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THERMALLY STIMULATED PROCESSES IN ORGANIC POLYMERS

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ABSTRACT

Emerging trends in the interpretation of measurements of thermally stimulated conductivity, luminescence and depolarization in organic polymers are reviewed, in the context of charge trapping and transport. Particular attention is given to the following:

(1) the advantage of making simultaneous measurements (say TSC and TSL) on the same sample,

(2) the determination of the forms of quasicontinuous distributions of trap activation energies, and

(3) the use of thermally stimulated processes to monitor ageing (degradation) of polymeric insulants in power distribution cables, and hence estimate their economic service lifetimes.

INTRODUCTION

Quantitative analysis of thermally stimulated luminescence (TSL) and conductivity (TSC) to yield charge trapping parameters dates from 1945 [1] and 1951 [2] respectively. An analysis of thermally stimulated current originating in the relaxation of impurity-defect dipoles in an ionic solid was published in 1964 [3], and by 1975 TSD was firmly established as an alternative method of studying charge trapping and transport is non-metallic solids in general [4]. Many papers have been published reporting trap depths, frequency (or pre-exponential) factors, kinetic order of recombination leading to TSL, and slow or fast retrapping associated with TSC; unfortunately, in most of them the single trap model [5] is assumed. Now it has been known since the early 1970s that a single TSL or TSC glow-curve can be satisfactorily

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fitted by a wide range of physically-realistic trapping parameters [6], and consequently very little significance can be attached to the results of an isolated curve-fitting exercise, no matter how sophisticated its algorithms. It is essential that the proposed trapping parameters be consistent with data gathered under widely varying heating programmes, e.g. different heating rates, varying delays between the end of irradiation and the commencement of heating, periods of isothermal decay during heating, and rapid cooling to the irradiation temperature followed by re-heating [7,8].

SIMULTANEOUS MEASUREMENT OF CORRELATED PHENOMENA

Most authors measure only one thermally stimulated process, e.g.TSL or TSD, and the information they gain is therefore of a very general nature and difficult to interpret unambiguously, particularly in polymers. The information harvest is much richer if two such correlated phenomena are measured simultaneously [9], and this can usually be achieved without unduly complex apparatus [10,11]. Separate measurements, even on the same sample, are less valuable because of the notorious marked dependence of polymer measurements on the detailed thermal history of the sample.

Consider the simultaneous measurement of TSL and TSC on a polymeric sample polarised by application of an external electric field at or above room temperature, cooled to liquid nitrogen temperature, exposed to ionizing radiation and heated with the field still applied. Both TSL and TSC require the release of charge carriers from traps; however, while geminate and non-geminate radiative recombination will both generate a TSL signal,only non-geminate recombination will generate a TSC current, assuming a homogeneous distribution of the separations of trapped electrons and geminate luminescence centres with respect to distance and direction. Thus the presence of a TSL peak and the absence of a TSC peak in a given temperature range (typically 50K between the two half-maximum points of a glow curve in polymers) together indicate a trap density sufficiently high to ensure that the electron is trapped within the Onsager radius of its parent luminescence centre, and so a lower estimate of that density can be calculated. (One must bear in mind here that a photomultiplier with a cooled photocathode is usually a much more sensitive detector than even a high quality electrometer, and therefore a measurable TSC current may require a much larger radiation dose than a measurable TSL signal). The reverse situation indicates that (a) the escaping electrons were injected into traps during polarisation or cooling, with no associated activated luminescence centres, or (b) the radiative recombination probability is zero over the temperature range of the TSC peak (this can be fairly easily checked by searching for phosphorescence), or (c) there is an absence of luminescence centres near the emptying traps. The latter case can arise in polymers if electrons are trapped well within the crystalline regions, from which impurities (forming the luminescence centres) are usually excluded.

The interpretation of simultaneous TSL and TSD measurements is a little more complex. (In TSD measurements the sample is heated in short circuit, after polarisation and cooling, and usually after exposure to ionizing radiation when cooled). Comparison of the TSC and TSD glow curves, with and without exposure of the sample to ionizing radiation, will usually indicate whether a given peak in the TSD glow curve originates in the thermal disorientation of dipoles oriented during polarisation, or in the movement of untrapped charge under its own electric field. In the latter case, comparison of the TSL and TSD glow curves leads to deductions similar to those outlined above for the TSL/TSC comparison. In the former case, the presence of a TSL and a TSD peak in a given temperature range in a semi-crystalline polymer strongly suggests that the electron traps are located very close to the disorienting dipoles on the polymer chains, the electron escape and the disorientation being driven by the same intra-chain molecular motion. (Many workers now accept that the electron traps in semi-crystalline polymers are formed by the polymer chains themselves, at least in the amorphous regions [12]). Presence of a TSL peak and absence of a TSD peak therefore together indicate that very few dipoles with significant dipole moment exist in or close to the regions in which the appropriate molecular motion occurs, while the reverse situation gives the same indication for electron traps.

TRAP ACTIVATION ENERGY AND FREQUENCY FACTOR DISTRIBUTION FUNCTIONS

Since the electron traps are formed by the polymer chains themselves, it is most unlikely that all traps will be identical, or that only a few discrete types of trap will exist; an immense variety of shape and size is to be expected, and with it a quasi-continuous distribution of activation energies, or frequency factors, or both. While the precise mathematical form of these distributions in a given polymer is unlikely to affect seriously its practical performance as an insulator or electret, there is scientific value in attempting to document them.

The use of space-charge-limited currents (SCLC) to probe trap activation energy distributions is well established [13]. In the recently introduced temperature-modulated SCLC method [14] the temperature-dependence of the SCLC is measured over a range of applied voltage ; experimental data for polycrystalline metal-free phthalocyanine, amorphous silicon and arsenic triselenide, and the deduced density of localised states (traps) plots, have been presented [15]. The experimental procedure is straightforward and the analysis of the resulting data uncomplicated. However, it is essential that an efficient charge-injecting (ohmic) contact be made with the sample. This implies a minimum applied voltage given by [16]

$$V\mathrm{min} = el^2(n_f+n_t)/\epsilon\epsilon_0$$

where l is the sample thickness, n_f and n_t are respectively the concentrations of free and trapped carriers at thermal equilibrium, and the other symbols have their usual meanings. Vmin could be as much as 100V for a 1μm thick polymer sample, and this perhaps explains why no report of the successful application of this technique to polymers has appeared in the literature.

Many authors have used TSC measurements to probe the energy distribution of traps in solid insulators, particularly semiconductors [17]. However, the analysis is complicated by the likely but unknown variation of the carrier mobility with temperature, and the possibility of extrinsic charge generation.

The use of this technique to obtain the form of the distribution in a polymer has yet to be reported.

We have deduced the activation energy distribution for occupied traps in polystyrene, shown in Fig. 1, from TSL measurements [7,8].

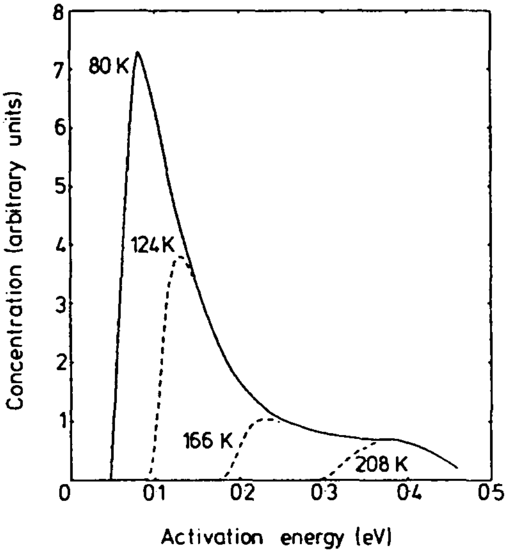

Fig. 1. Trap depth distribution in polystyrene.

We have also obtained the temperature dependence of the frequency factor, assumed the same for all traps. Since there is very little TSL emission from polymers above 273K approximately, the method is limited to "shallow" traps. This limitation originates in the decreasing probability of radiative recombination of an electron with an activated luminescence centre as the temperature increases, the luminescence centres in polymers frequently being aromatic impurity molecules ; attempts to dope the polymer with more efficient inorganic luminescence centres were unsuccessful. It should be pointed out that although first order kinetics was assumed in our earlier paper [7], i.e. every electron released from a trap recombines with a luminescence centre without first being retrapped, in agreement with the findings of most authors investigating TSL in polymers, this assumption is not necessary in our second method [8].

None of the methods mentioned above can distinguish between electron and hole traps, and it is always assumed that the traps are spatially homogeneously distributed (apart from the gross distinction between surface and bulk traps).However the recently developed pressure pulse methods of probing the spatial distribution of charge in insulators [18,19] can distinguish between positive and negative carriers, within the appropriate resolution limits, assuming no complications due to polarisation. It might therefore be possible to combine pressure pulse and TSC data, collected before and after a small rise in sample temperature, to obtain more accurate information on the distributions of interest.

DEGRADATION OF POLYMER INSULANTS

The use of polymeric insulants in electrical power distribution systems is wide-spread, e.g. cross-linked polyethylene (XLPE), ethylene-propylene rubber, and ethylene-propylene-diene monomer [20]. Power utilities worldwide have underwritten an enormous research effort in attempting to extend the lifetime of their cabling, such failure frequently originating in the insulant. The importance of excluding moisture, and thereby preventing the formation of water (electrochemical)trees in the insulant, has been known for many years. Breakdown may also occur in dry field-stressed insulant following the formation of electrical trees, particularly along crystalline /amorphous interfaces.

A pressing problem is the estimation of the economic service life-time of a given cable in the absence of water [21]. (A figure of at least forty years is presently being targeted for XLPE cables rated 15-35 kV). Thermal endurance analysis [22] is well established, but since the laid-down procedures extend over at least 5000 hr, a reliable shorter method would be of great value.

TSD has been used to study electrical/thermal ageing in XLPE samples cut from commercially-produced cables [23]. The samples, 50-100μm thick, were aged by applying an ac voltage, typically 60-90kv, for 3-13 hours. The TSD plots for a sample polarised for 1800s at 333K and 500V, before and after ageing, are shown in Fig.2. A doubling of the high temperature peak height will be

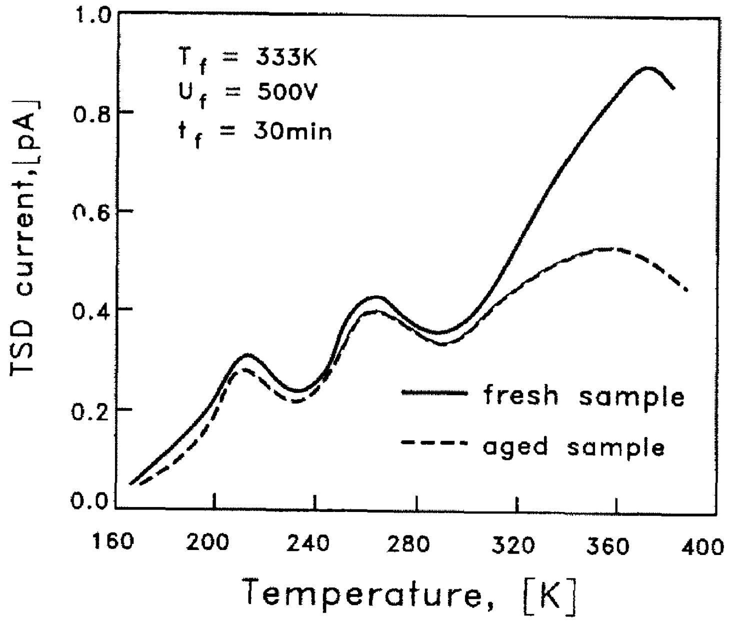

Fig.2. TSD of XLPE.

seen, with little change in the other two peaks. Other authors have reported a new TSD current peak around 340K in electrically stressed (ac and dc) XLPE [24]. A possible explanation of both results is that application of the field and the resultant temperature increase induce a change in the supermolecular structure of the samples. (It was found that ageing also produced increases in the molecular weight, degree of cross-linking and breakdown ac field strength [23]). This explanation is consistent with a recent study [25] of the morphology of chemically crosslinked XLPE, which showed that after annealing within 5K of the melting point (~380K), two different crystallite thicknesses (11nm and 24nm) were produced. (It was also shown that, contrary to earlier reports, spherulites are not formed in XLPE). This difference arises from the fundamental incompatibility of the crosslinked network and the low molecular weight sol (extractable) crystals. It was also found [26] that the concentration and maximum length of water trees almost doubled when the sample was annealed for 30 hours around 373K. The measurement and counting of such trees in a length of cable would be time-consuming, and would preclude measurements on the same cable after further ageing.

However, it may be that the growth of the high temperature TSD peak with time, as tabulated during an accelerated ageing programme, would provide a reliable and convenient yardstick with which to estimate the service lifetime of cable subsequently received from the manufacturers.

A study of ageing in polyethylene terephthalate (PET), also based on TSD measurements, has recently been reported [27]. Fig.3 shows the TSD plot for a 36µm thick PET foil polarised for 1800s at 100V and 390K. It is believed [4] that the composite β-peak covering the approximate range 80–220K is due to disorientation of polar side-groups below the glass transition, the α-peak at 360K to disorientation of (unidentified) main chain dipoles as a result of the glass transition, and the δ-peak around 410K to release of space charge from traps. Fig.4 shows the variation of the α-peak and δ-peak heights with ageing time at four different temperatures. The authors attribute the variation in the δ-peak height to changes in trap concentration originating in spherulite size and density changes during ageing, and cite independent morphological data as support. They deduced the empirical equation

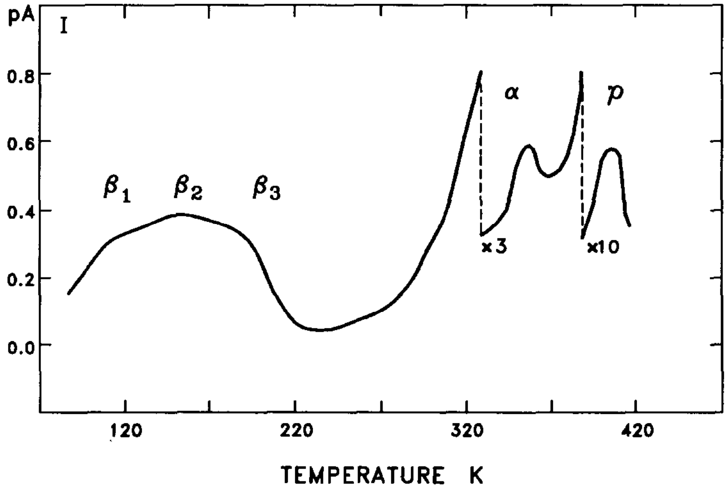

Fig.3. TSD of PET.

$$\log \tau = a - b\theta$$

relating life-time τ, as given by thermal endurance tensile

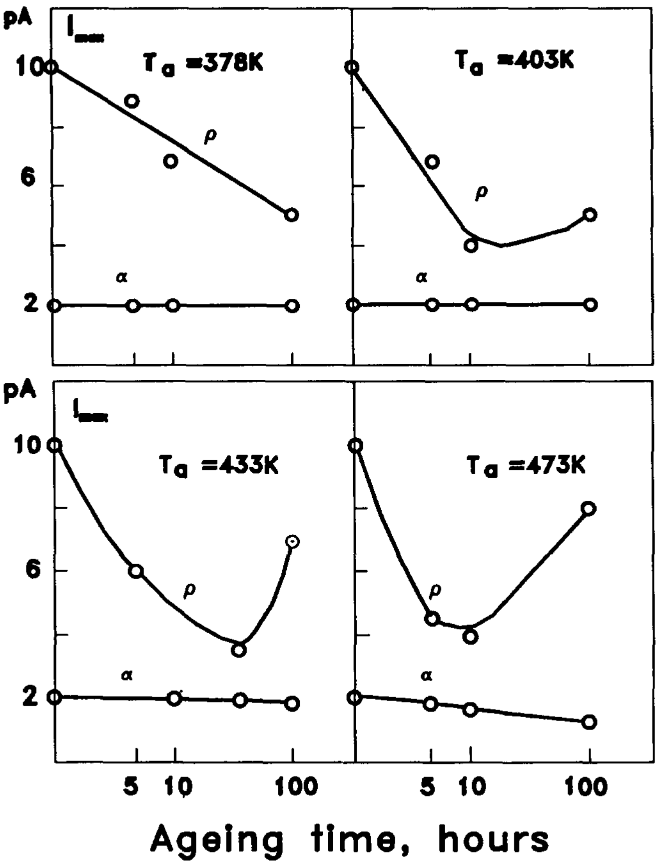

Fig.4. TSD peak height variation in PET.

strength measurements, and rate of increase θ of the δ-peak with ageing time between 10 and 100 hours (a and b are constants). Note that the dc conductivity, relative permittivity, loss factor and ac breakdown voltage of PET are not sensitive to short term (10-100 hours) ageing.

We have found recently that, when absorbed air is removed from chemically crosslinked unfilled XLPE, its TSL glow curve profile varies greatly with X-ray exposure in the range 25-150 kilo-Roentgen, contrasting with the glow-curves of low and high density PE which consistently show three peaks at constant temperatures over the same exposure-range. We have argued that the electron traps in low density PE are formed by the polymer chains themselves in the chain-fold regions of the samples [28], and thus the different result for XLPE is (a priori) consistent with a different morphology [25]. The glow curve of low density PE is sensitive to annealing close to the melting point [29], and we plan to study the effects of annealing and electrical stressing on the TSL, TSC and TSD glow curves of XLPE as part of a search for an alternative estimator of its service lifetime when used as an insulant in power distribution cables.

REFERENCES

[1] J.T.Randall and M.H.F.Wilkins, Proc.Roy.Soc.(London), A184,366(1945).
[2] R.H.Bube, Phys.Rev., 83,393(1951).
[3] C.Bucci,R.Fieschi and G.Guidi, Phys.Rev.,148,816(1966).
[4] J.van Turnhout, Thermally Stimulated Discharge of Polymer Electrets (Elsevier, Amsterdam 1975).
[5] R.Chen, J.Mat.Science,11,1521(1976).
[6] P.Kelly, M.Laubitz and P.Braunlich, Phys.Rev.,B4,1960(1971).
[7] L.F.Pender and R.J.Fleming, J.Phys.C:Solid State Phys.,10,1571(1977).
[8] R.J.Fleming and A.Markiewicz, IEEE Trans.Elec.Insulation, EI-22,29(1987).
[9] P.Braunlich, P.Kelly and J.-P.Fillard, Topics in Applied Physics,37,35(Springer-Verlag 1979).
[10] D.Ito and T.Nakakita, J.Appl.Phys., 51,3273(1980).
[11] A.Markiewicz and R.J.Fleming, J.Phys.D:Appl.Phys., 21,349(1988).
[12] R.H.Partridge, J.Poly.Sci.A3,2817(1965).
[13] K.C.Kao and W.Hwang, Electrical Transport in Solids (Oxford:Pergamon 1981).
[14] O.Zmeskal, F.Schauer and S.Nespurek, J.Phys.C:Solid State Phys.,18,1873(1985).
[15] F.Schauer, S.Nespurek and O.Zmeskal, J.Phys.C:Solid State Phys.,19,7231(1986).
[16] S.Nespurek, O.Zmeskal and F.Schauer, phys.stat.sol.(a),85, 619(1984).
[17] G.G.Roberts, N.Apsley and R.W.Munn, Phys.Rep.,60,59(1980).
[18] R.Gerhard-Multhaupt et al., J.Appl.Phys.,55,2769(1984).

[19] W.Eisenmenger and M.Haardt, Solid State Commun.,41,917(1982).

[20] Electrical Power Research Institute (EPRI) Report EL-4398, Long-life Cable Development : Cable Materials Survey (March 1986).

[21] W.F.Horton, IEEE Trans.PAS-101,472(1982).

[22] IEC Standard Publications 216-1 (2nd Ed.) 1974 and 216-3 (2nd Ed.) 1980.

[23] S.M.Gubanski and B.Masurek, Eur.Symp. on Polymeric Materials (European Polymer Federation), Lyon-France, September 1987.

[24] K.Doughty, D.K.Das-Gupta and D.E.Cooper, IEEE Conf. Elec. Insul.and Dielectric Phenomena, 56 (1986).

[25] R.M.Gohil and P.J.Phillips, Polymer, 27,1687(1986).

[26] P.J.Phillips, IEE 4th Intern.Conf.on Dielectric Materials, Measurements and Applications, 1984, Conf.Publ.No.239, p.187.

[27] S.M.Gubanski, R.Kacprzyk and Z.Zubel, Fifth Int. Symp. on High Voltage Eng., Braunschweig, August 1987.

[28] A.Markiewicz and R.J.Fleming, J.Poly.Sci. Part B, Poly.Phys.,24,1713(1986).

[29] A.Markiewicz and R.J.Fleming, J.Poly.Sci. Part B, Poly.Phys.,25,1885(1987).