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RELAXATION IN UNSATURATED POLYESTER RESINS STUDIED BY THERMALLY STIMULATED DEPOLARIZATION CURRENTS

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Abstract

Investigations involving thermally stimulated depolarization currents were performed on unsaturated polyester resins cured with styrene. Samples containing different amounts of Co octoate promoter were studied. The complex spectra revealed the classical β and the α dipolar relaxations. The peak characterizing the α dipolar relaxation was overlapped by a ρ peak of appreciable magnitude, due to the presence of impurities in the promoter solution [1]. However, study of the elementary spectra as concerns both α and β peaks for various samples containing different amounts of Co octoate demonstrated that the relaxation kinetics, and particularly the values of the apparent activation energies, do not depend on these impurities.

Keywords: TSDC, unsaturated polyester resins

Introduction

Unsaturated polyester resins (UPRs) cured with styrene are widely used in coating technology. Easily adaptable to specific applications by change of either the nature of the unsaturated polyester chain or the ratio of the amounts of styrene/polyester, they are also good candidates for systematic studies of physical relaxation phenomena.

The analysis of physical relaxation phenomena can be performed by means of thermal investigations (differential scanning calorimetry (DSC) or thermally stimulated depolarization currents (TSDC)) and/or spectroscopic investigations (dielectric, or mechanical). To carry out such investigations by DSC, the jump ΔC_p in the specific heat at the glass transition must be of sufficient magnitude, ($\Delta C_p = C_{pl} - C_{pg}$, where C_{pl} and C_{pg} are the heat capacities in the liquid state and the glassy state). Unfortunately, this is not really the case for this kind of three-dimensional network and an alternative way is to use dielectric or mechanical spectroscopy measurements. However, this needs specific sample preparations, which are not easy to perform in a reproducible

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way. For this reason, the first results involving the use of TSDC and reported in this work, were obtained on fully cured UPRs. To study the influence of the promoter on the TSDC signal, UPRs with different amounts of Co octoate were applied.

Material and methods

Technibat Co. (Gravigny, France) provided the UPR studied in this work. This polyester resin consists of maleic anhydride, isophthalic acid and propylene glycol, mixed in a styrene monomer solution. Both resins and styrene monomer were used as received without removal of the inhibitor. The initiator was methyl ethyl ketone peroxide (MEKP; AKZO, Compiègne, France) and the promoter a Co octoate (AKZO). To initiate the reaction, 0.19 m/m% of the promoter solution containing 6 m/m% of Co octoate was first mixed with the resin. Then, 1.5 m/m% of the initiator solution was added to the mixture (resin+styrene+promoter). In this way, we obtained the composition called the 'standard composition'. For TSDC, various samples were prepared with different amounts of promoter solution (from 0.09 to 0.5 m/m%). It is necessary to point out here that it is very difficult to prepare a solid-state resin without a promoter. Described elsewhere [2], the thermal cycle performed to obtain the solid state was isothermal curing at 25°C for 24 h, then a postcuring at 80°C for 6 h, and a second postcuring at 120°C for 2 h. With this method, the maximum degree of transformation is reached, but the structure is not fully stable, because approximately 5 m/m% of the initial styrene remains free in the solids [2]. These free radicals cannot react and a majority of them are extracted by keeping the final sample under vacuum for one week (for further details on the structure of the resin [1, 4]).

Largely described elsewhere [3], the TSDC measurements were performed with apparatus developed in our laboratory [4]. The sample was submitted to an electric field ($E=10^6$ V m^{-1}) for 2 min at a polarization temperature T_p=110°C. The temperature was then lowered to –150°C. The depolarization current I was measured during annealing up to 150°C at a constant rate of 10°C min^{-1} to obtain a complex spectrum. The conductivity σ (in S m^{-1}) was used instead of current I as normalized quantity ($\sigma=I/ES$ where S is the surface area of the sample); integration of the peaks provided the polarization P (μC m^{-2}), proportional to the concentration of the species polarized at T_p and depolaried during reheating. Elementary TSDC spectra were obtained by means of the fractional polarization method, which allows the selection of a small range of relaxing elements. The sample was submitted to the same electric field during 2 min at a temperature T_p' . The temperature was then lowered to $T_d=T_p'$–5°C and a short circuit was performed for 2 min. Under these conditions, mobile dipolar units with relaxation times greater than 2 min at T_p' were not oriented, while those with relaxation times shorter than 2 min were randomized by the short circuit. The sample was finally cooled (in short circuit) to $T_0=T_p'$–40°C. The depolarization current (in amperes) was measured during annealing up to T_p' at 10°C min^{-1}. The use of the same procedure with increasing T_p' (from 50 to 120°C for the α transition, and from –145 to –50°C for the β transition) allows exploration of the whole of the α and β transitions.

Results and discussion

Figure 1 displays an example of a complex TSDC spectrum obtained with the standard UPR (0.19 m/m% of Co octoate). Three peaks are observed. The first, of weak magnitude, observed at low-temperature (between –140 and –50°C), is characteristic of the non-cooperative β relaxations which are due to local molecular rearrange-

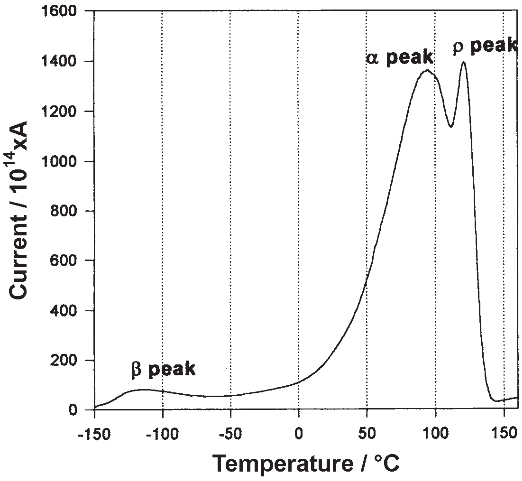

Fig. 1 Complex TSDC spectrum of UPR with the standard composition (0.19 m/m% of Co octoate in the promoter solution)

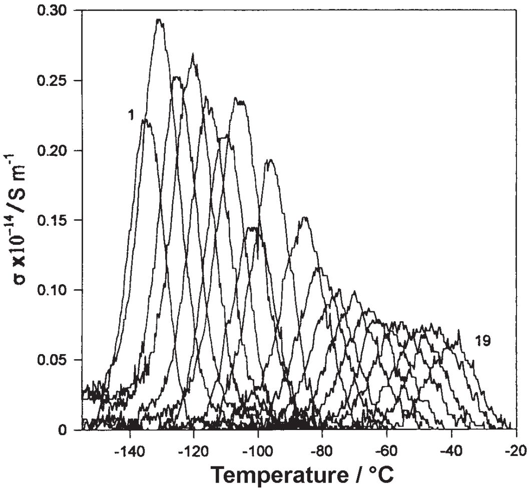

Fig. 2 Example of elementary TSDC spectra for β relaxation, obtained on a standard resin. The curves are numbered from 1 to 19. This corresponds to the variations of the polarization temperature from –140°C (curve 1) to –55°C in steps of 5°C

ments. At higher temperatures, the second peak, called α, corresponding to cooperative movements of the macromolecules, is the dielectric manifestation of the glass transition [3]. Unfortunately, this peak is overlapped by a third one, located a few degrees above the α peak. This third peak, called ρ, is the classically attributed to the conduction through motion of excess charges limited in space by drift and diffusion [3]. In a recent work [1], it was demonstrated via X-ray fluorescence spectroscopic investigations that the ρ peak can be directly connected to the whole amount of impurity existing in the Co octoate solution. It was also shown in [1] how to extract the α contribution from the signal and that this contribution does not depend on the amount of Co octoate in the resin.

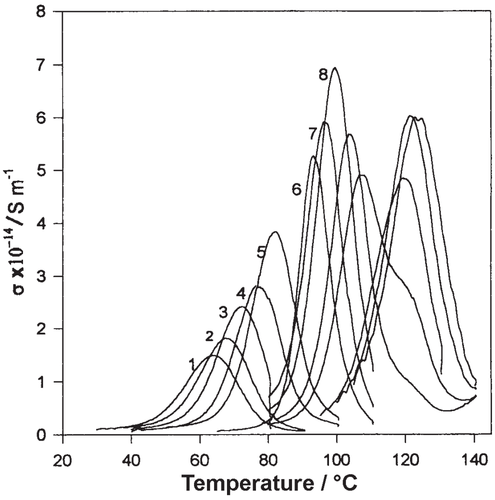

Fig. 3 Example of elementary TSDC spectra for α relaxation, obtained on a standard resin. The spectra are carried out from T_p=70°C (curve 1) to 130°C in steps of 5°C. The non-numbered curves illustrate the influence of the ρ overlapping

Then, in spite of the existence of this ρ peak, we performed an elementary TSDC analysis of the signal in both the α and β regions. Figures 2 and 3 present examples of the elementary spectra collected on the β and the α peaks, respectively, for a resin of standard composition.

At temperature *T*, the relaxation time τ(*T*) [5] is given by

$$\tau(T)=\left|\frac{P(T)}{\mathrm{d}P/\mathrm{d}t}\right|=\left|\frac{1}{r}\,\frac{P(T)}{\mathrm{d}P/\mathrm{d}T}\right| \tag{1}$$

where *P*(*T*) and d*P*/d*t* are the polarization at temperature *T* and its derivative, respectively. It is also possible to express this expression in terms of temperature; then, *r* is the heating rate.

The behaviour of the relaxing modes could be described in terms of Eyring's activated states equation, where the relaxation time is associated with the crossing of a barrier of height ΔG^*:

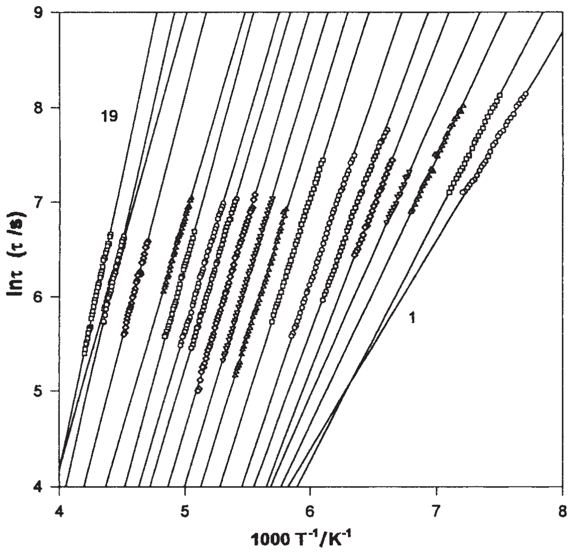

Fig. 4 Arrhenian plot of the relaxation time for all the β elementary spectra of Fig. 2. The quasi-parallelism of the lines already shows the non-cooperative nature of the β relaxation

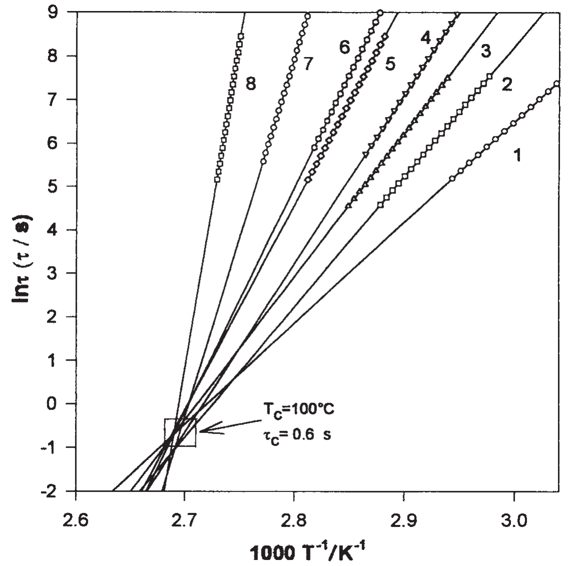

Fig. 5 Arrhenian plot of the relaxation time for α relaxation elementary spectra. To avoid the overlapping effect of the ρ relaxation, only the numbered curves in Fig. 3 are used to determine the apparent activation energy. The convergence of the lines towards the compensation point shows the cooperative behaviour of the α relaxation

$$\tau(T)=\left(\frac{h}{kT}\right)\exp\left(\frac{\Delta G^*}{RT}\right)=\left(\frac{h}{kT}\right)\exp\left(\frac{-\Delta S^*}{R}\right)\exp\left(\frac{\Delta H^*}{RT}\right) \tag{2}$$

where h, k and R are the Planck, Boltzmann and gas constants; respectively, and ΔS^* and ΔH^* are the apparent activation entropy and enthalpy.

To study the temperature behaviour of the relaxation time, it is useful to draw the Arrhenius plot $\ln\tau$ *vs.* $1/T$. For both β relaxation and α relaxation, we observe for each elementary spectrum a quasi-linear dependence of $\ln\tau$ on $1/T$. This leads to description of the behaviour by an Arrhenian relation [5], where the apparent activation energy ΔH can be derived from the slope of the straight lines observed in Figs 4 and 5.

$$\tau=\tau_0\exp\left(\frac{\Delta H}{RT}\right) \tag{3}$$

It then follows (from relations (2) and (3)) that

$$\Delta H=R\frac{\mathrm{d}(\ln\tau)}{\mathrm{d}(1/T)}=\Delta H^*+RT \tag{4}$$

To determine whether the relaxations are cooperative or non-cooperative, Starkweather [6] has rewritten the activated states equation

$$\Delta G^*=\Delta H^*-T\Delta S^*=RT\ln\left(\frac{\tau kT}{h}\right) \tag{5}$$

and

$$\Delta H=\Delta H^*+RT=RT\left[1+\ln\left(\frac{k}{h}\right)+\ln(\tau T)\right]+T\Delta S^* \tag{6}$$

Taking into account the values of the constants, Eq. (3) can be written

$$\Delta H^*=RT\left[22.92+\ln\left(\frac{T}{f_{\mathrm{eq}}}\right)\right]+T\Delta S^* \tag{7}$$

where $f_{\mathrm{eq}}=1/2\pi\tau$ is the equivalent measurement frequency.

Called the Starkweather relation, this relation is of prime importance: a localized relaxation, which does not imply any long-distance atom or chain movements, has an activation entropy of around zero, whereas a cooperative relaxation, which needs long-distance configurational rearrangements, has an activation entropy different from zero. It then follows that in cooperative relaxation the ΔH experimental points diverge from the zero entropy line ($\Delta H(\Delta S=0)$).

Derived from the slopes of the straight lines observed on the Arrhenian plot for β relaxation, the values of the apparent activation energy (which lie between 40 and 60 kJ mol^{-1} whatever the Co octoate amount), are well fitted by the zero activation entropy line (Fig. 6). These relatively weak values and the zero entropy activation are

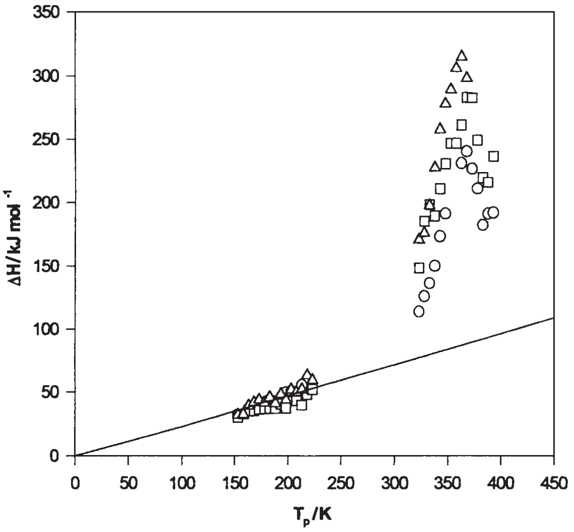

Fig. 6 Starkweather representation of the apparent activation energies *vs*. polarization temperature for both β and α relaxations. Full line – zero entropy; open squares – 0.19 m/m% Co octoate; open circles – 0.21 m/m% Co octoate; open triangles – 0.49 m/m% Co octoate

characteristic of non-cooperative movements [7, 8]. On the other hand, for the relaxation modes observed at around the glass transition, the lines converge to a single point called the compensation point (τ_c=0.6±0.3 s, T_c=100±4°C for the sample exhibited in Fig. 5, see caption). This compensation behaviour in a polymeric material is often considered to be representative of cooperative molecular movements. The values of the apparent activation enthalpy are higher than those observed for β relaxation (up to 320 kJ mol^{-1}) and diverge widely from the zero entropy line. This was the behaviour expected for the α relaxation. Moreover, the Starkweather representation also shows that the deviation occurs at the same temperature, whatever the Co octoate content. This is characteristic of the non-dependence of the α relaxation on the Co octoate amount in the resin. As concerns the β relaxation, the impurities in the promoter solution and their effect on the TSDC signal, revealed by the existence of an extra peak, do not modify the relaxation at the glass transition.

Conclusions

In this work, which is the second of a series devoted to a study of relaxation phenomena occurring in a three-dimensional network obtained with UPRs cured with styrene, we have observed that TSDC signals exhibit an important overlapping of α and ρ peaks. In a previous paper, the ρ peak was attributed to the presence of impurities in the Co octoate promoter solution. Using different Co octoate amounts in the samples, we have shown by an elementary spectrum analysis that the relaxations, and particularly the values of the apparent activation energies for both the β and the α relaxations, do not depend on these impurities.

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