

The Involvement of Oxygen in the Primary Decomposition Stage of Polymer Combustion

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ABSTRACT

The effects of oxygen on the thermal decomposition of organic polymers are first described. Evidence for the involvement of oxygen in the primary decomposition stage of polymer combustion is then reviewed and factors which determine whether or not oxygen is present during this stage are considered. Some suggestions are also made as to ways in which it might be possible to exclude oxygen from the region where polymer breakdown first occurs and thus decrease the readiness with which polymeric materials are initially ignited. Finally the desirability is stressed of further studies being made of the oxidative pyrolysis of organic polymers.

INTRODUCTION

There are at least two essential requirements for the development of any fire; one is a source of ignition and the other is one or more flammable materials. Although the principal ignition sources responsible for starting fires are fairly well known (1,2), there is still relatively little statistical information about the precise types of material involved in fires (3). Nevertheless, most of the flammable components of residential, public and commercial buildings consist largely of either natural or synthetic organic polymers, and these materials are therefore nearly always implicated in, if not directly responsible for, fires in urban areas.

The likelihood of fire developing depends not only on the magnitude and effectiveness of the ignition source but also on the ease with which the adjacent materials can be ignited and the readiness with which they subsequently burn and spread flame to other parts of the structure under consideration. Although all organic polymers will burn under sufficiently vigorous experimental conditions, there are substantial variations in the combustion reactivity of different polymeric materials; and, in order to assess the risks of fire developing, it is important to be able to identify the principal factors determining the readiness or otherwise with which a particular polymer burns.

The combustion of organic polymers is a very complex process, which involves a number of interrelated, although conceptually distinct, stages taking place both in the condensed phase and in the adjacent gas phase (4). In flaming combustion, the polymers first suffers breakdown in the condensed phase to give combustible volatile products; these then enter the flame zone above the decomposing polymer where they burn in the gas phase yielding final combustion products and

liberating heat; and finally at least some of this heat is transferred back to the polymer where it causes the evolution of a further supply of volatile breakdown products. Since in such a system it is in effect the gases formed from the polymeric material which burn rather than the polymer itself, factors which determine how readily a given polymer undergoes combustion will include its ease of breakdown and the extent to which its decomposition yields combustible gaseous products which can form flammable mixtures with the surrounding air or other gaseous oxidant.

Over the last 35 years or so, detailed studies have been made of both the kinetics and products of decomposition of numerous organic polymers, so that there is now a wealth of experimental evidence regarding the mechanisms of breakdown of polymeric materials and the nature and amounts of gaseous and other products formed from them (5-9). By far the greater part of the vast amount of work on thermal reactions of polymers in the condensed phase has been carried out either in a vacuum or in inert atmospheres. There is now however considerable evidence that, at least under certain combustion conditions and with some organic polymers, the initial breakdown of the polymer is a process which actively involves oxygen.

In this paper, therefore, an account is first included of the influence of oxygen on the thermal decomposition of some organic polymers. A review is then given of the evidence for the involvement of oxygen in the primary decomposition stage of the combustion of certain polymers and an attempt is made to identify at least some of the factors which determine whether or not oxygen is present during this stage. Suggestions are made too as to ways in which oxygen might be excluded from the region where breakdown of the polymer first occurs so as to decrease the readiness with which certain polymeric materials are initially ignited. Finally the need is emphasised for detailed studies of the kinetics and mechanisms of the oxygen-catalysed pyrolysis of many more organic polymers.

THE INFLUENCE OF OXYGEN ON THE THERMAL DECOMPOSITION OF ORGANIC POLYMERS

It has long been known that even stoichiometrically insignificant amounts of oxygen can considerably alter the rate and course of decomposition in the gas phase of hydrocarbons and other organic compounds. Probably one of the best-known examples of oxygen-catalysed pyrolysis is found with acetaldehyde (10-12), where as little as 10^{-3} vol% of oxygen can double the rate of decomposition, although methane and carbon monoxide remain the predominant breakdown products. Somewhat similar behaviour is observed with low molecular weight hydrocarbons (13-15), although the mechanism of action of the oxygen is complex and indeed the experimental results suggest that oxygen can act both homogeneously and heterogeneously and can terminate as well as initiate the free radical chains involved (16-18).

It is not perhaps surprising therefore that the kinetics and products of decomposition of many organic polymers are considerably affected by the presence of (often very small amounts of) oxygen. For example, with polypropylene, oxygen decreases the reaction temperature by some 200° and reduces the activation energy by about 150 kJ mol^{-1} (19,20); and similar behaviour is found with poly(vinylidene fluoride), where oxygen, in addition to causing a dramatic lowering of the activation energy and the pre-exponential factor, changes a normally second-order reaction to one of zero order (21). Among other common organic polymers whose decomposition is generally accelerated by oxygen are poly(vinyl chloride) (22), polyamides (23) (including wool (24)) and cellulose (25). Interesting behaviour is observed with styrene-based polymers, where the effect of oxygen appears to depend on the nature of the substituent groups attached to

the aromatic ring (26); with polystyrene itself, oxygen considerably decreases the thermal stability but poly(p-hydroxystyrene) breaks down at virtually the same rate in the absence and presence of oxygen (27). Polybutadiene is another polymer whose decomposition is very little affected by oxygen (28). However the complexity of the action of oxygen is shown by the fact that the gas tends to retard the decomposition of other polymers, such as polyacrylonitrile (29,30) and certain polyurethane foams (31,32).

It is thus clear that, with many but not all organic polymers, oxygen affects (and usually promotes) the thermal decomposition process. However, in general, the effects of the gas are less marked with thermosetting polymers than with thermoplastic polymers (33).

EVIDENCE FOR THE INVOLVEMENT OF OXYGEN IN THE PRIMARY DECOMPOSITION STAGE

Experimental evidence for the involvement of oxygen during the initial breakdown stage of polymer combustion is derived from several different types of measurement, which will now be considered in turn.

Studies of Stationary Flames above Burning Polymers

Measurements have been made of the chemical composition of the gases at various positions in the flames above candles of different organic polymers with both air and oxygen-enriched air as the supporting gas (34,35). With polyethylene burning in air, it was found that close to (i.e. within 1 mm of) the surface of the molten polymer, at least 70% of the flame gases consist of nitrogen, with less than 2% of oxygen, appreciable quantities of oxides of carbon and water and small amounts of several low molecular weight hydrocarbons. In other words, nearly all the oxygen originally associated with the nitrogen in the air had undergone chemical reaction and disappeared within a very short distance of the polymer surface. The possibility was considered that the oxygen oxidised the gaseous decomposition products of the polyethylene to carbon oxides and water as soon as they entered the gas phase. However calculation showed that the residence time of the gases in the first millimetre above the surface was only 5-10 ms, and separate experiments revealed that, at the temperatures in this region (ca. 400°C), negligible oxidation of simple hydrocarbons would take place within so short a time (36). It was therefore concluded that the carbon oxides and water were formed by oxidation reactions within the surface of the polymer melt rather than in the gas phase. On the other hand, similar experiments with both poly(methyl methacrylate) and polyoxymethylene showed that there were still substantial amounts of unchanged oxygen in the flame gases immediately adjacent to the polymer and that little or no surface oxidation took place. In other words, these polymers appeared to undergo principally thermal decomposition to the corresponding monomers, which then reacted with oxygen within the flame.

More detailed analysis of the flame gases only 0.1 mm above the surface of burning polyethylene and polypropylene (37) also showed very little residual oxygen and substantial amounts of oxides of carbon and water, strongly suggesting that, with both these polyolefins, significant amounts of oxygen diffuse through the flame to the polymer surface and are then absorbed into a well-defined surface layer in which an appreciable proportion of the polymer undergoes oxidative decomposition. However, it may be possible to explain the presence of the final gaseous products of combustion of the polymer close to its surface in terms of the relatively rapid diffusion of these species from the flame zone to other parts of the combustion region.

Analysis of Oxygen in the Condensed Phase during the Combustion of Polymers

Perhaps the most direct evidence for the presence of oxygen in the surface layer of burning polymers during combustion comes from experiments with both polyethylene and polypropylene (37). Burning candles of these polymers were extinguished by an excess of nitrogen or argon and then cooled in a stream of the inert gas. The oxygen content was then determined by neutron activation analysis of a section sliced lengthwise through the samples. In the case of one polypropylene sample, the oxygen content was about 0.3 wt%, 1.6 mm below the surface, but this rose to 12 wt% at a depth of 0.1 mm, and extrapolation suggested an oxygen concentration of about 26 wt% at the surface.

Another technique which may well prove useful for studying condensed-phase processes in polymers undergoing combustion is in situ continuous γ -radiometry, which can be used to monitor density changes in discrete isothermal layers of relatively large blocks of materials during their decomposition (38). This technique has recently been extended to the determination of the changing elemental composition of burning polymers and, although it has been used so far mainly to detect the chemical changes occurring in various types of wood, it can also be applied to measuring the oxygen concentration during the combustion of other polymers (39).

Measurement of Temperatures in the Condensed Phase of Burning Polymer Systems

More indirect evidence suggesting the intervention of oxygen in the decomposition stage of polymer combustion comes from measurement of the temperatures at and near the surface of polymeric materials when they burn. With polyethylene burning in air, for example, the temperature rose rapidly from about 200°C, 5 mm below the polymer surface, to approximately 400°C at the surface (35). Separate experiments have shown however that, in the absence of oxygen, polyethylene suffers scarcely any decrease in weight at this latter temperature (40). On the other hand, this polymer starts to break down at temperatures as low as 250°C when oxygen is present (40), and indeed most high molecular weight hydrocarbons undergo rapid oxidation in the liquid phase under these conditions (41,42). It is thus reasonable to assume that oxidation of the molten polymer could take place in the surface layer, whereas pure thermal decomposition could not. Another interesting finding was that the temperature of the surface of burning molten polyethylene increased rapidly when the oxygen content of the surrounding atmosphere was increased, whereas the maximum flame temperature remained more or less constant (35). This suggests that the additional oxygen becomes involved primarily in a direct reaction with the polymer in the condensed phase rather than in purely gaseous reactions. It is perhaps significant, however, that, in contrast to the behaviour observed with polyethylene, the surface temperature of burning poly(methyl methacrylate) decreases when the oxygen concentration is increased (43).

Determination of the Influence of Oxygen on Rates of Gasification of Polymers

In experiments involving the thermal irradiation of polyethylene, an increase in the oxygen concentration (from 0 to 40 vol%) in the surrounding atmosphere considerably increased the rate of gasification of the polymer (43). The results of a theoretical study suggest too that, with poly(methyl methacrylate), both oxidative and thermal degradation are responsible for the gasification of the polymer (44).

On the other hand, the use of a radiative pyrolysis technique has shown that,

when small-diameter rods of polystyrene decompose in the absence and presence of oxygen, the linear regression rates are the same (45). Interestingly, observation of the onset of ignition by means of high-speed cine-shadow photography, when a stream of hot oxygen was passed over a flat polymer plate, has indicated that ignition occurs mainly as a result of a gas-phase reaction in the boundary layer rather than at the surface of the polymeric material (46).

Consideration of the Energy Balances Involved in Polymer Combustion

A physical model has been proposed for the flaming combustion of organic polymers in which heat is transferred, mainly by conduction from the flame, to the polymer surface, where pyrolysis takes place to produce more gaseous fuel (47, 48). If all the oxygen in the surrounding atmosphere is consumed in the flame zone, so that decomposition of the polymer occurs in the absence of oxygen, the model predicts that the critical ratio of oxygen to inert gas needed to sustain combustion of the polymer should be a linear function of the heat capacity of the inert gas. Experiments with different inert gases showed that this was the case with poly(methyl methacrylate) and polyoxymethylene (49) but not with polytetrafluoroethylene (50). With the fluorinated polymer, it is therefore necessary to invoke exothermic oxidation reactions at the polymer surface in order to supply the missing energy. Consideration of the energy fluxes for both polyethylene and polypropylene burning in air (37) showed too that, on the assumption that a small amount of energy is provided by radiation from the flame envelope, it is possible to calculate the extents to which these polymers simultaneously undergo oxidative decomposition (which is exothermic (51)) and thermal decomposition (which is endothermic). Measurement of the composition profiles in an opposed-flow diffusion flame of polyethylene also indicate the appreciable contribution (i.e. up to 20%) which surface oxidation of the polymer makes to the total enthalpy required for production of the gaseous polymer breakdown products (52).

FACTORS AFFECTING THE ACCESS OF OXYGEN TO THE SURFACE OF BURNING POLYMERS

The factors which determine whether or not oxygen is present at the interface between the condensed and gaseous phases during the flaming combustion of polymers are not at all well understood. There must however be a delicate balance between various physical and chemical processes, including the rate at which oxygen diffuses towards the burning polymer surface, the rate at which the gaseous polymer breakdown products diffuse away from the surface and the rates of the different chemical reactions in the condensed phase, in the gas phase and at the interface between them.

The general conclusion seems to be that, at least with some organic polymers, oxygen is involved in the decomposition stage of flaming combustion which generates combustible gaseous fuel. However the extent of oxygen involvement varies considerably with the nature of the polymer, the size, shape and orientation of the sample being burnt and the combustion conditions, including the flame geometry.

One important factor which clearly influences whether or not oxygen reaches the surface of the polymer undergoing combustion is the vigorousness of the emission of the gaseous decomposition products. Thus, with poly(methyl methacrylate), as the rate of gasification becomes larger and the resulting counterflow of gaseous products allows less and less oxygen to reach the condensed phase, the effect of oxygen on the gasification process becomes less marked (43). This competition between the diffusion of oxygen to the surface and the convective flow of

product gases away from the surface clearly influences the magnitude of the effect of gas-phase oxygen on the rate of polymer gasification. Such an effect, which depends on the distance over which oxygen has to diffuse to the surface, is thus not surprisingly affected too by the size and shape of the polymer sample undergoing combustion. Thus, in a fire situation, where large areas of polymeric materials are generally involved, the role of oxygen in the decomposition stage of polymer combustion may well be much less important than during the candle-like burning of relatively small polymer samples.

Another factor is no doubt the ease with which oxygen, after it has successfully diffused to the surface of the condensed phase, can dissolve in the polymer. The molten surface layer of certain polymers becomes less viscous in an oxygen-containing environment (43,53). In the case of poly(methyl methacrylate), it has been observed that the bubbles then burst more frequently, leaving large holes which oxygen can enter; in these circumstances, oxygen penetrates a deeper layer of near-surface material than it could reach by diffusion alone (43).

It has already been mentioned that oxygen has in general a smaller effect on the decomposition of thermosets than it has on thermoplastics (33). The probable reason for this is that the melting which generally occurs when thermoplastics are heated tends to increase the surface area exposed to oxygen; this means that oxygen and volatile decomposition products can diffuse more readily through the polymeric material. In contrast, the surface area of thermosets, which do not melt, remains unchanged, so that gaseous diffusion in and out of the polymer remains difficult. In this context, the decreased flammability of aged polyurethane foams compared with newer ones may be due to the higher crosslink density caused by storage which makes diffusion even more difficult (54). Indeed, in a fire environment, the high temperatures attained may lead to further extensive crosslinking and hence even less access for oxygen.

The greater solubility of oxygen in the liquid as compared with the solid phase of the polymer probably explains why the involvement of oxygen is greater when poly(methyl methacrylate) is heated slowly, so that it remains molten for a relatively long time, than when heating is more rapid (55).

CONCLUSIONS

For oxygen catalysis of the primary decomposition stage of polymer combustion, not only must oxygen be present in the immediate vicinity of the surface of the burning material but the gas must react chemically with the polymer in such a way as to accelerate its decomposition. Paradoxically, with some polymers, whose breakdown is quite strongly catalysed by oxygen, no oxygen is apparently present to take part in the decomposition stage of polymer combustion. Conversely, there are other polymeric materials, where the presence of oxygen has no effect on decomposition and yet appreciable quantities of the gas are nevertheless present at the condensed phase - gas phase interface of the burning polymer. It is only in systems where oxygen is present at the polymer surface and catalyses the primary decomposition stage that it may be possible to decrease the ease with which the polymer burns by excluding oxygen from the polymer-gas interface.

Exclusion of air or oxygen is of course a universal method of preventing altogether the combustion of any flammable material. However, although in most real fire situations removal of all oxygen is not practicable, it may nevertheless be possible in certain burning polymer systems to reduce or even eliminate completely diffusion of oxygen to the polymer surface and thus help to prevent ignition of the underlying material. Perhaps the most obvious way of achieving this

is to incorporate into the polymer an additive which either decomposes (56) or volatilises (57) to yield a vigorous counterflow of non-flammable gaseous products. Another and perhaps simpler approach is to arrange that the surface of the polymer is or becomes completely covered with a non-flammable protective solid coating which effectively excludes oxygen (58).

On the basis of the simplest cycle for the flaming combustion of organic polymers, according to which the polymer first suffers simple thermal decomposition to yield combustible volatile products, good correlations might be expected between polymer flammability and (a) the thermal instability of the polymer, (b) the extent of formation of combustible gases therefrom and (c) the heat of combustion of these gaseous products (59). In practice such correlations do not exist (60). Since oxygen is often involved in the primary decomposition stage of polymer combustion, it is clearly necessary also to have quantitative information regarding the thermo-oxidative instability of polymeric materials as well as the nature, amounts and heats of combustion of the gaseous products of such initial oxygen-catalysed breakdown. It is thus very important, for a fuller understanding of the factors governing polymer flammability and of the fire risks associated with the use of polymeric materials, that at least some of the excellent detailed studies which have been made of the purely thermal decomposition of organic polymers should now be extended to conditions under which controlled quantities of oxygen are also present.

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