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EFFECT OF POLYMERS WITH A SYSTEM OF CONJUGATED BONDS ON THE THERMAL AND LIGHT STABILITY OF POLYVINYL CHLORIDE

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At present it may be regarded as established that the thermal and photooxidative destruction of halogen-containing carbocyclic polymers proceeds by a radical-chain mechanism (^{1}). Apparently, this process is initiated by radical products of macromolecular destruction, in particular by alkoxyl and hydroxyl radicals arising in the decomposition of polymeric hydroperoxides (^{2}, ^{3}). Chain propagation occurs as a result of the elimination of hydrogen and halogen atoms, which ultimately leads to dehydrochlorination, accumulation of double bonds, and breakdown of the macromolecules (^{1}–^{3}). Although at present there is still no unequivocal proof of the mechanism of chain initiation, propagation, and termination in the thermal and photooxidative destruction of polyvinyl chloride (PVC), it may nevertheless be asserted that the most effective inhibition of this process is possible only by using substances capable of accepting radicals. Naturally, radical acceptors can be used as effective stabilizers of the polymer only if, on heating or irradiation in the presence of air, they do not form hydroperoxides capable of initiating the destruction process.

In this connection, the study of the effect on the thermooxidative destruction of polyvinyl chloride of certain types of recently synthesized polyphenylvinylenes (PPV) (^{4}), as well as of products containing conjugated bonds and obtained by the destruction of certain high polymers, in particular polyvinyl chloride, is of great theoretical and practical interest.

The low activity of such quasi-radicals accounts for their ability to react only at comparatively high temperatures ($ 150–200°)(${}^{\{4\}).A study of the electron paramagnetic resonance spectra of PPV and dehydro}$ paramagnetic particles per 1 g), delocalized along the conjugation chain (^{5}). This circumstance permits the assumption that they may be highly effective inhibitors of the thermooxidative destruction processes of halogen-containing polymers. The experimental data given in Table 1 confirm the correctness of this assumption.

PPV obtained by thermal polymerization of phenylacetylene at 150° (I) is a very effective inhibitor of the thermooxidative destruction of PVC; a copolymer of phenylacetylene with *p*-diethynylbenzene (II), obtained at 300° and infusible and insoluble, as well as the product of exhaustive dehydrochlorination of PVC under vacuum at 300° (III), possess lower inhibiting ability.

Figure 1 gives kinetic curves for the elimination of hydrogen chloride from PVC at 175° in the presence of various stabilizers; these

curves show the high effectiveness of the inhibiting action of product I.

It should be noted that when large amounts of insoluble products are used, their stabilizing action weakens. Apparently, when insoluble and infusible polymers with conjugated bonds are used, contact between the radicals formed during the degradation of polyvinyl chloride and the active centers of the polymer stabilizers is hindered.

Table 1

Stabilizer: substance	Stabilizer: number of paramagnetic particles in 1 g	Amount of stabilizer, % relative to PVC	Temperature of the onset of PVC dehydrochlorination, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	V, $\frac{\text{mg HCl}}{\text{1 g PVC}}$	$\frac{V}{V_0} \cdot 100$, %
PVC without stabilizer	–	–	158	7	3,91	100
Polyphenylvinylene (I)	$2{,}41 \cdot 10^{17}$	0,1	–	8,5	2,16	55
Polyphenylvinylene (I)	$2{,}41 \cdot 10^{17}$	1,0	158	7	1,34	34
Polyphenylvinylene (I)	$2{,}41 \cdot 10^{17}$	5,0	–	7	1,30	33
Polyphenylvinylene (I)	$2{,}41 \cdot 10^{17}$	10,0	–	5	1,43	37

Stabilizer: substance	Stabilizer: number of paramagnetic particles in 1 g	Amount of stabilizer, % relative to PVC	Temperature of the onset of PVC dehydrochlorination, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	V, $\frac{\text{mg HCl}}{\text{1 g PVC}}$	$\frac{V}{V_0} \cdot 100$, %
Copolymer of phenylacetylene and paradiethynylbenzene (II)	$4,35 \cdot 10^{18}$	0,1	–	6	2,54	65
Copolymer of phenylacetylene and paradiethynylbenzene (II)	$4,35 \cdot 10^{18}$	1,0	153	7	2,53	65
Copolymer of phenylacetylene and paradiethynylbenzene (II)	$4,35 \cdot 10^{18}$	10,0	–	5	3,30	84

Stabilizer: substance	Stabilizer: number of paramagnetic particles in 1 g	Amount of stabilizer, % relative to PVC	Temperature of the onset of PVC dehydrochlorination, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	V, $\frac{\text{mg HCl}}{\text{1 g PVC}}$	$\frac{V}{V_0} \cdot 100$, %
PVC dehydrochlorination product (III)	$2,10 \cdot 10^{17}$	1,0	160	9	3,07	78
PVC dehydrochlorination product (III)	$2,10 \cdot 10^{17}$	5,0	–	8	2,44	65
PVC dehydrochlorination product (III)	$2,10 \cdot 10^{17}$	10,0	–	10	3,13	80

Note. The mean integral rates of PVC dehydrochlorination in the presence (V) and in the absence (V_0) of a stabilizer were determined at 175° in an air stream with an experiment duration of 180 min. The ratio $\frac{V}{V_0} \cdot 100$ characterizes the change in the rate of dehydrochlorination due to the introduction of the stabilizer.

Table 2

Stabilizer	Amount of stabilizer, % relative to PVC	Temperature at which the rate of dehydrochlorination was determined, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	$V, \frac{\text{mg HCl}}{\text{1 g PVC}}$	$\frac{V}{V_0} \cdot 100,\ \%$
PVC without stabilizer	–	175	7	3,91	100
PVC without stabilizer	–	185	6	10,0	100
PVC without stabilizer	–	195	5	20,7	100
Polyphenylvinylene (I)	1,0	175	7	1,34	34
Polyphenylvinylene (I)	1,0	185	5	6,30	63
Polyphenylvinylene (I)	5,0	185	6	6,20	62
Polyphenylvinylene (I)	10,0	185	7	6,17	62
Polyphenylvinylene (I)	1,0	195	3	19,0	92
Polyphenylvinylene (I)	5,0	195	3	20,0	96
Polyphenylvinylene (I)	10,0	195	3	20,8	100
PVC dehydrochlorination product (III)	1,0	175	9	3,07	78

Stabilizer	Amount of stabilizer, % relative to PVC	Temperature at which the rate of dehydrochlorination was determined, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	$V, \frac{\text{mg HCl}}{\text{1 g PVC}}$	$\frac{V}{V_0} \cdot 100,\ \%$
PVC dehydrochlorination product (III)	1,0	185	8	7,8	78
PVC dehydrochlorination product (III)	5,0	185	6	6,4	64
PVC dehydrochlorination product (III)	10,0	185	7	9,0	90
PVC dehydrochlorination product (III)	1,0	195	6	27,0	130
PVC dehydrochlorination product (III)	5,0	195	5	20,7	100

Fig. 1. Rate of dehydrochlorination of PVC at 175° in an air stream; 1 —without stabilizer, 2 —with 1% lead silicate, 3 —with 1% dibutyltin maleate, 4 —with 1% diphenylolpropane, 5 —with 1% PPV

Figure 1: Fig. 1. Rate of dehydrochlorination of PVC at 175° in an air stream; 1 —without stabilizer, 2 —with 1% lead silicate, 3 —with 1% dibutyltin maleate, 4 —with 1% diphenylolpropane, 5 —with 1% PPV

Stabilizer	Amount of stabilizer, % relative to PVC	Temperature at which the rate of dehydrochlorination was determined, °C	Duration of the induction period before the onset of PVC dehydrochlorination, min	$V, \dfrac{\text{mg HCl}}{\text{1 g PVC}}$	$\dfrac{V}{V_0} \cdot 100,\ \%$
PVC dehydrochlorination product (III)	10,0	195	6	31,2	151

Table 2 presents data characterizing the inhibiting influence of polyvinylenes I and III on the decomposition of PVC at various temperatures.

The data of Table 2 indicate a decrease in the effectiveness of the action of polyvinylenes with increasing temperature. Product I inhibits the thermal decomposition of PVC at 185° and does not accelerate it at 195°. In contrast to I, product III at 195° accelerates the destruction of PVC. This specific action of product III, obtained by dehydrochlorination of PVC, is apparently associated with the formation of active radicals during thermal cracking of the polymer. Such radicals can become trapped in the network of the dehydrochlorinated polymer and interact with oxygen with the formation of peroxide radicals that initiate the destruction of PVC at elevated temperatures.

Fig. 1. Rate of dehydrochlorination of PVC at 175° in an air stream; 1 —without stabilizer, 2 —with 1% lead silicate, 3 —with 1% dibutyltin maleate, 4 —with 1% diphenylolpropane, 5 —with 1% PPV.

Fig. 2. Rate of dehydrochlorination of PVC at 175° in an air stream in the presence of: 1 —PPV before thermal treatment, 2 —PPV after holding for 6 h at 300°, 3 —PPV after holding for 6 h at 400°.

Fig. 2. Rate of dehydrochlorination of PVC at 175° in an air stream in the presence of: 1 –PPV before thermal treatment, 2 –PPV after holding for 6 h at 300°, 3 –PPV after holding for 6 h at 400°

Figure 2: Fig. 2. Rate of dehydrochlorination of PVC at 175° in an air stream in the presence of: 1 –PPV before thermal treatment, 2 –PPV after holding for 6 h at 300°, 3 –PPV after holding for 6 h at 400°

In this connection it was of interest to determine the influence of thermal treatment of PPV (I) on its stabilizing activity. Experimental data show that when PPV is heated to 300 and 400°, an increase in the degree of conjugation is observed, as may be judged from the deepening of the polymer color from yellow to brown and black; at the same time the concentration of unpaired delocalized electrons increases from $2.4 \cdot 10^{17}$ to $4.2 \cdot 10^{18}$ and $3.4 \cdot 10^{19}$ paramagnetic particles per 1 g, respectively (4). Simultaneously, partial dehydrogenation of the polymer is observed, as indicated by a decrease in the hydrogen content from 6.12 to 5.88 and 5.16%, and, apparently, the possibility exists for the formation of radical centers. The data of Fig. 2 confirm the supposition that active radicals capable of initiating PVC destruction may be formed during the thermal treatment of polyphenylvinylene. The initial PPV remains an effective inhibitor within the concentration range from 0.1 to 10% (by weight of PVC); after treatment at 300° it initiates decomposition at concentrations of 8% and higher, while after treatment at 400° the initiation of decomposition begins already at a concentration of 6%.

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Note: Figure translations are in progress. See original paper for figures.