Crosslinking of Unsaturated Polyester Resins by Combinations of Vinyl Esters and Methacrylates

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Synopsis

The replacement of styrene by other crosslinking monomers in unsaturated polyester resins has been investigated because of the possible toxicity of this monomer and the strong smoke evolution of burning polyester materials. A theoretical study has been carried out to provide criteria for the applicability of classes of monomers in polyester curing. From this study it appeared that vinyl esters, vinyl ethers, N-vinyl lactams, and styrenes are suitable, whereas acrylic and methacrylic esters and allylic or olefinic compounds are not. Combinations of vinyl esters and (meth)acrylic esters of polyols should generate IPN-like structures. Polyesters cured by this combination of monomers gave materials with increased stiffness and strength relative to those obtained with the separate monomers and on the same level as styrene-cured polyesters.

INTRODUCTION

Styrene monomer is used for the crosslinking of unsaturated polyesters for over 30 years.[1,2] In recent years two problems have risen concerning the use of styrene. First, the toxicity of the monomer may be a possible threat to the health of workers in the polyester processing industries.[3] Secondly, the strong smoke evolution which occurs when styrene-cured polyesters are subjected to fire conditions[4] forms a serious limitation in the application of these materials in buildings.

Several solutions to both problems have been suggested, e.g., the use of waxes which might reduce styrene evaporation and the addition of smoke suppressing compounds. These methods have shortcomings and are not generally applicable. An alternative solution would be the total replacement of styrene by another monomer lacking the inherent disadvantages of styrene, whereas the original favorable properties of both uncured and cured resins should be retained as much as possible.

The use of other monomers than styrene is not unknown.[1,2,5,6] However, the attention has been focused either on the toxicity or the smoke problem, so that most alternative monomers which have been proposed are either "cleanburning" but volatile and/or toxic, e.g., methyl methacrylate,[6] or nonvolatile but not applicable in room-temperature curing techniques, e.g., allyl monomers.[1,2]

In this paper the problem of monomer selection for styrene replacement is first approached from copolymerization theory. Practical limitations as dictated by the processing conditions are considered next. Finally the experimental results with a monomer system resulting from this study are presented and discussed.

MONOMER SELECTION

Theoretical Aspects

The crosslinking of unsaturated polyester resins is equivalent to the copolymerization of the fumarate groups in the polyester molecule with the added monomer. Several studies[7,8] suggest that this crosslinking reaction can be described with copolymerization parameters of low-molecular fumarate esters, e.g., diethyl fumarate.

Representative values of the reactivity ratios for the diethyl fumarate (1) and styrene (2) copolymerization are $r_1 = 0.005 \pm 0.005$ and $r_2 = 0.35 \pm 0.02$.[9] As both r values are smaller than 1, the system possesses an azeotropic point, at which the mole fraction of fumarate is $f_1 = F_1 = 0.40 \pm 0.01$.

From the literature[10,11] it appears that styrene-containing unsaturated polyester resins with approximately the azeotropic composition show an optimum in their mechanical properties, which may be accounted for by the maximum in crosslinking density occurring at the azeotropic point.

For the replacement of styrene it seems desirable to have a monomer which can also form an azeotropic pair in its copolymerization with fumarate. The conditions for azeotropy are $r_1 < 1$ and $r_2 < 1$. As the number of published r values of fumarate copolymerizations is small, we have to resort to the Q–e approximation.[12] When fumarate is taken as monomer 1, the conditions for azeotropy can be written as

$$r_1 = (Q_1/Q_2) \exp[-e_1(e_1 - e_2)] < 1 \tag{1}$$

$$r_2 = (Q_2/Q_1) \exp[-e_2(e_2 - e_1)] < 1 \tag{2}$$

from which follows for monomer 2

$$\ln Q_2 > e_1 e_2 - e_1^2 + \ln Q_1 \tag{3}$$

$$\ln Q_2 < e_2^2 - e_1 e_2 + \ln Q_1 \tag{4}$$

The graphic representation of eqs. (3) and (4) with monomer 1 as the reference monomer is given in Figure 1. The monomers for which Q_2 and e_2 are lying in the shaded areas meet the conditions for azeotropy.

To apply these considerations to the selection of monomers for the curing of unsaturated polyesters, the values of Q_1 and e_1 for fumarate copolymerization should be substituted in eqs. (3) and (4). The graphic representation of these equations after substitution of $Q_1 = 0.61$, $e_1 = 1.25$ for diethyl fumarate[13] is given in Figure 2. In this figure the loci of the Q,e values of a number of classes of monomers are also indicated. From their position with respect to the boundaries (see Fig. 1) it can be concluded that vinyl esters, vinyl ethers, N-vinyl lactams, and styrenes fulfill the conditions for azeotropy with fumarate, contrarily to acrylic and methacrylic esters and allylic and olefinic compounds.

Monomer Combinations

Appropriate copolymerization behavior is not the only condition to which a styrene-replacing monomer must answer. Unfavorable qualities of monomers, e.g., in the mechanical properties of their copolymers (such as internal plastification), may be compensated for by using combinations of monomers.
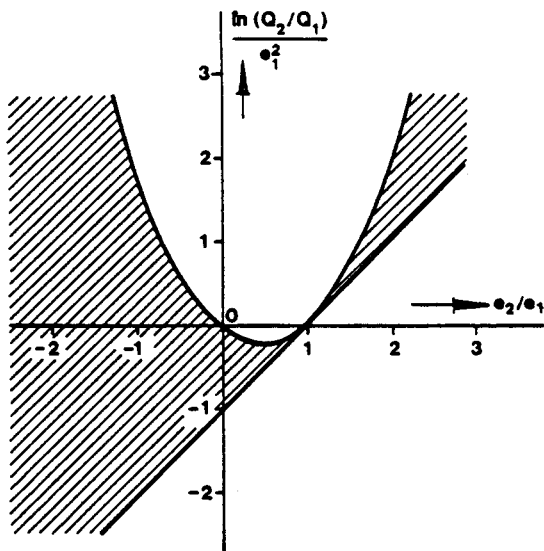
Fig. 1. General conditions for azeotropic copolymerization with a monomer with Q_1, e_1. The normalized Q_2, e_2 values of the second monomer must lie in the shaded areas.

A particularly interesting combination would be a mixture of two monomers giving little mutual copolymerization (e.g., a vinyl ester and a methacrylate), while only one of the monomers (in this example the vinyl ester) would copolymerize with the fumarate groups of the polyester (see Fig. 3). When a methacrylic ester of a polyol is used in this combination, two more or less independent networks will be formed. This is analogous to the formation of interpenetrating polymer networks (IPN's) by simultaneous polymerization of a monomer mixture through two distinct types of polymerization.[14]

The results of crosslinking an unsaturated polyester with the above-mentioned combination of monomers are reported in this paper.
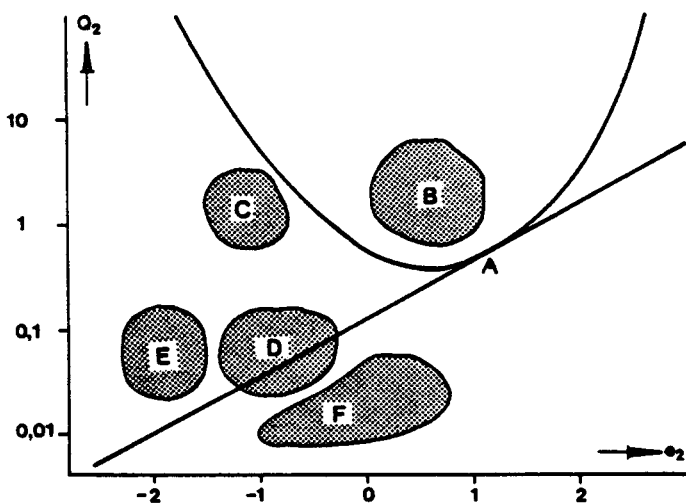

Fig. 2. Copolymerization with diethyl fumarate (A): (B) acrylates and methacrylates; (C) styrene and derivatives; (D) vinyl esters; (E) vinyl ethers and vinyl lactams; (F) allylic and olefinic monomers. Q and e values from Young.[13]
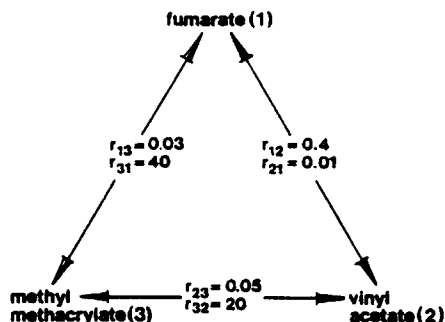
Fig. 3. Reactivity ratios for copolymerization of diethyl fumarate, vinyl acetate, and methyl methacrylate.[13]

Practical Considerations

In addition to the ability to copolymerize with the unsaturated polyester, a styrene-replacing monomer or mixture of monomers should meet a number of conditions dictated by the practice of polyester processing. The monomer should be miscible with the polyester, and the resulting solution must have a low viscosity. Both these requirements can be met by a suitable choice of monomer and by modification of the polyester.

The monomer must have a low vapor pressure and be nontoxic. Nonaromatic monomers are to be preferred, as aromatic groups contribute to the smoke development.[4]

EXPERIMENTAL

Monomers and Polyesters

Vinyl versatate (VeoVa 10, Shell) was used as main vinyl ester. This product consists of a mixture of vinyl esters of branched synthetic carboxylic acids with 10 carbon atoms. At the α-C atom there are one methyl and two alkyl groups.[15] The atmospheric boiling point of the mixture is 210°C, while the vapor pressure at 20°C is 53 Pa.[15] It is considered to be of low toxicity (Shell Chemical Co., private communication).

As methacrylic ester ethylene glycol dimethacrylate (Merck) was used. This monomer has an atmospheric boiling point of 240°C, while the vapor pressure at 20°C is less than 2 Pa (communicated by Rohm and Haas Co.). Other chemicals were of laboratory grade.

Unsaturated polyesters were prepared by conventional polycondensation reactions.[2] The solubility of the polyesters in some of the monomer mixtures was greatly improved by using less polar and/or monofunctional components in the polycondensation mixture. The polyesters were stabilized with 140 ppm by weight of hydroquinone. Details of the polyester preparation are given in Table I.

TABLE I
Polyester Preparation

Polyester no.	Alcohols (molar ratio)	Diacids (molar ratio)	OH/COOH (molar ratio)	Acid no. (mg KOH/g)
1	Propylene glycol, diethylene glycol (3/1)	Phthalic anhydride, maleic anhydride (4/6)	1.05	37
2	Neopentyl glycol	Isophthalic acid, maleic anhydride (4/6)	1.05	15
3	Neopentyl glycol, n-decanol (95/5)[a]	Terephthalic acid, maleic hydride (4/6)	1.05	—[b]

[a] On hydroxyl basis.
[b] Not determined because of modification with monofunctional compound.

Polyester Curing

The polyesters were dissolved in the appropriate quantity of monomer, and subsequently cured using two different procedures. In procedure A, 0.35 mL of a solution of cobalt(II)octoate in dioctyl phthalate (containing 1% by weight of cobalt) were added to 100 g of resin, followed by 1.4 mL of a 50% solution of methyl ethyl ketone peroxide in dimethyl phthalate (Butanox M50, Akzo Chemie). The solution was poured in poly(ethylene) molds measuring 15 × 15 × 0.3 cm^3 which were open only at one narrow side. The molds were kept at room temperature for 24 h, at 60°C for 24 h, and at 100°C for another 24 h. In procedure B, 100 g of polyester resin were cured by adding 0.44 mL of a solution of vanadyl acetyl acetonate in dimethyl phthalate (containing 0.3% of vanadium), 0.67 mL of acetyl acetone, and 1.4 mL of the afore-mentioned peroxide solution. The molds were kept at room temperature for 24 h, at 60°C for 24 h, and at 80°C for 24 h.

Testing Procedures

For mechanical and smoke tests the polyester plates were sawed with a water-cooled diamond saw. Impact strength according to the Charpy method (ISO R 179) and flexural properties (according to ASTM D 790, deformation rate 1.5 cm/min) were determined with samples of 6.35 × 1.27 cm^2. Smoke density was measured with samples of 15.0 × 0.65 cm^2 in a Stanton-Redcroft Smoke Density Unit. All samples had a thickness of 0.3 cm.

For determination of the unconverted polyester and monomer contents, the cured materials were ground after cooling with liquid nitrogen. Extractions were carried out in a Soxhlet apparatus with boiling acetone for 48 h. The polyester in the extract was determined by weighing of the residue after evaporation of the solvent. Residual monomers in the extract were determined by gas chromatography.

TABLE II
Properties of Cured Polyesters

Polyester[a]	Monomers[b] (%)[c]	Unconverted polyester (%)[d]	Flexural modulus (MPa)	Deflection at rupture (%)	Flexural strength at rupture (MPa)	Impact strength (kJ/m²)
1	Styrene (38)	9.5	4070	4.2	140	4.5
1	VP (31)	7.7	3300	—[e]	—[e]	1.8
1	GDMA (35)	21.2	1600	2.7	38	1.4
1	GDMA/VP (17/18)	7.5	4200	2.2	72	4.8
2	Styrene (40)	4.5	3640	4.3	142	6.5
2	GDMA (40)	16.8	—[e]	—[e]	—[e]	—[e]
2	GDMA/VV (20/20)	6.3	3320	4.0	107	10.4
3	Styrene (40)	3.8	2940	4.5	107	3.8
3	VV (40)	2.1	1590	4.0	50	5.3
3	GDMA (40)	16.9	2300	3.2	59	4.2
3	GDMA/VV (20/20)	3.5	2740	3.7	86	6.9

[a] Polyesters 1 and 2 cured by method A (see text); polyester 3 by method B.
[b] VP: vinyl propionate, GDMA:ethylene glycol dimethacrylate, VV: vinyl versatate.
[c] % by weight of monomers + polyester.
[d] % by weight of polyester.
[e] Sample is too brittle for the measurement.

RESULTS AND DISCUSSION

Mechanical properties and other characteristics of the cured materials are summarized in Table II. Monomer conversions were always more than 99%. Smoke densities of all styrene-cured polyesters were 0.50 ± 0.05 (expressed as optical density per gram of combusted material); with the other monomers the smoke density was 0.21 ± 0.02.

From Table II it appears that neither curing with vinyl esters nor curing with methacrylates gives mechanical properties comparable to curing with styrene. The combination of both types of monomers, however, shows a synergistic effect both on stiffness and toughness of the materials, which are on the same level as the styrene-cured polyesters, or in some cases even better.

The results of the extractions are consistent with the previous considerations on copolymerization: the azeotrope-forming monomers (styrene and vinyl esters) give low extraction yields, while crosslinking with methacrylate leaves a higher quantity of unconverted polyester in the material.

The synergistic effect of vinyl ester plus methacrylate on the flexural modulus might be explained as follows. The vinyl ester crosslinking yields a dense network, which is, however, internally plasticized by the side chains of the vinyl ester: the homopolymer of vinyl versatate has a T_g of $-3°C$.[15] The polymerization of the methacrylate/polyester combination gives rise to a dense and stiff network of methacylate homopolymer. As only a part of the polyester is crosslinked by the methacrylate, there remains a residue of unconverted polyester which acts as a plasticizer. The combination of both monomers gives a material containing only a small quantity of free polyester (due to the copolymerization with the vinyl ester) and having a stiffness which is due to the intrinsic stiffness of the methacrylate polymer.

The combination of vinyl ester and dimathacrylate might lead to an IPN-like structure, as explained above. From torsion pendulum measurements (unpublished results) we found no indication of separate glass and rubber phases. Phase separation should have lead to a greater increase in impact strength than observed. An explanation of the increased toughness should rather be found in a larger number of entanglements in the crosslinked structure.[16]

With regard to the problems related to the use of styrene as formulated in the Introduction, we have indicated in this paper that there may be a solution in the form of a monomer systems which lacks the disadvantages of toxicity, relative high vapor pressure, and smoke development inherent to styrene. For practical application much developmental work is still necessary, not only on the monomer side but also on the polyester. Work in this direction is in progress.

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