Note

Compatibility with Freon 11 of Oligoesteralcohols Synthesized from Waste Products from the Production of Dimethylterephthalate

INTRODUCTION

Oligoesteralcohols, employed in the preparation of polyurethane foams, can be synthesized by the preesterification of hydroxyl-containing compounds with the waste products obtained in the production of dimethylterephthalate.[1] The latter represents a mixture of diphenyltricarbonic, diphenyldicarbonic, and aromatic monocarbonic acids. The homogeneity of component A is of utmost importance for the normal reaction between the hydroxyl and the isocyanate groups during the synthesis of polyurethane-foams. The homogeneity is reduced by the low compatibility of the polyols based on polyester with freon 11.[2]

It is the aim of this paper to investigate the effect of the oligoesteralcohol structure on its compatibility with freon 11.

EXPERIMENTAL

Starting compounds: Oligoesteralcohols synthesized with the waste products from the production of dimethylterephthalate;[1] polyethyleneglycol with a molecular mass of 200 (commercial product); ethylene glycol, a commercial product; tris(β-chlorethyl) phosphate from "Bayer," FRG; freon 11, a commercial product; phosphorus-containing fire retardants.

Description of the Compatibility Test[3]

Add in portions of 0.5–1 g freon 11 to 20 $\mp$ 0.1 g of the oligoesteralcohol in a 100-mL beaker. Stir carefully after each portion of freon 11 so that only a small amount of air is introduced in the mixture. The weight ratio of freon 11 to oligoesteralcohol at which fine droplets of freon 11 become visible is critical for the mixture under study. The evaporation of freon 11 during the test should be accounted for by frequent control of the total weight of the mixture. The variation is followed for 24 hr at 20°C.

The viscosity was measured by a Brookfield LVT viscometer at 20°C. The dielectric constants were determined by a dielcometer GK at 7000 Hz and 20 $\mp$ 0.1°C.

RESULTS AND DISCUSSION

The use of polyesteralcohols in the synthesis of polyurethane foams is limited by their comparatively high viscosity as well as by their low compatibility with freon 11. The compatibility between different compounds is better when the components have similar dielectric constants.[4] However, as seen in Table I, the dielectric constants of the oligoesteralcohols synthesized with the waste products from the production of dimethylterephthalate are substantially higher than that of freon 11, which is only 2.3 at 20°C, and consequently only a low compatibility is to be expected.

The compatibility of two or more components can be improved[5,6] by the addition of definite kinds of low-molecular compounds. Thus, the compatibility of oligoesteralcohols with freon 11 is enhanced by the introduction of tris(β-chlorethyl)phosphate.

Because of the high viscosity of the oligoesteralcohols, we determined first the compatibility limits of oligoesteralcohols in mixtures containing various amounts of tris(β-chlorethyl) phosphate. Thereafter the compatibility of the pure oligoesteralcohols with freon 11 was evaluated by extrapolation.

The compatibility ratio of oligoesteralcohol no. 1 (Table I) is only 0.23 (Fig. 1, curve 1). This low value is probably associated with the high concentration of diethyleneglycol in the oligoesteralcohol. Low-molecular diols such as ethyleneglycol and diethyleneglycol[7] have a low compatibility ratio.

Journal of Applied Polymer Science, Vol. 28, 431–435 (1983)
 CCC 0021-8995/83/010431-05$01.50

TABLE I
Characteristics of Oligoesteralcohols, Synthesized from Waste Products in Production of Dimethylterephthalate

No.	Starting compounds	Molar ratios	Hydroxyl number, (mg KOH/g)	Viscosity at 20°C (cP)	Dielectric constant ϵ at 20°C	Compatibility at 20°C (g freon 11/g OEA[a])
1	Waste product: diethyleneglycol:trimethylolpropane	1:2.5:0.75	455	900	23.4	0.23
2	Waste product: diethyleneglycol:trimethylolpropane	1:1:1.5	435	308,000	22.1	0.26
3	Waste product:tall oil fatty acids: diethyleneglycol:trimethylolpropane	1:0.12:1:1.5	400	42,000	21.8	0.29
4	Waste product: diethyleneglycol:triethanolamine	1:2.5:1	450	306,000	21.4	0.28

[a] OEA = oligoesteralcohol.

The investigations of Fuchs[6] have revealed that diols with a side alkyl radical possess a high compatibility with freon 11. In order to improve the compatibility of the oligoesteralcohols, we prepared oligoesteralcohol no. 2 (Table I) with a lower content of diethyleneglycol and a higher content of trimethylolpropane. The compatibility (Fig. 1, curve 2) is higher than that of oligoesteralcohol No. 1. This improvement is attributed to the increased content of side chains in the molecule of oligoesteralcohol no. 2, inasmuch as the dielectric constants of no. 1 and no. 2 are very similar. The higher content of side chains lowers the molecular interaction, making it possible for the freon 11 molecules to be inserted more easily between the separated chains of oligoesteralcohol No. 2.

The introduction of tall oil fatty acids in the macromolecule of the oligoesteralcohols can considerably improve their compatibility with freon 11.[2] This finding was corroborated by our own experiments which revealed that oligoesteralcohol no. 3, containing tall oil fatty acids, shows a better compatibility than the previous two. This effect is attributed to the high compatibility of the tall oil fatty acids with various compounds.[8]

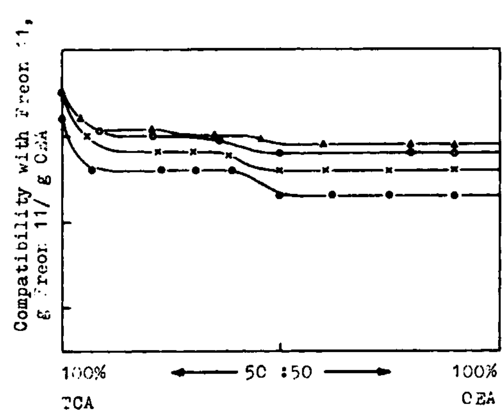


Fig. 1. Dependence of the compatibility with freon 11 of the mixture tris(β-chlorethyl)phosphate (TCA)–oligoesteralcohol on the ratio between TCA and oligoesteralcohol: (1, ●) oligoesteralcohol no. 1; (2, ×) oligoesteralcohol no. 2; (3, ▲) oligoesteralcohol no. 3; (4, O) oligoesteralcohol no. 4 (the numeration of the oligoesteralcohols corresponds to that in Table I).

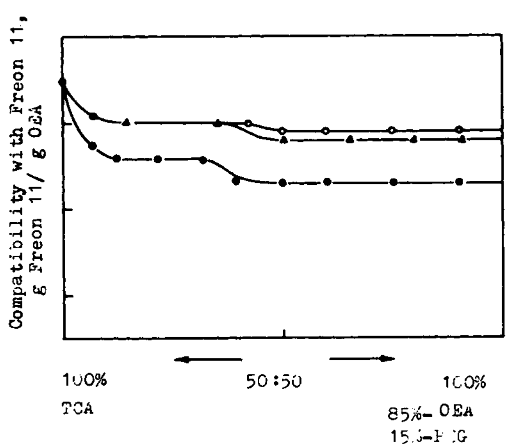
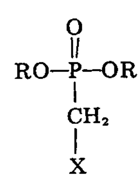


Fig. 2. Dependence of the compatibility with freon 11 of the mixture of tris(β-chlorethyl)phosphate (TCA)–oligoesteralcohol, containing 15% low-molecular poly(ethylene glycol) (PEG) on the ratio between TCA and oligoesteralcohol with 15% low-molecular poly(ethylene glycol (PEG): (1, ●) oligoesteralcohol no. 1, (2, O) oligoesteralcohol no. 2; (3 O) oligoesteralcohol no. 3; (4, ▲) oligoesteralcohol no. 4 (the numeration of the oligoesteralcohols corresponds to that in Table I).

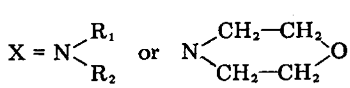
In order to enhance the rate of interaction between the hydroxyl and the isocyanate groups part of the aliphatic glycols were substituted by nitrogen-containing diols or triols, e.g., triethanolamine. Thus oligoesteralcohol no. 4 has the best compatibility, 0.28, as compared with all the rest of the oligoesteralcohols studied (Fig. 1, curve 4).

The physicomechanical properties of polyurethane foams can be improved by the addition of low-molecular polyesters to component A. The compatibility test of freon 11 with the mixture oligoesteralcohol–low-molecular polyol revealed that the introduction of 15% polyethyleneglycol in oligoesteralcohol no. 1 does not alter its compatibility with freon 11 (Fig. 2, curve 1), while the addition of the same amount of polyethyleneglycol to oligoesteralcohol no. 2 improved the compatibility of the latter (Fig. 2, curve 2). As assumed by Gommen et al.,[2] this effect is related to the solvation of the polar ester groups by the low-molecular polyethers. This leads to a reduction of the interaction between the molecules of the oligoesteralcohols and, consequently, to an improvement in the compatibility ratio of the mixture. This is not the case with oligoesteralcohol no. 1, since here the free diethyleneglycol suppresses the effect of the low-molecular polyethyleneglycol. The introduction of the low-molecular polyethyleneglycol in oligoesteralcohols no. 3 and 4 does not affect their compatibility with freon 11 (Fig. 2, curves 3, 4). In these two cases it may be assumed that the effect of the introduction of polyethyleneglycol is lower than that of the tall oil fatty acids of triethanolamine.

The combustion resistance of polyurethanes can be enhanced by the addition of phosphorus, or phosphorus- and chlorine-containing fire retardants. The introduction of the latter in the oligoesteralcohols necessitates the study of their influence on the compatibility of the mixture with freon 11. Both reactive and nonreactive fire retardants can be used. The structure of the nonreactive fire retardant used here is the following:



where



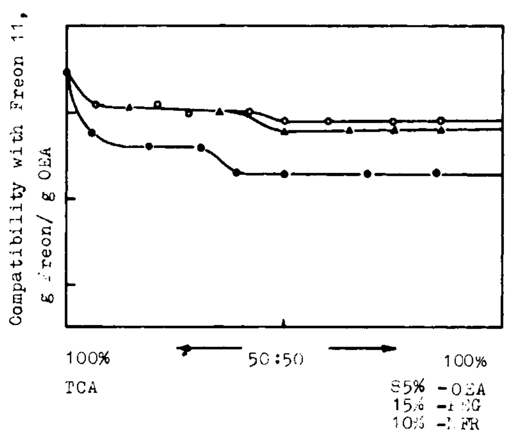


Fig. 3. Dependence of the compatibility with freon 11 of the mixture tris(β-chlorethyl)phosphate (TCA)–oligoesteralcohol, containing 15% low-molecular poly(ethylene glycol)(PEG) and 10% nonreactive fire retardants (NFR): (1, ●) oligoesteralcohol no. 1; (2, O) oligoesteralcohol no. 2; (3, O) oligoesteralcohol no. 3; (4, ▲) oligoesteralcohol no. 4 (the numeration of the oligoesteralcohols corresponds to that in Table I).

Their introduction into a mixture of oligoesteralcohol no. 1-low-molecular polyol up to 10% has no effect on either the compatibility with freon 11 (Fig. 3, curve 1) or the mixtures of oligoesteralcohols nos. 2, 3, and 4 (Fig. 3, curves 2, 3, and 4).

The use of reactive fire retardants having a structure

$$(OHCH_2CH_2)_3\overset{+}{N}H\bar{O}\underset{\displaystyle OR}{\underset{|}{P}}OCH_2CH_2OCH_2O\underset{\displaystyle OR}{\underset{|}{P}}\bar{O}H\overset{+}{N}(CH_2CH_2OH)_3$$

where R = CH_3 or CH_2CH_2Cl, reduces the compatibility of all the oligoesteralcohols studied (Fig. 4, curves 1–4). The deterioration is proportional to the content of the fire retardant introduced. The decrease in the compatibility is probably due to the saltlike character of the fire retardant, which raises the level of molecular interaction.

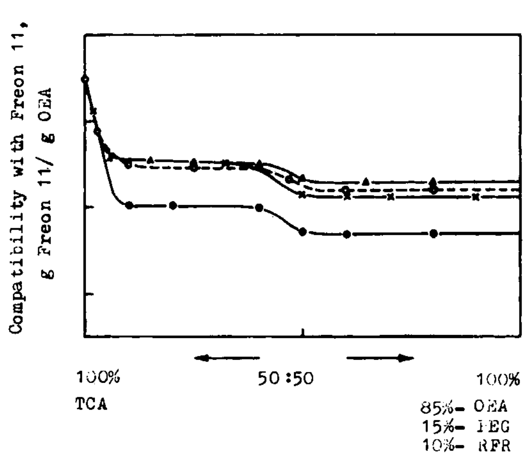


Fig. 4. Dependence of the compatibility with freon 11 of the mixture tris(β-chlorethyl)phosphate (TCA)—oligoesteralcohol, containing 15% low-molecular poly(ethylene glycol)(PEG) and 10% reactive fire retardants (RFR): (1, ●) oligoesteralcohol no. 1; (2, ×) oligoesteralcohol no. 2; (3, ▲) oligoesteralcohol no. 3; (4, O) oligoesteralcohol no. 4 (the numeration of the oligoesteralcohols corresponds to that in Table I).

An enhancement of the compatibility with freon 11 of oligoesteralcohols, synthesized from the waste products in the production of dimethylterephthalate can be achieved either by the introduction of tris(β-chlorethyl)phosphate or by insertion of tall oil fatty acids or nitrogen-containing alcohols in the chain of the oligoesteralcohol.

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Received April 12, 1982
Accepted July 23, 1982