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Optimizing Peroxide Performance for Vacuum Infusion

By
Dennis Fink
Syrgis Performance Initiators, Inc.

Target:

Large part vacuum molders. Filament winders, Equipment manufactures, Resin formulators, and Coring venders.

Abstract:

When used to harden unsaturated polyester (UPR) and vinyl ester resins (VER), high dimer methyl ethyl ketone peroxides (MEKP) alone, or in combination with cumyl hydroperoxide (CHP), give longer gel times, do not show a viscosity build up, and do not affect the green strength development as seen in high monomer and/or high hydrogen peroxide MEKPs, or blends of same with cumyl hydroperoxide. These advantages are seen in various resins used for the infusion process, including a VER, two Isophthalic (ISO) resins, one corrosion resistant resin, a high strength ISO resin, and an Orthophthalic resin.

Introduction:

Modern MEKP formulations are made up of various combinations of four active ingredients; hydrogen peroxide (H_2O_2) and the monomer, dimer and trimer forms of MEKP. The H_2O_2 primarily affects the gel time, more H_2O_2 usually gives a faster gel time, while less H_2O_2 slows the gel time. The MEKP monomer primarily drives the cure, but can also affect the gel time in some resin formulations. The dimer drives the cure through, while the trimer does not contribute to cure or gel to any significant degree in the resins studied. Orthophthalic UPR can usually be fully cured with the monomer of MEKP, while ISO and VE resins tend to require a significant amount of the dimer. Because of these characteristics, it has become common practice to use these "match ups" in most of the fabricating processes in use today. Another common practice is too reverse the products when one needs to slow down, or reduce the exotherm of a laminate, i.e., switch to a high monomer product to reduce the laminate exotherm of a resin that normally works best with a high dimer product.

As mentioned, monomer can also contribute to the gel time in some resin systems. This can be seen as a secondary exotherm, normally occurring one half to two thirds into the laminate gel time. This exotherm corresponds to cross linking occurring, and can be physically observed as an increase in viscosity. In open molding, this phenomena is commonly referred to as "the stickies" when the laminate gets harder to roll, and the resin sticks to the back side of the roller (See Figure 5). In RTM or vacuum Infusion, it is noted when the "leading edge" becomes thicker, and glass "wet out" and "air release" become much harder. In the past decade, blends of high monomer MEKP and CHP have become popular to extend the operating gel times and lower the process exotherm, and while reducing viscosity gain, do not completely control it (See Figure 4). For the infusion process to work properly, a long gel time is often useful, together with limited viscosity build before gel, so that the resin can flow where it's needed, wet-out is optimized, and air bubbles can leave the laminate before gel occurs. This holds true for the filament winding process, where a viscosity increase could entrap air between layers of glass on the mandrel, causing voids and dry spots.
The peroxide initiator formulation which demonstrated one, or more, of the desirable properties is a low H_2O_2, high dimer MEKP like MEKP-925H (See Figure 6). When blended with CHP, these properties were enhanced even further. As in blends of high monomer MEKP and CHP like MCP-75, gel time is lengthened and peak exotherm is reduced with the use of increased amounts of CHP, but the cure time is not affected as much. At fairly high MEKP content with a high dimer MEKP, it is possible to have a long gel time, a fairly quick green-strength development after gel, and an excellent cure after 24 hours.

Experimental:

The formulation parameters of the MEKPs and the MEKP/CHP blends which were studied are given in Table 1. Please note that for all tests, a high monomer MEKP was used, with about 1% hydrogen peroxide, for comparative purposes. For some resins a high monomer MEKP which had 2% hydrogen peroxide was also tested. The high dimer MEKP contained very low (0.3%) levels of hydrogen peroxide. Both hydrogen peroxide and MEKP monomer shorten gel time. Both MEKP monomer and MEKP dimer are important in achieving good cure, as is CHP, when present.

Gel times were taken using a Sunshine gel meter, Syrgis SOP 258A. (All Syrgis SOPs are available on request.) Viscosity changes in the initiated resin samples were measured using a Trombotech viscometer and/or a Brookfield model DV-I. Cure data was collected using Syrgis SOP 269.

Test results for a VE Infusion resin show that, as compared to the equivalent blends made with MEKP-9/CHP, blends using MEKP-925H/CHP give similar gel times, shorter time from gel to cure, and a 23°F higher exotherm (See Table 2). The magnified plot of the time between initiation and gel shows that the blends using the MEKP-9/CHP has an increased exotherm and showed a doubled viscosity for the last third of the time before gel, compared to the HDP-75 blend. As the graphs below show, both this viscosity build up and pre-gel exotherm are mainly absent in the HDP-75 blend (See Figure 4). Note that cure for the HDP-75 is as good as, or better, when compared to the MCP blends.

An Ortho infusion resin shows that High Dimer MEKPs have much longer gel times than High Monomer ones, and that the blends of MEKP-925H/CHP also have much longer gel times than the blends of MEKP-9/CHP. Excellent cure was obtained for all the initiators studied (See Table 3).

A "Standard Marine" grade infusion resin shows gel times of: 10 minutes with MEKP-900, 39 minutes with initiator MEKP-9H, and 70 minutes with initiator MEKP-925H. Note that the increase of gel time from 10 to 39 minutes for this resin is caused by a lowering of initiator hydrogen peroxide content only. Going to a high dimer initiator further lengthens the gel time to 70 minutes. The Gel to peak ratio remains the same for the last two. Interestingly, Pulcat, a high dimer product with 1% free hydrogen peroxide, also gives a long gel time of 60 minutes (See Table 4).

A 1:1 ISO (See Table 5) short to medium gel times, but an abnormally high initial exotherm accompanied by a large viscosity increase. Upon mixing initial exotherm increases ranged from 5 - 9 °F, accompanied by a viscosity increase of 4 times the starting viscosity. This phenomenon can explain the "leading edge" effect, why some resin systems cause wet out problems, increased back pressure, and reduce the flow rate after a short time.

Conclusion:

This study shows that for the variety of resins studied, the high dimer MEKP initiates with longer gel times and lower initial exotherm than their high monomer counterparts. This property can be further enhanced by blending the high dimer MEKP with CHP. The advantages to the fabricator should be obvious, lower initial exotherm, or lower viscosity increases due to the exotherm allow a cavity to be filled quicker, and probably with less back pressure (not in the scope of this study). A common "rule of thumb" is to have the cavity filled before one sees a 30% rise in viscosity. This is a good rule and has prevented many bad parts, but it has the built in time restraint of the last 70% of the gel time of nothing productive happening.

With a high dimer MEKP, or a blend of high dimer MEKP and CHP, it is suggested the time required to fill the cavity, with a 10% margin built in, becomes the new target gel time. This saves both time and associated labor. Current high monomer MEKP/CHP blends are effective in dramatically lowering the peak exotherm, a good attribute for thick sections, but at the expense of longer molding cycles. It is suggested the high dimer/CHP blends would be very efficient for thinner cross sections; i.e. "skins", "cored laminates", etc., both in the infusion and filament winding processes. There is no "magic bullet" in our industry, nor does "one size" fit all, but with proper selection and engineering, a low H2O2/hi dimer product, or blend with CHP, can help optimize many processes.

Table 1 – Initiator composition used in testing.

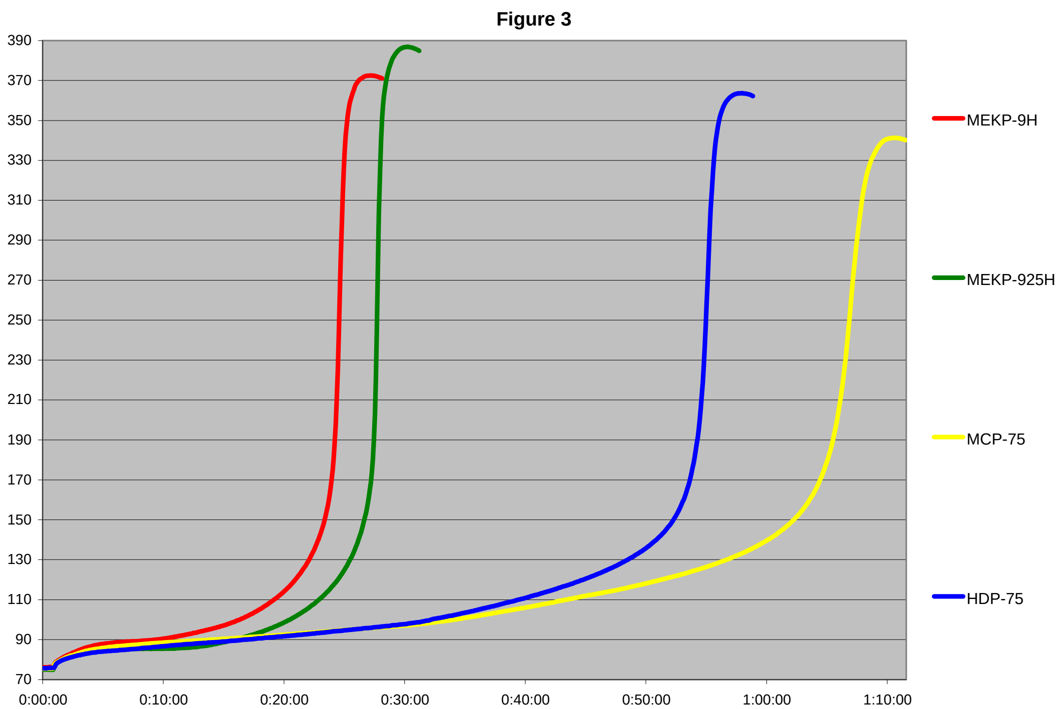
Initiator Name	%Active Oxygen	%Hydrogen Peroxide	% MEKP Monomer	%MEKP Dimer + Trimer	% CHP
MEKP-900	8.9-9.0	2.0	24	8	0
MEKP-9	8.9-9.0	0.9	25	9	0
MEKP-9H	8.9-9.0	0.5	26	9	0
MEKP-925H	8.9-9.0	0.2	18	18	0
MCP-75	8.9-9.0	0.7	19	7	22
HDP-75	8.9-9.0	0.2	14	14	22

Figure 1

Table 2 – VE VRTM Resin

Initiator	Gel Time	Cure Time	Time to Peak	Peak Temp	4 hr Barcol	24 hr Barcol
MEKP-9H	14.9	12.3	27.2	373°F	45-50(5)	10-15(4)
MEKP-925H	17.2	10.5	27.7	388°F	45-50(5)	10-15(4)
MCP-75	31.9	38.7	70.6	341°F	10-15(D)	15-20(4)
HDP-75	31.5	26.5	57.9	364°F	25-30(D)	15-20(4)

Figure 2 – (1.50% Initiator Level) @ 77°F



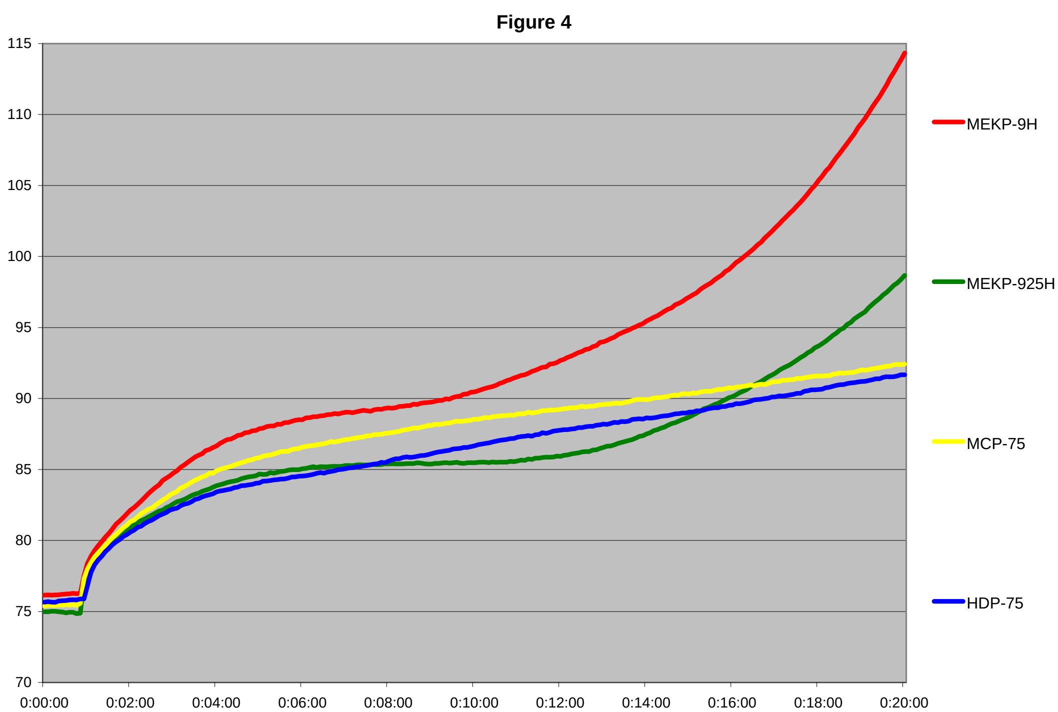


Figure 5 **MEKP-900**

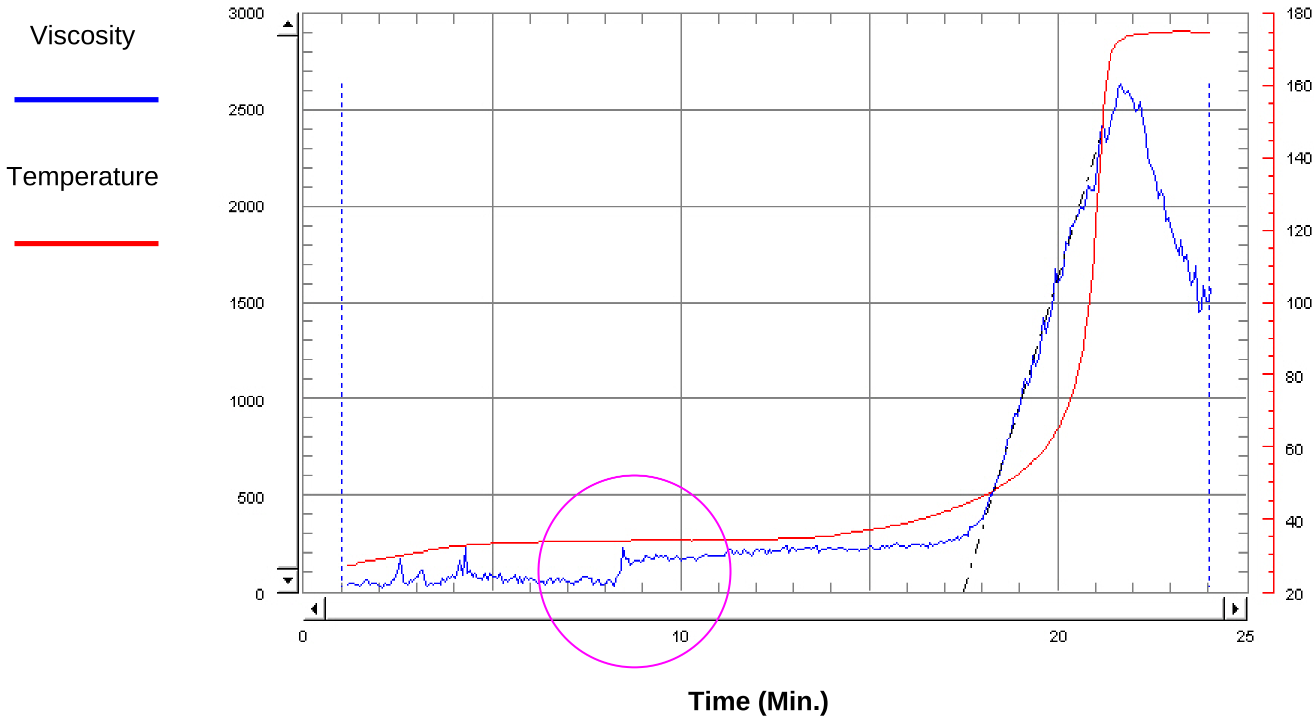


Figure 6 **HDP-75**

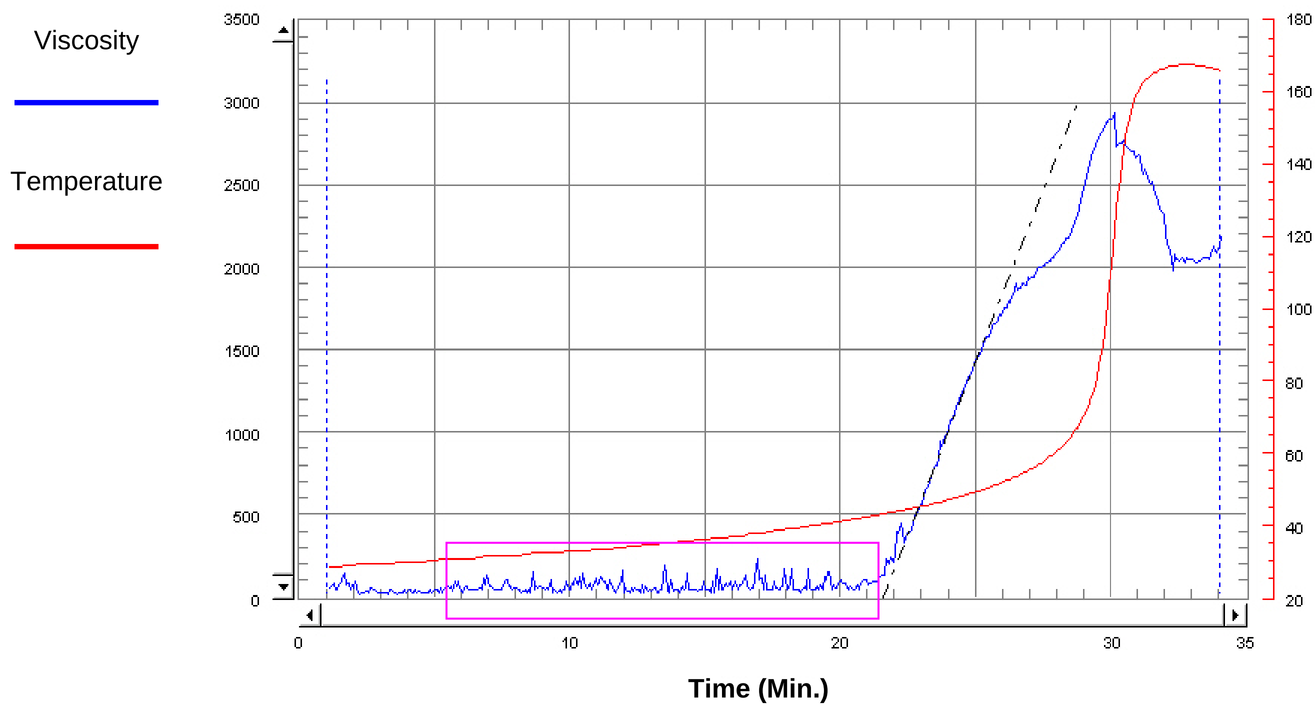
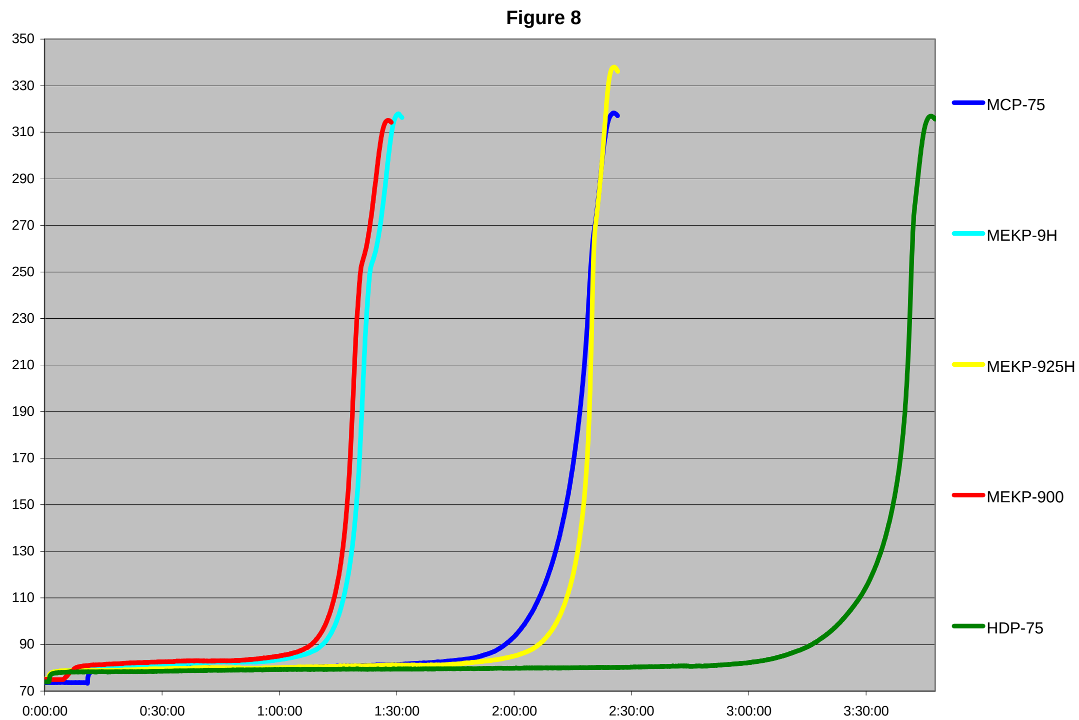


Table 3 – Ortho VRTM Resin

Initiator	Gel Time	Cure Time	Time to Peak	Peak Temp
MCP-75	120.5	15.0	135.5	318°F
MEKP-9H	79.0	11.4	90.4	318°F
MEKP-925H	127.9	17.7	145.6	338°F
MEKP-900	71.5	16.2	87.7	315°F
HDP-75	198.0	28.7	226.7	317°F

Figure 7 – (1.50% Initiator Level) @ 77°F



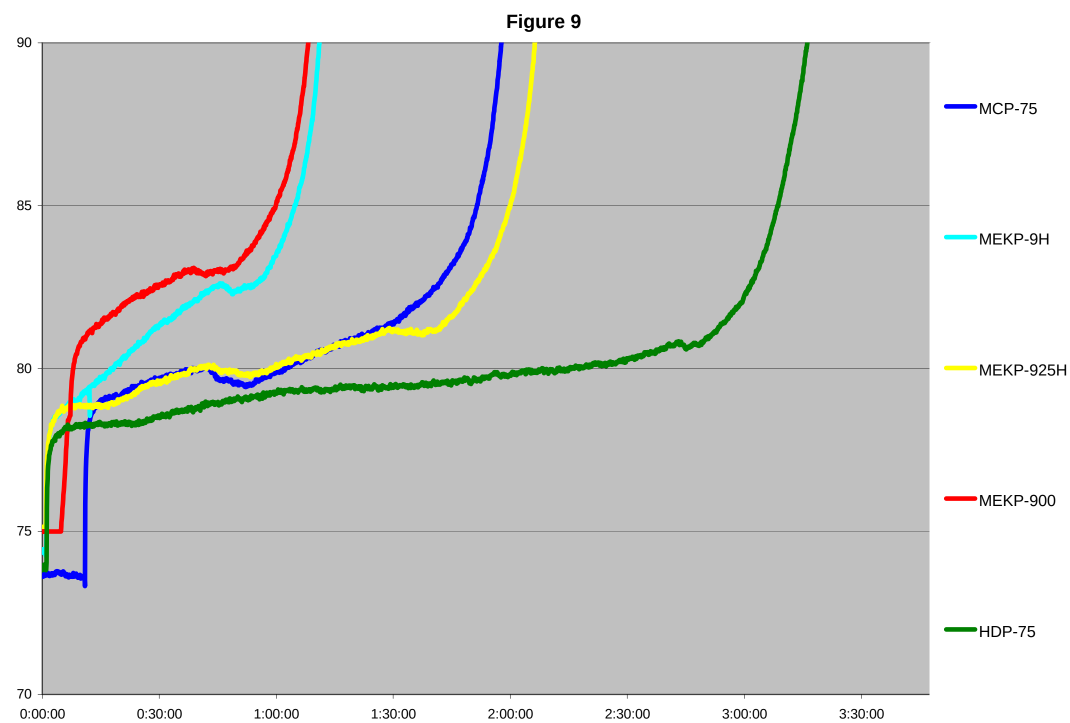
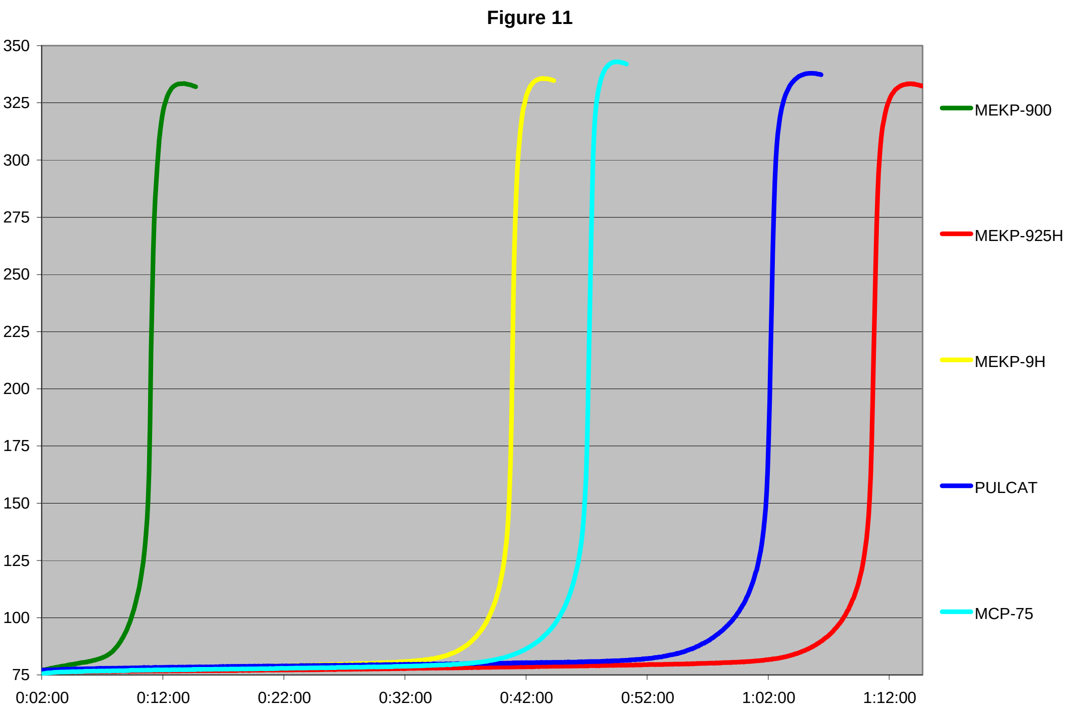


Table 4 – Standard Marine Infusion Resin

Initiator	Gel Time	Cure Time	Time to Peak	Peak Temp	1 hr Barcol	3 hr Barcol	24 hr Barcol
MEKP-900	10.0	3.8	13.8	333°F	25-30(4)	25-30(4)	25-30(4)
MEKP-925H	70.3	3.4	73.8	333°F	N/A	25-30(4)	25-30(4)
MEKP-9H	39.4	4.0	43.3	336°F	15-20(D)	25-30(4)	25-30(4)
PULCAT	60.2	5.2	65.4	338°F	N/A	25-30(4)	25-30(4)
MCP-75	44.1	5.2	49.3	343°F	N/A	25-30(4)	30-35(4)

Figure 10 – (2.00% Initiator Level) @ 77°F



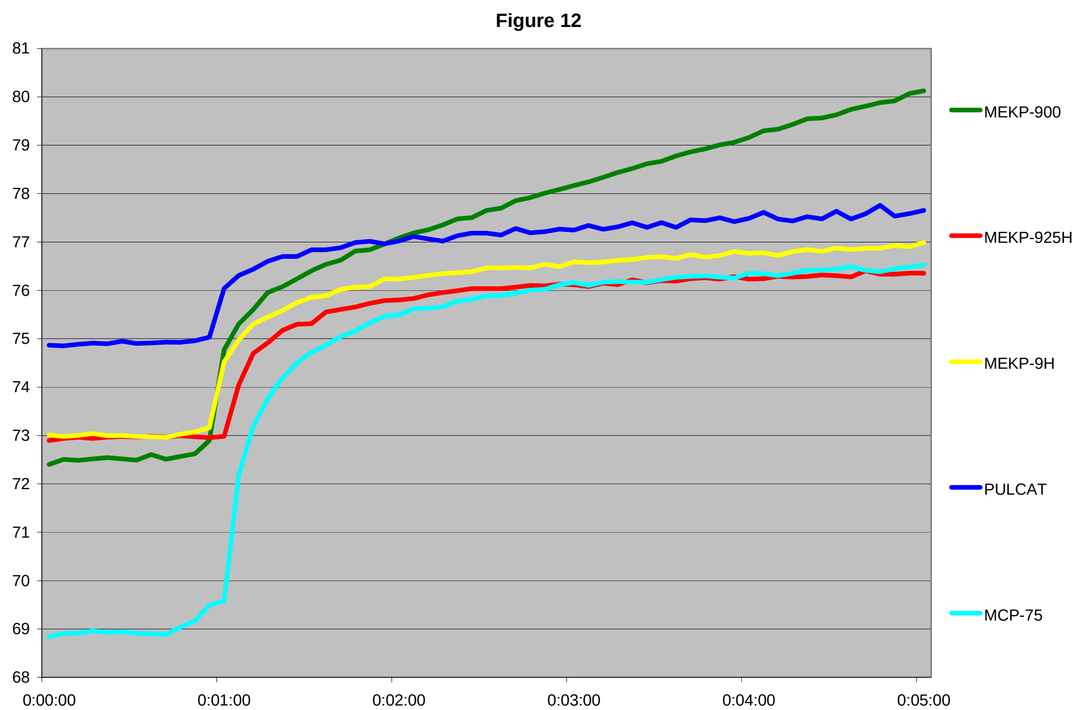


Table 5 – Isophthalic (1:1 ISO) RTM Resin

Initiator	Gel Time	Cure Time	Time to Peak	Peak Temp
MEKP-925	18.2	8.1	26.3	350°F
MEKP-925H	17.7	6.6	24.3	350°F
MEKP-9	24.8	7.9	32.8	335°F
MEKP-900	26.5	9.2	35.7	333°F
MEKP-9H	28.1	8.8	36.8	336°F
HDP-75	23.2	10.3	33.5	351°F

Figure 13 – (1.50% Initiator Level) @ 77°F

Figure 14

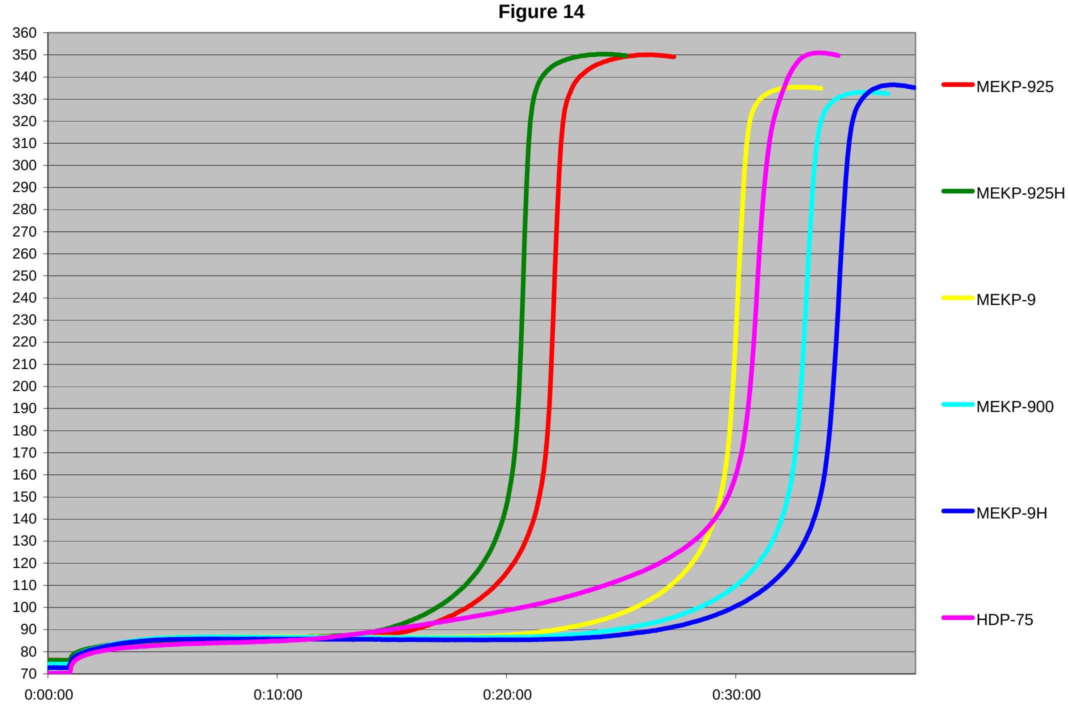
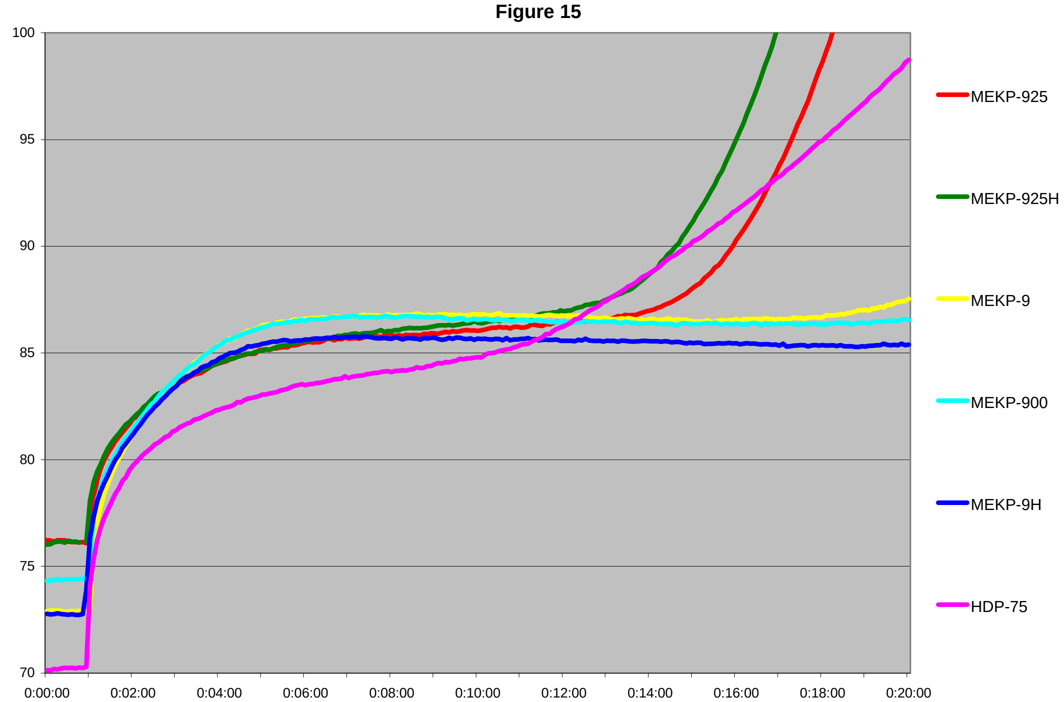


Figure 15



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