

## Short Communications

## Reactivity of Polyvinyl Chloride

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It was shown in a previous paper<sup>1</sup> that the thermal instability of polyvinyl chloride, prepared in emulsion systems, is related to the presence of polymeric (hydro)peroxides, formed by the occurrence of an induction period during the initiating step, by random copolymerization with oxygen as comonomer, or by deactivation of trapped polymer radicals at grinding and drying operations. As a consequence inhibition or retardation of color formation and decomposition on heating can be achieved by the formation of a redox system, where the polymer takes part as an active component. The same principle may be used in the preparation of graft copolymers by the interaction of polymeric peroxide radicals and acrylonitrile in an aqueous suspension at 32°C.

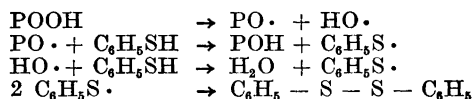
Complementary studies have been carried out from other points of view. A summary is given below. As earlier<sup>1</sup>, the rate of color formation and gelation in pyridine at 100°C is used to indicate the inhibitory action of coreactants or the change of thermal stability, caused by earlier operations in other media. Any discoloration arising from side reactions between solvent and additives is identified in a blank. The concentration of stabilizers in test solutions was kept high (1-10 % by wt of polymer) to make sure that an excess is at hand, compared to the amount of radical intermediates in the degradation cycle.

*New types of inhibitors.* a. *Carbon black.* Addition of *High Abrasion Furnace* or *Easy Processing Channel* blacks to a solution of polyvinyl chloride in pyridine gives a satisfactory inhibition of thermal degradation according to the standard schedule. This statement merely implies the nonappearance of the later steps — strong discoloration and gelation — in the degradation

cycle, as a weak color formation is visually undetectable for obvious reasons. The removal of suspended inhibitor by filtration is infeasible, because the average end to end distance of the polymer molecules far exceeds the diameter of a carbon particle.

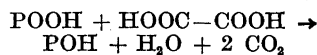
The inhibitory properties of carbon black are known from rubber chemistry. It has been recently shown that reinforcing carbon black fillers act as radical acceptors<sup>2</sup>. Analogous effects have also been reported on milling of polyethylene<sup>3</sup>.

b. *Thiophenol.* This compound gives a complete protection against thermal decomposition in pyridine. A prolonged heating beyond the standard schedule (more than 330 min) gives no other visible change but a light yellow color formation. This is expected from the type reactions of an aromatic modifier and a polymeric hydroperoxide (= POOH):



Arylmercaptans are known to react with alkenes<sup>4</sup>. When peroxides are present, addition occurs contrary to the Markownikoff rule. As technical grades of polyvinyl chloride always show a low, significant degree of unsaturation, this side reaction cannot be ignored. No distinction, however, between the separate contributions is made here, as they necessarily work in the same direction of improved stability. Moreover the quantitative relations would be obscured by a conceivable combination reaction between PO· and RS· radicals.

c. *Oxalic acid.* Oxidation of oxalic acid by free radicals is a case of hydrogen abstraction, where the transfer agent acquires radical character but loses its activity in a secondary step by thermal decomposition:



The inhibiting action of oxalic acid is comparable to that of thiophenol. An analy-

tical grade of highest purity (oxalic acid dihydrate) was used in order to exclude catalytic effects from metallic impurities, especially ferrous compounds.

*Deactivation of the polymer in an aqueous medium.* Hydroperoxides may decompose by thermal dissociation, by reduction activation and by acid or base catalysis. The influence of neutral, alkaline and acid water on the polymer properties was therefore considered, preferably in the vicinity of 100°C, because such treatments are believed to occur as routine methods of purification of technically produced material. An improvement of heat stability was observed in all three cases (pH range 1–12), but the most acid medium was distinctly superior, yet insufficient to impart a complete stability to the polymer when heated in pyridine. This statement is valid for aqueous media, containing hydrochloric, sulfuric or phosphoric acid. The necessary time of reaction seems to be short. The main improvement of heat stability is obtained within 15 min, followed by a moderate change of purity and whiteness of the sample when heating is continued for arbitrary periods.

Analogous effects are obtained by adding cobaltous chloride to the water. This reduction activator operates at a satisfactory rate in a neutral medium at a moderate temperature (35°C). Its action is enhanced by the presence of sulphur dioxide. Samples of polyvinyl chloride, soaked in this way for 8 h, or more, are stable in pyridine according to the actual testing schedule.

A variety of coreactants might be mentioned here, working in the same manner. *Vinyl acetate* is active in the presence of nonionic detergents, allowing solubilization of monomer in the polymer particles. This is particularly interesting, as no indication of graft copolymerization has been found. On the contrary a strict emulsion homopolymerization of vinyl acetate takes place by use of the activator system polyvinyl chloride-ferrous chloride-sodium pyrosulphite. Separation of the two polymers is preferably carried out by filtration in standard glass equipment. The opposite case-grafting — seems to be restricted to *acrylic* monomers (acrylonitrile, acrylic esters and related derivatives, such as *N,N'*-methylene-bis(acrylamide)).

*Graft copolymerization and interpolymerization in solution.* a. *N*-vinyl-2-pyrrolidone is a solvent for polyvinyl chloride at elevated temperature. When such a solution is

stored at 100°C for several hours in the absence of air, viscosity is gradually increased. At increasing time of reaction the water soluble fraction of the system gradually disappears, even when the weight ratio polymer/solvent is low. Practical working conditions are found in the concentration range of 2–5 %.

As no reduction activator is present, an attempt of interpretation is obscured by a number of conceivable overlapping cases. A thermally dissociating polymeric hydroperoxide would be able to initiate a graft copolymerization as well as a homopolymerization of the comonomer. The latter reaction might even be superposed by a pure thermal initiation of the monomer, resulting in an appreciable formation of water soluble homopolymer. No experimental evidence for the existence of such a fraction has been found at high extents of reaction. It is probable that growing macromolecules of this kind are deactivated by combination reaction with radical species of hydrophobic origin. The ultimate composition would then be undistinguishable from a graft copolymer, formed directly by a chain reaction between the primary components.

b. *Polyvinyl chloride-polyvinyl alcohol* interpolymers. Accumulated experience makes probable that a second vinyl polymer, added to a fresh solution of polyvinyl chloride in pyridine, would give a block copolymer on heating, provided the added compound is accessible to reactivation by hydrogen abstraction. Polyvinyl alcohol of low acetyl content was selected for this purpose. An equimolar mixture of the two components was heated at 100°C in pyridine, until turbidity had decreased to a low, constant value. At this interchange level the polyvinyl alcohol is no more extractable with water. The formation of an interpolymers is expected from previous studies<sup>5</sup> on reactivation of polyvinyl alcohol by free radicals.

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