Evolutions of Microstructure and Dielectric Behavior of Epoxy Based Insulator-Insulator Composites over Long Periods of Time

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ABSTRACT: Aging of epoxy based composites used as insulators in the industry are investigated. The analysis of a composite aged for 20 years in actual service conditions points out chemical degradations, a structural recovery, a tendency for particle debonding from the polymer matrix and with respect to the unaged sample, and no significant changes in the permittivity values measured at 50°C. To understand this latter result, a purely physical aging was carried out on fresh composites with similar formulation as the insulator aged 20 years in service. A detailed analysis of the changes in properties during physical aging is proposed.

It is concluded that the constant ε' value at 50°C found for the 20 years aged composite results from two opposite phenomena: an increase in the relative dipole amount due to structural recovery and/or the presence of polar species at the polymer/filler interface that both increase ε' and the loss of polar species in the bulk that decreases the ε'. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3454–3464, 2006

Key words: aging; composite; dielectric properties; interfaces; thermosets

INTRODUCTION

Epoxy based composites are commonly used for insulating applications because of their ability to withstand high electric fields over long periods of time.[1] Nevertheless, the resulting multi-stress constraints generate structural modifications within the insulating parts after a long term in service. Accordingly, the aging of such composites might eventually reduce the reliability of their insulating properties. It seems thus of interest to understand and to predict structural changes of this kind of composites when submitted to high electric fields over long periods.

Because of the low thermal conductivity of polymer networks, the application of high electric fields induces local temperature raises by the Joule effect.[2] Depending on the magnitude of these temperature increases, two kinds of structural modifications of the polymer network might be considered:

1. When the temperature T reached is higher than the glass transition temperature T_g of the polymer, chemical degradations of the polymer might occur, such as chain scissions, formations of polar groups, or recombination of chain segments.[3–7] In addition, degradation mechanisms depend on environmental conditions. For example, Ollier-Dureault and co-workers[6] showed that the superimposition of both electric stress and UV irradiations of epoxy based composites results in generation of carbonyl functions through a decarbonylation of the product stemming from photo-oxidation.

2. For $T < T_g$, the so-called physical aging of the amorphous phase occurs over time, resulting in a densification of the polymer network. The physical aging originates from the metastable state of amorphous materials below T_g. Vitreous materials indeed exhibit enthalpy, entropy, and specific volume excesses with respect to their respective values at the thermodynamic equilibrium for a given temperature. Accordingly, vitreous materials kept at temperatures below T_g tend to reach thermodynamic equilibrium over time. As a result, all thermodynamic parameters (enthalpy, entropy, and specific volume) exhibit a nonlinear decrease as a function of time.[8–10] This evolution is the well-known structural recovery. From a microstructural point of view, physical aging results in a network densification over time and leads to an increase of the brittleness of the material.[11] Because of the difficulty to accurately evaluate changes in specific volume, physical aging is

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usually quantified by calorimetric measurements. As a matter of fact, on the heating run immediately performed after aging, aged vitreous materials display an endothermic peak near T_g, the so-called structural relaxation. Montserrat and colleagues[12] have studied the influence of the aging temperature ($T < T_g$) on the kinetics and magnitude of the enthalpy relaxation phenomenon.

For aging temperatures below but near T_g, macromolecular chains exhibit some mobility and the enthalpy excess shown by the system is weak. Accordingly, the densification of the polymer network quickly occurs and, subsequently, the structural relaxation detected on heating exhibits a weak magnitude. In contrast, for aging temperatures significantly lower than T_g, the molecular mobility of the macromolecules is strongly reduced and the rate of the change in specific volume is slow. For these aging conditions, the magnitude of the endothermic peak is expected to become much larger than that measured for aging temperatures near T_g.

Few investigations[1] are reported in literature concerning the influence of physical aging on the dielectric properties of composite materials. Beyer[13] investigated the dielectric behavior of filled and unfilled epoxy first submitted to high electric fields. According to this author, the dielectric losses increase with the magnitude of the electrical field. This effect is magnified for the unfilled materials. Even if this author did not give a definitive explanation to this evolution, it could be suggested that such an effect rises from the formation of polar groups resulting from chemical degradations of the polymer. However, the possible contribution of physical aging to the changes in material behavior cannot be excluded.

In this article, it is first proposed to investigate the microstructure and electrical properties of a composite used as an insulator in actual service conditions for 20 years, which was submitted over this long time to various stresses. Then, to separate the relative contributions of chemical and physical aging on both microstructure and dielectric behavior, physical aging tests are performed under laboratory conditions on composites with similar compositions.

EXPERIMENTAL

Materials

As received materials

The resin and the hardener in this study were, respectively, a diglycidyl ether of bisphenol A (DGEBA) and an anhydride. Two systems of particle-filled composites were studied (Table I). The so-called C1 material is reinforced by 58.0 ± 0.5 wt % of mineral particles. The

TABLE I
Main Characteristics of the Composite Materials

	C1 M1	C2 M2	C1* M1
- Granulometry	$2–40\mu m$	$3–30\mu m$	$2–40\mu m$
- D50	$6\mu m$	$6.6\mu m$	$6\mu m$
- Graded shape	elongated	irregular	elongated
- wt %	58 ± 0.5	67 ± 0.5	67 ± 0.5

C2 material was processed with 67.0 ± 0.5 wt % of an alternative type of mineral filler, different in shape but similar in chemical nature. It is worth noticing that the chemical nature of the two matrices, somewhat different, leads to slightly different T_g.

Despite the different components (resin, hardener, and fillers), both systems were basically processed by the same way. The inorganic fillers were dried by placing them into an oven at 60°C for 48 h to reduce as much as possible the influence of water. The resin, the hardener, and inorganic materials were then mixed and stirred at 56°C and degasified under vacuum. The mixture was then injected under pressure at the bottom of a vertical mold and underwent the cure process at 140°C for 15 min for both composites C1 and C2. The composites were then post cured 8 h at 140°C and 12 h at 60°C to fulfill the crosslinking reaction.

Aged material under actual service conditions

An insulating material based on the same composite as the "as-received" material C1 but aged 20 years in service was supplied by the Areva T and D. This composite, defined as C1* in the following (Table I), has experienced multi-stresses (electrical, thermal, and mechanical as well as environmental constraints) over this long service period.

Laboratory aging

Physical aging was carried out on the as-received materials, that is, the C1 and C2 composites. The aging temperature was chosen to be Tg-18°C[12] to induce significant physical aging for limited aging periods. Aging was performed in an oven under nitrogen atmosphere to reduce the risk of chemical modifications. For each material, aging periods ranged from 9 h to 6 months. Seven samplings were taken out during these 6 months (Fig. 1).

Methods

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was carried out by using a DSC 7 Perkin–Elmer device. The calorimeter had previously been calibrated with the indium standard. The analysis was then carried out
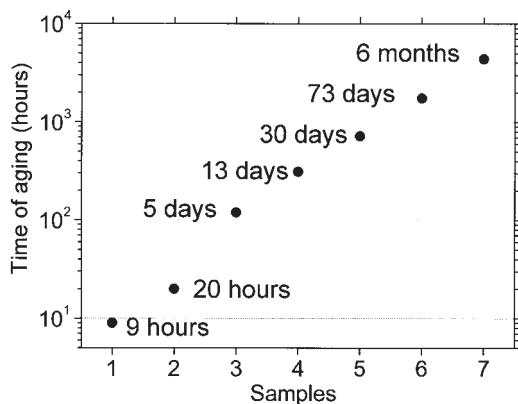
Figure 1 Samples for aging times ranging from 9 h to 6 months.

with samples containing 10 ± 1 mg of polymer. Thermograms were recorded under nitrogen atmosphere from 40°C to 170°C. Heat flows were measured at a heating rate of 10°C/min. For each sample, two successive heating runs were carried out with a 5 min hold stage at 170°C between each scan to erase the previous thermal history. From the thermogram recorded on the first heating run, the enthalpy excess related to the magnitude of the previous physical aging was determined. A second heating run was performed at a heating rate of 10°C/min, to verify that the first heating run followed by the hold stage at 170°C did not induce any chemical degradation. The DSC experiments were carried out twice on each sample (n = 2). In this article, T_g is taken as the onset value at which the thermogram splits from the base line.

Dielectric thermal analysis

Dielectric measurements were performed on parallel-epipedic samples $(25 \times 25 \times 3mm^3)$ under a low electric field by using a dielectric spectrometer (4284A Hewlett–Packard). The principle is to apply a 1V AC voltage to the sample and to record the dielectric permittivity (real (ε') and imaginary (ε'') parts and the loss angle tg $\delta = \varepsilon'' / \varepsilon')$ as a function of temperature and/or frequency. In this article only the ε' variations are reported as a function of temperature and/or frequency.

Analyses were carried out in a frequency range from 100 Hz to 1MHz and for temperatures ranging from 30 to 300°C. For each sample, two successive isochronal scans were performed. Uncertainties in permittivity values mainly result from sample dimension measurements. To avoid surface problems, the samples were metallized by a thin aluminum layer of 1.0 ± 0.2 μm thick by using cathode vaporization treatment.

Scanning electron microscopy

Morphology analysis was performed with the help of a scanning electron microscope Stereoscan 440 Leica. Samples were broken and the surface fracture was covered with a thin gold layer by cathode vaporization. This technique allows detecting some particle debonding tendency from the polymer matrix that could be related to the strength of interactions at the polymer/particle interface.

Dynamic mechanical analysis

Dynamic mechanical analysis was carried out on both the 20 years aged material, C1*, and on the corresponding unaged composite material, C1, to characterize the structural changes that could occur on heating at temperatures higher than T_g.

By using the Rheometric Scientific DMTA MK III analyzer, viscoelastic spectra were recorded from 30 to 300°C, with a heating rate of 1°C/min under nitrogen atmosphere. The device was used in a three point bending mode under isochronal conditions at frequencies of 0.3, 1, 3, and 10 Hz. The samples were 1.5 mm thick, 5 mm wide, and 45 mm long. In this article, only the evolution of the real part of the Young's modulus versus temperature at 10Hz recorded for both materials will be reported.

RESULTS AND DISCUSSION

First, to analyze the resulting effects of multi-stresses undergone by an insulator experienced under actual service conditions over a long time, microstructure and subsequent properties of a composite material aged for 20 years under actual service conditions were investigated.

20 years aged insulator

Microstructure investigated by DSC

Figure 2 shows the thermograms of the 20 years aged material (C1*) recorded on two successive heating runs. For comparison, the thermogram displayed by the as-received material C1 is superimposed.

Aging in actual service conditions leads to the two following effects:

1. On the first heating run, the aged material exhibits a large endothermic peak attributed to the physical aging undergone by the insulator over 20 years.
2. Comparing the thermogram displayed by the aged material on the second heating (rejuvenated sample) to that recorded in the same conditions for the as-received material, it can be observed that T_g of C1* is significantly
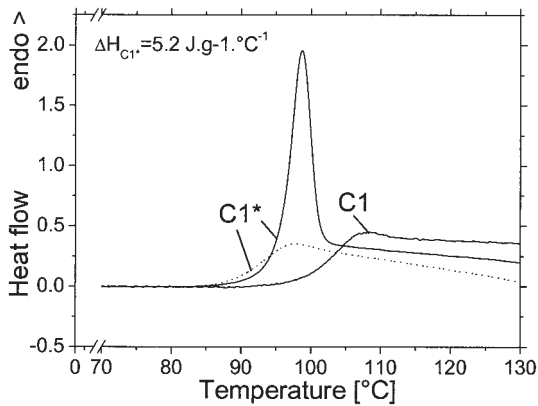
Figure 2 Thermograms recorded for the as-received material, C1 (second heating run), and for the 20-years-aged material, C1*, first (solid lines) and second (dashed line) ramp of temperature.

shifted towards lower temperatures. This behavior can be attributed to some chemical degradations of the polymer network, as, for example, chain scissions or uncrosslinking effects.

To identify the nature of these molecular structure modifications induced by aging, IRFT analyses[3] have been carried out on these samples. Unfortunately, recorded spectra show a low signal magnitude because of the high amount of inorganic particles. Accord-

ingly, it was not possible to accurately evaluate the exact nature of the chemical modifications.

To confirm the above-described structural changes, the microstructure of the epoxy matrix was analyzed in terms of molecular mobility with dynamic mechanical analysis.

Microstructure investigated by dynamic mechanical analysis

Figure 3 shows the plots of the normalized real parts of the Young's modulus E'/E'_0 (where E'_0 is the modulus at 50°C) versus the temperature at 10Hz displayed by the C1 and C1* materials.

The following features can be pointed out:

1. The drop in the modulus characteristic of the main relaxation related to T_g exhibited by the aged composite is shifted towards lower temperatures with respect to that displayed by the as-received material. This is consistent with DSC data, that is, the T_g of the aged material is located at a lower temperature than the T_g of the fresh composite because of some chemical degradations made, for example, chain scissions have occurred on aging in service conditions.
2. For temperatures higher than 190°C, a significant rise in the Young's modulus was observed on the aged material while the fresh one only shows a slight increase in its stiffness. This is
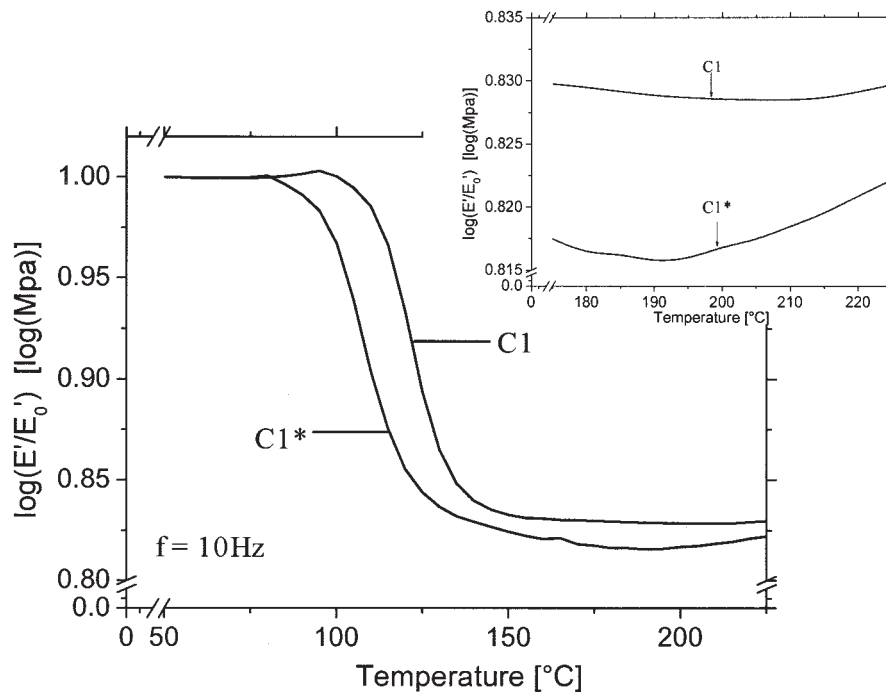

Figure 3 Real part of the dynamic mechanical modulus (E') versus temperature shown by the C1 and C1* samples at 10Hz.
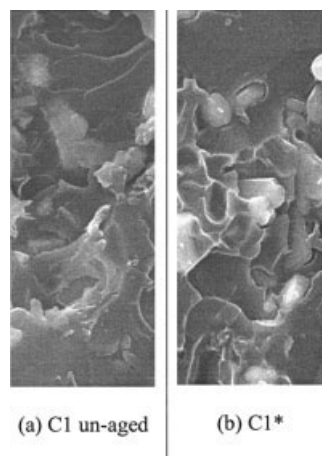
Figure 4 SEM observations of the fracture surface for the as-received (a) and aged (b) composites.

consistent with additional chain crosslinking effects, such as chain recombination that can occur on heating, and involving nonreacted groups and molecular species issued from the chemical degradations.

Accordingly, dynamic mechanical features are consistent with DSC characteristics and point out the chemical degradations that occurred in service. No influence of the physical aging on molecular mobility could be detected by dynamic mechanical analysis because the expected decrease in molecular mobility due to structural aging is counterbalanced by the increase in molecular motion related to chain scissions.

Morphology analysis

To complete these microstructure investigations, scanning electron microscopy observations were performed on fracture surfaces of both C_1 and C_1^* materials (Fig. 4).

It can be observed that fracture surfaces displayed by the aged material exhibit a particle debonding tendency from the polymer matrix, in contrast to those exhibited by the as-received material. This could indicate relatively weak interactions at the inorganic filler/polymer network interface. The poor adhesion between polymer and fillers might result from the physical and/or chemical changes induced by multistresses undergone by the insulator over a long time period.

Dielectric behavior

The dielectric behavior of this aged material was analyzed to determine the influence of the changes in microstructure (including the interface modifications) on the permittivity.

Figure 5 shows the evolutions of the real part of the permittivity (ε') versus temperature at 1kHz recorded on two successive heating runs for both the aged and as-received composites. Materials exhibit similar dielectric properties on the first and second heating runs.

The first increase in ε', occurring near 110°C, is attributed to the main relaxation (Tα) related to T$_g$. For the aged material, Tα is located at a lower temperature than Tα recorded for the as-received sample. This feature is consistent with DSC (and dynamic mechanical) analysis showing a shift of T$_g$ (and the main mechanical relaxation) towards lower temperature for C1*.

However, permittivity values of the aged sample recorded at 50°C and at various frequencies are not significantly different from those determined for the unaged sample in the same conditions (Fig. 5). This is unexpected because of the chemical degradations that could induce the formation of polar species and thereby result in an increase in ε' at service temperatures. This unexpected behavior might originate from the superimposition of opposite effects, and this will be discussed later.

Moreover, it can be observed that on the first heating runs, the C1 and C1* samples both exhibit a maximum in ε' close to 180°C for all measured frequencies.

This ε' peak shows no frequency dependence and is not detected on the second heating run, that is, after the first heating run up to 300°C and cooling. This maximum in ε' can thus originate from (i) the presence of polar species (including water molecules) and/or (ii) some structural evolution (including chain recombination) of the polymer network.

Because of the shift of the main relaxation towards higher temperatures detected for the two composites on the second heating run, this ε' maximum is consistent with additional chain crosslinkings, that is, with
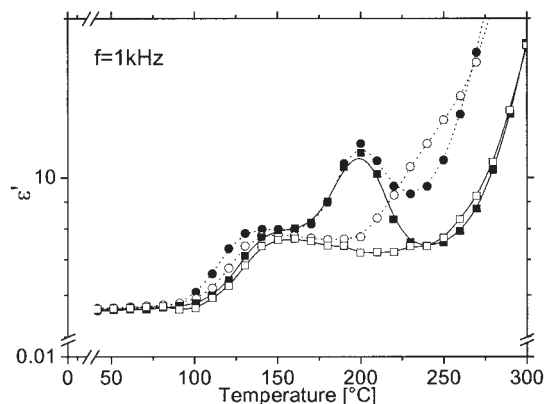

Figure 5 Dielectric permittivity ε' versus temperature recorded for C1 (■ first scan, □ second scan) and C1* (● first scan, ○ second scan) at 1kHz.
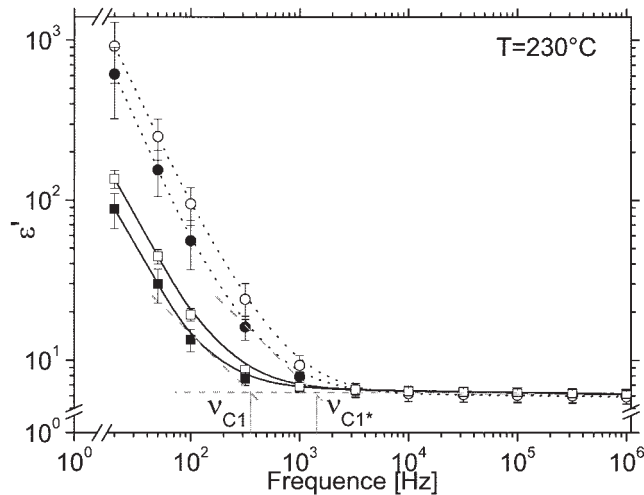
Figure 6 Dielectric permittivity ε' at 230°C against frequency for C1 (■ first heating run, □ second heating run) and C1* (● first heating run, ○ second heating run).

structural modification of the polymer network. It is also consistent with dynamic mechanical analysis showing a significant increase in the aged material stiffness at about the same temperature and characteristic of some chain recombination.

The strong rise in ε' value displayed by C1 as C1* composites at high temperatures, that is, at temperatures higher than 200°C (Fig. 5), is usually attributed to the diffusion of large polar species.[14]

In this temperature range, the ε' values displayed by the aged composite are always higher than those exhibited by the as-received sample for a given temperature and frequency. To better compare the dielectric behaviors of these two materials at high temperatures, plots of ε' versus frequency recorded at 230°C are shown in Figure 6.

For both materials, the permittivity first decreases with increasing the frequency and then reaches a plateau for higher frequencies, thus defining a critical frequency (ν). To interpret this behavior, two mechanisms can be proposed:

1. At low frequency, the high ε' values displayed by composites can result from the presence of mobile polar species. For a given frequency, the ε' value displayed by the aged material is higher than that measured for the as-received sample. This is consistent with a higher number and/or higher mobility of polar species shown by the aged material because of chemical degradation of the polymer matrix induced by the aging in service.
2. With increasing frequency, the decrease in ε' displayed by both materials could be related to the progressive decrease in the number of polar groups able to align along the alternating elec-

tric field direction. For frequencies higher than these critical values, polar groups cannot follow the alternating electric field any longer.

It can be observed that critical frequencies displayed by both the C1 and C1* materials, respectively, show no thermal history dependence. In addition, it is found that ν_{C1*} for the aged material is almost one order higher than ν_{C1} recorded for the fresh material under the same conditions. The critical frequency can thus be employed as a probe of the aging effects undergone by the composites.

To conclude, from a structural point of view, the aging in actual service conditions of an insulator based on epoxy resin reinforced by inorganic particles results in the followings effects:

1. A chemical degradation of the polymer matrix involving the formation of polar species.
2. A densification of the epoxy network due to physical aging.
3. Reduced interaction magnitude at the interface of polymer/inorganic particles.

The comparison between the dielectric behaviors displayed by the aged and the as-received materials can be summarized as follows:

1. At 230°C and for a given frequency, the aged material exhibits higher ε' values and a shift of the critical frequency, ν_c, towards higher values. This can originate from a higher number and/or higher mobility of polar species resulting from the chemical degradation of the polymer matrix occurring over a long service period.
2. The aged material exhibits no increase in ε' value measured at 50°C. This unexpected finding could result from opposite effects involving physical and chemical agings.

From these investigations, it is difficult to separate the relative contribution of chemical aging from that of physical aging on the overall structural changes and related dielectric properties shown by the composites.

To evaluate the sole influence of physical aging on the microstructure, including the polymer/particles interface, of the epoxy based composites and subsequently on the dielectric properties, laboratory structural aging tests were carried out.

Laboratory aging

Over a 6 month period, the C1 and C2 composites were sampled for various aging times.

It was first required to verify that no chemical degradation occurs over time before discussing the influence of the physical aging of the materials. From the

Aging time	C1	C2
0	88°	101°C
9 hours	88°	101°C
20 hours	89°	101°C
5 days	88°	98°C
13 days	87°	100°C
30 days	88°	102°C
73 days	87°	102°C
6 months	88°	101°C

thermograms recorded on the second heating runs (rejuvenated samples), it can be observed that T$_g$ remains almost constant whatever the aging time is, Table II. This is consistent with no significant chemical degradation of the polymer that could occur under laboratory aging conditions (under nitrogen, at a given temperature).

Microstructure evolution—Aging kinetics of the epoxy network

For all samples, the thermograms recorded immediately after aging exhibit an endothermic peak whose magnitude increases with the aging time, associated with a shift of T$_g$ towards higher temperatures (Fig. 7).

Aging kinetics can be evaluated[8,9,12] by plotting both T$_{g\ aged}$, that is, T$_{g\ onset}$ of the aged composites [Fig. 8(a)], and the related enthalpy excess ΔH, [Fig. 8(b)] recorded on the first heating run versus aging time.

With increasing aging time up to 30 days, the C1 and C2 composites first exhibit a linear shift of T$_{g\ aged}$ towards higher temperatures, accompanied by a linear increase in the enthalpy excess with time. Then, for aging periods ranging from 30 days to 6 months, the slopes of T$_{g\ aged}$ and ΔH curves versus aging time significantly increase. Based on data reported by Montserrat,[12] ΔH and T$_g$ are expected to reach constant values for long aging periods. In agreement with Kovacs[8] and Bauwens,[9] such an evolution of the enthalpy excess with aging time at T$_g$ - 18°C clearly shows that the structural relaxation, also called structural recovery, is a nonlinear phenomenon. Accordingly, it can be suggested that for aging times longer than 6 months at T$_g$ - 18°C, polymer networks in the C1 and C2 composite materials have almost reached their respective structural equilibrium states.

Thus, as described in the Introduction, such an evolution is related to a progressive and nonlinear increase in density undergone by the polymer.[11]

Dynamic mechanical analyses performed on the physically aged materials confirm that no chemical degradations of the polymer have occurred over time. Moreover, only a slight shift of the main relaxation

towards high temperatures is found with increasing aging time. Because of experimental uncertainties, the expected increase in the vitreous Young's modulus for aged materials has not been detected.

The influence of the densification of the polymer matrix due to physical aging on the adhesion quality at the polymer/filler interface was then investigated through SEM observations.

SEM observations

Figure 9 shows the surface fracture of the as-received and aged C1 composite materials.

It can be observed that the aged materials show a tendency to particle debonding from the polymer matrix even for the shortest aging time (13 days). Thus, it seems that physical aging may alter the adhesion quality at the particle/polymer interface. It would be of
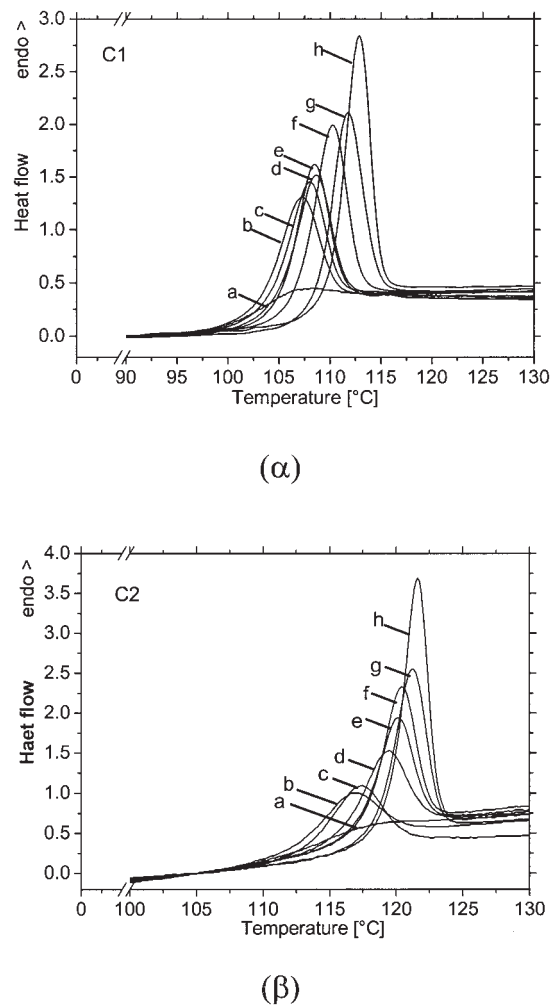

(α)

(β)

Figure 7 Thermograms of the as-received systems (a) and composites aged under laboratory conditions for (b) 9h, (c) 20h, (d) 5days, (e) 13 days, (f) 30 days, (g) 73 days, and (h) 6 months –1st heating run for the composites C1 (α) and C2 (β).
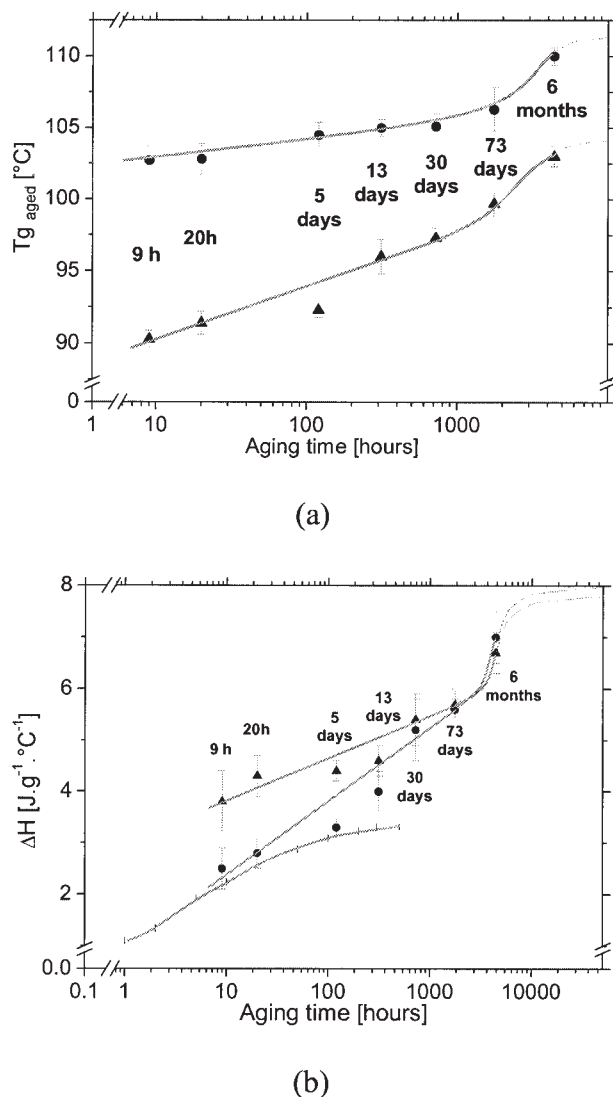
(a)

(b)

Figure 8 Evolutions of T_g (a) and enthalpy excess ΔH (b) values as a function of aging time for the composites C1 (▲) and C2 (●), compared to those displayed by an unfilled system based on a similar formulation as C2 reported by Montserrat (+).[12]

interest to precisely evaluate the evolution of the polymer/particles adhesion over aging time, but SEM observations are not well suited to quantify the eventual progressive decrease in the interaction strength between the polymer and the particles with time.

To determine the influence of such changes in microstructure (densification of the polymer network and interface modifications) on permittivity, the dielectric behavior of the aged composite materials was investigated.

Dielectric behavior

Figure 10 shows the evolution of the real part of the permittivity ε' versus temperature displayed by the

C1 composite aged for various times (the C2 composite exhibits a similar evolution).

At T_g - 18°C and for the longest aging times, the main relaxation located near 110°C at 320 Hz is significantly shifted towards higher temperatures. Such an evolution points out the decrease in the molecular mobility of chains segments of the polymer network due to the decrease in free volume accompanying the structural recovery.

The maximum in ε', located at about 170°C, exhibited by both composites is related to additional chain crosslinking reactions involving unreacted species. It can be noticed that the ε' maximum shown by the 6 months-aged material is located at a much higher temperature than that displayed by the unaged sample. This can be related to the shift of T_g towards the higher temperatures displayed by the aged material. As a matter of fact, additional chain crosslinking based on thermally activated diffusion of unreacted species should occur at even higher temperature than that displayed by the unaged material.

For higher temperatures, it can be noticed that the strong increase in ε' versus temperature related to the mobility of polar species displayed by both composites shows no significant aging time dependence. This is consistent with no chemical degradations of the polymer network induced by physical aging.

The influence of microstructural changes, that is, the densification of the polymer network and the decrease in the polymer/fillers adhesion quality, induced by physical aging on the permittivity at insulator service temperatures were analyzed.

Plots of ε' versus aging time measured at 50°C for various frequencies ranging from 100Hz to 1 MHz are shown in Figures 11 and 12 for both composites.

With increasing aging time up to 73 days, both composites exhibit an increase in the real part of the permittivity over the analyzed frequency range. It can be noticed that ε' values measured for the sample aged for 6 months tend to be slightly but significantly lower than that those determined for the 73 days aged sample. Such an evolution suggests than ε' could have gone through a maximum for aging time ranging between 73 days and 6 months. The influence of physical aging in the dielectric behavior of insulators in service conditions can be interpreted as follows.

The increase in ε' with increasing aging time up to 73 days may arise from the two following origins:

1. The decrease in volume induced by the structural recovery occurring on physical aging and leading to an increase in the relative volume ratio of molecular dipoles.
2. The presence of polar species in the polymer network that can migrate to the polymer/filler interface over time, leading to the formation of a "polar interphase." The comparison between
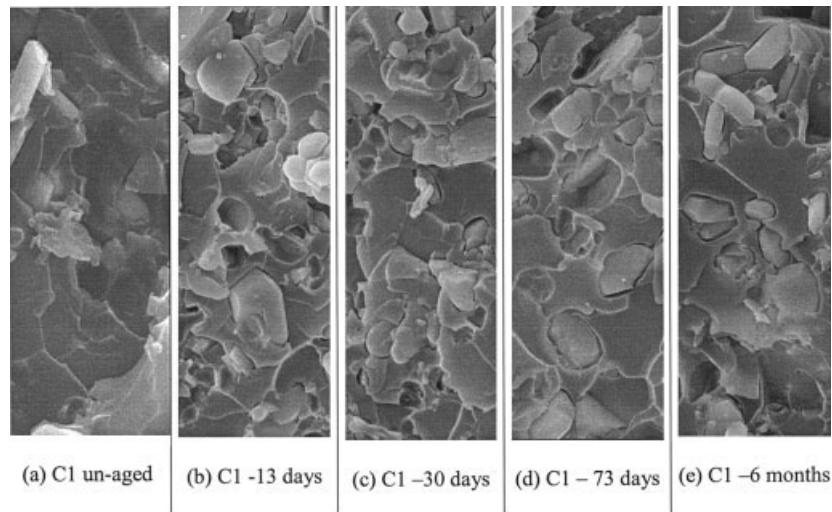
(a) C1 un-aged | (b) C1 -13 days | (c) C1 –30 days | (d) C1 – 73 days | (e) C1 –6 months

Figure 9 SEM observations of fracture surface displayed by the as-received C1 composite (a), aged in laboratory for 13 days (b), 30 days (c), 73 days (d), and 6 months (e).

the dielectric behavior of the unaged and aged composite suggests that the formation of such a "polar interphase" could be favored by the poor quality of the polymer/filler adhesion at the interface induced by the structural recovery occurring over the aging time (Fig. 13). The decrease in ε' detected for both composites aged for 6 months could result from the diffusion and the removal of volatile polar species favored by long aging time.

To elucidate the unexpected ε' value displayed at 50°C by the insulator aged in actual service conditions for 20 years, that is, ε' was found to be not significantly different from the permittivity measured on the fresh material in the same conditions, while it was expected to increase because of the presence of polar species, the dielectric behavior of the 20 years aged

material was compared to that displayed by the laboratory aged samples (Fig. 14).

It can be observed that ε' values at 50°C shown by the C1* composite are very close to those displayed by both the unaged and 30 days aged C1 materials.

Based on the previous analysis about the evolution of ε' versus laboratory aging times (Fig. 11), it can be suggested that the aging in actual service conditions results in two opposite effects on the dielectric behavior displayed by C1* at 50°C.

According to the first mechanism, ε' exhibited by the 20 years aged material at 50°C is expected to strongly increase because of the structural recovery that induces an increase in the amount of dipole per unit volume and/or that favors the formation of a
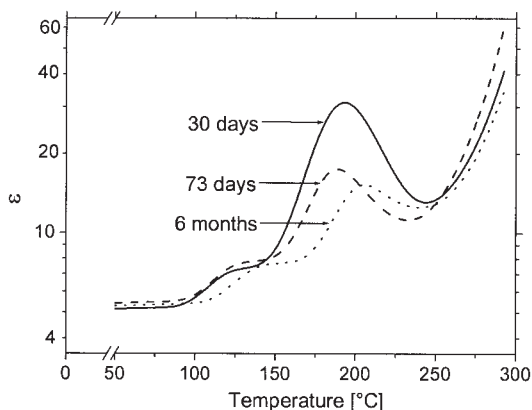

Figure 10 Plots of dielectric permittivity ε' (first heating run) versus temperature at 320 Hz of the aged composite C1for (—) 30 days, (- - -) 73 days, and (· · ·) 6 months.
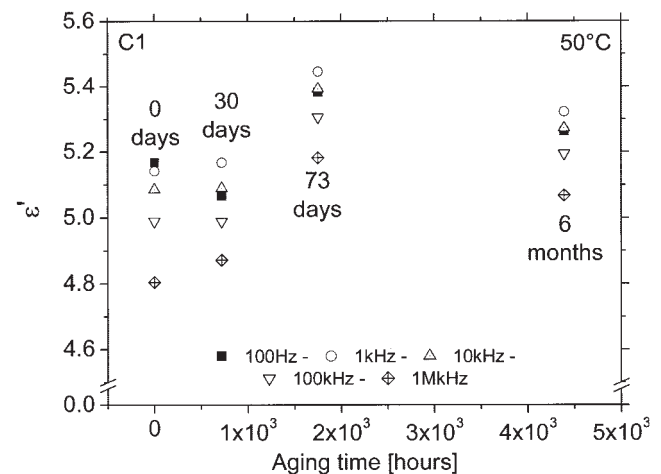

Figure 11 Evolution of dielectric permittivity ε' (first heating run) versus aging time for the sample C1 unaged, and aged for 30 days, 73 days, and 6 months, at 50°C and at several frequencies (ranging from 100Hz to 1MHz).
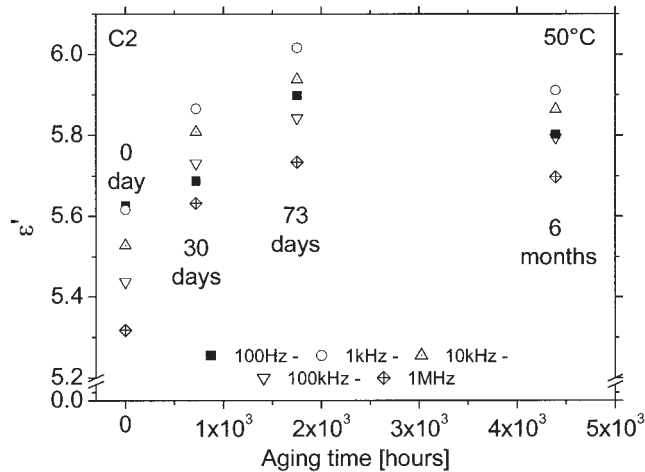
Figure 12 Evolution of the dielectric permittivity ε' (first heating run) versus aging time for the sample C2 unaged, and aged 30 days, 73 days, and 6 months at 50°C and at several frequencies (ranging from 100Hz to 1MHz).

Figure 14 Evolution of dielectric permittivity ε' (fist heating run) at 50°C and at several frequencies (ranging from 100Hz to 1MHz) versus aging time for the unaged, aged for 30 days, and C1* samples.

"polar interphase." In contrast, over this very long time, both the original volatile polar species and the polar group resulting from chemical degradation of the polymer network occurring on actual service conditions might be removed through diffusion mechanisms out of the material. This can result in a significant decrease in ε'. Accordingly, such opposite effects could counterbalance each other, resulting in constant ε' values at 50°C.

CONCLUSIONS

Microstructure and dielectric behavior changes undergone by an insulator based on epoxy reinforced by inorganic particles aged in actual service conditions over a long time, that is, 20 years, were investigated.

With respect to the characteristics displayed by the as-received material based on the same composition, aging in service conditions results in the following effects:

1. A chemical degradation of the polymer network characterized by a shift of T_g towards lower temperature. Such a chemical degradation gives rise to additional movable polar spe-
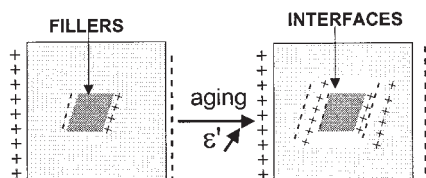

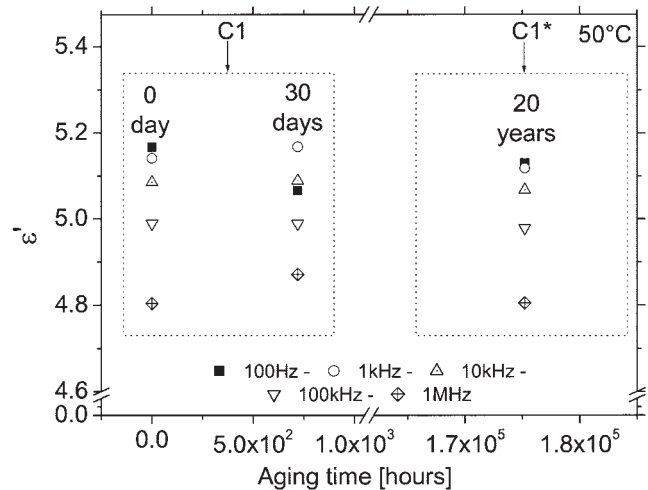**Figure 13** Schematic representation of dipoles pilling at the polymer/filler interface.

cies whose presence is detected from dielectric measurements performed at high temperature, that is, $T \geq 230°C$. As a matter of fact, the shift of the critical frequency towards the higher values exhibited by the aged sample can result from an increase in the number and/or motion ability of polar species. Such a critical frequency can constitute a probe of the chemical degradation of the polymer occurring over time in service conditions.

2. A structural recovery characterized by the presence of an endothermic peak near T_g on the thermograms.

3. A tendency to particle debonding from the polymer matrix that could originate from both chemical degradation and physical aging.

4. No apparent change in the permittivity value measured at 50°C. However, it was expected there would be an increase in ε' value because of the chemical degradation of the polymer that gives rise to polar species.

To identify the mechanisms leading to this unexpected result and in a more global way to evaluate the contribution of structural recovery only on the composite properties, laboratory physical aging tests were carried out on two epoxy-based composites. First, the aging kinetics study points out that enthalpy excess (and T_g) is found to be a nonlinear increasing function of aging time. This is in agreement with Kovacs[8] and Bauwens[9] data. Then, from SEM observations of fracture surfaces performed on aged samples, it was found that composites exhibit a tendency to particle debonding from the polymer matrix. Such a phenomenon could be related to matrix densification due to

structural recovery and resulting in stress concentration at the polymer/filler interface.

Analysis of the dielectric behavior of aged materials showed that ε' measured at 50°C and at various frequencies increases with increasing aging time up to 73 days. This was related to: (i) an increase in the relative volume ratio of dipoles because of the decrease in the polymer volume due to the structural recovery and/or (ii) the piling up of the original polar species at the matrix/filler interface that could be favored by the low adhesion quality between the polymer and inorganic particles.

The permittivity value at 50°C displayed by the longest aged sample, that is, aged for 6 months, was slightly but significantly lower than that measured for the 73 days aged sample. Such a decrease in ε' at 50°C for very long aging times could result from additional effects due to the removal through a diffusion process of volatile polar groups favored by long aging periods.

Accordingly, the mechanisms leading to apparently no change in permittivity values measured at 50°C (T $<$ T_g) exhibited by the 20 years aged insulator at various frequencies (Fig. 14) could result from the superimposition of the two following opposite effects:

1. The first one is related to an increase in the relative volume ratio of dipoles due to structural recovery and/or the piling up of polar species at the polymer/particle interface.
2. The second one acting in an opposite effect could be related to the removal of polar species, that is, original polar molecules and/or additional polar species due to chemical degradation occurring as the insulator underwent multi-stresses over a long time. This leads to a decrease that could counterbalance the ε' in-

crease and result in a constant value of permittivity at 50°C.

References

1. Dissado, L. A.; Fothergill, J. C. In Electrical Degradation and Breakdown in Polymers. IEE Materials and Devices Series 9, Vol. 9; Morgan, D. V.; Parkman, N.; Overshott, K., Eds.; London: The Redwood Press, 1992.
2. Las, T. Conference Record of the 2000 IEEE International Symposium on Electrical Insulation, 2000, p 324.
3. Hepburn, D. M.; Kemp, I. J.; Shields, A. J.; Cooper, J. M. IEE Proc Sci Meas Technol 2000, 147, 97.
4. Hepburn, D. M.; Kemp, I. J.; Cooper, J. M. Polym Degrad Stab 2000, 70, 245.
5. Hudon, C.; Bartnikas, R.; Wertheimer, M. R. IEEE Trans Electrical Insulation 1995, 2, 1083.
6. Ollier-Dureault, V.; Gosse, B. IEEE Trans Dielectrics and Electrical Insulation 1998, 5, 935.
7. Ollier-Dureault, V.; Gosse, B. J Appl Polym Sci 1998, 70, 1221.
8. Kovacs, A. J.; Hutchinson, J. M. J Polym Sci Polym Phys 1979, 17 2031.
9. Bauwens-Crowet, C.; Bauwens, J. C. Polymer 1986, 27, 709.
10. Heymans, N.; Dequenne, B. Polymer 2001, 42, 5337.
11. Hutchinson, J. M. Prog Polym Sci 1995, 20, 703.
12. Montserrat, S. J Polym Sci Part B: Polym Phys 1994, 32, 509.
13. Beyer, M. Electrical and Dielectric Behaviour of Cast Epoxy Resins; Institute of Electric Power Systems (Schering-Institute), Hannover University, Germany, 1991.
14. Pethrick, R. A.; Hayward, D. Prog Polym Sci 2002, 27, 1983.