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Short Communication

Determination of high- and low-molecular-mass plasticisers in stretch-type packaging films

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Abstract

A single analytical procedure is presented for determination of so-called monomeric plasticisers such as di(2-ethylhexyl) adipate, polymeric plasticisers such as poly(butylene adipate), and secondary plasticisers such as epoxidised soybean oil. The plasticisers are extracted from the film with concurrent derivatisation. Ester linkages are cleaved by treatment with potassium hydroxide in ethanol, epoxide moieties are opened using hydrochloric acid generated *in situ* by addition of acetyl chloride and, lastly, hydroxy groups are converted to silyl ethers using bis(trimethylsilyl)trifluoroacetamide. This reaction sequence is conveniently performed sequentially on a single sample leading to products that can be measured in a single GC analysis. The method has been applied to samples of known provenance and in a large survey of retail stretch-type films. The combined method offers significant savings in time compared with the separate analytical methods published earlier for monomeric and polymeric poly(vinyl chloride) plasticisers. The method is quantitative and gives results in good agreement with these earlier procedures.

1. Introduction

Thin stretch-type plastics films are widely used for packaging food in both home-use and retail applications [1]. The most common base polymers are poly(vinyl chloride) (PVC), vinylidene chloride co-polymerised with vinyl chloride (PVDC) and polyethylene (PE). Plasticisers are used in PVC and PVDC films to impart the desirable stretch and cling properties [2] while PE films are naturally flexible but may require tackifying agents ("cling additives") to impart cling properties [3,4].

Plasticisers for PVC and PVDC are typically esters and are incorporated into the plastic at quite high levels —percentage levels— in order to modify the basic physical properties of the polymer. For this reason the migration of these additives has been the topic of numerous studies [5,6] and manufacturers have tended in recent years to use higher-molecular-mass plasticisers to reduce migration levels [7]. Thus for PVC, it is now common to find di(2-ethylhexyl) adipate (DEHA) wholly or partially replaced by polymeric plasticisers prepared from adipic acid and

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glycols such as propane-1,2-diol or butane-1,3-diol. There is also a tendency to use higher levels of epoxidised soybean oil (ESBO) since this heat stabiliser has useful characteristics as a secondary plasticiser [8].

These changes have been successful in reducing migration levels but present the analyst with some difficulties. The polymeric plasticisers in particular are too high in molecular mass to be analysed successfully by GC and they lack a convenient chromophore for HPLC analysis. There are numerous methods published for the determination of the individual plasticisers. One of our laboratories has published methods for the analysis of plastic films and foods for DEHA [9], polymeric plasticisers [10] and ESBO [11,12]. It is time-consuming, however, to apply two or more separate methods if polymeric plasticisers are to be characterised according to their base monomers and then both monomeric and polymeric plasticiser levels are required. Bodies that require this information include industries' own quality control laboratories and enforcement authorities charged with ensuring food contact plastics meet applicable regulations. The present paper overcomes this analytical problem by the use of selective derivatisation procedures to allow a combined analysis of the additives to be performed.

2. Experimental

2.1. Materials

PVC films with declared plasticiser levels were available from earlier studies [7,13] and had been supplied by various manufacturers of stretch-type PVC films. The films were either production samples from the period 1987–1991 or experimental film formulations. The plasticisers DEHA, poly(propylene adipate) (PPA) and poly(butylene adipate) (PBA) were commercial samples obtained from these film manufacturers as were samples of the heat stabiliser and secondary plasticiser ESBO.

Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was from Pierce (Chester, UK) and ethanol (99.9%, v/v) was from Hayman (Witham, UK). Acetonitrile (HPLC grade) and chloroform (glass-distilled grade) were from Rathburn (Walkerburn, UK). Triheptadecanoin, butane-1,4-diol and acetyl chloride were from Sigma (Poole, UK).

2.2. Methods

A known area of film (0.25 dm^2) was weighed, cut into small pieces and placed in a crimp-cap vial (20 ml capacity) along with internal standards butane-1,4-diol (3 mg) and triheptadecanoin (1 mg) dissolved in chloroform (250 μl). The chloroform was evaporated just to dryness under a stream of nitrogen at 40°C whereupon ethanolic potassium hydroxide (0.2 *M*, 2 ml) was added and the vial then capped and heated for 1 h at 80°C. Acetyl chloride (100 μl) was then added to the mixture and the vial contents heated for a further period of 2 h at 60°C. An aliquot of the supernatant (5 μl) was transferred by syringe to a tapered vial (1.6 ml capacity) and derivatised by the addition of acetonitrile (100 μl) and BSTFA (100 μl) followed by a period of heating at 80°C for 2 h and a further period of 24 h at ambient temperature. The tapered vials were loaded directly into the GC autosampler (Fisons A200S, Crawley, UK) for analysis.

GC analysis employed a CPSil 5CB fused-silica capillary column (Chrompack, London, UK) of dimensions 18 m × 0.25 mm I.D., 0.12-μm phase. The column was installed in a Carlo Erba Mega Series 2 gas chromatograph (Fisons, Loughborough, UK) operated with hydrogen as the carrier gas at 1 ml/min. The column was held at 60°C for 4 min after injection and then programmed to rise at 40°C/min to 260°C (held 1 min) then at 50°C/min to 290°C to clean. Injections of 1 μl in volume were made in the split mode (20:1) with the injector block at 240°C. The flame ionization detector was held at 300°C. Quantitation was on the basis of integrated peak area ratios of analytes *versus* the internal standard(s) and used standard curves prepared by the analysis of plasticiser standards taken through the full analytical method. GC–MS analysis for confirmation of peak identity used a Hewlett-

Packard 5890II GC fitted with a 7673 autosampler and an HP5971 mass-selective detector.

3. Results and discussion

3.1. The reaction scheme selected

The concurrent GC analysis of monomeric and polymeric plasticisers is made possible by the chemistry shown in Fig. 1. The aim of the first reaction was to break down the polymeric plasticisers to their more volatile base monomer units, adipic acid (as the diethyl ester) along with the C-3 or C-4 diol for PPA and PBA, respectively. The conditions also convert high-molecular-mass epoxidised triglycerides such as ESBO to the individual epoxy fatty acid ethyl esters. The basic conditions of potassium hydroxide in ethanol were chosen so as to leave the epoxy moieties in ESBO intact [14]. The second step chosen was the acid-catalysed opening of these epoxide groups to the isomeric 1,2-ethoxyalcohols. This was conveniently achieved by the addition of acetyl chloride to the basic ethanolysis solution to generate an excess of HCl under anhydrous conditions. Finally, an aliquot of the reaction mixture was treated with BSTFA to provide good chromatography on a robust non-polar GC phase, by converting the polar hydroxy functions to the silyl ethers.

3.2. Measurement of DEHA and polymeric plasticisers

A typical chromatographic trace is shown as Fig. 2. DEHA was quantified as the TMS ether of 2-ethylhexanol and PPA and PBA as the TMS ethers of propane-1,2-diol and butane-1,3-diol respectively (Fig. 1). The yield of diethyl adipate was used as a check on the DEHA, PBA and PPA results since these three plasticisers combined should account for the total adipate found when calculated on a mole basis. In this work

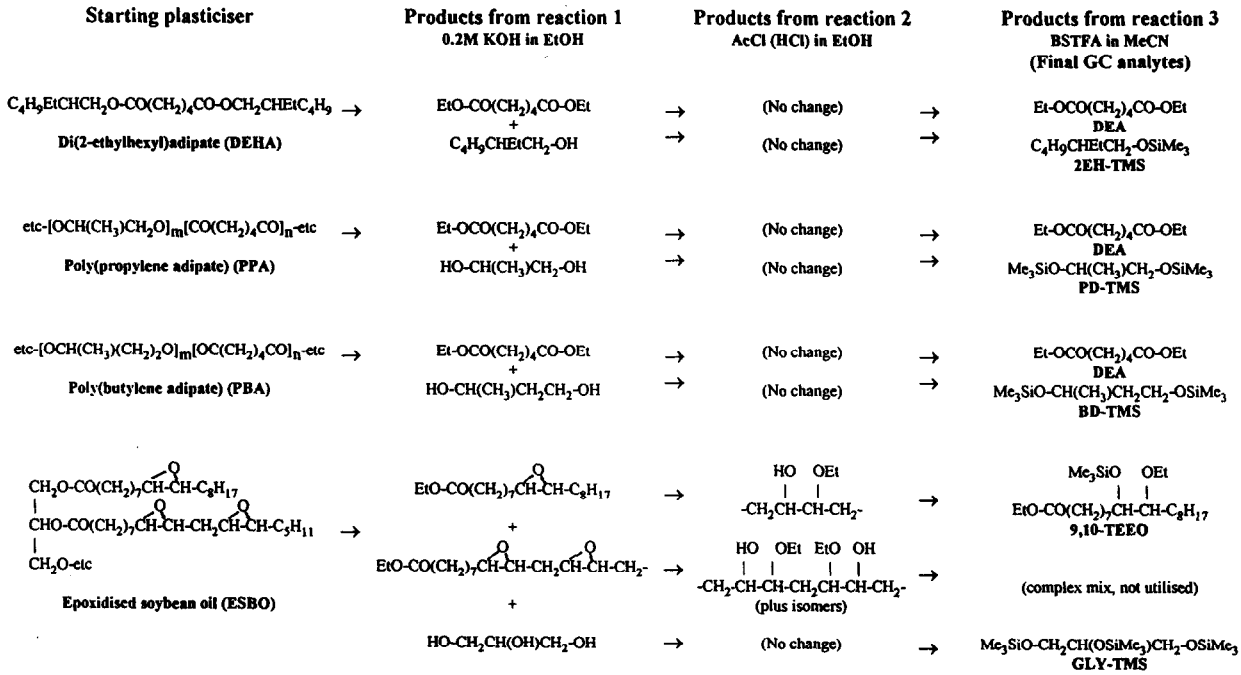

Fig. 1. Chemistry of analysis. DEA = Diethyladipate; 2EH-TMS = trimethylsilyl (TMS) derivative of 2-ethylhexanol; PD-TMS = TMS derivative of propane-1,2-diol; BD-TMS = TMS derivative of butane-1,3-diol; GLY-TMS = TMS derivative of glycerol; 9,10-TEEO = 9-trimethylsilyloxy-10-ethoxyethyl octadecanoate (and 10,9-isomer).

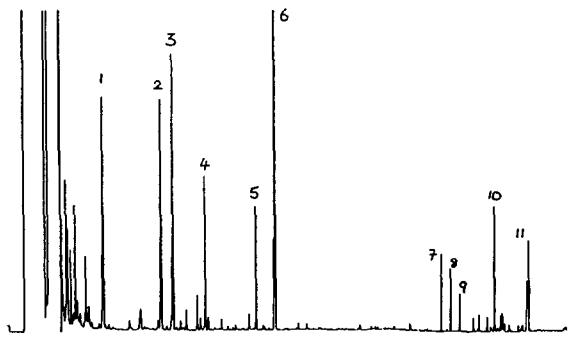

Fig. 2. GC trace of plasticiser standards taken through the method. Identification of peaks and the parent plasticisers: 1 = propane-1,2-diol-TMS from PPA; 2 = butane-1,3-diol-TMS from PBA; 3 = 2-ethylhexanol-TMS from DEHA; 4 = butane-1,4-diol-TMS internal standard; 5 = glycerol-TMS from ESBO and triheptadecanoin internal standard; 6 = diethyl adipate from DEHA, PPA and PBA; 7 = ethyl hexadecanoate from ESBO; 8 = ethyl heptadecanoate from triheptadecanoin internal standard; 9 = ethyl octadecanoate from ESBO; 10 = 9-trimethylsilyloxy-10-ethoxyethyl octadecanoate (and 10,9-isomer) from ESBO; 11 = complex products from diepoxide component of ESBO.

DEHA, PPA and PBA were the three main plasticisers encountered. If however the total yield of adipate did not tally as described above or if the chromatogram revealed the presence of phthalate, sebacate, azelate or citrate ethyl esters, for example, this served as an alert for the presence of alternative plasticisers such as di(2-ethylhexyl) phthalate, acetyl tributyl citrate, dioctyl azelate or dibutyl sebacate. These plasticisers are rarely found in PVC films for food contact but are used in certain other films, laminates, inks and varnishes [15, 16]. They can be quantified using the method described here with the appropriate standards.

3.3. Measurement of ESBO

The chromatogram in Fig. 2 shows a number of late-running peaks which are derived from ESBO and which were used to identify and quantify ESBO. GC–MS analysis identified ethyl hexadecanoate (peak 7) and ethyl octadecanoate (peak 9) derived from the saturated 16:0 and 18:0 fatty acids in ESBO. There were a number of other products identified by GC–MS and ascribed to the epoxy fatty acids in ESBO. The product of choice for determining ESBO was 9-trimethylsilyloxy,10-ethoxyethyl octadecanoate (TEEO, Fig. 1) derived from monoepoxy stearate (epoxidised oleate). The mass spectrum of this derivative showed no molecular ion but gave the expected [17] intense α-cleavage fragments at m/z 273 and 215 (base peaks) ascribed to positional isomers giving $[EtOOC(CH_2)_7CHOSiMe_3]^+$ and $[C_8H_{17}CHOSiMe_3]^+$ fragments from 9,10-TEEO and 10,9-TEEO respectively. These two isomers were the expected products arising from acid-catalysed attack of EtOH at the 10 and 9 carbons of the ESBO monoepoxy stearate (Fig. 1). The two isomers gave a single GC peak with good symmetry (peak 10). A number of closely related spectra were seen in the GC–MS analysis and these were attributed to positional and stereoisomeric forms of the derivatives from the diepoxy and triepoxy fatty acids in ESBO. These were less attractive for ESBO quantification because of their complexity (peaks 11, Fig. 2). This complexity was useful, however, as the characteristic fingerprint of peaks when expanded, served to confirm the presence of ESBO.

The fatty acid composition of soybean oil depends on source and cultivar. The 18:1 content can range from 14 to 35% [18] although a more typical 18:1 content is about 26% [19]. With this uncertainty, there is the possibility that only a semiquantitative calculation of ESBO can be made from the TEEO derivative unless the same ESBO as in the film is available as a calibration standard. Outside a manufacturer's own quality control laboratory this situation does not usually pertain. An alternative approach is to quantify ESBO via the TMS derivative of glycerol (Fig. 1). This should be done only if there is no evidence of triglycerides other than ESBO present in the plastic, and the triheptadecanoin internal standard should be omitted as it also yields glycerol. The butane-1,4-diol serves as the internal standard for glycerol.

3.4. Accuracy of the method

Results of analysis of film samples are shown in Table 1 along with information on plasticiser

Table 1
Comparison of results from the present method with known plasticiser levels

MFilm code	Composition as determined here (%, w/w)				Prior information (%, w/w)			
	DEHA	PPA	PBA	ESBO	DEHA	PPA	PBA	ESBO
Manufacturer A								
Film 1	18.3	<0.3	<0.3	7.8	17.6	na	na	7.3
Film 2	6.9	<0.3	7.4	3.8	10.2	na	na	na
Manufacturer B								
Film 3	<0.3	2.2	22.4	5.3	0	+	+	na
Film 4	24.0	<0.3	<0.3	6.7	+	0	0	+
Film 5	12.8	<0.3	2.4	5.7	na	na	na	na
Manufacturer C								
Film 6	9.8	5.7	2.4	7.8	10.0	9 (PPA + PBA)		8.0
Film 7	<0.3	21.7	<0.3	6.4	0	23 (PPA + PBA)		na
Film 8	12.0	5.0	<0.3	7.2	11.0	na	na	na

Levels as stated by the film manufacturer or determined in earlier studies using independent techniques. + = Stated as present by the manufacturer but no level revealed; na = no prior information available.

levels either supplied by the film manufacturers or obtained using alternative analytical methods [9–12]. There was good agreement in most cases indicating that the method presented here is reliable. The only major discrepancy was for film 2 where the manufacturer stated a DEHA content of 10.2% whereas our analysis indicated only 6.9%. Analysis by an independent technique [9] found 7% DEHA and so the manufacturer's figure appeared to be in error. For polymeric plasticiser analysis, the manufacturer of film 6 indicated a total polymeric content of 9% with both PPA and PBA used but gave no individual values. Analysis found 5.7% PPA and 2.4% PBA and so the total was very close to that expected. Similarly for film 7 where the manufacturer declared 23% polymeric plasticiser but did not state which type. PPA at 21.7% was found —again consistent with the declared composition.

For the determination of ESBO the agreement with the measured value and the expected value was good at 7.8 *versus* 7.3% and 7.8 *versus* 8% for films 1 and 6. The films had been supplied by two different manufacturers and the ESBO standard by a third manufacturer, at times separate by 2 or 3 years. This agreement between expected and found values suggests, therefore, that although the natural composition of soybean oil can vary quite markedly in principle, in practice the epoxy fatty acid composition of ESBO is rather consistent.

3.5. Precision and robustness of the method

In a survey of 170 films sold for home-use or used to package retail foodstuffs, every 10th film was analysed in triplicate. The precision of the method was in all cases ± 5% or better for DEHA, PPA, PBA and ESBO. The detailed results of this survey will be reported elsewhere. The limit of determination (LOD) was found to be about 0.3% (w/w) for each plasticiser in the films. The exact LOD value depended on the state of the film —some retail films had adhering food components and gave an LOD close to this 0.3% (w/w) figure while films sold on the roll for home-use were cleaner and had a lower LOD. The limiting factor in this LOD figure is dilution of the sample aliquot (5 μl) when reacted with BSTFA–MeCN (200 μl) according to Fig. 1. Since an additive below this 0.3% limit would serve almost no useful purpose as a plasticiser, the LOD figure is considered acceptable. The

lowest level of interest in practical terms is for ESBO in PVDC where a 1% level of the heat stabiliser would be typical [6].

In the aforementioned survey, the 170 film samples, along with replicates and calibration standards, were analysed without difficulties. A single capillary GC column was employed without any evidence of build-up of column residues. The whole procedure takes about 29 h but this is largely time required for the derivatisation and the method is not labour intensive. With the accuracy, precision and robustness thus established, it is considered that the combined method proposed here is suitable for general use and offers considerable time savings over the individual methods available to date.

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