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DSC AND TSDC STUDY OF UNSATURATED POLYESTER RESIN

Influence of the promoter content

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Abstract

This work reports on the curing kinetics of unsaturated polymer resins (UPRs) cured with styrene, studied by differential scanning calorimetry and Fourier transform infrared spectroscopy. The data lead to determination of the experimental conditions with which to obtain a fully cured material and open the way for study of the relaxation phenomena by means of thermally stimulated depolarization current analysis (TSDC). In relaxation studies on fully cured resins, the TSDC spectra revealed important overlapping of the main relaxation peak with an extra upper peak. The importance of this extra peak a priori prevents further analysis of the main relaxation. To identify the origins of this peak (space charge or other), the purity of the resin was checked by X-ray fluorescence spectroscopy. The use of UPR specimens with different compositions (in terms of the resin/activator/initiator ratio) demonstrated that the bulk of the impurities Cl, K, Ca, Sr, Zr and Ba are due to the promoter. Decoupling of the mixed peaks (α-relaxation and extra) revealed that the α peak is independent of the proportion of the promoter in the resin and that the extra peak is principally due to the presence of these impurities.

Keywords: DSC, TSDC, unsaturated polyester resin, X-ray fluorescence spectroscopy

Introduction

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

Before any physical analysis of such thermosets, it is important to characterize the kinetics of the different reactions leading to the final product. The formation of the three-dimensional network results (for this type of resin) from the competition of various reactions [1], such as (1) the co-polymerization of the unsaturated polyester and the styrene monomer, and (2) polystyrene formation by the polymerization of

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styrene. It has been shown that calorimetry and infrared analysis provide good means of studying the kinetics of the different reactions [2, 3], and we therefore apply these experimental methods to characterize our UPR samples.

On the other hand, the analysis of physical relaxation phenomena can be performed by thermal investigations (differential scanning calorimetry: DSC; thermally stimulated depolarization current: TSDC) and/or by spectroscopy (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, respectively). Unfortunately, this not generally the case for these kinds of three-dimensional networks and an alternative way may be given by dielectric or mechanical spectroscopic measurements. However, these techniques often need a specific sample preparation, which is not easy to perform in a reproducible way. For these reasons, the first results obtained by means of TSDC, reported in this paper, relate to fully cured UPR systems.

During the relaxation studies on fully cured resins, the TSDC spectra reveal important overlapping between the main relaxation peak (α) and an extra upper peak located a few degrees above the α peak. The magnitude of this extra peak a priori prevents further analysis of the main relaxation. What are the origins of this peak (space charge or others)? In this field, the purity of the resin was checked by X-way fluorescence spectroscopy in order to determine the major impurities which can exist in such commercial systems. With the use of UPR samples of various compositions (in terms of the resin/activator/initiator ratio), we propose an investigation of the role played by these impurities as concerns the TSDC signal obtained for such samples.

Materials and methods

The UPR studied in this work was provided by Technibat Co. (Gravigny, France). This polyester resin consists of maleic anhydride, isophthalic acid and propylene glycol mixed in a styrene monomer solution. The detailed composition of the material is given in Table 1. 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 cobalt octoate (Akzo). To initiate the reaction, 0.2 w/w% of the promoter solution containing 6 w/w% of Co octoate was first mixed with the resin. Then, 1.5 w/w% of the initiator solution was added to the mixture (resin+styrene+promoter). In this way, we obtained the composition referred to as the ‘standard composition’. For TSDC and X-ray fluorescence spectroscopy, the amount of promoter varied from 0.09 to 0.5 w/w%. Studies of the curing kinetics were performed according to the method described in [3]. It consists in isothermal DSC measurements of the exothermic cure reaction observed for different curing temperatures T_{iso} in the range 0–65°C. When the isotherm is completed, a dynamic scan up to 200°C is performed to achieve the curing. The fully cured resins studied by TSDC measurements are obtained after a curing duration of 24 h at 25°C, a post-curing at 80°C for 6 h and finally a second post-curing at 120°C for 2 h.

Table 1 Composition of the material used in this work

	Composition (molar ratio)
Maleic anhydride	1
Isophthalic acid	1
Propylene glycol	2
Styrene monomer	2.5
$\overline{M}_n$/g mol^{-1}	≈3000
M_w/mol C=C g mol^{-1}	362
Average number of C=C groups per polyester molecule	8.3

Despite this method giving the highest degree of transformation, about 5% of the initial styrene remains free in the resin and the structure is not fully stabilized [3]. For TSDC experiments, these free radicals are extracted before the measurement by keeping the samples under vacuum for one week.

All the experimental details concerning the DSC and Fourier transform infrared (FTIR) measurements used to characterize the curing kinetics have already been described elsewhere [3]. In brief, DSC is performed on a Perkin Elmer series 4 calorimeter; FTIR measurements are performed in transmission mode with a Nicolet 510M FTIR spectrophotometer, by collecting and averaging 30 scans at a resolution of 4 cm^{-1}. The spectra are collected on the same sample throughout its transformation from the liquid to the solid state with the thermal cycle specified previously. Already largely described [4], the TSDC measurements are performed with an apparatus developed in our laboratory [5]. The sample is submitted to an electric field E of 10^6 V m^{-1} for 2 min at a polarization temperature T_p of 110°C. The temperature is then lowered to –150°C, and a short circuit is applied for 2 min. The depolarization current I is measured during annealing up to T_p at a heating rate of 10°C min^{-1}.

The emission fluorescence X-spectra are obtained at the X-ray fluorescence station, by using the beam delivered from a bending magnet, at DCI, Lure (Orsay, France). Excitation energies of 10 and 20 keV are used with an acquisition time of 5 min and an angle beam of 45°. A deconvolution program, called ‘Symetrie’, developed at Lure [6], is used to perform both the qualitative and the quantitative analysis. This allows an accurate knowledge of the cobalt content and deduction of the amounts of the other elements.

Results and discussion

Curing

Figures 1a and 1b show typical calorimetric curves obtained during the isothermal curing period (1a) and during the heating scan performed to achieve the curing (1b), respectively. In accordance with Abadie *et al.* [2] and Delahaye *et al.* [3], we presume that the enthalpy determined from the area of the exothermic peak during the isother-

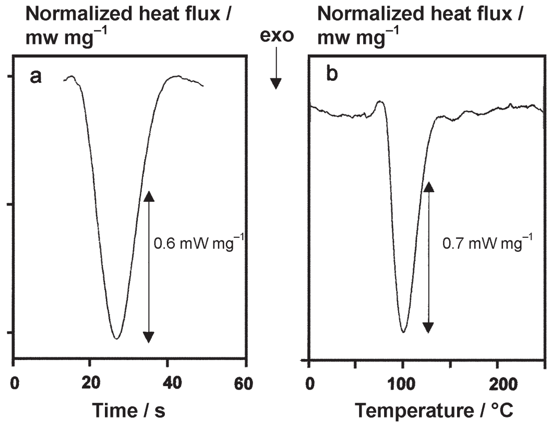

Fig. 1 a – Example of enthalpic curve obtained during the isothermal curing period for an UPR; b – Dynamic enthalpic curve obtained after the isothermal curing shown in Fig. 1a

mal period is mainly a result of styrene homopolymerization and its copolymerisation with the C=C double bonds of the unsaturated polyester chain.

The variations in this enthalpy (ΔH_{cop}) with the iso curing temperature T_{iso} are reported in Fig. 2. For T_{iso}<40°C, no evidence of an exothermic reaction is observed in the DSC trace. This fact can be interpreted in at least two different ways: either the enthalpy of the reaction is too weak to be detected, or there is no reaction during the experimental time. During the dynamic period, the enthalpy determined from the area of the exothermic peak is a result of the reactivity of the residual functions that have

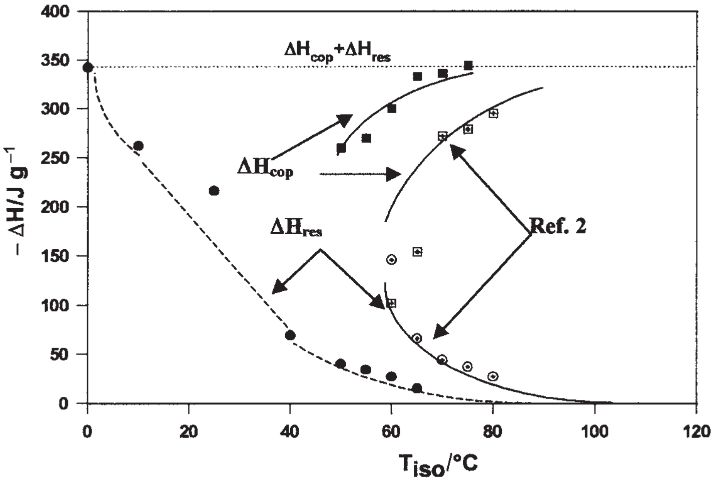

Fig. 2 Variations in ΔH_{cop} and ΔH_{res} with the curing temperature T_{iso}. Lines are drawn as a guide for the eye, and the results of Abadie *et al.* [2] are also included

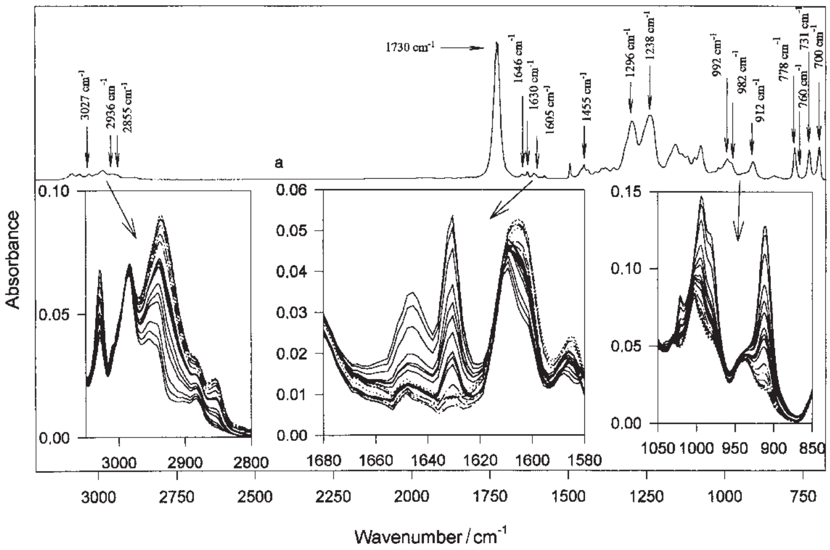

Fig. 3 FTIR spectrum obtained on the liquid resin before curing, and magnified parts of FTIR spectra obtained during curing

not reacted during the isothermal period. The variations in this quantity, called ΔH_{res}, with T_{iso} are also reported in Fig. 2. It is interesting that the quantity $\Delta H_{cop}+\Delta H_{res}$ remains practically constant for $T_{iso}>40°C$. On the other hand, although not observed during isothermal measurements at $T_{iso}>40°C$, we may suppose that copolymerization and homopolymerization reactions also occur in this range of temperature; this is suggested by the decrease in ΔH_{res}.

Table 2 Values of the maximum α_{max} of the rate of transformation and of the characteristic time τ for various reactions and for the curing period

$\bar{\nu}$/cm^{-1}	Function	α_{max}/%	τ/min
762	polystyrene	87	29
1455	polystyrene	86	33
1605	polystyrene	80	31
2936	polystyrene	73	35
982	C=C polyester	70	84
1646	C=C polyester	73	85
778	styrene	64	133
912	styrene	67	131

Figure 3 displays the FTIR spectrum obtained with the UPR in the liquid state before curing. In this spectrum, most of the characteristic features have been assigned according to Yang *et al.* [1], Mathias *et al.* [7], Urban *et al.* [8] and Bellamy [9]. Ta-

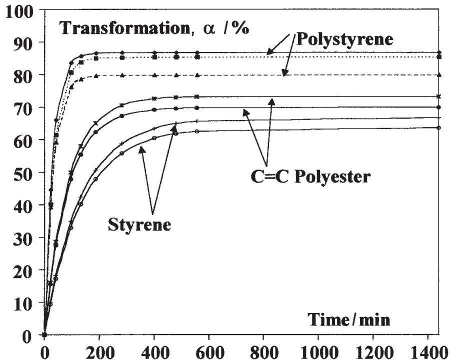

Fig. 4 Variations with time of the rate of transformation of the different functional groups, observed by means of FTIR. The Figure shows the experimental points (marks) and the fitted curves (full lines)

ble 2 reports the different wavenumbers and the assigned functions, which allow a kinetic analysis of the different reactions occurring during the curing process. The inserts at the bottom of Fig. 3 show three zoomed parts of the FTIR spectra collected during curing. Quantitative analysis of the variations in the degree of transformation for each assigned function was performed by using the method developed by Yang *et al.* [1], which requires normalization of the FTIR signal and extraction of the overlapping peaks. The variations with time of each function reported in Fig. 4 could then be fitted by the kinetic relationship proposed by Delahaye *et al.* [3]:

$$\alpha(t)=\alpha_{\max}(1-e^{-t/\tau}) \qquad (19$$

The values of the characteristic transformation time τ defined by expression (1) are also reported in Table 2. Comparison of these values allows conclusions on the different reactions and their kinetics that occur during the liquid-to-solid transformation:

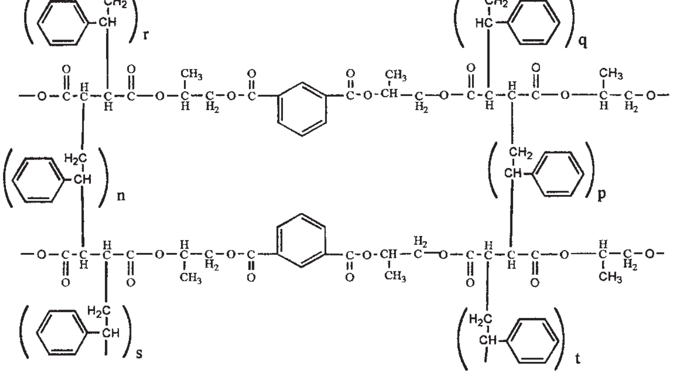

Fig. 5 Unsaturated polyester resin cured with styrene in the solid state (schematic)

1. the variations in enthalpy (ΔH_{cop}) with the curing temperature characterize styrene homopolymerization and its copolymerization with the polyester chains;
2. it is clear that polystyrene formation is faster than styrene-polyester copolymerization;
3. when homopolymerization of the styrene is achieved, the copolymerization remains active. After this curing period, the final product, in a solid state, may be drawn as shown in Fig. 5.

Relaxation

As revealed by DSC (Fig. 6), the glass transition of the standard UPR (0.2 w/w% Co octoate) occurs with a low ΔC_{p} value (characteristic of a fully cured thermosetting resin) in a wide range of temperature (between 50 and 100°C). This range of temperature for the glass transition is that expected for a fully cured UPR [10].

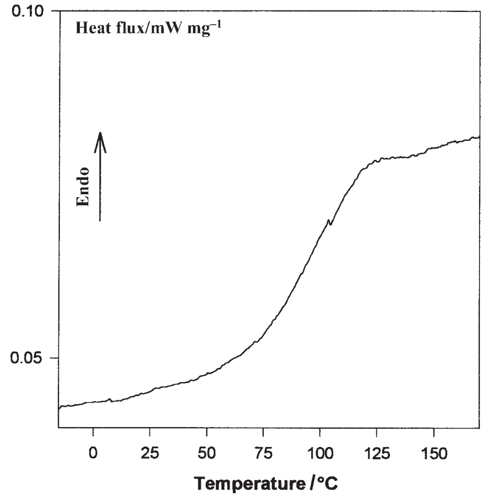

Fig. 6 DSC curve obtained on fully cured UPR (standard composition), showing the glass transition

On the other hand, Fig. 7 presents an example of the complex spectrum obtained with this standard UPR. This first peak, of weak magnitude, observed at low-temperature (between –140 and –100°C), fits with the relaxation β characterized by non-cooperative molecular motions due to local molecular rearrangements. The second peak, called α, observed at higher temperature (≈70°C) and due to the cooperative movements of the macromolecules, is the dielectric manifestation of the glass transition. This peak is overlapped by a third peak of considerable magnitude located a few degrees above the α peak. This third peak, generally called ρ, is classically related to the conduction through motions of excess charges limited in space by drift and diffusion [4]. This overlapping is an important problem and a priori limits further investigations of the α main peak, for instance through the use of elementary spectrum analysis.

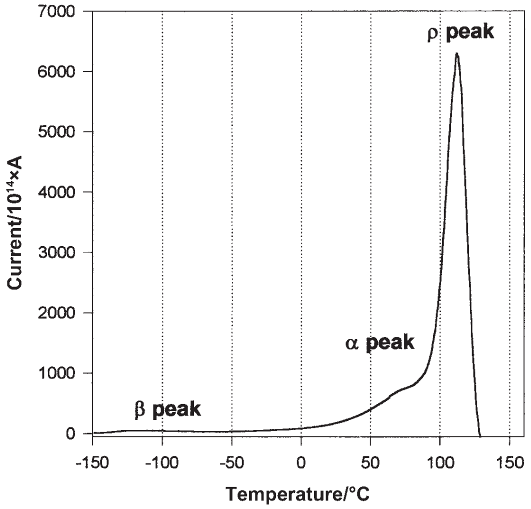

Fig. 7 TSDC spectrum obtained on a fully cured UPR (standard composition)

Table 3 Concentrations (in ppm) of the different elements determined by X-ray fluorescence spectroscopy as a function of the real amount of Co octoate

Element	UPR film Co octoate solution/%				
	1.9	0.5	0.23	0.19	0.09
17–Cl	12	7.5	6.6	2.3	3.6
19–K	4.9	1.4	2.2	0.5	0.2
20–Ca	10	2.6	1.3	1.1	0.9
19–Ti	0.1	0.1	–	–	0.1
24–Cr	5.4	6.1	5.4	9.2	7.1
25–Mn	0.5	–	0.1	0.1	0.1
26–Fe	2.3	0.5	0.4	0.6	0.6
27–Co	1140	300	138	96	42
29–Cu	2.6	0.4	0.4	0.4	0.3
30–Zn	2.5	1.8	1.4	1.8	1.3
38–Sr	3	0.9	0.4	0.2	–
40–Zr	2.4	0.8	0.2	0.3	–
56–Ba	5.8	1.1	0.7	0.4	–

In Fig. 8, which relates to several experiments performed under the same experimental conditions on samples prepared with various amounts of Co octoate, the magnitude of the α peak is seen to be unchanged, while the magnitude and the position of the ρ peak are greatly influenced by the amount Co octoate. Nevertheless, no correlation can be easily found between the magnitude of this ρ peak and the amount of Co octoate.

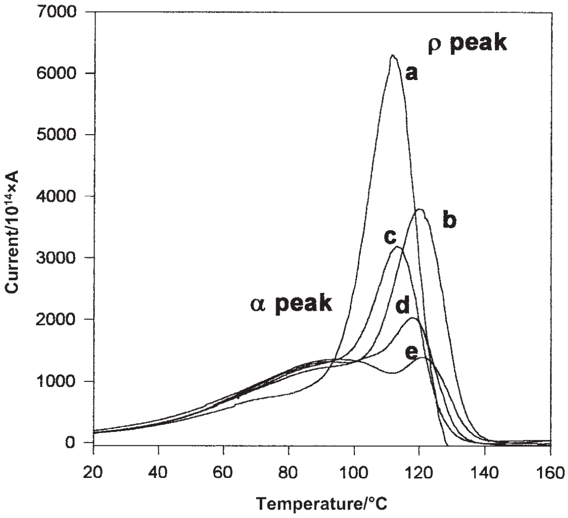

Fig. 8 Complex TSDC spectra obtained for UPR with different Co octoate contents: a – 1.9; b – 0.21; c – 0.49; d – 0.09; e – 0.19 w/w% nominal compositions

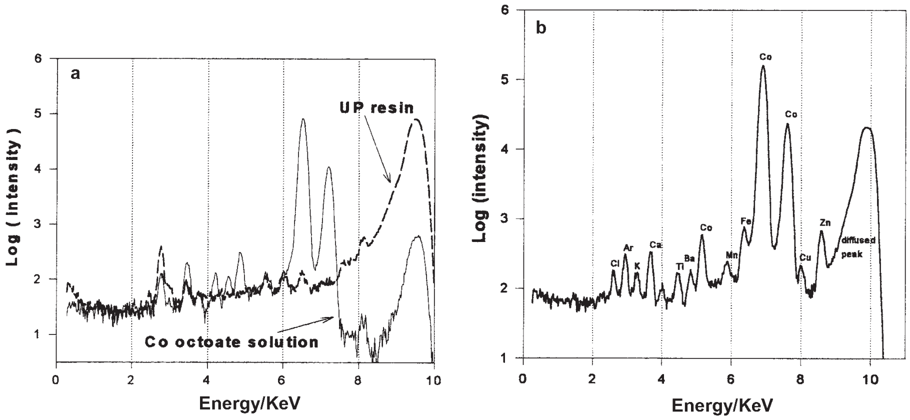

Fig. 9 a – X-ray fluorescence spectra for resin and Co octoate solutions; excitation energy=10 keV; b – X-ray fluorescence spectra for Co octoate solution, identification of the different elements

To study this point, we performed X-ray fluorescence spectroscopy measurements. Figure 9a displays the results obtained with this technique on the resin and on the Co octoate solutions, for an excitation energy of 10 keV. It is clear that a major part of each peak observed for the UPR occurs in the signal of the Co octoate solution. The following elements are found: Cl, Ar, K, Ca, Ti, Cr, Mn, Ba, Fe, Cu and Zn at an excitation energy of 10 keV (Fig. 9b) and Sr and Zr at an excitation energy of 20 keV. According to the calibration performed on the Co content, the quantitative analysis for each of these elements is reported in Table 3.

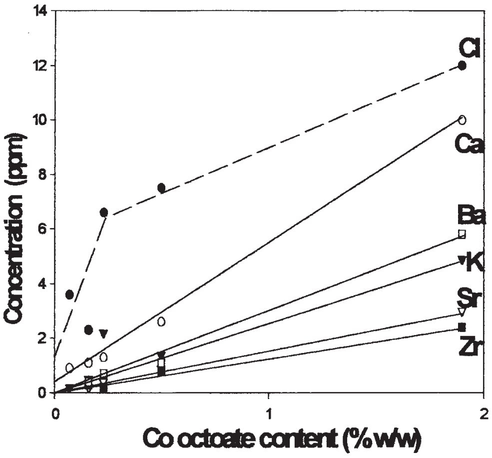

Fig. 10 Variations with the Co octoate content of the impurity amounts. For Cl, the line is drawn as a guide for the eye

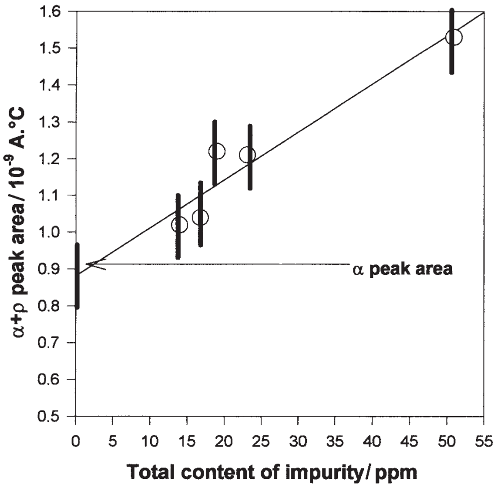

Fig. 11 Variations of α+ρ peak area with total content of impurity. This Figure also shows the correlation between the α+ρ area extrapolation to zero impurity amount and the α Gaussian-extrapolated area

The Ar revealed by the signal could be assigned to the experimental atmosphere of air and is not characteristic of the resin or of the Co octoate. On the other hand, the amounts of Ti are so small that the possible effects of this element could be neglected. There is no evidence for a correlation between the elements Fe, Cu, Zn, Mn and Cr and the concentration of Co octoate. The amount of Cl increases with the concentration of Co octoate. The elements K, Ca, Ba, Sr and Zr seem to vary linearly with the concentration of Co octoate (Fig. 10). Finally, the intercept at zero Co octoate content is at the origin, except for the cases of Cl and Ca. Thus, it may be concluded that Fe, Cu, Zn, Ti, Cr and Mn are present as contamination, Cl and Ca exist in both the resin and the promoter, while K, Ba, Sr and Zr occur in the promoter.

Instead of an analysis of the effects of these elements directly on the magnitude of the ρ peak, which requires a knowledge of its area independently of the α peak, and thus with a great possibility of error, we propose use of the total area, including both the α and ρ peaks. Since it is known that Co is surrounded by four oxygen atoms in the octoate solution, this element is not taken into account in this approach and it is not regarded as an impurity. Figure 11 shows that the variations in the total α+ρ area with the impurity content exhibit a spectacular quasi-linear dependence. At zero impurity, the extrapolation of the behaviour gives an α+ρ area of around $9\cdot10^{-10}$ A °C. This value, which is independent of the amount of impurities, must be compared with the fact mentioned earlier (Fig. 8) that the α peak seems to be independent of the promoter content. In order to estimate this peak, we presume to a first approximation that the α and ρ peaks can be described by Gaussian curves. Then, for each complex TSDC signal, curve fitting which gives the best value of the α area leads to a mean value of $9\pm2\cdot10^{-10}$ A °C. This value is remarkably close to that obtained by extrapolation to zero impurity of the α+ρ area variations (Fig. 11). Thus, it seems legitimate to assign the ρ peak to the role of impurities in TSDC measurements and to use the α-Gaussian value instead of the real one. This is an important result. In fact, high-energy X-ray fluorescence spectroscopy requires advanced and heavy equipment; in practice, therefore, it is impossible to carry out such a spectroscopic analysis on each studied TSDC complex spectrum and a fortiori on each elementary spectrum. The Gaussian extraction, which separates the contribution of the impurities from the contribution due to the motions occurring during the α relaxations, allows fine analysis of the relaxations by the technique of fractioned spectra.

Conclusions

By coupling DSC, TSDC and X-ray fluorescence spectroscopy measurements on unsaturated polyester resins with various amounts of Co octoate promoter, we have shown that impurities which occur in the formulation of the promoter are the main cause of the peak which overlaps the glass transition relaxation peak. Taking into account all these impurities within the resin (intrinsic or extrinsic), we have demonstrated that the α peak is independent of the amount promoter. Moreover, it is possible to extract the α peak from the complex signal by means of simple Gaussian analysis. As a consequence, this opens up the field to fine TSDC analysis by elementary spectra decomposition.

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