crease in crosslink density is presumably accompanied by increases in internal strain sufficient to increase the crystallization temperature. Another possible effect may arise from the fact that the formation of crosslinks inhibits the extreme flexibility of the PDMS chains and thus may help to promote the formation of nuclei. At high crosslink densities the chain segments are sufficiently constrained to prevent any further crystallization. This occurs above ~70 Mrad radiation dose where the chain length between links is 35 monomer units. The non-reappearance of crystallinity at room temperature following heating to 45°C is believed to be due to relaxation of the strain field.

The free energy of formation of a crystalline cluster, ΔF, is given by[12]:

$$\Delta F = \sum_i n_i \alpha_i \sigma_i + \frac{n}{N_\alpha}(\mu_c - \mu_a) \quad (1)$$

where the sum is over all the faces of the cluster. Referring to faces of type i, n_i is the number of molecules or molecular segments, α_i is the molecular cross-sectional area and σ_i is the interfacial tension. N_α is Avogrado's number, n is the total number of molecules in the cluster and μ_c and μ_a the chemical potentials in the crystalline and the amorphous state, respectively. The crosslinking process and associated strain field is expected to affect both terms in equation (1), the major effect through the parameter μ_a and a lesser effect through σ_i.

Extension of this work to lower temperatures in samples with different degrees of crosslinking will help understanding of the detail of this high temperature crystallization.

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The nature of the initiation process in the photo-oxidation of polypropylene

Two quite distinct initiation processes have been suggested to explain the sensitivity of polyolefins to light[1,2]. Both invoke the presence of adventitious photosensitive impurities formed in the polymer either during manufacture or as a consequence of oxidation during high temperature fabrication processes. The first class of sensitizing impurities encompasses the macromolecular peroxides which readily photolyse to give initiating free radicals[1,3–6]. The second class comprises the in-chain ketones[4,7–10] which are the major derived products formed by thermolysis or photolysis of hydroperoxides[1].

It has previously been shown[3] that polypropylene is markedly sensitized to photo-oxidation by the thermal processing sequence involved in its conversion to fabricated products. The absence of significant carbonyl formation during the early stages of this thermal oxidative treatment suggests that hydroperoxides rather than carbonyl compounds are responsible for the photoactivation process. Similar conclusions have been reached in the study of other polyolefins[5,6]. Other work has indicated[11], however, that conjugated carbonyl compounds formed as a result of thermal oxidation could be involved in the initiation step during the early stages of photo-oxidation and a relationship has been found between fluorescence intensity due to conjugated carbonyl initially present in the polymer and u.v. lifetime of polypropylene samples[12].

There is little doubt that carbonyl compounds may participate in photoinitiation processes in extensively photo-oxidized polyolefins which contain a substantial concentration of ketonic carbonyl[13]. However, the evidence is much less unequivocal during the early stages of photo-oxidation and it has been shown that in low density polyethylene allylic hydroperoxides are the primary photoinitiators[14].

An analogous study of polypropylene has shown a similar relationship between the rate of photo-oxidation and hydroperoxide concentration. *Figure 1* shows that the latter (measured by a chemical method), grows

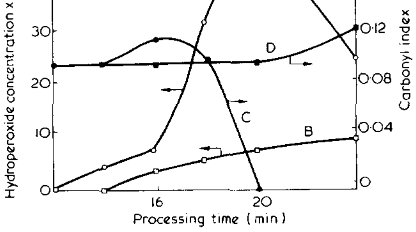

Figure 1 Effect of processing of polypropylene at 180°C in open mixer (○, ●) and closed mixer (□, ■) on peroxide concentration and conjugated carbonyl index (1685 cm^{-1})

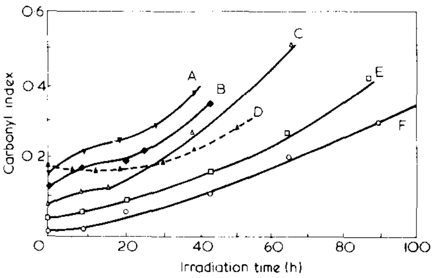

Figure 2 Effect of processing on the rate of carbonyl formation during the photo-oxidation of polypropylene. Processing times (min): A, 20; B, 15; C, 10; D, 15, heated in argon for 50h at 110°C; E, 5; F, compression moulded control

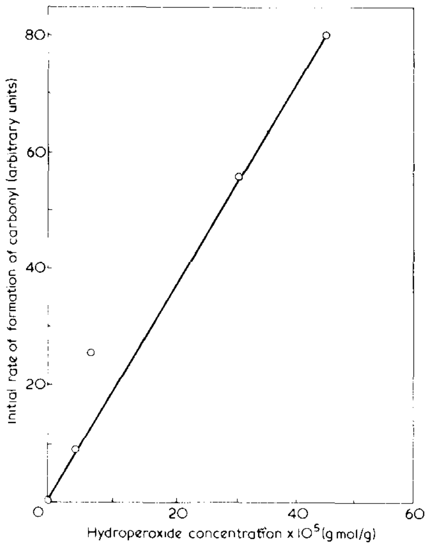

Figure 3 Initial rate of carbonyl formation as a function of peroxide concentration during the u.v. irradiation of polypropylene

rapidly in unstabilized polypropylene subjected to a severe (curve A) and a mild (curve B) processing operation in a simulated commercial mixing procedure (RAPRA Torque Rheometer). Under the latter conditions there is an induction period before hydroperoxide can be detected. Conjugated carbonyl (1685 cm^{-1}) which is initially present in the polymer shows a longer induction period to further growth under both sets of conditions and under severe conditions (curve C) it is destroyed after 20 min. The polypropylene samples for these experiments were compression moulded to films and the rate of photo-oxidation was measured by following the carbonyl index by the method previously described[3] (*Figure 2*). A plot of initial photo-oxidation rate against initial hydroperoxide concentration showed a linear relationship (*Figure 3*). No correlation was found between photo-

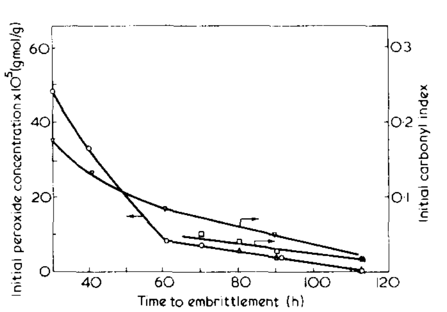

Figure 4 U.v. lifetimes of processed polypropylene films as a function of initial peroxide concentrations and carbonyl (1720 cm^{-1}) indices. ○, Peroxide concentration in samples mixed in an open chamber; △, peroxide concentrations in samples mixed in a closed chamber; ▽, carbonyl (1720 cm^{-1}) concentration in samples mixed in an open chamber; □, carbonyl (1720 cm^{-1}) concentration in samples mixed in a closed chamber

oxidation rate and initial conjugated carbonyl (1685 cm^{-1}) concentration.

A similar relationship was also found between initial hydroperoxide concentration and time to embrittlement under mild processing conditions (*Figure 4*) and, significantly, results obtained by processing in the presence of excess oxygen fell on the same straight line as those obtained in the presence of less oxygen. Embrittlement time also decreased as a function of initial ketonic carbonyl (1720 cm^{-1}) concentration but in this case two different curves were obtained for the two sets of processing conditions and samples with the same carbonyl concentration were found to degrade at very different rates (*Figure 4*).

This is consistent with the view that photo-oxidation rate is only dependent on ketonic carbonyl concentration in so far as carbonyl concentration is related to peroxide (the photoinitiator) concentration. The dominating importance of peroxides as photoinitiators was confirmed by heating in argon a film of polypropylene which contained a substantial amount of hydroperoxide (15 min processed in excess oxygen containing 33.0 g mol/g x 10^5) and which before this treatment photo-oxidized rapidly (*Figure 2*, curve B). This treatment destroyed the hydroperoxide completely with a corresponding increase in the ketonic carbonly concentration. In spite of the very high concentration of ketonic carbonyl the initial photo-oxidation rate of the resulting film was reduced to zero (*Figure 2*, curve D). Furthermore, this treatment introduced an induction period of almost 30 h before photo-oxidation recommenced, compared with about 10 h for a compression moulded control with a negligible initial carbonyl concentration.

The time to embrittlement for the argon heated sample (53 h) was longer than that of the untreated sample (40 h) but was less than that of the control (113 h). This is consistent with the observation that ketonic carbonyl (1720 cm^{-1}) plays some part as a secondary photoinitiator during the later stages of photodegradation[5,13] (presumably by Norrish I and II photolysis[8]). It is clear, however, from this and previous studies that, contrary to previous belief, thermally formed peroxides are the primary initiators in the photo-oxidation of polyolefins. The implications of this for the photostabilization of the polyethylenes has already been discussed[3,5,6,15] and will be considered further in a subsequent publication[16].

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