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Low Styrene Content Filled Resin Systems

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ABSTRACT

New low styrene unsaturated polyester resins have been developed for the filled market segment. These polyesters maintain viscosity and thix indexes of conventional systems while offering dramatic reduction in styrene content.

The next generation resin system has a styrene content of 30%. Although the styrene content has been dramatically reduced, rollout and wetout remain equal to the higher styrene systems. The cure profile is rapid while maintaining low peak temperatures. Shrinkage is minimal, and physical property test results are comparable to typical polyester resin used in filled applications. The Heat Distortion Temperature is dramatically improved over traditional filled resin systems that are available in the industry today, which contain a much higher level of styrene.

As the new generation of resin is introduced, liquid properties and physical properties will be compared to resins typically used in the filled market sector.

HISTORICAL BACKGROUND IN FILLED SYSTEMS

Filler was introduced to the market in the early seventies as a way of adding a degree of fire retardancy to a finished part. Alumina trihydrate was the filler of choice. The reason for using Alumina trihydrate was approximately 35% water is given off upon heating to temperatures of 300C or higher. Therefore provides fire retardant properties.

Later, filler was added similar to a diluent, that is, as a way of extending the resin system, which lowered the cost on the finished components produced. Additional attributes also contributed to the use of fillers. Opacity of filled systems improved the surface cosmetics, cracks were reduced in areas of tight radii, parts were more rigid and shrinkage was reduced.

Early on, resin systems used were typically orthophthalic in composition. The level of styrene in the systems averaged 50%. These resin systems had filler loading of 40%-50% using alumina trihydrate.

Many challenges were presented as filler was introduced to resin systems. Some of the obstacles to overcome were as follows; maintaining a workable viscosity for sprayability, optimizing the thix index to prevent “sliding” on horizontal surfaces, good wetout and rollout abilities, and the ability to keep the filler from packing in the day tanks and lines. As systems evolved, suppliers worked with fabricators to overcome these areas of concern.

Fabricators began to blend different types of fillers. Calcium carbonate was blended with alumina trihydrate. This allowed for an even further reduction in cost on the finished parts. Calcium sulfate (Gypsum) also was used. The Gypsum releases water molecules at 200°F when heated. Thus, it also is flame-retardant filler.

Glass contents on resin systems before filler was introduced were typically targeted at 25%. As the fabrication of parts evolved using fillers, glass contents were reduced to a range of 10 to 15%. Which again reduced the cost of the finished part.

The filled market segment of open molding has changed dramatically over the years. New chemistries of polymers were introduced. In 1980 polyester resin based on DCPD (dicyclopentadiene) as a raw material were introduced to the market. They were lower in molecular weight than the orthophthalic resins, thus allowing for an increase in filler loading. One of the attributes of the DCPD based systems was processability. These systems made the roll out and wet out of glass much less burdensome.

Figure #1 represents the evolution of filled resins systems. It compares a traditional orthophthalic system to the newer chemistries of resin that have evolved over the years.

Each system was thinned with styrene to a targeted filled viscosity of 1000-1200 cps with a thix index range of 2-3. The range is typical of specifications that most fabricators use. Each system was filled at 47% loading.

One of the reasons for the creation of a new polymer was increasing pressures on the industry by the government to reduce HAPS in a fabricator's shop. The new polymer has a styrene content of 30%. This is a 33% reduction in styrene over traditional orthophthalic resin systems.

INTRODUCTION OF NEW LOW STYRENE SYSTEM

One of the problems encountered when removing styrene from a system is that the physical properties are dramatically reduced. Testing indicates that a system can become styrene deficient, in that there is not enough styrene in a system for the necessary crosslinking to occur. As a result, parts are under cured and tend to be sticky. DSC results indicate that this is indeed true and the parts will tend to post print and distort. With this information taken into consideration, a new polymer was created by careful selection of glycol and acids at specific ratios to reduce styrene and maintain processability of the filled resin system. The viscosity and thix index are equal to that of the orthophthalic system; however, the styrene content has been reduced by 33%.

IMPACT ON PHYSICAL PROPERTIES

Figure #2 compares the physical properties of the different resins used in filled systems as they have evolved over the years.

The samples were made via the industry standard of clear casting, non-filled, promoted with cobalt 12% and 1.25-% MEKP. All samples were post cured.

As expected, the physical properties in a clear casting have dropped in value. The main point of interest is that the new system at 30% styrene has a higher HDT than any of the other systems at much higher levels of styrene. This is important for fabricators of truck caps and tonneau covers that are post cured and painted at higher temperatures. If the HDT is too low, the parts will sag or droop in the middle. The following photos (Figure #6, Figure #7) demonstrate a part bridged in the air with no middle support. The test bars were placed in a 90°C oven for one hour. As one can clearly see, the new polymer maintains its integrity, the system with the lower HDT sags dramatically in the middle.

LAMINATE PHYSICAL PROPERTIES

Clear cast physical properties have been accepted as an industry standard, however, they do not clearly reflect filled laminate physical properties. The following table lists the comparison properties of laminates on the same systems in the previous tables. Looking at the data in the clear cast table, one can see the reduction in some of the physical properties. The filled laminate physical property results portray a different picture. The "drop" in values are minimal. A slight increase in glass content can easily overcome any reduction in physical properties one may experience by using a lower styrene system. Figure #3 demonstrates those results.

The laminates were prepared in the same manner; filled at 47%, targeted 15% glass, and 21% glass on the new polymer. Analytical testing was performed on the laminate itself to determine the exact glass content of each laminate.

CURE PROFILE

Figure #4 lists the cure profile of filled resin systems that have evolved over the years.

Identical formulations were used to demonstrate the difference in cure profile and hardness progression. The only difference in the formulation is the level of styrene. Each system was thinned with styrene to meet the 1000-1200 cps viscosity and a thix index of 2.0 to 3.0.

As one can see by the test results, the new polymer meets and matches the cure profile of previous systems. The hardness development is improved, allowing for quicker throughput of parts. Formulations can be tailored to meet the customer's fitness criteria on peak temperature without adversely impacting the cure profile.

IMPACT ON SHRINKAGE

Reducing styrene and/or adding filler to a system reduces linear shrinkage.

Figure #5 demonstrates the differences in linear shrinkage from the traditional orthophthalic system to the new polymer. All samples were filled at 47% (contains no glass). The samples were room temperature cured.

Results indicate that as styrene is reduced from the system, linear shrinkage is reduced to a minimum. This translates to dimensional stability on the finished parts.

CONCLUSION

Fabricators are looking for ways to reduce HAPS in their process through many different avenues. A combination of technologies may be necessary to meet desired levels of HAPS. Non-atomizing spray equipment along with a reduced HAP resin system that maintains filler loading of traditional resin systems will offer the fabricator the most economic solution to HAP reductions in his production facility. Fabricators that are need of low styrene resin systems to meet permit issues or MACT standards set forth by government mandates, without loss of the integrity of the resin system, should consider the new low HAP system.

Figure 1.

Variables	Traditional Orthophthalic System	First DCPD Systems	Next Generation of DCPD	New Polymer
Styrene Content	45%	38%	36%	30%
Viscosity, LV #3 @ 60	1096	1144	1148	1120
Thix Index, 6/60	2.4	2.8	2.7	3.0

Figure 2.

Clear Casting Mechanical Test Results		Traditional Orthophthalic System	First DCPD Systems	Next Generation DCPD	New Polymer
ASTM-D 790					
Flexural Strength	**Psi**	21,000	18,000	15,000	13,000
	Mpa	145	124	103	90
Flexural Modulus	**Psi**	610,000	480,000	560,000	550,000
	Gpa	4.2	3.3	3.9	3.8
ASTM-D 638					
Tensile Strength	**Psi**	10,400	8,100	8,900	7,700
	Mpa	72	56	61	53
Tensile Modulus	**Psi**	510,000	450,000	500,000	520,000
	Gpa	3.5	3.1	3.4	3.6
Elongation	**%**	3.5	2.4	2.1	1.6
ASTM-D 648					
HDT	**°C**	59	83	93	105
	°F	138	181	200	221
ASTM-2583					
Barcol Hardness	**934-1**	47	43	45	50

Figure 3.

Laminate Physical Property Test Results		Orthophthalic System at 14.4% Glass	Early DCPD System at 16.3% Glass	New Polymer at 16.7% Glass	New Polymer at 19.5% Glass
ASTM-D 790					
Flexural Strength	Psi	17,700	18,900	17,600	23,700
	Mpa	122	130	121	163
Flexural Modulus	Psi	1,300,000	1,300,000	1,300,000	1,300,000
	Gpa	9.0	9.0	9.0	9.0

Figure 4.

Styrene Content Cure Profile		Traditional Orthophthalic System	Early DCPD System	Next Generation DCPD System	New Polymer
Styrene Content	%	45%	38%	36%	30%
Gel Time 1.25% DDM-9, 100g cup		19.0	22.5	20.0	18.4
Gel to Peak		23.0	14.5	12.2	8.4
Peak Temperature	°C	120	124	142	136
	°F	150	256	287	276
Barcol Hardness 934-1 ASTM-2583 40g, 1 hour, room temp. cure		62 SD	25 HB	25 HB	38 HB

Figure 5.

Linear Shrinkage	Traditional Orthophthalic System	Early DCPD System	Next Generation DCPD System	New Polymer
Percent	12.9	7.5	4.6	2.0
Styrene Content	45%	38%	36%	30%

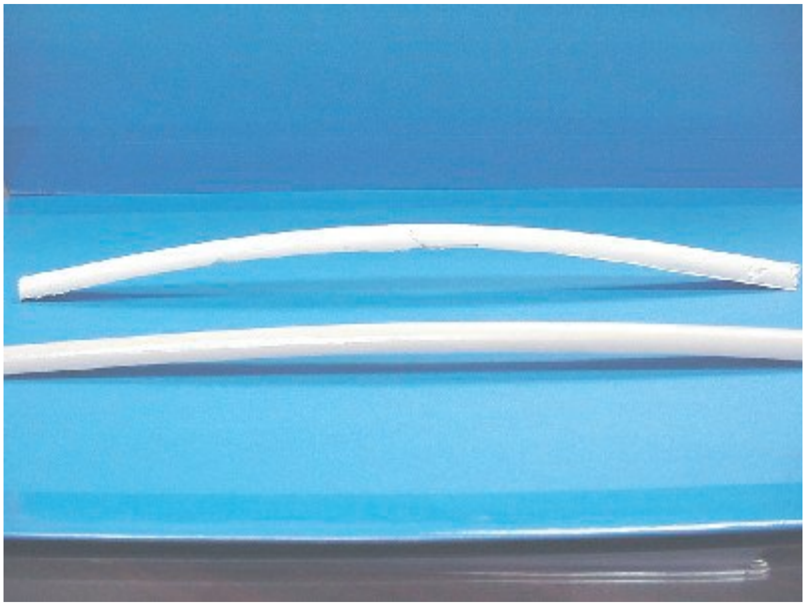

Figure 6. The photo above demonstrates the improved Heat Distortion Temperature of the new polymer filled. The front specimen is the new polyester. The specimen in the background is a sample from the traditional polyester resin system.

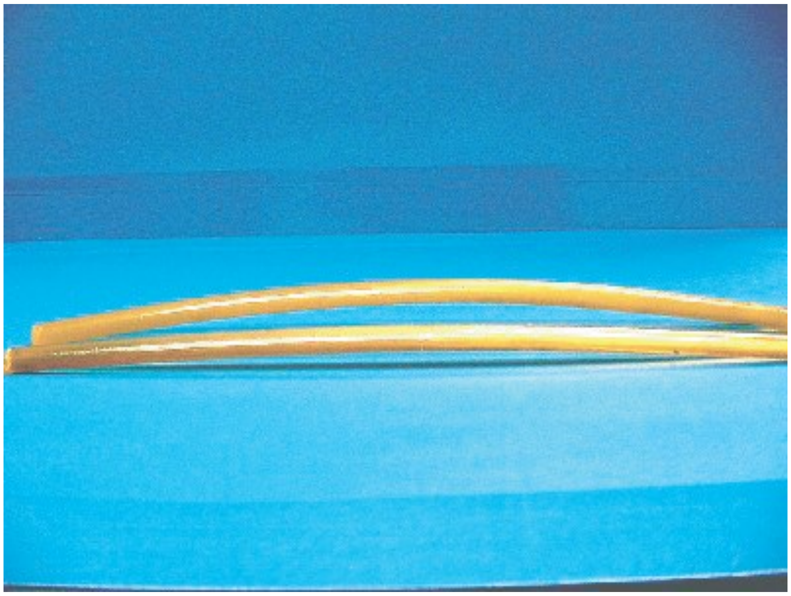

Figure 7. The photo above demonstrates the improved HDT of the new polymer without the addition of filler. The front test bar is the new polymer. The specimen in the background is an example of traditional resin systems that have lower HDT temperatures.