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SIMULTANEOUS DIFFERENTIAL SCANNING CALORIMETRY AND REFLECTED LIGHT INTENSITY MEASUREMENTS IN POLYMER STUDIES

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ABSTRACT

DSC and Reflected Light Intensity curves are given for a variety of polymers and the uses of this simultaneous method are shown for both phase changes and for decomposition and additive studies on polymer systems.

INTRODUCTION

The application of simultaneous techniques will often give far more information than the separate experiments and the large number of uses of differential scanning calorimetry (DSC) and of optical microscopy suggest that techniques combining these would be very useful, especially for polymer systems. [1]

The use of reflectance microscopy, rather than transmission, allows the study of opaque and highly coloured materials and there is less need for special sample preparation. Changes in reflected light intensity (RLI) may be caused by alterations in colour or refractive index, by expansion or textural changes on the surface. In a slow reaction the colour may change gradually, but this is still detectable by RLI which is an additive method, although little is shown on the DSC trace. Galwey [2] has pointed out, in connection with kinetic studies, that "Microscopic observations can also be used to resolve ambiguities concerning interface geometry deduced from other methods".

The applications of microscopic methods to polymers has recently been reviewed [3] and many of the multitude of DSC studies are noted and discussed by Turi.[4]

EXPERIMENTAL

The original studies were carried out using a Perkin-Elmer DSC 1B combined with a Beck Binomax stereo microscope.[1] A newer system is capable of using several types of DSC, particularly the Perkin-Elmer DSC 7, the Du Pont 990, and the Mettler DSC 20 with a more sophisticated Olympus SZ-TR stereo zoom microscope, a Schott fibre-optic light source and better facilities for photography. The light intensity is measured using a simple photometer based on a CdS cell. An increase in light is conventionally plotted upwards.

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A larger sample than usual for DSC is found to give better results, partly because this will fill the entire field of view of the microscope. Also, this allows use of a lower sensitivity which compensates for the need to run an "open" system without covers or lids which produces a more curved DSC baseline, although this can be corrected by using a linked computer system. Samples were generally run in nitrogen flowing at $20cm^3min^{-1}$.

APPLICATIONS

1. Phase Changes in Thermoplastic Polymers

Polyethylene

Small samples of low-density polyethylene bead of about 10mg were pre-melted into the DSC pans and flattened. As reported for low molecular weight organics, the melting endotherm on DSC has a corresponding increase in RLI, although for this polymer it is rather small and variable.(Fig. 1a) Cooling reverses the sequence although the transition is sharper which may assist discrimination.[5] Samples annealed below the melting point of 107°C showed multiple melting peaks on DSC but the RLI showed an almost continuous increase throughout the meltings. This is shown for a sample annealed for 1 hour at 72°C in Fig. 1b.

Polypropylene

To illustrate the isothermal operation of DSC-RLI, a sample of polypropylene was fully melted by heating to 177°C and then rapidly cooled to 117°C and held at that temperature. Observation showed that the polymer was still liquid when the DSC baseline returned to zero prior to the exotherm usually seen.[6] The RLI trace however showed two changes. Initially, while very small nuclei and spherulites were being formed the RLI increased. However, as the spherulites grew and became space-filling there was an almost equal decrease (Fig. 2). This is similar to the Depolarised Light Intensity (DLI) curves reported by Magill for nylons.[7]

Polystyrene

Samples of atactic polystyrene were premelted on the DSC at 227°C and quench-cooled to room temperature. DSC observation of the T_g at about 87°C showed as an endothermic step on the DSC while the RLI trace began a downward trend at the T_g. Although there was no thermal evidence of a melting, the RLI curve showed a broad increase in reflection in the region of 217°C, perhaps indicating that flow takes place more readily above this temperature (Fig. 3). This corresponds to the melting temperature of isotactic PS reported by Currie and Dole.[8]

Poly(ethylene terephthalate); (PET)

The familiar DSC trace of this polymer shows typical transitions of crystalline or semi-crystalline polymers. For a sample of PET of about 10mg rapidly quenched from the melt the DSC trace (Fig. 4) shows the T_g step at 80°C,

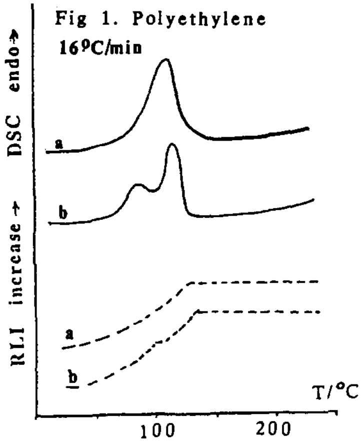


Fig 1. Polyethylene

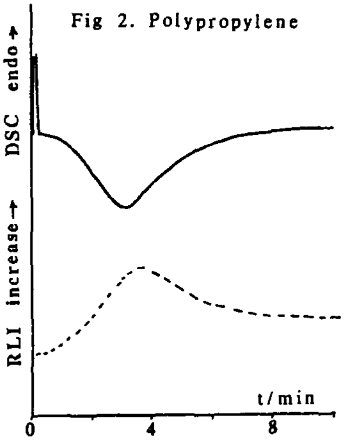


Fig 2. Polypropylene

Fig 3. Polystyrene

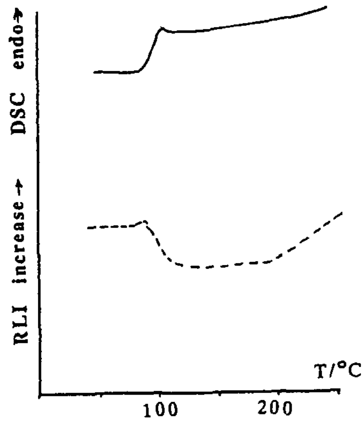
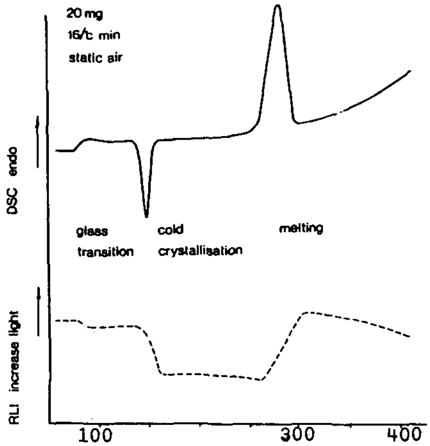


Fig 4. Polyethylene terephthalate



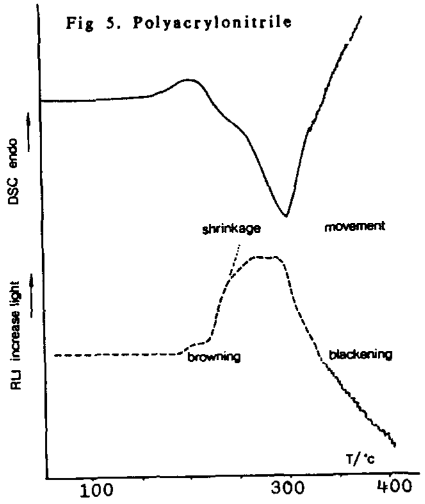
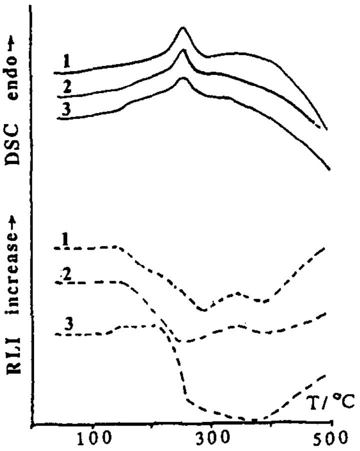


Fig 5. Polyacrylonitrile

Fig 6. Polyvinylchloride



the cold crystallisation exotherm at 150°C and the melting endotherm at 250°C. The simultaneous RLI trace and observation confirms the nature of these transitions. The T_g gives a small decrease due to relaxation in surface texture. The crystallisation caused a large decrease due to the formation of extremely small scattering centres of colloidal size which gave the sample "brown" appearance. The melting removed this colour and gave a large increase in RLI, closely followed by some decomposition.

2. Decomposition studies on thermosets

Poly(acrylonitrile); (PAN)

This polymer was studied as a carbon fibre precursor and the original fibres ('Dralon', Bayer (UK) Ltd) were crimped into a DSC pan with a metal washer which had been heated previously. This avoided any effects due to reaction of the washer or due to the fibres curling up or moving during the run. The complex DSC trace corresponded in every case to the observed changes on the RLI trace, including the sharp jumps as the fibres shrunk (Fig. 5). The colour changes reported by Madorsky [9] were all observed and recorded. Kinetic plots derived from the DSC and from the RLI traces both fitted a diffusion controlled reaction for the early part of the decomposition [1,10].

Poly(vinyl chloride);(PVC)

The decomposition of PVC may be altered by the addition of fire-retardant or smoke suppressant additives.[11-13] Thermogravimetry and evolved gas studies show that the major loss of HCl occurs at about 573K and results in the formation of conjugated structures involved in the production of flammable, smoky materials.[4]

Three commercial samples of semi-rigid PVC board were studied containing Geon 103 (BP Ltd.), phthalate plasticiser, and additives. Sample 1 had no fire retardant, Sample 2 had 2 phr Sb_2O_3 and Sample 3 had 4 phr MoO_3. These have been shown to increase the Critical Oxygen Index and the molybdenum oxide decreases the smoke produced.[14]

Figure 6 shows the behaviour of these samples under DSC-RLI investigation. They all gradually brown above 177°C and melt at 257°C. Above this temperature frothing occurs which causes both traces to be uneven and leaves a bubble-filled brown-black mass. Slight increases in RLI above 377°C are seen although the present apparatus does not reach a temperature high enough for complete oxidation of the char.

Samples 1 and 2 give very similar DSC and RLI traces but Sample 4 shows considerable changes, confirming parallel studies on TG. There is a small, sharp increase at 150°C and the decrease at 250°C is more rapid corresponding to catalysis of the HCl evolution. The final char residue is also different showing a more rigid, stable structure.

Unsaturated Polyester Resins(PER)

These are prepared from a variety of monomers but particularly maleic anhydride, phthalic anhydride and either neopentyl glycol or dibromo-neopentyl glycol. The effects of additives, especially Sb_2O_3 and MoO_3 have been investigated.[15] As with the PVC, it has been shown that MoO_3 reduces smoke evolution especially with halogen present by a mechanism not yet fully understood. Samples of powdered PER with and without additives were run in air (Fig. 7).

Cellulose

The effects of various flame retardant additives on cellulose fibres and powder have been studied extensively by thermal methods.[16, 17] Using paper samples (Whatman No. 1) treated with solutions of flame retardant chemicals and dried very clear differences in behaviour were seen by DSC-RLI. The untreated paper lost adsorbed moisture first and then combined water which gave little DSC change but a large decrease in RLI due to browning of the sample. Oxidative degradation at higher temperatures produced a large exothermic DSC peak and an increase in RLI due to shrinkage of the sample. It has also been shown that, under high heat-flux and oxygen-rich conditions, ignition of the sample will occur, producing a bright flash.[1]

The results for original paper and for samples treated with 2% $AlCl_3$ solution and with 4% ammonium molybdate solution are shown in Fig. 8. The reagents make little change to the DSC trace, but the RLI which starts to decrease at about 300°C for untreated, now changes at just about 127°C. This difference can be seen by using half-circles of each in the same DSC cell. The later stages of reaction also occur at lower temperatures with the treated material. It seems probable that the $AlCl_3$ becomes hydrolysed on the surface and is effectively the hydroxide which agrees with studies of alumina trihydrate as a fire retardant in polyester resins now in progress.

CONCLUSION

The use of the DSC-RLI method for polymers has been shown to give a large amount of additional information with little increase in complexity, cost or time. Direct observation allows proper assignment of the nature of changes and comparison of samples having different treatment or additives. Future work could extend the use to study of polymer cure, of catalysts and of further additives.

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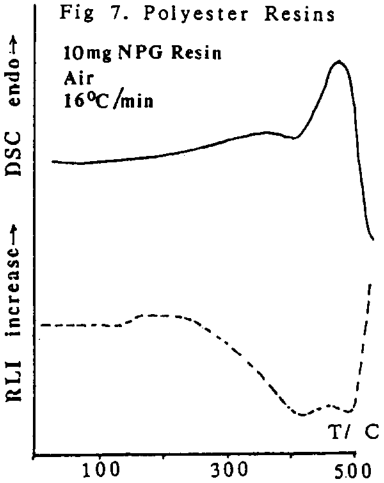

Fig 7. Polyester Resins

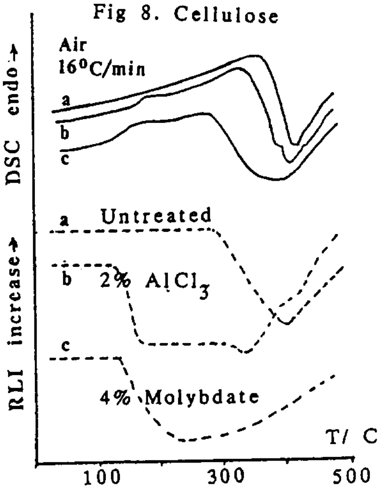

Fig 8. Cellulose

REFERENCES

1. P.J. Haines and G.A. Skinner, Thermochim Acta 59 (1982) 343.
2. A.K. Galwey, "Thermal Analysis", Vol. 1: B. Miller (ed); proceedings of 7th ICTA, Toronto 1982. J. Wiley.
3. L.C. Sawyer and D.T. Grubb, "Polymer Microscopy", Chapman and Hall, London, 1987.
4. E. Turi (ed) "Thermal Characterisation of Polymeric Materials", Academic Press, New York, 1981.
5. T.J. Lever (Private Communication)
6. J.R. Knox, "Analytical Calorimetry:, Vol. 1, p. 45: R.S. Porter and J.F. Johnson (ed), Plenum Press, New York, 1968.
7. J.H. Magill, Polymer, 2 (1961) 221.
8. J.A. Currie and M. Dole, "Analytical Calorimetry" Vol. 1, p. 56: R.S. Porter and J.F. Johnson (ed); Plenum Press, New York, 1968.
9. S.L. Madorsky, "Thermal Degradation of Organic Polymers", Interscience, New York, 1964, 1.
10. B. Danner and J. Meybeck, "Int. Conf. on Carbon Fibres, 1971", Paper 6. Plastics Inst. London, 1971.
11. P.J. Haines and G.A. Skinner, Analyt. Proc. 23 (1968) 121.
12. W.H. Starns and D. Edelson, Macromol. Rev., 5 (1979) 12.
13. T. Iida and K. Gota, J. Poly Sci., 14 (1977) 2427.
14. D.A. Church and F.W. Moore, Plastics Eng. 31 (1975) 36.
15. P.J. Haines, G.A. Skinner and T.J. Lever, Thermochim Acta, 59 (1982) 331.
16. D. Dollimore and J.M. Hoath, Thermochim Acta, 45 (1981) 87, 103.
17. W.K. Tang and W.K. Neill, J. Poly. Sci., C 6 (1964) 65.