

Renfil™'s Affinity for Styrene

Abstract

Renfil™ is the mechanically modified residue of cotton plants produced during the stripping of the cotton bolls at harvest. A patented process to produce a free flowing, low aspect fiber/filler called Renfil™ for use in unsaturated polyester composites is used to upgrade this natural, plant material. Renfil™ has been found to have an affinity for the styrene fraction of the common commercial grades of unsaturated polyester resin. This affinity for styrene is an indication that the use of Renfil™ in polyester spray up operations can reduce VOC emission. Several laboratory scale experiments were designed to demonstrate this principle. Draeger tube sniff tests indicated that styrene emissions could be reduced by ~75% with the use of Renfil™. More quantitative adsorption/desorption measurements at ambient temperatures indicated that Renfil™ has an oil adsorption number of ~2.5 for liquid styrene. The equilibrium adsorption of styrene vapors over liquid styrene (vapor pressure ~ 9 mm Hg) at ~25 °C (76 °F) was recorded as 0.06 gram styrene/gram of Renfil™ for the -80 mesh product. Based on the findings of these experiments, it is proposed that a "green" adsorption filter can be designed to trap styrene vapor emissions during polyester spray-up processes. The Renfil™ containing the adsorbed styrene could either be regenerated or used as is as filler in the composites being fabricated without the need to remove the adsorbed styrene vapors.

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This paper represents a preliminary study on the adsorption/desorption capacity of Renfil™ products for liquid styrene and styrene vapors at ambient temperature.

Introduction: It is well known that styrene emissions are a common environmental concern during the use of unsaturated polyester resins. Emissions from spray up fiberglass systems becomes even more intractable due to the large surface areas generated by the small droplets of uncured resin. In most cases spray booths are required with exhaust gases and vapors being collected and sent through an oxidation unit. Styrene removal efficiencies of 93% have been achieved through this type of oxidation process. (Niezodski, 1997). Even so, styrene emissions remain a major concern for unsaturated polyester polymer processors (Patel and Xanthos, 2001) (Shoemaker and Krishnan, 1991). Hence, there was more than casual interest registered when an organic fiber product called "Renfil™" demonstrated an unusual ability to suppress styrene vapor emissions from unsaturated polyester resins.

Our laboratory and field observations appear to indicate that Renfil™ products have a strong affinity for styrene monomer. This affinity is particularly evident whenever a Renfil™ product is utilized during glass fiber/polyester resin spray-up applications. This behavior was first observed in the field where a Renfil™ product was being used as fiber/filler with a traditional polyester resin containing 42% by weight of styrene. When a dusting of Renfil™ 30/80 was applied to the wet, uncured surface of the composite structure, the smell of styrene vapor in the immediate work area was noticeably reduced. In addition, it was observed that the mixing of the product Renfil™ 80 with the uncured polyester resin prior to spray-up dramatically prolonged the onset of the mixture's gel time when the recommended amount of activator was used. Both of these observations have been confirmed under laboratory conditions, which supports the initial hypothesis that Renfil™ products were functioning as an adsorbent for the styrene monomer contained in the uncured, polyester resin liquid. The adsorption of liquid styrene and styrene vapors may represent a plausible explanation for the reduced olfactory response to styrene following the dusting of the Renfil™ 30/80 onto a wet polyester surface. However, the retardation of gel time for a thermoset polyester resin system may also arise from inhibitors being extracted from the Renfil™ by styrene acting as a solvent in the polyester resin. This second scenario is more plausible than to the physical removal of the styrene monomer from the reacting polyester mix.

The interaction of Renfil™ with styrene monomer in both of the instances just described was, however, of sufficient interest to warrant further laboratory studies. For example, if the application of Renfil™ during a polyester spray-up operation can substantially reduce the VOC (styrene monomer) emissions

during processing, then both the immediate work area and the environment would benefit. Moreover, any prolonging of cure or gel times during the use of Renfil™ in thermoset polyester resins is important to the timing of the production process and, therefore, must be fully understood if Renfil™ is to be an integral part of the final composite structure. For these reasons, therefore, some additional laboratory studies were undertaken to more thoroughly study the adsorption/desorption characteristics of Renfil™ products with respect to its affinity for the styrene monomer used in thermoset polyester resins.

Experimental: Several simple experiments were designed to quantify the interactions of Renfil™ products with styrene monomer. These tests used the liquid solutions of styrene-polyester resin and a liquid, inhibited styrene monomer as sources of styrene vapor and liquid. Four Renfil™ products, Renfil™ -16, Renfil™ 30/80, Renfil™ -80, and Renfil™ Fluff, were tested for their affinity for styrene. All of the experiments were conducted in a vented hood and at ambient temperatures except for those instances where exotherms were generated during the curing of the polyester resin.

Vapor Suppression

Our initial experiment involved pouring the liquid polyester resin into a laboratory beaker. The concentration of styrene vapors in the headspace directly above the top of the liquid solution was then measured with sniff probes manufactured by Drager. These detector tubes can be utilized only once, were specific to styrene vapor, and are usually used to screen gas spaces. Table 1 shows the results obtained with the Drager tubes.

Table 1: Styrene Sniff Tests with Drager Tubes

<u>Test #</u>	<u>Description</u>	<u>Results, Styrene Detected</u>
1	~100 grams of polyester resin (42% styrene by weight) were placed in a 500 ml beaker.	~35 ppm
2	~5 grams of Renfil™ 30/80 (4.8% by weight) were dusted on top of the resin in #1.	~10 ppm (-70%)
3	~15.4 more grams of Renfil™ 30/80 were added to the beaker in #2 to give ~ 17% by weight. This resin filler mixture was stirred for fifteen minutes and retested with a sniff tube.	~9 ppm. (-75%)
4	Sample #3 was again tested after 15 minutes.	~10 ppm. (-70%)
5	After an additional 15 minutes another sniff test was performed on sample #3.	~10 ppm (-70%)

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| 6 | After setting for ~ 11 hours, Sample #3 was sniff tested again. | ~8 ppm. (-80%) |
| 7 | A fresh 25 grams of resin were placed in a second Beaker and sniffed twice. | ~40 ppm. |

The information embodied in Table I suggests that Renfil™ 30/80 can suppress the emissions of styrene vapor to a level in excess of 70% over the levels of styrene vapor emitted from the base resin. This level of reduction remains effective even when the Renfil™ is blended with the liquid resin and the suspension is allowed to stand. The porous structure of the Renfil™ appears to adsorb the liquid styrene from the uncured polyester and prevents the styrene from out gassing. Undoubtedly, the much larger polyester molecules in the uncured resin lack the smaller styrene's ability to penetrate the porous Renfil™ structure. Perhaps after being left on the filler's surface these polyester molecules form an outer thin film of denser polyester molecules, which further retards the tendency for the adsorbed styrene to out gas to the environment.

Adsorption/Desorption Rate Data

Based on the preliminary data with the Drager sniff tubes, a second series of experiments were design to quantify the interaction of styrene with the Renfil™ product. In these tests, production grade, inhibited liquid styrene monomer was used. For the adsorption studies, known masses of Renfil™ were placed in metal wire baskets and suspended over 200 ml of liquid styrene contained in a 2.0-liter beaker and placed in a vented hood. The draft of air through the hood was sufficient to draw styrene vapors from the liquid surface, past the suspended Renfil™, and on out the vent. The sample baskets containing the Renfil™ were then removed periodically from the hood and beaker, quickly weighed to the nearest 0.01 gram, repositioned in the beaker above the liquid styrene, and returned to the hood. Over time the adsorbed styrene was thereby recorded as a weight gain in grams of styrene per gram of Renfil™.

In a similar fashion, the desorption studies were conducted by first saturating known masses of Renfil™ with the inhibited liquid styrene. The saturation process was accomplished by adding a known mass of a Renfil™ product to a 250 ml beaker. Beakers containing the Renfil™ was then placed inside a vacuum oven, heated to 80 °C (~ 175 °F), and left under a vacuum of ~27 inches of mercury for five hours. This preconditioning step was intended to remove any residual adsorbed moisture or volatiles from the Renfil™ product. The beakers containing the samples of Renfil™ were then removed from the vacuum oven, cooled to ambient temperature, and reweighed. Renfil™ dried in this manner adsorbed the liquid styrene to a much greater degree. In so far as possible, 2.5 grams of styrene per gram of dried Renfil™ were then added to each sample beaker. The mass ratio of 2.5/1.0 is approximately the oil

adsorption number for the Renfil™ filler. Hence, very little if any free-standing, liquid styrene could be seen on the top surface of the Renfil™ in each beaker. The beakers were positioned in the vent hood so that the forced airflow passed over the tops of the beakers and provided a continuous driving force for evaporation from the filler's exposed surfaces. The desorption process was measured as a mass loss in grams of styrene per gram of pre-dried Renfil™ as a function of elapsed time.

Experimental Results

Adsorption: The results of the adsorption measurements are shown in the appended Figure I for four Renfil™ products. These data are represented as grams of styrene adsorbed per gram of Renfil™ product as a function of time. The amount of styrene adsorbed for each product rises from zero to a level of ~0.06 grams/gram. The vapor pressure of pure liquid styrene is ~9 mm Hg at 25 °C (~76°F), which is not a large driving force for adsorption. The total elapsed time covered just over three days.

The curves for the four Renfil™ samples demonstrated some erratic behavior as the result of experimental variation and error. These curves could be smoothed to give better appearing adsorption rate curves. However, the data as plotted suggest that that the finer ground Renfil™ product (-80) adsorbs a greater mass of styrene vapors and at a faster rate than the other three products. Also except for the Fluff product, nearly half of the total styrene adsorbed accumulates on the Renfil™ materials during the first twenty minutes.

The data shown on Figure I were lumped into five average time groups (four groups if the zero point time is excluded) and the average amount of styrene adsorbed was then calculated. These reduced data are given in Table 2 and depicted in Figure 2.

Table 2: Adsorption Rate Data for Styrene on Renfil™ Products

Avg. Time (hr) <u>(min)</u>	Avg. Amount/Rate of Styrene Adsorbed (g Styrene/ 100gRenfil™)			
	<u>Renfil™ Fluff</u>	<u>Renfil™ (-16)</u>	<u>Renfil™ (-80)</u>	<u>Renfil™ (30/80)</u>
0	0	0	0	0
60	0.380	0.600	1.55	0.891
600	0.157	0.210	0.154	0.186
1300	0.078	0.042	0.029	0.018

Table 2 and Figure 2 suggest again that the finer the particles of Renfil™ Product, the more rapid the adsorption of the styrene vapor. The suggestion by

the depicted data that the maximum rate of adsorption occurs at approximately one hour is, however, an artifact of data averaging. The most rapid rate of take up will always occur following the instantaneous contact between the adsorbent, Renfil™, the styrene vapors, after which the sites available for adsorption diminish. Even so the averaged rate of 1.55 gr/100gr/hr for the Renfil™ (-80) is almost double that of the Renfil™ (30/80) and the Renfil™ (-16).

Figure 3 depicts the data obtained from the desorption experiments over a time period of approximately three days at ambient temperatures. The data at the extended time of three days is roughly equivalent to the data obtain at maximum adsorption as one might expect. The data for the initial portion of the desorption curves indicate some instabilities typical of systems not being at equilibrium. This is particularly true for larger Renfil™ (-16) product with its delayed release of styrene vapor. It is as if the styrene is being drawn into the porous structure of these larger particles faster than it can evaporate from the surface. However, after the first ten hours the desorption rates for all four of the samples are roughly parallel. Therefore, if all the data between 500 minutes and 2500 minutes are lumped together and fit to a linear line, the desorption rate for all the products is ~5.4 (grams/100gram/hour). This value is approximately equivalent to the adsorption rate, considering that the latter was determined by an averaging reduction of the data. Finally, these desorption data indicate as the adsorption data did that the finer screen size of Renfil™ (-80) with its increased surface area results in a greater desorption rate of the adsorbed styrene.

Conclusions

It has been demonstrated that the organic filler, Renfil™, has a strong affinity for liquid styrene and styrene vapors. This was documented for unsaturated polyester resins that contain 42% by weight of styrene monomer. The affinity was further quantified with inhibited, liquid styrene monomer and four Renfil™ products. Based on these data it appears that Renfil™ material could be used as a "green filter" to suppress and/or adsorb styrene emissions from unsaturated polyester spray-up processes. The suppression of vapor losses is probably best accomplished by spreading the Renfil™ powder on the wet uncured resin. This approach will draw the styrene at the contact surface into the porous structure of the Renfil™ and thereby create a diffusion barrier or thin skin enriched in the high molecular weight polyester molecules at the resin-air interface.

If the Renfil™ product is added to the polyester/styrene resin solution, then the high oil adsorption number of Renfil™ for styrene (2.5/1.0) will also strongly retard styrene from being volatilized. The amount of styrene retarded in this fashion depends on both the amount of Renfil™ added and the level of styrene in the base resin. Also, as noted earlier, if the Renfil™ is added directly to unsaturated resin solution, there may be a corresponding retardation in resin

cure time due to inhibitors leached from the Renfil™. This latter topic has been observed in the field, but needs further experimental investigation.

The use of Renfil™ in a "green" adsorption bed is particularly attractive for polyester resin spray-up processes. In this scenario, whenever the Renfil™ bed becomes saturated, it can simply be added to the spray up process. Since the Renfil™ is already saturated with styrene, it simply adds to the composite structure as it cures.

Bibliography

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