

Stabilization of Poly(vinyl chloride) by Elemental Sulfur

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ABSTRACT: The process of stabilization of a poly(vinylchloride) elemental sulfur in thermal and thermooxidative destruction conditions is investigated. The high stabilizing efficiency of elemental sulfur is revealed at the destruction of plasticized poly(vinylchloride) compared with the efficiency

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Key words: poly(vinyl chloride); antioxidant; stabilization

INTRODUCTION

Various compounds of sulfur have found wide application in the chemical industry as initial components at the synthesis of new products or as chemical additions, in particular, to increase thermal and thermooxidative stability of poly(vinyl chloride) (PVC). Some compounds of sulfur as dialkylsulphides and sulfur-included derivants of dialkyl tin are used as thermal and thermooxidative stabilizers.^{1,2} In the practice of processing polymers, elemental sulfur is used only as the curing agent.³ However, the ability of element sulfur to inhibit thermooxidative destruction of polyethylene has been shown in the literature.⁴ Practical use of sulfur for the stabilization of polymers is attractive because of its low cost and is the basis of this investigation of the influence of elemental sulfur on process of thermal and thermooxidative dehydrochloration of hard and plasticized PVC.

EXPERIMENTAL

Thermal and thermooxidative dehydrochloration of hard and plasticized PVC was carried out at 175°C in a bubbling-type reactor in a current of nitrogen or oxygen (3.3 L/h). The rate of dehydrochloration was determined as described in Minsker et al.⁵ Titration of hydroperoxide was carried out according to Antonovsky and Buzlanova.⁶

RESULTS AND DISCUSSION

By thermooxidative destruction of PVC in the presence of sulfur along with the process of dehydrochloration of the polymer, the formation of sulfur dioxide is possible, which can influence the results of acid–base titration and therefore the rate of dehydrochloration of the polymer. However, in a model experiment on oxidation of individual sulfur the qualitative test on discoloration of a KMnO_4 solution by oxidates of sulfur at 175°C over at least 60 minutes, yielded a negative result. The oxidates of sulfur (175°C), bubbled through an alkaline solution, did not decolorize the indicator of acid–base titration (when a mixture of bromkrezol green and methyl red). The products of thermooxidative destruction of sulfur in the chosen conditions (175°C) also did not change the color of Congo red indicator paper. On the basis of obtained results it was possible to ascertain that, under these conditions, sulfur dioxide was not formed and the obtained results of the rate of dehydrochloration of PVC are correct.

The introduction of sulfur to PVC led to an insignificant decrease of the rate of thermal dehydrochloration of the polymer (Fig. 1), thus the kinetic dependencies of process of elimination HCl are linear. The indicator method GOST 14041-91 shows that under conditions of PVC destruction, sulfur did not accept eliminated HCl.

By thermooxidative destruction of PVC the stabilizing efficiency of sulfur noticeably grows and, in particular, surpasses efficiency of the known antioxidant diphenylolpropan (DFP) (Fig. 1), producing a linear kinetic curve.

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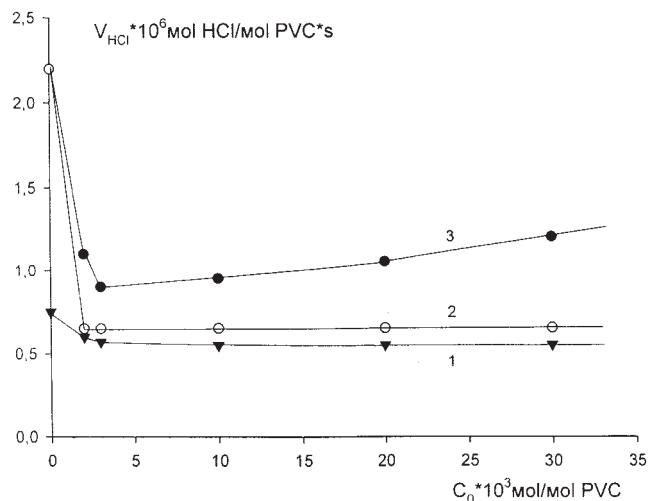


Figure 1 Dependence of the rate of thermal (1) and thermooxidative dehydrochlorination of PVC from the contents of element sulfur (1,2) and diphenylpropan (3).

The maximal decrease in the rate of thermooxidative dehydrochlorination of PVC is observed at values of 2 mmol/mol sulfur in PVC and does not change with further increase of sulfur in polymer. The decrease in rate of thermooxidative dehydrochlorination of PVC at the presence of sulfur is observed practically up to rates appropriate to rates of destruction PVC, which is characteristic for stabilizers-antioxidants.

The problem of stabilizing plasticized PVC by production of soft products is appreciably deals with decreasing the oxidizing destruction of plastifier in polymeric compositions by applying antioxidants.

Introduction of elemental sulfur in PVC, plasticized by ester plastifiers [dioctylphthalate (DOF), dioctylsebacinate (DOS)] leads to a decrease in the rate of thermooxidative dehydrochlorination of the polymer (Fig. 2). The maximal decrease of the rate of dehydrochlorination of the plasticized polymer, as well as in the case of destruction of unplasticized PVC, is observed at values of 2 mmol/mol sulfur PVC. The stabilizing efficiency of sulfur in PVC plasticates is practically identical with the efficiency of diphenylpropan. It is necessary to note that the stabilizing effect is achieved by the introduction of sulfur in polymeric compositions within the limits of 0.02–0.05 wt parts/100 wt parts PVC, which is less than the phenolic stabilizers-antioxidants for PVC usually used. Thus, the origin of sulfur (gas lumps or natural lumps) is not reflected in its stabilizing efficiency (Figure 2).

The decrease of the rate of thermooxidative destruction of PVC in the presence of elemental sulfur is observed up to much lower meanings appropriate to the rate of thermooxidative destruction of unplasticized PVC. Apparently, the elemental sulfur effec-

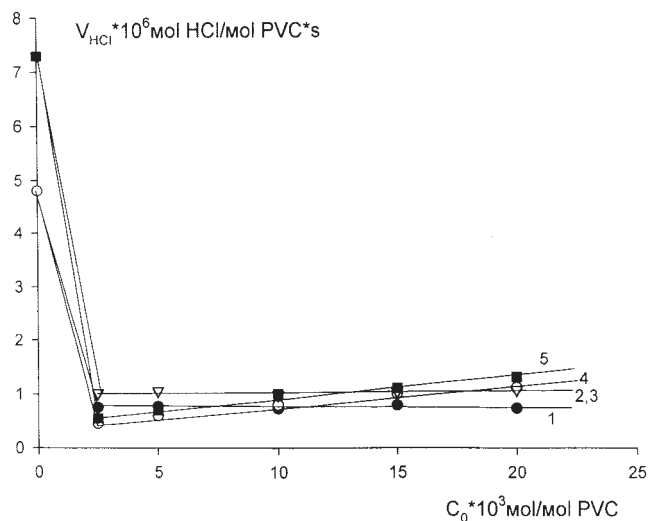


Figure 2 Dependence of the rate of thermooxidative dehydrochlorination of PVC, plasticized (40 wt parts/100 wt part of PVC) by DOF (1,4) and DOS (2,3,5) from the contents of gas lumps sulfur (1,2), natural lumps sulfur (3), and diphenylpropan (4,5).

tively protects the plastifier from oxidation (stabilizer-antioxidant), which in its turn stabilization increases the heat stability of PVC by stabilization (known as "echo - stabilization" of PVC.⁷

CONCLUSIONS

With the help of iodometric titration of hydroperoxide at spontaneous oxidation of the ester-plastifiers, dioctylphthalate and dioctylsebacinate, in the presence of

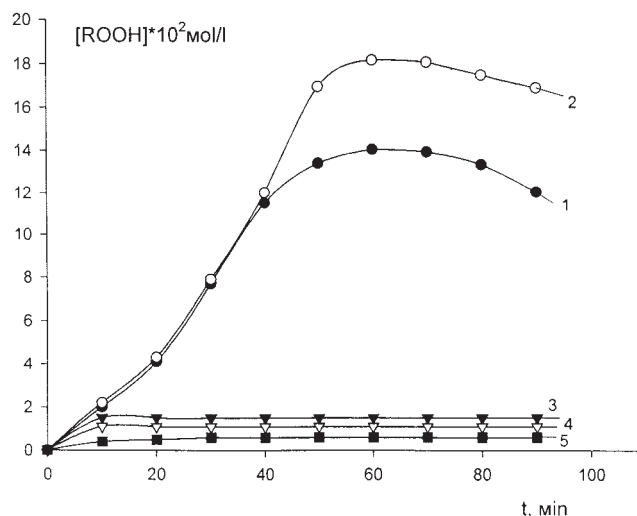


Figure 3 Kinetic curves of accumulation of hydroperoxides by oxidation of individual plastifiers (DOF-1, DOS-2) and plastifiers at the presence of gas lumps sulfur (DOF-3, DOS-4) and diphenylpropan (DOF-5) (oxygen, 3.3 L/h, 165°C).

elemental sulfur it is shown that the introduction of elemental sulfur of various origins (gas lumps or natural lumps) to esters in a wide interval of concentrations inhibits the process of accumulation of hydroperoxide products (Fig. 3). The elemental sulfur is comparable with phenolic antioxidant diphenylolpropan in the efficiency of inhibition of the oxidation process of ester-plastifiers.

Thus, elemental sulfur has a high inhibiting action in the process of thermooxidative dehydrochloration for hard and plasticized PVC and is of interest practical use in the production of polymeric materials in view of its availability and low cost.

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