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CHANGES IN THERMOLUMINESCENCE (TL) DURING AGEING OF EPIDIAN-2 EPOXY RESIN

1. Introduction

The ever wider application of new materials, mainly polymers, in insulation calls for new techniques of studying their properties and behaviour. Problems of new criteria for polymers selection and for the evaluation of their behaviour when applied are evoked as well. For example, a criterion most frequently used to evaluate the degree of ageing in classic insulation is to measure the dielectric loss factor tg δ . However, as shown by [1,2] and by the present work, the factor remains virtually unchanged during thermal ageing of certain polymers. Similar is the case with the through resistivity, arc resistance, and creep current resistance.

The present work is an attempt to gain, through TL curves plotting, an increased amount of information on changes taking place during thermal ageing of Epidian-2 epoxy resin. The measurements may be useful in determining, e.g. epoxy composition total thermal use-up criterion or working temperature effects on ageing.

2. Methods and subject of study

Epidian-2 epoxy resin, phthal anhydride cured, was used in the study. The cured resin was sibjected to thermal ageing for 0–720 h at 423 K. When measuring thermoluminescence (TL), the temperature of samples was raised at a constant speed $\beta = 5$ K/min. The temperature measurement error was estimated at ± 1 K. The dielectric loss factor tg δ was measured at the 1000 Hz frequency.

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Results

The TL curves plotted for samples subject to various ageing times are shown in Fig.1.

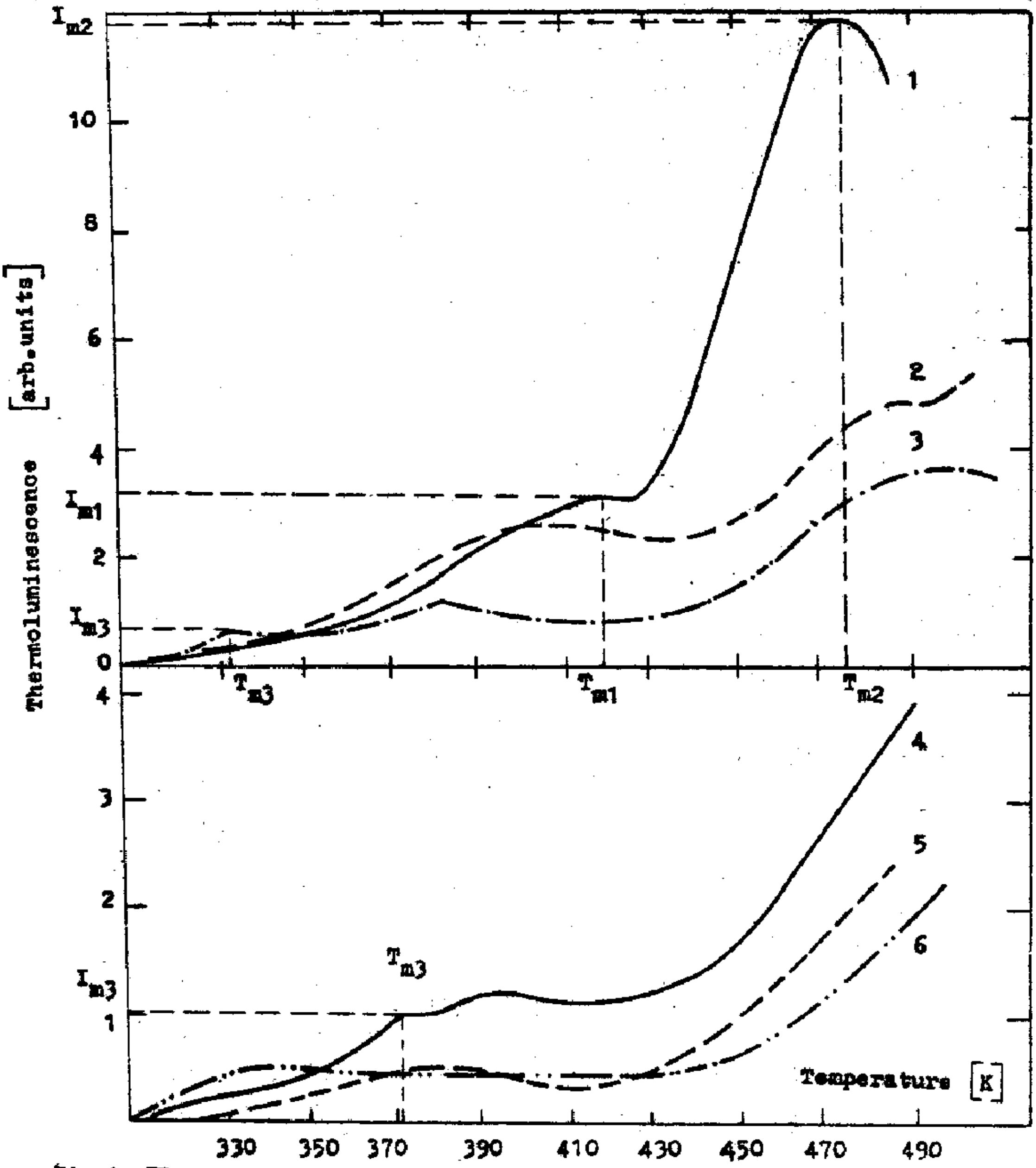

Fig.1. TL curves in thermally aged Epidian-2 epoxy resin
1 - 0 h, 2 - 144 h, 3 - 288 h, 4 , 432 h, 5 - 576 h, 6 - 720 h

According to the ealier works on TL in polymers [3,4,5,6], local extremes on the TL curves obtained, occurring at temperatures lower than 440K are brought about by processes of dopant traps release in non-saturated terminal groupings of a resin or in its non- "looped" linear bonds. On the other hand, the TL extremes at high temperatures are a result of re-trapping during resin thermooxidation [7,8,9].

The energetic depth of TL dopant and oxidative centres was calculated from the formula [10]:

$$E = \frac{T_1 \cdot T_m}{7940\ (T_m - T_1)} - \frac{T_1}{14866} \quad [eV] \qquad (1)$$

where: T_m - temperature of a local TL extreme,
T_1 - temperature of $I = 0,5 \cdot I_m$ at $T < T_m$.

The ageing time- dependent values of E calculated are given in Table1 and Fig2. As seen in the table and in the figure, the ageing process in Epidian-2 causes a constant reduction in the trap depth.

Table 1

The parametrs of TL curves and depth traps during Epidian-2 ageing

Ageing time [h]	0	144	288	432	576
TL dopant peaks temperature (T_{m1}) [K]	409	397	382	389	381
Temperature (T_1) of $I = 0,5.I_{m1}$ [K]	381	365	350	352	346
TL oxidative peaks temperature (T_{m2}) [K]	466	489	490	-	-
Temperature (T_2) of $I = 0,5.I_{m2}$ [K]	441	449	431	-	-
Dopant traps [eV]	0,67	0,53	0,51	0,45	0,45
Oxidative traps [eV]	1,02	0,64	0,42	-	-

A larger decrease in energy levels of thermooxidative traps, as compared to that of the dopant ones (from 1,02 eV to 0,42 eV and from 0,67 eV to 0,51 eV, respectively, after 288 hours of ageing) confirms earlier suggestions as to the relationships between high terperature TL centres and terminal units, the carbon-carbon bonds in aliphatic fragments of the resin [8] in particular. Disintegration of those bondings, and also their replacement by new ones, presumedly causes a TL quenching during ageing (Fig.3, curve 2) and a shift of the TL peak toward higher temperatures (Fig.4, curve 2).

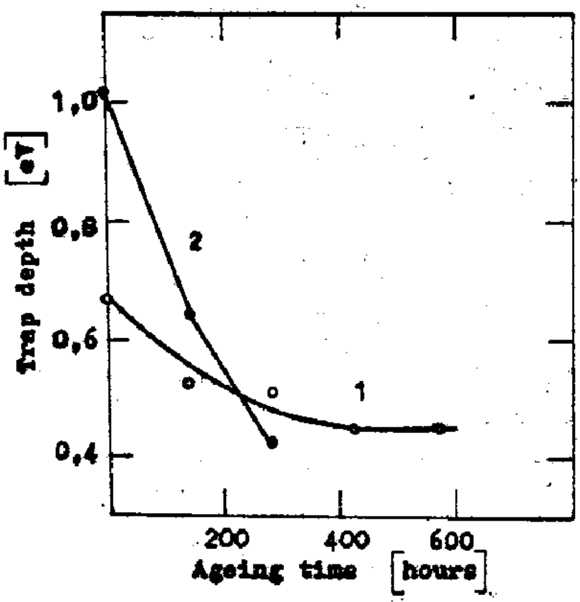

Fig.2. Changes in trap depth during Epidian-2 ageing
1 - dopant traps, 2 - oxidative traps

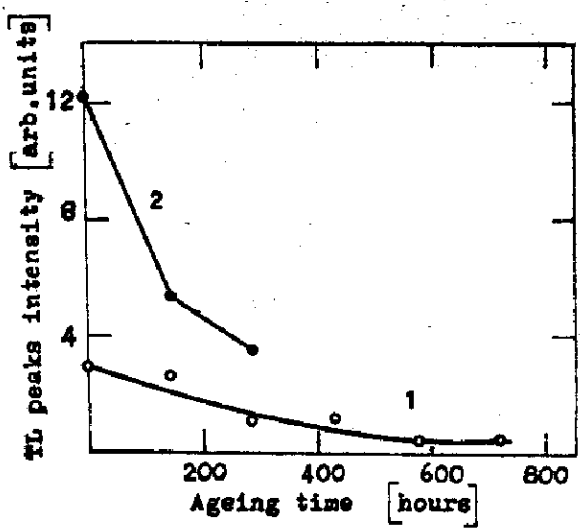

Fig.3. Changes in TL peaks intensity during Epidian-2 ageing
1 - dopant peaks, 2 - oxidative peaks.

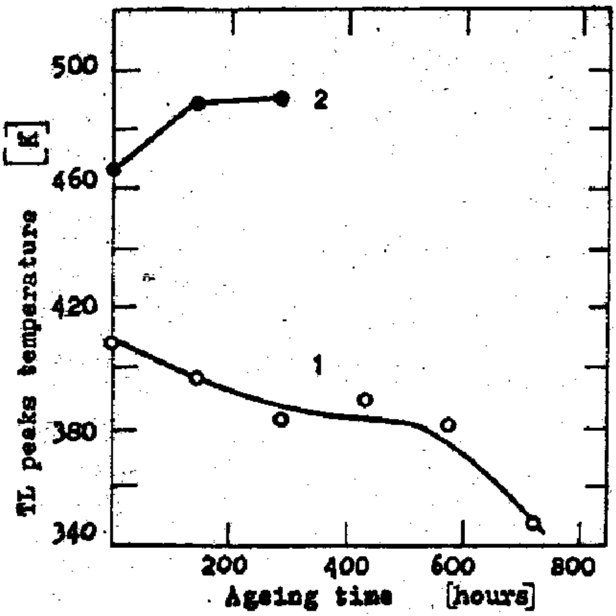

Fig.4. TL peaks temperature (T_m) - ageing time relationship in Epidian-2
1 - dopant peaks, 2 - oxidative peaks.

When the TL curves in Fig.1 are compared, dopant TL peaks are observed to expand and to shift toward lower temperatures (Fig.4, curve 1). Finally, after 720 hours of ageing, the samples glowed with a virtually constant TL intensity within a wide range of temperatures (340 - 440 K). Moreover, no further quenching of dopants-associated TL was observed (Fig.3, curve 1). This is doubtless an additive effect of a number of TL peaks located close to one another within this temperature range, particularly that an extra TL peak (I_{m3}, T_{m3}) was observed after 288 h of ageing. During further ageing, the peak shifted to higher temperatures and merged with the first TL peak (Fig.1, curves 3,4,5). A similar expansion in energy distribution of trapping centres with a simultaneous reduction in peak height was observed in [1] ; that study dealts with thermal depolarisation currents in aged polypropylene films.

As found in [12], the absence of clear glowing extremes is typical of amorphous centres radiative recombination. Thus a constant TL intensity over a wide range of temperatures may evidence the disintegration of terminal groupings and linear bondings to an almost amorphous form. The formation of such an amorphous phase as a result of thermal ageing of polyethylene insulation is described in detail in [13].

It is worth mentioning that the estimated energetic depth of centres in the additional TL peak after 288 h of ageing was much larger than the dopants depth and amounted to about 2,5 eV. Such transformation of dopants brought about by higher temperatures was observed also at an excessively long curing of epoxy compositions [5].

Simultaneously to TL measurements, tg δ changes during ageing were measured. As shown in Fig.5, tg δ underwent no changes during thermal ageing as opposed to those occurring in the curing process, which may be an evidence of a carbonyl group stability in the process [14].

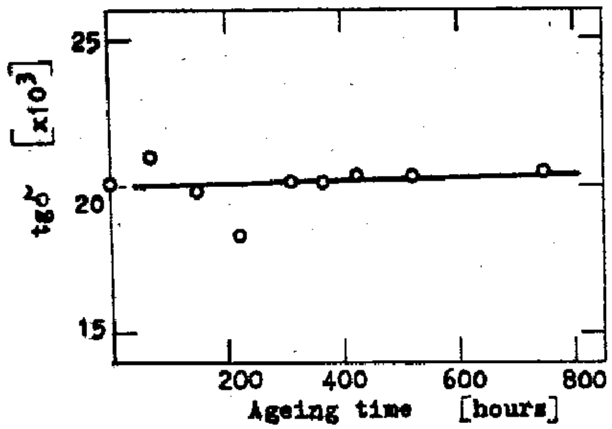

Fig.5. Changes in dielectric loss factor tg δ during Epidian-2 ageing

Thus tg δ cannot be taken as a resin ageing indicator. This is particularly important with respect to strongly filled epoxy compositions in which it is mainly the inorganic filling that decides on the tg δ value.

4. Conclusions

1. TL curves may be successfully used to follow ageing processes occurring at elevated temperatures in Epidian-2 epoxy resin.

2. The processes are manifest as, i.e., expanded energy distribution of trapping centres and TL quenching. In consequence, they lead to the formation of amorphous phase in the resin.

3. Values of tg δ as measured during ageing are unreliable indicators of the Epidian-2 epoxy resin ageing.

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