Thermochimica Acta, 148 (1989) 365-373
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL ANALYSIS OF POLYMERIC MATERIALS

Papers presented at the 9th ICTA, Jerusalem, 1988

P J HAINES
Faculty of Science
Kingston Polytechnic
Kingston upon Thames
Surrey
KT1 2EE
England

ABSTRACT

The contents of over thirty papers related to polymer systems are reviewed. They reflect many of the interests and applications of polymer chemistry worldwide, and the uses for which thermoanalytical techniques have proved valuable. The continuing development of new instrumentation, and new and improved polymers has increased the need for the analytical use of thermal methods.

INTRODUCTION

The major areas of interest in polymer chemistry for which thermal methods contribute to our understanding may broadly be classified as quality control of materials and as characterisation of material properties. The early investigations into the cure, phase behaviour and degradation of polymers (1) have been followed by later investigations using more sophisticated instrumentation or new polymeric materials. The effects of additives and of reinforcement on the chemical and physical properties of polymers have been investigated by thermal analysis and pyrolysis and much important data assembled concerning fire retardants and stabilisers.

After 8th ICTA, Sasanov (2) described derivatographic applications to polymer studies and stressed the increase in the amount and range of uses of polymeric materials, the improvement in thermal analysis instrumentation and the interest in new materials such as polyimides.

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21-25 August 1988.

0040-6031/89/$03.50

The papers presented at 9th ICTA follow similar trends and may be divided roughly into four sections: cure, phase properties, degradation studies and specialist techniques and applications.

CURE STUDIES

Bachman and Houlihan (3) describe TG studies of the cure of polyamic acid esters produced by a novel synthetic route. Their DTG results show an earlier maximum for the esters than for the acid, and they note the effects of solvent retention. DSC, TG and TMA were applied by Ennis et al (4) to the cure of epoxide film adhesives. They found that the presence of small amounts of absorbed water produced anomalous curves. A simple adaptation of a TMA system followed changes in flow during cure and low temperature curing was considered. They stress that 'the greatest value is obtained from direct measurement of the properties of interest (e.g. extent of cure, T_g)'.

Malavasic and co-workers (5) investigated the effects of solvents on curing. The solvents ranged from hexane to DMF and the effects on cure of methacrylate polymers correlated well with the solubility parameters of these solvents. In a second paper the effects of trioctyl methyl ammonium salts on initiator decomposition were measured (6).

Ninan and Krishnan (7) studied both the cure and the decomposition of bismaleimide-diamine adduct polymers using IR, viscosity, DSC and TG. Their kinetic results for E_a and A of decomposition are consistent, except that the Horowitz-Metzger method gives considerably higher values.

A calorimetric analysis of polyester resin cure by DSC was made by Salla et al (8), comparing benzoyl peroxide with dimethyl aniline to MEKP with cobalt octanoate. The curing in presence of the promotors gave more complex DSC curves. Schneider (9) analysed the curing and decomposition of silicone resins by DSC, TG and EGD systems and the resins and residues were studied by spectroscopic techniques to give a ull picture of the behaviour of this system.

DTA and TG were used by Sickfeld and Neubert (10) in a study of the curing of epoxy powder coatings and to distinguish between curing types. The overlapping curves were analysed mathematically.
Cui Guo-Liang and Wang Wen-ju (11) looked at the cure of epoxy resins with a new dicyanamine-tertiary amine curing system and determined the optimum curing temperature and reagent ratios.

In these studies of cure, it seems that the attention is now being focussed on use of spectroscopic and other analytical techniques as well as thermal analysis to unravel the complex chemistry of the cure processes and to give meaning to the kinetic parameters derived.

CRYSTALLISATION AND PHASE STUDIES

Wunderlich (12) showed in his Ankor Plenary lecture the extremely careful work which enables thermodynamic functions to be measured and calculated and conformational disorder to be studied in crystals such as polyethylene and in liquid-crystal forming molecules. With Cheng (13) the values of Cp for PEEK, PET and other polymers were considered and crystallisation and melting behaviour, together with glass transition were related to the "rigid amorphous fraction".

Porter (14) discussed phase behaviour in polymer blends, stressing the possibilities of reaction between components which might give better properties. Polyarylates (PA) with PET showed phase separation, whereas with PBT they gave a blend with nematic order. Blends with liquid crystals were also studied. Bogdanov et al (15) used DSC to investigate block copolymers and found that crystallisation of blocks in the copolymer of oligo(ethylene terephthalate) and oligo (oxyethylene) was more difficult than for the homopolymers under the same conditions.

Two papers showed the effects of additives on crystallisation behaviour. Wlochowics and Eder (16) found that pigment particles accelerated the crystallisation of dyed Nylon 6, and Zerjal et al (17) showed that calcium carbonate had small effects on the melting point and crystallisation temperatures of polypropylene and PP/EPDM, but decrease H (fusion) markedly.

Bello and co-workers, in two papers looked at the glass transition of substituted polyoxetanes (18), where bulky substituents may increase T_g from -71°C to -4°C, and the glass transition of poly-(ditrimethylene terephthalate) (19) and used viscometry, osmometry and thermal analysis to relate the T_g to molecular weight. They find that although at high molecular weights T_g varies linearly with the inverse of MW, the Gibbs-DiMarzio theory of supercooled liquids (20) shows best agreement over the full range. Schneider (21) also looked at mathematical equations for T_g of polymer blends. DSC was applied by Qui Mingbi et al (22) to the crystallisation of PEEK and its carbon fibre composite. They fit their results to the Avrami equation and conclude that crystallisation is easier in the composite than for PEEK alone.

Selivansky (23) described a novel apparatus to measure shrinkage stress of high speed spun PET yarns as a function of time, which gave more appropriate results for large samples and was useful for quality control.

DEGRADATION

The development of linked thermal analysis-spectroscopic methods, such as TG-FTIR and TG-MS, as well as advances in data handling and chemometrics have made the task of abstracting data from measurements easier and more meaningful. The controversy which still surrounds the evaluation of kinetic parameters from scanning thermoanalytical techniques, or even their isothermal variants may cast doubt on the values of some activation energies derived, but the value of TG, DTA and TMA as construments for the comparison of materials is not in doubt.

In discussing the problems of lifetime prediction from thermal analysis experiments, Flynn (24) points out the need for accelerated ageing tests to take into account the nature of the ageing process, the factors causing ageing and methods of intensifying these. Consideration of work reported on polystyrene, polyurethane and PEEK showed that heating rate, atmosphere and errors in the Arrhenius extrapolation may all produce incorrect predictions of polymer lifetimes.

Popovic (25) reported work on the thermal degradation of poly-(dihexyl itaconate) and obtained evidence for two stages in the decomposition. The thermal stability of polyazines and polyazomethines was studied by Dumitriu (26) and co-workers and they found that polyazomethines were generally more stable than the corresponding polyazines. The investigation by Howell (27) into the principal site for "Saran", poly(vinylidine chloride) degradation involved addition of small amounts (0.05 - 0.40 W/%) of phenylacetylene to provide controlled amounts of unsaturated sites, and addition of methyl acrylate to limit dehydrochlorination. Using molecular weight, DSC, TG and NMR spectra, he shows convincingly that unsaturation greatly facilitates the dehydrochlorination reaction.

Applications of thermal methods to the more applied areas are typified by three papers. Popescu and Simion (28) studied quick-drying, waterproof adhesives from vinyl chloride-vinyl acetate copolymers and characterised them by TG/DTG and DTA together with the effects of solvent, plasticizer and pigments. Horrocks and D'Souza (29) illustrated the use of DTA and TG in investigating ageing of polypropylene film and conclude that TG offers a means of studying the small physico-chemical structural changes which take place prior to failure. The recovery of chemicals from polymeric waste was shown by Simionescu et al (30) to be greatly improved by the use of metal and oxide catalysts for pyrolysis. With styrenic polymers a CuO catalyst gives better yield of styrene and catalytic pyrolysis of PE and PP produced high-grade carburants and raw petrochemical materials. Abstracts report of work by Gronowski (31) on the effect on stability of metal acrylate copolymers with styrene; by Tomi et al (32) on the thermal stability of epoxy resins; by Vilcu et al (33) on the decomposition of acrylamide-maleic anhydride copolymers and by Kaminska et al (34) on the effects on thermal stability of photochemical transformations.

SPECIALIST TECHNIQUES AND APPLICATIONS

Thermally stimulated processes in polymers were discussed by Fleming (35) and measurement of thermally stimulated conductivity, luminescence and depolarisation on PE, EPDM and PET were described together with their use to study ageing and morphology of polymeric insulants. In his Landseas Plenary Lecture, Wendlandt (36) also described experimental details and gave applications of thermally stimulated light emission measurements to materials including polymers.

Haines and Skinner (37) showed how reflected light measurements can give useful additional data on many physical and chemical changes simultaneously with DSC curves.

Two papers concerned with drugs and polymers were very interesting. Daringa and co-workers (38) looked at drugs such as ampicillin and streptomycin on macromolecular supports of PVA, PS and polysacharides and were able to analyse the destruction process stages, in some cases quantitatively. Drug delivery systems based on cellulose polymers with various plasticisers were tested using DSC and TMA by Selinger and Brine (39) and this method could be used to screen plasticisers.

The importance of linked techniques is well illustrated by the paper of Jensen et al (40) who used thermal desorption and GC with FTIR or MS to detect and identify products produced from TG. Polyester urethanes gave CO_2,H_2O, THF and others and cured silicone rubbers gave some PCB.

CONCLUSION

It was somewhat surprising to have no papers dealing directly with fire retardant and smoke suppressant materials, especially in view of the interest in the use of thermal methods in their evaluation in recent years (41-43), and the development of TG-FTIR instrumentation seems to be slow in reaching polymer publications.

A review of uses of polymers by Manley (44) summarised the striking advances of the last 25 years. Besides the general review by Dollimore (45), particular polymer applications have been recently reviewed by Campanella and Tomasetti (46) who concentrate on TG, by Todoki (47) for plastics and rubbers and by Osawa (48) who looks at kinetic data.

It is a measure of the success of any conference that one leaves stimulated with new ideas, techniques and theories to try and integrate into one's own work. The 9th ICTA was certainly a success in this respect.

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