Stabilization of Polymers of Vinylchloride with Sulfur

Rinat M. Akhmetkhanov,[1] Natalya N. Kabalnova,[2] Ruslan R. Akhmetkhanov,[1]
Sergey V. Kolesov,[1] Gennadi E. Zaikov[3]

[1]The Bashkir State University, Ufa 450074, Russia
[2]Institute of Organic Chemistry URC RAS, Ufa 450054, Russia
[3]Institute of Biophysical Chemistry RAS, Moscow 119991, Russia

Received 9 August 2004; accepted 29 April 2005
DOI 10.1002/app.22835

ABSTRACT: The high stabilizing efficiency of element sulfur was revealed by the thermooxidative destruction of polymers of vinylchloride (VC). It was shown that the stabilizing efficiency of sulfur in compositions of polymers of VC is comparable with the efficiency of phenolic antioxidants. Element sulfur inhibits process of autooxidation of esters-plastifiers of polymers of VC, apparently, because of destruction of formed hydroperoxides. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4538–4542, 2006

Key words: polymers of vinylchloride; sulfur; stabilization

INTRODUCTION

To increase thermal and thermooxidative stabilities of polymers of VC, some disulfides and sulfur derivants of dialkyl tin are used as heat stabilizers and antioxidants.[1,2] Element sulfur has not found applications till now, as a chemical-additive to polymers, except for as curing agent for rubbers[3], although in the scientific literature there is an information about the ability of element sulfur to inhibit thermooxidative destruction of polyethylene because of destruction of hydrooxides.[4] That is why it was expedient to study the influence of element sulfur on the process of thermal and thermooxidative dehydrochlorinations of hard and plasticized poly(vinylchloride) and some copolymers of VC.

EXPERIMENTAL

Thermal and thermooxidative dehydrochlorinations of the hard and plasticized polymers of VC were carried out at 175°C in a bubbling-type reactor in a current of nitrogen or air (3.3 L/h). The rate of dehydrochlorination and deacetylations were determined as described by Minisker et al.[5] Destruction of copolymer VC with 11.1 mol % vinyl acetate (VCVA-11.1) was estimated on total speed of elimination of HCl and CH_3COOH. Definition of melt flow rate (MFI) of compositions was carried out on the IIRT device using a standard technique. Titration of hydroperoxides was carried out according to Antonovsky et al.[6] The polymers of VC (PVC C7059M, copolymer VCVA-11.1, and copolymer of VC with 28.3 mol % of methyl acrylate VCMA-28.3) were purified by washing with ethanol in a Soxhlet apparatus. Ester plastifiers dioctyl phthalate (DOP) and dioctyl sebacate (DOS) were elutriated through a column filled with Al_2O_3.

In conditions of the thermooxidative destruction of polymers of VC in the presence of sulfur along with the process of dehydrochlorination or deacetylation of polymer, the formation of sulfur dioxide is possible, which can influence the results of acid–base titration and thereby increase the rate of destruction of polymers. However, in model experiment, by oxidation of individual sulfur in an atmosphere of air, the qualitative test on discoloration of a solution of $KMnO_4$, by oxidates of sulfur at 175°C for at least 80 min has yielded negative result. The oxidates of sulfur (175°C), by barbotage through distilled water, did not decolorize the indicator of acid–base titration (mix of bromocresol green and methyl red). Also, the products of the thermooxidative decomposition of sulfur (175°C) do not decolorize the congo-red indicator paper. On the basis of obtained results, it is possible to ascertain that under experimental conditions, the sulfur dioxide has not formed, and the obtained results on the rates of dehydrochlorination of polymers of VC are correct.

RESULTS AND DISCUSSION

The introduction of the sulfur in PVC leads to an insignificant decrease in the rate of thermal dehydrochlorination of polymer (Fig. 1); thus, the kinetic dependences of process of elimination of HCl have a

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Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

Journal of Applied Polymer Science, Vol. 101, 4538–4542 (2006)

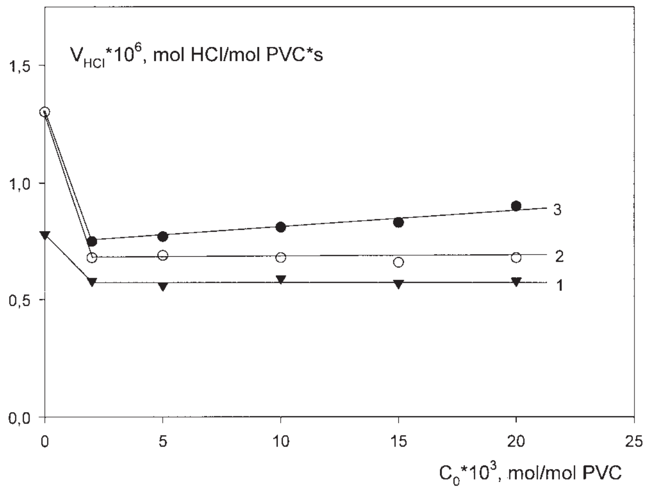

Figure 1 Dependence of the rate of thermal (1) and thermooxidative (2,3) dehydrochlorination of PVC from the contents of elemental sulfur (1,2) and DPP (3).

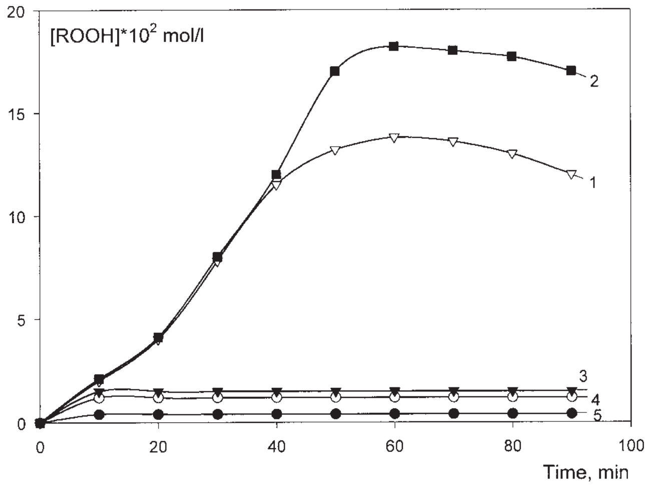

Figure 3 The kinetic curves of accumulation of hydroperoxides by the oxidation of individual plastifiers (DOP-1, DOS-2), and plastifiers in the presence of elemental sulfur (3.1 mmol/L, DOP-3, DOS-4) and 4-methyl-2,6-ditertbutylphenol (1.4 mmol/L, DOP-5; oxygen 3.3 L/h, 165°C).

linear kind. By an indicator method with congo-red, it is shown that sulfur, under conditions of destruction of PVC, has no accept action in relation to allocated HCl.

By thermooxidative destruction of PVC, the stabilizing efficiency of sulfur grows, and in particular, surpasses the efficiency of known antioxidant—diphenylolpropane (DPP) (Fig. 1). The kind of the kinetic curves of the thermooxidative dehydrochlorination process of PVC in the presence of sulfur is linear.

The maximal decrease in the rate of dehydrochlorination of PVC is observed at the contents of sulfur of the order 2 mmol/mol PVC and does not change with the further increase of the contents of sulfur in polymer. The influence of the rate of thermooxidative dehydrochlorination of PVC from the contents of sulfur after achievement of minimum rate of V_{HCl} when compared with that of phenolic antioxidants, for which this dependence is extreme, has a linear kind. The decrease of the rate of thermooxidative dehydrochlorination of PVC in the presence of sulfur occurs practically up to meanings appropriate to the rate of thermal decomposition of PVC, that is characteristic for stabilizers and antioxidants.

The problem of stabilization of the plasticized polymers of VC by production of soft and semifixed prod-

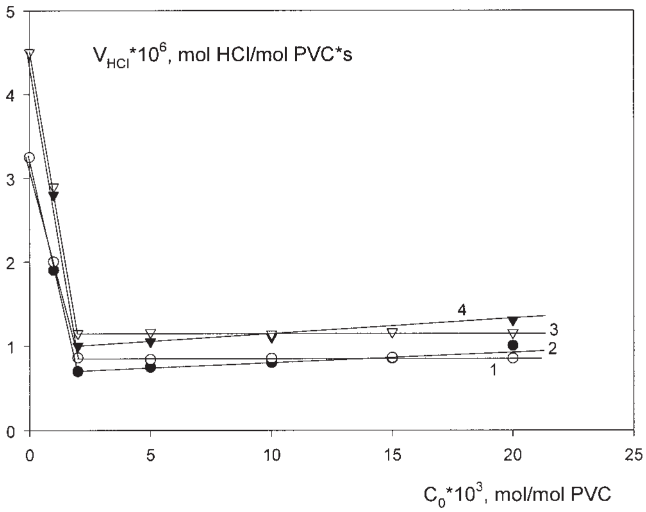

Figure 2 Dependence of the rate of thermooxidative dehydrochlorination of PVC plasticized (40 weights parts/100 weights parts PVC) by DOP (1,2) and DOS (3,4) from the contents of elemental sulfur (1,3) and DPP (2,4).

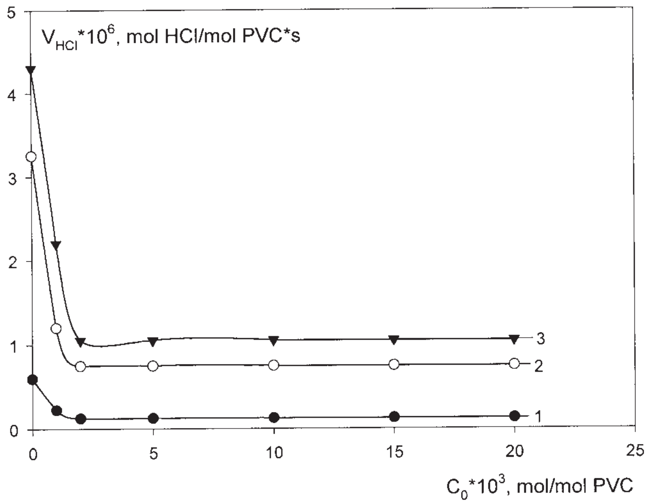

Figure 4 Dependence of the rate of thermooxidative dehydrochlorination of PVC plasticized 40 weights parts/100 weights parts PVC by DOP from the contents of elemental sulfur at different temperatures (1–150°C, 2–175°C, 3–190°C).

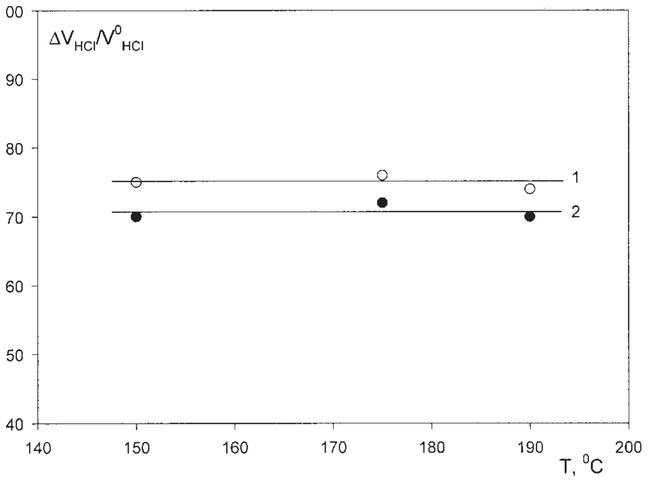

Figure 5 Dependence of limiting stabilizing efficiency of element sulfur on an index $\Delta V_{HCl}/V^0_{HCl}$ from temperature by thermooxidative destruction (air, 3.3 L/h) PVC plasticized by DOP (1) and DOS (2) (40 weights parts/100 weights parts PVC).

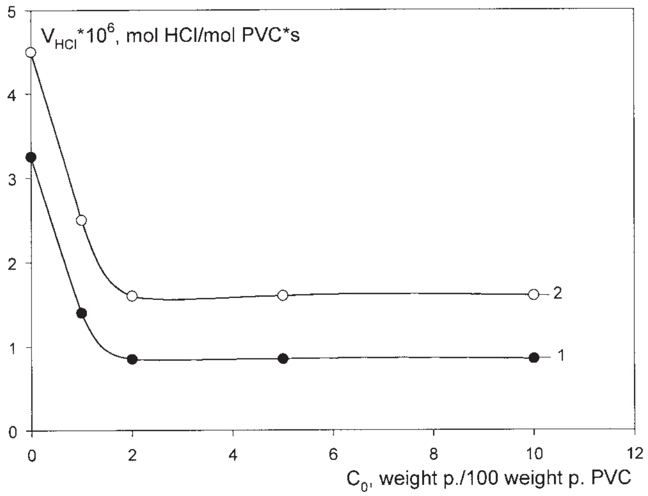

Figure 6 Dependence of the rate of thermooxidative dehydrochloration of PVC, plasticized 40 weights parts/100 weights parts PVC by DOP (1) and DOS (2) from the contents of polymeric sulfur "Crystex OT-33."

ucts appreciably connected to prevention of oxidizing destruction of plastifier in polymeric compositions, by application of antioxidants.

The introduction of element sulfur in PVC plasticized by ester-plastifiers leads to the fall off of the rate of thermooxidative dehydrochlorination of PVC (Fig. 2). The maximal decrease in the rate of dehydrochlorination of the plasticized polymer, as well as in case of destruction, unplasticized PVC is observed by the contents of sulfur $\geq$2 mmol/mol PVC. The stabilizing efficiency of sulfur in PVC-plasticates is practically identical with the efficiency of DPP. The maximal stabilizing effect is reached by the introduction of 0.02 weights parts of sulfur/100 weights parts of PVC, which is less than the percentage by weight of known organic stabilizers and antioxidants for PVC in polymeric compositions. Thus, the origin of sulfur (gas or natural) is not reflected on its stabilizing efficiency.

The decrease in rate of thermooxidative destruction of PVC by the presence of element sulfur is observed up to much lower meanings appropriate to the rate of thermooxidative destruction of unplasticized PVC. Apparently, the element sulfur effectively protects plastifier from oxidation (stabilizer and antioxidant), and this improves the thermofeatures of PVC (known effect "an echo - stabilization" PVC).[7]

The introduction of element sulfur in esters by their autooxidation inhibits the process of accumulation of hydropyroxide products. The efficiency of element sulfur to inhibit the process of oxidation of ester-plastifiers is comparable with those of the phenolic antioxidant 2,6-ditert-butyl-methylphenol (Fig. 3).

It is known that element sulfur, at various temperatures, passes from one modification to another.[8]

TABLE I
The Time of Heat Stability of PVC Compositions

Composition (weight parts/100 weight parts of PVC) index	1	2	3	4	5	6	7	8	9	10	11	12
PVC	100	100	100	100	100	100	100	100	100	100	100	100
DOP	40	40	40	40	40	40	40	40	40	40	40	40
Sulfur	—	0.02	—	—	0.02	—	—	0.02	—	0.02	—	0.02
DPP	—	—	0.1	—	—	0.1	—	—	—	—	—	—
Tribasic lead sulfate	2	2	2	—	—	—	—	—	—	—	—	—
$CaSt_2$	—	—	—	2	2	2	—	—	—	—	—	—
$CdSt_2$	—	—	—	—	—	—	2	2	—	—	—	—
$PbSt_2$	—	—	—	—	—	—	—	—	2	2	—	—
$BaSt_2$	—	—	—	—	—	—	—	—	—	—	2	2
Time at 175°C (min)	106	257	252	22	50	54	32	93	43	150	27	85

TABLE II
Dependence of Melt Flow Rate of PVC Plasticates from the Contents of Sulfur

Composition (weight parts/100 weight parts of PVC) index	1	2	3	4	5	6	7	8	9	10
PVC	100	100	100	100	100	100	100	100	100	100
DOP	40	40	40	40	40	—	—	—	—	—
DOS	—	—	—	—	—	40	40	40	40	40
Tribasic lead sulfate	2	2	2	2	2	2	2	2	2	2
Sulfur	—	0.02	0.05	0.1	1.0	—	0.02	0.05	0.1	1.0
MFI at 190 °C (g/10 min)	2.34	1.78	1.46	2.03	3.70	2.80	2.60	2.45	2.75	4.10

Most typical transferring is observed at a temperature range of 159–160°C, when soluble carbon bisulfide S_λ, representing cyclooctasulfur S_8 turns to insoluble (polymeric) S_μ, consisting high molecular weight circuits and rings. At the temperature interval of 159–188°C, an abnormal increase of melt viscosity of sulfur on fourth order reaching 93.2 Pa s is observed,[9] which is explained by tearing up 8-parts cycles of sulfur with formation of polymeric circuits. That is why it was interesting to study the influence of sulfur on the process of dehydrochlorination of plasticized PVC at various temperatures, when transferring from one modification of sulfur to another.

The process of thermooxidative dehydrochlorination of PVC, plasticized by DOP and DOS in presence of element sulfur was carried out at 150, 175, and 190°C. At 150°C, S_λ basically is a 8-parts of rings, at 175°C, the sulfur is intensively polymerized and mainly is in polymeric modification, and at 190°C, it is completely in polymeric modification.

From obtained data (Fig. 4), it was found that independent of the temperature, at which the destruction was carried out and independent of the modification of sulfur (elemental or polymeric), the sulfur effectively inhibits the process of thermooxidative destruction of PVC-plasticates. Stabilizing efficiency of sulfur on an index $\Delta V_{HCl}/V^0_{HCl}$ practically does not depend on temperature of destruction and reaches 75% and 69% for PVC plasticized by DOP and DOS, respectively (Fig. 5).

In Figure 6 are shown the results of thermooxidative dehydrochlorination of PVC-plasticates in the presence of polymeric sulfur of industrial production "Crystex OT-33," used during vulcanization of polydienes. The polymeric sulfur as well as elemental sulfur effectively inhibits the process of thermooxidative dehydrochlorination of PVC-plasticates. The kinetic laws of process of thermooxidative dehydrochlorination of plasticized PVC in presence of polymeric sulfur do not differ from the laws of inhibiting action of element sulfur.

In practical, with the use of small amounts of element sulfur in PVC-compositions (0.02 weights parts/100 weights parts of PVC), there is a problem of its exact dosing and uniform distribution in a polymeric composition. It is obviously possible to expedient introduction of sulfur in the plasticized PVC-compositions through its predissolution in plastifier.

The solubility limit of sulfur in DOP and DOS at 20°C was 0.41% and 0.13% mass, respectively. For comparison, the solubility of sulfur in benzol and hexane at 20°C was 1.77% and 0.25% of weights, respectively.[9] The limiting concentration of solutions of sulfur in esters, at some times, exceeds maximum effective concentration of sulfur in PVC-plasticates, which allows to dissolve the designed amounts of sulfur in plastifier, and then to mix a ready solution of sulfur in plastifier with a PVC.

Experiments have shown identical inhibiting efficiency for sulfur injected into a composition as a solution in plastifier and that at separate introduction into a composition.

The high inhibiting efficiency of element sulfur and polymeric sulfur of the mark "Crystex OT-33" in the

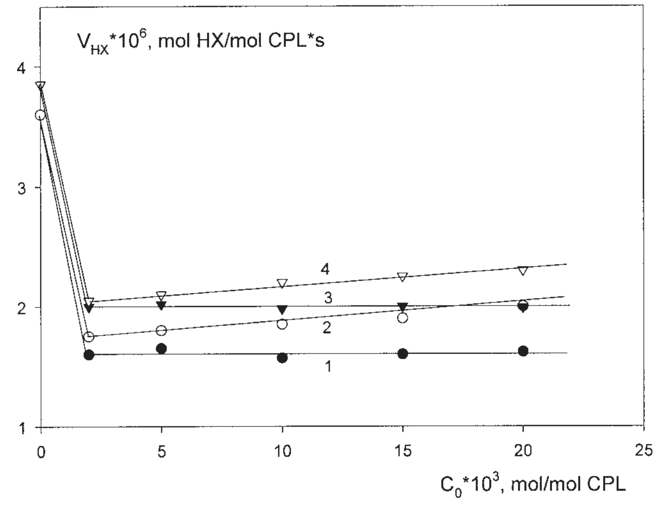

Figure 7 Dependence of the rate of thermooxidative dehydrochlorination of VCMA-28.3 (1,2) and dehydrochlorination + deacetylation VCVA-11.1 (3,4) from the contents of element sulfur (1,3) and DPP (2,4).

TABLE III
Meanings of the Time of Heat Stability of Compositions on the basis of Copolymers VC

Composition (weight parts/100 weight parts of CPL) index	1	2	3	4	5	6	7	8	9	10	11	12	13
VCVA-11.1	100	100	100	100	100	100	100	—	—	—	—	—	—
VCMA-28.3	—	—	—	—	—	—	—	100	100	100	100	100	100
DOP	40	40	40	40	40	40	40	40	40	40	40	40	40
Tribasic lead sulfate	—	—	—	—	2	2	2	—	—	—	2	2	2
$CaSt_2$	2	2	2	2	—	—	—	2	2	2	—	—	—
Sulfur	—	0.02	0.05	—	—	0.02	—	—	0.02	—	—	0.02	—
DPP	—	—	—	0.1	—	—	0.1	—	—	0.1	—	—	0.1
Time at 175°C (min)	10	15	16	18	19	35	31	12	18	22	16	21	24

process of thermooxidative dehydrochlorination of PVC-plasticates is confirmed in compositions containing various metal contained heat stabilizers, on an index "time of heat stability" (Table I). Introduction of sulfur in amount upto 0.02–0.05 weight parts/100 weight parts of PVC in the stabilized PVC-plasticates increases the time of heat stability of PVC-compositions upto 2.27–3.48 times, depending on the nature of a metal contained heat stabilizer. On the basis of the efficiency, sulfur does not concede to the efficiency of a phenolic antioxidant DPP.

By using of element sulfur as the stabilizer, an increase of the thermooxidative stability of compositions and a change in the melt flow index (MFI) of PVC-compositions (Table II) are observed. Introduction of sulfur in amounts up to 0.05 weights parts/100 weights parts of PVC leads to the reduction of MFI compositions. If the contents of sulfur amounts more than 0.05 weights parts/100 weights parts of PVC, an increase in the MFI compositions is observed. The reduction of MFI occurs because of the presence of sulfur, which apparently leads to an increase in the molecular weight of polymer because of interaction of sulfur with internal olefinic linkages in PVC. As the concentration of internal olefinic linkages in PVC is small (10^{-4} mol/mol PVC[10]), complete crosslink of polymer with loss of fluidity does not occur. At large contents of sulfur, its surplus plays the role of a lubricant, thus increasing meaning MFI.

The introduction of elemental sulfur in copolymers of VC, 11.1 mol % of vinyl acetate (VCVA-11.1) and 28.3 mol % of methyl acrylate (VCMA-28.3), leads to the decrease in the rate of their thermooxidative destruction (Fig. 7).

In case of stabilization of thermooxidative destruction of homopolymer-PVC with the element sulfur, maximal decrease of the rate of dehydrochlorination and deacetylation of copolymers VC is observed by concentration of sulfur of about 2 mmol/mol of copolymer. The inhibiting efficiency of sulfur in copolymers VC is also comparable with the efficiency of antioxidant DPP (Fig. 7).

The introduction of element sulfur in plasticates on the basis of copolymers VC containing metal included heat stabilizers, improves their thermostability on an index "time of heat stability" (Table III).

However, it is necessary to note that the efficiency of sulfur by inhibition of thermooxidative destruction of copolymers VCVA-11.1 and VCMA-28.3 is much lower in comparison with its efficiency of inhibition of destruction of a PVC as on an index "speed of destruction" and on an index "time of heat stability." This fact deals with the known law of reduction of effect of inhibition of stabilizers in copolymers VC in comparison with a PVC.[11]

Thus, the element sulfur is the effective stabilizer - antioxidant for the thermooxidative destruction process of hard and plasticized polymers VC, and it is interesting for practical use during the production of polymeric materials.

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