DEGRADATION AND STABILISATION OF POLYMERS

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DEGRADATION AND STABILISATION OF POLYMERS

The Proceedings of the plenary and main lectures presented at the International Symposium held in Brussels, Belgium

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Opening Remarks

During the last two decades, the production of polymers has been increasing at a rate of about 10% a year. During the same period, the main feature of chemical industry has been the increasing importance of petroleum as a source of organic chemicals. Presently, polymers represent about 80% of the final petrochemical products and consequently the rise of crude oil cost has resulted in increased prices for raw materials for the polymer industry. Polymers can no more be considered as low cost substitutes to traditional materials: they have to meet challenges never presented before and it can be expected that an increased lifetime will have to counterbalance the increase in price.

Nowadays, problems related to degradation and stabilisation of polymers are getting more and more important. Although experience gained by trial and error gradually evolved in the recognition of different types of stabilisers, a better understanding of the mechanism of degradation will undoubtedly lead to new methods for preventing the deterioration of polymers under various environmental conditions.

The aim of this Symposium was to provide a broad survey of recent developments in the field of degradation and stabilisation of polymers. These papers covered all aspects of polymer degradation: thermal, oxidative, photochemical and mechanical. The Scientific Committee is very grateful to all invited lecturers for their important contribution to the success of this Symposium.

G. GEUSKENS
Chairman of the Symposium

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A Review of Present Trends in Polymer Degradation

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INTRODUCTION

Systematic studies of polymer degradation, which started about 25 years ago, were originally confined to thermal degradation and were seriously limited in scope by problems of chemical analyses. Manufacturers preferred to solve their problems of polymer instability by the use of stabilisers discovered by trial and error methods, rather than through an understanding of the mechanism of the degradation process. The new instrumental techniques of the 1950s and 1960s, such as u.v., i.r., n.m.r., e.s.r., and mass spectrometry, the various thermal analyses techniques, high speed osmometry, g.l.c., g.p.c., etc., gradually made the solution of problems of polymer degradation more readily accessible. The area of research on polymer degradation was further extended as synthetic materials of increasing chemical complexity began to be synthesised. These are the products of a continuing search for materials which are more resistant to the many degradative agencies to which synthetic polymers are exposed in their commercial applications—agencies such as light, oxygen, ozone, high energy radiation, mechanical stress, moisture, atmospheric pollutants of industrial origin and the various combinations of these.

While, in the past, the ultimate purpose of degradation studies has been to assist in the formulation of more stable materials, a new aspect has emerged during the past few years in response to pressures against pollution of the environment. This is concerned with the synthesis of materials which are readily photo- or bio-degradable and any review of the present position of polymer degradation must take account of this.

In looking through the recent literature in order to try to decide how I should approach my task of presenting the opening lecture of this Conference, I was much impressed by the novelty and diversity of current work on polymer degradation. I therefore decided to bring to your notice some of the highlights which interest me particularly. This review will of necessity be subjective because it will be impossible to give a comprehensive account in the time available. However, I shall try to set the scene for the many interesting contributions which the programme promises us. I am very conscious of one very great danger of a review of this kind, namely, that I may intrude on some of the material of later lecturers. However, I shall approach my subject in a very general and highly selective way in the hope that any such intrusion will be minimal.

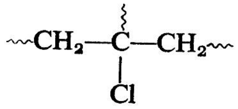
THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)

Over the years, interest in the thermal degradation of various homopolymers has come and gone, but it seems that the problem of poly(vinyl chloride) is to go on for ever and it has quite rightly been given a prominent place in this Conference. The basic question concerning PVC is what are the structural abnormalities which cause it to be so very much less stable than one would expect by comparison with model compounds representing the saturated linear chains of PVC.

$$\sim CH_2\text{—}CHCl\text{—}CH_2\text{—}CHCl\sim$$

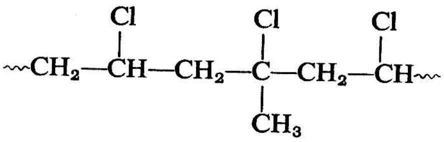
Extensive work on small molecular model compounds has demonstrated that unsaturated structures and chain branches involving labile tertiary chlorine atoms:

$$\sim CH{=}CH\text{—}CHCl\text{—}CH_2\sim;$$



$$\sim CH_2\text{—}\underset{\displaystyle Cl}{\overset{\displaystyle \wr}{C}}\text{—}CH_2\sim$$

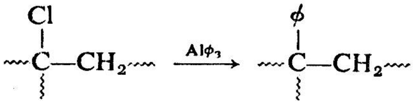
are probably the answer. Emphasis seems now to be moving back to investigating the polymer itself. Values of 0·05 and 0·2–1·2 double bonds per 1000 chain carbon atoms have been quoted by Michel, Schmidt and Guyot[1] and by Braun and Quarg.[2] Berens[3] has shown, by comparison of PVC and copolymers of vinyl chloride and 2-chloropropene:



$$\sim CH_2\text{—}\overset{\displaystyle Cl}{CH}\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{C}}\text{—}CH_2\text{—}\overset{\displaystyle Cl}{CH}\sim$$

that 0·1 mole % of units incorporating tertiary carbon atoms is sufficient to account for the instability of PVC.

If the structures responsible for instability could be positively identified, then, in principle, a new approach to stabilisation of PVC seems possible. This would attempt to eliminate the unstable structures either by modifying the polymerisation process or by treatment of the polymer with suitable reagents. This contrasts with the present rather inefficient approach to stabilisation which usually consists of nullifying the effects of degradation once it has taken place. Perhaps the seeds of this new approach are to be found in the report by Kennedy and Ishikawa[4] that PVC may be stabilised by treatment with triphenylaluminium which replaces tertiary chlorine atoms by phenyl groups.



$$\sim\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{—CH}_2\sim \xrightarrow{\text{Al}\phi_3} \sim\overset{\phi}{\overset{|}{\text{C}}}\text{—CH}_2\sim$$

COPOLYMERS AND POLYBLENDS

Of course degradation studies are also being carried out on a large variety of other commercially important homopolymers and these studies have been extended to copolymers as more and more copolymer systems have been exploited commercially. Although a copolymer often has superior physical properties to either of its related homopolymers the thermal stability is often impaired. Thus Fig. 1 shows that the introduction of vinyl acetate into poly(vinyl chloride) or vinyl chloride into poly(vinyl acetate) results in a loss in stability (as measured by rate of loss of acetic acid or hydrogen chloride) and stability is at a minimum in copolymer containing approximately 40% vinyl acetate.[5]

In recent years certain mixtures or blends of polymers have been found to have especially favourable physical properties and new classes of materials like the ABS polymers are coming into prominence. This has stimulated an interest in the stability of polymer blends. It is often surprising how the polymers in the blend influence the stability of each other in spite of the fact that this influence must usually act across the discrete phase boundary which exists between the constituents of the blend. This is quite different from the situation in copolymers in which the constituent monomers are chemically bonded to each other.

Typical TGA thermograms for poly(vinyl chloride) and poly(vinyl acetate) are illustrated in Fig. 2(a).[6] The two regions of weight loss represent acids (acetic acid and hydrogen chloride) and the decomposition of

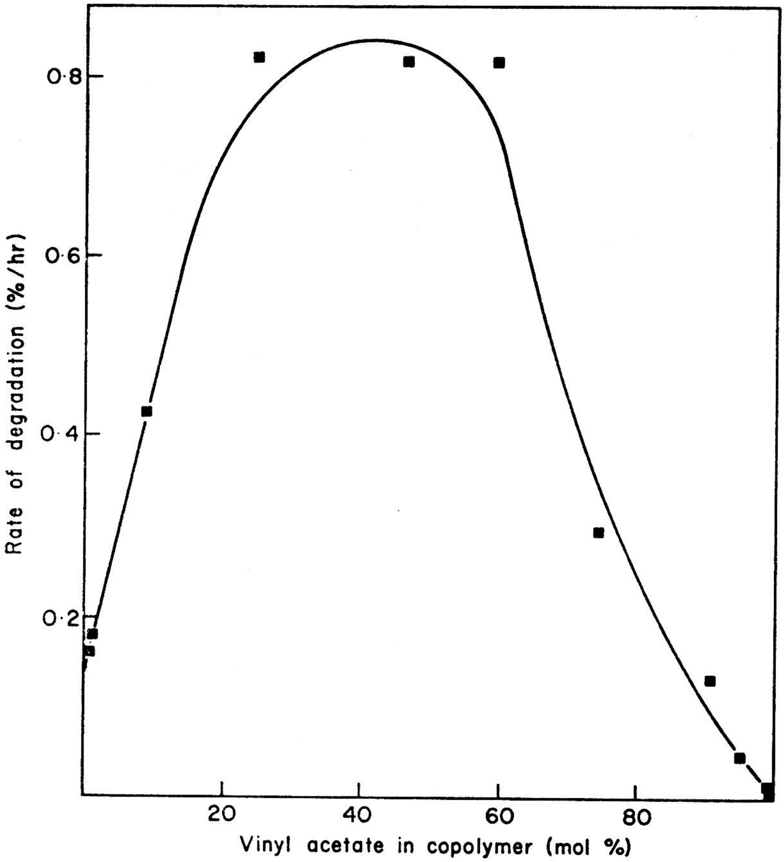


FIG. 1. Effect of composition on the rates of degradation of copolymers of vinyl chloride and vinyl acetate at 180°C.

the subsequent unsaturated chain. The 'expected' curve in Fig. 2(b) has been constructed from the data in Fig. 2(a) assuming a 1:1 mixture of the two homopolymers. The 'observed' curve demonstrates that the mixture is much less stable than predicted. Thermal volatilisation analysis (TVA) thermograms of unmixed and mixed polymers, illustrated in Fig. 3, confirm this behaviour and give further information about the nature of the gaseous products. The TVA technique involves heating a polymer sample through a linear temperature programme in a continuously evacu-

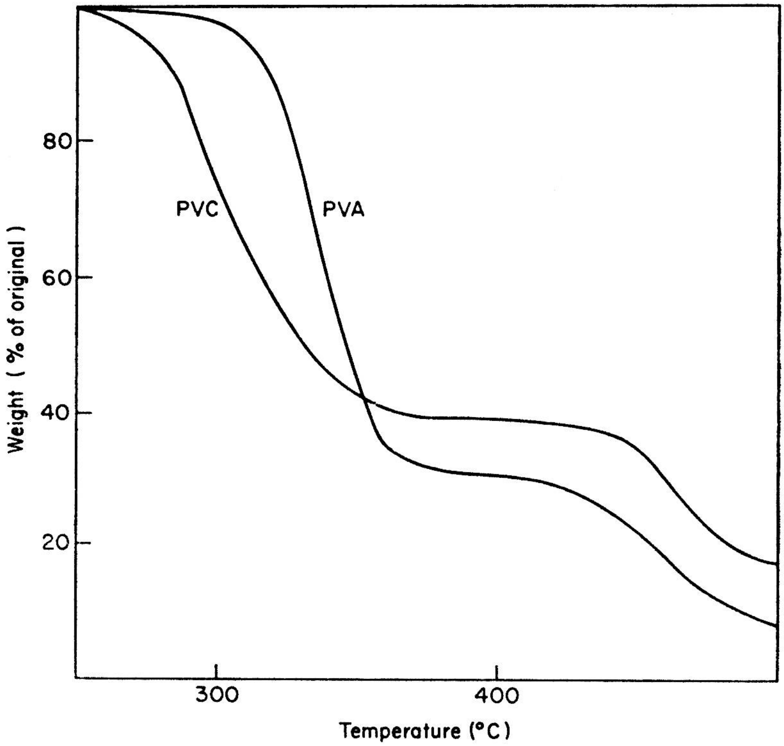


FIG. 2. (a) TG curves for poly(vinyl acetate) and poly(vinyl chloride).

ated system and continuously measuring the pressure of gaseous products by means of a Pirani gauge.[7] The various curves on the thermograms represent the pressures of products which are volatile at the temperatures indicated.

In Fig. 3(a) the product responsible for the first peak is clearly pure hydrogen chloride since it is involatile at −196°C but completely volatile at −100°C. The second peak is typical of the degradation products of poly(vinyl acetate), namely acetic acid (volatile at −45°C but involatile at −75°C) with smaller quantities of ketene, water, carbon monoxide and methane.[8] Figure 3(b) confirms that the polymer mixture is very much less stable and suggests that some acetic acid is appearing along with the hydrogen chloride in the low temperature phase of the reaction. Thus the

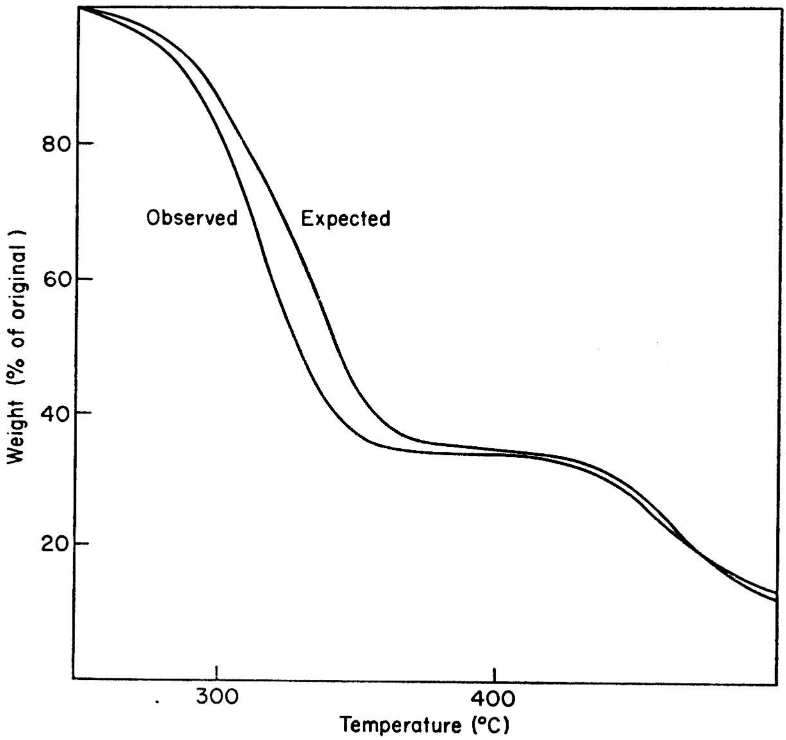


FIG. 2 (b). Comparison of 'expected' and 'observed' TG curves for a 1:1 mixture of poly(vinyl acetate) and poly(vinyl chloride).

presence of each polymer is making the other less stable. Since it is unlikely that the polymers themselves could interact across the phase boundary between them, an explanation of these phenomena has been given in terms of catalysis by the volatile products, acetic acid and hydrogen chloride which will readily diffuse across the phase boundaries.

STRUCTURE AND STABILITY

The continuing search for new synthetic materials with enhanced stability has created much interest in the relationships which exist between stability

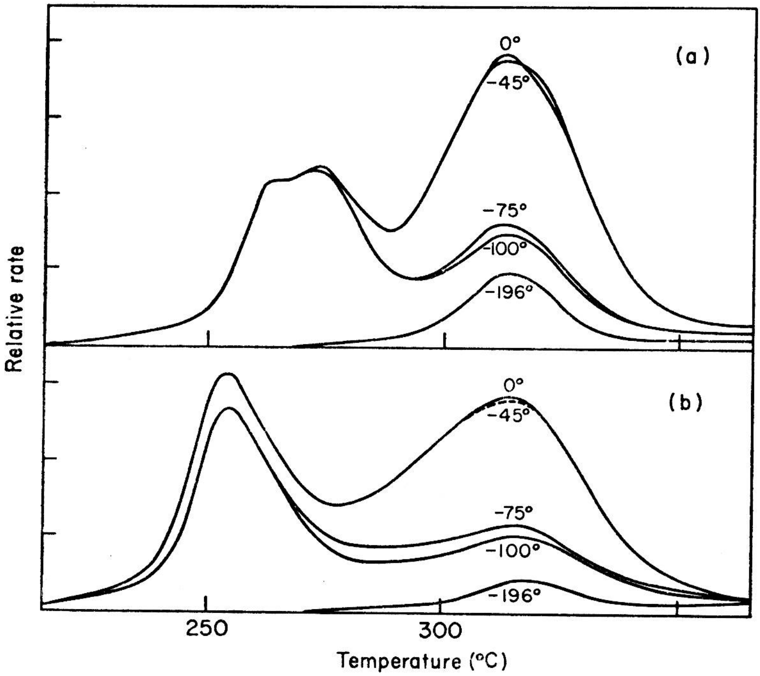
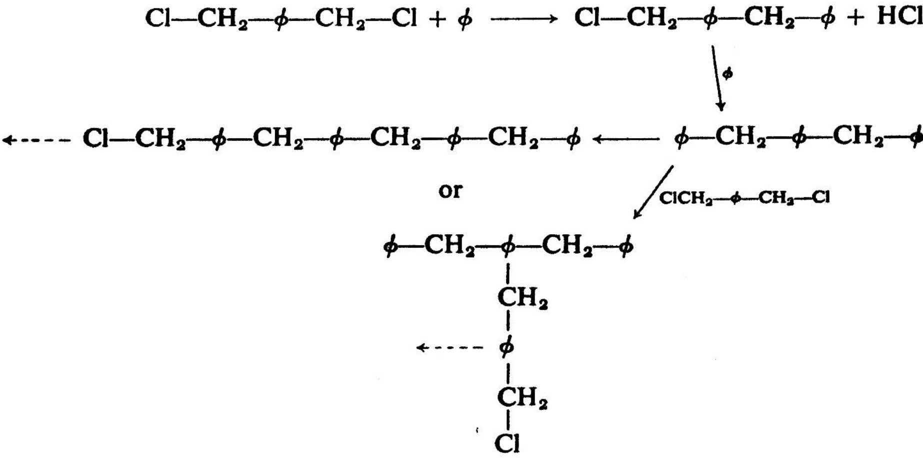


FIG. 3. TVA thermograms for equal amounts of poly(vinyl acetate) and poly(vinyl chloride). (a): unmixed; (b): mixed.

(or degradability) and chemical structure in polymers and a great deal is now known about the structural features necessary for optimum stability. For example, it is quite clear that aromatic and ladder structures built into the main chain are especially desirable. Some recent work in the field of Friedel-Crafts polymers has shown how different stabilities in chemically similar polymers may be accounted for in terms of basic structural differences built in during the polymerisation process.

Thus the polymers obtained by copolymerising di(chloromethyl) benzene (DCMB) with benzene in the presence of stannic chloride as a catalyst is approximately 50° less stable than the polymer obtained when benzene is replaced by thiophene. The basic reactions are obviously as follows:



$$\mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}Cl} + \phi \longrightarrow \mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi + \mathrm{HCl}$$

$$\Big\downarrow \phi$$

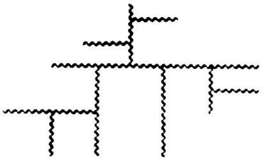
$$\dashleftarrow \mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi \longleftarrow \phi\mathrm{{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi$$

or

$$\swarrow \mathrm{ClCH_2{-}}\phi\mathrm{{-}CH_2{-}Cl}$$

$$\begin{array}{c} \phi\mathrm{{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}}\phi \\ | \\ \mathrm{CH_2} \\ | \\ \dashleftarrow \phi \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{Cl} \end{array}$$

Using gel permeation chromatography it has been possible to separate the various products of reaction as in Fig. 4. All the products with molecular weights up to about 1000 have been identified using various spectroscopic techniques and it has been established that the polymer has essentially a randomly branched structure which may be represented thus:



When benzene is replaced by thiophene[10] (T) the first two steps in the polymerisation process are:

$$\mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}Cl} + \mathrm{T} \longrightarrow \mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}T} \xrightarrow{\mathrm{T}} \mathrm{T{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}T}$$

But the thiophene nucleus is 20–30 times more reactive than the benzene nucleus so that the next stage in the reaction is almost exclusively:

$$\mathrm{T{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}T} + \mathrm{Cl{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}Cl} \longrightarrow \mathrm{T{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}T{-}CH_2{-}}\phi\mathrm{{-}CH_2{-}Cl}$$