Styrene-free UV cured Resin systems for Composites

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Introduction:

The use of styrene containing resins systems while common has a number of areas of concern in industrial applications. A number of Federal, State, and possibly local regulations can require a significant effort to control and/or monitor emissions of the material. There are also health concerns regarding worker exposure to styrene. Despite these drawbacks the use of Styrene in conjunction with unsaturated polyester resins or vinyl ester resins is still common in many composite applications. The relative cost of Styrene compared or other diluents is low and the material possesses a good cure speed both in thermally and radiation cured systems compared with many mono-functional materials. Combine these attributes with the generally good physical properties obtained of these resin systems employing styrene and it is no surprise that it use remains quite significant.

This paper discusses a number of alternative resin systems that have been employed many in conjunction with UV (Ultraviolet) curing as an alternative to thermal curing to eliminate styrene without a significant negative impact on costs and generally a positive impact of productivity and capacity.

Background and Definition:

Three basic types of resin systems are compared in this paper. The first (Type I) is the reference material which is a thermally cured unsaturated polyester resin containing roughly 40 – 45 weight percent styrene utilizing a peroxide-Cobalt accelerator cure system common in the industry. The second (Type II) consists of thermally cured resin formulations based on acrylate or methacrylate functional materials and cured by utilizing the same peroxide-Cobalt accelerator cure system as the first resin system type. The third resin system (Type III) consists of UV cured resin formulations based on acrylate or methacrylate functional materials and cured by UV radiation using a variety of free radical type Photoinitiators commonly available to the industry at large. A list of the specific initiators evaluated and their chemical structures can be found in Appendix A. The choice of initiator system was an important factor in formulation cost of the resin system and will be discussed separately later in this paper. Although as a practical matter not specifically tested in this work, the resin systems employed in the second and third types could as easily be cured by EB (Electron Beam) irradiation in the first author's educated opinion and experience.

Type I resin system consists of only one control formula for purposes of this paper and is the reference point for the comparison of the various formulations of Type II and Type III resin systems. A sample designation of II-A or III-A-1 will refer to the same base resin formulation, that is oligomer, monomer, and non-curing additive composition but will of

course utilize different cure packages. Type II resins for simplicity of the data presented within the scope of this paper will all consist of exactly the same type and concentration of the peroxide-Cobalt cure system as Type I resin unless specifically noted. The additional numeric designator for Type III resin systems will refer to a specific type of photoinitiator package. For example, III-A-1, and III-B-1 will be samples of differing oligomer, monomer, and non-curing additive composition but exactly the same type and concentration of photoinitiator package. Likewise III-A-1 and III-A-2 will be of identical oligomer, monomer, and non-curing additive composition but utilize different photoinitiator packages. A photoinitiator package will consist of at least one free radical photoinitiator responding to light in a 250 – 430 nanometer wavelength range and possibly more such initiators or some combination with either a photosensitizer, amine synergist or both.

All thermally cured resins were cured using the same thermal processing regardless of whether they were Type I or Type II resins. All UV cured sleeves were cured using a simultaneous exposure to two Fusion UV Curing Systems Model F300S units, one equipped with a Type "D" bulb and the other with a Type "H+" bulb. All cure conditions were identical for all Type III resin samples.

The model composite construction was a simple cylindrical tube consisting of fiberglass reinforcement. In type I & II resin systems this fiberglass reinforcement was of a woven tape form while the Type III resins utilized fiberglass rovings. While this is admittedly a very different type of reinforcement the two different methods of reinforcement were carefully chosen to best represent the needed physical properties for the finished cylinder and the conclusions made in this paper are independent of any influence of the differing reinforcement layer based on testing not included in the scope of this paper. Conclusions that are drawn where the type of reinforcement would certainly have an effect are drawn only within a particular reinforced type cylinder not between cylinders with differing reinforcements.

Objectives and Limitations of Study:

The objectives of this study were twofold. The first was to evaluate the impact on overall operational cost per unit of thermal cured materials and styrene-free UV cured materials. The second was to look at factors influencing the cost of the styrene-free UV curable resin systems with emphasis on minimizing the cost premium over the standard thermal cured system. While the two objectives are not mutually exclusive it should be recognized that in the context presented certain constraints are not specifically identify in terms of actual costs but rather in terms of relative costs and efficiencies, et cetera so as to protect the proprietary information and trade secrets of Day International, Inc. Every effort was taken to treat the variables in the most objective manner to demonstrate the most significant effects of formulation or process changes.

Effects of Process: UV versus thermal

The primary impact of the process is that of throughput. The nature of the curing parameters of Type I and Type II resins is that the cure speed of the resin needs to allow sufficient working time to allow the cylinder to be constructed. This then affects the cure speed of the resin in the oven cure cycle. For some systems oven cure time may be much shorter than those listed here based on looser specifications on final structural dimensions, but for the tolerances allowed for in these parts the following times are required at a minimum.

The following table summarizes the difference in the relative time units between the two processes. A total of 113 units are used for the thermal process versus 3 units associated with the UV curing process. Of this difference it is important to note that this difference in actually direct labor time units is only 7 for thermal versus 2 for UV but still significantly improved on a per part basis. In this case, if we assume even a 50:50 split between material and labor costs in the overall cost per part and if we were to further assume that the resin component is 50% of all the materials in question, then the tolerable resin price should be approximately four times that of the standard thermal cured resin cost if all else is equal.

Process Type	Time Category	Build/Cure Cycle 1	Cure Cycle 2
Thermally cured	Labor Time	6 units	1 units
Thermally cured	Process Time	9 units	96 units
UV cured	Labor Time	2 units	N/A
UV cured	Process Time	1 units	N/A

Perhaps more importantly for many business models, the impact on turn around time per part is a major factor here. The UV cured part is completed in one-hundredth the time of the corresponding thermally cured part. The degree of cure of the parts was determined in several ways including bulk hardness, surface cure or tackiness, and via dynamic mechanical testing. Functional testing of the parts in its intended use was also an integral determination so these times are based on comparable form and function in all cases and all parts were deemed suitable for use as finished product.

Another capacity related phenomenon implicit in this result is a diminished requirement for tooling. Parts are required to remain on tooling through Cure Cycle 1. This can lead to a situation where the demand for a certain part may necessitate multiple tools of the same dimensions. This translates into a higher level of capital employed per unit production and ultimately translates into higher costs. The most significant factor can be seen in terms of part turn around time. As demands by customer continue to drive delivery times to practical minimums it is clear that the UV process affords much swifter response times and as a practical matter has a much higher production capacity per unit labor.

Resin properties and Costs:

Several variables were considered to minimize cost premium of a UV curable resin system over that of the cheaper styrene containing resin formulations. The first was choice of base resin or oligomer material. A wide range of products is available to the formulator of acrylate or methacrylate functional oligomer systems from the usual suppliers. In addition, there is the possibility of employing a number of resin systems that are not acrylate or methacrylate functional but which participate in a free radical curing reaction to such an extent and with favorable kinetics to be considered. A few unsaturated polyester and vinyl ester resins fall into this category as just two examples suitable for our application; there are more depending on the physical property requirements of the individual application.

The table below summarizes the results generically:

Sample ID	Surface Cure	Hardness	Physical Prop.	Cost
I-A (Control)	0	0	0	0
II-B	0	0	0	+++
II-C	0	0	0	++
III-B-1	+	-	-	+++
III-B-2	0	-	0	++
III-B-3	0	-	-	+
III-C-1	0	-	-	+++
III-C-2	0	-	0	++
III-C-3	0	-	-	+
III-D-1	+	0	0	+++
III-D-2	+	0	0	++
III-D-3	+	0	0	++
III-E-1	+	+	+	+++
III-E-2	+	0	+	++
III-E-3	+	0	0	++
III-E-4	0	+	+	++
III-E-5	+	0	+	+

0 = Acceptable Value
+ = More than acceptable Value; Acceptable Cost
++, +++ = Higher and much higher than desired costs

The major contributing factors to cost were (1) Photoinitiator Package Cost(s), and (2) Oligomer cost. While Photoinitiator choice had its primary effect on surface cure and hardness of the finished composite, it was the base oligomer that had the controlling influence on physical properties. Interestingly enough and perhaps obvious as well, the number of candidates that could achieve all the desired performance characteristics was far higher than the number of systems that could meet the cost constraint. However, it was possible to exceed the control values on most of the performance criteria and still achieve a desirable cost.

Conclusions and Recommendations

We were able to achieve our key performance and cost targets by a more complete understanding of not only the formulation properties, but also the impact on operational costs and capacities realized by the change in technology from thermal curing to UV curing. In addition, having a growing business allows the cost advantages to be phased in over time so that capital outlay and cash flow are more easily managed. There are several other benefits that also applied to our situation such as the desire to eliminate styrene from the working environment as well as the regulatory requirements of the manufacturing operation. Each of these has cost savings benefits in addition to the effect on unit manufacturing costs.

Our strategy was to quantify the opportunity from an overall benefit to operations perspective. We then derived how the cost structure of each of the different technologies would differ and the impact on the capacity of operations against forecasts. At this point it was possible to determine the proper cost target of the new raw materials needed to implement the new technology. Finally, careful experiments were designed around key product performance criteria to achieve desired properties and costs.
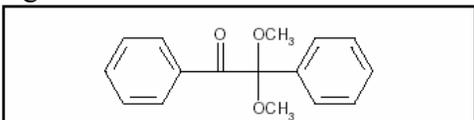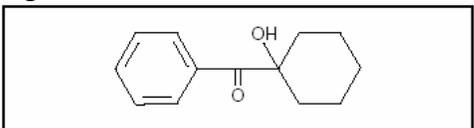
Appendix A:

Irgacure 819
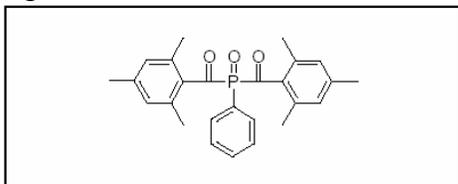
Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide

Irgacure 651

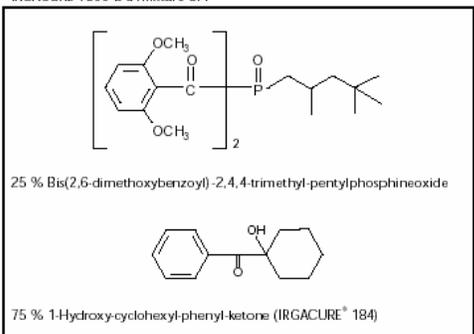2,2-Dimethoxy-1,2-diphenylethan-1-one

Irgacure 184

1-Hydroxy-cyclohexyl-phenyl-ketone
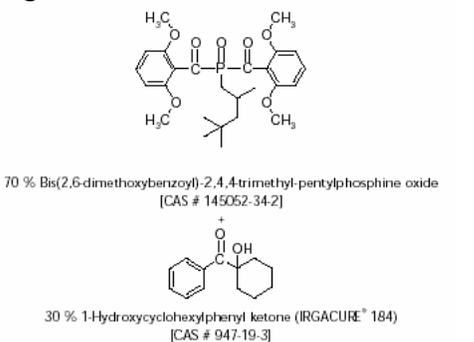Molecular weight: 204.3   CAS No. 947-19-3

Irgacure 1800

IRGACURE 1800 is a mixture of :

25 % Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphineoxide

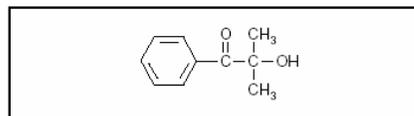75 % 1-Hydroxy-cyclohexyl-phenyl-ketone (IRGACURE® 184)

Irgacure 1870

70 % Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphine oxide
[CAS # 145052-34-2]
+
30 % 1-Hydroxycyclohexylphenyl ketone (IRGACURE® 184)
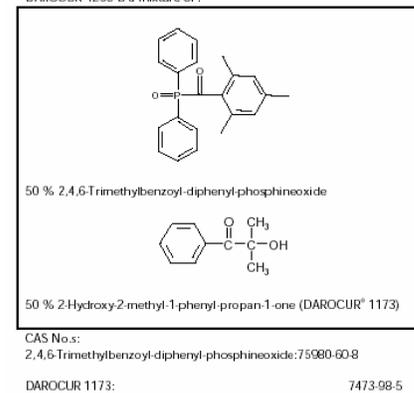[CAS # 947-19-3]

Darocur 1173

2-Hydroxy-2-methyl-1-phenyl-propan-1-one
Molecular weight: 164.2   CAS No. 7473-98-5
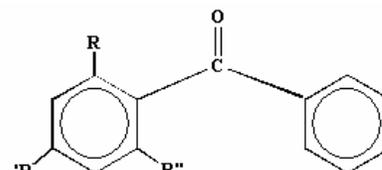
Darocur 4265

DAROCUR 4265 is a mixture of :

50 % 2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide

50 % 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (DAROCUR® 1173)

CAS No.s:
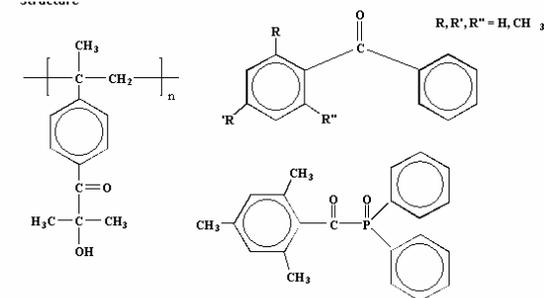2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide:75980-60-8

DAROCUR 1173:   7473-98-5

Esacure TZT

R, R', R" = H, CH₃

Esacure KTO 46

R, R', R" = H, CH₃

(Boxes have no significance)