

Stabilization of Vulcanized Polyethylene

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SYNOPSIS

Some polyaminedisulphides were studied as thermal stabilizers of polyethylene vulcanized by dicumyl peroxide. The effects of temperature, time, and concentration were investigated. A reaction mechanism is suggested.

INTRODUCTION

Like common polyethylene, polyethylene vulcanized by chemical and radiation-chemical methods undergoes thermal destruction under heating. However, the stabilization of vulcanized polyethylene has some specific features. Thermal stabilizers must have thermal stability from 300 to 350°C and should not prevent vulcanization, i.e., react with a vulcanizing agent.¹ Besides, they must have good compatibility and low volatility, and should not sweat out of the bulk polyethylene. The agents used at present to stabilize polyethylene such as alkyl phenols, aromatic amines and diamines, and sulfur- and phosphorous-containing stabilizers have thermal stabilities up to 200–250°C, above which they decompose and initiate thermal destruction. They react with a vulcanizing agent, most often with a peroxide, which leads to the mutual consumption of the peroxide and thermal stabilizer. So, for instance, the use of the di(β -naphthyl-*n*-phenyldiamine (diaphene NN) stabilizer in compositions with dicumyl peroxide results in a 15–40% inhibition of the gel fraction, depending on the dicumyl peroxide concentration.¹

At present, there are very few available compounds which are used as thermal stabilizers for vulcanized polyethylene. These are 1,3-dihydro-2,2,4-trimethylquinoline, di(β -naphthyl), *n*-phenyldiamine, and zincmercaptobenzimidazole.^{2–4}

EXPERIMENTAL

The study was carried out to test poly(amine disulfide)s as thermal stabilizers produced in the condensation reaction of series of aromatic and aliphatic amines and diamines with monochloride sulfur.^{5–7} Poly(amine disulfide)s do not prevent the peroxide vulcanization of polyethylene. They are stable in the air to 300–350°C, have good compatibility, and do not sweat out of the bulk polyethylene.

The gel fraction was calculated according to the formula

$$\gamma = (g/g_0) \times 100\%$$

where g_0 = weight of sample of vulcanized polyethylene and g = weight of undissolved polymer after boiling in *p*-xylene for 1 h.

Endurance tests by rupture and specific elongation by rupture were conducted on a tensile-testing machine RPU-1. Calculation was done according to the formulas

$$G_p = P_p/S$$

$$p = (l_p/l_0) \times 100$$

where P_p = load at which specimen breaks, S = minimum initial cross-sectional area of the sample, l_0 = initial calculated length of the specimen, and l_p = increment of initial calculated length of the specimen at rupture.

The arithmetic average of five determinations was taken for the test results.

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Table I Inhibition of Thermal Degradation of Vulcanized Low-Density Polyethylene (380°C, 120 min, 10⁻³ torr/1% Inhibitor)

	Gel Fraction (%)		Gel Fraction Decrease (%)
	Before Degradation	After Degradation	
Poly(aniline disulfide)	84	68	19
Poly(paraphenylene diamine disulfide)	82	60	27
Poly(amine disulfide)	64	50	22
Poly(carbamide disulfide)	70	44	39
Poly(thiocarbamide disulfide)	59	67	24
Poly(ethylene diamine disulfide)	70	52	26
Without stabilizer	87	43	41
Neozon D	78	49	62
Santonox R	75	39	49

RESULTS AND DISCUSSION

The efficiencies of poly(amine disulfide)s as thermal stabilizers of vulcanized polyethylene are compared in Table I. A number of poly(amine disulfide)s such as poly(aniline disulfide), poly(amine disulfide) and poly(paraphenylene diamine disulfide) are efficient thermal stabilizers of the vulcanized polyethylene in the presence of which the gel fraction decrease is 2.5–3 times smaller than in the case of uninhibited thermal degradation. The stabilizers for common polyethylene such as neozone and Santonox R, are not efficient for stabilization of vulcanized polyethylene. On the contrary, they decompose and even initiate thermal destruction.

Poly(amine disulfide)s are efficient thermal stabilizers of vulcanized polyethylene up to 400°C (Fig. 1). In the range of 350–380°C the gel fraction decreases in the presence of poly(amine disulfide)s to a half or one third that of unstabilized vulcanized polyethylene.⁵

Poly(aniline disulfide) is most efficient because in its presence the gel fraction decreases by 7% at 350°C, 19% at 380°C, and 60% at 400°C, whereas without the inhibitor the gel fraction decrease amounts to 24% at 350°C, 41% at 380°C, and 92% at 400°C.⁶

The studies performed to investigate the influence of poly(amine disulfide) on the inhibition of thermal destruction of vulcanized polyethylene have shown that poly(amine disulfide) is efficient at concentrations as low as 0.25%. Increasing concentrations increase its efficiency, but still further increase of the concentration slightly diminishes the inhibition (Fig. 2).

Poly(amine disulfide)s continue to be efficient inhibitors of thermal destruction of vulcanized polyethylene for a long time (Fig. 3). After a 10-h exposure, a decrease of the gel fraction without inhibitor amounts to 40% whereas, in the presence of poly(aniline disulfide)s, the decrease is as low as 8%.

The high efficiency of poly(aniline disulfide) is confirmed by studying the changes of the strength

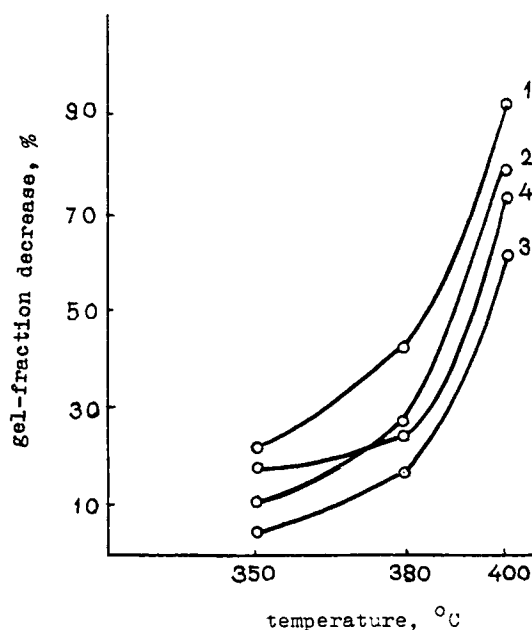


Figure 1 Thermal destruction of vulcanized polyethylene vs. temperature (120 min; inhibitor concentration of 1 wt %): (1) without inhibitor; (2, 3, 4) with inhibitors: (2) poly(paraaminophenylene disulfide); (3) poly(aniline disulfide); (4) poly(amine disulfide).

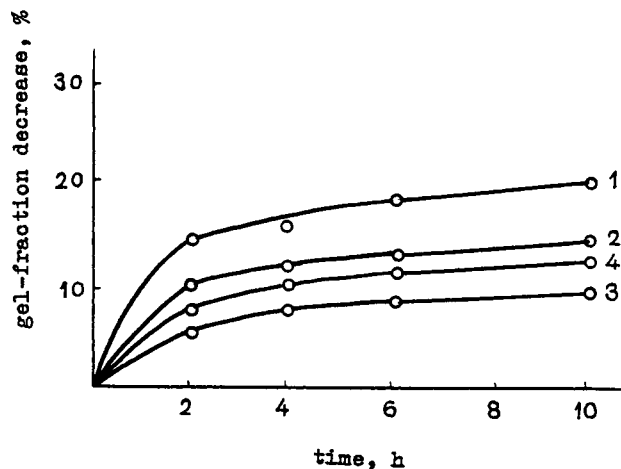


Figure 2 The influence of polyaniline disulfide concentration (wt %) on the inhibition of thermal destruction of vulcanized polyethylene (350°C): (1) 0.25; (2) 0.5; (3) 1.0; (4) 2.0.

properties of vulcanized polyethylene (Fig. 4). At 300°C in vacuum, the tensile strength of vulcanized polyethylene, containing poly(aniline disulfide), decreases insignificantly, and after a 10-h exposure is 192 kg/cm². Without inhibitor, the tensile strength markedly drops as a function of time; after a 10-h exposure it appears to be as small as 58 kg/cm². With poly(aniline disulfide), relative elongation at rupture drops slowly with time and after a 10-h exposure it amounts to 90% of its initial value.

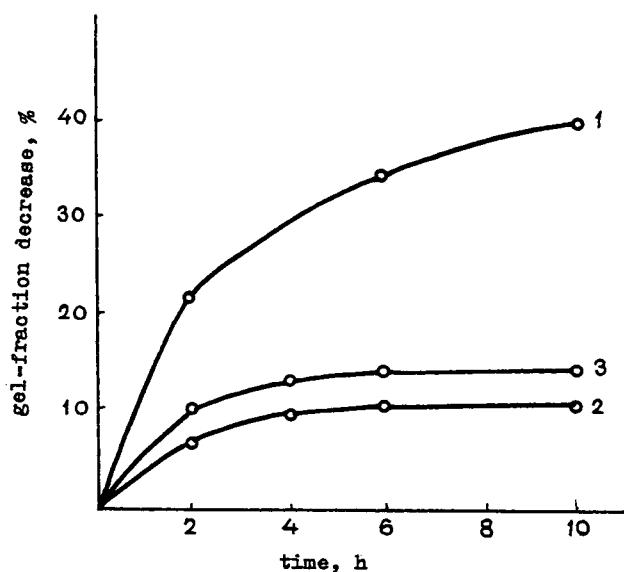


Figure 3 Time effect on the thermal destruction depth of vulcanized polyethylene (350°C, inhibitor concentration of 1 wt %): (1) without stabilizer; (2) poly(aniline disulfide); (3) poly(paraphenylene diamine disulfide).

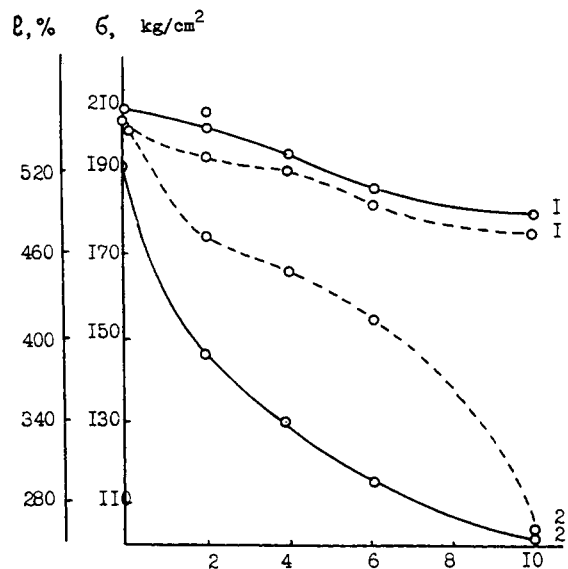


Figure 4 Changes of the strength properties of vulcanized polyethylene under thermal destruction (300°C): (—) tensile strength; (---) relative elongation; 1,1': aniline polydisulphide as an inhibitor; 2,2': without inhibitor.

Without inhibitor the relative elongation drastically drops with time, and after 10-h exposure amounts to 40% of its initial value (Fig. 4). The poly(aniline disulfide) efficiently inhibits the thermal aging of vulcanized polyethylene (Table II).

In unstabilized vulcanized polyethylene, the decrease in gel fraction amounts to 50% as early as after 25-h exposure, 75% after 50-h exposure, and after 75 h complete absence of gel is observed. In the presence of poly(aniline disulfide) the gel fraction begins decreasing only after a 50-h exposure and is as small as 2%; after a 100-h exposure it is down 10%.⁷

The high efficiency of poly(amine disulfide)s as thermal stabilizers of chemically linked polyethylene may be ascribed to their ability to accept macrorad-

Table II Thermal Aging of Vulcanized Polyethylene in Air [150°C; Poly(aniline disulfide concentration 0.8 wt %)]

Time (h)	Gel Fraction Decrease (%)	
	Without Inhibitor	With Inhibitor
25	53	0
50	76	2
75	100	5
100	—	10

icals on the disulfide bridge and amino group. Moreover, the presence of paramagnetic sites induces the adhesion of macroradicals and ensures an additional stability effect.

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