Influence of the Glycol Component in Dibenzoate Plasticizers on the Properties of Plasticized PVC Films

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ABSTRACT: A series of glycol dibenzoates was synthesized by transesterification of glycols with methyl benzoate. PVC films were prepared from suspension grade PVC and the dibenzoates at a constant content of the dibenzoates. The mechanical properties of the films were measured. In addition, the extractability and the absorption of various liquids was determined. The effect of the structure of the glycol component in the dibenzoates on the mechanical properties of the films and the plasticizing efficiency was investigated. Neopentyl glycol dibenzoate exhibits the highest plasticizing effect, followed by triethylene and ethylene glycol dibenzoates and the 2-(*n*-butyl)-2-ethyl-1,3-propanediol derivative. It was found that the ether linkages in the dibenzoates mainly contribute to the plasticization of PVC. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 822–824, 2005

INTRODUCTION

Phthalic acid esters, in particular di(2-ethylhexyl)phthalate, which are the most used plasticizers for poly(vinyl chloride) (PVC), are suspected of being toxic. In some applications, like articles from plasticized PVC, being in contact with blood or with the skin of babies, the use of phthalate plasticizers is forbidden.

Thus, benzoic acid esters have been proposed. A broad range of benzoates is marketed by Velsicol Chemical Corp. under the trade name "Benzoflex."[1–4] These products are particularly suitable as plasticizers for PVC. Other applications have also been mentioned, namely plasticization of urethane elastomers, poly(vinyl acetate)-based latex and hotmelt adhesives, and sealants from polyacrylates and vinyl/acrylate copolymers.

Most benzoates being offered by Velsicol Chem. Corp. are liquid glycol dibenzoates and mixtures of glycol dibenzoates. A low-viscosity monobenzoate, isodecyl benzoate Benzoflex B-131, is an exception. As the glycol components in the dibenzoates, the following diols have been listed: 1,2-propylene, diethylene, dipropylene, and triethylene glycol, and 2,2,4-trimethyl-1,3-pentanediol. Velsicol stresses the suitability of Benzoflex 2888 (a mixture of diethylene, triethylene, and dipropylene glycol dibenzoates) as a plasticizer for PVC toys.

Benzoflex 2888 has the following advantages in comparison with diisononyl phthalate (DINP): accelerated melting, excellent staining resistance, high UV resistance, faint odor, low emission of volatile organic compounds, excellent processing characteristics, and high efficiency.

In a recently published paper, the low toxicity of benzoate plasticizers was stressed.[5]

It seemed to us to be purposeful to evaluate the effect of the glycol component in dibenzoate plasticizers for PVC on the properties of plasticized PVC in a systematic way and to determine the structure–properties relationships.

RESULTS AND CONCLUSIONS

We synthesized the individual dibenzoates in a laboratory scale by the transesterification of glycols with commercial methyl benzoate. The volatile side products were distilled off *in vacuo*.

A list of the investigated dibenzoates comprising the structural elements thereof is given in Table I. The number of the following structural elements: aromatic rings, ester and ether bonds, and carbon atoms in aliphatic chains, neopentyl structures, and side groups, as well is presented.

The most important measuring results, namely the tensile strength, the stress at 100% elongation, elongation at break in tensile test, and Shore D hardness of the plasticized PVC films are set down in Table II.

The plasticizers are put into sequence in Table III relating to the plasticizing and flexibilizing efficiency,

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TABLE I
The Synthesized Glycol Dibenzoates

Glycol component	Structural elements			
	Benzene rings	Ester bonds	Ether bonds	Carbon atoms in the aliphatic chains, central neopentyl structures, and side groups
A. Ethylene glycol	2	2	—	2
B. Diethylene glycol	2	2	1	4
C. Triethylene glycol	2	2	2	6
D. 1,2-Propylene glycol	2	2	—	3
E. Dipropylene glycol	2	2	1	6
F. 1,3-Propylene glycol	2	2	—	3
G. 2-Methyl-1,3-propanediol	2	2	—	4
H. Neopentyl glycol	2	2	—	5
I. 2-(n-Butyl)-2-ethyl-1,3-propanediol (BEPD)	2	2	—	9
J. Di(n-butyl)phthalate (DBP)	1	2	—	8
K. Di(2-ethylhexyl)phthalate (DOP)	1	2	—	16
L. Di(undecyl)phthalate (DUDP)	1	2	—	22

according to the results given in Table II. In Table III, the sequence of plasticizers is set in such a way that the elongation at break decreases from the left to the right, whereas the other values increase.

The structure and the plasticizing efficiency of individual plasticizers are compared in Tables II and III, respectively. It can be seen that the mechanical properties are affected by the glycol component in the dibenzoates. That relationship concerns all four investigated mechanical properties. Neopentyl glycol dibenzoate exhibits, in general, the highest plasticizing efficiency. Then follow triethylene glycol, ethylene glycol, and BEPD dibenzoates.

The plasticizing efficiency can be evaluated taking into account the flexibility of films. The values of tensile strength, Shore hardness. and elongation at break (the last values in "reverse" direction) show the highest flexibility trend. However, the stress (at 100% elongation) values show some irregularities as far as certain plasticizers are concerned.

Ether bonds in the glycol component, in particular in the triethylene glycol units, are the strongest flexi-

TABLE II
Mechanical Properties of Plasticized PVC Film

Plasticizer (see Table I)	Tensile strength (MPa)	Stress at 100% elongation in tensile test (MPa)	Elongation at break (%)	Shore D hardness
A	23.4	9.5	303	36.3
B	24.3	7.9	371	31.6
C	23.6	10.9	328	36.0
D	24.0	9.3	315	37.8
E	22.7	8.0	352	31.1
F	20.6	7.5	322	31.5
G	22.0	7.5	339	29.7
H	24.6	10.6	302	40.8
I	23.3	10.3	339	29.7
K	17.7	6.0	386	30.2

TABLE III
Sequence of Plasticizers, After the Increase in Plasticizing Efficiency and in Flexibilizing Efficiency

	1	2	3	4	5	6	7	8	9	10
After tensile strength	H	B	D	C	A	I	E	G	F	K
After stress at 100% elongation in tensile test	C	H	I	A	D	E	B	G	F	K
After elongation at break	H	A	D	I	F	C	G	E	B	K
After Shore D hardness	H	D	I	A	C	B	F	E	K	G

TABLE IV
Weight Change (+Absorption/−Extraction) of Plasticized PVC Film Samples

Dibenzoate (see Table I)	Water	Ethanol	Motor oil	Gasoline with ethanol added
A	+0.08	−0.25	−0.47	−0.80
B	−0.70	−0.20	−0.71	−1.05
C	+3.00	−0.26	−0.92	−0.94
D	−0.04	+0.95	−0.10	+0.40
E	−0.20	+1.12	−0.21	+1.56
F	+0.02	−0.07	−0.15	−0.63
G	−0.05	+0.19	−0.15	+0.46
H	+0.02	+1.22	−0.47	+1.81
I	+0.02	+2.91	−0.40	+8.20
K (DOP)	+0.01	+2.64	−2.07	−9.09

bilizing elements. The increased flexibilizing efficiency is, moreover, reached in the way that the high content of polar groups like ester bonds is compensated by incorporation of unpolar hydrocarbon units, for example, in neopentyl glycol or BEPD.

It is understood that the plasticizing efficiency of plasticizers depends on the ratio of particular components in the molecule, namely of polar groups (esters and ethers), unpolar polarizable groups (benzene rings), and unpolar nonpolarizable groups (alkyls and alkylene chains).

The corresponding information about the structure of glycol dibenzoate plasticizers is given in Table I. The structures were compared with the structure of the commercially used phthalate plasticizers. It can be seen that the relative content of unpolar groups in almost all dibenzoates is much lower than in the phthalic esters. However, the relative content of polar ester bonds and polarizable unpolar aromatic cycles in higher. Some dibenzoates contain, moreover, a fraction of the ether bonds.

The mechanical properties of plasticized PVC films are presented in Table II. All tested films had the same composition: 100 wt. parts PVC, 45 wt. Plasticizer, and 4 wt. parts dibasic lead phthalate.

There is a correlation between the values of mechanical properties: higher Shore hardness and higher tensile strength values correspond in general to lower elongation at break. However, in the tensile test, a lower stress at 100% elongation corresponds mostly to lower tensile strength and lower Shore hardness. The relationships have rather an approximate character.

The measurement results of extraction and absorption on soaking in various polar (water, ethanol) and unpolar (motor oil, gasoline) liquids are given in Table IV. The PVC film plasticized with the highly polar triethylene glycol dibenzoate exhibits the highest water absorption. This phenomenon could obviously be expected. The highest extraction values of PVC film plasticized with diethylene glycol dibenzoate are hardly possible to explain. The highest ethanol absorption values of the PVC films plasticized with BEPD, neopentyl glycol, and 1,2-propylene glycol dibenzoates comport with the branched unpolar structure of the glycol component.

The DOP plasticized PVC film exhibited the highest extraction values in ethanol.

All dibenzoates are better than DOP, as far as behavior in unpolar liquids (motor oil, gasoline) is concerned, the difference being particularly distinct. High extraction values in ethanol containing gasoline of BEPD dibenzoate plasticized PVC films are noteworthy. This phenomenon results assumedly from the effect of the unpolar BEPD component.

Similar investigations of mechanical properties were performed for a series of polyester plasticizers for PVC at a constant plastification degree.[6]

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