielectric loss ε'' versus the filler content of styrenated PE_L and PE_C at 100 Hz.

Also the conductivity (δ) and the relaxation time (τ_2) against the filler content are presented in Figure 7. From this figure it is seen that:

- The conductivity (δ) of the composites increases by increasing filler content, which may be due to the increase in the mobility of polar groups.
- The δ values for composites containing talc are higher than those containing kaolin.
- The relaxation time τ_2 increases by increasing filler content. This increase indicates filler–polymer interaction, which led to an increase in the molar volume of the rotating units and consequently increases the relaxation time.
- The relaxation time τ_2 detected in case of PE_C composites is higher than those for PE_L composites. This is due to the larger volume of the cyclic diol when compared with linear one.

Effect of aging

The permittivity ε' and the dielectric loss ε'' were measured in the frequency range of 100 Hz up to

100 kHz for PE_L and PE_C loaded with either talc or kaolin with concentrations ranging from 60 to 80% after exposing to thermal aging for 7 days at 90°C. The obtained data are illustrated graphically in Figure 8. Comparing Figure 4 (a,b) with Figure 8 (a,b) it is clear that the values of both ε' and ε'' for PE_L and PE_C and those loaded with either talc or kaolin with concentration 60% are affected negatively by thermal aging while other percentages were not.

It is also found from Figure 6 that presents ε' and ε'' versus filler content at frequency 100 Hz, no significant change was observed in the values for the composites containing 70 and 80% talc and kaolin, while ε' decreases and ε'' increase for polyesters free from fillers and those containing 60% filler.

In the same manner, the conductivity (δ) increases and the relaxation time (τ_2) decreases for both polyesters free from fillers and those contains 60% fillers when compared with those before aging, see Figure 7. This decrease indicates that some sort of degradation
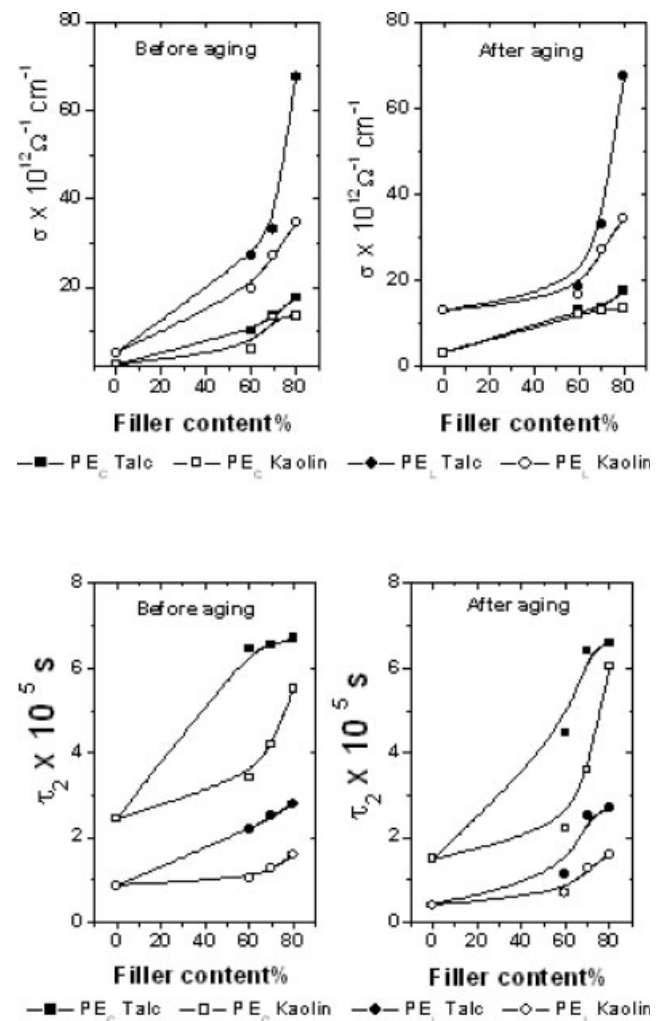

Figure 7 Variation of the conductivity (σ) and the second relaxation time (τ_2) versus the filler content of styrenated PE_L and PE_C.
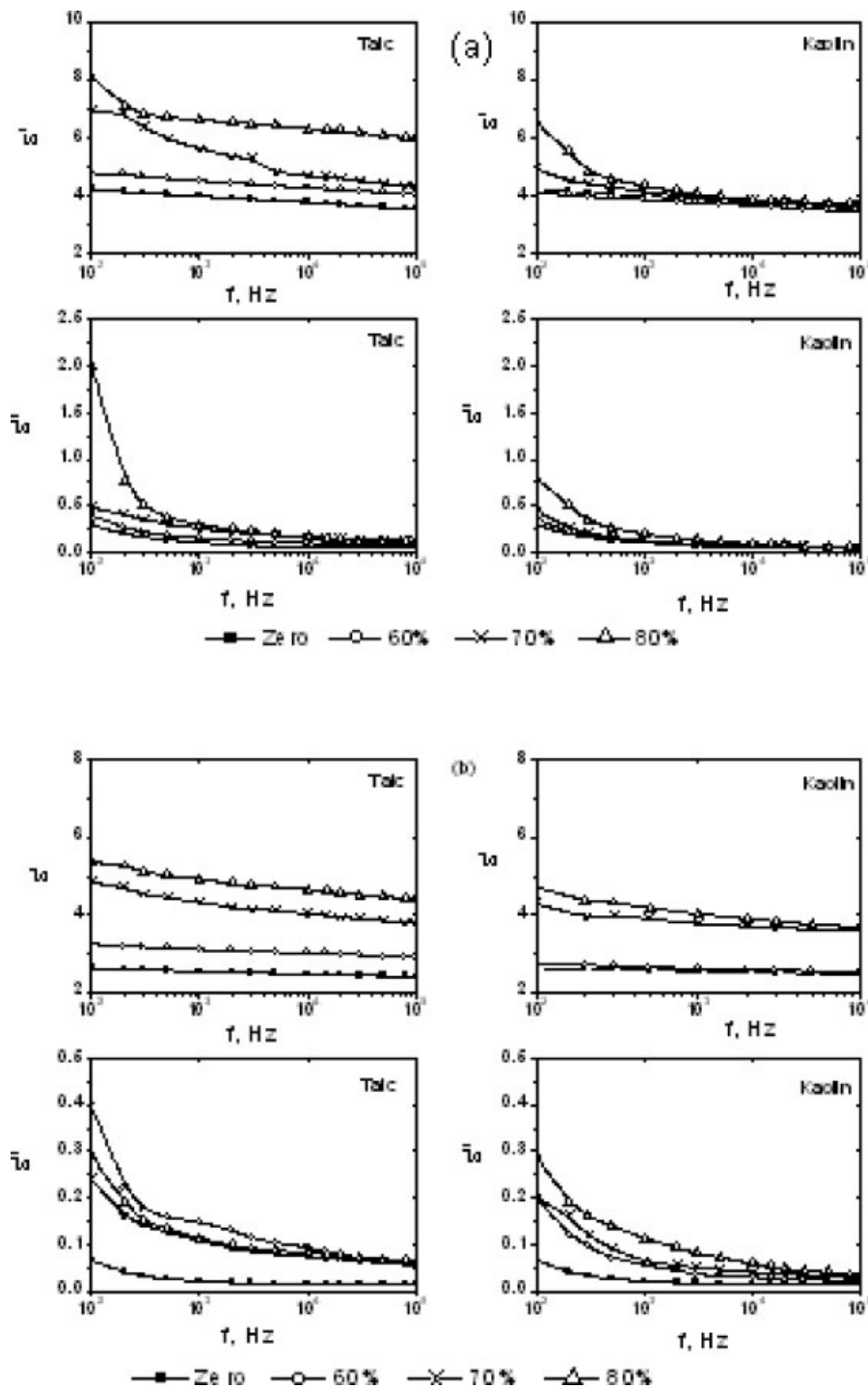
Figure 8 Permittivity ε' and dielectric loss ε'' at different frequencies for styrenated polyesters [(a) PE_L and (b) PE_C] loaded with different percentages of filler after aging.

could be happened by thermal aging for these samples. On the other hand, no significant change in either δ or τ_2 was observed for composites containing higher values of filler. This indicates that both talc and kaolin at higher concentration (70 and 80%) are characterized by thermal stability leading to high resistance to thermal aging.

These results leads to the conclusion that the most recommended composites for electrical insulating

purposes are those containing 70% of either talc or kaolin for the two polyesters under investigation. For such reason this ratio was chosen in TGA.

Thermal stability

To asses the thermal stability, TGA was performed for the styrenated polyesters (PE_L, PE_C) and their polymeric composites containing 70% fillers (talc

TABLE III
Thermal Degradation of Polyester Composites

Samples	T_{max}	Char yield % at 450°C
PE_L	339	2
PE_L/talc	402	70
PE_L/kaolin	400	70.3
PE_C	345	10.87
PE_C/talc	347	71.03
PE_C/kaolin	347	70.69

Figure 10 TGA curves of styrenated PE_C and its composites loaded with 70% fillers.

and kaolin). The temperature rate of maximum decomposition (T_{max}) and the char yield were listed in Table III. Figures 9 and 10 show only one degradation step for all samples, corresponding to a number of reactions leading to monomer units until the styrenated polyester volatilize completely. The char yield was 2 and 11% for unloaded PE_L, PE_C, and about 70 and 71% for their composites loaded with 70% filler, respectively. After this degradation step a thermal stability was observed between 450 and 800°C for composite samples loaded with both fillers, i.e., it does not lose weight, and a stable residue was formed corresponding to the filler content. It was also noticed that PE_L based on linear glycol and its polymeric composites are more stable than PE_C based on cyclic glycol and its polymeric composites, i.e., the stability increased with the length of carbon chain and the straight chain of glycol.[17,18] It is clear that the presences of fillers increase the thermal stability of polymeric composites. The char yield of composites was found to be higher than those of unfilled polyesters at higher temperatures.

Hardness

The hardness tests were done for the styrenated polyesters (PE_L, PE_C) and their composites before and after aging. Figure 11 indicates that among the two fillers used (kaolin and talc) the hardness values increased by increasing filler contents of polyester
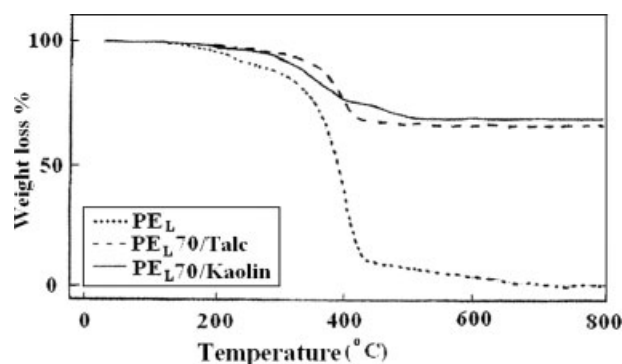
composites PE_L and PE_C. This result is expected as more filler is incorporated into the matrix the more the rigid composites obtained. It was also observed that the values of PE_C based on cyclic glycol and its composites were higher than those of PE_L based on linear glycol and the highest one was with PE_C containing 80% kaolin. The study also showed that the same trend after aging was occurred and the values were to some extent higher. This indicates that further curing may be occurred.

CONCLUSIONS

- The type of the glycol plays a role in the properties of the resulting polymer, e.g., the linear one (1,6-hexanediol) improves the electrical properties, while the cyclic (1,4-cyclohexanediol) improves the hardness.
- ε' and ε'' increase by increasing the filler content.
- After exposing to thermal aging for 7 days at 90°C, ε' and ε'' were found to be unchanged for

Figure 9 TGA curves of styrenated PE_L and its composites loaded with 70% fillers.

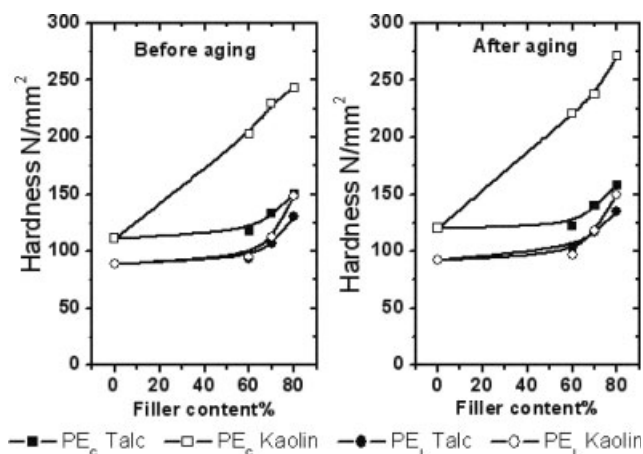**Figure 11** The variation of hardness with filler content for styrenated PE_L and PE_C composites before and after aging.

higher concentrations of both fillers (70 and 80%).

- The presence of both fillers increases the thermal stability of the prepared polyester composite.
- The filler type and concentration affect the hardness before and after aging. The highest value was with PE$_C$ containing 80% kaolin before and after aging.

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