Synthesis of New Free-Radical Initiators for Polymerization

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ABSTRACT: Synthesis and properties of new initiating systems formed from commercially available ketones, glycols, and hydrogen peroxide (60%) are presented. In preparation of free radical initiators methyl ethyl ketone, which was oxidized by hydrogen peroxide, was used. Reaction was carried out in etanodiol or 1,4-butanodiol as diluent. The obtained initiators with cobalt octoate as a promotor were applied for crosslinking of the commercially available unsaturated polyester resin. Properties of the resin were compared with those obtained while it was hardened by the typical curing system containing methyl ethyl ketone hydroperoxide and cobalt octoate. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2238–2243, 2003

Key words: radical polymerization; initiators; curing of polymers

INTRODUCTION

Unsaturated polyester resins are step-growth products formed by unsaturated and saturated diacids or anhydrides with difunctional alcohols. They have good mechanical properties and weather resistance, and thus they are widely used in the composite industry. These resins can be easily handled, pigmented, filled, and fiber-reinforced in a liquid form.[1–3]

Unsaturated polyester resins can be hardened either at an elevated temperature or at room temperature with the use of a suitable initiating system. To cure polyester resins at room temperature, initiators and promotors are used to generate free radicals through redox mechanisms.[4] The most common source of free radicals, which are needed to initiate the curing reactions in polyesters is organic peroxide, frequently methyl ethyl ketone peroxide. Promotors, usually cobalt salts (octoate or naphthenate), are required to cure polyester resins at low temperatures because they decompose the initiators rapidly under ambient conditions.

In the presence of water another hardening system is used. This comprises dibenzoyl peroxide in combination with tertiary aromatic amines,[5] or less toxic adducts of aromatic amines with epoxide compounds.[6] Unfortunately, at low temperatures the latter hardening systems are uneffective. When unsaturated polyester resins are handled at a temperature close to 0°C or when they have contact with wet fillers, hydrogen peroxide in the redox system is proposed to be used as an initiator for their polymerization.[7–9] According to the patent literature, hydrogen peroxide in concentration of 70% mixed with diluted phosphoric or phthalate esters can be applied as a source of free radicals.[10] Another solution consists in using the anhydrous solution of hydrogen peroxide for curing unsaturated polyester resins.[11]

In this article we present synthesis and properties of the initiating systems formed from commercially available ketones, glycols, and hydrogen peroxide (60%). In preparation of free radical initiators, methyl ethyl ketone, etanodiol and 1,4-butanodiol as diluents, were used. Their production is ecological because no by-products are released.

The obtained initiators with cobalt salt were applied for crosslinking of the unsaturated polyester resin manufactured by the Polifarb-Becker, Dębica. Properties of the resin were compared with those obtained while it was hardened by the typical curing system containing methyl ethyl ketone hydroperoxide and cobalt octoate.

EXPERIMENTAL

Chemicals

The unsaturated polyester resin D-1103 was generously obtained from the Chemical Plant Polifarb-Becker, Dębica (Dębica, Poland). It is a typical orthophthalic polyester resin. Methyl ethyl ketone and cobalt octoate (1% solution in styrene) were from POCh (Gliwice, Poland). Etanodiol and 1,4-butanodiol were from Fluka AG (Buchs, Switzerland). Luperox (50% solution of methyl ethyl ketone hydroperoxide in dimethyl phthalate) was from "Luperox" (Günzburg,

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TABLE I
Chemical Composition of the Obtained Initiators

Initiator no.	Substrates (g)			
	Hydrogen peroxide	Methyl ethyl ketone	Etanodiol	1,4-Butanodiol
1	60	20	40	—
2	60	30	30	—
3	60	40	20	—
4	60	20	—	40
5	60	30	—	30
6	60	40	—	20

Germany). Hydrogen peroxide (60%) was bought from "Azoty" Nitrogen Works (Puławy, Poland).

Preparation of initiators

Synthesis of an initiator containing etanodiol

Hydrogen peroxide (60%) was dropped in the reactor containing methyl ethyl ketone and etanodiol, while stirring. The addition drop by drop was made in such a rate that the temperature of reactor content was 32°C. The homogeneous solution was maintained at this temperature for 3.5 h while stirring. The obtained raw product was used as an initiator for free radical polymerizations of unsaturated polyester resin.

In this way, three initiators were obtained. The amounts of substrates used for their preparation are shown in Table I.

Synthesis of an initiator containing 1,4-butanodiol

The synthesis was carried out in the same way. Only etanodiol was replaced by 1,4-butanodiol. The detailed recipe is presented in Table I.

Active oxygen determination

Concentrations of active oxygen in all the obtained initiators were determined according to the procedure described by Królikowski et al.[12] The determination consists in titration of an initiator sample (dissolved in acetic anhydride) by sodium thiosulfate in the presence of potassium iodine and starch.

TABLE II
Concentration of the Active Oxygen in the Studied Initiators

Initiator no.	Oxygen concentration (%)	
	Real	Calculated
1	13.8	14.1
2	13.9	14.1
3	13.1	14.1
4	13.7	14.1
5	13.5	14.1
6	13.0	14.1

Curing procedure

The obtained initiators were used for crosslinking of the commercially available unsaturated polyester resin D-1103. The resin was crosslinked at 25°C using 0.5, 1.0, 1.5, 2.0, and 2.5% of the initiator. For each concentration of the initiator, the following concentrations of the promotor (1% cobalt octoate) were used: 0.2, 0.4, 0.6, and 1.0% (Tables III–VIII).

To determine efficiency of the initiators, gelation times of the resin were compared with those obtained for the resin cured in the presence of Luperox and cobalt octoate. The gelation times and peak exotherm temperatures of the resin were determined in the temperature-controlled bath (25°C) according to the Polish Standard PN-87/C-89082.

Thermomechanical properties of the cured resins

After curing, the following were examined: the impact strength according to the Charpy method (PN-81/C-89029), heat resistance by the Martens method (PN-90/C-89025), and ball indentation hardness (PN-84/C-89030). Thermal stability of the resins was determined using the derivatograph MOM (Budapest, Hungary). The heating rate was 5°C/min in the air. The initial decomposition temperatures were determined from the course of the TG curves.

RESULTS AND DISCUSSION

Decomposition of hydrogen peroxide by salts of metal of changing valency is presented in Figure 1. It is believed that the mechanism of this reaction is a free-radical.[13] Hydrogen peroxide with the redox system can be used as a source of free-radicals for initiating the reaction of polymerization. Such initiating systems can be used when solubility of initiator in water is required.

In the case of unsaturated polyester resins only organic peroxides are applied. In the presence of water traces polymerization of these resins is inhibited or even impossible. On the other hand, organic peroxides are explosive and special precautions should be undertaken during their storage and handling.

TABLE III
Influence of Concentrations of Initiator No. 1 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
1.1	0.5	0.2	12.2	56.3
1.2	1.0		11.3	67.5
1.3	1.5		10.0	75.8
1.4	2.0		9.5	78.0
1.5	2.5		9.0	78.8
1.6	0.5	0.4	8.6	68.5
1.7	1.0		8.3	96.0
1.8	1.5		7.2	105.0
1.9	2.0		7.1	118.8
1.10	2.5		7.0	120.0
1.11	0.5	0.6	6.6	70.2
1.12	1.0		6.5	97.3
1.13	1.5		6.3	122.5
1.14	2.0		6.2	130.0
1.15	2.5		5.8	133.8
1.16	0.5	1.0	6.2	72.5
1.17	1.0		6.0	98.8
1.18	1.5		5.3	132.2
1.19	2.0		5.1	136.3
1.20	2.5		4.5	142.5

The initiators proposed by us could be prepared just before the use. In the presence of 60% hydrogen peroxide methyl ethyl ketone oxidizes to methyl ethyl ketone peroxide. Water formed in this reaction is not removed. It is dissolved in glycol served as a solvent. Their production is wasteless.

Concentration of active oxygen in six initiators synthesized by us are presented in Table II. From these data one can see that they are characterized by similar activities.

These initators were used for polymerization of unsaturated polyester resin in the presence of different

TABLE IV
Influence of Concentrations of Initiator No. 2 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
2.1	0.5	0.2	10.5	53.5
2.2	1.0		10.0	70.0
2.3	1.5		9.5	95.0
2.4	2.0		9.0	100.0
2.5	2.5		8.6	120.0
2.6	0.5	0.4	8.4	80.3
2.7	1.0		8.2	108.8
2.8	1.5		8.1	125.0
2.9	2.0		7.5	138.0
2.10	2.5		6.6	165.3
2.11	0.5	0.6	7.0	110.3
2.12	1.0		6.5	125.3
2.13	1.5		6.3	145.8
2.14	2.0		6.0	168.3
2.15	2.5		5.7	182.5
2.16	0.5	1.0	6.0	150.0
2.17	1.0		5.7	168.8
2.18	1.5		5.0	175.0
2.19	2.0		4.5	182.3
2.20	2.5		4.3	185.7

TABLE V
**Influence of Concentrations of Initiator No. 3 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin**

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
3.1	0.5	0.2	10.2	45.9
3.2	1.0		9.9	62.5
3.3	1.5		9.4	95.0
3.4	2.0		8.8	118.8
3.5	2.5		8.0	123.3
3.6	0.5	0.4	7.8	82.8
3.7	1.0		7.4	115.0
3.8	1.5		7.1	131.0
3.9	2.0		6.5	139.5
3.10	2.5		5.6	148.7
3.11	0.5	0.6	6.0	105.3
3.12	1.0		5.5	125.3
3.13	1.5		5.3	142.0
3.14	2.0		5.1	152.2
3.15	2.5		5.0	170.2
3.16	0.5	1.0	5.0	120.0
3.17	1.0		4.8	153.5
3.18	1.5		4.5	161.5
3.19	2.0		4.3	167.5
3.20	2.5		4.1	172.0

amounts of cobalt octoate. In Tables III–VIII the influence of initiator concentrations on the gelation times and peak exotherm temperatures is presented. Studies were made in the presence of different promotor concentrations. From these data one can see that with an increase of initiator concentration gelation times of the resin decrease. The increase of peak exotherm temperatures is also observed. Such behavior of the resin is probably caused by synergistic effect of these new initiators, which are richer in free radicals than conventional organic peroxides.[14] In these cases free radicals are evolved both by hydrogen peroxide and methyl ethyl ketone peroxide formed by oxidation of methyl ethyl ketone by hydrogen peroxide. For initiators Nos. 1–3 (containing etanodiol) a smaller increase of peak exotherm temperatures is observed. The release of the least heat comes from initiator No. 1 even with the maximum amount of promotor. Initiators Nos. 2–6 guarantee a right course of polymerization. Such initiators can be used in production of resin mine charges where large heat effects are required.[15]

TABLE VI
**Influence of Concentrations of Initiator No. 4 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin**

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
4.1	0.5	0.4	7.0	126.5
4.2	1.0		6.4	155.0
4.3	1.5		5.7	167.5
4.4	2.0		5.3	170.0
4.5	2.5		5.0	177.2
4.6	0.5	0.6	6.0	137.3
4.7	1.0		5.7	160.0
4.8	1.5		5.1	170.0
4.9	2.0		4.6	173.8
4.10	2.5		4.4	178.8
4.11	0.5	1.0	5.9	140.7
4.12	1.0		5.1	166.3
4.13	1.5		4.6	172.5
4.14	2.0		4.4	178.3
4.15	2.5		4.2	180.5

TABLE VII
**Influence of Concentrations of Initiator No. 5 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin**

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
5.1	0.5	0.4	6.7	142.5
5.2	1.0		6.0	158.5
5.3	1.5		5.5	170.5
5.4	2.0		5.1	177.5
5.5	2.5		4.7	180.2
5.6	0.5	0.6	5.7	145.0
5.7	1.0		5.3	161.2
5.8	1.5		5.0	171.0
5.9	2.0		4.6	180.0
5.10	2.5		4.3	182.5
5.11	0.5	1.0	5.2	151.3
5.12	1.0		5.0	165.3
5.13	1.5		4.5	176.5
5.14	2.0		4.2	181.7
5.15	2.5		4.0	183.5

TABLE VIII
**Influence of Concentrations of Initiator No. 6 and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin**

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
6.1	0.5	0.4	5.6	147.5
6.2	1.0		5.3	165.0
6.3	1.5		5.2	175.0
6.4	2.0		5.1	180.0
6.5	2.5		5.0	183.8
6.6	0.5	0.6	5.2	151.3
6.7	1.0		5.0	170.4
6.8	1.5		4.6	177.7
6.9	2.0		4.4	182.8
6.10	2.5		4.2	188.5
6.11	0.5	1.0	4.8	152.5
6.12	1.0		4.5	172.0
6.13	1.5		4.2	178.5
6.14	2.0		3.6	184.0
6.15	2.5		3.3	190.0

In Table IX the results obtained during curing the resin in the presence of Luperox and cobalt octoate are presented. The data show that an increase of initiator concentration also causes the decrease of gelation time. Comparing the data in Tables III–IX one can see that the gelation time of the resin obtained with 0.5% of initiator and 0.4% of promotor is significantly longer than those obtained with the initiators synthesized by us. Peak exotherm temperatures are also smaller. Only for the highest concentrations of initiator and promotor the peak exotherm temperature of polymerization exceeds 100°C.

In Table X thermomechanical properties of the cured resin are presented. These data show that the initiators containing etanodiol (Nos. 1–3) have different properties than those containig 1,4-butanodiol

(Nos. 4–6). The resins cured with initiators Nos. 1–3 have higher ball indentation hardness and thermal resistance according to Martens. Their impact strengths are smaller. The resin cured with Luperox
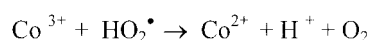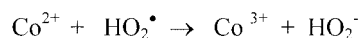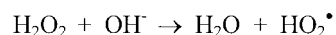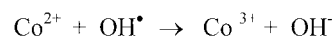
$$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + OH^- + OH^\bullet$$

$$Co^{2+} + OH^\bullet \rightarrow Co^{3+} + OH^-$$

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^\bullet$$

$$Co^{2+} + HO_2^\bullet \rightarrow Co^{3+} + HO_2^-$$

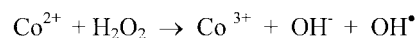$$Co^{3+} + HO_2^\bullet \rightarrow Co^{2+} + H^+ + O_2$$

Figure 1 Scheme of hydrogen peroxide decomposition.

TABLE IX
**Influence of Concentrations of Luperox and Promotor on the Gelation Times
and Peak Exotherm Temperatures of the Resin**

No. of curing system	Initiator concentration (%)	Promotor concentration (%)	Gelation time (min)	Peak exotherm. temperature (°C)
7.1	0.5	0.4	25.6	—
7.2	1.0		15.3	—
7.3	1.5		11.2	—
7.4	2.5		9.9	51.0
7.5	0.5	0.6	12.3	48.5
7.6	1.0		8.5	52.5
7.7	1.5		6.4	59.7
7.8	2.5		4.2	98.5
7.9	1.0	1.0	4.8	102.5
7.10	2.5		3.3	118.5

TABLE X
Thermomechanical Properties of the Cured Resin

No. of curing system	Initial decomposition temperature (°C)	Thermal resistance according to Martens (°C)	Impact strength according to Charpy (kJ/m^2)	Bal indentation hardness (MPa)
1.1	90	46	2.1	117.8
1.5	100	48	2.5	122.1
1.16	100	49	2.4	116.6
1.20	110	52	3.2	134.0
2.1	120	50	2.4	128.1
2.5	120	56	3.2	109.2
2.16	110	53	2.0	113.2
2.20	120	56	2.1	124.3
3.1	120	57	3.6	123.5
3.5	130	56	2.6	121.6
3.16	130	54	2.6	118.8
3.20	120	53	2.0	112.7
4.15	—	41	5.9	76.7
5.15	—	45	4.4	79.9
6.15	—	46	3.9	93.0
7.8	90	47	3.1	113.1

has properties comparable to those obtained while the resin was cured with initiator No. 1.

The results presented here indicate that the initiators based on 60% hydrogen peroxide can be used in polymerization of unsaturated polyester resins. Thermomechanical properties of the cured resin are comparable to those obtained when the typical initiating system composed of organic peroxide and cobalt salt is used. Additionally, these new initiators are safer in manufacturing and handling. It is important that during their preparation no by-product are produced.

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