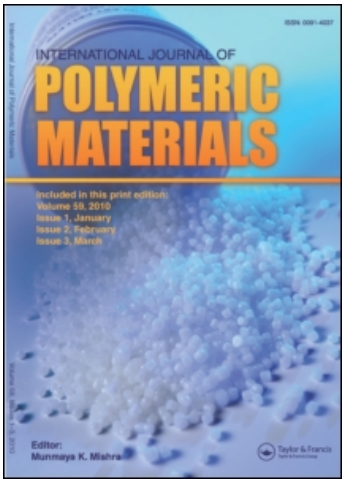

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Inhibitors in Curing of High Reactive Unsaturated Polyester Resin

T. Matynia[a]; B. Gawdzik[a]; J. Osypiuk[a]
[a] Faculty of Chemistry, M. C. S. University, Lublin, Poland

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Inhibitors in Curing of High Reactive Unsaturated Polyester Resin

T. MATYNIA*, B. GAWDZIK and J. OSYPIUK

Faculty of Chemistry, M. C. S. University, pl. Marii Curie-Skłodowskiej 3, 20-031 Lublin, Poland

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The behaviour of 16 hydroquinone–quinone systems used as inhibitors in the curing of unsaturated polyester resin catalyzed by dibenzoyl peroxide was studied. The resin used in the experiments did not contain any inhibitor added in the manufacture process. To increase its reactivity the resin was accelerated by tertiary aromatic amines. In order to determine the influence of the inhibitors mixture on the resin properties induction times at 70°C, viscosities and gelation times were measured.

Keywords: Unsaturated polyesters; curing; inhibitors; hydroquinone–quinones

INTRODUCTION

It is known that the addition of certain substances may prolong the lifetime of the polymers. These substances react with the radicals of initiation and/or propagation, becoming non-radical species or radicals of very low reactivity. The compounds that cause a great decrease in a polymerization rate when added in small quantities can be classified as inhibitors or retarders according to the mechanism of how they work. Inhibitors neutralize all the free radicals, whether they come from the initiator, the active centers of the prepolymer chains or the monomer. The polymerization is completely stopped until the inhibitor has been consumed. Retarders are less effective than inhibitors and only neutralize a fraction of the radicals. In this case polymerization is continued but at a lower rate.

*Corresponding author.

Choice of effective inhibitors is very important in case of reactive polymers such as unsaturated polyester resins. For these polymers, quinones are the class of inhibitors widely used. Novak *et al.* [1] studied the behaviour of hydroquinone and 1,4-benzoquinone during the curing of unsaturated polyester resins with an organic peroxide as an initiator. They proposed the following mechanism of inhibition for hydroquinone: Each molecule of hydroquinone reacts with two radicals of the peroxide, forming a molecule of 1,4-benzoquinone. While hydroquinone is in the reaction medium the polymerization is completely arrested. When the hydroquinone is exhausted, the curing starts. It occurs at a lower rate than without an inhibitor owing to the retarding effect of the 1,4-benzoquinone that is formed and reacts with the propagation radicals of the growing chains.

According to Ramis and Salla [2, 3] an inhibitor plays an important role in the curing of unsaturated polyester resins and any study of this process must state clearly the amount and type of inhibitor present in the resin. One of the problems is the fact that it is difficult to establish the amount of inhibitor in commercial resins, since it is incorporated during the manufacture and storage of the resin. This means that the amount of inhibitor is variable over time.

Novak [4] stressed that the type and amount of the inhibitor can modify the reactivity of the resin, the temperature of the mould, the colour, viscosity and mechanical properties of the cured materials.

In this paper we have studied the influence of the type and amount of hydroquinone–quinone systems on the curing of unsaturated polyester resin catalyzed with dibenzoyl peroxide. The unsaturated polyester resin used in these studies did not contain any inhibitors. It was specially manufactured in such a form by Chemical Plant Polifarb-Debica S. A. (Debica, Poland). To determine the influence of type and amount of the inhibitor system on the properties of resins, their stability at 70°C, viscosity and gelation times were controlled.

EXPERIMENTAL

Materials

The unsaturated polyester resin containing 35% of styrene came from the Chemical Plant Polifarb-Debica S. A. (Debica, Poland). This resin

does not contain any inhibitor. It was produced in such a form on purpose. Before experiments the resin was accelerated by the addition of 2% of *p*-toluidine and 2% of the adduct of *p*-toluidine and Epidian 5. The glycidyl amine adduct used as an accelerator was prepared by us from *p*-toluidine (POCh, Gliwice, Poland) and epoxy resin Epidian 5 came from the Chemical Plant "*Organika-Sarzyna*" (New Sarzyna, Poland) [5].

The compounds used as inhibitors: hydroquinone, *tert*-butylhydroquinone and 4-*tert*-butylpyrocatechol were from Merck (Schuchardt, Germany), 1,4-naphthohydroquinone from Aldrich (Steinheim, Germany) and 1,4-benzoquinone, 1,4-naphthoquinone, anthraquinone, 9, 10-phenanthrenequinone from Fluka (Buchs, Switzerland).

Benzoyl peroxide (50% paste) used as an initiator was from the Chemical Plant "*Organika-Sarzyna*"

Thermal Stability Determinations

To characterize thermal stability of the resin, induction times of the resin at 70°C were determined. For the aim 0.01, 0.02, 0.03, 0.04 and 0.05 mole of the inhibitors mixture containing equivalent amounts of the proper hydroquinone and quinone were solved in 100 g of the resin. All resin samples were maintained under nitrogen atmosphere. The samples were controlled every 4 hours.

Viscosity Measurements

Selected in the previous experiment samples of the longest induction times containing 0.01, 0.03, and 0.05 mole of inhibitors mixture were prepared once again. These were also placed into a dryer at 70°C under nitrogen. Every five days their viscosities were measured using a Brookfield programmable cone/plate rheometer Model DV-III (Brookfield, USA). For this determinations 0.5 ml of the resin sample was used.

Gelation Times Determinations

The gelation times were measured for newly produced unsaturated polyester resin accelerated by *p*-toluidine and aromatic amine adduct

and every five days for the samples maintained in a dryer at 70°C, which contain maximum concentration of inhibitors. These determinations were made in a temperature-controlled bath according to Polish Standard PN-87/C-89082/15.

RESULTS AND DISCUSSION

The kinetics of curing polyester resins is normally very complex because many reactive processes occur simultaneously [6, 7]. In the initiation stage, the initiator decomposes chemically, giving out free radicals that can react with the inhibitor, which can react as a retarder of the polymerization or as an inhibitor, reacting with all the radicals that have formed until it is exhausted. In the propagation or polymerization stage the initiator radicals can react well with the styrene or with the polyester. From this moment the chains of polymer will grow and cross each other, according to three possible reactive processes: styrene-polyester copolymerization, styrene homopolymerization, and polyester homopolymerization [8 – 11].

Studies on an influence of the kind and concentration of the inhibitors system on the properties of unsaturated polyester resin was made for the resin of high reactivity. Before adding any inhibitors gelation and induction times of the resin were 18 s and ca. 0.4 h, respectively.

In Table I the relationships between the inhibitors concentration and the resin induction times are summarized. Of 16 inhibitor systems those which contain 1,4-naphthohydroquinone or 1,4-naphthoquinone are the most effective. The highest stability is indicated by samples I, V, IX, X, XIII and XI. For the maximum concentration of inhibitors their induction times exceed 500 hrs at 70°C. For the resin containing 0.01% of the inhibitor mixture induction times are generally shorter than 1 hour. Only in the case of the sample containing 0.01% of 1,4-naphthohydroquinone + 1,4-naphthoquinone induction time is higher than 300 hrs. This inhibition system behaves exceptionally as the increase of its concentration causes rather a proportional increase of the resin stability. For others a double increase of inhibitors concentration causes a multiple increase of the resin induction time. This phenomenon is not observed only for the

TABLE I Influence of the type and concentration of the inhibitor system on the resin induction time

	Inhibitor system (1:1) (*g*)		*Induction time* (*h*)
I	4-*tert*-butylpyrocatechol	+ 1,4-naphthoquinone	
0.01%	0.0083	0.0079	1
0.02%	0.0166	0.0158	56
0.03%	0.0249	0.0237	296
0.04%	0.0332	0.0316	320
0.05%	0.0415	0.0395	447
II	4-*tert*-butylpyrocatechol	+ 1,4-benzoquinone	
0.01%	0.0083	0.0054	0.5
0.02%	0.0166	0.0108	0.5
0.03%	0.0249	0.0162	0.5
0.04%	0.0332	0.0216	0.5
0.05%	0.0415	0.0270	0.5
III	4-*tert*-butylpyrocatechol	+ anthraquinone	
0.01%	0.0083	0.0104	0.4
0.02%	0.0166	0.0208	0.4
0.03%	0.0249	0.0312	0.4
0.04%	0.0332	0.0416	0.4
0.05%	0.0415	0.0520	0.4
IV	4-*tert*-butylpyrocatechol	+ 9,10-phenanthrenequinone	
0.01%	0.0083	0.0104	4
0.02%	0.0166	0.0208	22
0.03%	0.0249	0.0312	23.3
0.04%	0.0332	0.0416	41.3
0.05%	0.0415	0.0520	45
V	*tert*-butylhydroquinone	+ 1,4-naphthoquinone	
0.01%	0.0083	0.0079	2.2
0.02%	0.0166	0.0158	13.5
0.03%	0.0249	0.0237	339.2
0.04%	0.0332	0.0316	452.3
0.05%	0.0415	0.0395	470.3
VI	*tert*-butylhydroquinone	+ 1,4-benzoquinone	
0.01%	0.0083	0.0054	1.5
0.02%	0.0166	0.0108	1.5
0.03%	0.0249	0.0162	1.5
0.04%	0.0332	0.0216	2.2
0.05%	0.0415	0.0270	18
VII	*tert*-butylhydroquinone	+ anthraquinone	
0.01%	0.0083	0.0104	0.5
0.02%	0.0166	0.0208	0.5
0.03%	0.0249	0.0312	0.5
0.04%	0.0332	0.0416	0.5
0.05%	0.0415	0.0520	0.5

TABLE I (Continued)

	Inhibitor system (1:1) (*g*)		*Induction time* (*h*)
VIII	*tert*-butylhydroquinone	+ 9,10-phenanthrenequinone	
0.01%	0.0083	0.0104	23
0.02%	0.0166	0.0208	23
0.03%	0.0249	0.0312	48
0.04%	0.0332	0.0416	53
0.05%	0.0415	0.0520	53
IX	1,4-naphthohydroquinone	+ 1,4-naphthoquinone	
0.01%	0.0080	0.0079	336
0.02%	0.0160	0.0158	477
0.03%	0.0240	0.0237	548
0.04%	0.0320	0.0316	522
0.05%	0.0400	0.0395	581
X	1,4-naphthohydroquinone	+ 1,4-benzoquinone	
0.01%	0.0080	0.0054	1
0.02%	0.0160	0.0108	114.3
0.03%	0.0240	0.0162	381
0.04%	0.0320	0.0216	405.3
0.05%	0.0400	0.0270	501
XI	1,4-naphthohydroquinone	+ anthraquinone	
0.01%	0.0080	0.0104	16.3
0.02%	0.0160	0.0208	161
0.03%	0.0240	0.0312	184
0.04%	0.0320	0.0416	256
0.05%	0.0400	0.0520	256.3
XII	1,4-naphthohydroquinone	+ 9,10-phenanthrenequinone	
0.01%	0.0080	0.0104	14.5
0.02%	0.0160	0.0208	14.5
0.03%	0.0240	0.0312	14.5
0.04%	0.0320	0.0416	14.5
0.05%	0.0400	0.0520	14.5
XIII	hydroquinone	+ 1,4-naphthoquinone	
0.01%	0.0055	0.0079	1
0.02%	0.0110	0.0158	67
0.03%	0.0165	0.0237	359
0.04%	0.0220	0.0316	359
0.05%	0.0275	0.0395	502
XIV	hydroquinone	+ 1,4-benzoquinone	
0.01%	0.0055	0.0054	0.4
0.02%	0.0110	0.0108	0.4
0.03%	0.0165	0.0162	1.1
0.04%	0.0220	0.0216	1.1
0.05%	0.0275	0.0270	1.2

TABLE I (Continued)

	Inhibitor system (1:1) (*g*)		*Induction time* (*h*)
XV	hydroquinone	+ anthraquinone	
0.01%	0.0055	0.0104	0.4
0.02%	0.0110	0.0208	0.4
0.03%	0.0165	0.0312	0.4
0.04%	0.0220	0.0416	0.4
0.05%	0.0275	0.0520	0.4
XVI	hydroquinone	9,10-phenanthrenequinone	
0.01%	0.0055	0.0104	18.3
0.02%	0.0110	0.0208	21
0.03%	0.0165	0.0312	24.3
0.04%	0.0220	0.0416	49
0.05%	0.0275	0.0520	71

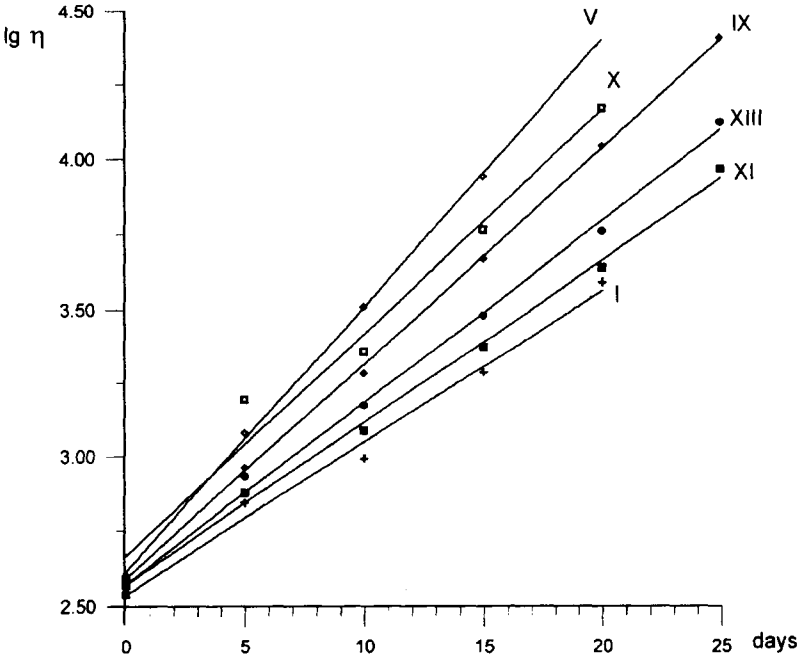

FIGURE 1 Changes of the resin viscosity in time. Numbers correspond to the inhibitor systems from Table I.

TABLE II Changes of viscosity and gelation time for the most stable resin samples

Inhibitor system	*Time (days)*	*Viscosity (cP)*			*Gelation time (s)*
		0.01%	0.03%	0.05%	0.05%
I 4-*tert*-butylpyrocatechol + 1,4-naphthoquinone	0	344.6	344.2	339.4	55
	5	–	837.5	696.0	50
	10	–	1491.4	980.9	48
	15	–	2998.0	1927.3	49
	20	–	–	3869.9	
V *tert*-butylhydroquinone + 1,4-naphthoquinone	0	388.0	395.8	395.8	40
	5			1199.0	39
	10			3222.0	39
	15			8720.7	39
IX 1,4-naphthohydroquinone + 1,4-naphthoquinone	0	386.2	386.2	399.6	45
	5	–	967.5	913.9	41
	10	–	2246.6	1912.0	40
	15	–	6646.2	4632.2	40
	20	–	–	11004.0	
	25	–	–	25200.0	
X 1,4-naphthohydroquinone + 1,4-benzoquinone	0	380.0	380.5	382.4	40
	5	–	–	1560.2	38
	10	–	–	2277.3	38
	15			5800.2	38
	20			14800.0	
XI 1,4-naphthohydroquinone + anthraquinone	0	363.3	361.4	370.9	50
	5	–	898.6	753.3	48
	10	–	–	1218.9	46
	15	–	–	2353.5	46
	20	–	–	4321.1	48
	25	–	–	9189.1	
XIII hydroquinone + 1,4-naphthoquinone	0	346.5	351.8	348.9	48
	5	–	818.3	856.6	45
	10	–	2110.8	1485.6	45
	15	–	–	3013.3	46
	20	–	–	5690.1	45
	25	–	–	13192.8	

systems containing anthraquinone because independently of the inhibitor concentration stability of the resin is the same. (Exceptional behaviour of the system XI is associated with the presence of 1,4-naphthohydroquinone). Insignificant influence of the inhibitor concentration on the resin stability is also observed for the most popular system hydroquinone + 1,4-benzoquinone.

In Table II the changes of the resin viscosities and gelation times are presented. These results are determined for the most stable samples of

the resin. From these data one can see that each of the studied inhibitor system causes an increase of the resin viscosity. The smallest increase is visible for the sample inhibited by the mixture: 4-*tert*-butylpyrocatechol + 1,4-naphthoquinone (Fig. 1). On the other hand, these inhibitors cause a significant increase of the resin gelation time.

Changes of the resin gelation times confirm that an inhibitor exhausts in time and curing can start faster. In each case, the gelation times of the resin after 5 days shorten significantly. Then the process runs more slowly. This means that after some time the concentration of free radicals is so low that they have not influence on the inhibitor concentration.

The results presented here indicate that for inhibition of unsaturated polyester resins of high reactivity inhibitor systems containing 1,4-naphthohydroquinone or 1,4-naphthoquinone should be used.

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