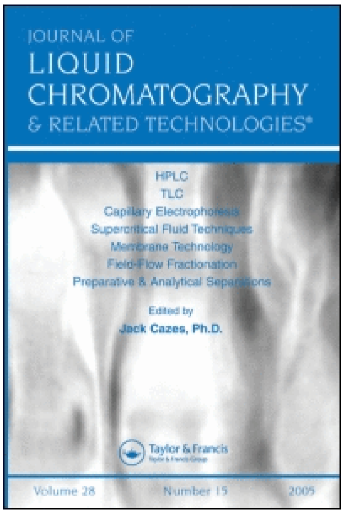

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CHARACTERIZATION OF PVC BY SEC. II. ONE SHOT CHROMATOGRAPHY OF THE ORGANIC COMPONENTS OF PVC COMPOUNDS

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ABSTRACT

1,2,4-Trichlorobenzene at 90 °C proved to be a universal solvent for the common organic components of PVC compounds except crosslinked impact modifiers. Size exclusion chromatography was carried out with 8 different components, with a PVC-U compound and plate out formed during its extrusion using both RI and IR detection. In the RI detector PVC shows a very low detector response. It is therefore possible to analyze the whole organic fraction of the compound without prior precipitation of PVC. Using RI/IR double detection, an "one shot" analysis of the PVC matrix and of all the soluble additives can be accomplished.

INTRODUCTION

Conventional analysis of polyvinylchloride (PVC) compounds requires the subsequent use of various solvents for extraction of the different organic components used as additives, e.g. plasticizer, lubricants and stabilizers (1). The solvents used do however not allow a selective separation of the individual additives. Furthermore, these solvents are often nonsolvents for PVC, except for fractions with very low molar mass, and several repetitions of a certain extraction are necessary to insure its completion. Braun and Bezdadea (2) therefore developed a procedure for the analysis of plate-out formed during PVC extrusion starting with complete dissolution of all the organic components in tetrahydrofurane (THF). THF is however a nonsolvent for some organic components of PVC compounds, e.g. outer lubricants of very low polarity such as oxidized polyethylene wax.

For the analysis of PVC compounds containing additives with a very wide range of polarity, 1,2,4-trichlorobenzene at 90 °C was found to be a more universal solvent. As this solvent is commonly used in the high temperature size exclusion chromatography (SEC), a systematic SEC study of PVC, of PVC additives, of a unplasticized polyvinylchloride (PVC-U) compound, and of plate-out formed during PVC extrusion was undertaken using both a refractive index (RI) and an infrared (IR) detector.

MATERIALS

The test samples of the components for conventional PVC compounds given in Tab. 1 and 2 were each of technical grade and were gift samples of various companies without more detailed specification. 1,2,4-Trichlorobenzene, reagent grade (Merck, Darmstadt, FRG), was used as solvent.

TABLE 1

Relative detector response (peak area of component)/(peak area of PVC) for various components fo PVC compounds . in 1,2,4-trichlorobenzene at 110 °C.

		relative detector response	
No	component	RI	IR
1	polyvinylchloride	-1.00	1.00
2	acrylate based processing aid	23.3	
3	oxidized polyethylene wax	44.7	
4	oxidized paraffin wax	69.1	15.7
5	ester wax	103.6	16.0
6	12-hydroxy stearic acid	81.9	
7	Ba/Cd laurate	63.9	
8	neutral lead stearate	42.6	
9	di-2-ethyl-hexyl-phthalate	77 *)	
10	epoxidized soya oil	82 *)	
11	stearic acid	127 *)	
12	di-n-butyl tin mercaptide	58 *)	
13	glycerol monooleate	84 *)	

*) estimated from measurement of the refractive index increment with λ = 546 nm at ~90 °C

TABLE 2

Composition of a typical PVC-U compound used for extrusion of window frame profiles. Content of components given in parts per hundred (phr) and mass percent (m %).

No	Component	phr	m %
	soluble *):		
1	polyvinylchloride (K=65)	100.0	80.71
2	acrylate based processing aid	2.0	1.61
3	oxidized polyethylene wax	0.2	0.16
4	oxidized paraffin wax	0.2	0.16
5	ester wax	0.5	0.40
6	12-hydroxystearic acid	0.4	0.32
7	Ba/Cd laurate	1.2	0.97
	insoluble *):		
VIII	acrylate modifier	8.7	7.02
IX	titanium dioxide	4.5	3.63
X	coated chalk	4.0	3.23
XI	two-basic lead phosphite/sulfite	2.2	1.78

*) in 1,2,4-trichlorobenzene at 110 °C

The sample of an extruded window profile and of plate-out formed during the production of this profile was made available through Chemson Polymer-Additive Ges.m.b.H. (Arnoldstein, Austria); the composition of the respective PVC-U compound is given in Tab. 2.

METHODS

Refractive index increment

The refractive index increment was measured using a Brice-Phoenix Differential Refractometer (model BP-2000-V, Phoenix Precision Instruments, Philadelphia, Penn.) at a wave length λ = 546 nm at 90 °C. The concentration of the individual components was about 2 g/dl.

Size exclusion chromatography

The apparatus for SEC consisted of the following components:

- HPLC pump (Constametric II, Milton Roy, Hasselroth, FRG) set to a flow rate of 0.800 ml/min,

- injection valve (Rh 7010, Rheodyne, Berkley, Cal.) with a sample loop of 20 μl.

- SEC column for separation of oligomers (Lichrogel PS 4, Merck, Darmstadt, FRG: particle diameter 5 μm, length 250 mm, inner diameter 7.0 mm) kept at 110 °C in a HPLC-oven (Knauer, Berlin).

- RI detector with a light (λ_{max} = 950 nm) emitting semiconductor diode (Hochtemperatur-Differential Refractometer, Knauer, Berlin), or

- IR detector (Du Pont Comp., Wilmington, Del.) set at λ = 3.41 μm with a modified detector cell (reduced thickness, volume = 30 μl)

Sample preparation for SEC

The individual components were dissolved by weighing about 50 mg in a 50 ml Erlenmeyer flask, adding

50 g of 1,2,4-trichlorobenzene, and keeping the closed flask for 4 h at 90 °C. The components 1-7 in Table 2 proved to be completely soluble with the content of individual components (mg/g solvent) given in Table 2, and the respective clear solutions were injected in SEC without filtration after quick heating to 110 °C.

The components VIII-XI in Tab.2 proved as insoluble in 1,2,4-trichlorobenzene at 110 °C, apart from a small soluble fraction of component VIII.

The sample solutions of the extruded profile and the plate-out sample were prepared with a content of 7.31 mg/g solvent and 7.10 mg/g solvent, respectively. The sample solutions were kept at 90 °C for 4 h and then filtered (45 µm Fluoropore filter, Millipore, Bedford, Mass.) at this temperature under a pressure of 3 bar. Prior to injection in SEC, these sample solutions were also quickly heated to 110 °C.

RESULTS

The SEC eluograms of the individual components 1-8 given in Tab. 1 are shown in Fig. 1. Taking into account the content of the individual sample solutions (cf. legend to Fig.1), the values for the relative response of the refractive index (RI) detector given in Tab. 1 for the components 1-8 can be calculated from the corresponding peak ar~~e~~eas. From earlier measurements of the refractive index increment, the relative response of the RI detector for the components No 9-13 was estimated.

As can be seen from Fig. 1 and Tab. 1, polyvinylchloride gives a very small response of negative sign

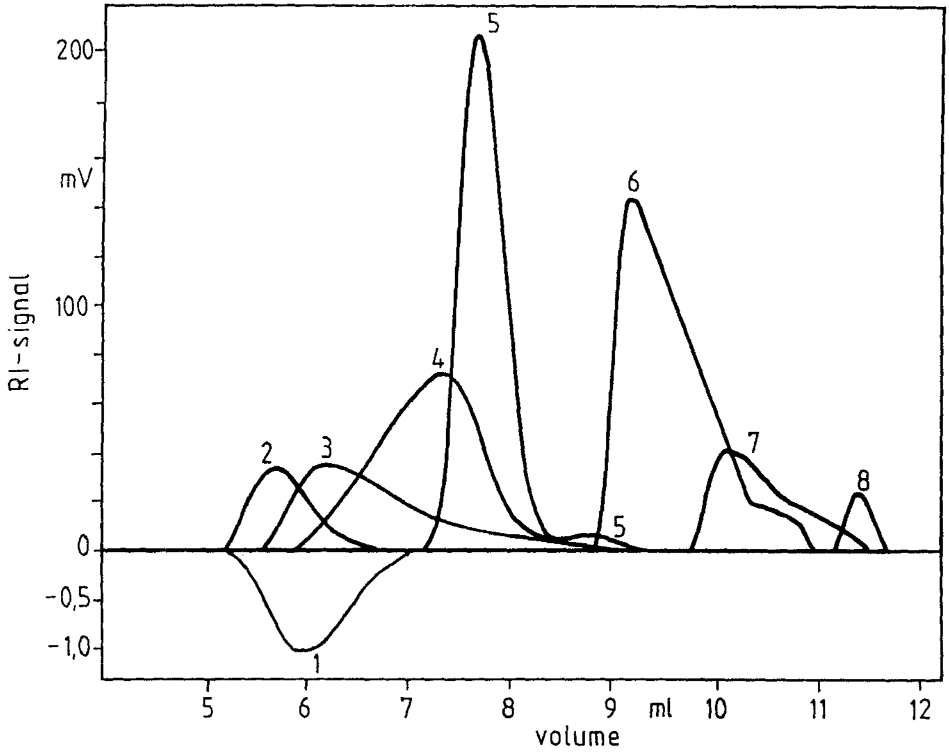

FIGURE 1

Eluograms recorded with the refractive index detector of components No 1-8 (cf. Tab.1). Content of sample solutions (mg/g solvent): 0.947 (No 1), 0.753 (2), 0.798 (3), 0.975 (4), 0.874 (5), 1.210 (6), 0.890 (7), 0.640 (8).

compared to the other soluble components No 1-8 of table 1 and 2. The peaks of the individual components show considerable overlap, and it is obvious that not only component 1 (PVC), but also component 2,3,4,6 and 8 are of considerable polydispersity.

Fig. 2. shows eluograms of component 1,4 and 5 given in Tab. 1 which were recorded by the IR detector.

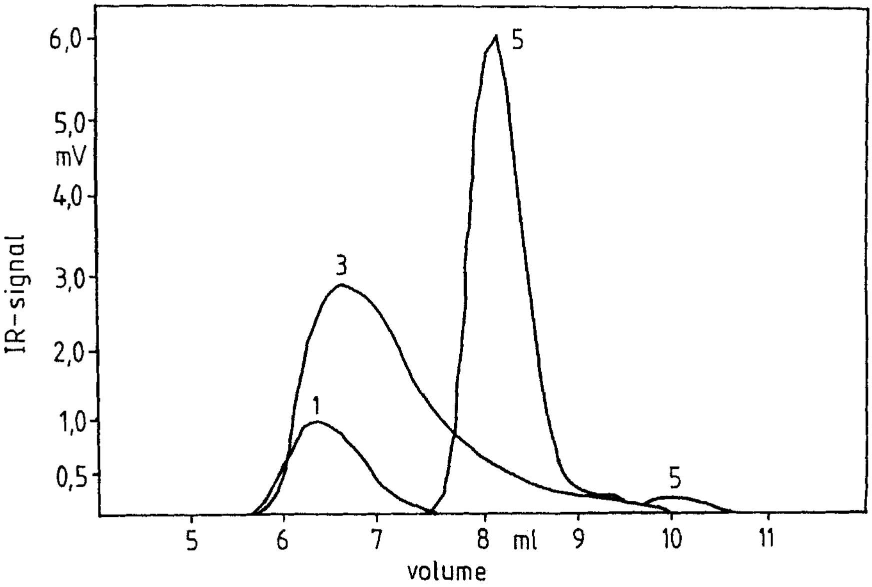

FIGURE 2

Eluograms recorded with the infrared detector of components No 1,4 and 5 (cf. Tab.1). Content of sample solutions (mg/g solvent): 3.566 (No 1), 0.975 (4), 0.879 (5).

From these eluograms, the values for the relative detector response of the IR detector given in Tab. 1 were calculated. The eluograms shown in Fig. 1 and Fig. 2 were both recorded with nearly the same signal to noise ratio when measuring component No 3. Therefore, direct comparison of the sensitivity of both detectors is possible; the response of the IR-detector for PVC is about 6.5 times larger than the response of the RI detector.

Fig. 3 shows the eluogram of a sample taken from an extruded window frame profile ("after extrusion")

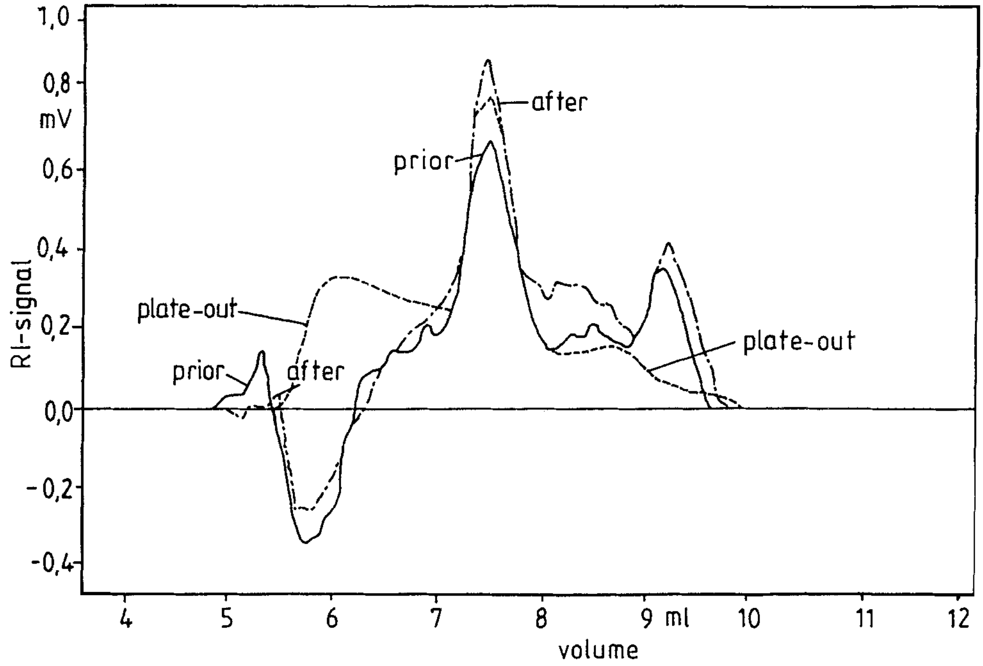

FIGURE 3

Eluograms recorded with the refractive index detector of samples from an extruded profile ("after extrusion"), and from plate-out ("plate-out") formed during the extrusion of this profile in comparison to the eluogram calculated from the formulation of the compound and the peaks 1-7 in Fig.1 ("prior to extrusion"). Content of sample solutions (mg/g solvent): 7.31 ("after extrusion" and "prior extrusion"), 7.10 ("plate-out").

recorded by the RI detector in comparison to the eluogram ("prior to extrusion") calculated by superposition of the peaks of individual components (No 1 -7 in Fig. 1) according to their content in the respective PVC-U compound (cf. Tab. 2). From this comparison, it can be stated that the sample from the extruded profile contains less of component No 2 and more of component No 5 than given in the formulation of the compound.

Also in Fig. 3, the eluogram of a sample taken from plate-out formed during extrusion of the window frame profile is shown which was recorded by the RI detector. It is obvious, that this plate-out sample exhibits a considerably lower content of component No 1,2 and 6 and a higher content of component 3 and 4 than the extruded profile.

DISCUSSION

These findings demonstrate, that high temperature SEC with 1,2,4-trichlorobenzene as eluent, which is common practice for the analysis of molar mass distribution of polyolefins, is an apt separation system for the analysis of PVC compounds. 1,2,4-Trichlorobenzene is a solvent for nearly all the organic components used in PVC compounds including for example Pb, Cd, Ba and Zn salts of fatty acids; the only exception of this rule found in this study were acrylate impact modifiers, which is probably due to the cross linked network structure of these additives.

The low relative detector response of PVC, especially in the RI detector, allows the "one shot chromatography" of most organic and metal organic components of PVC compounds without extraction procedures from the PVC matrix. This may be very useful for verification of the composition in case of unexpected failure of a product made of PVC. Furthermore this method is able to detect compositional changes of components with special impact on the rheological properties, e.g. inner and outer lubricants. Although these compounds vary strongly in polarity, they are all soluble in 1,2,4-trichlorobenzene at a temperature above 90 °C.

This separation system also appears to be suited for the elucidation of the plate-out phenomenon in PVC processing. This phenomenon is a phase separation process influenced by the inorganic components and by processing conditions, e.g. a sudden pressure drop in a certain zone of the extrusion tool. As can be seen from Fig. 3, direct comparison of the content of all the components which are miscible or at least partially miscible with PVC has become feasible with considerably smaller sample size than necessary for conventional analysis based on solvent extraction. Though the data shown in Fig. 3 lend themselves for the present to qualitative interpretation only, improvement for quantitative analysis appears feasible by the use of double detection (RI and IR detector) due to the different detector responses (cf. Tab.1).

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