

Using Multiple Peroxides with Complementing Resin to Provide Improved Laminate Cure and Part Profile

by

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Abstract

One of the challenges fiberglass reinforced plastic (FRP) manufacturers face is how to get the resins they use to perform in the varying applications typically found in a fabrication shop. How do you get the same resin to cure quickly and completely in a thin skincoat laminate and still provide enough working time to complete the application of subsequent thicker laminates, while maintaining a low enough exotherm to provide for a good surface profile?

Changing the peroxide level has been used to attempt to address these issues, but with limited effectiveness. This paper evaluates the effectiveness of using one peroxide for the application of the skincoat, and a different peroxide for the subsequent thicker laminates used to build the part. These peroxides were evaluated for their influence on the exotherm, hardness development, and degree of cure in laminates made to the varying thicknesses that are typically used in the fabrication process. How the resin interacts with the peroxides and the importance of designing the resin to work with both peroxides to achieve maximum performance were examined. The improvements in processing speed and part quality that are possible when using multiple peroxides will be demonstrated. The methods and equipment that can be implemented in a fabrication plant to allow the use of multiple peroxides will be discussed.

Background

Most fabricators apply a thin laminate behind the gel coat before applying the bulk of the laminate structure. This first laminate application, called a skincoat, is used for two primary reasons:

1) A thin first laminate application allows laminators to easily see any air in the laminate and remove it.

2) It improves the surface profile of a part.

Because the skincoat laminate is thin, the heat developed during its curing process is moderate and the shrink rate is reduced. If the skincoat is allowed to cure before the application of the bulk laminate, it provides a barrier to fiberglass print through from the bulk laminate applied behind it. To provide an optimum barrier to the print through of the bulk laminate, the skincoat must have a high degree of cure when the bulk laminate is applied. Skincoat laminates typically are applied in a thickness of 30-90mils (0.76-2.29mm). The low mass of the skincoat can make getting a high degree of cure a challenge. To help fully cure the skincoat, fabricators typically use higher levels, typically two percent, of peroxide in the skincoat.

To provide a faster cure in the skincoat, a resin manufacturer will put additional promoters in the resin. However, the promoter level that can be used in a resin is limited by the impact the promoter will have on the exotherm and rate of cure of the bulk laminate. Since there is much greater mass to the bulk laminate, it will cure faster and at higher temperatures than the skincoat laminate. The cure and exotherm of the bulk laminate can be reduced by lowering the peroxide level for the application of the bulk laminate. However, fabricators are limited in how low they can go with the peroxide level. Typically 1.25% is the lowest for a mechanical application and 1.0% for hand application. The end result is the fabricator is left with having either a longer cure time then desired in the skincoat or excessive exotherm in the bulk laminate.

Objective

The objective of this work was to find a means for the fabricator to use one resin to achieve a rapid cure in the thin skincoat laminate, while maintaining a moderate exotherm in the thick bulk laminate. The goal of this work was to determine which peroxides would help to achieve this objective. Another goal was to evaluate the interactions of the peroxides with the additives used in the resin.

Previous work on the effects of peroxide on the gel and cure of resin focused on testing different peroxides on one resin. The resin was not optimized for each of the peroxides being tested. The resin additive package was not adjusted for the effects of the peroxide.

In this work, the resin additives were modified to optimize the performance with each peroxide combination and to achieve a similar gel time in the skincoat application.

Experiment

Initial screening was done on numerous peroxide types to determine which would provide the rapid cure in thin laminates and which would provide lower exotherms in thick laminates. It quickly became apparent that each peroxide behaved differently depending on the additives present in the resin in which it was being used. For example, one peroxide might provide a lower exotherm with one resin, but when it was used with another resin, just the opposite might occur. Therefore, the peroxides were tested with multiple resin systems.

Various resin additives were evaluated to find the combination that would optimize the effect of each peroxide. This testing was limited to the peroxides with the best potentials to provide the properties desired.

The following peroxides were evaluated for skincoat application: acetyl acetone peroxide (AAP), sometimes referred to as 2,4 pentanedione peroxide; and a methyl ethyl ketone peroxide (MEKP) with a high dimer/low hydrogen peroxide content.

For the bulk laminate, a mixture of MEKP and cumene hydroperoxide (CHP) was evaluated.

A standard MEKP was used as a control in both the skincoat and bulk laminate.

A standard dicyclopentadiene (DCPD) resin blend was used in all the tests.

Three resin additive systems were also tested. An additive package was developed for use with the AAP in the skin coat. Since the AAP provides for a rapid cure in a thin laminate, the additive system did require an aggressive promoter to get a rapid cure in a thin laminate. The moderate promoter system should provide lower exotherms in the thick laminates. This resin matrix was designated Resin A.

An additive package for the resin used with the MEKP/CHP blend in the bulk laminate was developed that would not interfere with the exotherm reducing properties of the CHP. This resin matrix was designated Resin B.

A traditional additive package was used for the control resin for use with the standard MEKP in both the thick and thin laminates. This resin matrix was designated Resin C.

Testing Procedure

Six-inch by six-inch (152 mm x 152 mm) plies of fiberglass mat were used to make test laminates. To emulate the properties that will be seen in a production

part, the tests laminates must be thicker than the thickness of the part being emulated.

To evaluate cure levels in a thin laminate, tests were done using 2 plies of 2 oz. chopped strand mat. For the bulk laminate, 3 plies each of 1.5 oz. mat and 18 oz. woven roving were used for one set of test coupons, and 5 plies of 1.5 oz. mat and 5 plies of 18 oz. woven roving were used for the other set.

The laminates were evaluated for gel time, heat of cure (exotherm), hardness development and in some cases, for percent of cure. The gel time of the laminate was determined by folding it. When the laminate resisted folding, it was determined to be gelled. The exotherm of the laminate was monitored using an infrared pyrometer. A 934 Barcol meter was used to determine hardness development on all the laminates. The Barcol meter is a common tool used in fabrication shops to determine laminate cure. It is an easy to use, nondestructive method. Since the reading on a Barcol meter is determined by the degree of penetration of a needle into the laminate, it may not directly relate to the laminate's degree of cure. At the same degree of cure, a more flexible resin will have a lower Barcol reading than a more rigid resin. Since the meter is measuring surface penetration, a resin with more air inhibition will have a lower Barcol reading than a resin that is not air inhibited. The same polymer blend was used in all the testing for this paper. All the samples tested had good surface cure. Therefore, the readings obtained with the Barcol meter should reflect the relative degree of cure of the resins. As a check to assure the Barcol readings did indeed reflect the degree of cure, samples were taken from some test laminates and tested with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to determine the percent cure of the laminate. The DSC/TGA data correlated very well with the Barcol data. Those laminates with a high reading on the Barcol meter also had a high degree of cure.

Results and Discussion

1) Thin laminate test results

The 2 ply laminate tests were run first. Laminates were made with the control resin (Resin C) using AAP, a high dimer low hydrogen peroxide MEKP, and a standard MEKP as a control. The gel time, time from gel-to-peak exotherm, peak exotherm, and hardness development were recorded. The hardness development with the high dimer low hydrogen peroxide MEKP was approximately 30 minutes faster than that achieved with the standard MEKP. The hardness development was approximately one hour faster with the AAP than with the standard MEKP. The results are shown in Table 1. The gel-to-peak for the tests with the AAP was much shorter

than that of the control. The exotherm was also higher with the AAP.

The testing proceeded with the evaluating various additive combinations in the resin to lower the exotherm and extend the gel-to-peak without significantly changing the hardness development when using the AAP.

An additive system was developed that resulted in a lower exotherm while still providing a very rapid laminate cure in the thin laminate. The thin laminate gel time was longer than observed with the control resin. This additive system also had to provide a good cure with a low exotherm in a thick laminate using a standard MEKP. The test results with this resin using AAP in a thin laminate are shown in Table 2. Of note is that when using the new additive system, the gel time with the AAP was shorter than that of the MEKP. With the control resin additive system, using the AAP gave a longer gel time than when obtained with the MEKP.

To determine the optimum peroxide level for the AAP, thin laminates were made using 1.25%, 1.50%, 1.75% and 2.00% of the AAP. The test results are shown on Table 3 and illustrate that an AAP level of 1.5% to 1.75% provides the best cure development with Resin A in a thin laminate. However, even at a 1.25% level of AAP, the hardness development is faster than was achieved with the control resin using 2.0% MEKP.

An additive system was developed for use in the resin to optimize the resin's performance with the high dimer low hydrogen peroxide MEKP in the thin laminate and the MEKP/CHP in the thick laminate. Various levels of the high dimer low hydrogen peroxide MEKP were used in a thin laminate to determine the level needed for the optimum cure development. Table 4 contains the results of this testing. The optimum level of the high dimer low hydrogen peroxide MEKP with the resin with the modified additive system (Resin B) is 2.00%.

Thin laminate tests were run using 1.75%, 2.00%, 2.25%, and 2.50% levels of a standard MEKP in the resin with the standard additive package. The optimum MEKP level for cure in a thin laminates was 2.00%. This data is shown in Table 5.

Table 6 contains a side by side comparison of the best performing combinations of resin, peroxide, and peroxide level. The AAP provided by far the fastest thin laminate cure. It also had the highest thin laminate exotherm. The high dimer low hydrogen peroxide MEKP had a slower hardness development than the AAP. The hardness development with the high dimer low hydrogen peroxide MEKP was faster than the control resin with the standard MEKP.

Thick laminate test results:

The three resin systems used in the thin laminate testing were also evaluated in thick laminates. These laminates were made using alternating layers of 1.5 oz chopped strand mat and 18 oz. woven roving. Three layers of each were used for the first round of thick laminate testing. A glass resin ratio of 60:40 was used for this testing. The same resin systems that were used in the thin laminate testing were used in the thick laminate testing. Table 7 contains the test results of the control resin with 1.25% and 1.50% levels of the standard MEKP. As expected the exotherms were considerably higher than was observed during the thin laminate testing. To provide a uniform distribution of the peroxide using mechanical application equipment a minimum level of 1.25% of peroxide is required. Therefore, laminate tests were not conducted below that level.

Resin A, which was designed to provide a rapid cure in the thin laminate with the AAP, was tested for gel and cure in the thick laminate with a standard MEKP initiator. This resin gave an extended gel time in the thick laminate with MEKP levels at 1.25% and 1.50%, so a higher level of 1.75% was included in the testing. Table 8 contains the test results.

The exotherm with Resin A was lower and the gel time and gel-to-peak exotherm were longer than observed with the control resin. This is a function of the additive system used in the resin which does not need to be as aggressive as the system used in the control resin to achieve a fast cure in the thin laminate.

At the same level of peroxide, Resin A has a slower hardness development than the control resin. When a 1.75% MEKP level was used with Resin A, a hardness development similar to that of the control resin with 1.25% level was achieved.

Resin B was evaluated with a peroxide blend of MEKP and CHP in at a 3:1 ratio. This blend was used at a 1.25% and 1.5% level in the thick laminate. This combination produced the lowest exotherm. The exotherm of Resin B with the 1.25% level of the MEKP/CHP was 95°F/35°C. This was 25°F/14°C lower than the exotherm measured on the control laminate made with 1.25% MEKP. The exotherms of the Resin C laminates using the MEKP/CHP were also lower than those recorded on the laminates made with Resin A and the standard MEKP. The results of the thick laminate tests using the MEKP/CHP peroxide blend with Resin B are reported in Table 9.

Table 10 contains a summary of the three resin/peroxide systems using peroxide levels that resulted in similar gel times and time from gel-to-peak. This shows that Resin A with 1.75% MEKP has a similar peak exotherm and cure development to the control resin

with 1.25% MEKP even though it had a higher peroxide level. Resin B, using 1.5% of the MEKP/CHP blend, had a lower exotherm and started developing hardness one hour later than other two combination. However, at two and a half hours, the hardness of the laminate made with the Resin B and the MEKP/CHP blend was equal to that of the laminate made with the control resin and MEKP.

Occasionally in the field, it has been observed that a laminate with a moderate thickness might have lower exotherm when using the MEKP/CHP compared to the same laminate made using only MEKP. However a thicker laminate might have a higher exotherm with the MEKP/CHP than with a MEKP only initiator. To determine if this would occur with the resin system developed in this work, laminates were made using 5 alternating plies of woven roving and chopped strand mat. The same procedures and values recorded were used with the 5 ply laminate as were used in the 3 ply laminate tests. The results are reported in Table 11.

The exotherms of the 5 ply laminate made with the MEKP/CHP blend were much lower than the laminate made with the standard MEKP. The gel times were also longer. The effect of the MEKP/CHP in the 5 ply laminate was similar to those observed in the 3 ply laminate

Commercial Application

Some fabricators have expressed a reluctance to use two peroxides in their laminating process. They are concerned about how to handle switching between the two peroxides and the possibility of using the incorrect peroxide for the application.

In plants where the parts move down a production line, changing the peroxide in the spray equipment at the skincoat station is all that is required.

For those fabricators that apply the skincoat and bulk laminate at one station, a change in equipment is required before two peroxides can be used. A separate gun can be used for the skincoat application, but it is not required. The current one-peroxide equipment can be modified to use two different peroxides. An additional slave arm and peroxide line can be added to existing equipment. A valve at the pump and the gun head allows switching between the two peroxides with only a very small amount of residual material in the lines.

After the equipment issues have been resolved, the fabricator's next concern is the possibility of using the wrong peroxide for a lamination step. With the AAP, there is a distinct laminate color difference that would make it apparent very quickly if the AAP is being used.

There is no such visual difference in laminate color between the high dimer low hydrogen peroxide MEKP, and the CHP/MEKP blend. Separate storage and clear markings on the peroxide containers in storage and on the containers on the application equipment will help prevent inadvertently using the wrong peroxide.

Conclusions

The test results clearly demonstrate that when the additives in the resin are specifically designed to work with the selected peroxide, a wide range of gel, exotherm, and cure development can be achieved in thick and thin laminates. Resin A, when used with AAP, provides a very rapid cure in a thin laminate such as a skincoat, at varying levels of the AAP. At a 1.75% level, Resin A can be used on simple parts where a fast skincoat gel time is desired to speed up the fabrication process. On complex parts that require more working time, the level of the AAP can be lowered to 1.25% to provide a 25% longer gel time and still have a cure rate in a thin laminate that is faster than that achieved with a standard resin using 2.0% MEKP. On thick laminates the fabricator has the option of using the same level of MEKP as used in a standard system and getting a 50% longer gel time with a reduction of almost 20% in the exotherm, or using a higher level of MEKP and get similar gel and cure properties as the standard system. Resin A allows more flexibility to compensate for changing ambient temperatures. During periods of high ambient temperature, the MEKP level in the thick bulk laminate can be lowered to 1.25% to provide the needed working time.

In the thick laminate, the exotherm with Resin B using the MEKP/CHP blend peroxide is by far the lowest. The reduction in exotherm comes with a price. The cure development of the thick laminate made with Resin B and the MEKP/CHP blend was the slowest of all the systems. This system is the best option for manufacturers that are getting higher exotherms in their thick laminate and want to lower it. The extension of cure development in the thick laminate make this system best suited for operations that have thick bulk laminates and adequate time between the application of the bulk laminate and removal of the part from the mold.

The faster cure of the skincoat laminate with the AAP system makes it ideal for fabricators who want to speed up their lamination process while maintaining or improving surface profile. For those fabricators with issues with high exotherms in thick laminates, the use of the MEKP/CHP greatly reduces the exotherm in the thick laminate.

This work clearly demonstrates that widely varying gel, exotherm, and cure properties can be achieved with one resin by using different peroxides and by optimizing the resin to work with these peroxides. The peroxide that

is selected by the fabricator will depend on which of these properties best fulfills the requirements of the fabricator's lamination process.

Reference

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Bibliography

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Table 1: Resin C 2 plies 2 oz mat laminate

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development				
						Min.	°F/°C	Min.	75'	90'
Standard MEKP	2.00	C	36.5	90/32	15.5	0	0	10	25	28
AAP	2.00	C	38.0	100/38	8.0	15	20	27	33	38
HDLH* MEKP	2.00	C	39.0	93/34	14.0	0	15	20	25	32

* high dimer low hydrogen peroxide

Table 2: Resin A 2 plies 2 oz mat laminate

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development				
						Min.	°F/°C	Min.	75'	90'
AAP	2.00	A	45.5	95/35	9.0	15	15	25	33	38
Standard MEKP	2.00	A	52.0	82/28	12.0	0	0	5	15	18

Table 3: Comparing different levels of AAP 2 plies 2 oz mat

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development				
						Min.	°F/°C	Min.	75'	90'
AAP	2.00	A	43.5	94/34	9.0	15	15	25	33	38
AAP	1.75	A	38.5	96/36	9.0	15	20	27	38	38
AAP	1.50	A	42.0	96/36	12.0	15	20	27	38	38
AAP	1.25	A	48.5	95/35	13.5	5	15	25	33	38

Table 4: Comparing different levels of HDLH MEKP 2 plies 2 oz mat laminate

Peroxide	%	Resin	Gel time Min.	Peak Exotherm Temp. °F/°C	Gel to Peak Min.	934 Barcol Development				
						75'	90'	120'	150'	180'
HDLH* MEKP	1.75	B	39.0	85/29	12.0	0	11	10	28	28
HDLH MEKP	2.00	B	36.0	86/30	16.0	0	13	20	25	28
HDLH MEKP	2.25	B	32.5	87/31	14.5	0	8	15	20	25
HDLH MEKP	2.50	B	30.5	83/28	11.0	0	0	15	18	24

* high dimer low hydrogen peroxide

Table 5: Comparison of varying standard MEKP 2 plies 2 oz mat

Peroxide	%	Resin	Gel time Min.	Peak Exotherm Temp. °F/°C	Gel to Peak Min.	934 Barcol Development				
						75'	90'	120'	150'	180'
Standard MEKP	1.75	C	40.5	86/30	18.5	0	0	7	20	26
Standard MEKP	2.00	C	36.5	90/32	15.5	0	8	17	25	28
Standard MEKP	2.25	C	33.0	89/32	10.0	0	5	15	20	25
Standard MEKP	2.50	C	27.0	93/34	11.0	0	0	10	20	23

Table 6: Comparison of properties at the similar gel times 2 plies 2 oz mat

Peroxide	%	Resin	Gel time Min.	Peak Exotherm Temp. °F/°C	Gel to Peak Min.	934 Barcol Development				
						75'	90'	120'	150'	180'
AAP	1.75	A	38.5	96/36	9.0	15	20	27	38	38
HDLH* MEKP	2.00	B	36.0	86/30	16.0	0	13	20	25	28
Standard MEKP	2.00	C	36.5	90/32	15.5	0	8	17	25	28

* high dimer low hydrogen peroxide

Table 7: 3 plies 18 oz woven roving, 3 plies 1.5 oz chopped strand mat
Control resin with standard MEKP

Peroxide	%	Resin	Gel time Min.	Peak Exotherm Temp. °F/°C	Gel to Peak Min.	934 Barcol Development							
						90'	105'	120'	135'	150'	180'	210'	240'
MEKP	1.25	C	51	120/49	18.0	8	12	18	24	32	33	35	38
MEKP	1.50	C	43	127/53	15.0	18	23	30	30	32	37	40	40

Table 8: 3 plies 18 oz woven roving, 3 plies 1.5 oz chopped strand mat
Varying levels of MEKP with resin A

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development							
						Min.	°F/°C	Min.	90'	105'	120'	135'	150'
MEKP	1.25	A	79	99/37	33	0	0	0	0	5	8	18	32
MEKP	1.50	A	68	109/43	27	0	0	5	21	25	32	40	40
MEKP	1.75	A	61	117/47	19	5	13	18	27	32	38	40	40

Table 9: 3 plies 18 oz woven roving, 3 plies 1.5 oz chopped strand mat
Resin B with MEKP/CHP blend

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development							
						Min.	°F/°C	Min.	90'	105'	120'	135'	150'
MEKP/CHP	1.25	B	65	95/35	32	0	0	0	0	2	18	24	32
MEKP/CHP	1.50	B	55	102/39	21	0	0	0	0	15	25	35	38

Table 10: 3 plies 18 oz woven roving, 3 plies 1.5 oz chopped strand mat
Comparison of systems with similar gel times

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development							
						Min.	°F/°C	Min.	90'	105'	120'	135'	150'
MEKP	1.75	A	61	117/47	19	5	13	18	27	32	38	40	40
MEKP/CHP	1.50	B	55	102/39	21	0	0	0	0	15	25	35	38
MEKP	1.25	C	51	120/49	18	8	12	18	24	32	33	35	38

Table 11: 5 plies 18 oz woven roving, 5 plies 1.5 oz chopped strand mat
Comparison of MEKP to MEKP blend in resin system A and B

Peroxide	%	Resin	Gel time	Peak Exotherm Temp.	Gel to Peak	934 Barcol Development									
						Min.	°F	Min.	90'	105'	120'	135'	150'	180'	210'
MCP-75	1.25	B	62	116	26	0	0	3	12	25	28	32	33	36	40
MEKP-9	1.25	B	49	159	18	12	32	45	45	45	45	45	45	45	45
MEKP/CHP	1.50	A	80	104	34	0	0	0	0	2	20	27	29	35	40
MEKP	1.50	A	65	130	24	0	3	24	30	34	38	40	45	45	45