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Environmental degradation of the electrical and thermal properties of organic insulating materials

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The sorption behaviour of water molecules in epoxy-based thermosetting networks is discussed and related to the modifications of the polymer properties. The hypothesized sorption modes and the corresponding mechanisms of plasticization are discussed on the basis of experimental liquid-sorption tests, differential scanning calorimetry (DSC), and electrical analyses. Two modes of moisture sorption are assumed: a sorption leading to an increase in the free volume of the system, and adsorption of the water molecules due to hydrogen bonding to hydrophilic groups present in the network and to the surfaces of "holes" which make up the excess free volume of the glassy polymer. Electrical investigation improved the understanding of the hygrothermal ageing phenomena. Water conditioning of the composites modified the surface and bulk resistivities as a consequence of microstructural damage and plasticization.

1. Introduction

The chemical nature of the reagent monomers and their processing conditions influence the structure of the thermosetting networks and hence their mechanical and durability properties. Theoretically, a homogeneous infinite network should result from the cure reactions of a prepolymer, however, highly crosslinked nodules immersed in a lower density matrix are actually formed. The morphology of the polymeric matrix influences the durability in aggressive environments, mode of failure and electrical properties of a composite. The exposure of such inhomogeneous materials to humid environments induces different changes of the polymeric phase due to its affinity for and mode of sorption of water molecules [1–3].

In order to evaluate the effect of hygrothermal fatigue on physical and electrical properties of composites in actual service conditions, it is crucial to resolve the basic phenomena driving the complex sorption behaviour and degradation mechanism in various combinations of moist environment and temperature.

The moisture sensitivity of the epoxies, which are the dominant matrices for composites, is due to the strong mutual interactions between water molecules and polar groups present in the polymeric network. The water molecules act both as plasticizers and crazing agents, and their presence is often the principal cause of the modified material response in stress fatigue tests.

In general, polymeric materials differ from other structural materials in that, at ambient temperature, low molecular weight substances can easily migrate in them. Studies of the transport properties of low molecular weight substances in polymers have been developed in order to clarify the actual mechanisms of the diffusion process and to identify factors which influence the rate of migration and equilibrium sorption of the penetrant. The degradation of the mechanical properties of the epoxy polymers is associated with the plasticization [1–3] and micromechanical damage [4–17] induced by the sorbed moisture. The cure of a reactive prepolymer involves the transformation of low molecular weight reactive substances from liquid to rubber and solid states as a result of the formation of a polymer network by a chemical reaction of some groups in the system. The final post-cure of complex commercial formulations is often diffusion controlled, leading to the formation of inhomogeneous structures that influence the behaviour of the cured resins under actual service conditions [6]. The differences in properties between desiccated and soaked samples reinforce the concept that physical modifications occur in the polymer network by hygrothermal ageing. Although the exact nature of these changes has not yet been completely identified, previous investigations have led to explanations relating them to either the microvoiding and crazing of the polymer [10–18] or a dual state of water in the epoxy [17–23]. In the latter case, the material retains the penetrant even at high temperatures due to strong polar interactions between the epoxy and the water molecules water system [22–24]. It is expected that greater than normal depressions of the glass transition temperature should be observed in systems where such interactions are present. In such cases prediction based exclusively on the analysis of the free volume [25] often fail [1, 2, 26, 27, 29–31].

1.1. Moisture solubility and plasticization

Plasticization is the process of depression of the glass transition temperature and reduction of the mechanical properties associated with the sorption of moisture or, more generally, of a solvent. The diffusion of water in

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glassy polymers capable of strong interactions with the penetrant molecules is characterized by a complex mechanism of sorption and plasticization. The molecules of the penetrant can both form an ordinary polymer–diluent solution and be adsorbed on hydrophilic sites. Because of the multiplicity of the possible polymer–diluent interactions, it is our opinion that the degree of plasticization is not directly related to the overall water uptake. It can be readily inferred, in fact, that the same amount of water absorbed by different mechanisms is not expected to induce the same degree of plasticization.

The generally accepted mechanism describing the transport of a gaseous penetrant in a polymeric material is an activated solution–diffusion process (see Fig. 1). The molecules are first dissolved into the polymer surface and then diffuse through the bulk by a series of activated steps under the driving force of a concentration gradient. In this case, it is clear that both solubility and diffusivities are involved in the process, and that the polymer molecular and morphological features influence the penetrant transport behaviour. When water is transported through an epoxy, however, both steps are complicated by the multiplicity of the molecular interactions.

First, let us consider the ordinary dissolution of a substance in a polymer, using the Flory–Huggins theory, which treats the random mixing of a disoriented polymer and a solvent. If a_s is the penetran external activity, v_p, is the polymer volume fraction and X_s, is the solvent–polymer interaction parameter, the relationship relating these variables in the case of an infinite molecular weight polymer is

$$\ln a_s = \ln(1 - v_p) + v_p + X_s v_p^2 \qquad (1)$$

When the penetrant concentration is very low, as is the case of sorption from vapour phases, Equation 1 becomes the limiting Henry's law and a linear sorption behaviour is expected. Initial equilibrium moisture sorption data for commonly used bisphenolic epoxy matrices exposed to humid environments are adequately described by Equation 1 with a single interaction parameter of about 2.6. A second cycle of sorptions, after desorption, however, often shows a significant increase equilibrium moisture content [17, 18]. The strong curvature at high activities in a plot of the equilibrium uptakes against penetrant activity observed in the first cycle of sorption is attributed to an irreversible expansion of the polymer network due to the water sorption at temperatures below T_g. A fast rate of desorption of the dissolved water molecules from the expanded structure compared to the polymer relaxation leaves an excess free volume frozen in the resin.

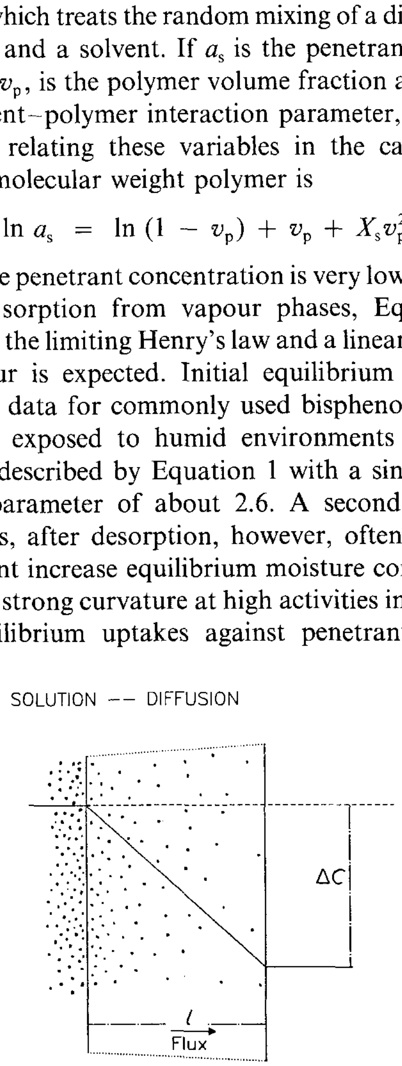

Figure 1 Mechanism of diffusion of a low molecular weight substance in a polymer. $J = -D\Delta C/l$, where J = mass flux, D = diffusion coefficient, $\Delta C/l$ = concentration gradient.

Moreover, the Flory–Huggins theory is not adequate for a polymer containing strongly polar groups, especially at high penetrant uptakes. In such cases the positive deviations from Henry's law are explained by the clustering of the penetrant and crazing of the resin [27–39]. In particular, the clustering of water molecules has been supposed to produce an irreversible microvoiding in the epoxies. A Langmuir mode of sorption is associated with regions of localized lower density frozen into the glass. Additional preferential adsorption is also associated with strong mutual interactions between polymer groups and diffusant molecules. The preferential adsorption on these sites gives rise to deviations from the normal behaviour evident as negative deviations from Henry's law. Sorption of an interacting vapour is therefore described by superimposing Henry's law and Langmuir isotherms [40–42].

The investigation of the mechanisms of polymerization of the epoxy prepolymers gives an insight into the chemistry of the system and then into the potential interactions that can arise between the penetrant molecules and the polymer. The cured epoxy resins have in their structure a large number of polar groups, whose exact nature depends on the specific hardeners and additives used as curing co-agents. Chain extension and cross-linking of the epoxy resins are due to the reaction of epoxides between themselves and with the hydrogens of donor compound, such as amine or acid hardeners. The nucleophilic addition of primary amines results in the formation of highly hydrophilic amino alcohols. Etherification sometimes competes with the secondary amine addition leaving the unreacted amino alcohols capable of strong interactions with water molecules. Organic acids or, more commonly, their anhydrides, induce chain extension and cross-linking either by catalysing the homopolymerization or by directly reacting with epoxide to form polyesters.

The possible active groups present in the structure generated in the reaction of an epoxy with an amine are reported in Fig. 2. The formation of intrachain hydrogen bonds between hydroxyls, amines or carboxylic groups (in the case of the anhydride cure), reduces the internal segmental mobility leading to an increase in the chain stiffness and hence in the glass transition temperature. Conversely, the breakdown of these bonds by the sorbed water molecules can greatly depress the glass transition temperature of the system. In particular, a greater depression of the glass transition temperature upon equilibration with water can be expected for systems prepared with higher concentrations of amino or anhydride hardeners.

As indicated before, the plasticization of the network structure depends on the dilution process as well as on the intermolecular bond formation. The former is

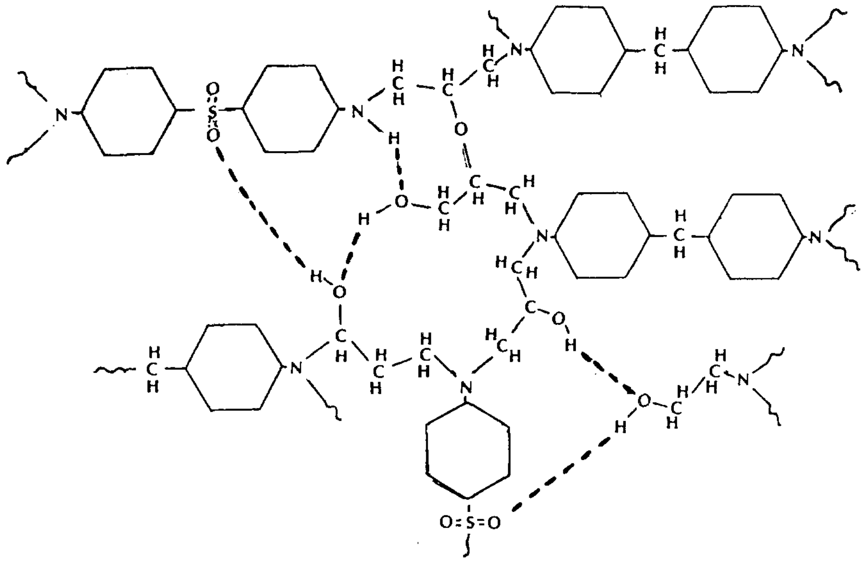

Figure 2 Structure and intra-molecular interactions of an epoxy–amine system, inducing reducing segmental mobility and an increase of the glass transition temperature.

governed by the diluent volume fraction and by the incremental change of the thermal expansion coefficients at the glass transition. The higher the incremental change in the polymer thermal expansion coefficient at T_g, the lower will be the influence of the diluent volume fraction [25]. This is due to the fact that the glass transition temperature of the wet polymer is calculated as the mean value of the characteristic temperatures of the constituents weighed by the product of the volume fraction and thermal expansion coefficient. Moreover, when the hardener concentration is increased, the network becomes more tightly cross-linked, but a larger number of hardener groups remain unreacted. When low hardener concentrations are used, plasticization occurs primarily by dilution, while the influence of hydrogen bonding on hydrophilic sites, which occurs at very low water activities [31], is less important. Conversely, the sorption and plasticization of hardener-rich materials are primarily related to the presence of unreacted hydrophilic species.

Recently, alternative theoretical expressions have been developed using classical thermodynamic treatments to describe the compositional dependence of the glass transition in miscible blends, further extended also to the epoxy–water systems [27, 43]. The studies carried out on bisphenolic epoxy resins of relatively low glass transition have shown that the plasticization induced by water sorption may be related to the incremental change in the specific heat at the glass transition. The smaller this change, the greater is the expected depression of the glass transition temperature. Ellis and Karasz [25] have calculated theoretical T_g depressions of 10 to 15 K per wt % water content for the less cross-linked epoxy systems and of 25 K per wt % water content for highly cross-linked systems, using a value of the incremental change in the specific heat at the glass transition of 1.94 J g^{-1} K^{-1} [44] for the water and values ranging from 0.34 to 0.35 J g^{-1} K^{-1} for the epoxies.

1.2. Sorption kinetics

While sorption of gas and vapours in rubbers follows the ordinary Henry's law, a dual-mode sorption theory is required to explain the negative deviations frequently observed in glassy polymers. Sorption is then visualized as a process in which two modes are present: the molecules of penetrant are either dissolved and free to diffuse in the bulk polymer, or immobilized as in a sink giving rise to the deviation from the Henry's law.

The process of water diffusion and sorption in glassy polymers capable of bonding the penetrant molecules should therefore be analysed by considering all the possible interactions. When the penetrant molecules are equally dispersed in the bulk and adsorbed on hydrophilic sites and surfaces, a diffusion equation can be written for the actual rate of sorption, which accounts for the two modes of sorption and contains the capacity (C'_h) and affinity (b) constants in addition to Henry's constant (k_d)

$$C_d = k_d a \tag{2}$$

$$C_h = \frac{C'_h b a}{1 + b a} \tag{3}$$

$$\frac{D\,d^2C_d}{dx^2} = \frac{d(C_d + C_h)}{dt} \tag{4}$$

where D is the diffusion coefficient, a = penetrant activity, x = space, t = time, C_d = concentration of dissolved molecules, and C_h = concentration of trapped molecules.

Glassy polymers exhibit linear equilibrium isotherms for low and high values of penetrant activity [1–3, 42]. In these cases the previous differential equation assumes the form of the ordinary Fick's second law with the same analytical solution, although the effective diffusion coefficient (D_{eff}) assumes different physical meaning

$$D_{\text{eff}} \frac{d^2C_d}{dx^2} = \frac{dC_d}{dt} \tag{5}$$

For low activities, $D_{\text{eff}} = Dk_d/(k_d + C'_h b)$. For high activities, $D_{\text{eff}} = D$.

Usually, the analysis of the sorption kinetics is used as a criterion to distinguish between the Fickian and anomalous behaviour. A first criterion states that the plot of the initial penetrant uptake or loss, is a linear function of the square root of time

$$M_t/M_\infty = 4(D_{\mathrm{eff}}t/\pi L^2)^{1/2} \qquad (6)$$

where M_t = water uptake at time t, M_∞ = overall water uptake, t = time, and L^2 = thickness.

Equation 6 is a simplified form of a more complex analytical solution of Equation 5 which holds for values of a fraction penetrant uptake lower than 0.60 [47]. A second criterion for the definition of a Fickian sorption is inferred from the observation that the analytical solutions always contain the time normalized to the square of the thickness (L). Sorption kinetics obtained for samples of different thickness are then reduced to a single curve when the per cent uptake is plotted against the square root of the time divided by the sample thickness. Anomalous sorption, conversely, produces different curves.

2. Experimental

2.1. Materials

Tests were performed on the following materials:

(a) Solid bisphenolic epoxy prepolymer (10 parts) cured with phtalic anhydride (3 parts) and filled with 60% by weight quartz powder.

(b) Liquid bisphenolic epoxy prepolymer (10 parts) cured with a modified carboxylic anhydride (8 parts) and filled with 60% by weight quartz powder.

(c) The same matrix used in (b) filled with 60% by weight calcinated alumina powder using a dispersing agent.

(d) A liquid isocyanate polymerized with polyols to obtain a polyurethane matrix filled with 60% by weight dolomia powder.

2.2. Apparatus and procedure

A differential scanning calorimeter, Mettler DSC 30, has been used to determine the glass transition temperature of the water-conditioned and desiccated samples. Sealed pans were used to scan 15 mg material at 20° C min^{-1} from −20 to 250° C.

Liquid sorptions were monitored by repeatedly weighing on an analytical balance samples immersed in distilled water held at constant temperature.

TABLE I Water uptake and diffusion coefficients (D_{eff})

	Water uptake (%)			D (10^9 cm^2 sec^{-1})		
	20° C	40° C	100° C	20° C	40° C	100° C
Epoxy (a)	0.36	0.62	1.85	1.0	4.2	20.0
(b)	0.42	0.51	0.82	2.1	4.2	64.0
(c)	0.51	0.65	3.71	1.5	4.0	19.0
Polyurethane (d)	3.00	4.10	5.76	1.5	3.0	200.0

The electrical tests were run on a flat disc of about 3 mm thickness and 63 mm diameter using an automated measuring system controlled by a personal computer HP 86 A. The dielectric properties were measured in the frequency range 100 Hz to 1 MHz by an impedance analyser HP 4192 A, connected to a suitable shielded cell equipped with a temperature control. To estimate the electrical resistivity, a high input resistance electrometer Keithley 610c was employed. D.c. measurements were performed according to the ASTM D 257–78 for d.c. conductance of insulating materials by using a three electrode shielded cell. The specimens were charged using a d.c. power supply (0 to 3000 V).

3. Results and discussion

3.1. Moisture sorption and property degradation

The moisture uptake by epoxy and polyurethane samples from liquid environments thermostatically controlled at 20, 40, and 100° C have been investigated. Typical sorption curves are shown in Fig. 3. According to the previous discussion, a Fickian mechanism drives moisture uptake, because a linear behaviour is observed in the initial stages of the sorption at the three temperatures investigated. The equilibrium uptake and the diffusion coefficients derived from the linear part of the sorption curve are reported in Table I.

It can be observed that all four systems show higher water uptake in the tests carried out at 100° C. Moreover, at all three temperatures the polyurethane sample shows weight gains significantly higher than those of the epoxy systems. First let us analyse the

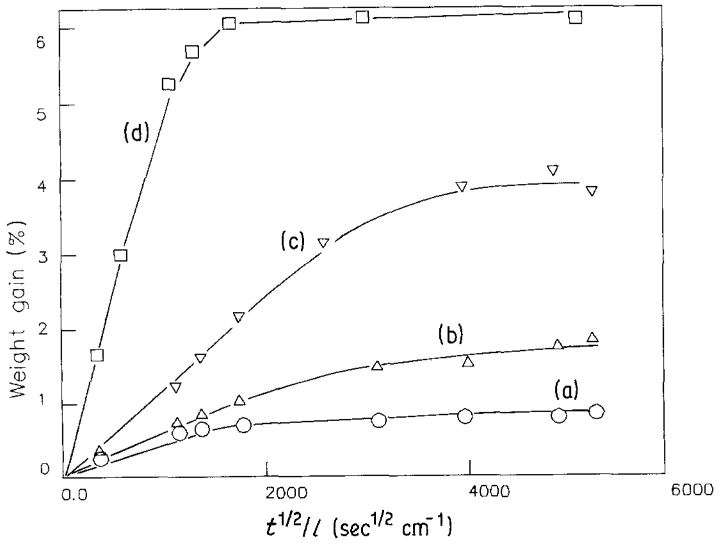

Figure 3 Water uptake in epoxy (a), (b) and (c), and polyurethane (d) composites at 100° C.

TABLE II Equilibrium water uptake for the polymer composites (a), (b), (c) and (d) at 20° C

	Water uptake (%) in samples			
	(a)	(b)	(c)	(d)
Equilibrated at 20° C	0.36	0.42	0.51	3.00
Previously conditioned at 100° C and then at 20° C	1.85	0.87	3.70	5.78

sorption characteristics of the epoxy composites as a function of temperature; at the lower test temperature, 20° C, a slightly lower water uptake characterizes the polymer matrix obtained from the solid bisphenolic epoxy resin when compared to those obtained from the liquid prepolymer, i.e. 0.36% compared to 0.42 and 0.50%, but when the test temperature is increased, sample b made with the more flexible epoxy matrix and quartz powder shows a less pronounced weight increase. The same flexible matrix, however, behaves differently when filled with the calcined alumina powder; at the highest test temperature, in fact, the water uptake for sample c reaches the value of 3.71 which is four times greater than for the composite made with the quartz powder. It can be inferred that this additional weight gain is due to a poorer adhesion of the alumina fillers which induces a debonding of the particles and then an accumulation of water at the boundary between the matrix and fillers [31–34]. The composite made with the stiffer resin and filled with quartz powder shows a behaviour similar to sample c, but less pronounced.

Moreover, further equilibration of the samples tested at 100° C in water held at 20° C showed that the apparent saturation occurred at values higher than for the samples equilibrated exclusively at the lower temperature, as indicated in Table II.

The difference between the two saturation uptakes at the same temperature for the samples with different hygrothermal history is caused by excess water trapped in microcavities that have been formed around the debonded fillers. Because this water should not contribute to the plasticization of the polymeric matrix, the glass transition temperatures of the conditioned samples, calorimetrically measured, do not change significantly (Table III).

3.2. Thermal properties and plasticization

Differential scanning calorimetry (DSC) has been carried out on the dry and water-conditioned materials in order to identify the polymer glass transition temperature depression induced by the water actually dissolved in the bulk. The values of the glass transition temperature for the dry and water-conditioned materials are reported in Table III.

TABLE III Glass transition temperatures of dry and water-conditioned materials

	Dry	Water conditioned at		
		20° C	40° C	100° C
(a)	105	100	103	103
(b)	105	93	95	96
(c)	105	93	94	94
(d)	35	33	31	22

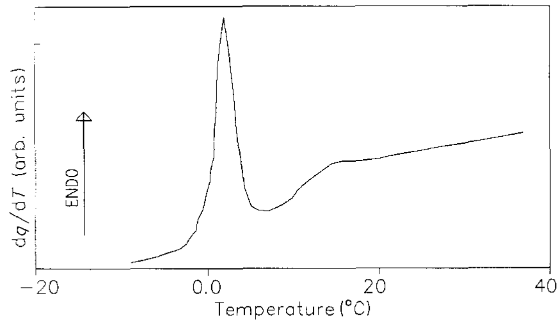

Figure 4 DSC trace of the polyurethane composite after equilibration in water at 100° C.

Although the water uptake observed for the samples conditioned at increasing temperatures is significantly different, the measured differences in the glass transition temperatures are less evident. This observation further confirms that all the sorbed water is not completely dissolved in the resin, but is also dispersed and confined in microcavities.

For the polyurethane system, in fact, the large excess of water is evident in the DSC thermograms as melting peaks of the water free to freeze near 0° C, Fig. 4. Moreover, it should be noted that while the polyurethane matrix is tested in a range of temperatures well above its glass transition, the epoxy systems remain in the glassy state during the tests, although they are in the range of T_g in the tests at 100° C.

3.3. Electrical properties

The moisture sorption and the morphological modifications induced in the polymeric structure by the hygrothermal ageing reduce their electrical performance. In order to analyse the changes of the electrical characteristics after the water conditioning at different temperatures, volume (ϱ_v) and surface (ϱ_s) resistivities, permittivities (ε) and dissipation factors (tan δ) have been measured and compared with the values relative to the unaged materials.

Equilibrium resistivities under an electrical field of about 3.5 kV cm^{-1} were reached by the aged and unaged samples after 500 sec. The values measured for the four types of materials investigated were equivalent in the dry state but differ significantly after the water conditioning, especially at higher ageing temperatures (see Table IV).

The conditioned samples showed decreased resistivities as a consequence of the water sorption. While samples a and b showed decreased but still acceptable resistivities, also after the severe ageing at 100° C, the samples c and d of aged composites, characterized by much higher water contents, were seriously degraded by plasticization. For the latter, the resistivity collapse is also affected by the wet material glass transition and by the presence of a large excess of unbonded water, as previously discussed.

The surface resistivities were adversely affected only after the severe 100° C water conditioning. This behaviour can be attributed to microscopic damage at the surface which increases the surface wettability and hence the surface conductivity.

TABLE IV Volume (ϱ_v) and surface (ϱ_s) resistivities of the dry and water-conditioned polymeric composites

	Unaged		Aged in water at:			
			40° C		100° C	
	ϱ_v (Ω)	ϱ_s (Ω)	ϱ_v (Ω)	ϱ_s (Ω)	ϱ_v (Ω)	ϱ_s (Ω)
(a)	3.9×10^{14}	3.6×10^{16}	9.5×10^{13}	6.4×10^{15}	8.8×10^{12}	9.5×10^{12}
(b)	2.7×10^{14}	3.6×10^{15}	2.0×10^{13}	9.1×10^{14}	5.0×10^{12}	3.5×10^{11}
(c)	4.4×10^{14}	2.7×10^{15}	7.2×10^{12}	1.7×10^{15}	5.4×10^{12}	8.3×10^{9}
(d)	3.1×10^{14}	1.1×10^{16}	1.1×10^{8}	4.8×10^{10}	7.3×10^{7}	6.1×10^{8}

Evidence of this microstructural damage is reported in the literature [48] where the scanning electron microscopy of samples aged in humid environments and made with the same materials showed the formation of microcracks in the polymer matrix and at the grain–matrix interfaces.

The presence of sorbed water in the aged samples alters the frequency response of the dielectric properties. A significant increase of the permittivity is observed at low frequencies in the water-conditioned samples, while there is virtually no change in the desiccated materials. The permittivity against frequency plots for dry and water-conditioned samples c and d are shown in Fig. 5. The same considerations hold true for the dissipation factor (see Fig. 5).

4. Conclusions

The properties of thermosetting resins are adversely affected by water sorption from humid environments. Degradation under temperature, humidity and stress fatigue tests has been related to water-induced plasticization and micromechanical damage. Sorbed moisture which acts as a plasticizer and swelling agent for the resins leads to significant changes in the electrical properties.

The presence of sorbed water alters the frequency response of the resins in dielectric tests reducing the permittivity at low frequencies. These changes were recovered upon drying. The surface conductivities were also dramatically influenced by the hygrothermal ageing.

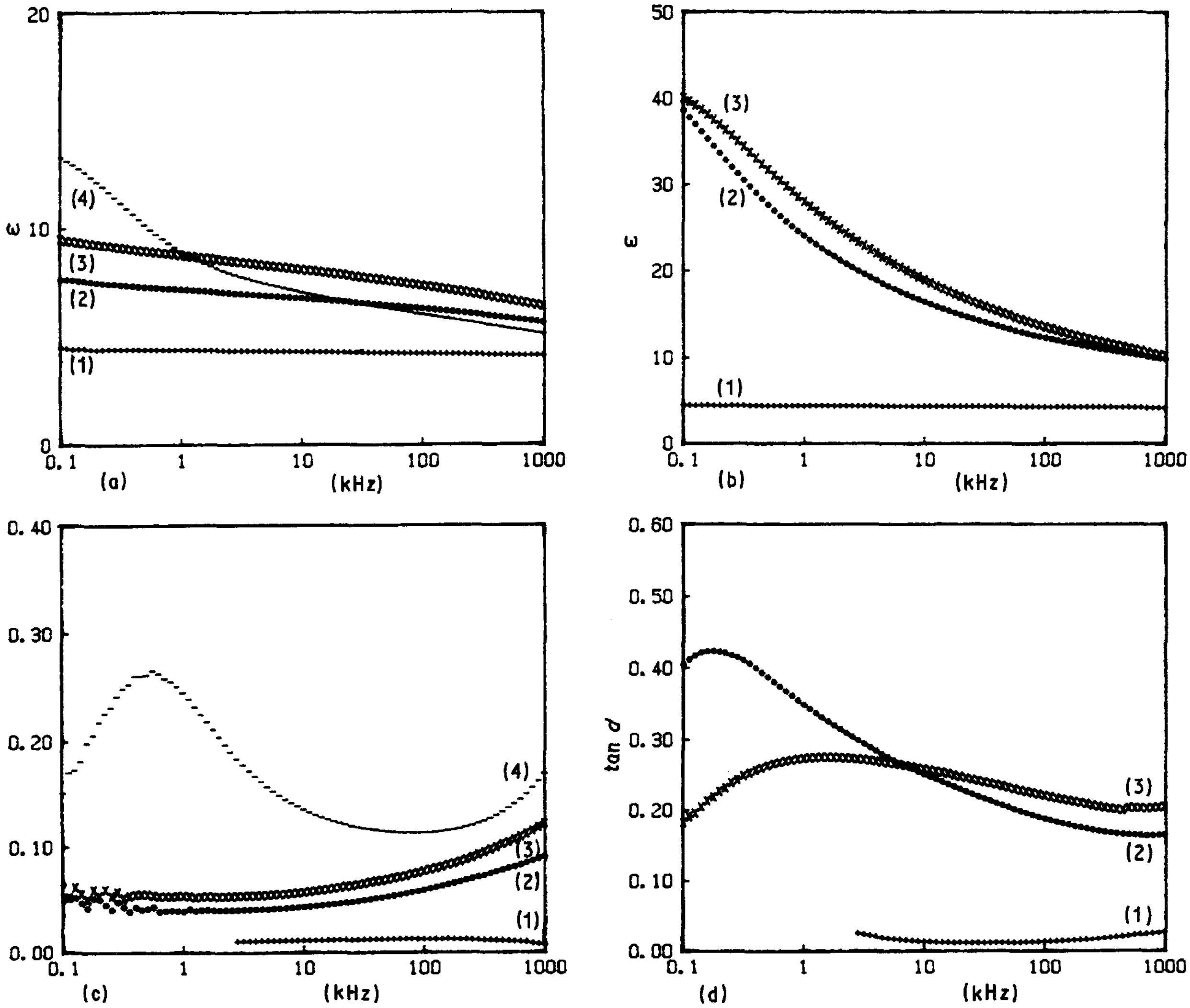

Figure 5 (a), (b) Permittivities (ε), and (c), (d) dissipation factors (tan *d*), for dry and water-aged composites. (a) and (c) Epoxy sample (c), (b) and (d) polyurethane. (a): (1) dry, (2) aged 20° C, (3) aged 40° C, (4) aged 100° C. (b): (1) dry, (2) aged 20° C, (3) aged 40° C. (c): (1) dry, (2) aged 20° C, (3) aged 40° C, (4) aged 100° C. (d): (1) dry, (2) aged 20° C, (3) aged 40° C.

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