

Effect of Washing on the Photo-oxidation Resistance of Stabilized Polypropylene Fibers

J. LUSTOŇ and Z. MAŇÁSEK, *Polymer Institute, Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia,*
and Z. SAMUHELOVÁ, *VÚCHV, 059 21 Svit, Czechoslovakia*

Synopsis

The effect of aqueous detergent and benzene washing on the photo-oxidation stability of stabilized polypropylene fibers was studied. The fibers were stabilized by higher molecular weight light stabilizers based on 2-hydroxybenzophenones and by thermo-oxidative stabilizers. The content of the light stabilizers in washed fibers was determined, and photo-oxidation curves of the original and washed fibers were measured. The effectiveness of stabilization of the original and the washed fibers was compared with that of 2-hydroxy-4-*n*-octyloxybenzophenone at identical content of 2-hydroxybenzophenone structural units. Another criterion was comparison of washed and unwashed fibers. Photo-oxidation curves of accelerated aging and induction periods showed that washing with either aqueous detergent or benzene decreases the resistance of fibers to photo-oxidation, i.e., washing lowers the content of stabilizers in fibers. Extraction with benzene exerts a more pronounced effect than washing with water. Extractability by benzene of higher molecular weight stabilizers is considerably lower than with low molecular weight stabilizer. On the basis of experimental results it is assumed that washing of fibers leads to leaching not only of thermo-oxidative stabilizers but also to a decrease in the content of light stabilizers. Derivatives alkylated by *tert*-butyl are more extractable by benzene, while the nonalkylated derivatives are more extractable by washing with water.

INTRODUCTION

It is well known that the lifetime of polypropylene (PP) products depends on the amount and effectiveness of the stabilization systems used. The stabilization systems commonly employed at present are composed of thermo-oxidative stabilizers and a light stabilizer. Of the light stabilizers, various substituted derivatives of 2-hydroxybenzophenone and 2-hydroxyphenylbenzotriazole are used most often. Of the 2-hydroxybenzophenone derivatives, mainly 4-alkoxy derivatives are employed. It has also been shown that 2-hydroxybenzophenones do not behave as absorbers of incident light only.¹⁻³ They function as excited-state quenchers of carbonyl chromophores⁴⁻⁶ and as scavengers of radicals formed during polyolefin photo-oxidation.⁷⁻⁹

Irrespective of the mechanism of the action of benzophenones and benzotriazoles, it is evident that in polymer processing and in their long-term use the content of the stabilizers in the polymer decreases. For instance, during PP fiber formation, stabilizers are evaporated around the extrusion die, leading to a decrease in the real content of stabilizers in the polymer. As the molecular weight increases, volatility of stabilizers decreases during storage,¹⁰ thermal treatment at 60–120°C,¹⁰ or at processing temperatures (280°C).¹¹ Volatility of stabilizers has been studied elsewhere.¹²⁻¹⁹ In addition, the decrease in stabilizer content may result from migration of stabilizers to the polymer surface due to incompatibility.¹⁰

Formation of a thin surface layer of the stabilizer on the surface of the polymer would improve the effectiveness of a compound,²⁰⁻²² but abrasion of the polymer or washing lead to removal of the protective layer and thus to a reduction in the effectiveness of incompatible stabilizers. Washing with water²³ or dry cleaning in organic solvents²⁴ decrease the content of low molecular weight stabilizers in the polymer.

The polymer lifetime in photo-oxidation is affected by the possibility of benzophenone derivatives reacting with low molecular and polymeric radicals,^{7,9,25} leading to a decrease in the stabilizer concentration in the polymer and also in the polymer lifetime.

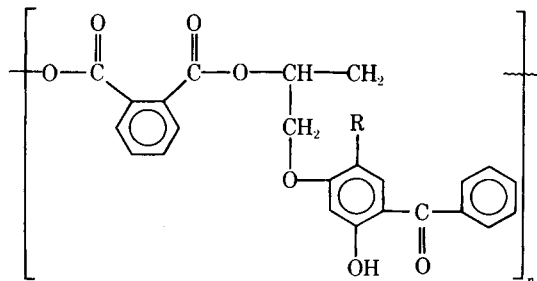
The bonding of stabilizers into a chain of the polymer or the use of higher molecular weight (oligomeric or polymeric) stabilizers can solve the problem of the loss of stabilizers in the polymer, of course, but will not protect against their reduction in concentration by radical reactions. Copolymerization of benzophenone derivatives with PP does not give the expected results.²⁶ Even at low comonomer concentration (0.5-1%) the polymerization rate is considerably reduced and the content of nonisotactic polymer increases. Therefore, the use of higher molecular weight stabilizers, where the molecular weight prevents volatilization from the polymer and reduces extractability and migration to the polymer surface, seems to be more suitable, especially for semicrystalline polymers.

In this paper we discuss the effect of extractability with aqueous detergent and benzene on the photo-oxidation of PP fibers stabilized by higher molecular weight benzophenone derivatives.

EXPERIMENTAL

PP fibers were prepared from powder polymer Tatren HPF (Slovnaft, Czechoslovakia). Distearyl-3,3'-thiodipropionate (0.55 wt %), 2,6-di-*tert*-butyl-4-methylphenol (0.1 wt %), and calcium stearate (0.15 wt %) were used as basic stabilization system. 2-Hydroxy-4-*n*-octyloxybenzophenone (9.2×10^{-4} mole/100 g, 0.3 wt %) was used as the standard light stabilizer. The following derivatives were used as higher molecular weight stabilizers:

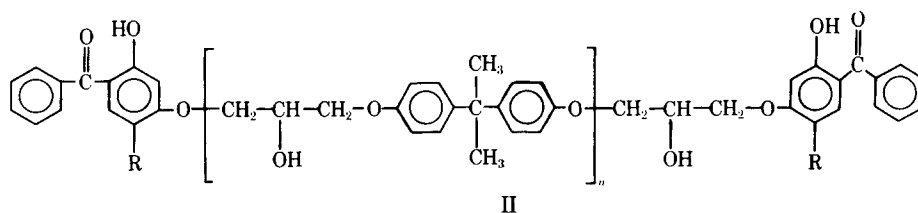
1. Polyesters of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with phthalic anhydride prepared according to references 24 and 27 of general formula I:



I

2. Addition products of epoxide resins with 2,4-dihydroxy-5-*tert*-butylben-

zophenone prepared according to reference 28 of general formula II:



3. Doubled benzophenones prepared according to reference 29, of general formula III:

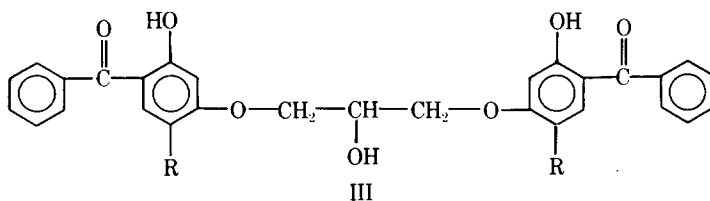


Table I shows the properties of the stabilizers. Stabilizers were dosed so that the content of benzophenone structural units was the same as for a reference sample stabilized by 2-hydroxy-4-*n*-octyloxybenzophenone (sample S).

The stabilizers were mixed with PP on a laboratory high-speed mixer, and the mixtures were then melted with an extruder 35 mm in diameter to granules and then spun with an extruder 30 mm in diameter. Temperatures ranged between 300° and 327°C to obtain a melt flow index of polymer under the die of 20–25 g/10 min. The prepared fibers were drawn to a 1:4 ratio and mechanically crimped with KK-2 equipment and then annealed in an autoclave (temperature 120°C, 20 min). The titer of the stabilized fibers was 5.5–6 dtex. Stabilization systems in PP fibers are given in Table II. There are some indications that the tested stabilizers also act as thermo-oxidative stabilizers, as follows from thermoanalytical curves of the stabilized PP. However, the difference in the melt flow index of the standard stabilized polymer and the other samples is due to the different PP used.

Washing of fibers was performed at ambient temperature for 30 min with a

TABLE I
Properties of Light Stabilizers

Formula	Stabilizer		Molecular weight ^b	mp, °C	
	Type	R ^a		Koffler	DTA
I	A	H	1800	—	—
I	AT	<i>tert</i> -butyl	2300	—	—
II	33T	<i>tert</i> -butyl	1450	—	—
II	16T	<i>tert</i> -butyl	2390	—	—
III	T	H, <i>tert</i> -butyl	— (541)	187–9	192
III	2T	<i>tert</i> -butyl, <i>tert</i> -butyl	586 (597)	199–201	206
—	S ^c	—	— (326)	—	51

^a In formulas I, II, and III.

^b Determined by VPO Knauer; data in brackets are calculated molecular weights.

^c 2-Hydroxy-4-*n*-octyloxybenzophenone.

TABLE II
Stabilization Systems in Polypropylene Fibers^a

Kind	Stabilizer		Melt flow index of granules, g/10 min
	Concentration, ^b wt %		
S	0.3		10.4
A	0.38		7.0
AT	0.44		8.4
33T	0.67		7.4
16T	1.1		7.3
T	0.25		6.9
2T	0.28		7.9

^a Basic stabilization system: 0.1 wt % 2,6-di-*tert*-butyl-4-methylphenol, 0.55 wt % distearyl-3,3'-thiodipropionate, 0.15 wt % calcium stearate.

^b Equal molar concentration of 2-hydroxybenzophenone structural units.

shaking machine in aqueous detergent (Tix, Czechoslovakia) at 2 g/dm³ concentration and in petroleum benzine (boiling range 50–75°C) at a sample-to-bath ratio of 1:40. Fibers were dried at ambient temperature. Washing was repeated after 24 hr of drying.

The content of the light stabilizers in the original and washed fibers was determined as follows. The weighed fiber was dissolved in hot toluene of UV purity. On cooling, PP was precipitated and filtered through a sintered glass filter S4. The filtrates were transferred into a graduated flask and the flask was filled with toluene. The content of the light stabilizers was determined spectroscopically (Specord UV Vis, Carl Zeiss, Jena, GDR) at wavelengths of 328 nm (S, A), 335 nm (T), and 340 nm (AT, 2T, 33T, 16T) in the range of the linear plots of the Lambert–Beer law.

The photo-oxidation of fibers was carried out by the method described earlier.²⁴ The weighed amount was 0.1 g of crimped and annealed fibers. Photo-oxidation proceeded at 60°C in an oxygen atmosphere (1013 kPa, 750 torr). Induction periods *I* were determined as intersections of the tangents of the photo-oxidation curves at the beginning and in the advanced phase of degradation, similarly to that described elsewhere.⁹

The effectiveness of the stabilization of higher molecular weight stabilizers for the original and extracted fibers was compared with the stability of fibers stabilized by standard stabilizer S according to the relation

$$E_S = I_i/I_S \quad (1)$$

where *I_i* is the induction period of photo-oxidation of fibers stabilized by higher molecular weight stabilizers (original or extracted), and *I_S* is the induction period of equally extracted standard fibers. Another criterion was a comparison of induction periods of the extracted fibers, *I_i*, with that of the original fibers, *I₀*, stabilized with the same stabilizer according to eq. (2):

$$E_i = I_i/I_0 \quad (2)$$

The effectiveness expressed by eqs. (1) and (2) which are nondimensional numbers shows the effect of washing on the stabilization effectiveness or, in other words, on the extractability of stabilizers from fibers.

TABLE III
Decrease in Concentration of Light Stabilizers After Washing of Polypropylene Fibers by Aqueous Detergent and by Benzine

Stabilizer	Decrease in concentration, ^a %			
	3w	5w	1b	3b
S	20	26	86	95
A	21	26	46	60
AT	16	19	54	74
33T	7	9	30	46
16T	5	6	33	42
T	32	38	58	76
2T	16	18	50	75

^a 3w and 5w denote values after three and five washings with aqueous detergent; 1b and 3b denote one and three extractions with benzine, respectively.

RESULTS AND DISCUSSION

Table III gives the results of the spectral determination of the content of the light stabilizers in washed fibers. The effect of the repeated washing on the reduction of the concentration of stabilizers in polymer is evident. Aqueous detergent washing has a smaller effect on washability than extraction with benzine.

Evaluation of the accelerated aging was performed by volumetric measurements on a photo-oxidation apparatus²⁴ with four measuring cells. For the purpose of their reproducibility, a reference sample was evaluated in each measurement. After extraction, the samples stabilized by the same stabilizer were placed in the same cell during photo-oxidation.

Figures 1 and 2 show the results of the photo-oxidation of stabilized PP fibers—original or washed three to five times with aqueous detergent (model washing) and one to three times extracted with benzine (model dry cleaning). Similar curves were also obtained with the other stabilized fibers. It is obvious from the figures that washing and extraction influence the photo-oxidation of fibers stabilized by the light stabilizers employed. During extraction with

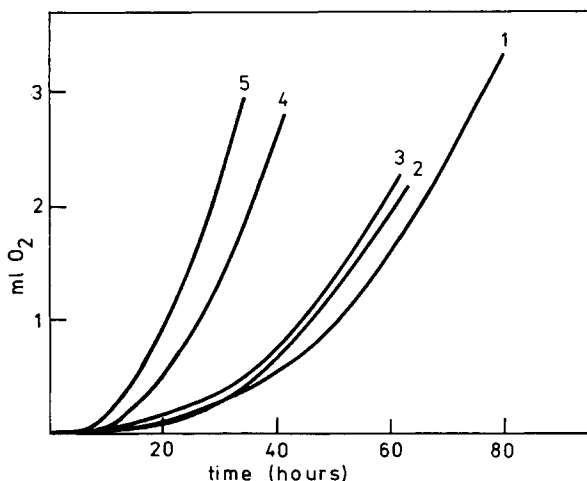


Fig. 1. Photo-oxidation of PP fibers stabilized by 2-hydroxy-4-*n*-octyloxybenzophenone: 1, original fibers; 2, three washings; 3, five washings with aqueous detergent; 4, one extraction with benzine; 5, three extractions with benzine.

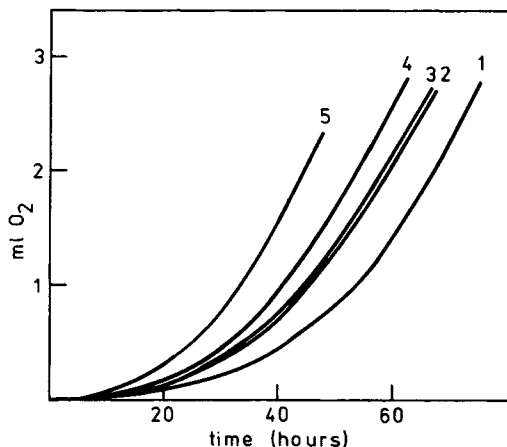


Fig. 2. Photo-oxidation of PP fibers stabilized by sample A: 1, original fibers; 2, three washings; 3, five washings with aqueous detergent; 4, one extraction with benzene; 5, three extractions with benzene.

benzene, the resistance of fibers to photo-oxidation is especially lowered as a result of one or three extractions of the stabilization systems from fibers. Table IV contains quantitative data on induction periods (I_i) and relative effectiveness with respect to standard (E_S) or unextracted samples (E_i).

It is seen from Tables III and IV that the effect of washing on the decrease in concentration of stabilizers in PP fibers is similar to the decrease in the stabilization efficiency of the extracted fibers.

The data in Table IV show that the effectiveness of the stabilization of higher molecular weight stabilizers for original unextracted fibers is, in the process of accelerated aging, similar to that for the standard commercial stabilizer. For fibers washed with aqueous detergent, the effect of washing on the concentration of stabilizers and the stability of fibers is less significant. Stabilizers 33T and 16T show the best resistance to washing; here, washing had no observable effect on photo-oxidation of fibers, and the decrease in concentration of light stabilizers was less than 10%. The decrease in the efficiency and concentration during washing by ca. 20% is evident for samples A, AT, and 2T and for standard sample S. Washing affects most of the stability of fibers stabilized by compound T, where the induction period decreases by 30–40%.

The reduction of the stabilizer content and of the resistance to photo-oxidation is more marked in the extraction of fibers with benzene. The most significant reduction is that of standard fibers, where the induction period decreases to 40% or 30% and the concentration to 14% and 5% of the original value. The effectiveness of the stabilization by higher molecular weight stabilizers ranges between 60% and 70% of the original value during the first extraction or between 50% and 60% after three extractions with benzene. High molecular weight addition products of reactions of epoxide resins with 2,4-dihydroxybenzophenone (samples 33T and 16T) exhibit the best resistance to extraction.

It is seen from Table III that the difference in the content of the standard stabilizer S is lower in one- and threefold extractions with benzene than in the case of the higher molecular weight stabilizers. According to the Weimer-Conner model of the extractability of stabilizers from polymers,³⁰ this is connected with a decrease in the concentration gradient between the polymer surface and its

TABLE IV
 Induction Periods of Photo-oxidation and Relative Effectiveness of Stabilized Polypropylene Original Fibers and after Washing by Aqueous Detergent or Extraction with Benzine^a

Stabi- lizer	I_0 , hr	I_{3w} , hr	I_{5w} , hr	I_{1b} , hr	I_{3b} , hr	E_i^b			E_s^c					
						3w	5w	1b	3b	Orig.	3w	5w	1b	3b
S	50.5	41	39	21	15	0.81	0.77	0.42	0.30	1	1	1	1	1
A	51.5	41	39	33.5	27	0.80	0.76	0.65	0.52	1.02	1	1	1.60	1.80
AT	50.5	43.5	40.5	32	25	0.86	0.80	0.63	0.50	1	1.06	1.04	1.52	1.67
33T	52.5	52.5	52.5	37.5	32	1	1	0.71	0.61	1.04	1.28	1.35	1.79	2.13
16T	54.5	54	53.5	37	31.5	0.99	0.98	0.68	0.58	1.08	1.32	1.37	1.76	2.03
T	50	34	31.5	32.5	27.5	0.68	0.63	0.65	0.55	0.99	0.83	0.81	1.55	1.83
2T	51	43	41	30.5	26	0.84	0.80	0.60	0.51	1.01	1.05	1.05	1.45	1.73

^a Polymer properties are given in Table II; i denotes original fibers; 3w and 5w denote values after three and five washings with water; and 1b and 3b denote one and three extractions with benzine, respectively.

^b Calculated according to eq. (2).

^c Calculated according to eq. (1).

interior. This decrease lowers the diffusion rate of the stabilizer in the polymer and reduces its concentration in surface layers.

A comparison of the effectiveness of higher molecular weight stabilizers with that of the standard with fibers of the same history (Table IV, E_S data) shows differences in the extractability of low and higher molecular weight stabilizers. In the case of washing with aqueous detergent, the washability of polyester stabilizers (formula I) is the same as for the standard. For compounds of formula II, E_S is higher by ca. 30% than the standard and for formula III, the less substituted sample T is more leached than the standard, while sample 2T is at the same level. Great differences were observed during extraction with benzene. The lower extractability of higher molecular weight stabilizers as a function of the induction period will be observed in the first extraction, and E_S will increase after three extractions with benzene. The best stabilizers are those of formula II, where the effectiveness is twofold with respect to the standard. The E_S values for compounds of formulas I and III are between 1.7 and 1.8, which reflects the lowering of the extractability of these types of stabilizers.

In view of the chemical structure it is interesting to compare the effect of alkyl substituents on the extractability of individual compounds. The compounds of formulas I and III differ in either the presence or the number of *tert*-butyl groups in the molecule. It is evident for both types that alkylation influences the decrease in extractability of stabilizers in aqueous solutions of detergent, while in benzene the alkylated derivatives are more extracted. This effect is reasonable if we consider the differences in the polarity of both extraction media and thus also their influence on the solubility of individual derivatives.

The use of oligomeric light stabilizers is generally considered as sufficient for ensuring long-term resistance of polymers to photo-oxidation since they show only a very low extractability in methanol,³¹ perchloroethylene,³¹ or trichloroethylene.^{24,32} Low extractability was also observed for polymeric and oligomeric antioxidants.²³ On the other hand, the content of the low molecular weight stabilizers strongly decreases after washing with water or organic solvents.^{23,31-33} We can say that the molecular weight of the stabilizer plays a significant role in its extractability and effectiveness.

However, this study of the effect of fiber washing on their photo-oxidation stability showed that the use of higher molecular weight stabilizers leads to a decrease in the induction periods (Table IV) and in their concentration (Table III). The stabilization system contained an antioxidant of phenolic type, a peroxide decomposer, and a light stabilizer. From the point of view of synergistic effect of such stabilizer mixtures, each change in the concentration of an arbitrary component of the stabilization mixture causes a decrease in the stabilization effect. The lowering of the photo-oxidation stability might also be due a decrease in the content of antioxidant and synergistic component. Mizutani and Kusumoto³² interpreted their results in this way and assigned the reduction of the resistance of PP films with respect to photo-oxidation after extraction with trichloroethylene to leaching of antioxidant and sulfur compound and assume a preservation of the light stabilizer in polymer. In spite of this, results in Tables III and IV show that under the given experimental conditions, a washing out of light stabilizers has to take place. Large fiber surface and small fiber thickness enable solvents to leach stabilizers from fibers, resulting in a decrease in the stability of fibers stabilized by higher molecular weight stabilizers.

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Received February 2, 1979

Revised June 18, 1979