

AMBIENT TEMPERATURE CURING OF CORROSION RESISTANT UNSATURATED POLYESTER RESINS

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Summary

The application of unsaturated polyester resins as construction material for chemical aggressive environments is a very important and steadily growing market.

Application areas are for instance storage tanks and pipes for the chemical processing industry, scrubbers for electricity power plants, chemical resistant coatings and so on.

As the chemical resistance of general purpose unsaturated polyester resins based on orthophthalic acid/fumaric acid/propylene glycol is in general not sufficient to guarantee a long lifetime of the mouldings, special UP resin types have been developed for these kind of applications, ranging from isophthalic resins up to bisphenol A and vinylester resins.

It will be obvious that an optimal use of the various resins is only possible when, after the processing, optimal end properties of the moulding are achieved. Apart from optimal working conditions during the moulding process, extra attention should be paid in this respect to the choice of the cure system.

It will be described in this lecture:

- how the curing process of the various resins can be influenced by the choice of the cure system
- how important a good cure is
- how an optimal cure can be achieved

Introduction

By changing the raw materials for the production of unsaturated polyester resins (UP resins), it is possible to create resins which can be used for the manufacturing of mouldings with a wide range of mechanical and chemical properties e.g. from very flexible parts to very strong and tough parts and products which can withstand a wide range of chemicals like strong acids, solvents.

For the production of corrosion resistant mouldings, UP resins of the following general types are available:

- isophthalic acid/fumaric acid/standard glycol based resins
- isophthalic acid/fumaric acid/neopentylglycol based resins
- bisphenol A/fumarate resins
- vinylester resins, which can be divided in : bisphenol A/epoxy resins and novolak based resins.

Which type of resin is most suitable for a certain application can best be discussed with the resin supplier.

The excellent chemical and mechanical properties are potentially present in the resins via the backbone.

Full use of these properties is, however, only made when the resins are processed in the correct way and last but not least are cured in the correct way.

Of special importance in this respect is a crosslinking as complete as possible of all fumarate (meth)acrylate groups in the resin backbone via reactive diluents like styrene .

Experimental

For the various cure experiments, use was made of the following UP resins:

Resin type	Abbreviation	Styrene content (%)	Acid value	HDT (°C)
Isophthalic acid/standard glycol	ISO	35	16	98
Isophthalic acid/neopentyl glycol	ISO/NPG	43	12	109
Bisphenol A/fumarate	BA	50	14	130
Bisphenol A/epoxy vinylester	Epoxy VE resin	45	8	102
Novolak vinylester	Novolak VE resin	36	12	145

HDT = Heat Distortion Temperature acc. to ISO R/75A.

The cure systems were based on:

the ketone peroxides:

Butanox M-50, Butanox LPT and Trigonox 44B

the dibenzoyl peroxide formulation:

Lucidol CH-50

the special peroxides:

Trigonox 42PR and Trigonox 239

The peroxides were used in combination with the accelerators:

Accelerator NL-51P: Cobalt 2-ethyl hexanoate containing 6% cobalt
Accelerator NL-63-100: N,N dimethyl aniline (100%).

The following experiments were carried out:

-gel times at 20°C in the pure resin

-curing of 4 mm laminates at 20°C.

- Determined were:
- * the time temperature curve
 - * the time to achieve a Barcol 934-1 hardness of 0-5 as an indication for the initial cure speed
 - * the residual styrene content as a function of the cure cycle.

Results

In the attached Tables 1, 2 and 3, the results of the cure experiments with various peroxides in respectively an iso/npg, an epoxy based vinylester resin and a novolak based vinylester resin are summarized.

The gel time in the pure resin was, in all cases, adjusted on an average practical gel time of 20-25 min.

From the figures in the tables, some general conclusions can be drawn:

- Butanox LPT gives, of the ketone peroxides tested, in general the best overall results.
- try to adjust the gel time with a cobalt accelerator only, the use of an aromatic amine results in a faster initial cure but also in higher residual styrene figures especially after a postcure.
- Trigonox 239 is a very good alternative for Butanox LPT in vinyl ester resins. Trigonox 239 does not give a gassing as is always observed with ketone peroxides. Moreover, lower residual styrene figures are achieved.
- Trigonox 42PR is, in vinylester resins, by its high peak exotherm, very suitable when low residual styrene figures are required without a post cure.
- the use of a dibenzoyl peroxide like Lucidol CH-50 is not recommended for the cure of corrosion resistant resins. The risk of undercure and hence not optimal physical and chemical properties is very big.

In Table 4, the cure characteristics of the various UP resins is compared. The cure system was in all cases based on Butanox LPT. The gel time in the pure resin was adjusted on approx. 20 min. by means of the accelerator dosage level.

Cure system	Time Temperature curve			Cure speed	Residual styrene content		
	Gel time (min.)	Time to peak (min.)	Peak exotherm (°C)		1 week at 20°C (%)	6 months at 20°C (%)	1 week at 20°C + 8 hours at 80°C (%)
ISO resin 2% Butanox LPT + 0.7% Acc. NL-51P	18	42	55	<1	3.6	1.8	0.01
ISO/NPG resin 2% Butanox LPT + 0.5% Acc. NL-51P	25	52	29	3.5	5.8	2.9	0.2
Bisphenol A resin 2% Butanox LPT + 1% Acc. NL-51P + 0.1% Acc. NL-63-100	17	51	38	5.5	4.9	2.1	0.1
Epoxy VE resin 2% Butanox LPT + 0.7% Acc. NL51P	37	120	36	3	5.9	4.9	0.1
Novolak VE resin 2% Butanox LPT + 0.5% Acc. NL-51P	28	42	84	<1	2.0	1.6	0.1

Table 4. Cure experiments with various corrosion resistant resins at 20°C.

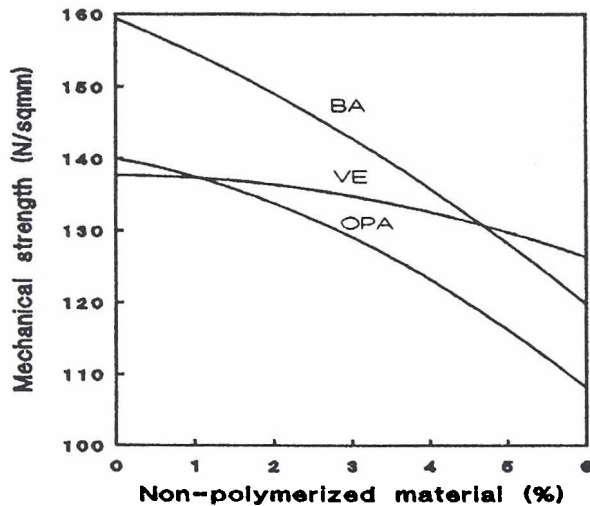
It is clearly demonstrated that each resin has its own cure characteristics. Although all resins can be properly cured with a cure system based on Butanox LPT, a further optimisation can possibly be worked out in cooperation with your peroxide supplier. Price differences between the various peroxides available are in this kind of applications and resins of minor importance. The cost of the peroxide is in general not more than 2-3% of the total raw material costs. This is in general negligible in comparison with benefits as higher quality of the endproduct and an increase of the production speed.

Residual styrene content.

It has already been discussed in various previous articles that an optimal performance of a cured UP resin is only obtained when the product is optimally cured. Optimal cure means a residual styrene and residual fumarate unsaturation as low as possible. It is well accepted to use the residual styrene content as a measure for the degree of cure under the assumption that styrene and fumarate unsaturation decrease proportionally. The residual styrene content is easy and very accurate to measure by means of a gaschromatographical analysis after an extraction of the cured UP part.

From numerous experiments with a large number of curing systems it has been established that also in corrosion resistant resins a good correlation exist between the content of non-polymerized material and the physical properties of the cured resin. Non-polymerized material is residual styrene content plus phlegmatizers added via the cure system.

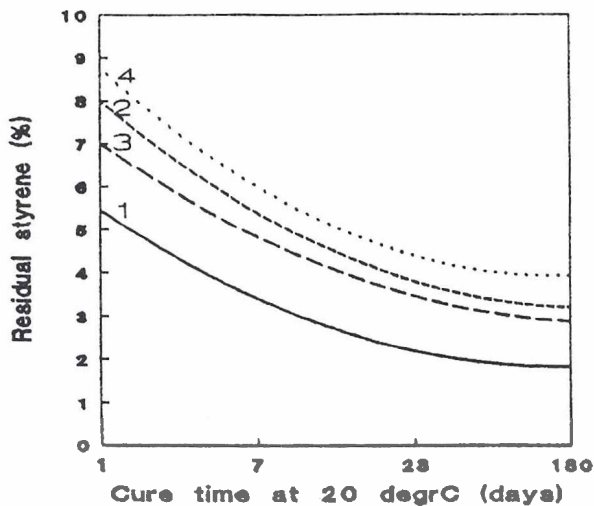
The correlation is demonstrated in Graph 1.



Graph 1: The effect of the quantity non-polymerized material in cured UP resins on the flexural strength.
 VE = Epoxy based vinylester resin
 BA = Bisphenol A resin
 OPA = Standard orthophthalic resin

The negative effect of the non-polymerized material on the flexural strength is very obvious. Interesting is the observation that the flexural strength of the vinylester resin is less influenced by the presence of non-polymerized materials than the one of both the other two resins. It can be assumed that the same kind of dependency exist between the chemical resistance and the amount of non-polymerized material in a cured UP part.

The production and initial curing of GRP products is in general done at ambient temperatures. In the first days, up to a few weeks, the styrene will be build-in very quickly. After that, the polymerization reaction will slow down and almost come to a stand-still. This is caused by the increasing rigidity of the polyester network, by which the free styrene is almost frozen-in. It is obvious that the heat distortion temperature (HDT) of a UP resin is a measure for the rigidity. Corrosion resistant resin have, as demonstrated in Table 1, high HDT values. The consequence of this all is that an optimal cure with residual styrene figures of less than e.g. 0.1% can not be obtained during an ambient temperature cure process. The development of the residual styrene content in 4 mm laminates produced with some UP resin types is demonstrated in Graph 2.



Graph 2: The effect of the cure time at 20 °C on the development of the residual styrene content in 4 mm laminates based on:

1. OPA resin + 2% Butanox LPT + 1% Accelerator NL 49P
2. ISO/NPG resin + 2% Butanox LPT + 1% Accelerator NL 49P
3. BA resin + 2% Butanox LPT + 1% Accelerator NL 51P + 0.05% Accelerator NL 63-100
4. Epoxy VE resin + 2% Butanox LPT + 0.5% Accelerator NL-51P.

The graph demonstrates that when a GRP product is put into use e.g. 1-2 months after production, the residual styrene content is in general still about 3-5%. An exception can be vinylester resin based parts in which during the production a peak exotherm of about 100-120°C has been evolved. A residual styrene content of 3-5% is for corrosion resistant parts in general unacceptably high. To guarantee a long lifetime of the product, the residual styrene content should be about 0.5% or lower. It is obvious that when the polymerisation reaction almost stops because of the rigidity of the network, the reaction continues when the network is to some extent flexibilized again. This is the principle of post curing. In Graph 3, 4 and 5 the effect of the post cure time and temperature on the development of the residual styrene content is demonstrated. All resins show the same pattern viz. a low residual styrene content is in general only achieved after a post cure at 80°C during several hours.

Remark: The information in this article has mainly been focussed on the cure of 4 mm laminates. The same cure systems are of course, with comparable reactivities and reactivity differences, also applicable for the cure of coatings, glass flake applications and thin laminates.

Conclusions.

1. To achieve the optimal physical properties of a corrosion resistant GRP product, special attention should be paid to the selection of the cure system.
2. The best overall results in the various resins are achieved with Butanox LPT, preferably only in combination with a cobalt accelerator.
3. A combined cobalt/tert. amine accelerator gives a fast initial cure but higher residual styrene figures than a cobalt accelerator alone.
4. For vinylester resins, an improvement of the cure can be achieved by using Trigonox 239 or Trigonox 42PR instead of Butanox LPT.
5. To obtain low residual styrene figures a post cure of several hours at 80°C is a must.

Cure system	Time Temperature curve			Cure speed Time to reach a Barcol 934-1 of 0-5 (hours)	Residual styrene content after		
	Gel time (min.)	Time to peak (min.)	Peak exotherm (°C)		1 week at 20°C (%)	6 months at 20°C (%)	1 week at 20°C + 8 hours at 80°C (%)
2% Butanox M-50 + 0.1% Acc. NL-51P	22	48	28	4	6.2	3.4	0.8
2% Butanox LPT + 0.5% Acc. NL-51P	25	52	29	3.5	5.8	2.9	0.2
2% Trigonox 448 + 0.2% Acc. NL-51P	28	50	32	3	5.9	3.8	0.7
3% Lucidol CH-50 + 0.4% Acc. NL-63-100	22	39	88	<1	5.8	5.2	3.3

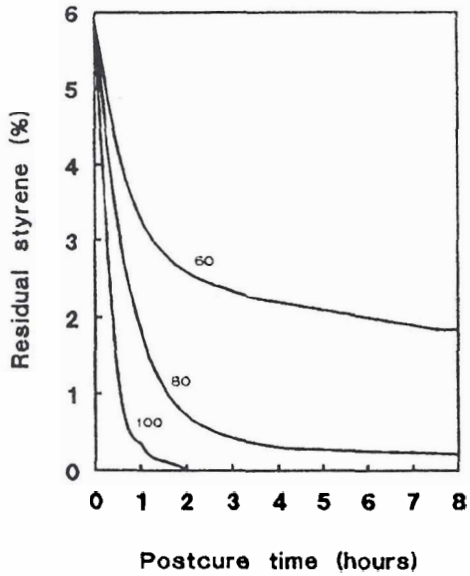
Table 1: Cure experiments with various cure systems in an iso/npg resin at 20°C.

Cure system	Time Temperature curve			Cure speed Time to reach a Barcol 934-1 of 0-5 (hours)	Residual styrene content		
	Gel time (min.)	Time to peak (min.)	Peak exotherm (°C)		1 week at 20°C (%)	6 months at 20°C (%)	1 week at 20°C + 8 hours at 80°C (%)
2% Butanox M-50 + 0.3% Acc. NL-51P + 0.1% Acc. NL-63-100	36	80	40	3.5	6.0	4.2	0.9
2% Butanox LPT + 0.2% Acc. NL-51P + 0.1% Acc. NL-63-100	38	96	38	4	6.2	4.0	0.7
2% Butanox LPT + 0.5% Acc. NL-51P	42	134	36	5	5.9	3.6	0.1
2% Trigonox 239 + 0.6% Acc. NL-51P	37	128	49	3	5.0	2.9	0.1
2% Trigonox 42PR + 0.5% Acc. NL-51P + 0.6% Acc. NL-63-100	42	60	126	<1.5	0.2	0.2	0.02
3% Lucidol CH-50 + 0.1% Acc. NL-63-100	40	135	50	4	8.1	6.8	2.4

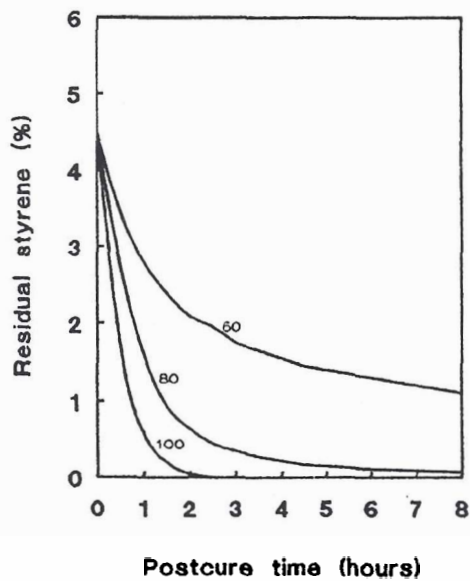
Table 2: Cure experiments with various cure systems in an Epoxy VE resin at 20°C.

Cure system	Time Temperature curve			Cure speed Time to reach a Barcol 934-1 of 0-5 (hours)	Residual styrene content		
	Gel time (min.)	Time to peak (min.)	Peak exotherm (°C)		1 week at 20°C (%)	6 months at 20°C (%)	1 week at 20°C + 8 hours at 80°C (%)
2% Butanox M-50 + 0.3% Acc. NL-51P + 0.1% Acc. NL-63-100	26	34	110	<1	2.0	1.9	0.9
2% Butanox LPT + 0.2% Acc. NL-51P + 0.1% Acc. NL-63-100	27	36	108	<1	2.1	1.7	0.8
2% Butanox LPT + 0.4% Acc. NL-51P	29	45	94	<1	2.8	1.6	0.1
2% Trigonox 239 + 0.2% Acc. NL-51P	44	75	43	<2	1.3	1.0	0.03
3% Lucidol CH-50 + 0.1% Acc. NL-63-100	28	37	128	<1	2.5	2.4	1.8

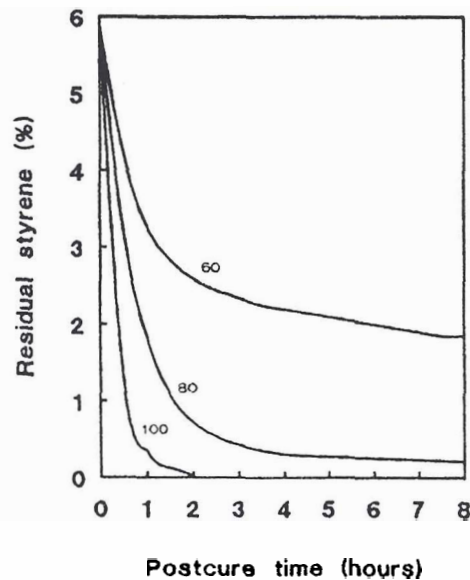
Table 3: Cure experiments with various cure systems in a Novolak VE resin at 20°C.



Graph 3: The effect of the postcure time and temperature on the residual styrene content in 4 mm laminates based on the ISO/NPG resin cured with:
2% Butanox LPT + 1% Accelerator NL-49P



Graph 4: The effect of the postcure time and temperature on the residual styrene content in 4 mm laminates based on the BA resin cured with:
2% Butanox LPT + 1% Accelerator NL 51P + 0.05% Accelerator NL 63-100.



Graph 5: The effect of the postcure time and temperature on the residual styrene content in 4 mm laminates based on the Epoxy vinyl ester resin cured with:
2% Butanox LPT + 0.5% Accelerator NL-51P.