# Effect of moisture and electronic packaging exhalates on the electrical conductivity of epoxy laminate

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The temperature dependence of the d.c. conductivity of epoxy laminate has been studied before and after exposing the samples to moisture (relative humidity 70 to 95%) and various exhalates (HCl, $HNO_3$, HCOOH, $CH_3COOH$, $NH_3$ and $SO_2$ vapours) which are generally released by electronic packaging materials. The d.c. conductivity increases with increase of temperature. At a particular temperature the d.c. conductivity increases after exposing the samples to moisture and exhalates, the increase being more at higher exposure times. The results have been explained on the basis of Fickian adsorption of moisture and consequent dissolution of the exhalate vapours in it, which possibly increases the conductivity due to ion formation.

## 1. Introduction

Epoxy resins and composite materials are in great demand for electronic circuitory. They are used as substrates for integrated circuits, conformal coatings, encapsulants, insulants and sealants. An electronic circuit assembly used outdoors is not only subjected to atmospheric humidity and atmospheric pollutants but also to the exhalations evolved by the organic materials comprising the packaging such as wood, insulating tape, synthetic adhesives and resins, paints, and varnishes. 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 from certain incompletely cured plastics. These substances may be the volatile components of the organic materials themselves (outgassing) or products of attack by micro-organisms [3].

In our earlier communication [4], we reported the effect of moisture and various exhalates (HCl, $HNO_3$, HCOOH, $CH_3COOH$, $NH_3$ and $SO_2$ vapours) on the dielectric behaviour of epoxy and polyester laminates and found that the dielectric loss increases after exposing these materials to moisture and exhalates. From the same study we also conclude that except for $CH_3COOH$ and HCOOH vapours, the epoxy seemed to be less glossy than polyester after exposing the samples to humidity and exhalates. We have, therefore, chosen epoxy laminate for further study of the effect of moisture and exhalates.

In the present paper we report the d.c. conductivity behaviour of epoxy laminate before and after expos-

ing the samples to moisture and various exhalates. Two types of experiments have been conducted for this study:

(i) The d.c. conductivity is measured at room temperature before and after exposing the samples to moisture and exhalates. This is done without vacuum to allow for the realistic situation in open service conditions in the tropics.

(ii) The temperature dependence of d.c. conductivity is measured in a vacuum of $\sim 10^{-2}$ torr before and after exposing the samples to moisture and exhalates.

These two types of experiment are conducted for various exposure times (6 h, 18 h, 3 days and 5 days). The effect of moisture and exhalates is studied on the annealed samples.

## 2. Experimental details

### 2.1. Sample preparation

The resin used for the laminate was DGEBA (Araldite LY556) and the hardner used was the polyamine HY951 (both from Ciba-Geigy). Plain-weave glass fabric was used for the composite. 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 45% resin and 55% glass fabric was made for the purpose at room temperature and allowed to cure in air for 72 h.

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 dessicator of 3 litres capacity, in which 500 ml of solution was kept. The samples were kept on a porcelain disc with holes in such a way that they were open to the vapour phase. The lid was tightly closed
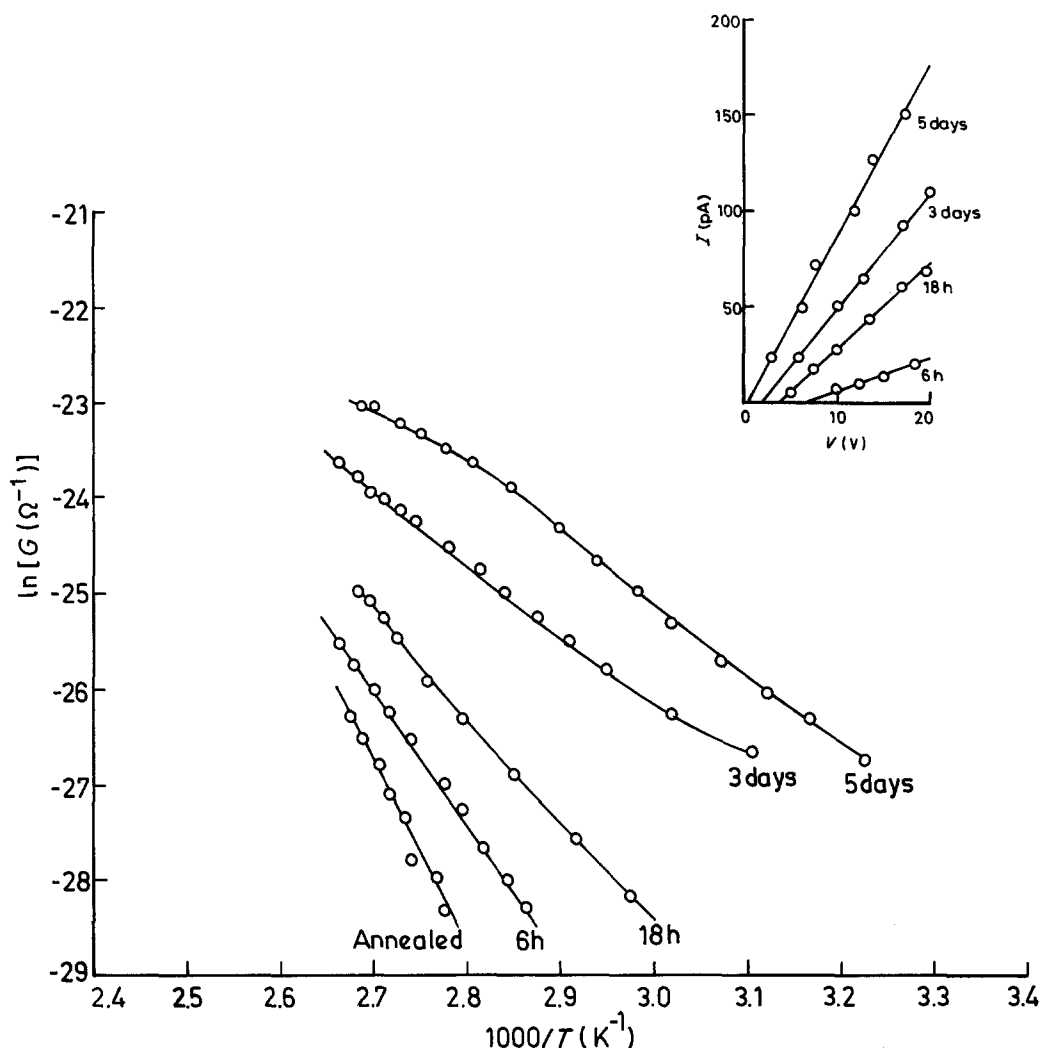
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*Figure 1* Temperature dependence of d.c. conductance for annealed and moisture-exposed sample of epoxy laminate for different exposure times (RH 70%). The inset shows the *I–V* characteristics at room temperature.

and was opened only for a time just long enough to pick up the sample for testing. Sulphur dioxide gas was produced inside a conical flask with a rubber bung having a glass hook from which the sample could be hung, by neutralizing a 10% excess solution of sodium thiosulphate with 0.1 N $H_2SO_4$. The $SO_2$ generated in the flask was 0.06 wt %. Whenever the sample was taken out for testing, a fresh charge of $SO_2$ gas was generated. Various percentages of relative humidity (RH) were created by different percentages of $H_2SO_4$ (AR grade, specific gravity 1.86).

## 2.2. Electrical conductivity measurements

D.c. conductivity was measured by mounting the samples (sandwiched between two steel electrodes of diameter 1.5 cm) inside a metallic sample holder. The temperature was varied by mounting a heater outside the sample holder, and was measured by mounting a chromel–alumel thermocouple very close to the sample. A d.c. voltage of 20 V was applied across the sample and the resulting current was measured by a digital ($3\frac{1}{2}$ digit) pico-ammeter (Achme, Model SD-100) having a least count of 1 pA.

To measure the temperature dependence of d.c. conductivity on annealed samples, the samples were

first annealed at 100° C for 2 h in the same sample holder in a vacuum $\sim 10^{-2}$ torr. After annealing, the measurements were made in the same vacuum. To study the effect of moisture on the d.c. conductivity, each time the sample was taken out of the sample holder and kept for exposure to various humidity conditions (RH 70 to 95%). Firstly, the *I–V* characteristics of moisture-exposed samples were determined at room temperature without having any vacuum inside the sample holder. Thereafter, a vacuum of $\sim 10^{-2}$ torr was maintained and the temperature dependence of d.c. conductivity was measured.

To study the effect of exhalates, identical samples were taken and exposed to various exhalates in their respective desiccators. In this case also, first, measurements were made at room temperature without vacuum and then the temperature dependence was measured in a vacuum of $\sim 10^{-2}$ torr.

Uncoated samples were preferred for the present study so that the effect of moisture and exhalates could be observed clearly. As the measurements on all the samples are done under identical conditions, the errors due to contact may not affect the conclusions of the present work. To check the reproducibility of the measured parameters, various pieces of the same
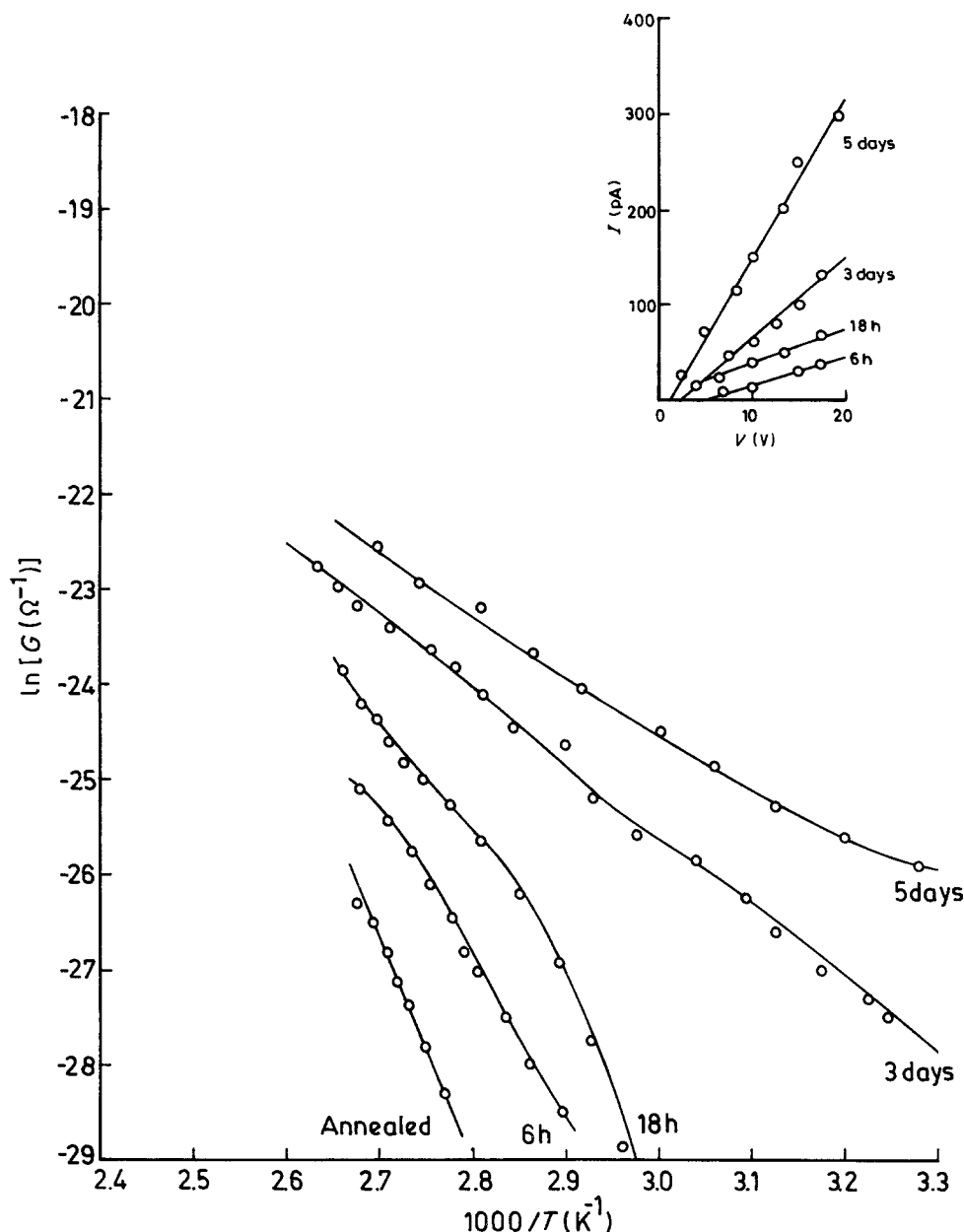
*Figure 2* Temperature dependence of d.c. conductance for annealed and moisture-exposed sample of epoxy laminate for different exposure times (RH 85%). The inset shows the $I$-$V$ characteristics at room temperature.

material were subjected to the same experimental conditions and the results were found to be within ± 2% experimental error.

## 3. Results and discussion

### 3.1. Effect of humidity

Epoxy resins may absorb water from the ambient atmosphere, with the surface layer reaching equilibrium with the surrounding environment very quickly. To study the effect of surface adsorption of water, we measured the $I$-$V$ characteristics at room temperature without vacuum after exposing the sample to different relative humidities. The insets of Figs 1 to 3 show the results of these measurements. The conductances calculated from the slopes of these curves and the values under different RH conditions and at different exposure times are given in Table I. It is clear from this table that the conductance goes on increasing as the exposure time increases.

Table I also indicates that the conductance for the same time of exposure increases as the RH increases. This may be understood in terms of the vapour pressure of the humid air which increases as RH increases. A higher vapour pressure may help in settling more moisture on the surface of the material.

After evacuating the sample holder to $\sim 10^{-2}$ torr, the conductance decreases significantly showing the evaporation of adsorbed water from the surface of the material. However, the conductance does not come back to the original annealed state just by evacuating the sample holder. This indicates that water vapour is not only adsorbed on the surface but also diffuses into the bulk.

To study the effect of diffused water vapour, we made conductivity measurements in a vacuum of $\sim 10^{-2}$ torr at different temperatures for moisture-exposed samples under different RH conditions and for different exposure times. The results of these measurements are plotted in Figs 1 to 3. It is clear from these figures that the conductance $G$ increases
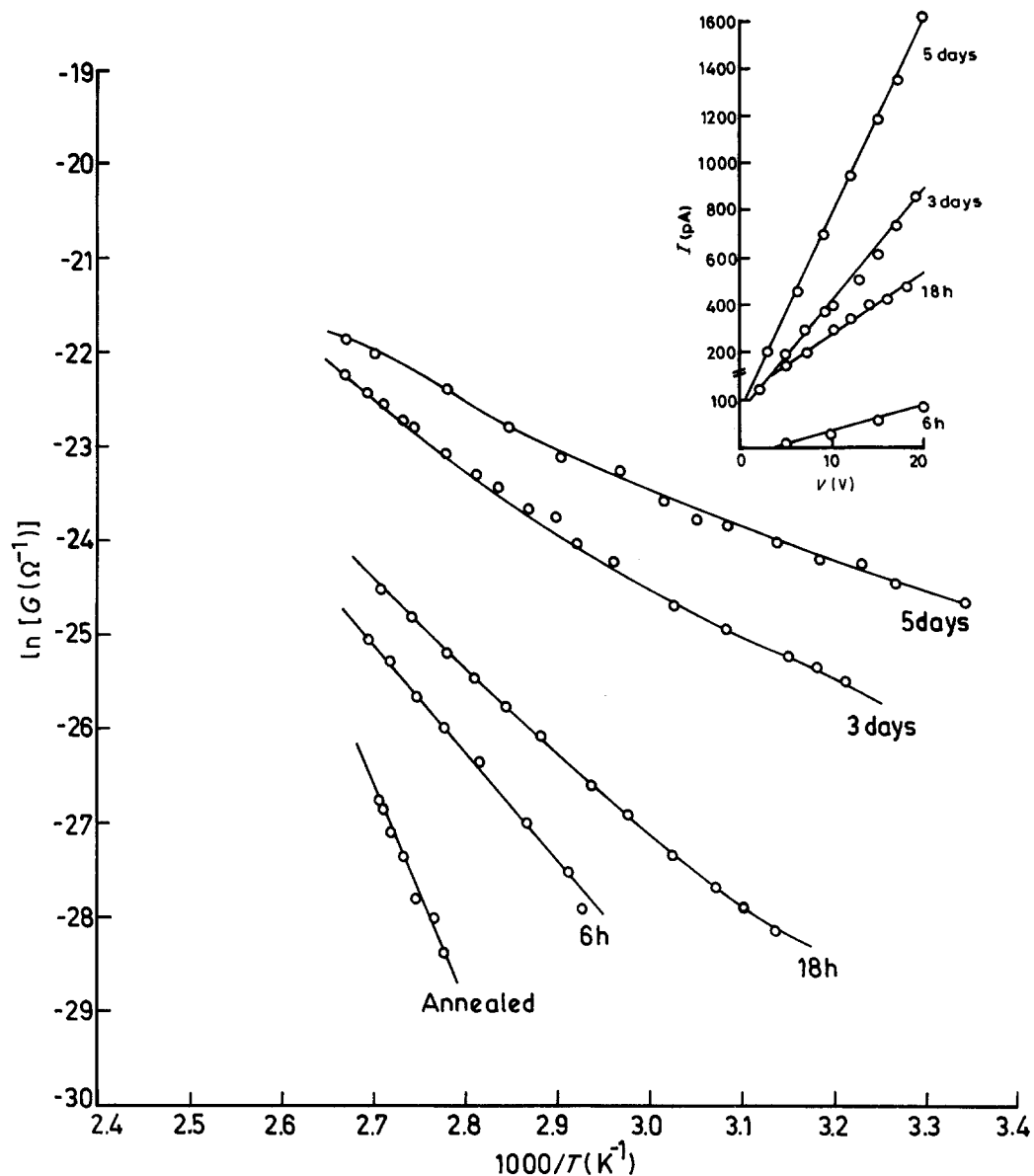
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*Figure 3* Temperature dependence of d.c. conductance for annealed and moisture-exposed sample of epoxy laminate for different exposure times (RH 95%). The inset shows the *I-V* characteristics at room temperature.

exponentially with temperature $T$ for annealed samples, as the ln$G$ against 1000/$T$ curves are straight lines. Such curves for the exposed samples show slight deviations from straight lines as the absorbed water may start coming out of the material at different temperatures. With an increase of the exposure time the conductance increases, for various RH values, at all temperatures. Fig. 4 confirms this statement where

the ln$G$ against exposure time curves are plotted at two temperatures (80 and 100° C).

Kohn [5] has pointed out that epoxy resins absorb very little water but may be quite permeable to the passage of moisture. It is also reported [6] that the diffusion of water may obey Fick's law in epoxy, so that the water concentration gradient between the environment and the material is responsible for the

TABLE I Conductance values ($G = I/V$) at room temperature without vacuum after exposing the epoxy laminate sample to humidity and exhalate vapours for different exposure times

| Vapour | $G$ ($\Omega^{-1}$) | | | |
|---|---|---|---|---|
| | 6 h | 18 h | 3 days | 5 days |
| 70% RH | $1.7 \times 10^{-12}$ | $4.3 \times 10^{-12}$ | $5.9 \times 10^{-12}$ | $8.7 \times 10^{-12}$ |
| 85% RH | $3.0 \times 10^{-12}$ | $6.0 \times 10^{-12}$ | $8.6 \times 10^{-12}$ | $1.8 \times 10^{-11}$ |
| 95% RH | $5.3 \times 10^{-12}$ | $2.2 \times 10^{-11}$ | $4.7 \times 10^{-11}$ | $8.2 \times 10^{-11}$ |
| HCl | $7.3 \times 10^{-12}$ | $1.3 \times 10^{-11}$ | $6.0 \times 10^{-11}$ | $1.5 \times 10^{-10}$ |
| $HNO_3$ | $1.0 \times 10^{-11}$ | $3.0 \times 10^{-11}$ | $3.3 \times 10^{-10}$ | $1.5 \times 10^{-9}$ |
| $SO_2$ | $4.1 \times 10^{-11}$ | $2.0 \times 10^{-10}$ | $7.4 \times 10^{-10}$ | $8.2 \times 10^{-9}$ |
| $NH_3$ | $7.6 \times 10^{-11}$ | $6.3 \times 10^{-10}$ | $7.5 \times 10^{-10}$ | $1.4 \times 10^{-9}$ |
| $CH_3COOH$ | $8.0 \times 10^{-10}$ | $1.7 \times 10^{-9}$ | $1.6 \times 10^{-8}$ | $1.4 \times 10^{-6}$ |
| HCOOH | $3.3 \times 10^{-11}$ | $2.7 \times 10^{-8}$ | $1.8 \times 10^{-6}$ | $1.3 \times 10^{-5}$ |

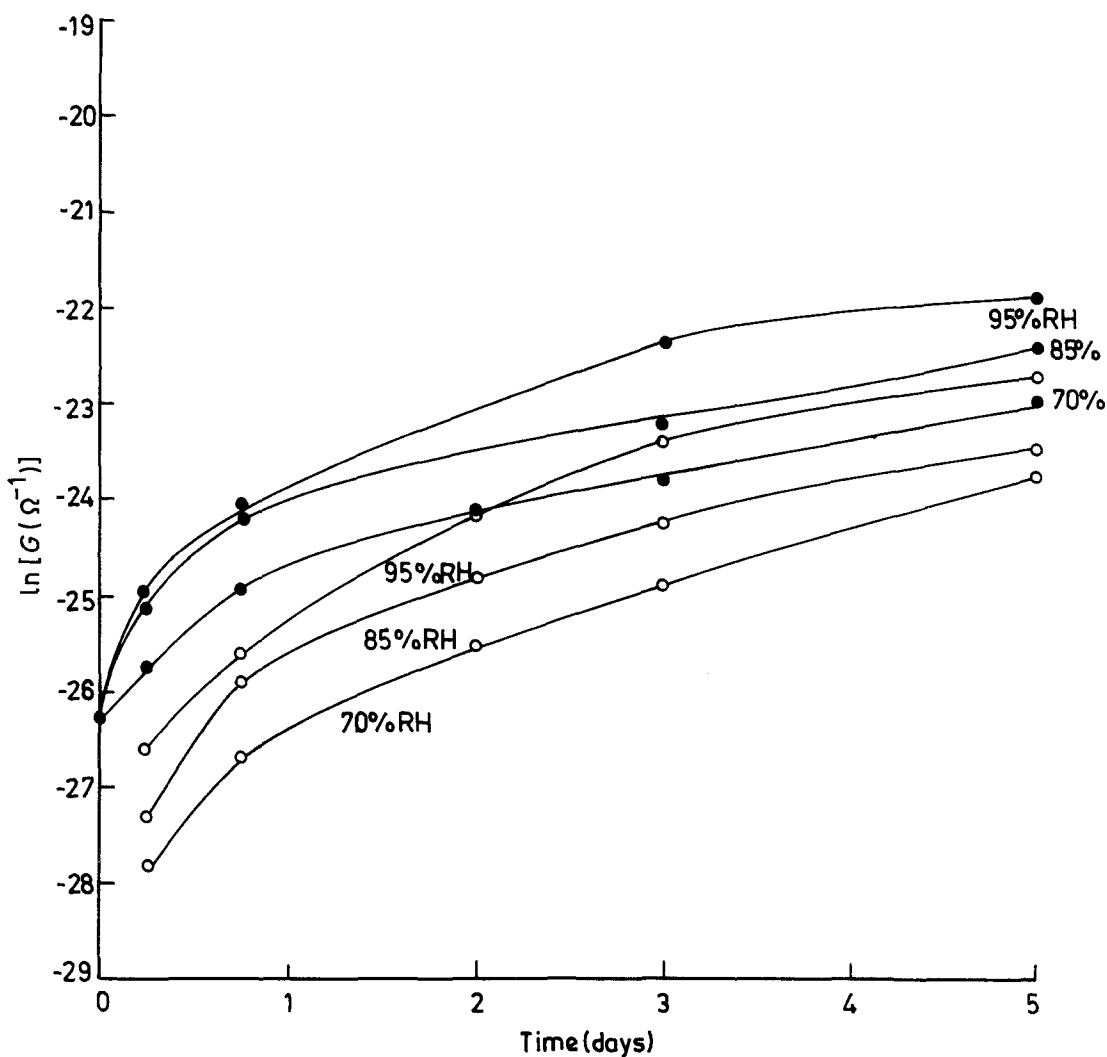*Figure 4* lnG against exposure time at (O) 80 and (●) 100°C for moisture-exposed samples of epoxy laminate at different RH values.

diffusion of water into the material until saturation is reached. Studies made by various workers [7-10] have established that the water absorbed is not usually in the liquid form but consists of molecules or groups of molecules linked by hydrogen bonds to the polymer. In addition, liquid water can be absorbed by capillary action along cracks or along the fibre–matrix interface.

The increase in the conductivity after exposing the samples to moisure can be understood in terms of a heterogeneous system (sample + water molecules). Water is known to be conducting, especially in an impure state. Absorption of water, therefore, increases the measured conductance of the sample.

We also performed recovery studies by airing the exposed samples for a few days in an open atmosphere and then annealing them as before. Our results of these studies show that samples return back 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.

### 3.2. Effect of exhalates
To study the effect of exhalates on the d.c. conductivity behaviour of epoxy laminates, annealed samples were exposed to similar conditions of temperature and exhalate vapours. The diurnal temperature changes

produced similar condensations of the exhalate vapours. As in the case of moisture, two types of study are made in this case also: (i) $I$-$V$ characteristics have been studied at room temperature without vacuum and (ii) the temperature dependence of conductivity is studied in a vacuum of $\sim 10^{-2}$ torr. Both types of measurement have been made for various exposure times (6 h to 5 days) in all the exhalate vapours used. Figs 5 to 10 show the results of this study. From the slopes of the $I$-$V$ characteristics at room temperature (see insets of Figs 5 to 10) the conductance has been calculated and the values have been inserted in Table I for different exposure times. It is clear from this table that the conductance at room temperature increases as the exposure time increases in all types of exhalate vapour.

Table I indicates that HCl vapours affect the conductivity the least among all the exhalate vapours used in the present study. The effect in this case is slightly higher than what one observes in the case of humidity alone. This is accounted for by the fact that the partial vapour pressure of the evolved HCl gas (0.00024 mm Hg) at room temperature is very low, and as such it is primarily moisture which is effective. The initially higher value in the case of HCl vapours (4 times that of 70% RH for an exposure time of 6 h) may be on account of the high dissociation constant of HCl.
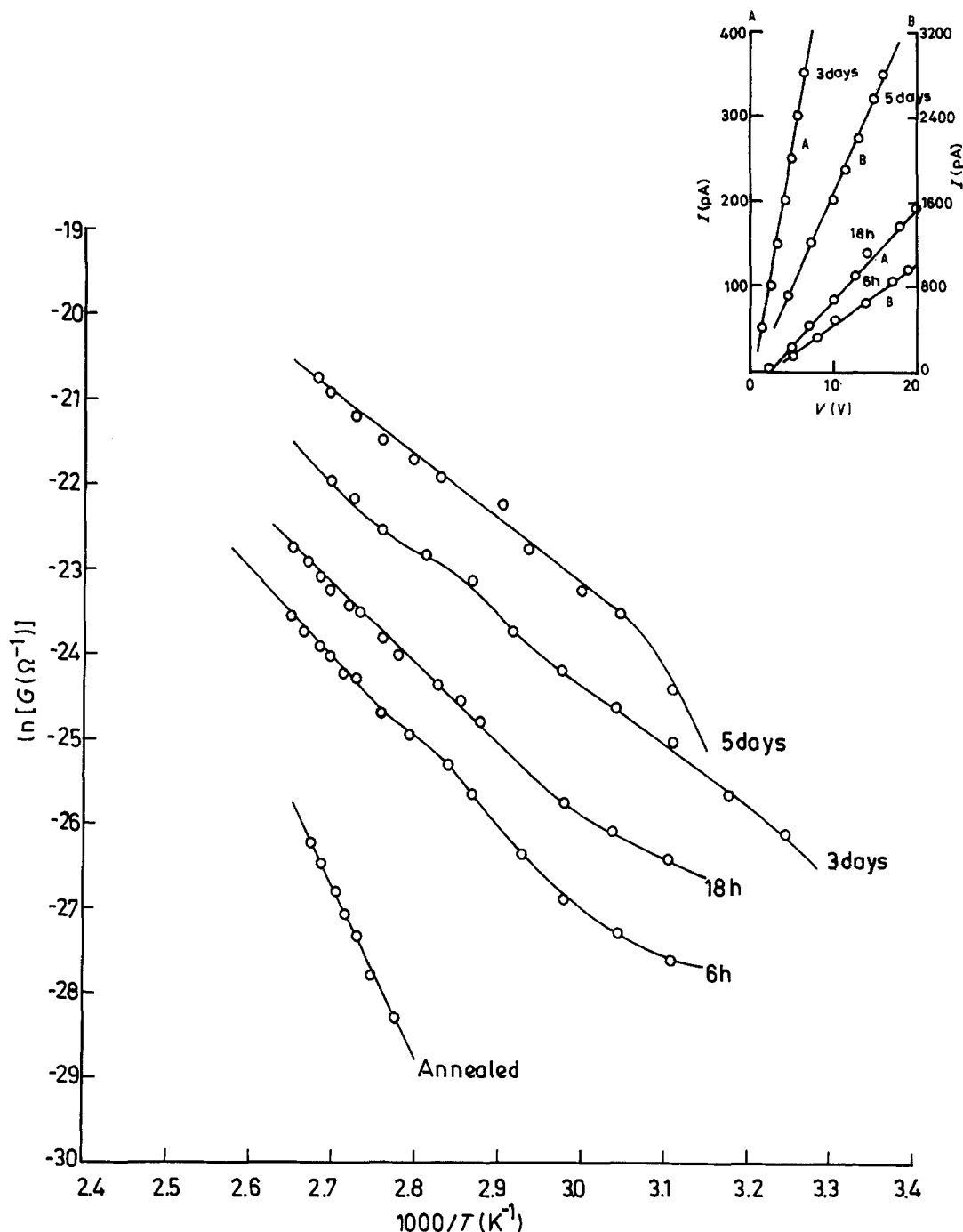
*Figure 5* Temperature dependence of d.c. conductance for annealed and HCl vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the $I-V$ characteristics at room temperature.

Table I also indicates that $HNO_3$ vapours produce an increase of about one order of magnitude as compared to that of HCl vapours. The effects of $SO_2$ and $NH_3$ vapours are also of the same order of magnitude.

Barkatakova and Hranickova [11], in a study of the insulation resistance of phenol- and epoxy-based compounds exposed to gases like $SO_2$, $NH_3$, HCl and $HNO_3$ vapours, have explained the increase in conductivity in terms of dissociation constant and ionic mobility. Although the dissociation constant of $SO_2$ is more than that of $NH_3$, the higher mobility of the latter may be responsible for producing a similar effect in both cases.

$CH_3COOH$ and HCOOH acid vapours produce the greatest effects on the conductivity (see Table I) among all the exhalate vapours used in the present study. Formic acid in the long run (exposure time 5 days) makes the sample more conducting than $CH_3COOH$ exposure, primarily because of the higher vapour pressure of the former as compared to the latter. The higher mobility of HCOOH and the higher dissociation constant ($1.8 \times 10^{-4}$ for HCOOH compared with $1.8 \times 10^{-5}$ for $CH_3COOH$) are also responsible for this behaviour.

In the case of exhalates we also found that the conductivity decreases significantly on evacuating the sample holder. This decrease may be associated with the evaporation of exhalate vapours adsorbed on the surface of the material. To study the exhalate vapours absorbed by the material, we measured the temperature dependence of conductivity in a vacuum of $\sim 10^{-2}$ torr for various exposure times (6 h to 5 days).
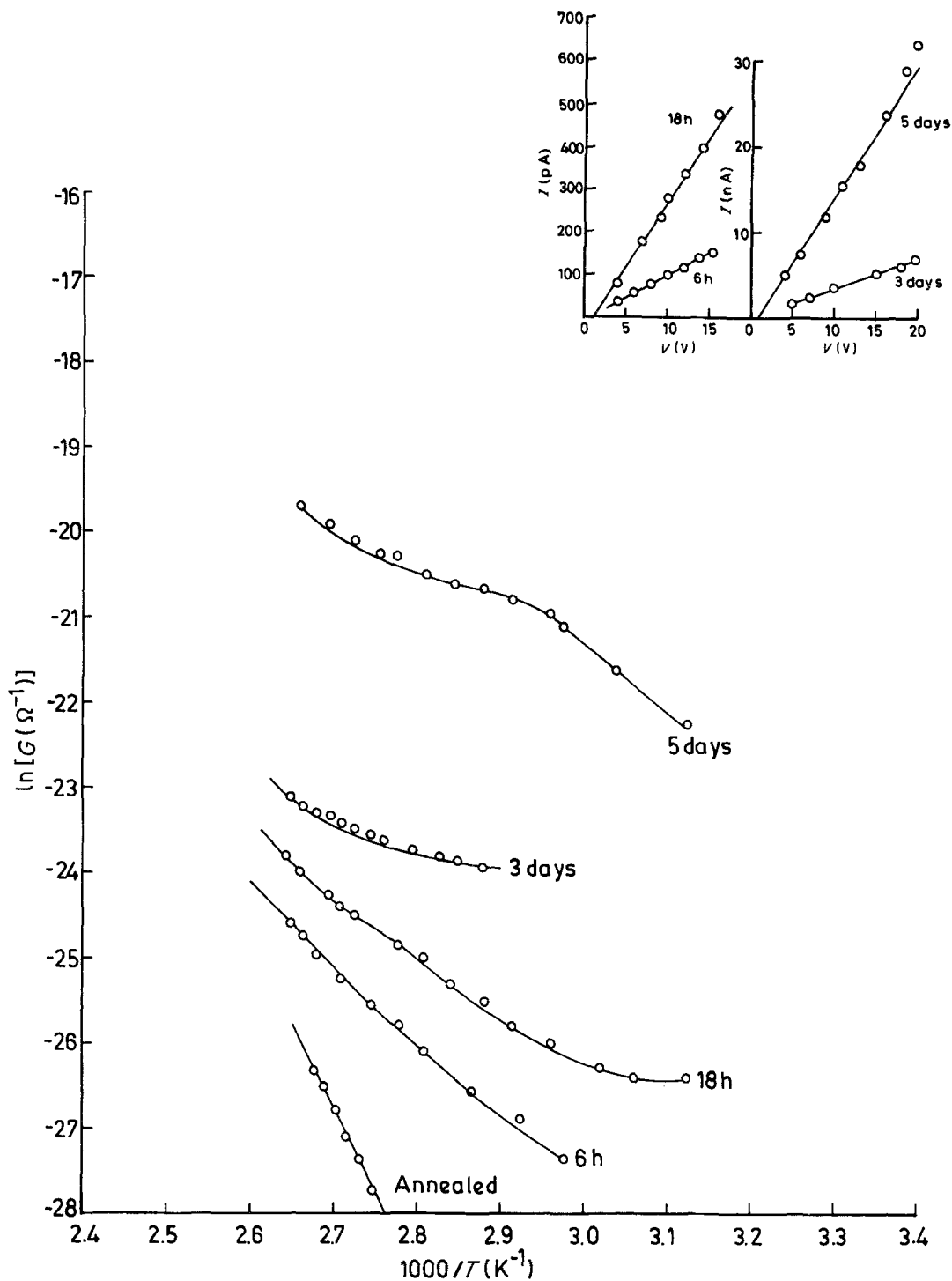
*Figure 6* Temperature dependence of d.c. conductance for annealed and HNO$_3$ vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the *I–V* characteristics at room temperature.

The results of these measurements are shown in Figs 5 to 10. It is clear from these figures that the conductivity increases with temperature in annealed as well as in exposed samples. The increase in conductivity on account of the exhalate vapours can be understood in terms of the absorption of moisture present in the desiccator, and the consequent dissolution of exhalate vapours in the moisture. This may increase the ionic conductivity in the material. The magnitude of the conductivity is higher in exposed samples as compared to the annealed sample in the entire range of temperature used. Fig. 11 depicts the exposure-time dependence of d.c. conductance in the case of various exhalate vapours. This plot has been

made at 100°C. However, at other temperatures also, similar results were obtained. It is clear from this figure that the conductance increases as the exposure time increases for all exhalate vapours. A comparative study of this figure indicates that the effects of HCOOH and CH$_3$COOH vapours are the greatest, even in the case of absorbed/permeated exhalate vapours, as observed in the case of surface adsorption discussed earlier in this paper. The partial vapour pressure of an aqueous solution of HCOOH is more than that of CH$_3$COOH [12]. Fick's law says that the rate of permeation of a gas is proportional to its concentration gradient. This, coupled with the higher dissociation constant of HCOOH, explains
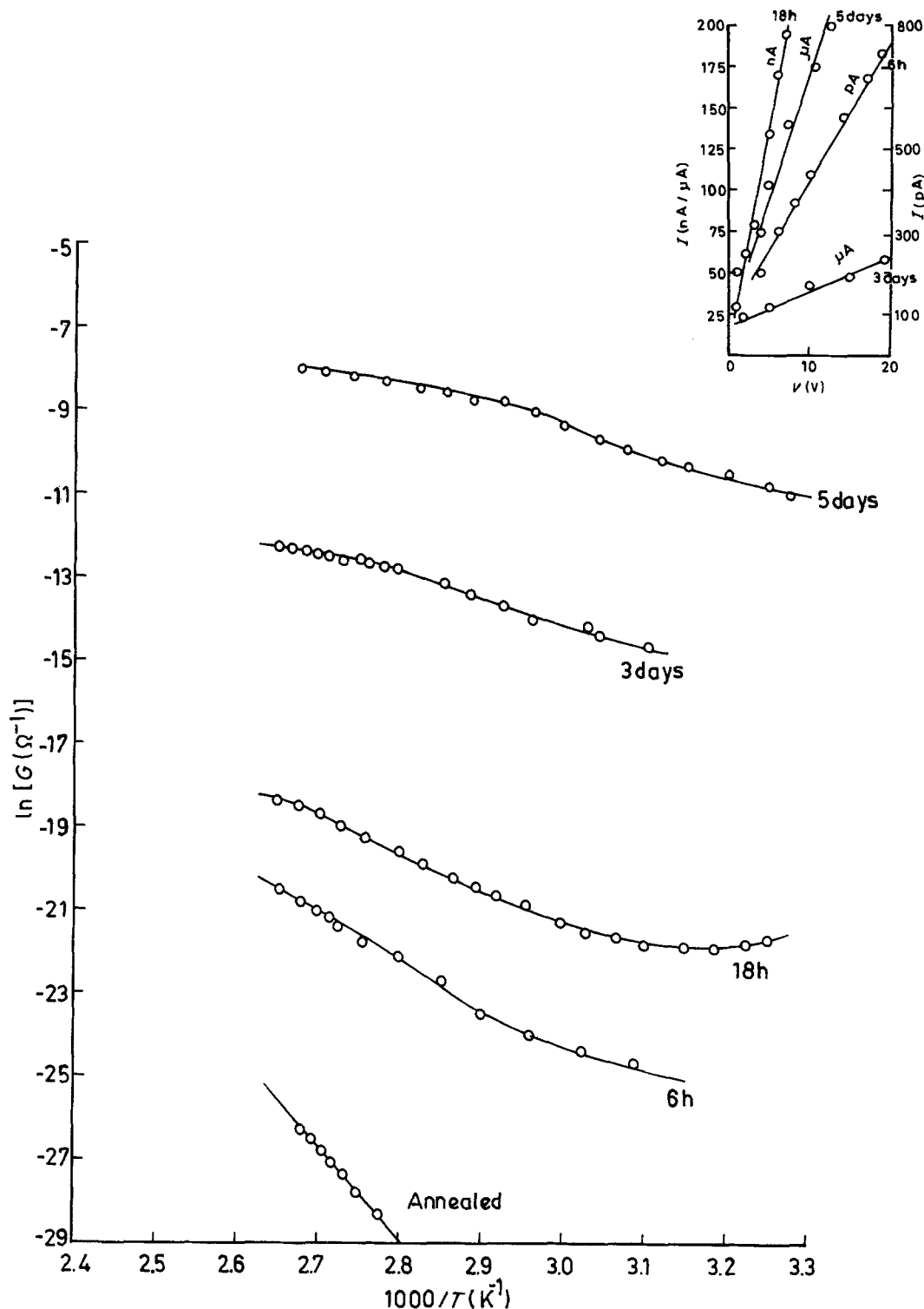
*Figure 7* Temperature dependence of d.c. conductance for annealed and HCOOH vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the *I-V* characteristics at room temperature.

the higher conductivity of epoxy under HCOOH vapours.

The partial pressures of inorganic acids are in general quite low. The vapour pressure of the ambient atmosphere in the desiccator will be nearly the same as that of water (15 mm Hg at 20°C). The conductivity of epoxy under HCl and $HNO_3$ vapours is therefore of the same order as that due to water alone. The higher conductivity of the former compared to the latter at initial stages (see Fig. 11) may be on account of the comparatively higher mobility of HCl. It appears, however, that being strong acids

(dissociation constant $\simeq 1$) the difference in their ionic activity will depend on their $H^+$ ion concentration. There seems to be competition between the $H^+$ ion concentration and the mobility, and as time passes the ionic concentration probably plays a predominant role and the conductivity of epoxy in $HNO_3$ exhalates exceeds that under HCl exhalates (see Fig. 11). Amongst gases, the slightly higher conductances in the case of $SO_2$ and $NH_3$ may be on account of the more polar character of $H_2SO_4$, which may be formed inside the sample due to moisture vapours.
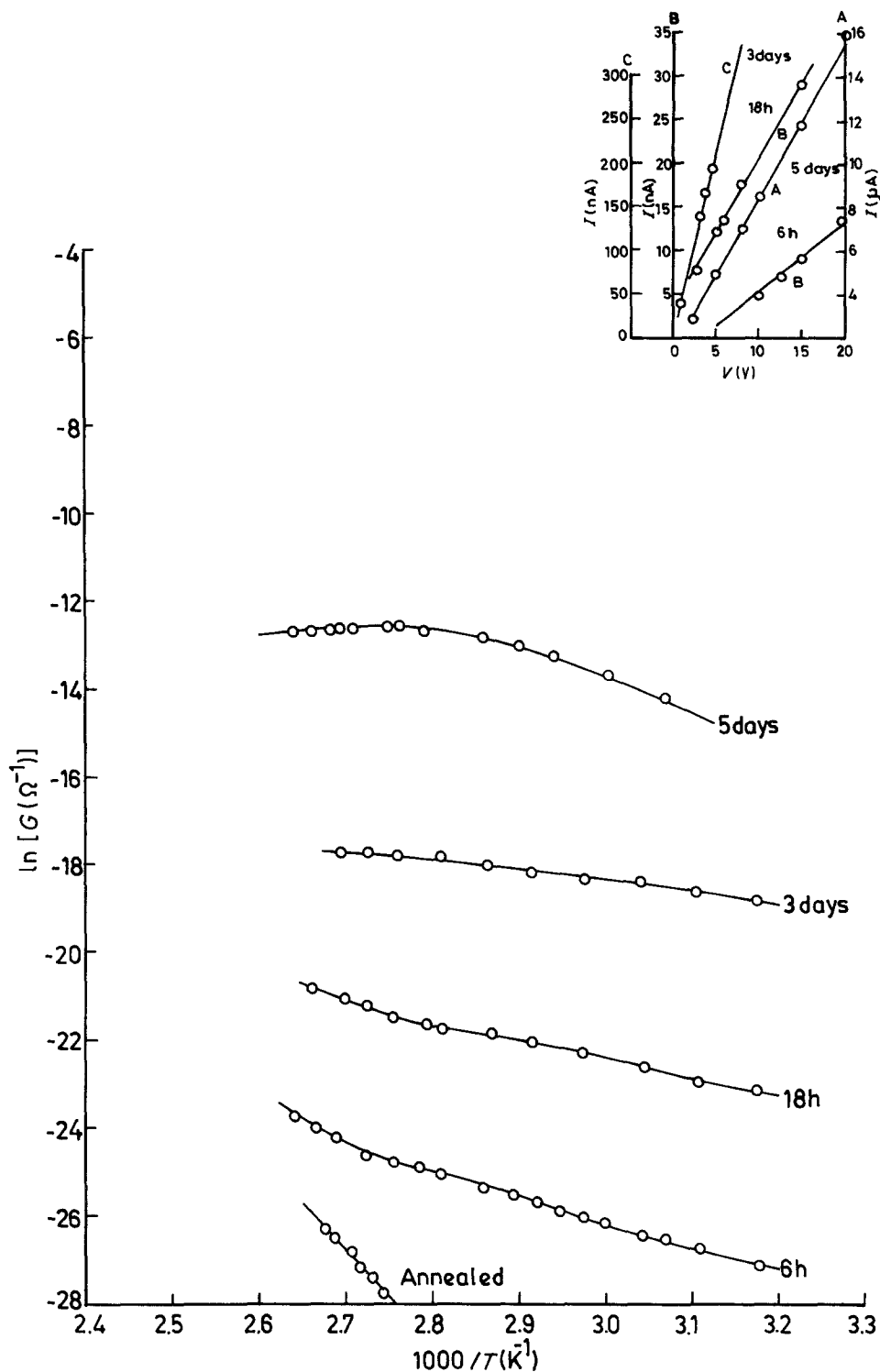
*Figure 8* Temperature dependence of d.c. conductance for annealed and $CH_3COOH$ vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the $I$–$V$ characteristics at room temperature.

We performed recovery studies in the case of exhalate exposure as well. We found that the conductances come back to their original values in most cases. In case of HCOOH and $CH_3COOH$ vapours, some irreversible changes were observed in the d.c. conductivity. This indicates some sort of chemical change in the specimens. In our earlier study [4] of dielectric behaviour, such types of irreversible change were also observed in these cases. In the case of $SO_2$, though the value of the conductivity returned to the original value, some opacity was observed. This may be because of the lodging of sulphur particles in the

material. The material lost its clarity and became slightly yellowish.

## 4. Conclusions

The d.c. conductivity measurements made on annealed and moisture-exposed samples of epoxy laminate having a woven glass content of 55% showed that the d.c. conductivity increases with increase of relative humidity. The values depend on the exposure time as well. There is a complete recovery of the samples from the humidity effect. Our results indicate that moisture is not only adsorbed on the surface but also diffuses
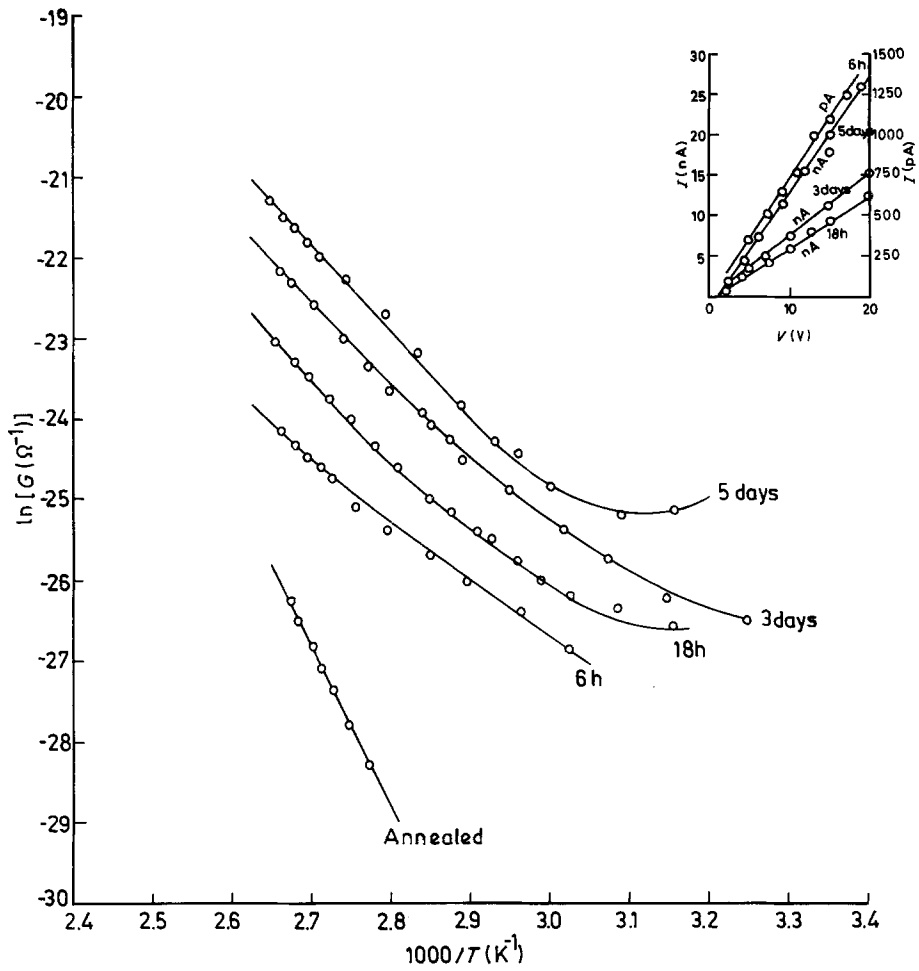
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*Figure 9* Temperature dependence of d.c. conductance for annealed and $NH_3$ vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the $I$-$V$ characteristics at room temperature.



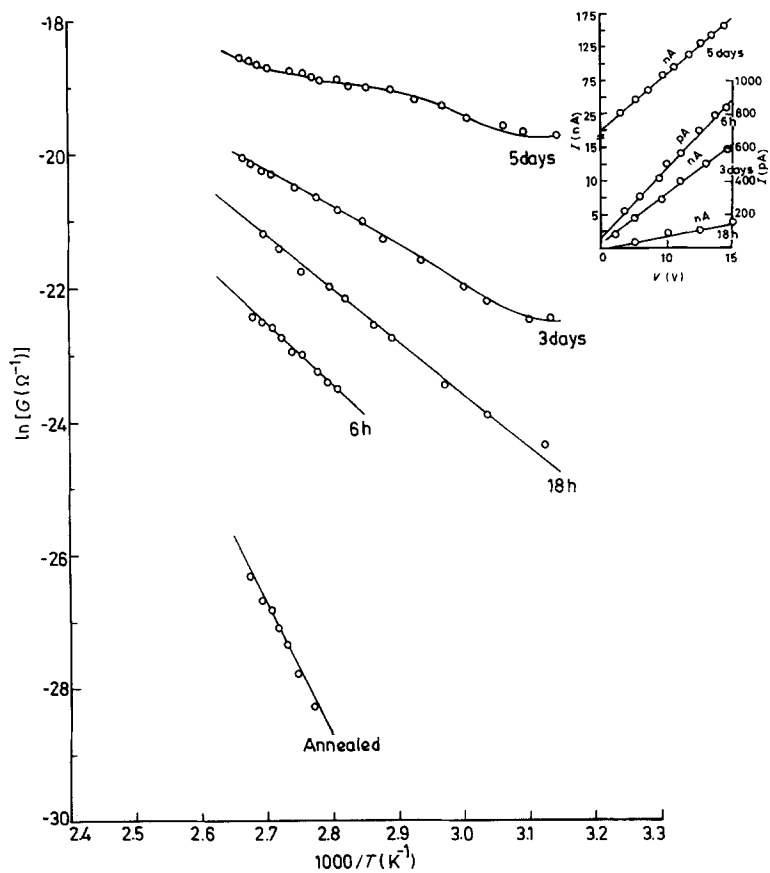*Figure 10* Temperature dependence of d.c. conductance for annealed and $SO_2$ vapour-exposed sample of epoxy laminate for different exposure times. The inset shows the $I$-$V$ characteristics at room temperature.

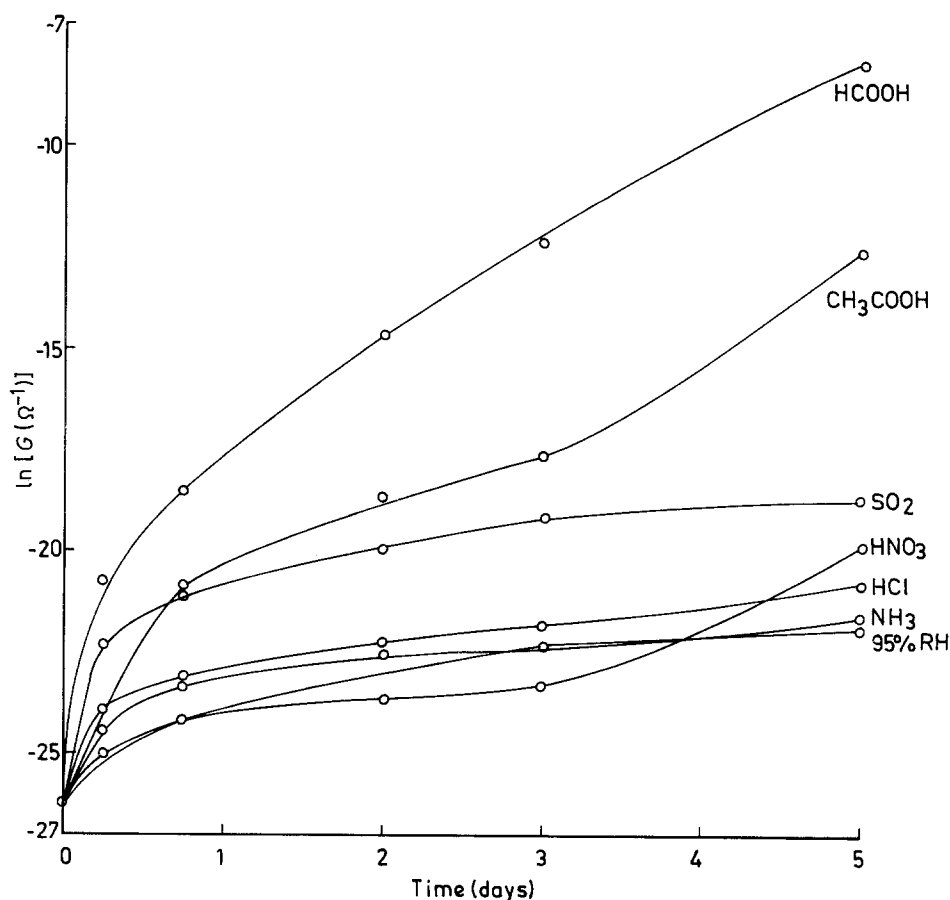*Figure 11* ln$G$ against exposure time at 100°C after exposing the sample of epoxy laminate to various exhalates.

into the sample, and thus shows a higher conductivity in vacuum as well as at higher temperatures.

In the case of exhalate vapours ($HCl$, $HNO_3$, $HCOOH$, $CH_3COOH$, $NH_3$ and $SO_2$), the increase in conductivity is not only higher than for the annealed sample but also higher than what one observes in the case of humidity alone. The greatest effect is seen in the case of HCOOH vapour. There is a near-complete recovery from the exposure of exhalates except in the cases of $CH_3COOH$ and HCOOH. Some chemical changes might have taken place in these cases. The exact chemical composition after reacting with these exhalates is, however, not known from the present measurements.

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