Poly(vinyl chloride) (PVC) has found wide use in various fields. The multipurpose application of PVC is determined by its ability to endure high mechanical stresses, good dielectric characteristics, and corrosion stability. At the same time, PVC features a very high melt viscosity and possesses insufficient stability at temperatures of its processing into products. The hydrogen chloride that evolves during heating of PVC catalyzes the further degradation of the polymer. The softening temperature of PVC is higher than its degradation temperature; therefore, it practically cannot be processed in the individual pure state. The majority of the materials based on PVC are composites; they necessarily include plasticizers, which facilitate the mobility of macromolecules, and stabilizers, which serve as binders of evolving hydrogen chloride and prevent the development of degradation. One of the main problems encountered in the use of these compositions is the high toxicity of stabilizers (lead, cadmium, and barium compounds). Therefore, an increase in the thermal stability of PVC and preservation of its valuable properties is a topical problem of polymer chemistry.

It is expected that the sulfurization of PVC will considerably increase its thermal stability, while preserving its main performance and processing characteristics.

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In this study, we attempted to investigate the reaction of PVC with elemental sulfur and to characterize the products of the reaction.

**EXPERIMENTAL**

We used commercial PVC, which was obtained by emulsion polymerization at OOO Usol’e Khimprom. This PVC is well soluble in DMF, DMSO, cyclohexanone (CH), and 1,2,4-trichlorobenzene (TCB) and has the following characteristics: a Fikentscher constant of \( K_f = 62–63 \), \( T_{\text{deg}} = 120°C \), and a specific surface area of 1.81 cm\(^2\)/g.

The reaction of sulfur with PVC was performed in TCB or without any solvent. The process in the solvent was conducted under intense stirring for 3 or 6 h at 213°C and at different molar ratios of S : PVC = 1 : 1, 2 : 1, and 3 : 1. At this temperature, sulfur and PVC completely transferred into the solution. The reaction of the powderlike mixture of sulfur and PVC in the absence of solvent was performed at 300°C and PVC : S = 1 : 2.3 or 1 : 10 (mol/mol).

In both cases, intense evolution of hydrogen sulfide and hydrogen chloride occurred during the first hour. Then, the formation of gas stopped. The conditions of reaction and the yield of the product (polymer) containing S and Cl are given in the table.

The products of sulfurization are black powders insoluble in organic solvents.

The unreacted sulfur was washed from the polymer with hot benzene in a Soxhlet extractor. Then, the contents of C, H, S, and Cl in the purified polymer were determined (table).

The thermal gravimetric analysis curves of the samples were recorded on a Q-1500 derivatograph (MOM, Hungary). The maximum temperature was 850°C, and the heating rate in air was 10 K/min.

Diffraction curves were recorded on a Shimadzu XRD-7000 instrument (Japan) in the range of scattering angles 20 = 0–70°; focusing was performed according to Bragg–Brentano.

The films were obtained on laboratory rolls. Dioctyl phthalate was used as a plasticizer. The temperatures and times of rolling were 160–250°C and 10–30 min, respectively.

**RESULTS AND DISCUSSION**

When the reaction of sulfur with PVC was performed at ratios of 1 : 1 and 2 : 1 mol sulfur/base-mol PVC in boiling TCB (213°C) for 3 h, the contents of chemically bonded sulfur in the resulting polymer were 3.8 and 2.3% (table, experiments 1, 2). When the same experiment was conducted at an equimolar ratio of sulfur and PVC for 6 h, the amount of the chemically bonded sulfur in the sulfurized polymer was maximum (21.1%) (table, experiment 3). In this case, the polymer contained 16.3% chlorine, while the initial PVC contained 56.8% chlorine.

Under the same conditions, increases in S : PVC to 2 : 1 and 3 : 1 (table, experiments 4, 5) led to decreases in the sulfur contents in the polymer to 7.8 and 7.0%, respectively.

When the reaction of sulfur with PVC was performed in the absence of solvent for 6 h and at molar ratios of the reagents of 2.3 : 1.0 (213°C) and 10 : 1 (300°C), the sulfurization process was more intense (table, experiments 6, 7). The contents of the chemically bonded sulfur in the polymers were 57.6 and 48.0%; the chlorine contents, 1.9 and 0.6%.

Thus, the above experimental data suggest that the reaction of the powderlike mixture of sulfur and PVC makes it possible to obtain a polymer containing 50–