SIMULTANEOUS DSC-REFLECTED LIGHT INTENSITY OF POLYMER SYSTEMS
Part II

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Abstract

It has been shown that simultaneous measurements of reflected light intensity (RLI) with DSC can give additional and valuable information for the thermal analysis of materials including pure organic and inorganic chemicals, natural and synthetic polymers and foods.

This paper extends the range of polymers studied and examines the possibility of improving the reproducibility and quantitative nature of RLI measurements. Polymer crystallisation, the curing of epoxy resins, the action of fire retardant additives and the degradation of polymers and proteins are among the systems studied.

Keywords: curing, degradation, polymers, thermal analysis, thermomicroscopy

Introduction

The use of simultaneous techniques has been shown to give more information than either technique separately. Combining differential scanning calorimetry (DSC) with optical microscopy, particularly in the reflectance mode with measurement of reflected light intensity (RLI) has proved most useful for inorganic and organic compounds, polymers and foods [1–4].

The advantages of combining these techniques are that while the DSC can detect the sign, magnitude, temperature and rate of change, the RLI can detect colour, texture and surface changes. Direct observation of the nature of any change is possible and use of the reflectance mode allows study of opaque materials such as filled polymers.

The recent interest in micro-thermal analysis [5] and photo visual DSC [6] has shown the importance of combining observation of the image of material studied with determination of the thermal properties. While not giving such high magnification, RLI provides an average view and measurement of the material throughout the experiment. Similar arguments apply to the simultaneous measurement of DSC and Fourier transform infrared spectrometry (FTIR) [7].

The observation and qualitative study of physical changes such as melting, crystallization, expansion and crack formation are readily accomplished, and allow more

confident assignment of the nature of such changes. Quantitative measurements using RLI present more difficulties, since the intensity of reflected light depends on both the absorbance characteristics of the sample, and hence on the path length, absorptivity and the concentrations of absorbing species and also on the reflectance characteristics, refractive index and particle size [1, 8]. Calibration is difficult unless the sample remains in the same physical form, for example, a solid powder, throughout the experiment. Reproducibility depends on accurate placement of samples of similar size and shape, which poses problems when studying samples such as fibres. However, in a single experiment, the illumination, the sample placement and other experimental parameters should be constant and capable of comparison to the DSC experiment taking place simultaneously.

Photo-visual examination of pharmaceuticals and foods at low temperatures [6] has shown that different physical changes may be distinguished. One additional benefit of recording the reflected light intensity is that very slow changes may be studied, since RLI is an 'integrating' technique.

Experimental

The present work was carried out using a Perkin Elmer DSC 1-B combined with a Beck Binomax stereo microscope as previously described [1]. Modifications were made to allow measurements at lower temperatures by including a coolant chamber in the head cover. Scan conditions were generally 16°C min^{-1} in air flowing at 40 ml min^{-1}.

Open aluminium pans were generally used, but samples were also observed through transparent discs of mica punched to fit into the pan. Where fibre samples were studied, it was advantageous to crimp them into place, either using the aluminium pan alone, or by placing a small steel lock washer on top of the fibres before crimping. This gives a similar arrangement to that used for DSC-FTIR [7]. Where sealed pans were required, for example in experiments on aqueous solutions, the Perkin Elmer volatile sample pans were used. A very small amount of 'Loctite' cyanoacrylate adhesive was smeared onto the top surface, the sample injected into the central well using a syringe, and a transparent mica lid placed on top and lightly pressed onto the adhesive. This proved satisfactory up to a temperature just below the boiling point of the solvent.

In order to improve the reproducibility and quantitative evaluation of the RLI trace, the apparatus was adjusted so that the size and position of the sample in the cell holder, the placement and focusing of the microscope above the sample in each dimension and the illumination were maintained as nearly constant as possible.

Calibration of the DSC for temperature and power was carried out in the usual way with standard calibration materials, chiefly pure indium, tin and lead metals. Calibration of the RLI was attempted by using mixtures of magnesium carbonate and carbon black, giving a range from an opaque white powder to black. This is not entirely satisfactory, since in the case of transparent materials, some light is transmitted through the sample, and reflected back to the sensor, obeying a Beer–Lambert law.

Additionally, colour changes during reaction and decomposition will change the response of the sensor. These factors are well discussed by Kealey [8]. For quantitative experiments, the results were normalised by dividing the reflectance change at time t, $(R_t–R_o)$ by the total change $(R_\infty–R_o)$. Where light absorption predominates, the absorbance A was calculated from:

$$A=\log ((R_t–R_o)/(R_\infty–R_o))$$

where the sample was practically opaque, a 'white light' reflectance was estimated from the calibration outlined above.

Results and discussion

Synthetic polymers

Poly(ethylene terephthalate)

Samples of about 10 mg were obtained from an injection-blow moulded bottle by punching discs to fit the DSC pan. These were heated to just above the melting temperature (ca 280°C), flattened in the pan and quench-cooled. Very reproducible curves for both DSC and RLI were obtained as shown in Fig. 1. Both traces show the glass transition, cold crystallization and melting clearly.
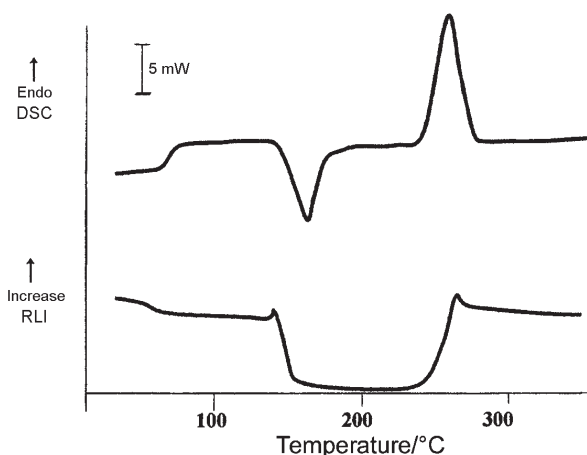

Fig. 1 DSC-RLI curves for poly(ethylene terephthalate), 10 mg quenched sample, 16 K min^{-1}, air

The isothermal crystallisation of polymers has proved the usefulness of DSC and microscopic measurements. Magill [9] showed that depolarised light intensity measurements of Nylon 66 could give good results fitting the Avrami kinetic law:

$$\ln (1–x)=–kt^n$$

where $(1-x)$ is the fraction of uncrystallized material, k the rate constant, t the time and n a constant characteristic of the system studied. Martins and Cruz-Pinto [10] used both DSC and optical microscopy to study spherulite growth parameters of poly(oxymethylene), recording the radius of the spherulites as a function of time.

The samples were cooled rapidly from the melt to temperatures just above the cold crystallization temperature shown in Fig. 1. The isothermal DSC and RLI curves were then recorded and are shown in Fig. 2a. From the plot of $\ln(-\ln(1-x))$ *vs.* $\ln(t)$ as shown in Fig. 2b reasonable agreement is found between the two techniques, especially over the region $0.2<x<0.5$ and the average Avrami constant n was evaluated as 2.5 ± 0.2. This is within the expected range [11, 12].
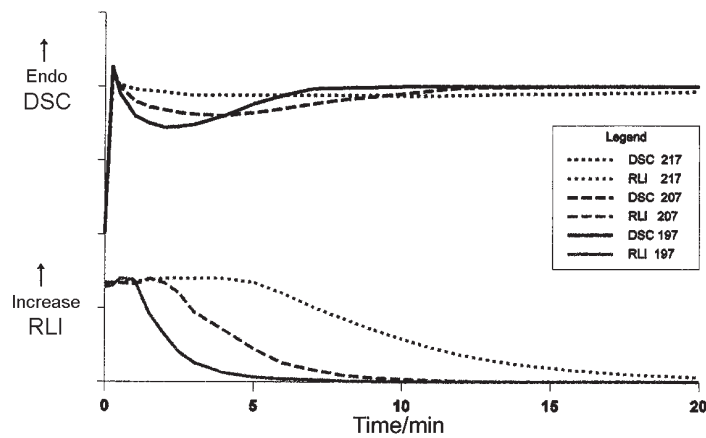

Fig. 2a DSC and RLI curves for isothermal crystallization of poly(ethylene terephthalate)
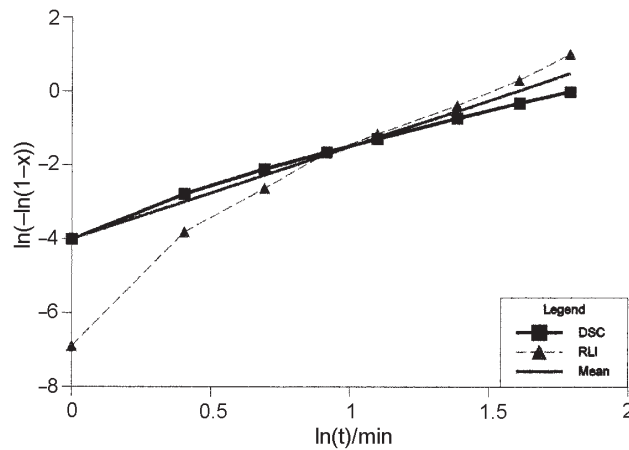

Fig. 2b Avrami plots for isothermal crystallization at 207°C

Nylon 11, (poly(ω-undecanoamide))

Samples of about 5 mg were cut from granular material using a scalpel and run directly. The melting peak occurs between 180 and 200°C, and for this material appears to be an endothermic doublet. Further heating in air to above 300°C causes oxidative decomposition, giving an exothermic trend on the DSC and considerable darkening to a brown-black colour recorded on the RLI. This is shown in Fig. 3. This may be a possible alternative method of measuring oxidative stability according to the ASTM D3350 method [13].
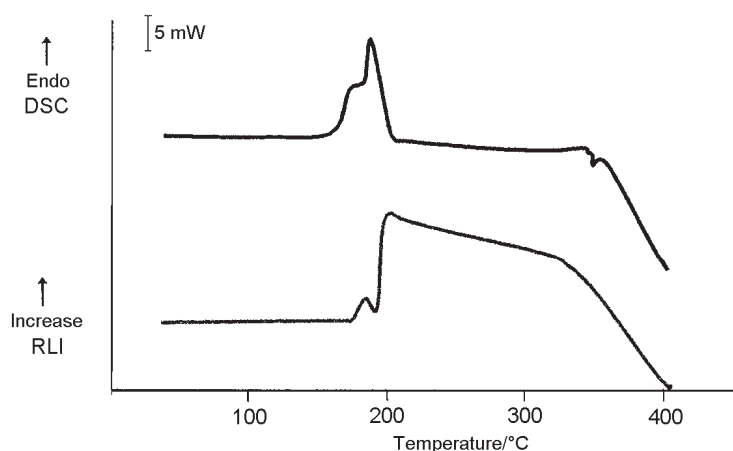

Fig. 3 DSC-RLI curves for Nylon 11. 5 mg slice, 16 K min^{-1}, flowing air at 50 ml min^{-1}

Epoxy resins

In order to check the performance of the apparatus, samples of 'Araldite Precision', that is, Bisphenol A-epichlorhydrin resin with N-(3-dimethylaminopropyl)-1,3-propylene diamine as hardener, were run under the same conditions. A large exotherm on the DSC, peaking at around 100°C was accompanied by a small increase in the RLI, probably indicating the clearing of the mix as curing progressed.

A mixture of a Bisphenol A-epichlorhydrin resin, Epikote 828 (100 parts mass/mass) and piperidine (5 parts) was prepared by mixing at room temperature. Samples of the uncured mix were carefully transferred into the centre of the pan and then run in the apparatus up to 400°C at 16 K min^{-1} in flowing air. No exotherm was observed until the temperature reached 200°C, when an exothermic trend commenced. The RLI trace showed a decrease from 200°C, corresponding to the development of a 'honey' brown colour. The colour continued to darken until the entire mixture was very dark, and decomposition had started. This is shown in Fig. 4. It is evident that, for this system, separation of curing and decomposition is difficult under scanning conditions. Isothermal cure at 200 and at 215°C gave dark, hard resins.
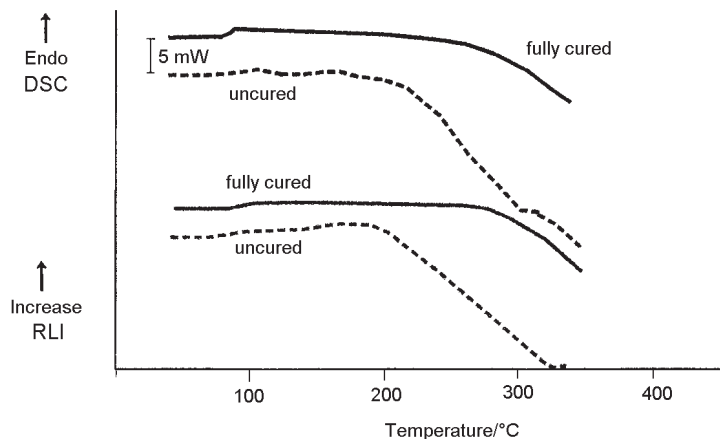
Fig. 4 DSC-RLI curves for Epoxy resin. Epikote 828 (100 parts)+piperidine (5 parts) 16 K min^{-1}, air

The resin mix is usually cured at 140°C for 16 h. Samples were cured under these conditions in DSC cells. The hard resin had a light, honey-brown colour, and gave the curves shown in Fig. 4, showing a glass transition around 95°C but no further change until around 300°C, where decomposition commenced. It is reported [14] that this curing agent operates by a two-part reaction, first forming a tertiary amine, which then initiates polymerisation through the epoxy groups. The colour generation may be due to the tertiary amine formation.

Natural polymers

Cellulose

Investigations of fire retardant additives for several polymer systems, particularly polyester resins [15] have been carried out using many thermoanalytical methods. The use of molybdenum compounds was investigated, and their effects on natural polymers such as cellulose were evaluated. measurement of the limiting oxygen index (LOI) for paper samples showed that treating the paper with a 4% mass/mass solution of ammonium paramolybdate raised the LOI from 18.3 to 29.5 and increased the amount of char remaining.

Samples of paper (Whatman #1) were obtained by punching circles to fit the DSC pan. Papers treated with solutions of ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O)$ were prepared by soaking in 0.5, 1, 2 or 4% aqueous solutions for 30 min, air drying for 3 h and then drying at 60°C for 2 h. The resultant DSC and RLI curves run in flowing air are shown in Fig. 5. The DSC traces show a shallow endotherm between 200 and 300°C followed by an exothermic effect. The RLI traces show more clearly that the molybdate treated samples start to decompose and blacken at progressive lower temperatures with increasing additive. While untreated cellulose commences to decompose around 250°C,
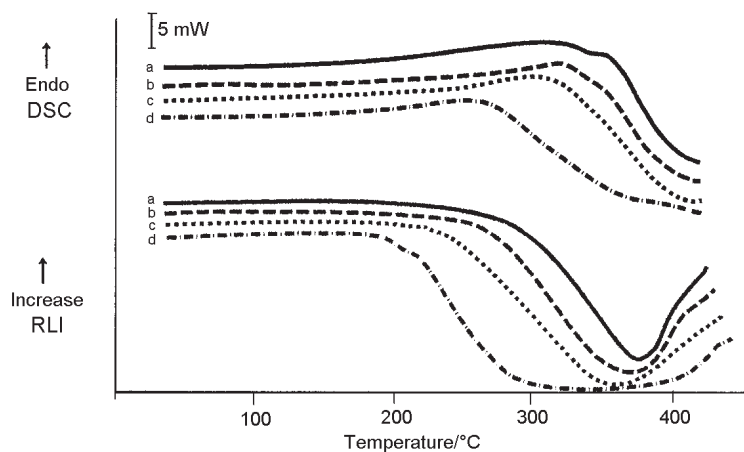
Fig. 5 DSC-RLI curves for cellulose treated with ammonium paramolybdate.
a – solid line=untreated; b – dashed line=0.5%; c – dotted line=1%;
d – dot/dash line=4%. 3 mg samples, 16 K min^{-1}, flowing air at 20 ml min^{-1}

paper treated with 4% molybdate starts some 100°C lower. Additionally, the amount by which the RLI increases at higher temperatures is decreased, suggesting that the mechanism is affected and char formation increased by the additive. This behaviour follows that reported by Dollimore and Hoath [16].

Ovalbumin

The extension of investigations into complex mixtures of natural polymers, such as proteins and foods has been commenced [3]. Early work showed that protein reactions and denaturation [17, 18] could be followed by careful DTA or DSC study. Ini-
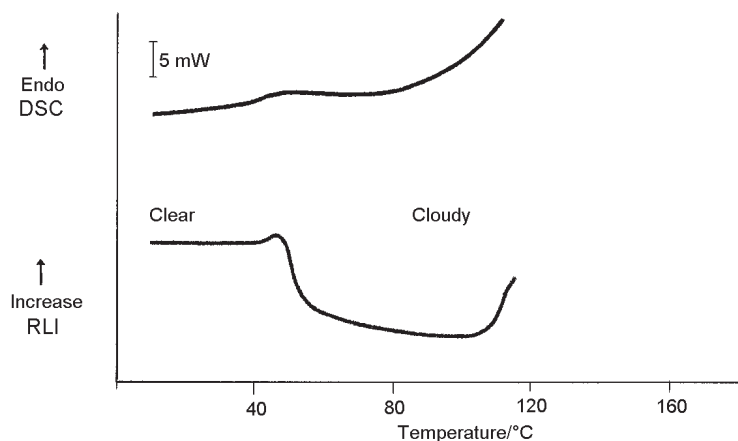

Fig. 6 DSC-RLI curves for ovalbumin: 20% aqueous solution; sealed pan, 16 K min^{-1}

tially, using a single component, such as the globular protein, ovalbumin, demonstrates the technique. An aqueous solution of 20% ovalbumin powder was prepared and added to the volatile pan by syringe. A mica lid was sealed on, as detailed above, and the sample heated to 100°C . The denaturation reaction produces a barely detectable DSC peak endotherm at 50°C at the sensitivity used, but the decrease in RLI is very marked. This is shown in Fig. 6.

Further work on protein mixtures, such as egg white, and connective tissue has confirmed that more complex changes can be studied by this technique.

Wool

Wool fibres are formed of the protein keratin. This is reported [19] as containing leucine, glutamic acid, cystine and arginine as major components. Thermal analysis, particularly by Crighton and co-workers [20, 21] has identified several characteristic peaks in the temperature range 160 to 321°C, which have been related to the physicochemical processes in the keratin. The need for supporting techniques to characterization is also stressed, especially rigorous drying.

Two types of fibres were studied. Natural wool, from Highland Blackfaced sheep was washed in mild detergent and dried, but otherwise untreated. Commercial wool, 3-ply pure 'baby' wool (Paton & Baldwins), treated to be shrink resistant, and made from Merino wool. In order to obtain reproducible results, similar methods to those outlined for poly(acrylonitrile) fibres were used, and the fibres aligned and crimped in the DSC pans.
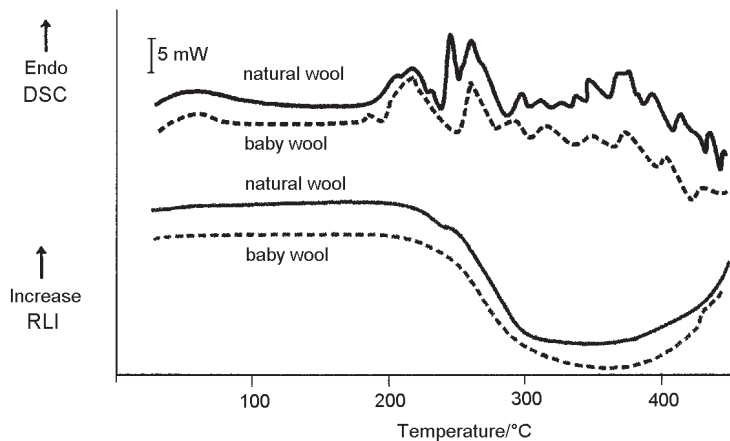

Fig. 7 DSC-RLI curves for wool. Solid lines: natural wool from blackfaced sheep; dashed lines: 3-ply baby wool from merino sheep. 16 K min^{-1}, flowing air at 50 ml min^{-1}

The traces in Fig. 7 show an extremely complex behaviour. The initial loss of adsorbed water gave a slight increase in reflectance, and the complex pattern of endo-

thermic peaks in the temperature range 200 to 300°C follow a similar pattern to those reported by Jaffe *et al.* [22].

The RLI trace reaches a minimum for the natural wool around 300°C, and remains steady until 360°C, whereas the baby wool trace curves down to a minimum around 350°C. Decomposition and shrinkage above 350°C is extremely complex in both cases.

In a parallel investigation using the TA Instruments TA2990 MicroThermal Analyser, Warrington [23] has shown that both materials show steady contraction from 50°C to 200°C, followed by expansion up to 300°C, and that the amount of contraction was more than five times greater for the shrink resist treated baby wool.

Conclusions

The observation and measurement of physical and chemical changes occurring in the temperature range 0–450°C using the simultaneous DSC-RLI arrangement has proved of value for several investigations of synthetic and natural polymer systems. Reproducible results may be obtained, provided care is taken in the preparation and placement of samples and in the operation of the equipment. Quantitative results have proved more difficult to obtain, although supporting evidence is noted for kinetic behaviour.

This simultaneous technique has advantages in studying slow isothermal changes, which are difficult to observe with conventional DSC. It has also demonstrated subtle differences between complex materials which have been subjected to different processing regimes. However, the major advantage lies in the direct observation and recording of changes, which enables distinctions to be drawn between physical, chemical and mechanical changes in the sample.

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