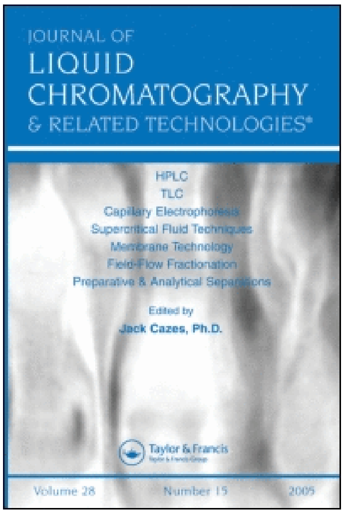

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Simultaneous Determination of the Antioxidant, the Crosslinking-Agent and Decomposition Products in Polyethylene by Reverse-Phase HPLC

Michel Duval[a]; Yves Giguère[a]
[a] Institut de recherche d'hydro-Québec, Canada

To cite this Article Duval, Michel and Giguère, Yves(1982) 'Simultaneous Determination of the Antioxidant, the Crosslinking-Agent and Decomposition Products in Polyethylene by Reverse-Phase HPLC', Journal of Liquid Chromatography & Related Technologies, 5: 10, 1847 — 1854

To link to this Article: DOI: 10.1080/01483918208062858

URL: http://dx.doi.org/10.1080/01483918208062858

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(10), 1847-1854 (1982)

SIMULTANEOUS DETERMINATION OF THE ANTIOXIDANT, THE CROSSLINKING-AGENT AND DECOMPOSITION PRODUCTS IN POLYETHYLENE BY REVERSE-PHASE HPLC

Michel Duval and Yves Giguère

Institut de recherche d'hydro-Québec,
Varennes, Québec, Canada J0L 2P0

ABSTRACT

A method has been developed for the extraction and analysis of the antioxidant, the peroxide crosslinking agent and some decomposition products in crosslinked polyethylene. The method involves the use of high-performance liquid chromatography (HPLC) in the reverse-phase mode, with a mixture of methanol and water as the mobile phase. Samples of polyethylene are ground at low temperature into a fine powder prior to extraction by methanol. The accuracy and sensitivity limits are given for each of the separated components.

INTRODUCTION

The initial formulation of chemically crosslinked polyethylene generally contains a peroxide crosslinking agent such as dicumylperoxide, and an antioxidant of the unhindered-phenol, sulfur-containing type. During the curing process, peroxide decomposition products are formed, e.g., acetophenone, cumylalcohol and α-methylstyrene (1).

The mechanical integrity of the crosslinked polyethylene (XLPE), as well as its resistance to oxidation, depend on the remaining amounts of the above compounds, and these must therefore be carefully controlled.

The analytical procedures used in the determination of antioxidants in polyolefins, and the problems associated with them, have been discussed in several review paper (2-4). Most modern methods involve the use of high-performance liquid chromatography (HPLC) and differ mainly with regard to the extraction methods and phases used (4-9). HPLC has also been employed for the analysis of some organic peroxides (10-13). However, none of these methods can readily be applied to the case of XLPE.

A method has therefore been specially developed at IREQ for that purpose, allowing simultaneous determination of the antioxidant, the peroxide and decomposition products in XLPE, using reverse-phase HPLC. Applications to the more limited case of high voltage cables are described elsewhere (14).

EXPERIMENTAL

Materials

Commercial pellets of uncrosslinked polyethylene containing Di Cup$^{(R)}$R dicumylperoxide crosslinking agent and Santonox$^{(R)}$R antioxidant were obtained from Union Carbide Corp. (grade 4201B). Samples of partially and fully crosslinked polyethylene were prepared by heating pellets in a mold under pressure, at 160°C and 190°C respectively.

Standard samples of Di Cup$^{(R)}$R dicumylperoxide and Santonox$^{(R)}$ R antioxidant were obtained from Hercules Inc. and Monsanto Chemical Co., respectively. Acetophenone, and 2-phenyl-2-propanol (cumylalcohol) were purchased from Aldrich Chemical Co., and α-methylstyrene from J.T. Baker Chemical Co.

HPLC and extraction solvents (methanol and water) were Omnisolv-grade from BDH (Canada), filtered on 0.4-μm Millipore filters prior to use.

Apparatus

A Waters Associates Model ALC-GPC 301 liquid chromatograph fitted with a Model 6000 high-pressure pump (0-40 MPa), a Model 7120 Rheodyne sample injector and a Lichrosorb RP 18 (10 μm) reversed-phase column was used with a 80 : 20 (v/v) methanol : water solution as the mobile phase. The flow rate was 1 mℓ/min and typical back pressure 17 MPa. The UV absorbance of the sample was monitored at 254 nm.

Cumylalcohol was analyzed by gas chromatography on Carbowax 20 M (1-m column, 160°C, FID detector).

Extraction Method

Additives cannot be recovered from XLPE by dissolution and selective precipitation of the polymer, because XLPE is cross-linked and consequently not soluble, and solvent extraction must be used.

XLPE samples were thus ground to 20 to 30 mesh powder in a blade grinder cooled with liquid nitrogen to avoid heat degradation, covered with methanol and stirred for 48 h at room temperature in amber glassware, then filtered and washed with methanol; the methanol solutions were subsequently concentrated to a known volume in a rotating evaporator at 30°C under vacuum, and injected directly into the liquid chromatograph.

Extractions performed directly on pellets or unpowdered specimens of XLPE were incomplete, and Sohxlet extraction with boiling methanol was not quantitative, even under a nitrogen atmosphere, possibly owing to the reaction of antioxidant and peroxide at that temperature.

RESULTS AND DISCUSSION

Qualitative Analysis

Typical chromatograms of XLPE samples are shown in Figure 1. In the reverse-phase mode, separation is according to polarity,

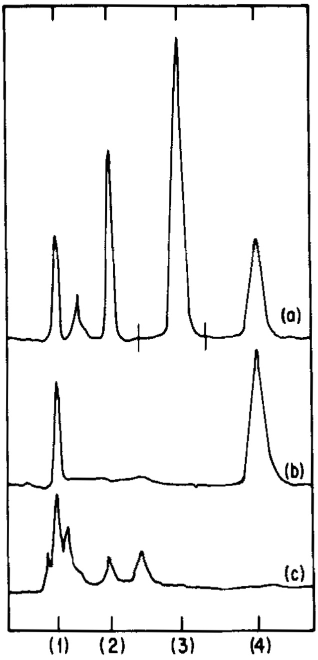

FIGURE 1 : Typical HPLC chromatograms of XLPE samples: (1) Acetophenone + cumylalcohol; (2) α-methylstyrene; (3) Santonox antioxidant; (4) Dicumylperoxide; (a) PE pellets, uncured, 0.08, 0.64 and 0.32 AUFS; (b) XLPE, partially cured, 0.08 AUFS; (c) XLPE fully cured, 0.08 AUFS.

i.e. the more polar compounds are eluted first: the peroxide decomposition products, mainly acetophenone, cumylalcohol and α-methylstyrene, then the antioxidant (Santonox$^{(R)}$R) and the crosslinking agent (dicumylperoxide). Other decomposition products in a few cases were identified by mass spectrometric analysis of the eluting fraction, e.g., phtalates for the fully cured sample.

Quantitative Analysis

The antioxidant (Santonox$^{(R)}$R), the crosslinking agent (dicumylperoxide) and α-methylstyrene are well separated. Acetophone and cumylalcohol elute together. However the UV absorption coefficient of cumylalcoohol is very low, about 1000 times lower than that of acetophenone, while its concentration is only 1 to 5 times higher in all XLPE samples studied, as evaluated by gas chromatography. The contribution of cumylalcohol to the peak surface therefore is negligible (0.5%, i.e., less than the accuracy on the HPLC analysis) and this peak can be considered due to acetophenone only.

Quantitative HPLC results are obtained by calibrating with standard solutions of pure compounds. Accuracy on repeated injections is ±2%. The minimum amounts that can be determined by HPLC are 1 - 2 ng for acetophone and α-methylstyrene, 10 ng for the antioxidant and 400 ng for dicumylperoxide, at 0.04 AUFS.

HPLC values must be multiplied by a conversion factor, owing to the fact that extraction is not 100% complete after the 48 h extraction period chosen as a practical limit in the experimental procedure. A typical extraction curve relating the amount of additive extracted as a function of time is shown in Figure 2. Such curves are quite reproducible and a fairly reliable extraction value of 86% (±3%) is reached after 48 h.

The overall accuracy on XLPE analysis, combining the accuracy on extraction and on HPLC analysis, is ±5%. The sensitivity, i.e., the minimum concentration of additives and decomposition

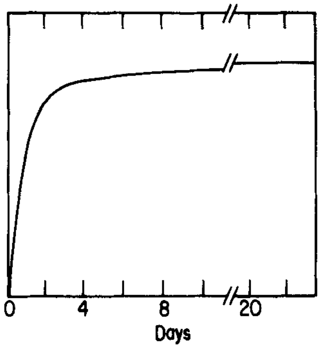

FIGURE 2 : Typical curve of extraction of the additives as a function of time.

TABLE 1
Sensitivity Limits on XLPE Analysis (in ppm)

Dicumyl-peroxide	Anti-oxidant	Aceto-phenone	α-methyl-styrene
100	2	0.5	0.5

TABLE 2
HPLC Quantitative Analysis of Various XLPE Samples

Ref Fig. 1	HPLC analysis / Samples	Dicumyl-peroxide %	Anti-oxidant %	Aceto-phenone ppm	α-methyl-styrene ppm
	Di-Cup R$^{(R)}$ Dicumylperoxide	100	-	3170	720
(a)	PE pellets uncured	1.2	0.14	25	3
(b)	XLPE sample partially cured	0.4	-	15	-
(c)	XLPE sample fully cured	-	-	5	22

products in XLPE that can be analyzed, is a function not only of the sensitivity of the HPLC analysis (values given above) but also of practical considerations such as the HPLC injection volume (20 μℓ max.), volume of concentrated extract (10 mℓ min.) and amount of XLPE which can be powdered (2 g min.). The sensitivity limits thus obtained are indicated in Table 1.

Application to the Curing Process

The quantitative values obtained for the XLPE samples shown in Figure 1 are listed in Table 2.

As expected, the peroxide content, starting from a measured value of 1.2% in uncured pellets, falls to 0.4% in the partially cured sample, then to 0% in the fully cured sample.

The amounts of the peroxide decomposition products vary slightly, with acetophenone present in all cases and α-methylstyrene being formed in the fully cured sample. Commercial dicumylperoxide itself contains relatively large amounts of acetophenone and α-methylstyrene.

The antioxidant, surprinsingly, starting from an initial value of 0.14%, seems to disappear in partially as well as in fully cured samples. Extended studies, however, have shown that it does not in fact disappear but is grafted to the polymer chain during the curing process and is not extracted by methanol (14).

ACKNOWLEDGMENTS

The authors would like to thank Dr. H. St-Onge for providing samples of XLPE, and Mrs. Lesley Regnier for reviewing the manuscript.

The cooperation of Union Carbide Corp., Hercules Inc. and the Monsanto Chemical Co., in providing materials and information, is also gratefully acknowledged.

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