

REDUCTION OF STYRENE EVOLUTION FROM THERMOSET POLYESTER RESIN COMPOSITES

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Abstract

The incomplete reaction of polyester resins in fiber reinforced composites results in residual styrene monomer that slowly evolves from the polymer matrix over many years. In cars and trucks where extensive use of such composites are open to the interior of the passenger compartment, the odor of styrene can become strong enough to be objectionable to the vehicle occupants. A design goal for the development of coupe sports car, which makes extensive use of polyester SMC and liquid molded composites, was to assure that the styrene concentration in the passenger compartment is not offensive. Simple test methods were devised to assess styrene evolution at the material, component and vehicle levels. Through the systematic study of resin paste formulations, process modifications, coatings and part design features, this design goal was met before the launch of the vehicle.

Introduction

The presence of volatile organic compounds (VOC) in the passenger compartments of vehicles is well-known and is commonly associated with “new car smell” or window “fogging.” However, in some instances the concentration of a particular VOC can become high enough to be a nuisance to some passengers. The odor of styrene from thermoset polyester composites can present such an issue to customers. Styrene has a distinctive strong odor and humans have a low threshold of detection (the lowest concentration at which a chemical can be detected). Reported threshold values for styrene vary widely, but some are as low as 0.01 to 0.08 parts per million by volume (ppm) (1,2).

Most thermoset polyester composite parts contain some residual styrene monomer due to incomplete polymerization. This styrene will slowly migrate through the polymer network to the atmosphere through Fickian diffusion (3). If the styrene evolves into a closed environment the concentration will slowly build over time and can become noticeable. The rate of diffusion, and thus, the rate of evolution depend on temperature, time, the concentration gradient through the thickness of the composite part and the styrene concentration in the surrounding atmosphere.

During the development of a coupe sports car derived from a convertible, the potential for a styrene odor issue was identified. The smell of styrene was evident in the trunk area of the convertible presumably from the trunk pan assembly, which is composed of glass fiber reinforced polyester liquid molded composite. In addition, numerous polyester SMC parts (lift

gate, roof, doors, door surround and windshield surround) would also be in contact with the interior air confined in the passenger compartment of the coupe. Despite the absence of an established allowable styrene concentration in the vehicle and reliable means to relate it to styrene evolution rates from individual parts, a program was undertaken to minimize the styrene evolution from the primary composite components.

Test Methods

Evolution of a styrene from composite samples was quantified by both “dynamic” and “static” test methods. In the dynamic tests a known volume of a dry carrier gas such as helium or argon is passed over a material sample (solid piece(s) or powdered) at a particular temperature and the VOC are trapped for analysis by gas chromatography/mass spectrometry (gc/ms). The micro scale of this laboratory test results in considerable sample-to-sample variation for composites, especially if the material is cut into small pieces or ground to a powder.

In the static tests an amount of material with a specific surface area is exposed to an enclosed volume of air (headspace) at a given temperature. The concentration of styrene in the air is then measured at a particular point(s) in time. Several detection methods were employed to measure styrene concentrations in static tests. The first was an infrared spectrometer set to measure absorption at a particular frequency. The second approach was to collect the styrene on activated charcoal (Tenax Tube) for later desorption and gc/ms analysis. A third method was direct injection of a gas sample from the headspace onto the gc column. The static approach can be used in the laboratory for micro samples, but can also be used to study molded plaques, components or the interior of a vehicle.

Many of the experiments in this study were conducted with simple static chambers fabricated from five-gallon metal cans sealed with air-tight lids. Threaded fittings with sealing faces were installed on the side of each can, one near the top and one near the bottom. Threaded caps provided an air tight seal. When styrene measurements were made the caps were replaced with fittings that connected plastic tubing from the inlet and outlet ports of the infrared (IR) detector (Figure 1). The IR detector, a Foxboro MIRAN 203 with a fixed wavelength of 10.1 microns, contained a pump that circulated the air from the can into the detection cell and back to the test chamber.



Figure 1. The test set-up used to measure styrene evolution from molded plaques over time with an IR detector.

One or more molded composite plaques measuring 30.5 cm by 30.5 cm were cut in half and placed in the can such that essentially all of the surface area was exposed to the air. The can was then sealed and the time was recorded. The cans with the test specimens were stored in a temperature controlled room. Periodically over a number of days the concentration of the styrene was measured with the infrared detector. Use of this method assumes that styrene is the only VOC absorbing at 10.1 microns.

The geometry of untrimmed trunk pans provided a convenient means of creating a nearly constant headspace. A piece of styrene impermeable SMC carrier film (polyethylene/nylon co-extruded sheet) was tightly sealed over the opening of the pan (Figure 2). Periodically, tubes connected to the inlet and outlet ports of the IR detector were inserted into the headspace to sample the air for styrene concentration. Due to the various test methods used and their dependence on many variables, no attempt was made to develop quantitative correlations among them. Likewise, quantitative comparisons among variables are only made within a single experiment.



Figure 2. A trunk pan sealed with SMC carrier film to monitor styrene concentration over time using an IR detector.

Results and Discussion

Data Analysis

Typical plots of styrene concentration versus time in hours measured in two static headspace tests are shown in Figure 3. Clearly, the rate of styrene emission decreases with time, which indicates that the closed system is approaching equilibrium. The same data presented as a plot of styrene concentration versus the logarithm of time in hours shows a linear relationship (Figure 4). This proved to be the case in almost every experiment performed. To simplify comparisons among different samples an arbitrary parameter, styrene concentration at 100 hours ($\log 100 = 2$) calculated from the regression of the styrene concentration versus time in $\log(\text{hours})$, was used.

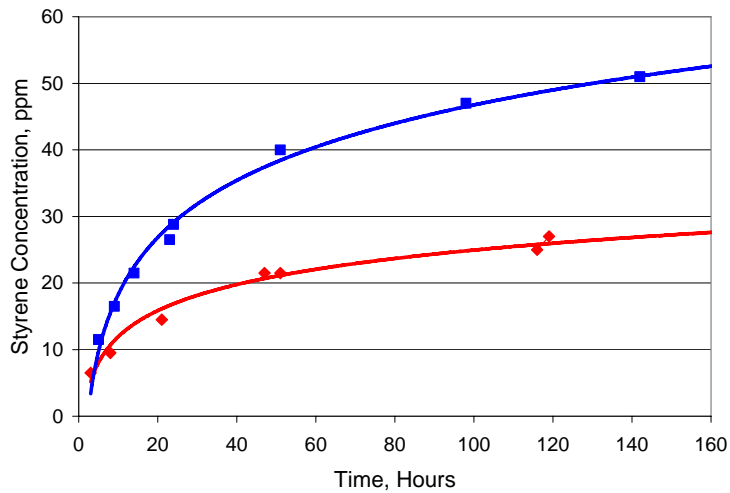


Figure 3. Typical plots of styrene concentration over time in hours as measured in a headspace experiment using an IR detector.

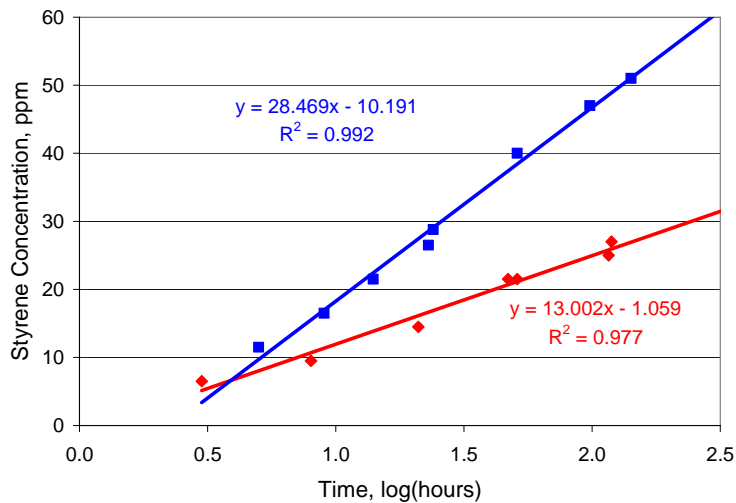


Figure 4. The same data in Figure 3 plotted as styrene concentration versus log(hours).

Effect of Time

The rate of styrene evolution from a given part will decrease over time as the monomer diffuses into the atmosphere and its concentration in the polymer matrix is reduced. A trunk pan was allowed to age at ambient indoor conditions and at different points in time, 6, 26, 96 and 258 days after molding, the pan was sealed with film and the styrene concentration was measured over time. The plot of the 100-hour styrene concentration against log(days) exhibits an exponential decrease (Figure 5). The most rapid styrene evolution occurs immediately after a part is molded. Thus, it is important for the comparison of different composite systems that the age of the molded samples be the same. For rigorous experiments storing sealed samples at

very low temperature between molding and testing would be advisable, but was not practical for these studies.

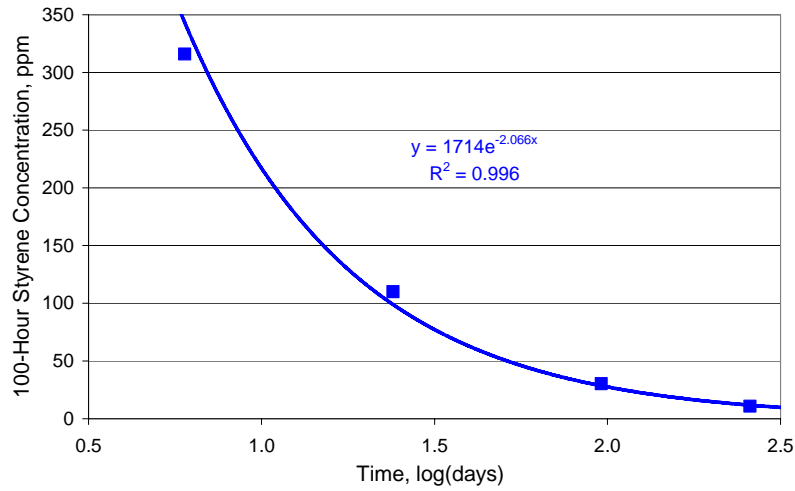


Figure 5. 100-Hour styrene concentration measured with time in log(days) for a composite trunk pan.

Effect of Temperature

The rate of monomer diffusion through a polymer network is strongly dependent on temperature. Styrene evolution was monitored for a sealed trunk pan held at 4°C, 22°C and 40°C. Styrene concentration after 100 hours at temperature increased with temperature and was more than ten times greater at 40°C than at 4°C (Figure 6). These data emphasize the need to hold the temperature constant during such measurements. Where adequate temperature control can not be maintained, comparisons among data collected at different times may contain scatter due to temperature changes.

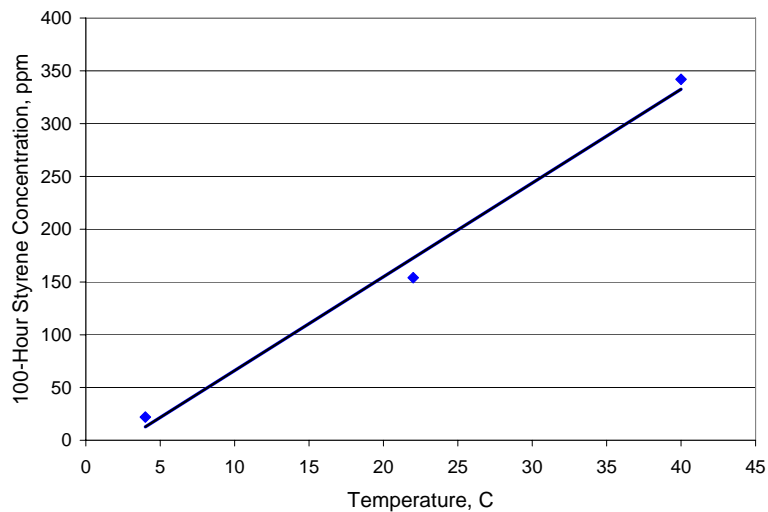


Figure 6. 100-Hour styrene concentration in a trunk pan held at different temperatures.

Trunk Pan Formulation

Sequential Dynamic Mechanical Analysis (DMA) scans of the trunk pan composite samples confirmed a measurable amount of undercure of the resin. A series of resin paste formulation experiments were conducted to improve the degree of resin cure and thus reduce the rate of styrene evolution from molded parts. Styrene emissions were measured using dynamic and static methods. Variables examined included resin type, thermoplastic additive, initiator, inhibitor, promoter, filler level, and glass bubble content. A number of these factors had significant impact on residual styrene evolution as evidenced by the data presented in Figure 7.

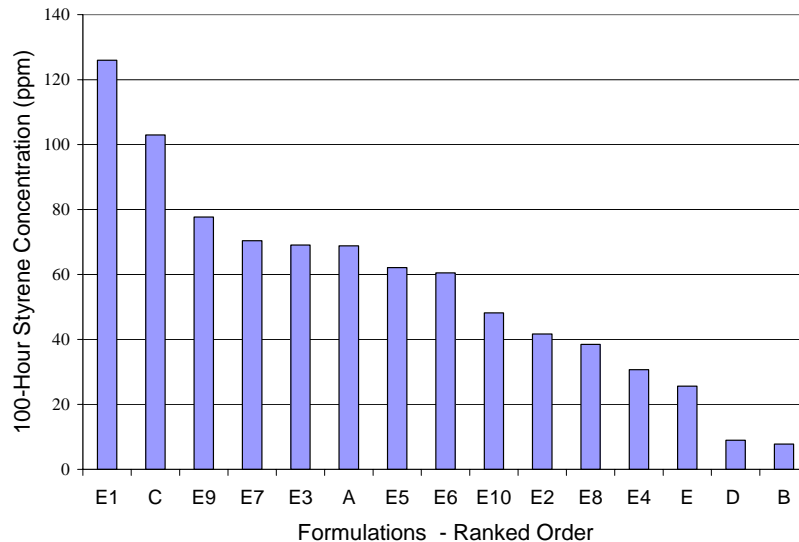


Figure 7. 100-Hour styrene concentration measured for plaques as part of a resin paste formulation experiment.

The initial experiments were followed-up with a refined formulation experiment and finally a confirming experiment with extensive replication. Unfortunately, the resin paste formulation that exhibited the lowest rate of styrene emission was determined to gel too rapidly for production feasible molding. Therefore, it was necessary to increase the amount of inhibitor in the resin paste formulation, which resulted in a modest increase in styrene evolution rate for the composite. The final formulation exhibited a 75% reduction in the rate of styrene emission from the original production material. This represented a significant odor reduction in the trunk of the convertible, but was judged to be insufficient for the coupe.

Trunk Pan Processing

Experiments examining the effect of cure time and cure temperature showed that this was not an effective means to increase the degree of cure of the trunk pan material system. However, a post bake of the composite parts proved to be very effective. A plot of 100-hour styrene concentration for plaques of one formulation post baked at three different temperatures (149°C, 163°C and 177°C) for four different lengths of time (30, 60, 90 and 120 minutes) is presented in Figure 8. It was observed that effectiveness of post bake in decreasing styrene evolution varied among different resin paste formulations. After a two-hour post bake at 177°C the formulations presented in Figure 7 show a different rank ordering and relative range of 100-hour styrene concentrations (Figure 9).

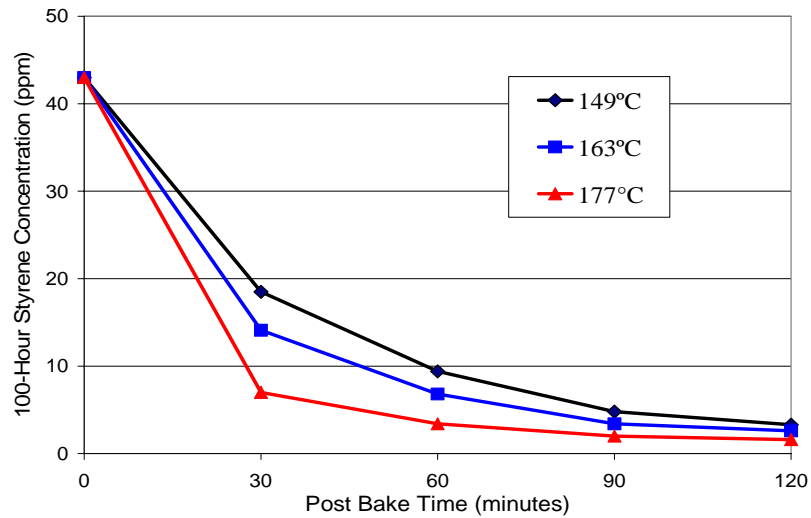


Figure 8. Effect of post bake time and temperature on 100-hour styrene concentration measured on plaques molded from one resin paste formulation.

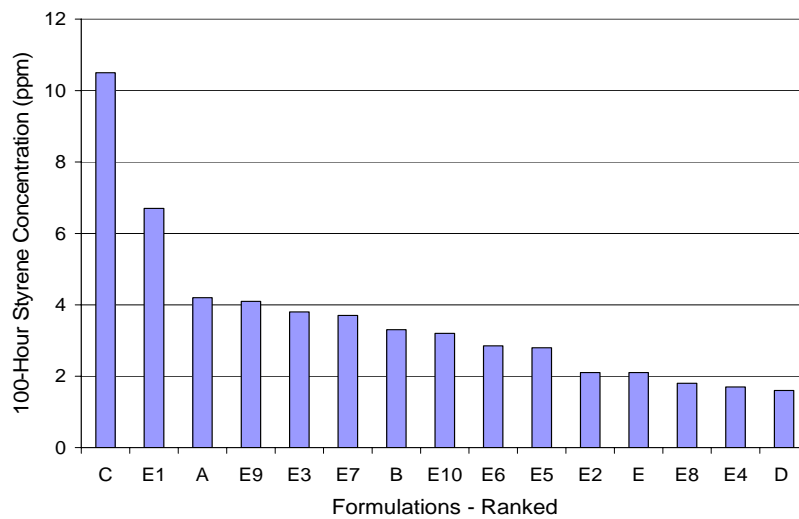


Figure 9. 100-Hour styrene concentration measured for plaques from a resin paste formulation experiment (same formulations as in Figure 7) after a two-hour post bake at 177°C.

From these experiments a post bake temperature and time were selected for production trunk pan assembly parts for the coupe. Mechanical property testing confirmed an acceptable level of strength for the post baked material. Overall, the combination of the formulation change and the post bake cycle resulted in more than a 95% reduction in the styrene evolution rate relative to the original convertible trunk pan.

No doubt a number of mechanisms are operating to reduce the rate of residual styrene emission following a post bake cycle at or above the cure temperature. These include (1) acceleration of the rate of styrene diffusion to the composite surface, (2) free radical reaction of the styrene, which builds molecular weight and reduces free styrene concentration, and (3) increased polymer crosslink density which retards the diffusion of remaining residual styrene. The relative contributions of the different mechanisms in these systems are not known.

Roof and Liftgate Formulation/Processing

The coupe required new SMC outer and inner panels for the roof and liftgate assemblies. A major factor in the selection of an SMC for these parts was the rate of styrene evolution from the molded composite. Two candidate suppliers of low-pressure “Class A” SMC were considered. Each compounder used resin from a different manufacturer. Pre-screening tests were done by the resin manufacturers to measure residual styrene by gc/ms and to determine degree of cure with a Perkin-Elmer Diamond Differential Scanning Calorimeter. From the preliminary work candidate formulations were selected.

Plaques of five different formulations were provided by one compounder/resin manufacturer (A) and plaques of four formulations were supplied by the second (B). Each examined formulation factors such as the initiator package. The effect of cure time at 149°C (90, 160, 240 seconds) and the influence of a post bake time at 163°C (0, 30, 60 minutes) were examined for each of the nine formulations. Thus, a total of 45 different material and processing combinations were studied in this designed experiment. All of the molded panels were subjected to 45 minutes at 95°C, then a cool down, followed by 60 minutes at 99°C to simulate the low bake prime and topcoat paint cycles. Styrene concentration in the headspace over plaques of each formulation/processing treatment combination was measured over time with an IR detector.

This experiment revealed a clear difference between the formulations of compounder/resin manufacturers A and B (Figure 10). Without a post bake, the A systems exhibited much higher rates of styrene evolution than the B formulations. In fact, most of the A formulations exhibited higher rates of styrene evolution after a post bake than the B systems did without a post bake. Thus, an SMC formulation from compounder/resin manufacturer B was selected for the production parts. However, since a post bake only produced a modest reduction in styrene evolution for the B formulation, an alternative approach to achieve further reduction—use of paint as a styrene barrier—was investigated.

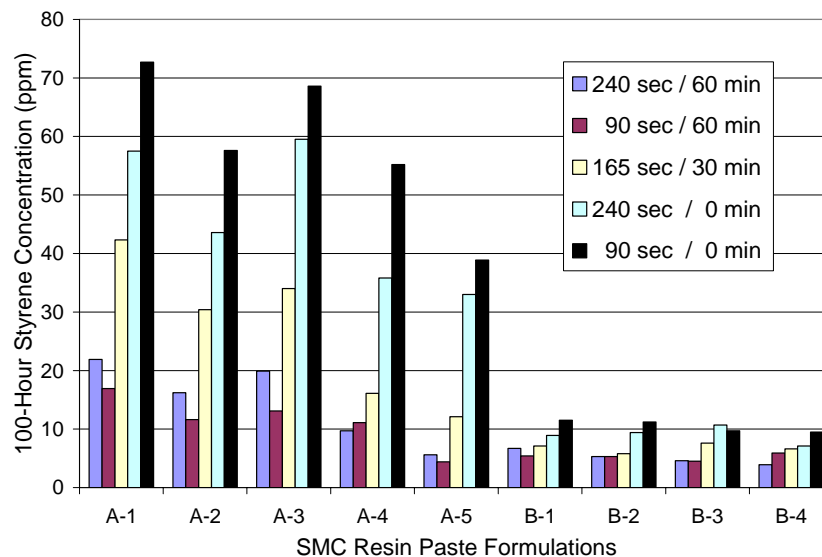


Figure 10. 100-Hour styrene concentration for formulations from two SMC compounders/resin manufacturers subjected to different cure times at 149°C and different post bake times at 163°C

Effect of Coatings

Prior Tier One program experience had shown that coatings were an effective styrene barrier and that the least porous coatings understandably provided the best barrier. An experiment was performed to quantify the effectiveness of the low-bake base/clear paint to be used on these production parts. Unfortunately, residual VOC in the paint exhibited IR absorption at 10.1 microns which interfered with the measurement of styrene.

In a separate experiment the effectiveness of a paint coating to block styrene emission was demonstrated. The SMC windshield surround is painted with a low-bake primer and flat black urethane-based monocoat paint. Six molded plaques of this particular SMC were cut in half. One half of each plaque was painted on all surfaces. The unpainted halves were subjected to the same bake cycles as the painted plaques. Plaques were tested in pairs so there were three painted and three unpainted measurements. The 100-hour styrene concentration as measured by IR for the painted panels was 6.1 ppm (s = 3.0 ppm) and for the unpainted panels the average was 23 ppm (s = 4.2 ppm). Early experience proved that a paint system using a clear coat provides a more effective barrier to styrene diffusion than primers and monocoats.

The decision was made to paint the underside of the coupe roof and liftgate assemblies with the top coat system. The parts were not post baked after molding as only marginal reduction in styrene emissions would be achieved at a significant cost. Tests conducted on fully painted parts at the vehicle level validated this approach.

Design Features

While painting the backside of assemblies covers most of surface area, styrene concentration can build-up inside of channels created by the mating of the inner and outer panels. Access openings and attachment holes in these panels can allow this styrene to diffuse into the passenger compartment. Early identification of this potential allowed the design to close-off channels, incorporate plugs to seal holes and the venting of closed sections outside of the passenger compartment.

Vehicle Level Testing

Ultimately the styrene evolution from composite parts in the vehicle under typical conditions is most important. At the outset of the program there was no established test procedure and no known target value for styrene concentration in the vehicle. Through an iterative process with different levels of prototype vehicles a test method and a target allowable level of styrene concentration were developed.

Many factors were considered in establishing the test conditions. To accelerate the styrene evolution, a vehicle soak temperature of 49°C +/-1°C was selected as it could be reproducibly controlled in a test cell, it is a safe temperature for unprotected workers, and it will not damage vehicle components. A heat soak time of 66 +/- 4 hours was established to allow this to be performed over a weekend. During the heat soak all doors, windows and vents were closed. At the end of the heat soak period, air from the passenger compartment was passed through a Tenax tube to collect VOC and the residual air was pumped back into the vehicle. The sealed Tenax tube was then submitted to a test laboratory (Clayton Group Services) for VOC

desorption, separation by gas chromatography, and identification by mass spectrometry. Results were reported in ppm by volume as well as g/m³.

After the VOC samples were collected a jury of about six individuals from engineering and management evaluated the air in the vehicle. An individual quickly entered the vehicle and closed the door. A numerical rating was made on the level of styrene odor perceived. Over the period of this study several sessions with juries and VOC analyses were conducted. Based on the results of these tests, a styrene concentration limit of 0.15 ppm was established as a target.

A vehicle from the final preproduction build was determined have a styrene concentration of 0.10 ppm in the passenger compartment after the 49°C heat soak. The styrene odor level in the passenger compartment of this vehicle was judged to be commercially acceptable.

Conclusions

Various test methods were employed to conduct a series of experiments on the evolution of styrene from thermoset polyester composites. The effect of fundamental parameters such as time and temperature were identified. Key variables such as resin paste formulation, cure time, post bake conditions and coatings were found to effect the rate styrene evolution from fiber-reinforced polyester resin composites. The application of the knowledge gained in these studies resulted in the cost-effective production of vehicles with sufficiently low concentrations of styrene in the enclosed passenger compartment to be acceptable to customers.

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