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Dielectric behaviour of epoxy and polyester laminates in moisture and electronic packaging exhalates

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The dielectric behaviour of epoxy and polyester laminates has been studied before and after exposing the samples to moisture (relative humidity 60 to 95%) and various exhalates (HCl, HNO_3, HCOOH, CH_3COOH, NH_3 and SO_2 vapours) which are normally released by electronic packaging materials. A strong dielectric dispersion at room temperature is observed after exposing the samples to moisture and various exhalates. The dissipation factor also increases quite appreciably, the increase being more at higher exposure times. The results have been explained in terms of the ionic conductivity due to the dissociation of the exhalates. Recovery studies have also been made and it was found that the changes were reversible except in the case of HCOOH and CH_3COOH for epoxy and in the case of NH_3 for polyester. These results indicate some chemical changes in these cases.

1. Introduction

The conventional inorganic insulators and dielectrics have, to a large extent, been replaced by polymers on account of their unique ability to be tailor-made for specific needs. Epoxies and polyesters have been used in electronics as insulators, dielectrics, substrates, potting compounds, embedding materials and conformal coatings. An electronic circuit assembly used outdoors is not only subjected to atmospheric humidity and atmospheric pollutants but also the exhalations evolved by the organic materials comprising the packaging such as wood, insulating tape, synthetic adhesives and resins, paints and varnishes etc. Troublesome vapours given out by them include phenol, formaldehyde, formic acid, acetic acid (particularly from wood), higher fatty acids and alkaline vapours such as ammonia [1, 2]. HCl is produced by the soldering vapour environment as well as by the hydrolysis of chloride radicals of certain not fully cured plastics. These substances may be the volatile components of the organic materials themselves (outgassing) or products of attack by micro-organisms [3].

Out of these manifold exhalates, the effect of acetic acid, formic acid, hydrochloric acid, nitric acid, sulphur dioxide and ammonia on the dielectric behaviour of epoxy and polyester laminates has been studied in the present paper. The experiments were conducted at room temperature to allow for the realistic situation in open service conditions in the tropics. Two types of study were made: (i) the effect of moisture and (ii) the effect of exhalates. The effect of moisture is studied on the annealed samples. However, the effect of exhalates has been studied on the samples which were pre-exposed to atmospheric humidity (r.h. ~ 70%). To see the effect of exhalates over and above the moisture, results have been compared with 85% r.h. as inside the desiccator, where the samples were exposed to various exhalates, the relative humidity may be higher than the atmospheric humidity.

2. Experimental details

2.1. Sample preparation

Bisphenol A/Epichlorohydrin (BPA/ECH) resin was selected as the epoxy laminate. Curing was done by acid anhydride and woven glass fabric was used for the composite. We chose acid anhydride-cured epoxy resin because the electrical properties are better and are not as sensitive to stoichiometry and cure as those of amine-cured epoxy resin [4]. No filler was used so that the properties of the fillers do not affect our experimental results. A 1.5 mm thick laminate of epoxy with 48% resin and 52% glass fabric was prepared at room temperature and allowed to cure in air for 72 h.

Similarly, bisphenol fumerate polyester resin was used for the polyester laminate. A 1.5 mm thick laminate was prepared with 45% resin and 55% glass fabric content. The curing was done at room temperature for 72 h. Void- and defect-free specimens (3/4 in. × 3/4 in., ~ 1.9 cm × 1.9 cm) were cut from the laminates for the study.

The specimens were exposed to the vapours of 1 N solutions of analytical grade HCl, HCOOH, CH_3COOH, HNO_3 and ammoniacal liquor inside a desiccator of 3 litres capacity, in which 500 ml of solution was kept. The samples were positioned on a porcelain disc with holes in it, in such a way that they were open to the vapour phase. The lid was tightly placed and was opened only for sufficient time to pick up the sample for testing. Sulphur dioxide gas was

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produced inside a conical flask fitted with a rubber bung having a glass hook from which the sample could be hung, by neutralizing a 10% excess solution of sodium thiosulphate by 0.1 N H_2SO_4. The SO_2 generated in the flask was 0.06 g %. Whenever the sample was taken out for testing, a fresh charge of SO_2 gas was generated. Environments of different r.h. were created using different percentages of H_2SO_4 (AR grade, specific gravity 1.86).

2.2. Dielectric measurements

Dielectric measurements were made by mounting the samples (sandwiched between two steel electrodes diameter ~ 1.5 cm) inside a metallic sample holder. Three terminal measurements were made to avoid stray capacitances by grounding the metallic sample holder. A GR 1620 – A.P. capacitance measuring assembly was used to measure the capacitance and the dissipation factor. The instrument was used in the parallel capacitance mode where parallel conductance could be measured directly. The values of tanδ were calculated using the measured conductance at various frequencies. Lead capacitance (~ 2.5 pF) was subtracted from the measured capacitance before calculating the dielectric constant.

To measure dielectric behaviour on annealed samples, the samples were first annealed at 100° C for 2 h in the same sample holder in a vacuum of ~ 10^{-2} torr. After annealing, the measurements were made in the same vacuum. To study the effect of moisture on the dielectric behaviour, a sample was also each time taken out of the sample holder and kept for exposure to various humidity conditions (r.h. 60% to 95%). Measurements on moisture-exposed samples were made with no vacuum inside the sample holder. To study the effect of exhalates, identical samples were taken and exposed to various exhalates in their respective desiccators. The dielectric measurements on exposed samples were also made with no vacuum inside the sample holder. Uncoated samples were preferred so that the effect of exhalates could be observed clearly. As the measurements on all the samples were done under the same conditions, error due to contact should not affect the conclusions of the present work. To check the reproducibility of the measured parameters, various pieces of the same material were subjected to the same experimental conditions and the results were found to be within ± 2% experimental error.

3. Results and discussions

3.1. Effect of humidity

To study the effect of humidity on dielectric behaviour of epoxy and polyester laminates, the dielectric constant (ε') and dissipation factor (tanδ) were measured as a function of frequency (60 Hz to 10 kHz). Such measurements have been made on annealed samples (no moisture) and after exposing the samples to humidity (r.h. 60% to 95%) for different exposure times (1 to 8 days). Frequency dependence of ε' and tanδ at room temperature for epoxy and polyester laminates, in the annealed state and after exposure to moisture, is shown in Figs 1 and 2. Only values of ε' and tanδ for a particular exposure time (5 days) have been plotted in these figures. Results were found of the same nature at other exposure times.

It is clear from Figs 1 and 2 that ε' and tanδ decrease with increasing frequency for annealed and moisture-exposed samples of epoxy and polyester laminates. These results indicate that the dielectric dispersion occurs even in the annealed samples where moisture may be absent. The dielectric dispersion in annealed samples of epoxy and polyester laminates may be because of the polar character of these materials [4].

It is also evident from Figs 1 and 2 that moisture affects the dielectric behaviour quite appreciably. The dielectric dispersion becomes quite strong as the samples of epoxy and polyester laminates are exposed to higher relative humidity. The values of ε' and tan δ, at a particular frequency, continue to increase as the percentage of relative humidity increases (see Figs 1 and 2). In the case of epoxy, it can be seen that ε' against frequency curves for 85% and 95% r.h. are close together whereas, in polyester, the difference between these curves is very large (see Fig. 1). At all r.h. the increase in the values of ε' with increasing r.h. is more in the case of polyester than epoxy. Fig. 2 shows that, in the case of polyester, even a peak in the tanδ against frequency curves is observed when r.h. increases to 95%. Such peaks are not seen in the case of epoxy. Comparatively more absorption of water vapour by the polyester may be responsible for such drastic changes in ε' and tanδ, compared to epoxy.

Kohn [5] has pointed out that epoxy resins, used for protective coatings, may absorb very little water but are quite permeable to the passage of moisture. The increase in the dielectric constant and tanδ due to moisture absorption may, therefore, be understood in the present case in terms of an heterogeneous system (sample + water molecules) which might result in Maxwell–Wagner-type losses as the conductivity of water is quite large compared to the materials used in the present study. A peak in the tanδ against frequency curve in the case of polyester can, therefore, be interpreted in terms of Maxwell–Wagner losses. Because of these losses, the apparent value of ε' also increases.

We have also studied the effect of exposure time of moisture on the dielectric behaviour of epoxy and polyester laminates. Our results (not shown here) indicate that the values of ε' and tanδ go on increasing as the time of exposure increases and then become stable after a very long time (> 5 days). The effect was found to be maximum at the highest relative humidity. Although epoxides are glassy polymers and can absorb a significant amount of water, diffusion of water in them seems invariably Fickian [4].

We also performed recovery studies by airing the exposed samples for a few days in open atmosphere and then annealing them as before. The results of these studies show that samples return to their original annealed state. The reversible nature of the moisture effect indicates that no chemical change takes place after exposing the samples to moisture.

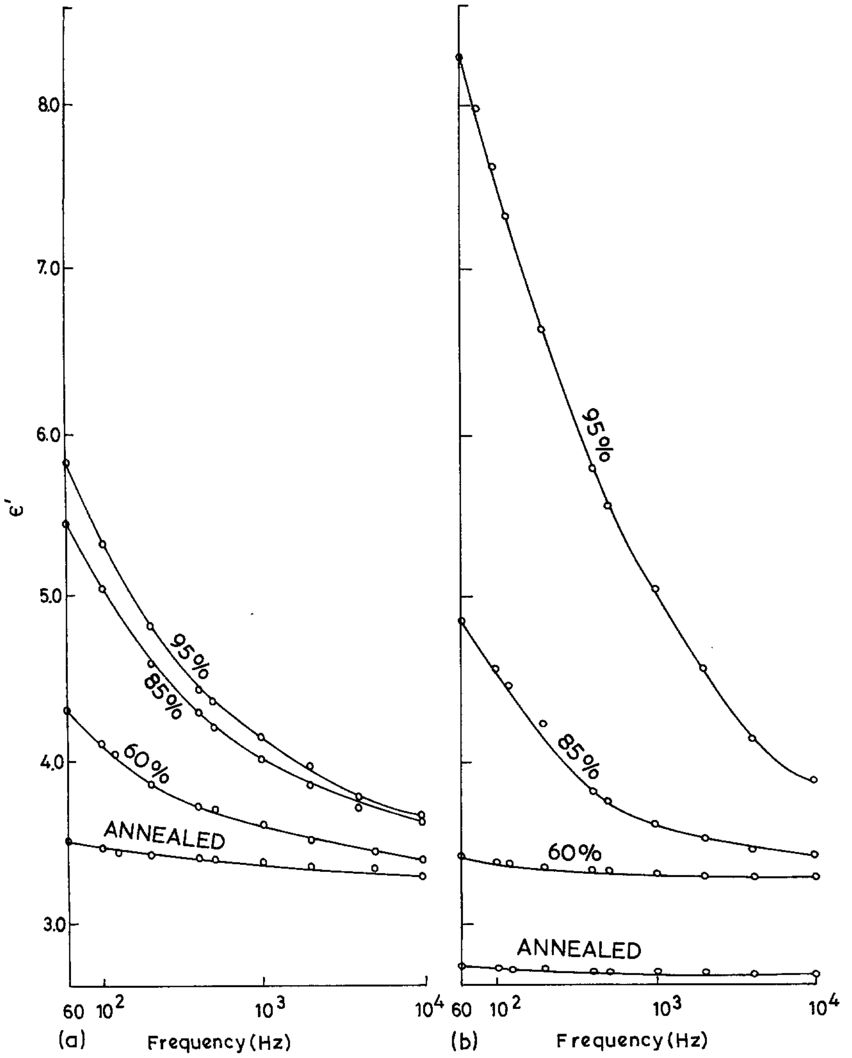

Figure 1 Frequency dependence of dielectric constant for (a) epoxy and (b) polyester laminates in annealed and moisture-exposed samples; exposure time 5 days.

3.2. Effect of exhalates

To study the effect of exhalates on the dielectric behaviour of epoxy and polyester laminates, both materials were subjected to similar conditions of temperature and exhalate vapours. The diurnal temperature changes produced similar condensations of the exhalates. The frequency dependence of dielectric constant and tanδ was studied for the samples exposed to various exhalates for varied times for a period of 8 days. The results for a particular time period of exposure (48 h) are plotted in Figs 3 to 6. The results are of a similar nature at other exposure times. These figures also depict the variation of ε' and tanδ with 85% r.h. which has been taken as the base line for the tropics. This was done to assess the effect of exhalates over and above the prevailing atmospheric humidity. Before exposing to exhalates, the samples were conditioned in atmospheric humidity for about a month (average r.h. 70%).

Figs 3 and 5 show that dielectric dispersion increases in both epoxy and polyester after exposing to various exhalates. The values of tanδ also increase in all cases (see Figs 4 and 6). A comparative study of Figs 3 and 5 shows that the dielectric dispersion is greater in polyester than in epoxy in all cases. In the case of epoxy, except for CH_3COOH and HCOOH vapours, all the curves are close together and the values do not differ widely from that of 85% r.h. (see Fig. 3). The slightly higher dispersion in SO_2 than HCl, HNO_3, NH_3 may be on account of the higher polar character of the H_2SO_4 which is formed on the sample due to the condensation of vapours. In the case of polyester, the values of ε' are very much higher than the values at 85% r.h. in all cases. The highest is NH_3 followed by HCOOH, CH_3COOH, HCl, HNO_3 and SO_2 (see Fig. 5).

The variations in tanδ in the case of epoxy are close to each other, except in CH_3COOH and HCOOH (see Fig. 4). On the other hand, variations in tanδ in the case of polyester are quite large (see Fig. 6). In this case, peaks in tanδ are also seen at lower frequencies for HCl, HNO_3 and CH_3COOH. This type of behaviour makes it unsuitable for use as a substrate for ICs, etc.

To assess the effect of exposure time of exhalates, we have plotted ε' and tan δ (at 10 kHz) against time of exposure in Figs 7 and 8 for both the materials. It is seen that in most cases, the saturation in the values of ε' and tan δ is reached after one week. Similar results were observed at other frequencies. It is clear from Fig. 7 that the variation in ε' and tan δ in epoxy for HCl, HNO_3 and NH_3 are very close together, but more than 85% r.h., whereas in the case of SO_2, CH_3COOH and HCOOH, the variations are quite large. The maximum change in tan δ is observed in the case of HCOOH followed by CH_3COOH and SO_2. On the other hand, in the case of polyester laminate, the variations in all other exhalates except for NH_3 are

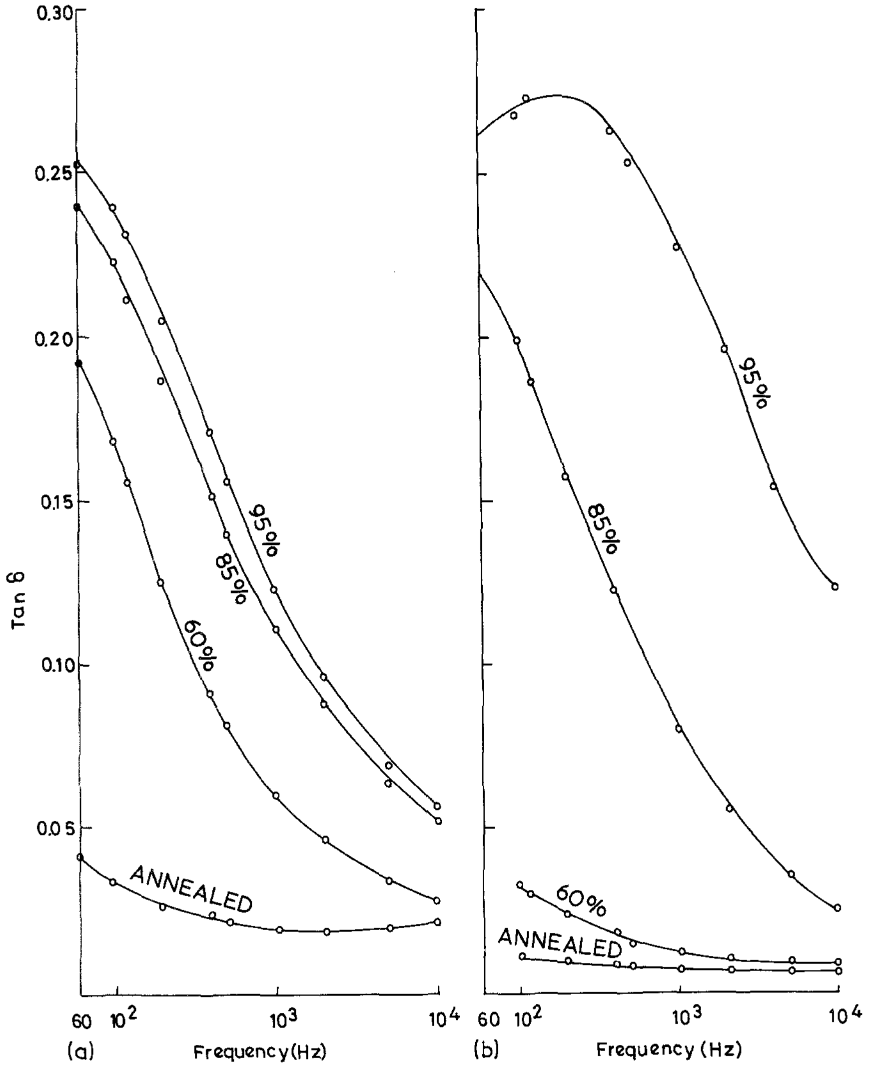

Figure 2 Frequency dependence of dissipation factor for (a) epoxy and (b) polyester laminates in annealed and moisture-exposed samples; exposure time 5 days.

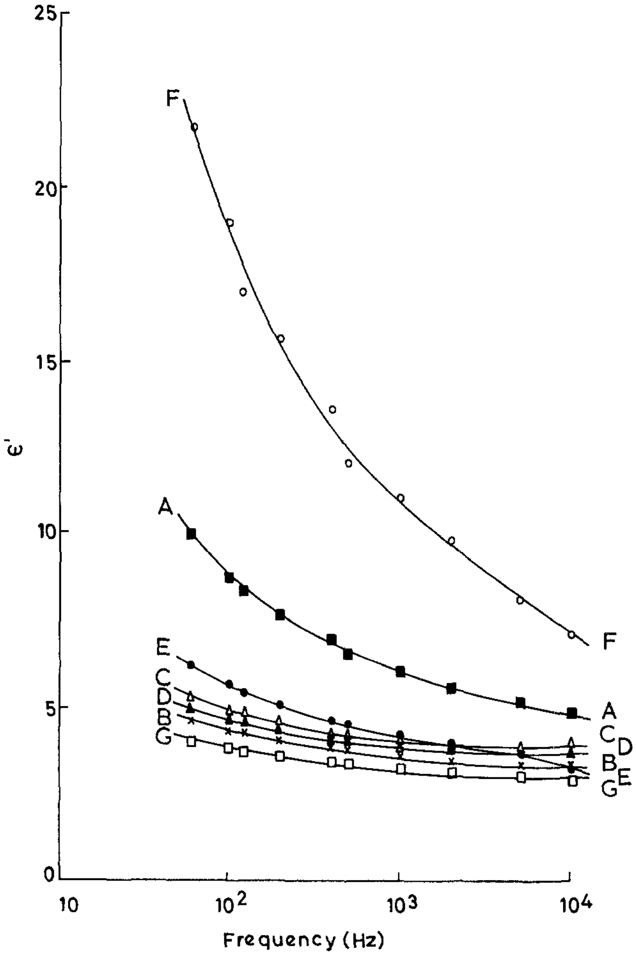

Figure 3 Frequency dependence of dielectric constant for epoxy laminate exposed for 48 h to various exhalates. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

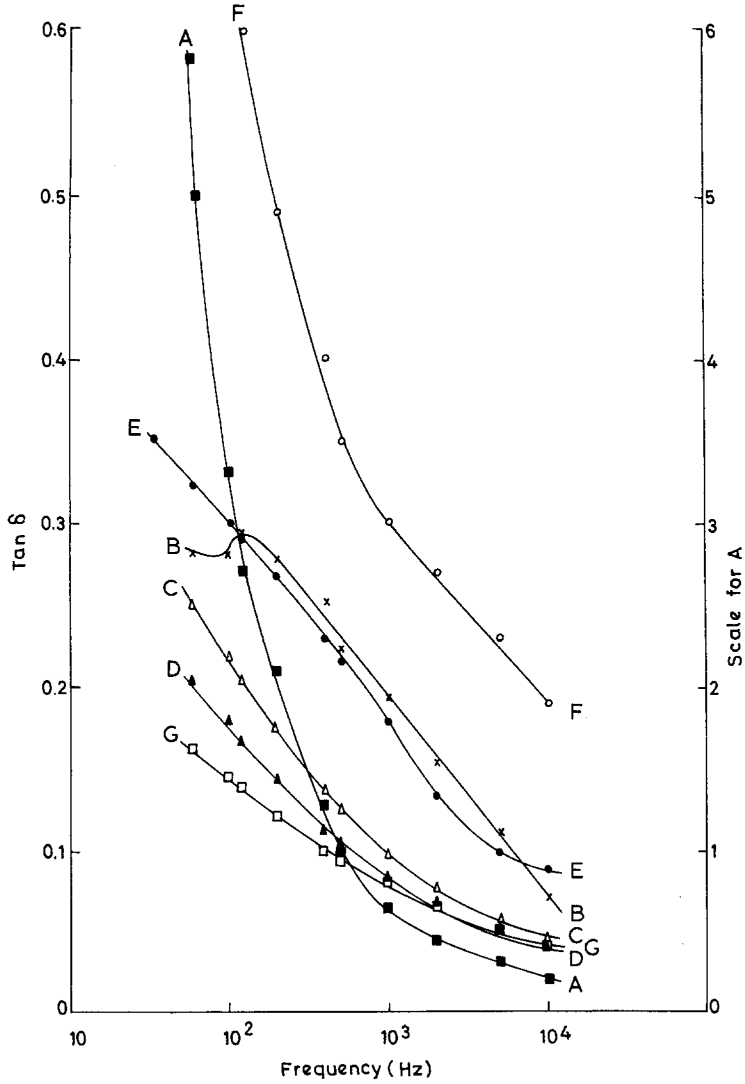

Figure 4 Frequency dependence of dissipation factor for epoxy laminate exposed for 48 h to various exhalates. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

very close to each other but much larger than 85% r.h. (see Fig. 8).

A comparison of Figs 7 and 8 shows that, except for formic and acetic acid, the changes in ε' in polyester are more than in the case of epoxy, and the changes in tan δ are also several orders larger. From these results, it seems that epoxy poses lesser problems on account of exhalation than polyester.

Recovery studies (results not shown here) were also performed by keeping the exposed samples in an open container. We found that in most of the cases, the dielectric parameters (ε' and tan δ) return back to their original value. In the case of CH_3COOH and HCOOH in epoxy and NH_3 in polyester, some irreversible changes were observed. This indicates some sort of chemical change in the specimens. In the case of SO_2, for both samples, though the values of ε' and tan δ returned to values very close to the original ones, some opacity was observed. This may be because of lodging of sulphur particles in the material. The material lost clarity and became slightly yellowish.

Barkatakova and Hranickova [6] have also studied the effect of exhalates (HCl, NH_3, SO_2 and HNO_3) on the dielectric loss and various other parameters in case of phenol-based and epoxy-based compounds. They also observed an increase in dielectric loss after exposing the samples to these exhalates over and above the humidity. They explained the increase in dielectric loss as due to an increase in ionic conductivity which arises due to the dissociation of these exhalates. Their study showed that the dissociation constant and the mobility of ions are important parameters on which the increase of ionic conductivity depends.

According to the above point of view, NH_3, which has a lower dissociation constant than HCl and HNO_3, should have a lesser effect on tan δ in the sample of epoxy, but probably because of the higher mobility of ammonium ions (due to lower molecular weight), the increase in tan δ approaches the same value as in the case of HCl and HNO_3 (see Fig. 7). The enormous rise in tan δ in the case of HCOOH and CH_3COOH may be associated with a chemical change in the sample [7]. Similarly, in the case of polyester, the maximum change in tan δ for NH_3 may be due to some sort of chemical change [7]. The exact chemical composition after reacting with these exhalates is, however, not known from the present measurements.

4. Conclusions

Dielectric constant and tan δ measurements, made on annealed and moisture-exposed samples of polyester and epoxy laminates, having a woven glass content of 55% and 52%, respectively, showed that the dielectric constant and tan δ increase with increasing relative humidity. The values also depend on the exposure time. The process is Fickian in nature and

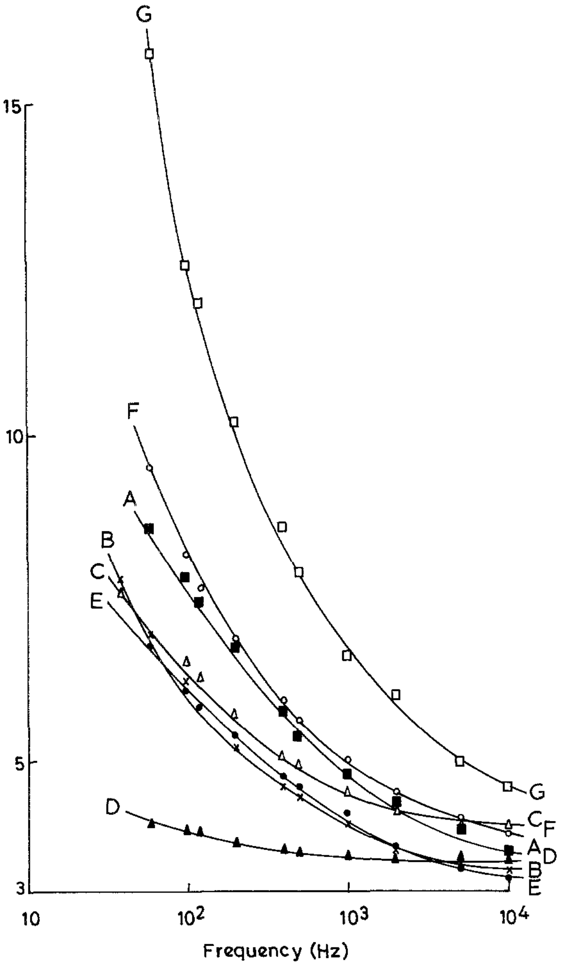

Figure 5 Frequency dependence of dielectric constant for polyester laminate exposed for 48 h to various exhalates. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

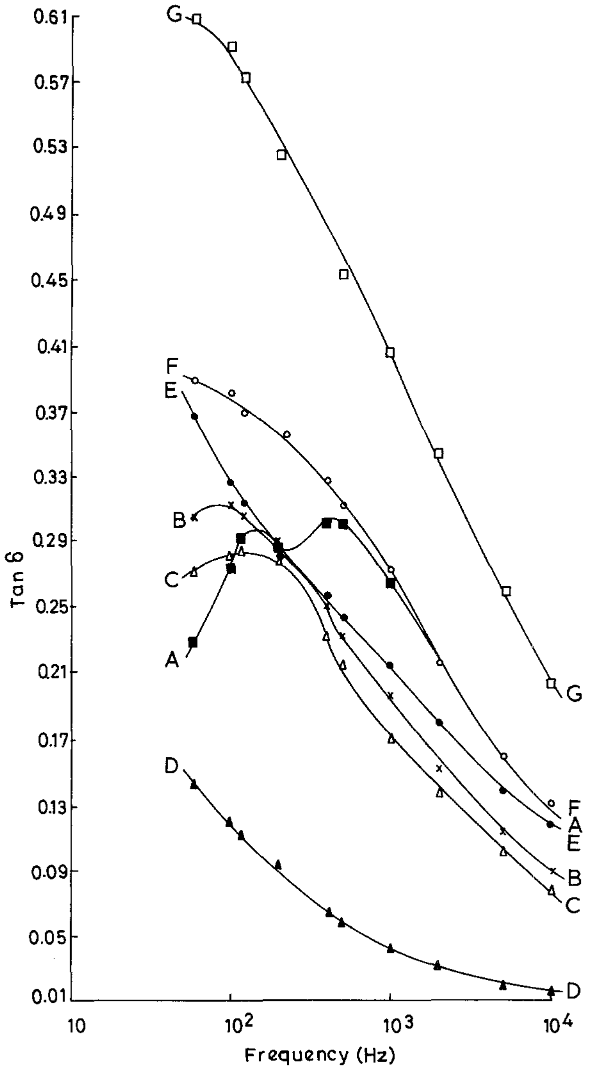

Figure 6 Frequency dependence of dissipation factor for polyester laminate exposed for 48 h to various exhalates. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

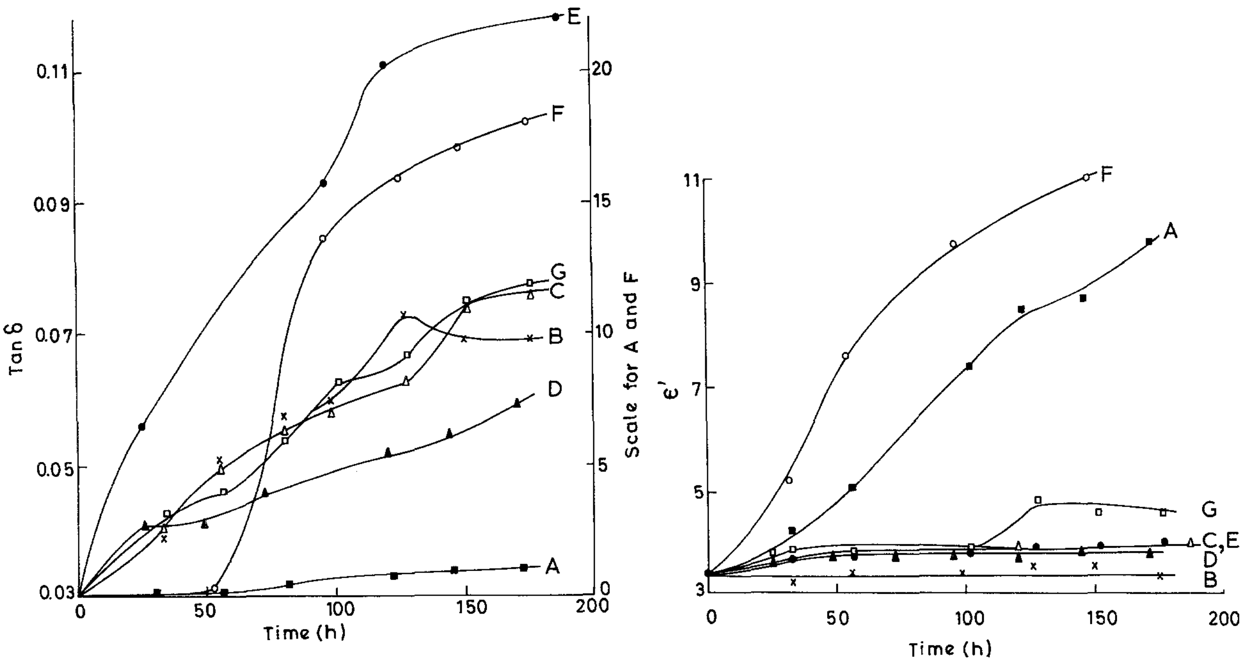

Figure 7 Exposure time dependence of dielectric constant and dissipation factor at 10 kHz for epoxy laminate exposed to various exhaltes. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

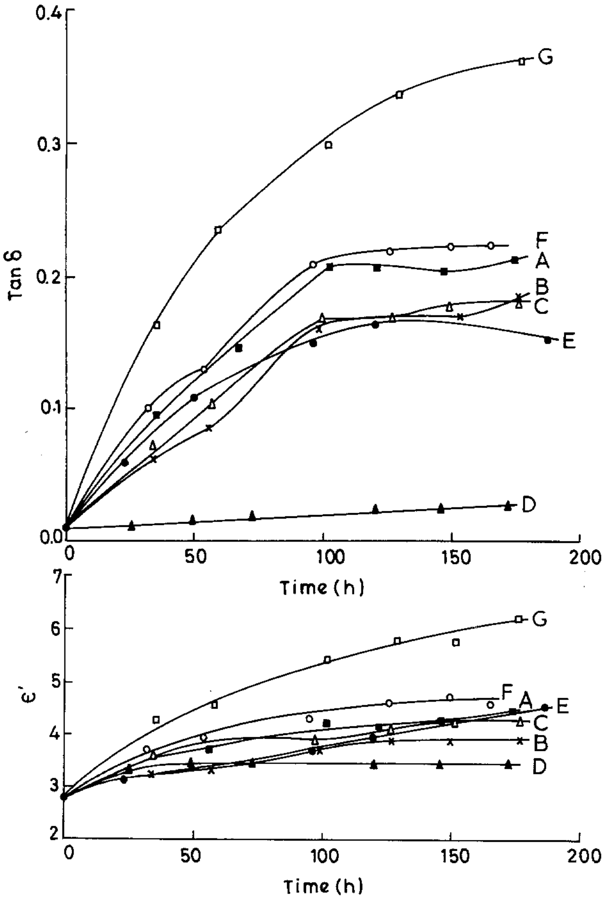

Figure 8 Exposure time dependence of dielectric constant and dissipation factor at 10 kHz for polyester laminate exposed to various exhalates. (A) CH_3COOH, (B) HNO_3, (C) HCl, (D) 85% r.h., (E) SO_2, (F) HCOOH, (G) NH_3.

it is observed that the saturation is reached in approximately one week. There is a complete recovery of the samples from the humidity effect. The effect of moisture is less in epoxy than in polyester.

In the case of exhalates, the increase in ε' and tan δ is much more than what one observes in humidity alone. The values of ε' and tan δ also increase with time of exposure in the case of exhalates. The effect of vapours of 1 N solutions of HNO_3, HCl and SO_2 on epoxy and polyester laminates are similar, except that the values of ε' and tan δ are higher in the latter case.

In the case of vapours from ammonia solution, the effect is not much in epoxy but in polyester the values of ε' and tan δ are much higher than the humidity alone. The polyester sample also loses its texture.

In the case of vapours from 1 N solutions of CH_3COOH and HCOOH, the changes are quite large in epoxy. For polyester, however, their effect is the same as in the case of other exhalates except that it is slightly higher than the others barring the case of ammonia where maximum effect is seen.

There is a near complete recovery from the exposure of exhalates, except in the case of epoxy exposed to CH_3COOH and HCOOH and polyester exposed to NH_3. Some chemical changes might have taken place in these cases.

The present study shows that except for CH_3COOH and HCOOH vapours, the epoxy seems to be less lossy than polyester in annealed samples and after exposing the samples to humidity and exhalates.

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