Reactions of Polyester Resins and the Effects of Lignin Fillers

By Randy Lee

Composite Technology

-

January 2001

Introduction

Glass fiber reinforced composites, often loosely referred to simply as 'fiberglass', have been used throughout industry for many decades. While 'e-type' glass fibers or the slightly stronger 's-type' series are the most prevalent fiber/fabric reinforcements incorporated into these materials, a number of polymers have been employed as binders or matrix resins. Epoxies, acrylics, vinyl-esters, cyanate-esters and phthalate-esters are perhaps the more common resins used for most fiberglass fabrications throughout the world. In all cases, the manufacturing lifetimes of these synthetic polymer systems involves two phases – formation (synthesis) of the basic, uncured polyester mixture by the resin manufacturer, and then crosslinking or curing of the resin after incorporation into the fiber/fabric network by the end user or fabricator.

The basic resin is often formed by the reaction of two or more specialized monomers to form a viscous liquid solution of linear polymer chains grown to a predetermined molecular weight. At least one of these monomers will contain unsaturated units or double bonds which partake in the final crosslinking phase later on. Before final packaging, a final monomer is added to the solution which can be activated by the end user through the application of heat and/or the addition of a catalyst. Prevalent crosslinking monomers used throughout industry include compounds from the styrenic and acrylic families. In addition to the crosslinking monomer, uncured, industrial resins may also contain activators, inhibitors, surfactants and other agents designed to enhance the processing and field performance of these materials.

Since the crosslinking process involves permanent, irreversible bond formation between polymer chains, these types of two phase polymer systems are classified as 'thermosets', as opposed to 'thermoplastics' which are non-crosslinking polymers that simply harden when cooled and re-flow upon heating. For cost reasons, the most common commercial fiberglass thermosets are based on the phthalate-ester family of styrene-crosslinked polyesters in which the curing/crosslinking reaction is initiated or 'kicked-off' when the end user adds a small amount of peroxide catalyst. In particular, peroxide-catalyzed, styrene-crosslinked, phthalate-maleate-ethylene polyester thermosets are the primary subject matter for this project.

This study was initiated at the request of product managers from Composite Technology Inc of Texas to accomplish two goals. The primary objective was to document and/or derived the basic reactions and mechanisms associated with the synthesis and curing of common phthalate-based, styrene-crosslinked polyester resins. Supplemental to this analysis was the effort to evaluate the cure-altering behavior of a new natural-based, lignin-type filler material which has seemingly exhibited synergistic effects with styrene-crosslinked fiberglass resins. For this part of the study, no expenses were allocated to undertake any forms of advanced chemical characterization methods, outside laboratory testing or instrumental analysis. Rather, the author's wet lab facility was utilized to conduct elementary, small sample evaluations.

This new filler material is an agricultural by-product derived from cotton husks that has been marketed under the name *LignoFil* as a cost- reduction filler and performance-enhancing additive designed to be mixed into styrene-monomer-crosslinked polyester resins during the fabrication of fiberglass structures. Previously, laboratory tests conducted by other researchers have demonstrated some very unusual properties when LignoFil particles were allowed to come in contact with monomeric styrene. Supposedly, this was due to the presence of natural styrenic-alcohol oligomers comprising LignoFil which eventually act as lignin precursors. During these previous tests, LignoFil particles were found to (1) exhibit high oil (and styrene) absorption properties, (2) significantly reduce styrene VOC emissions (an environmental concern), and (3) provide slight improvements in fiberglass composite impact strength and toughness.

Prior to this project, questions were raised and issues were discussed regarding the effects of LignoFil on the application work time (pot life) and handlability of catalyzed resin during the fabrication process. Characteristics dealing with field/life performance, reliability or net mechanical property changes could not be addressed or confirmed in this study due to budget restrictions and time limitations. While there was an initial indication to determine the *chemical* effects that this natural filler might have on the curing process, it was suggested by the author that this effect was essentially *physical* in form, having little or no actual influence on primary chemical reaction rates or or products formed during the crosslinking process. However, chemical interactions between LignoFil and styrene molecules *outside of the primary crosslinking process* are a distinct possibility. LignoFil may chemically interact with free styrene monomer within the overall system, but it is believed that that no changes actually occur to the crosslinking reaction properties, i.e... while LignoFil may have significant effects on the overall curing process, the basic crosslinking reactions proceed as usual.

In the forthcoming section, *Polyester Reaction Chemistry*, the classical chemistry of styrene-crosslinked phthalate-ester resins is formulated and covers the most likely reaction pathways, mechanisms and associated kinetics for these types of resins. As requested, this is done for academic in reference and to supplement the following section, *Analysis of LignoFil*, in which results are briefly reviewed covering the series of crude and elementary wet-lab tests that were conducted for this study using LignoFil as a blended component in the raw resin mixture. The tests were intended to explore basic curing effects of LignoFil, at various loading levels, in terms of resin exotherm temperature, gel time and gel temperature in the peroxide-catalyzed crosslinking process. These properties are believed to be the best indicators related to pot life, handlability and processability. Finally, in the section, *Summary & Conclusions*, a brief synopsis of the two objectives or subject areas is provided to sum up the project effort. This short study project is not intended to be a tool for any major decision-making processes, but should serve only as a supplement to prior and forthcoming research studies in this area.

Polyester Reaction Chemistry

The resin manufacturer has a wide choice of reactive monomers with which to choose for the production of linear unsaturated polyesters depending on the properties desired for end product applications as well as handlability. Some of the more common monomers include phthalic anhydride, maleic anhydride, furmaric anhydride, acrylic acid, ethylene glycol, propylene glycol, diethylene glycol and others, where phthalic anhydride is the primary monomer employed for the synthesis of phthalate-based (high aromatic) polyester resins.

The resin production process involves the classic ester formation reaction between a di-acid and a di-alcohol in a step-wise polymerization process that produces an alternating sequence of reactant units along linear polymer chains (ideally). In practice, anhydrides or dichlorides are used rather than their acid forms (for safety and handling purposes) and sometimes epoxides are used in place of the di-alcohol. The reaction is considered to be a condensation process since a water molecule is generated for each complete reaction step. A simple scenario is illustrated below utilizing phthalic and maleic anhydrides with ethylene glycol...
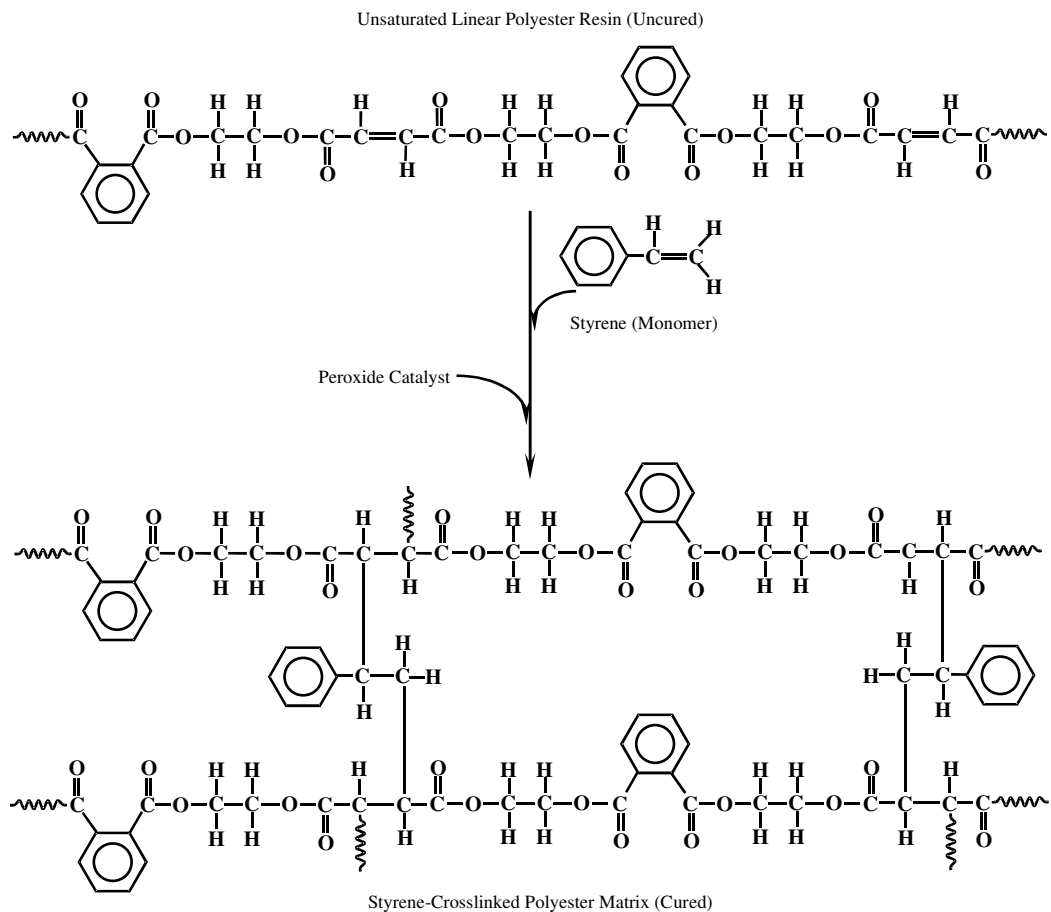

Unsaturated Linear Polyester
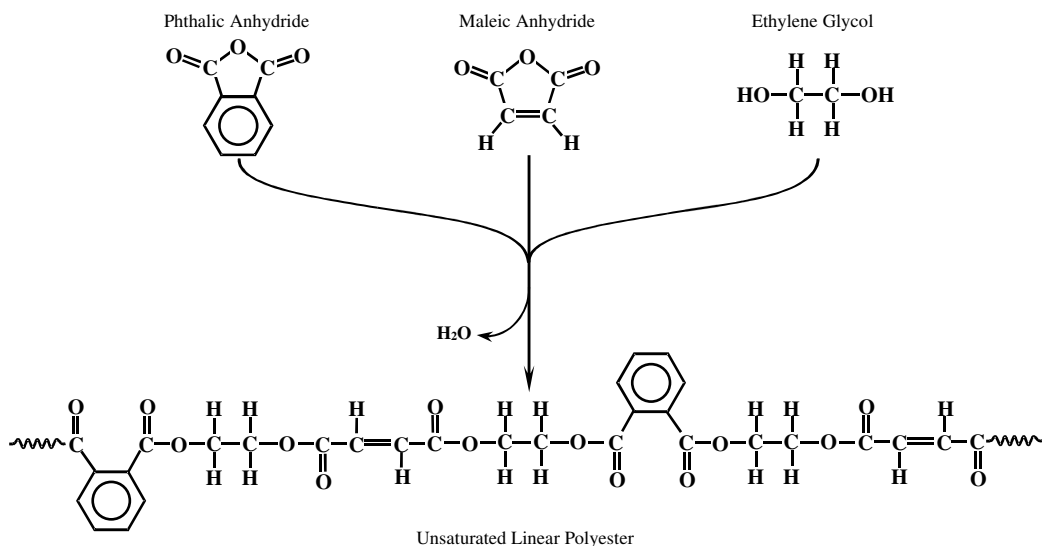
In a typical general purpose polyester resin, a 10% excess of ethylene glycol is cooked with an equimolar mixture of maleic and phthalic anhydrides for eight hours or more at 150-200°C to produce a viscous liquid polyester of 1000-5000 molecular weight. After the polyester is reacted to the specified molecular weight, the resin manufacturer may add promoters, inhibitors (preservatives) and/or other agents to enhance the desired properties. Cobalt napthanate is the most common promoter used for room curing systems.

Lastly, the mixture is diluted with 30%-50% styrene solvent (styrene monomer). Styrene not only acts as a necessary dilutent for the super-thick, thixotropic product, but is the monomeric agent that subsequently forms the crosslinks between adjacent polymer chains during

the final cure. In some cases, methyl acrylate may also be added to modify the final crosslinked properties. Both of these monomers themselves contain double bonds which will react with the linear polymer double bonds of the resin (maleic units) during cure. However, for most common polyester resins, crosslinking does not begin until an adequate initiator (or catalyst) is incorporated into the system, the most common being solutions containing methyl ethyl ketone (MEK) peroxide or benzoyl peroxide.

When heat can be applied during the user fabrication process, the most common initiator used is benzoyl peroxide. For room temperature curing resins, the more reactive MEK peroxide is mixed in by the fabricator and, in conjunction with the existing promoting agent (cobalt napthanate), a completely cured system can be achieved without the application of heat. Typically, addition of styrene solvent is the final step performed by the resin producer (prior to packaging) so that the end user or fabricator simply mixes a small quantity of liquid peroxide initiator (0.5-1%) to the resin solution to 'kick it off'. This process is illustrated below...

Unsaturated Linear Polyester Resin (Uncured)

Styrene (Monomer)

Peroxide Catalyst

Styrene-Crosslinked Polyester Matrix (Cured)

Crosslinking reactions transform the liquid linear polymers into a cured, solid three-dimensional network by linking all of the polymers together into one large molecule. The crosslinking process is itself a polymerization process specifically characterized as a 'free radical' polymerization chain reaction process which generally begins after addition of the peroxide initiator. At the onset, the initiator itself decomposes into free radicals (molecules containing an unpaired electron). Each peroxide free radical reacts with the double bond of a styrene molecule (producing a larger free radical) which combines with the double bond on a polymer chain (producing a larger free radical) which then joins to the double bond on an adjacent polymer, and so on. The process is auto propagating in classical chain reaction style. Availability of reaction sites eventually becomes hindered as the system viscosity skyrockets and the crosslinking reactions increasingly become dependent on diffusion. When the network hardens, there are inevitably, a certain number of unreacted (residual) double bonds throughout the cured system.

Thus, the process leading the the cured, crosslinked resin is a two step process. (1) The copolycondensation of a glycol (or its oxide) with one or more difunctional acids (or their anhydrides), where at least one of the anhydrides contains carbon-carbon double bonds. This step leads to a viscous solution of unsaturated linear polyester chains. (2) The free radical copolyaddition of styrene monomer with unsaturated polyester chains to result in a rigid, crosslinked structure.

For simplicity, this study will only consider reactions leading to an 'ideal' crosslinked polyester using ethylene oxide, maleic and phthalic anhydrides, styrene and benzoyl peroxide to form a classical phthalate-based system.

## Mechanism and Kinetics of Polyester Formation

The mechanism of condensation polymerization using maleic anhydride and ethylene oxide consists of the ionic ring-opening polyesterification of the anhydride with the oxide by use of a small amount of tertiary amine catalyst. Tertiary amines represent good anionic initiators. The first step involves ring-opening activation of the anhydride by the amine. During the course of polyesterification, most of the maleate isomerizes into fumarate. The vast excess of anhydride over the amine causes the equilibrium to be shifted to the right in formation of the fumarate-amine complex...

(1)
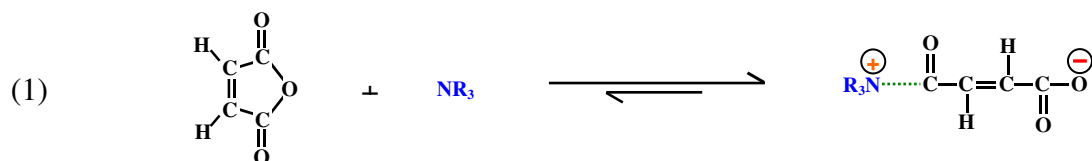
Step two involves the reaction of the carboxyl ion with the epoxide...

(2)
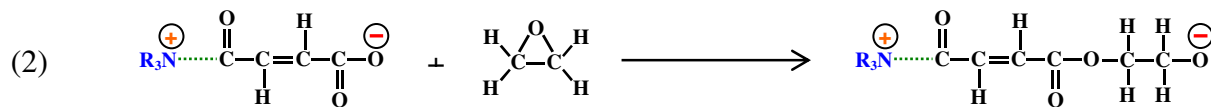
In step three, the alkoxide ion reacts with another anhydride molecule...

(3)
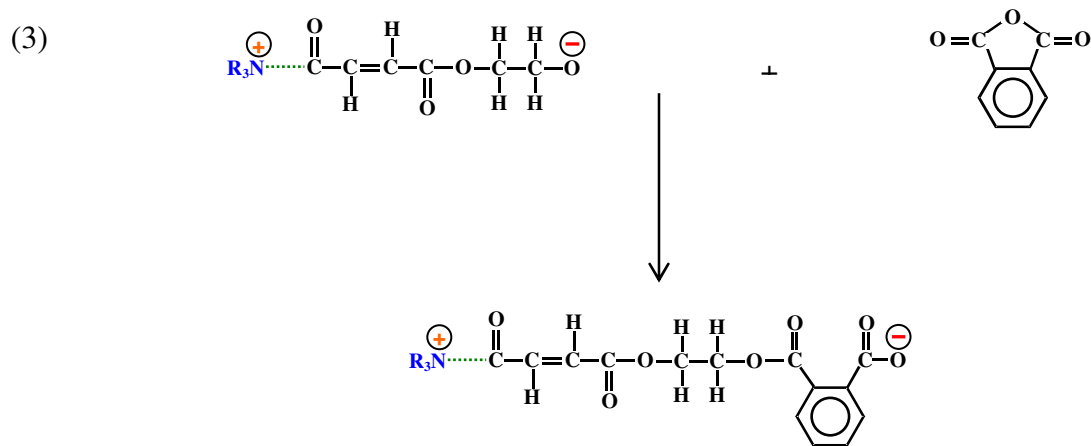
This product can then react with another epoxide molecule so that a continuation of these three steps should produce a linear polyester.

A fourth step would involve displacement of the amine catalyst by the alkoxide ion and should also lead to polyester formation...

(4)

8
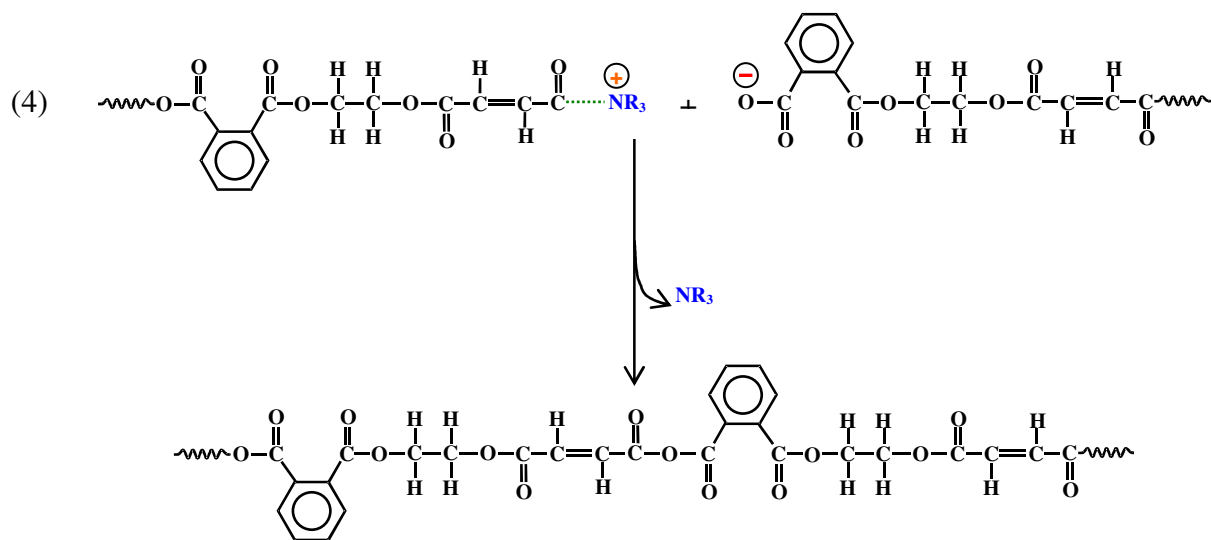
It is a fundamental point in the theory of polycondensation that the reactivity of the functional groups is unaffected by the chain length and so all the functional groups in the system react at random. Then we can expect the condensation product to be viscous solution of linear polyesters each consisting (approximately) of an alternating sequence of ethyl-maleate-ethyl-phthalate units...
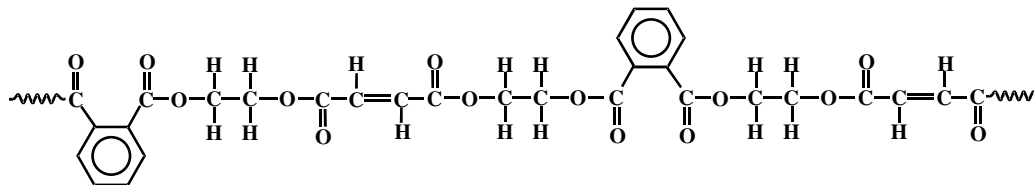
The kinetics of the polycondensation process can be approached from a statistical point of view by considering the probability that a given random monomer is part of a growing molecule consisting 'n' units. During the course of the reaction, the mixture will consist of unreacted monomers, dimers, trimers, oligomers and so on. If there are initially N_0 unreacted monomers and N total molecules in the system (of all sizes), then the number average degree of polymerization is given by...

$$\langle R \rangle = \frac{N_0}{N} \tag{1}$$

Since we consider all functional sites in the system equally reactive (approximately), then at any point in the reaction, there will be a distribution of molecules at various degrees of polymerization. If we select at random any functional site in the system, the probability that it has reacted is equal to the fraction of reacted functional sites...

$$P = \frac{\text{number of reacted sites (or ester links)}}{\text{number of reacted and unreacted sites}}$$

The probability of selecting an unreacted functional site is $(1 - p)$ according to the normalization condition...

$$p + (1 - p) = 1$$

Now, throughout the reaction process, p increases according to the degree of polymerization...

$$p = 1 - \frac{N}{N_0}$$

and the total number of molecules can be expressed as the product...

$$N = N_0 (1 - p) \tag{2}$$

If we select at random a polymer consisting of n units then there are $(n-1)$ ester links and two unreacted terminal ends so that the total number of '$n-$ mers' is proportional to the product of the probabilities...

$$N_n = N_0 p^{n-1} (1-p)^2$$

Then the weight fraction of $n-$ mers is equal to the ratio of $n-$ mers' to initial monomer times n ...

$$W_n = n \frac{N_n}{N_0} = n p^{n-1} (1-p)^2$$

and using equation (2), the mole fraction of $n-$ mers is...

$$X_n = \frac{N_n}{N} = p^{n-1} (1-p)$$

Using (1) and (2), we can express the average degree of polymerization as a function of the extent of the reaction...

$$\langle R \rangle = (1-p)^{-1}$$

This expression shows that, even at fairly high degrees of conversion, the degree of polymerization is low.

From kinetic studies of linear condensation polymerization, it has been shown that the catalyzed reaction follows second order kinetics and gives a bimolecular differential expression...

$$\frac{dN}{dt} = -kN^2$$

Integration of this equation allows us to write the number of molecules at any point in the reaction as a function of time...

$$\int_{N_0}^{N} N^{-2} dN = -k \int_0^t dt$$

$$\frac{1}{N} - \frac{1}{N_0} = kt$$

Then we can express the average degree of polymerization as a function of time...

$$\langle R \rangle = \frac{N_0}{N} = N_0 kt + 1$$

which defines the resin synthesis phase of our linear polyester resin system.

Mechanism and Kinetics of Styrene Crosslinking

The second phase leads to the formation of the crosslinked polyester and involves the free radical copolymerization of styrene with carbon-carbon double bonds in the polyester chains. A double bond will react with a styrene free radical many times faster than it will with a styrene molecule. Consequently, crosslinking reactions are initiated by the addition of a small amount of peroxide and/or the application of heat or light which generates highly reactive free radicals...


Benzoyl Peroxide
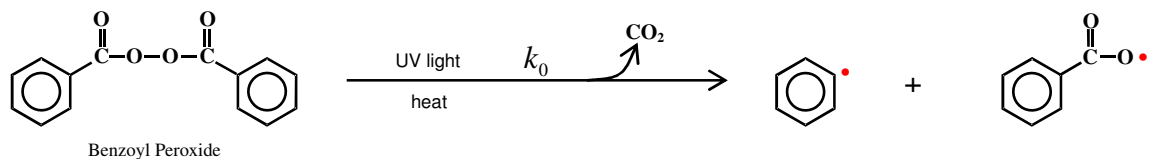
the rate constants k will be addressed shortly

These free radicals will react readily with styrene molecules to produce a new free radical that is strongly stabilized by resonance...
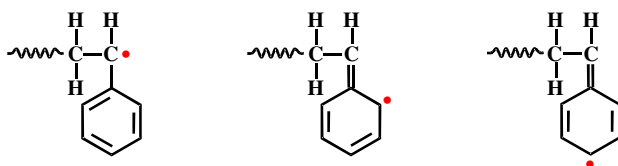

Due to the substituents on both sides of each double bond in the polyester chains, steric hindrance prohibits reactions between polyester molecules. So the rate constant for this type of reaction is essentially zero. As a result, there are three possible propagating reactions to be considered. The first two reactions are the most important and the most likely to occur.

The reaction of a styrene radical end group with a double bond in a polyester chain to form a 'graft' bond...

(1)

$\sim M_1 \bullet$ M_2 $\sim M_1 M_2 \bullet$
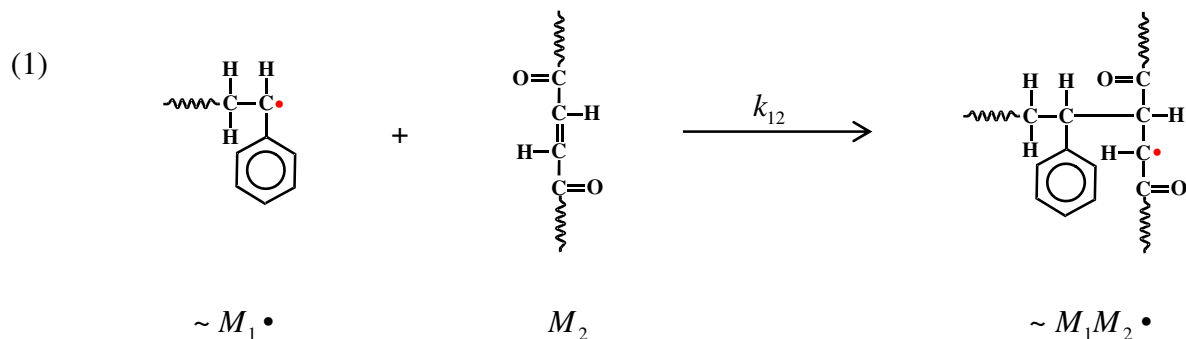
The symbols below each structure here will be used to represent that molecular entity in the forthcoming treatment concerning the kinetic properties of the crosslinking process.

The reaction of a polyester chain containing a radical group with a styrene molecule...

(2) $\sim M_2 \bullet$ + M_1 $\xrightarrow{\ k_{21}\ }$ $\sim M_2 M_1 \bullet$
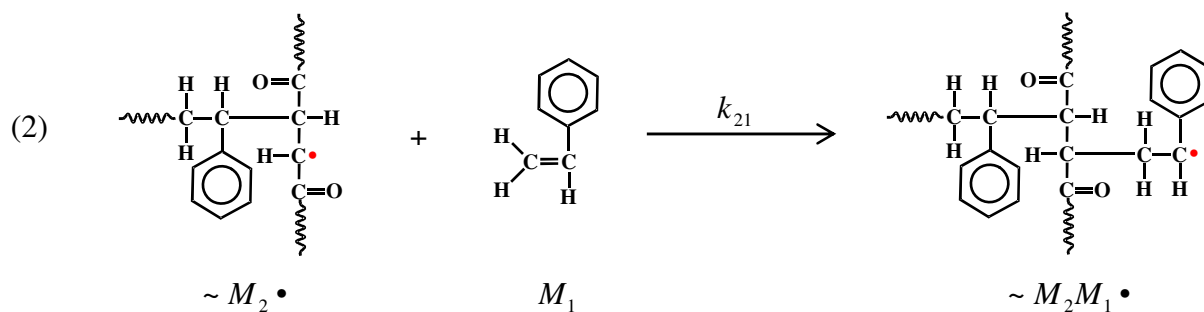
The reaction of a styrene radical end group with a styrene molecule...

(3) $\sim M_1 \bullet$ + $M_2 \bullet$ $\xrightarrow{\ k_{11}\ }$ $\sim M_1 M_2 \bullet$
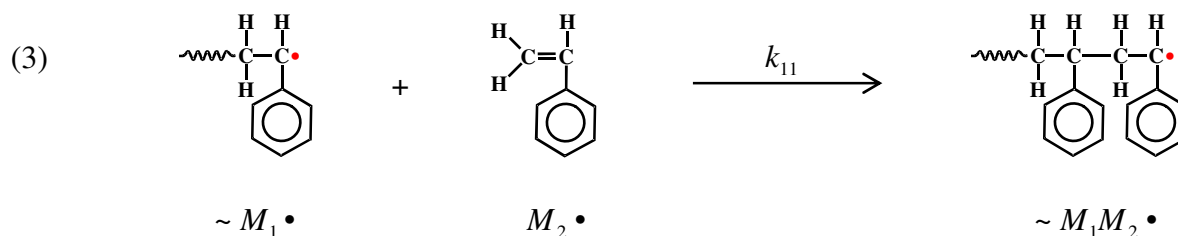
For the free radical copolymerization of styrene with phthalate linear polyesters, it has been shown that the constant for reaction (3) is very small and on the order of $k_{11} \sim 10^{-2}$. This suggests that the transition state could involve ionic free radicals of the type...
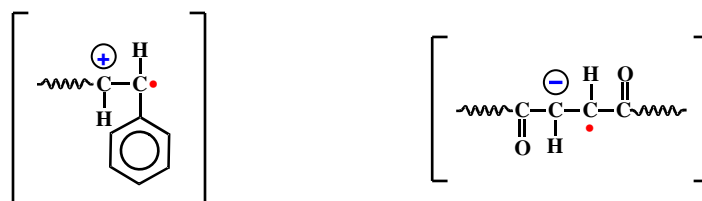
which could explain the high reactivity of styrene radicals for carbon-carbon double bonds.

When we impose the conditions for ideal crosslinking, we can assume that termination of the process most likely takes place by disproportionation...

(4) $\sim M_1 \bullet$ + $\sim M_2 \bullet$ $\xrightarrow{\ k_{31}\ }$ $\sim M_1{}'$ + $\sim M_2{}'$
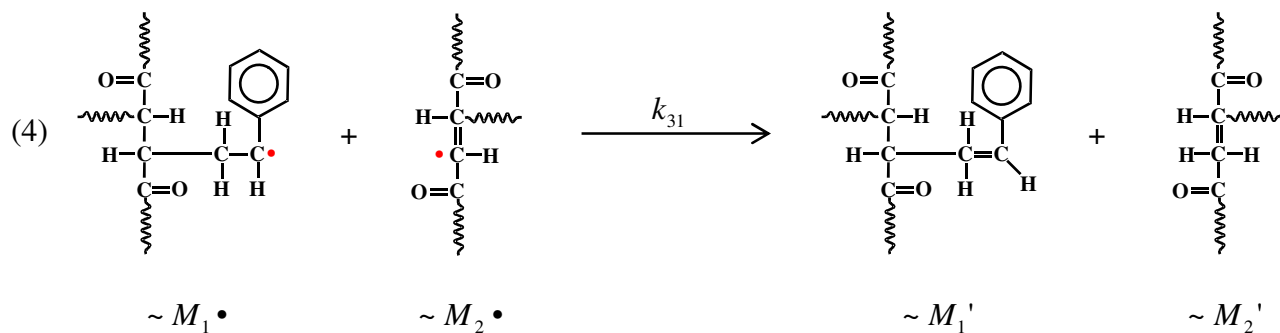
To start our evaluation of the crosslinking kinetics, let us take $k_{11} \approx 0$, then the rate of styrene consumption becomes...

$$\frac{d[M_1]}{dt} = -k_{21}[\sim M_2 \bullet][M_1]$$

and the rate of consumption of double bonds in the polyester is...

$$\frac{d[M_2]}{dt} = -k_{12}[\sim M_1 \bullet][M_2]$$

If we assume a steady state condition, the two, rates are essentially equal...

$$\frac{d[M_1]}{dt} = \frac{d[M_2]}{dt}$$

Also, the rate of radical production is balance by the rate of radical disappearance, so that the rate of peroxide decomposition is equal to the rate of rate termination by disproportionation...

$$2k_0 B = k_{31}[\sim M_1 \bullet][\sim M_2 \bullet] \tag{3}$$

where B is Boltzman's constant.

Since the rates of the two main propagating reactions are (approximately) equal...

$$k_{12}[\sim M_1 \bullet][M_2] = k_{31}[\sim M_2 \bullet][M_1]$$

we can solve for one of the radical end groups...

$$[\sim M_2 \bullet] = \frac{k_{12}}{k_{21}}\frac{[M_2]}{[M_1]}[\sim M_1 \bullet] = D[\sim M_1 \bullet]$$

and define a new parameter...

$$D = \frac{k_{12}}{k_{21}}\frac{[M_2]}{[M_1]}$$

Now we can express equation (3) in terms of $[\sim M_1 \bullet]$ ...

$$2k_0 B = [\sim M_1 \bullet]^2 D k_{31}$$

and derive expressions for both radical end groups...

$$[\sim M_1 \bullet] = \left(\frac{2k_0 B}{k_{31}D}\right)^{\frac{1}{2}} \tag{4}$$

$$[\sim M_2 \bullet] = D[\sim M_1 \bullet] = D\left(\frac{2k_0 B}{k_{31}D}\right)^{\frac{1}{2}} \tag{5}$$

The total rate of copolymerization is equal to the sum of the individual rates...

$$Rate = \frac{d(M_1 + M_2)}{dt} = 2k_{12}[\sim M_1 \bullet][M_2]$$

Using equation (4), we can write the rate in this form...

$$Rate = k_{12}[M_2]\left(\frac{8k_0 B}{k_{31} D}\right)^{\frac{1}{2}}$$

For this particular mechanism, there is a direct relationship between the rate and the degree of polymerization...

$$\langle R \rangle = (\text{constant})(Rate)$$

It has previously been determined that this constant is of the order of radical production, that is...

$$\text{constant} \sim k_0 B$$

Then the number average degree of polymerization can written in this form...

$$\langle R \rangle = \frac{k_{12}[M_2]}{\sqrt{k_0 k_{31} BD}}$$

In the alternating-type of copolymerization treated here, a 1:1 copolymer is formed and both monomer reactivity ratios are essentially zero; a monomer can add only to the opposite type of monomer. For the formation of the ideal crosslinked polyester considered in this project, the alternating tendency in copolymerization has been based on three main assumptions. (1) The low reactivity of the double bonds in the polyester chains with themselves due to steric hindrance. (2) Stabilization of the styrene-fumarate link due to resonance and complex formation in the transition state. (3) The assumption that the relative reactivity of styrene radical end groups for styrene monomer is insignificant.

Analysis of LignoFil

For this phase of the study, simple room temperature laboratory trials were performed using 50 gram resin samples to physically demonstrate the behavior of LignoFil-filled resins regarding the expected increases in gel time and associated effects on early exotherm cure temperature. At the onset, it should be noted that the crosslinking phase is characterized as an exothermic (heat evolving) process since each free radical reaction generates a certain amount of heat (the 'heat of reaction'). In cast polyester resin articles and fiberglass laminates, system temperatures can increase to as high as 285°F (140°C) at 'peak exotherm'.

The first test in this study utilized unfilled, over-catalyzed resin samples to acquire the initial exotherm curve (Figure 1). Typical peroxide levels for industrial applications range from 0.3%-1%. For this project however, an accelerated level of 3% was used to expedite the results. The temperature of resin samples was periodically monitored just after addition and adequate mixing of MEK peroxide catalyst. At the onset of gellation (the gel point), the test was ended. The crosslinking process is essentially isotropic throughout the resin matrix until the system begins to gel (noted by a rapid increase in viscosity). Even though heat is generated with each reaction, it is not readily noticeable (or measurable) until many reactions have already occurred. Shortly after heat begins to evolve, the resin system rapidly increases in viscosity and begins to expand in volume. This marks the 'gel point' or gel time. The evolution of heat is gradual at first and then increases almost exponentially as the system begins to harden. When the typical 0.3-0.5% level of peroxide initiator is used, gellation may occur in 15-20 minutes and the peak 'exotherm' may occur in about 30-40 minutes. At the 3% levels used in this study, the gel point was marked at around five minutes after addition/mixing of the initiator and peak exotherm sometime thereafter (data was not taken beyond the observed gel point).
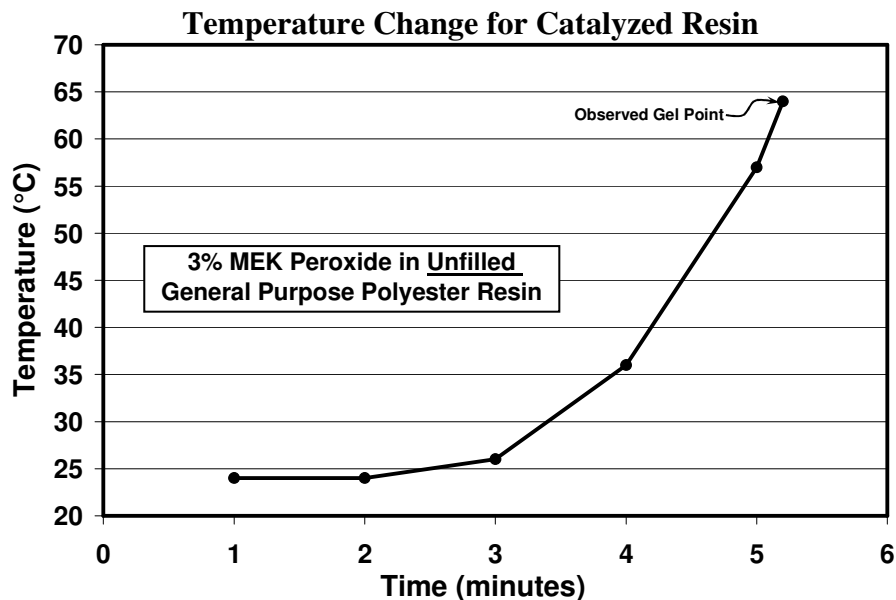

Figure 1 – Graph illustrating resin temperature change after addition of peroxide catalyst.

After the peak exotherm is reached, the matrix continues to harden as the temperature gradually begins to decrease. However, the hardened resin matrix also begins to shrink in volume, and stresses are initiated in the matrix which gradually increase in number and magnitude throughout the cool down period. In the end, the cooled system is inevitably under the influence of significant internal stresses, which sometimes manifest themselves as cracks. To remedy the problem, particulate or fibrous fillers are often incorporated into to the resin which facilitate the distribution of internal cure stresses throughout the filled composite system thus relieving the resin phase significantly during the hardening process.

Most fillers are inert but may exhibit very slight changes in the cure properties due to particle surface adsorption effects. However, vast differences were noted in the observed gel point when LignoFil particles were used as filler (Figure 2). Retardation of the gel point at low LignoFil levels is quite significant (130%), and at typical filler levels (~20%), LignoFil appears to exhibit the properties of an inhibitor.
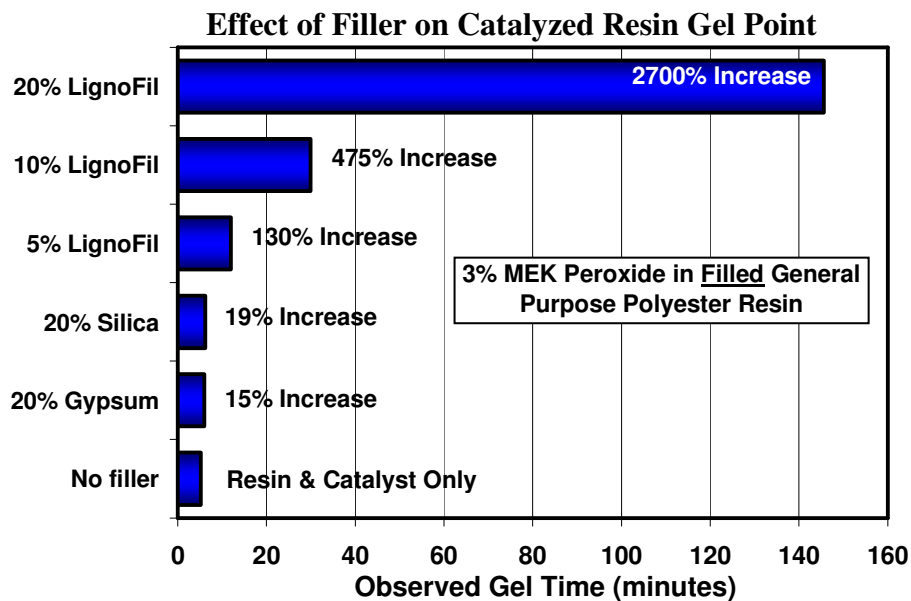
Effect of Filler on Catalyzed Resin Gel Point

Figure 2 – Graph illustrating the effects of various fillers on gel point observations.

Peroxide initiators are sometimes referred to as 'catalysts' (incorrectly). Technically speaking, catalysts are not consumed in a reaction and are often recoverable afterwards. On the other hand, peroxide molecules become permanently fixed in the cured polyester network (both terms will be used interchangeably here for simplicity). If the quantity of peroxide initiator/catalyst is too small (less than about 0.1%), or too large (greater than about 5%), there is a risk that the system will not cure properly. The extent of cure in both cases could be classified as incomplete, but the end results are different.

An under-catalyzed system could possibly result in only partial curing throughout the body due to high levels of residual, unreacted double bonds which could however, be saturated by heat application since the under-cured body might still retain some flowable properties. When excessive catalyst amounts are used, the system hardens too quickly. Many unreacted sites become inaccessible and remain unsaturated. In addition, the degree of internal stresses is abnormally high in rapidly cured systems, which decreases the product's mechanical properties and increases the risk of failure downline. Ideally, the crosslinking process should be allowed to progress at a moderate speed rather than being forced to take place rapidly. As mentioned earlier, even properly catalyzed systems contain unreacted sites. However, many of these double bonds can be saturated by applying a heated follow-up 'postcure' or by placing the article out in the hot sun to advance the crosslinking process.

With this being said, a series of tests was performed where the peroxide levels were intentionally increased for LignoFil-filled resin samples in an attempt to compensate for the extended gel time exhibited by the effects of the LignoFil (Figure 3).
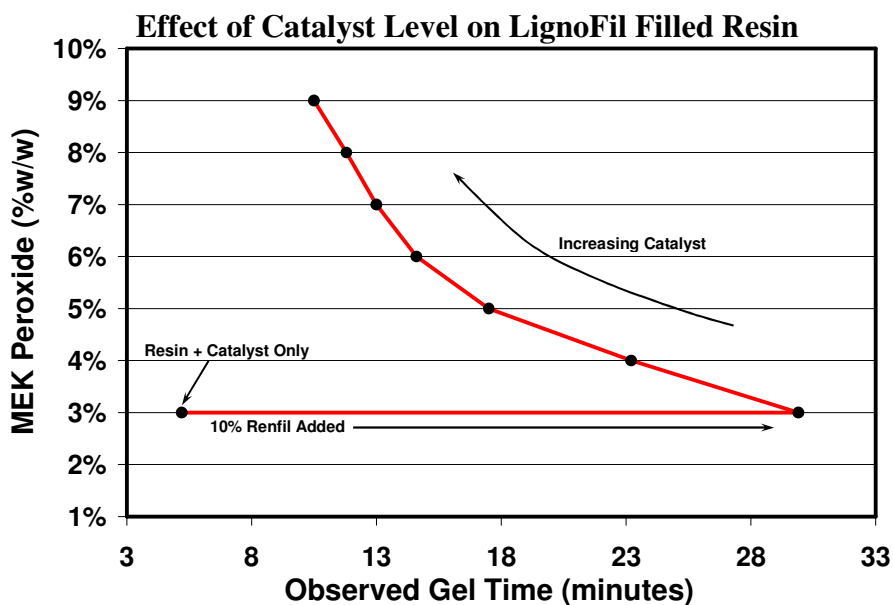

Figure 3 – Graph illustrating the effects of peroxide level on LignoFil-filled resin samples.

Even at exceedingly high levels of peroxide, the original gel time (corresponding to unfilled resin) was not obtainable. It is clear that the presence of LignoFil permanently retards the setting time, even at low levels.

The data also indicated that LignoFil played a role in slightly lowering the observed temperature at gel (Figure 4).
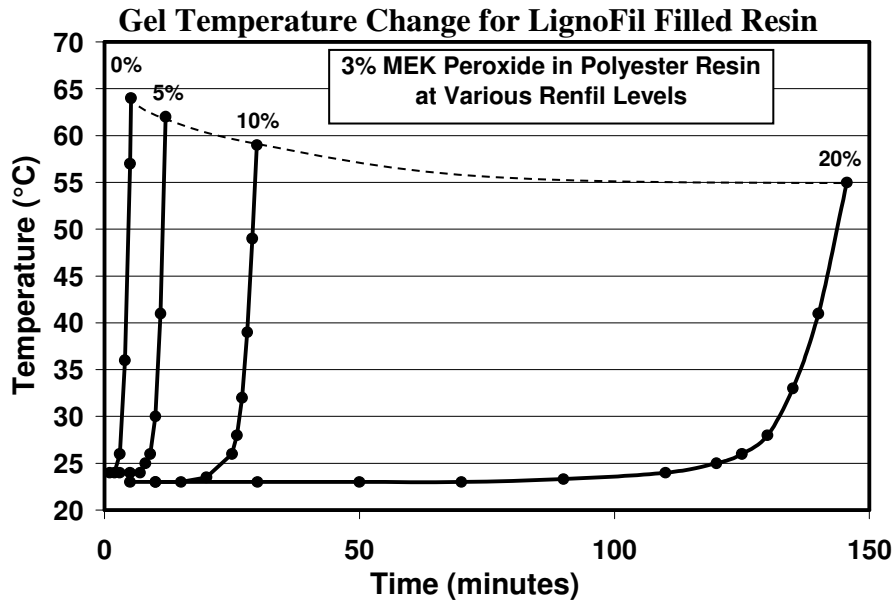
Gel Temperature Change for LignoFil Filled Resin

Figure 4 – Graph illustrating the change in gel temperature due to LignoFil loading.

Summary & Conclusions

The most likely reactions, mechanisms and kinetics are documented and/or derived for the synthesis of phthalate-based linear polyester resins and the subsequent crosslinking process via peroxide-initiated styrene copolymerization which occurs during the end user fabrication phase. The most relevant reactions for both the synthesis and crosslinking phases have been illustrated and analyzed in detail. In addition, probable expressions for critical kinetic parameters and reaction rates have been derived for each of the two phases. This effort may serve as an educational reference and a resource for future studies in this area.

A series of simple wet-lab tests were conducted on small resin samples to provide some preliminary experimental results for evaluation. The gross effects of LignoFil on the curing properties were measured at several loading levels. While higher level chemical analysis and instrumental methods were not available for this study, attempts are made to obtain the best possible results from the data and information that was gathered.

As Figure 2 indicates, addition of LignoFil particles to the resin has an enormous effect on the observed gel point. This is believed to be due, not only to the absorption (porosity) properties of LignoFil, but also to the possibility that specific chemical entities within the LignoFil microstructure exhibit an affinity for styrene molecules. This interaction would explain the reductions in VOC levels observed in previous studies and could possibly aid in fabrication applications requiring longer working (pot) times. On the other hand however, it could be detrimental to room temperature manufacturing operations which are dependent upon quick setting times where the application of heat is not possible or feasible.

Gellation represents the very early stages of the curing sequence. Figure 3 shows that retardation of the gellation process due to the presence (and action) of LignoFil is quite significant and cannot be compensated for by the use of additional peroxide catalyst. As indicated earlier, there is a window of peroxide concentration required to produce an adequately crosslinked structure. While recommended peroxide levels range from 0.3 to 1%, a level of 3% was used in this study to expedite the results. This rather high level appeared to produce adequate sample results for this quick study, but anything above about 1.5% would be unacceptable for industrial applications. As the data in Figure 3 indicate, peroxide levels at an abnormally high 9% do not even come close to the gel point of non-LignoFil-filled resin.

Figure 4 shows that the presence of LignoFil slightly decreases the temperature that gellation occurs which is probably associated with conduction effects. Whether or not LignoFil exhibits a similar effect on the peak exotherm temperature was not determined in this study (utilization of DSC and DTA would have revealed these properties). It is therefore recommended that instrumental techniques be investigated to further understand the benefits as well as the possible drawbacks of LignoFil-filled polyester resins.

A general synopsis might be formulated as follows. LignoFil permanently associates with styrene molecules through some sort of affinity interaction. Perhaps functional groups within the LignoFil structure actually bond with and saturate the styrene during this process. While some swelling of slurry samples was noted after addition of LignoFil particles, this may be due almost completely to the physical absorption effects or perhaps LignoFil actually induces polymerization of styrene within the particle porosity. In any case, this project, as well as previous studies, have demonstrated that LignoFil has a phenomenological affinity for styrene monomer, beyond that of simple absorption effects.

However, there is absolutely no indication that LignoFil interferes with or otherwise alters the raw chemistry or basic crosslinking reactions (or their chemical rates) in any fashion. While the overall (net) curing process may be altered, these reactions are assumed to occur outside of the particle phase as usual – when there is available styrene. Inside the particle, it may be a different story. If styrene is permanently bonded to LignoFil functional groups, then crosslinking reactions are starved and may not even occur. On the other hand, if the styrene is temporarily tied-up by the LignoFil, then the reactions are *regulated* by the LignoFil. In this sense, LignoFil is a physical curing inhibitor rather than a chemical one, and its action on the overall curing process may be that of a physical regulator.

The resin manufacturer adds styrene solvent to the freshly synthesized polyester product to serve two primary purposes with regard to end user fabrication operations. To provide the necessary crosslinking co-monomer agent for the cure process, and to dilute the highly viscous resin product for handleability purposes so the fabricator is able to pour, transfer and apply the resin appropriately (the resin manufacturer also needs these properties to convert the reaction product into its packaged form). This last reason is important for our discussion since the amount of styrene required for crosslinking is very small compared to the total amount added to the pre-packaged resin. In other words, a vast amount of styrene is added to the system just to meet the dilution requirements while the portion needed to complete the subsequent crosslinking process is relatively small. Thus, the undesirable environmental concern associated with these types of resins is due essentially to the excess of styrene monomer added for handleability properties. It is this area where LignoFil may have its greatest benefits.

Since no physical, structural or mechanical tests were available for this project, nothing can be said here regarding the positive or negative effects of LignoFil-filled resins. If there are any adverse influences in these areas, then the benefits of LignoFil may become trivial. However, notable reductions in VOC emissions of free styrene along with the longer work times (if needed for particular applications) appear to be the primary benefits associated with the use of this agent in phthalate-based, styrene-crosslinked polyester resin systems.

References

"Organic Chemistry", 3rd Edition, Morrison and Boyd, New York University, Allyn and Bacon Inc., 1973
"Physical Chemistry", 4th Edition, Gordon M. Barrow, McGraw-Hill Book Company, 1979