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CHARACTERIZATION AND MODELING OF STYRENE EMISSION FROM A THERMOSET COMPOSITE MATERIAL

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DOCTOR OF PHILOSOPHY

ABSTRACT

Diffusive emissions of volatile compounds from building materials have been well documented as a source of indoor air pollution. While laboratory testing can quantify these emissions and predict volatile concentrations in indoor air, the ability to precisely model emission rates from any given building material would provide a useful tool to air quality professionals to anticipate, identify and mitigate potential sources of indoor air pollution. Composite materials, some made with vinyl ester resins, are replacing metal in transportation applications (bus bodies, airplane fuselages) but contain volatile styrene. Here, a mass transfer model for predicting volatile emissions from a “dry” building material is presented, validated and expanded for use over a range of temperatures. A vinyl ester resin (VER) composite material containing 38% styrene by weight, reinforced with E-glass fiber and formed by a vacuum assisted resin transfer method is characterized for styrene emissions using small environmental test chamber (ETC) methodology. Styrene concentrations in the ETC were collected at regular intervals for a range of temperatures using charcoal sampling tubes analyzed by gas chromatography. The VER composite material parameters and emission profiles were applied to an existing mass transfer model for validation at 23°C. Total mass of styrene emitted, as well as emission factor, increased at each test temperature. Total mass of styrene emitted ranged from 2.76 mg at 10°C to 15.5 mg at 50°C over a two week period. The styrene emission factor ranged from 0.029 mg m^{-2} hr^{-1} at 10°C to 0.079 mg m^{-2} hr^{-1} at 50°C. The VER composite emission factors over a temperature range were then applied to scale the model over varied environmental conditions. Results show that the modeled data fit the chamber data at 23°C, but underestimate chamber data by as much as 10^{-6} at the highest temperature tested (50°C). Empirical adjustments to the model show that, for VERTCM, the modeled data can be made to fit the chamber data to within a factor of no more than 2.8. This scalable model allows for the prediction of volatile emissions and resultant concentrations in indoor air over a temperature range with few (material, environmental) parameter inputs.

Keywords: Vinyl ester resin, volatile emissions, environmental test chamber, styrene, VOC, indoor air

DEDICATION

I dedicate this work to my family and our future together.

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LIST OF ABBREVIATIONS

A	Area
ACGIH	American Conference of Governmental Industrial Hygienists
ACH	Air Changes per Hour
ATSDR	Agency for Toxic Substances and Disease Registry
CA DHS	California Dept. of Health Services
Ce	Emitted Concentration
Ce,df	Emitted Concentration, diffusive fraction
CFD	Computational Fluid Dynamics
Co	Initial Concentration
D	Diffusion Coefficient
Da	Diffusion Coefficient of Air
Dk	Knudson Diffusion Coefficient
Dm	Molecular Diffusion Coefficient
ETC	Environmental Test Chamber
HAP	Hazardous Air Pollutant
Kv	Partition Coefficient
L	Linear Thickness of Material
MRL	Minimal Risk Level
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
Q	Air Flow

LIST OF ABBREVIATIONS
- CONTINUED -

REL	Recommended Exposure Limit
STEL	Short Term Exposure Limit
TCM(s)	Themoset Composite Material(s)
TLV	Threshold Limit Value
TWA	Time Weighted Average
USEPA	United States Environmental Protection Agency
V	Volume
VERTCM	Vinyl Ester Resin Thermoset Composite Material
VOC(s)	Volatile Organic Compound(s)
x	Linear VOC Pathlength (designated here as L/2)

CHAPTER 1

INTRODUCTION

Background

This course of study evaluates styrene vapor emission from vinyl ester resin thermoset composite material (VERTCM) over a temperature range (10°C to 50°C) using small environmental test chamber (ETC) methodology. Data generated by this study are used to model styrene emission from VERTCM. Estimation of the potential for adverse human health effects from styrene exposures in indoor environments is also performed.

The main purpose of this research is threefold. First, air styrene concentrations produced by emission from VERTCM at varied temperature are quantified and the resultant emission profiles are developed to determine total emission mass and emission factor over a period of time (Chapter 2). Second, an existing mass transfer model is validated against the experimental data, and, where needed, modified to accommodate temperature variation to predict potential indoor air styrene concentrations given a relatively few physical and environmental parameter inputs into the model (Chapters 3 and 4). Third, the emission data are applied in order to predict the potential for indoor air styrene concentrations from like VERTCM to exceed non-occupational guidelines for acute, intermediate and chronic styrene inhalation exposures (Chapter 5).

It would be beneficial to have a simple method to estimate the potential for exposure to indoor volatile organic compounds (VOC), including styrene, especially in non-occupational settings where susceptible populations may be exposed to low-level VOC concentrations for a long period of time. A model that could predict the indoor air concentrations of VOC without having to perform time-consuming and expensive analyses would be extremely useful. The ability of such a model to predict indoor air VOC concentrations at various temperatures is equally as important because temperature has a significant effect on the diffusion coefficient (D) and partition coefficient (Kv) of VOC for dry building materials and therefore, on the resultant indoor air VOC concentrations for any given point in time.

Vinyl Ester Resins

Thermoset composite materials are lighter and often stronger than common metals of similar dimension, and are being researched and developed as a replacement for metal (e.g. steel, aluminum) in military, transportation and civilian uses. Buses, trains, trucks, aircraft, and boats are a few examples of current transportation applications utilizing vinyl ester resin materials. Polymer resin composites are also currently used in many consumer applications such as patio furniture, shower units, ceiling and wall panels, institutional seating, stairs and wall partitions, and in components of toys and games, among other uses.

As the acceptance of these materials increase, production and use of polymers and polymer-based composites is expected to increase. Polymer-based composites are increasingly found in larger quantities and wider ranges of products for public use. One downside of these materials and other volatile-containing building materials is that they can emit volatile organic compounds (VOCs) into the air for a considerable period after installation in indoor environments. Several researchers are currently working on developing physical-based mass transfer models to accurately predict indoor air VOC concentrations given a minimal number of physical parameters.

Thermoset composite materials (TCMs) consist of cross-linked polymers containing VOCs that are cured either at room temperature or under high heat and/or pressure conditions. High temperature and pressure curing would be expected to volatilize more VOCs from the finished product than room temperature curing; however, many commercial TCMs are room temperature cured because of their typically large sizes (e.g. auto body parts) and increased manufacturing costs associated with high temperature and pressure curing. TCMs may also contain filler material such as powders or fibers to improve strength and durability. Fibers may be chopped, wound or woven, and may include fibers such as glass, Fiberglass™, cloth, Kevlar™ or other filler material.

Styrene is used in large quantities in the processing of vinyl ester resin thermoset composite materials (VERTCMs). Vinyl ester resin generally contains 30 to 60% styrene by weight. Styrene is added to the vinyl ester resin, serving as a diluent to reduce the viscosity of the resin and enabling processing by methods such as vacuum assisted resin infusion. Styrene monomer also enhances linear chain extension in the resin allowing for liquid mold processing and room temperature curing.

Vinyl ester resins offer corrosion resistance and strength, and are formed by reacting an epoxy resin with methacrylic acid. Styrene is added to the resin as a reactive diluent, not only decreasing the viscosity of the resin for forming, but also acting as a "bridge" during the crosslinking process. Crosslinking occurs when an initiator opens up double carbon bonds on both the vinyl ester and styrene molecules, allowing these free radicals to link and crosslink. Complete crosslinking results in a final, cured material with high strength and resistance to degradation. Complete crosslinking is unrealistic, however, and some “free” styrene remains in the polymer with the potential to diffuse out of pore spaces within the material.

As vinyl ester resins are subjected to increased post-manufacture temperatures, hydrogen bonding is overcome, and diffusion in and emission from the material increase. Because of the large amounts of styrene typically present in these materials, Ziaee and Palmese (1999) showed that as much as 50% by weight of the styrene in finished materials remains un-reacted after room temperature curing. Un-reacted styrene under high temperature conditions could result in unhealthy levels of styrene released into post-production indoor environments.

Styrene Health and Environmental Considerations

Styrene has been called one of the most important industrial chemicals with a global production of more than 17.8 million tons in 1993 (Miller, *et al*. 1994). Styrene is produced in very large amounts (10 billion pounds in 1993) by nine companies in the United States (USEPA, 1994). Styrene is used in large quantities in the production of vinyl ester resins, a component of thermoset composite materials (TCMs). Production of polymers and polymer-based composites (TCMs) was expected to reach 3 billion pounds per year by 2010 (Vaidya, 2006).

Styrene (also known as vinylbenzene) is a colorless liquid with a sweet smell, low odor threshold (0.32 ppm or 1.36 mg m^{-3}) and a vapor pressure of 5 mm Hg at 23^{o}C

(Table 1, Figure 1). Liquid styrene readily partitions into air, and studies have shown that the halflife by direct photolysis on styrene is on the order of fifty years and the halflife by photooxidation is as long as thirteen hours (ATSDR, 1992). This means that, once in air, styrene is readily available for inhalation exposures. The most likely mode of exposure of the general population to styrene is by inhalation of indoor air (USEPA, 1988).

Table 1. Properties of styrene (CAS# 100-42-5) syn. vinylbenzene

Structural Formula	$C_6H_5CH=CH_2$
Molecular Weight	104.2
Boiling Point (^oC, 1 atm)	145.0
Vapor Pressure (mmHg, 23^oC)	5.0
Specific Gravity (g/ml, 20^oC)	0.906

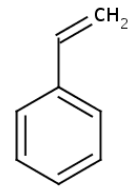


Figure 1. Styrene

Styrene has a high blood to air partition coefficient (48±7.6 at 37^oC), and it has been estimated that 60 to 70% of inhaled styrene passes to the circulatory system and accumulates in fat tissue (Lof, A. *et al.*, 1986). The health effects of various inhalation styrene exposures have been well-documented and can be referenced in the available literature, such as the Agency for Toxic Substances and Disease Registry's Toxicological Profile for Styrene (ATSDR, 1992). Styrene is generally characterized as a central nervous system toxicant and possible carcinogen. The International Agency for Research on Cancer has listed styrene as a possible (2B) human carcinogen; however, this designation relied on oral exposure of rats to styrene, and there is no known correlation between the carcinogenic potential of styrene and inhalation exposures in humans (IARC, 2002).

Styrene Health Effects

Most information on the effects of inhalation exposure to styrene in humans comes from studies of workers exposed to styrene vapors in the production and use of plastics and resins, especially polystyrene resins. Persons with preexisting respiratory or neurological problems would be at risk for the irritant action and central nervous system depressant effects of styrene, respectively. Styrene metabolism is known to be inhibited by the presence of other VOCs such as toluene, trichloromethylene, and ethyl benzene (ATSDR, 1992). Most of the occupational health effects to styrene described below occur at exposure levels below most current U.S. occupational guidelines (Table 2).

Table 2. Occupational exposure limits for styrene

NIOSH REL	TWA	50 ppm*	STEL	100 ppm*
ACGIH	TLV	50 ppm	STEL	100 ppm
OSHA PEL	TWA	100 ppm	Ceiling	200 ppm

* (50 ppm ≈ 213 mg m^{-3}, 100 ppm ≈ 425 mg m^{-3} at ambient temperatures)

Respiratory Effects. Several human studies have examined the respiratory effects caused by inhalation exposure to styrene. The most commonly reported general symptom is mucous membrane irritation (ATSDR, 1992). Obstructive lung changes were reported for workers exposed to styrene for about 10 years (Chmielewski and Renke, 1975; Chmielewski *et al.* 1977).

Neurological Effects. Epidemiological and clinical studies on workers have demonstrated that inhalation exposure to styrene may cause alterations of central nervous system function (ATSDR, 1992). The symptoms are typical of central nervous system depression, and appear to be the most sensitive endpoint for styrene exposure via the inhalation route (Kulig, 1988; Pryor *et al.*, 1987). Chronic exposure of workers to styrene resulted in an increased incidence of abnormal electroencephalograms at exposure levels as low as 31 ppm (Harkonen *et al.*, 1978). Based on the Lowest Observed Adverse Effect Level (LOAEL) of 25 ppm from Mutti *et al.* (1984), a chronic inhalation minimal risk level (MRL) of 0.06 ppm was derived for nonoccupational exposures (ATSDR, 1992).

Central nervous system symptoms attributed to acute styrene exposure include headaches, fatigue, nausea, weakness and dizziness. These and other neurological effects may play a role in the rate of workplace accidents and the level of worker performance. To assess psychomotor function, Chia, *et al.* (1994) performed the Santa Ana test on 21 styrene-exposed workers (mean styrene concentration <30 ppm) and compared the results to 21 matched nonexposed controls. The exposed group did poorly compared to the control group.

Recently, there have been reports about the effects of styrene on visual function. In a study at a fiber-reinforced plastics boat manufacturing plant, employees exposed to <30 ppm styrene in air suggested an impairment in color vision (Chia *et al.*, 1994). Jegarden (1993) found that workers with a mean exposure to styrene of approximately 22.7 ppm performed significantly less well than the control group in the morning ($p<0.02$) and in the evening ($p<0.01$). For Swedish workers exposed to a mean styrene concentration of 8.6 ppm, a color vigilance test indicated a somewhat prolonged reaction time for the exposed group when compared with the control; however, this difference was not statistically significant (Edling, *et al.* 1990).

Otoxicity of styrene and the synergistic action of styrene and noise have been shown in rats (Makitie, 2003). Muijser, *et al*. (1988) found a statistically significant difference in hearing thresholds between workers exposed directly to mean styrene concentrations of 138 mg m^{-3} and those exposed indirectly to mean styrene concentrations of 61 mg m^{-3}. Occupational exposure to styrene and combined exposures to styrene and noise produced an odds ratio of approximately 4x higher for exposed workers than for unexposed controls for developing hearing loss (Sliwinska-Kowalska, 2003). Johnson *et al*. (2006) found in a study of 313 workers exposed to styrene, those who were also exposed to noise had a significantly lower pure tone threshold in the high frequency range (3 - 8 kHz).

Chromosomal Effects. Another health effect at moderately low air styrene concentrations is related to the genotoxicity of styrene. There is evidence that both DNA adducts and DNA single strand breaks are induced in styrene workers (Henderson, 1995). Eighteen workers exposed to less than 50 ppm styrene were found to have a significant increase in chromosome gaps (Hansteen *et al*. 1984). Increased frequency of lymphocyte micronuclei in workers exposed to a mean of 13 ppm styrene has also been reported (Hogstedt *et al*. 1983).

Increased chromosome aberrations (Relative Risk = 2.44; 95% C.I., 1.26 - 4.70) and sister chromatid exchanges (Relative Risk = 1.26; 95% C.I., 1.07 - 1.47) were measured in peripheral blood lymphocytes of 46 male workers employed in a fiber-reinforced plastic boat building factory and exposed to styrene concentrations of 86 – 1,389 mg m^3 in ambient air (Artuso, 1995).

Hematological Effects. Lowered erythrocyte counts, hemoglobin, platelets, and neutrophils, and slightly higher mean corpuscular red cell volumes and neutrophil band counts were observed in workers exposed to mean styrene concentrations in a styrene-butadiene rubber manufacturing plant (Checkoway and Williams, 1982). Interpretation of this study is limited, however, because multiple-chemical exposures were involved and exposure and clinical signs were measured at the same time and only once (ATSDR, 1992).

Hepatic Effects. Liver enzyme levels were measured in 57 workers exposed to 1 to 100 ppm styrene in the polyester industry for l to 20 years (Hotz *et al*. 1980). This study suggests hepatic injury at exposure levels of 100 ppm and less (ATSDR, 1992).

Non-Occupational Exposure Guidelines. Styrene is regulated under the U.S. Clean Air Act (CAA) as a hazardous air pollutant (HAP) and, as a volatile organic compound, styrene falls under National Ambient Air Quality Standards (NAAQS) provisions. Styrene is the most common HAP found in materials made from vinyl ester resins (La Scala *et al*., 2006). As such, there is a need to determine the emission characteristics of styrene and potential resultant indoor air concentrations of styrene from composite materials that are increasingly finding their way into contact with human populations.

There is very little literature on the chronic exposure effects in humans to low levels of styrene in air. Based on the available literature and to protect humans in nonoccupational environments, the ATSDR (2008) has established a chronic (> 364 days) inhalation exposure Minimal Risk Level (MRL) of 0.06 ppm (0.25 mg m^{-3}) for styrene

(Table 3). The Environmental Protection Agency's Reference Concentration (RfC) for inhaled styrene is 0.20 ppm (0.85 mg m^{-3}) for intermediate exposures (14 - 354 days). The California Department of Health Services, Office of Environmental Health Hazard Assessment (California DHS, 1996), a state agency, has established a nonbinding guideline for acute (1 - 13 day) exposures to airborne styrene at 5.1 ppm (21.7 mg m^{-3}).

Table 3. Nonoccupational styrene inhalation exposure guidelines

Agency	Exposure	mg m^{-3}	ppm
CA DHS	Acute (1 – 13 days)	21.7	5.1
US EPA	Intermediate (14 – 364 days)	0.85	0.20
ATSDR	Chronic (> 365 days)	0.25	0.06

Sparks (1992) demonstrated that for a steady state (constant) emission source, daily ventilation rates can have a profound effect on the pollutant concentrations relative to the indoor environment having a constant air exchange rate, stressing the importance of determining not only the indoor air concentrations but also individual activity patterns to estimate exposures. La Scala *et al*. (2006) determined that total inhalation exposure is not only a function of exposure time, but also of lung ventilation rate (i.e. breathing rate).

There are several guidelines and publications for assessing the potential for indoor occupant exposure to VOCs emitted from building materials. The California Department of Health Services (California DHS, 1996) released nonbinding guidelines for reducing occupant exposure to VOCs, including a section specific for styrene. Other national and international guidelines exist for referencing and estimating indoor air exposures to VOCs from building materials (Tichenor, 2006; AgBB, 2005).

Environmental Test Chamber Studies

Emission testing of indoor building materials using small environmental test chamber (ETC) methodology is well documented since the 1980s. Matthews (1987) described one of the first ETC methodologies for organic vapor characterization of solid emission sources. He concluded that, compared to large scale ETCs (> 15 m^3), small-scale chambers (≤ 1 m^3) are more appropriate for comparing emissions from a large number of samples, while more accurately controlling environmental test conditions (temperature, humidity and air exchange rate). He also concluded that temperature, humidity, air flow and exchange rate can have profound effects on the rate of emissions both from the products being tested and from sink effects inside the chamber and sampling apparatus. Matthews suggested that a temperature range of 18 to 35^{o}C and humidity range of 20 to 80% relative humidity (RH) represent reasonable conditions for indoor environments with partial climate control and that standard test conditions of 23^{o}C and 50% RH should be achievable.

Colombo *et al*. (1990) sampled particle board with glued-on carpet, gypsum board with glued-on wallpaper, and plywood sandwich with stain and lacquer in 450 liter glass chambers. The results for materials received two to seven months after manufacture and encased in foil wrapping showed a conditioning period in the ETC of two to seven days before the ratio of the slope to concentration was ≤ 10% per day. They concluded that while following the emission profile to concentration equals zero is best for determining absolute mass loss, this is not pragmatic for chamber tests and that using steady state chamber concentration profiles at the end of the test period, where the slope of the emission profile is near zero, can be used with confidence to estimate volatile emissions at some future point in time. This is especially true for dry building materials that approximate steady state emission conditions.

Tichenor (1989) conducted small chamber tests on clear acrylic latex caulk with silicone. Tests conducted at 23°C, 50% RH and 1.8 air changes per hour (ACH) for 1,230 hours revealed that for materials with multiple VOC present, individual VOC concentrations vary with time. This was to be expected as the chemical components had varied vapor pressures and emissions may vary with the vertical concentration profile in the caulk.

Guo *et al*. (2004) evaluated total VOC emissions from carpet samples with polypropylene backing. Molecular diffusion was determined to be the dominant force for VOC transport in dry materials, and the driving forces of diffusion in dry materials were determined to be concentration gradient, pressure gradient and density gradient. Also, the age of material and storage temperature were determined to have profound effects on the emission concentrations of tested materials. Two studies describe the challenges of estimating an accurate quasi-static emission rate from dry (dry paint and wood stain on impervious substrates) building materials (Afshari, 2003; Yang, *et al*. 1998). These researchers stress the importance of allowing sufficient time at test conditions before attempting to quantify emission rates based on air velocity and mixing rates at the early stage.

Tichenor and Guo (1988) determined that for materials where emissions are diffusion driven and the rate of diffusion is very slow, changing the air exchange rate will have little effect on emission rate. Similarly, the air velocity over the surface of the material will have little effect on the rate of diffusion and partitioning of VOC within a diffusion-driven dry building material, whereas air velocity is much more important for wet materials such as paints, caulks and adhesives applied to the surface of dry building materials. More recently, change in temperature has been cited as the most important factor for influencing the diffusion (D) and partitioning (Kv) of VOC from dry building materials (Zhang *et al*., 2007; Deng *et al*., 2009).

There are sufficient standards and guidelines available for referencing ETC construction and analysis. The American Society for Testing and Materials (ASTM, 1997 and 2006) issued a Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products in 1997 (D 5116-97) with a revision in 2006 (D 5116-06). This standard covers equipment, experimental procedures, data analysis and QA/QC. According to a contractor report issued to the U.S. Environmental Protection Agency (Tichenor, 2006), there are both national and international assessment and certification programs for the testing of emissions to determine impacts on indoor air quality. There are currently four U.S. testing facilities with “approved” certification programs. One of these is the Greenguard Environmental Institute which issued its own guidelines for small-chamber testing and on which a portion of are relied upon in the completion of this study (GEI, 2006).

Modeling VOC Emissions

Researchers have attempted to model the characteristics of VOC emissions from building materials in indoor environments. Several researchers have argued that a mass transfer (physical-based) model can better predict VOC emissions for materials of known physical parameters at various environmental conditions (Clausen *et al*., 1991; Little *et* *al*., 1994; Huang and Haghighat, 2002; Zhang and Xu, 2003). This is because empirical models, such as the first-order decay model obtained from chamber data, cannot be easily scaled to “real world” building conditions. Further discussion of the details in applying mass transfer models to predict VOC emissions from building materials, as well as obtaining the necessary parameters to run the models, is contained in Chapters 3 and 4.

Previous characterization and modeling of VOC emissions from dry building material has yielded insight into the driving forces behind volatile emission rates and the parameters needed to predict resultant indoor air VOC concentrations. Virtually all of the data generated has occurred within a very narrow range of experimental temperature. In fact, most of the research to date has been developed using two to three datasets generated at approximately 23^{o}C and 50% RH. Only recently have researchers studied the effect of temperature on the diffusion (D) and partitioning (Kv) of volatiles from dry building materials.

Preliminary Studies

The primary purpose of this preliminary study was to verify that the chamber air samples contained enough styrene to be detected with sufficient confidence over the sampling period proposed for this research. As illustrated in Figures 2 and 3 below, styrene could be measured and quantified in the chamber air up to seven days after initiation. Replicate ETC air styrene sampling showed uniformity throughout the test, especially in the diffusive phase (≥48 h).

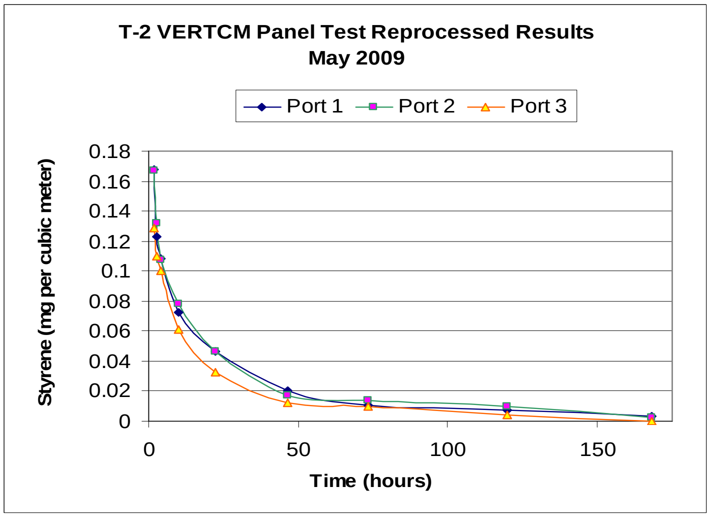


Figure 2. 2-panel VERTCM styrene profiles

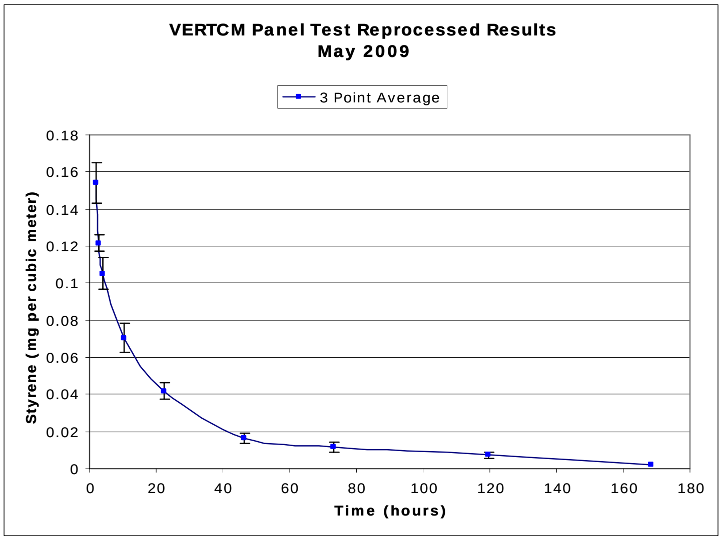


Figure 3. 2-panel VERTCM styrene average

As a result of this preliminary study, it was concluded that a minimum of 4 VERTCM panels placed inside the chamber for each experiment would ensure that an adequate concentration profile could be developed from the experimental data. Also, one experimental condition in this exercise that differed from previous experiments was that this experimental chamber data consisted of two panels suspended upright (i.e. on edge) in the chamber, and thus diffusion occurred from both sides of the panel rather than from a single layer, the latter method being the basis around which previous models have been developed. This parameter is accounted for in the model inputs and taken into consideration with the results.

Goals and Objectives

To date there is no known literature regarding the characterization of styrene emission from VERTCM using small environmental test chamber methodology and the subsequent modeling of potential indoor air concentrations for this novel material at varied temperature. As well, there are no data on the effect of temperature on the diffusion (D) and partitioning (Kv) of styrene from VERTCM, and analysis of the potential for modeling and predicting indoor air styrene emission from VERTCM. This course of study aims to fill this data gap.

References

Afshari A., Lundgren B., Eckberg L.E. 2003. Comparison of three small chamber test methods for the measurement of VOC emission rates from paint. Indoor Air, 13:156-165.

AgBB. 2005. Health-related evaluation procedure for volatile organic compounds emissions (VOC and SVOC) from building products. Committee for Health-related Evaluation of Building Products. 21 pp.

Agency for Toxic Substances and Disease Registry (ATSDR). 1992. Toxicological Profile for Styrene. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry (ATSDR). 2008. ATSDR HazDat, Air Comparison Values in ppb (for VOC Compounds Only). February 12, 2008. Page 2 of 3.

American Society for Testing and Materials (ASTM). 1997. ASTM Designation: D 5116-97. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.

American Society for Testing and Materials (ASTM). 2006. ASTM Designation: D 5116-06. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.

Artuso M., Angotzi G. Bonassi S. et al. 1995. Cytogenic biomonitoring of styrene-exposed plastic boat builders. Archive of Environmental Contaminant Toxicology, 29(2), 270-274.

California DHS. 1996. Reducing Occupant Exposure to Volatile Organic Compounds from Office Building Construction Materials: Non-Binding Guidelines; Office of Environmental Health Hazard Assessment, Indoor Air Quality Section. July 1996.

Chia, S.E. Jeyaratnam J., Ong C.N. et al. 1994. Impairment of colour vision among workers exposed to low concentrations of styrene. American Journal of Industrial Medicine, **26**: 481-488.

Checkoway H, Williams TM. 1982. A hematology survey of workers at a styrene-butadiene synthetic rubber manufacturing plant. Am Ind Hyg Assoc J, 43:164-169.

Chmielewski J, Renke W. 1975. Clinical and experimental studies on the pathogenesis of toxic effects of styrene. II. The effect of styrene on the respiratory system. Bull Inst Marit Trop Med Gdynia 26:299-302.

Chmielewski J, Dolmicrski R, Renke W, et al. 1977. Long-term effects of styrene on workers at the workplace. Z Gesnmte Hyg 23:639-643.

Clausen P.A., Wolkoff P., Holst E., Nielsen P.A. 1991. Long-term emission of volatile organic compounds from waterborne paints – methods of comparison. Indoor Air, 4:562-576.

Colombo A., De Bartoli M., Pecchio E., Schauenburg H., Schlitt H., Vissers H. 1990. Chamber testing of organic emission from building and furnishing materials. The Science of the Total Environment, 91:237-249.

Deng Q., Yang X., Zhang J. 2009. Study on a new correlation between diffusion coefficient and temperature in porous building materials. Atmospheric Environment (in press), doi:10.1016/j.atmosenv.2008.12.052.

Edling C., Ekberg K., Ahlborg G. et al. 1990. Long term follow up of workers exposed to solvents. British Journal of Industrial Medicine, 47:75-82.

Greenguard Environmental Institute (GEI). 2006. Laboratory Qualifications and Proficiency Requirements. Greenguard Product Certification Program. GG Publications, Inc. 14 pp.

Guo H., Murray F., Lee S.C. Wilkinson S. 2004. Evaluation of emissions of total volatile organic compounds from carpets in an environmental chamber. Building and Environment, 39:179-187.

Hansteen IL, Jelmert 0, Torgrimsen T, et al. 1984. Low human exposure to styrene in relation to chromosome breaks, gaps and sister-chromatid exchanges. Hereditas 100:87-91.

Harkonen H, Lindstrom K, Seppalainen AM, et al. 1978. Exposure-response relationship between styrene exposure and central nervous functions. Stand J Work Environ Health 4:53-59.

Henderson J.N. 1995. Styrene–butadiene rubbers, Rubber Technology, Chapman and Hall, London, p. 209.

Hogstedt B, Akesson B, Axe11 K, et al. 1983. Increased frequency of lymphocyte micronuclei in workers producing reinforced polyester resin with low exposure to styrene. Standard Journal of Work Environ Health 9:241-246.

Hotz P, Guillemin MP, Lob M. 1980. Study of some hepatic effects (induction and toxicity) caused by occupational exposure to styrene in the polyester industry. Journal of Work Environment and Health, 6:206-215.

Huang H., Haghighat F. 2002 . Modeling of volatile organic compounds emission from dry building material. Building and Environment, 37(12):1349-1360

International Agency for Research on Cancer (IARC). 2002. IARC Monographs Volumes 1-88. Styrene [100-42-5]; 60(82).

Jegaden D., Amann D., Simon J.F. et al. 1993. Study of neurobehavioral toxicity of styrene at low levels of exposure. International Archives of Occupational and Environmental Health, 64(7):527-531

Johnson A.C., Morata T.C., Lindblad A.C., et al. 2006. Audiological findings in workers exposed to styrene alone or in concert with noise. Noise Health; 8(30):45-57.

Kulig BM. 1988. The neurobehavioral effects of chronic styrene exposure in the rat. Neurotoxicology and Teratology, 10:511-517.

La Scala U.C., Orlicki J., Jain R., Palmese G., Vaidya U., Sands J.M. 2006. Emission modeling of styrene from vinyl ester resins. Clean Technology Environmental Policy. DOI 10.1007/s10098-006-0076-1.

Little J.C., Hodgson A.T., Gadgil A.J. 1994. Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment, 28(2):227-234.

Lof A., Lundgren E., Nydahl E.M. 1986. Biological monitoring of styrene metabolites in blood. Scand J W Environ Health, 12:70-74.

Makitie A. 1997. The ototoxic effect of styrene and its interaction with noise. Published by the University of Helsinki, Finland, Thesis.

Matthews T.G. 1987. Environmental chamber test methodology for characterizing organic vapors from solid emission sources. Atmospheric Environment, 21(2); 321-329.

Miller R., Newhook R., Poole A. 1994. Styrene production, use, and human exposure. Critical Review of Toxicology, 24:1-10.

Muijser H., Hoogendijk EMG., Hooiisma J. 1988. The effects of occupational exposure to styrene on high frequency thresholds. Toxicology, 49 : 331-340.

Mutti A, Mazzucchi A, Rustichelli P, et al. 1984. Exposure-effect and exposure-response relationships between occupational exposure to styrene and neuropsychological functions. American Journal of Industrial Medicine, 5:275-286.

Pryor GT, Rebert CS, Howd RA. 1987. Hearing loss in rats caused by inhalation of mixed xylenes and styrene. Journal of Applied Toxicology, 7:55-61.

Sliwinska-Kowalska M., Zamyslowska-Szmytke E., Szymczak W., et al. 2003. Ototoxic effects of occupational exposure to styrene and co-exposure to styrene and noise. Journal of Occupational and Environmental Medicine, 45(1), 15-24.

Sparks, Leslie E. 1992. Modeling Indoor Concentrations and Exposures. USEPA Indoor Air Branch. Research Triangle Park, NC: 102-111.

Tichenor B.A. Guo Z. 1988. The effect of ventilation on emission rates of wood finishing materials. Healthy Buildings 77(5):423-432.

Tichenor B.A. 1989. Measurement of organic emissions from indoor materials – Small chamber studies. Procedures from the Symposium on Measurement of Toxic Air Pollutants. EPA/APCA.

Tichenor B.A. 2006. Criteria for Evaluating Programs that Assess Materials/Products to Determine Impacts on Indoor Air Quality: Contractor Report (final) submitted to USEPA; Macon, NC.

USEPA. 1994. Pollution Prevention and Toxics, Styrene Fact Sheet; 749-F-95-019.

Vaidya U. 2006. Personal communication.

Yang X., Chen Q., Zhang J.S. 1998. Impact of early stage incomplete mixing on estimating VOC emissions in small test chambers. Indoor Air, 8:180-189.

Zhang Y., Xu Y. 2003. Characteristics and correlations of VOC emissions from building materials. International Journal of Heat and Mass Transfer, 46:4877-4883.

Zhang Y., Luo X., Wang X., Qian K., Zhao R. 2007. Influence of temperature on formaldehyde emission parameters of dry building materials. Atmospheric Environment, 41:3203-3216.

Ziaee S, Palmese G.R. 1999. Effects of temperature on cure kinetics and mechanical properties of vinyl ester resins. Journal of Polymer Science, 37:725-744.

CHAPTER 2

INFLUENCE OF TEMPERATURE ON STYRENE EMISSION FROM A VINYL ESTER RESIN THERMOSET COMPOSITE MATERIAL

Abstract

Composite materials made with vinyl ester resins are lighter, stronger and corrosion resistant compared to most metals, and are increasingly being used as building materials and in public transportation. Styrene monomer is used as both a diluent and strengthener in the production of vinyl ester resin (VER) composites. Some researchers contend that free styrene in VER composites is available to diffuse out of the material into air, perhaps leading to adverse health effects via inhalation exposures in humans, yet there are no known data on styrene emissions from these materials in the literature. In this study, a typical VER composite made with resin containing 38% by weight styrene, reinforced with E-glass fiber and formed using a vacuum assisted resin transfer method was characterized for styrene emissions by environmental test chamber (ETC) methodology. Styrene concentrations in the ETC were measured over a temperature range of 10 to 50°C. Initial evaporative styrene emissions increase with increasing temperature. There is a nearly linear relationship in the total mass of styrene emitted and emission factor as emissions increase with increasing temperature. Styrene emission factors appear to vary for different materials, which could indicate more complex processes or the influence of material physical properties on emission rates. These results can be used to validate and improve mass transfer emissions models for the prediction of volatile organic compound concentrations in indoor environments.

Keywords: vinyl ester resin, volatile emissions, environmental test chamber, styrene, VOC, indoor air

Introduction

The emission of volatile organic compounds (VOCs) from building materials, especially composite materials that contain binders or adhesives, has been well documented and researched over the past few decades. Thermoset composite materials typically consist of chopped, wound or woven fibers infused with a liquid resin which hardens to form a rigid material capable of withstanding high stresses and temperatures without failure. Novel composites are lighter and stronger than most metals of similar dimensions (e.g. thickness), and are being developed for military, transportation and civilian uses.

Vinyl ester resins are formed by reacting an epoxy resin with methacrylic acid. Styrene, a volatile organic compound (Table 1), is used in large quantities in the processing of vinyl ester resin thermoset composite material (VERTCM). Vinyl ester resin generally contains 30 to 60 percent styrene by weight. Styrene in vinyl ester resin serves as a diluent to reduce the viscosity of the resin and enabling processing by methods such as vacuum assisted resin infusion, and enhances linear chain extension in the resin allowing for liquid mold processing and room temperature curing.

Styrene in vinyl ester resin also acts as a “bridge” during the crosslinking process. Crosslinking occurs when an initiator opens up double carbon bonds on both the vinyl ester and styrene molecules, allowing these free radicals to link and crosslink, resulting in a cured material with high strength and resistance to degradation. Complete cure is unrealistic, however, and some "free" styrene remains in the polymer and has the potential to diffuse out of pore spaces within the material.

Table 1. Properties of styrene (CAS# 100-42-5) syn. vinylbenzene

Structural Formula	$C_6H_5CH=CH_2$
Molecular Weight (g/mol)	104.2
Boiling Point (°C, 1 atm)	145.0
Vapor Pressure (mmHg, 23°C)	5.0
Specific Gravity (g/ml, 20°C)	0.906

As vinyl ester resin is subjected to increased post-manufacture temperatures, hydrogen bonding is overcome and styrene diffuses through and is emitted from the material more rapidly with increase in temperature. Some researchers have shown that as much as 50% by weight of the styrene remains un-reacted in VERTCM and could result in unhealthy levels of styrene emitted into indoor environments (Ziaee and Palmese, 1999). Because styrene is categorized as a central nervous system toxicant and hepatotoxin (ATSDR, 1992), ototoxin (Johnson *et al*., 2006), and possible human carcinogen (IARC, 2002), there is a need to study the emission characteristics of styrene and determine the potential indoor air concentrations of styrene emitted from composite materials that are increasingly finding their way into contact with human populations.

Emission testing of indoor building materials using small environmental test chamber (ETC) methodology is well documented since the 1980s (Matthews 1987, Colombo *et al.* 1990, Guo *et al.* 2004) There are standards and guidelines available for referencing ETC construction and analysis. The American Society for Testing and

Materials (ASTM) issued a standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products in 1997 (D 5116-97) and a revision in 2006 (D 5116-06). The Greenguard Environmental Institute issued its own guidelines for small chamber testing, a portion of which are relied upon in the completion of this project (GEI, 2006).

Styrene emissions from building materials have been associated with carpet backing, carpet adhesive and styrene-containing resin. Hodgson *et al.* (1993) measured volatile emissions at room temperature from two new carpet samples using a large-scale environmental test chamber and determined emission factors for styrene over 168 hours of 0.002 and 0.016 mg m^{-2} hr^{-1}. Wallace *et al.* (1987) reported styrene emissions from carpet adhesive of 0.006 mg m^{-2} hr^{-1}. La Scala *et al.* (2006) measured evaporation rate and calculated the diffusion coefficient (D) of styrene from resins of varying styrene concentration over a temperature range. Evaporation rate and diffusion coefficient both increased with increased temperature and styrene concentration in the resin.

Change in temperature has been cited as one of the most important factors influencing the diffusion and partitioning of VOCs from dry building materials (Zhang *et al.*, 2007 and Deng *et al.*, 2009). To date, there is no known research in the scientific literature examining the effect of temperature on styrene emissions from finished vinyl ester resin thermoset composite material or other dry building material. The objectives of this research were to characterize, over a temperature range, styrene emissions from a vinyl ester resin thermoset composite material (VERTCM) using environmental test chamber methodology, and to quantify emission factors for points along the temperature range.

Materials and Methods

VERTCM Manufacture

Vinyl ester resin thermoset composite material (VERTCM) panels were prepared at the UAB School of Engineering's Department of Materials Science and Engineering laboratory. Squares of E-90 course weave glass fiber (E-glass) measuring approximately 120 cm x 120 cm were cut to size and set aside for lay-up. Fiber panel lay-up consisted of cleaning the glass work area with acetone and applying three coats of a releasing interface (Freekote 700-NC, Henkel Corp.) with a lint-free cloth. The resin used consisted of Derakane® 510A-40 (Ashland Chemical) containing 38% styrene by weight mixed with promoter (Trigonox 239, AkzoNobel Polymer Chemicals), accelerator (Cobalt Nap-all, Ashland Chemical) and inhibitor (Acetylacetone +99%, Sigma-A) in ratios to every gram of resin of 0.015, 0.002 and 0.001, respectively.

To form the panels, one layer of E-glass was placed onto the work area on top of a Teflon™ panel and the resin mixture applied by hand pouring and spreading with a plastic trowel until the fiber was completely covered and saturated. This process was repeated until eight layers of fiber formed the panel, with the resin amount equal to approximately twice the fabric weight. Each fiber layer weighed approximately 350 grams. After layup, the panels were topped with Teflon™ and breather cloth and sealed under vacuum to allow for overnight curing at room temperature.

The following day, the cured panels were removed from the work area and cut on a wet saw to form test panels suitable for upright placement in the environmental chamber (Figure 1). The final cured panel thickness measured approximately 0.60 (±0.01) cm and panel width ranged from 19.2 to 26.0 (±0.01) cm. After cutting, all four edges of the test panels were sealed with a non-VOC emitting metallic tape. Individual panels were immediately wrapped in two layers of heavy-duty aluminum foil, double-bagged in sealed 4 mm polyethylene sheeting, marked with identification numbers, and stored at -80°C.

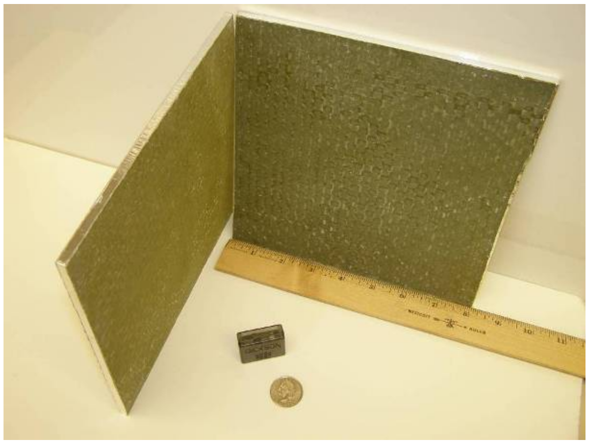


Figure 1. E-Glass VERTCM panels used for chamber emission data

Environmental Test Chamber (ETC) Performance

The ETC used in this research consisted of a LH-6 Laboratory Humidity Chamber (Associated Environmental Systems, Inc., Ayer, MA) modified to meet the definition of an environmental test chamber for use in emission studies (Figure 2). The chamber has an internal volume of 175.5 liters (0.176 m^3) and is temperature (0 – 90°C ± 1°C) and humidity (10 – 98%RH, ± 5%) controlled. The interior consists of stainless steel walls with a retrofitted door of anodized aluminum. Ports for inlet air (split inlet) are located on one side of the chamber, and air sampling ports are located on the top of the chamber. Chamber air is mixed with two internal fans and a diffuser, as well as the split inlet air supply. In order to meet the requirements of an airtight and well-mixed chamber, performance verification tests were conducted to ensure that the chamber to be used met these definitions.

The airtightness of the chamber was evaluated by closing the chamber, plugging all port openings and pressurizing the chamber with supply air. Using an inclined manometer attached to the chamber, a pressure loss of 0.5 inches of water over 525 seconds was recorded. By the Ideal Gas Law at constant temperature ($P_1V_1 = P_2V_2$), the rate of volumetric air loss inside the chamber was calculated to be 4.04 L hr^{-1}. The Greenguard Environmental Institute (2006) standard stipulates that the chamber should have an air leakage rate of less than 0.03 air changes per hour (ACH). For a 175.5 liter chamber, the leakage rate should be less than 5.26 L hr^{-1}. The calculated leakage rate of 4.04 L hr^{-1} confirms that the chamber meets the definition of being air tight.

Figure 2. Environmental test chamber

An air mixing test was performed by injecting inert sulfur hexafluoride (SF_6) gas into the inlet air of the chamber. When an equilibrium concentration was reached, the SF_6 supply was stopped, and the decay rate of gas in the chamber was monitored and logged for a period of one hour with a MIRAN Sapphire infrared spectrometer. The comparison between the theoretical model for a well-mixed chamber and the chamber data indicated that the chamber achieved 92.4% mixing, well above the minimum 80% suggested for a well-mixed chamber (ASTM, 2006).

VERTCM Panel Testing

Previous research has shown styrene and other VOC emissions to be temperature dependent (La Scala *et al.*, 2006; Zhang *et al.*, 2007). Therefore, panel emission tests were conducted at 10°C, 23°C, 30°C, 40°C and 50°C (±1°C) with an air exchange rate of 1 (±5%) air change per hour (ACH). Because high relative humidity levels at high temperature (≥40°C) were observed to be affecting the absorptive capacity of the charcoal sampling tubes, test chamber relative humidity values for the 40°C and 50°C tests were reduced to 15% RH and 10% RH, respectively. All other chamber tests were conducted at 50% RH. While humidity may have a slight influence on the evaporative phase of the volatile emission process, humidity has been shown to have a negligible influence on the diffusive emission rate process (Wirten, 2006). Ultimately, all tests were conducted within a humidity ratio range of 0.004 (10°C) to 0.014 (30°C) grams of water per grams of dry air (10-50% relative humidity).

The chamber was allowed to condition to the test parameters overnight. Panels were allowed to reach room temperature before being unsealed and placed into the chamber. Before placing a test panel into the chamber, a 12 liter background sample of chamber air was collected for analysis of VOCs. After collection of the clearance sample, four VERTCM panels were suspended upright in the chamber, along with a temperature and humidity data logger (Dickson TK120, Addison, IL). The air velocity over the face of the panels was measured with a hot-wire anemometer (TSI 8386, Shoreview, MN). The total average velocity of five measurements over each panel face ranged from 0.40 m s^{-1} to 0.65 m s^{-1}. Table 2 contains the various panel properties for each sample run, including test temperatures, humidity, exposed panel surface areas and the loading factor (exposed material surface area per volume of chamber air, or m^2 m^{-3}).

Table 2. Chamber test conditions, panel surface area and loading factor

Temperature (±1°C)	Relative Humidity (±5%)	Surface Area (m^2)	Loading Factor (m^{-1})
10	50	0.32	1.82
23	50	0.41	2.33
30	50	0.33	1.88
40	15	0.33	1.88
50	10	0.32	1.82

The experiment start time began immediately upon closing the chamber door. Interior chamber air was sampled at 1, 2, 4, 6, and 12 hours the first day, as well as on days 2, 3, 4, 5, 8, 9, 10, 11 and 12, for a total of 14 sample points over 264 hours. Three simultaneous samples of chamber air were collected on SKC 226-01 (Lot 2000) charcoal sorbent tubes using SKC AirChek XR5000 personal sampling pumps precalibrated to 1.0 ± 0.05 liter per minute for a minimum 12 liter air sample. The pumps were postcalibrated to average sampling flow rate. Chamber inlet flow, temperature and humidity were monitored and recorded for the duration of each test. The air flow and sampling train are illustrated in Figure 3.

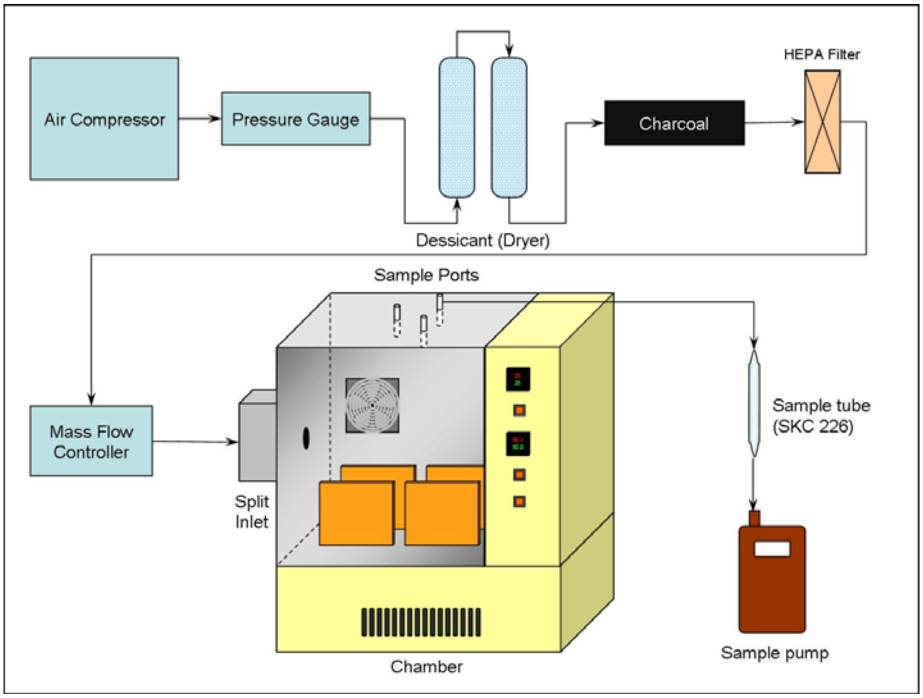


Figure 3. Air flow and sampling diagram for small test chamber experiment

Chamber air analysis for styrene was conducted using gas chromatography with flame ionization detection (Agilent 6850, Atlanta, GA). Desorbed samples were analyzed by 1.0 µl syringe injections onto a splitless inlet at 250°C. The capillary column (Agilent 19091Z-413E) of 0.25 µm internal diameter was heated to 70°C for 0.5 minutes and ramped at 60°C per minute for 2.5 minutes to a maximum temperature of 250°C. Styrene elution time was approximately 1.90 minutes. Chromatograph peaks were quantified with a flame ionization detector at 250°C against a 6-point calibration curve with a minimum correlation of $R^2 = 0.997$ and a limit of quantification (LOQ) of 0.1 µg. No significant peaks other than the desorbent carbon disulfide (CS_2), an internal standard of 4-Chlorobenzotrifluoride (4-CBTF) and styrene, were observed over a total method run time of approximately 5 minutes. Reported styrene concentrations are adjusted and presented here based on a laboratory desorption efficiency (DE) study conducted over the temperature range.

Determination of Emission Factor

Emission factor (EF) is the amount of styrene emitted from the exposed surface area of a material over time (mg m^{-2} h^{-1}) and was derived from the chamber concentration data using the following equation,

$$EF(t_i) = \frac{\left(\frac{\Delta C_i}{\Delta t_i} + NC_i \right)}{L} \qquad (1)$$

where EF(t_i) is the emission factor over the time interval t_{i+1}-t_i (mg m^{-2} h^{-1}), $\Delta C_i/\Delta t_i$ is the slope of the time-concentration curve over the time interval t_{i+1}-t_i, N is the air change rate (h^{-1}), C_i is chamber concentration at time t_i (mg m^{-3}), and L is the loading factor (m^2 m^{-3}). The emission factor is not a constant and varies over the emission profile. Emission factor is higher during the early stages of the test (1 - 48 hrs) and represents an evaporative emission process occurring at the surface of the air-material interface.

Determination of the emission factor during the latter stages of the emission profile, where the slope of the profile becomes quasi-linear, allows for the calculation of potential indoor air concentrations given a known material exposed surface area and room air exchange rate at a specific point in time. For these materials, emissions after 48 hours were chosen as representative of diffusion-driven emissions where styrene migrates through and out of the material, which is the primary process relevant to longer term indoor air quality concerns (Deng *et al.*, 2009).

Results and Discussion

The styrene concentrations and profiles reported here represent an average of three simultaneous samples for any given sampling period during the panel tests. An example of the 23°C averaged styrene emission profile is given as Figure 4. An example of the 23°C averaged styrene emission profile from 48 hours to 264 hours, representative of the diffusive emission profile used to generate emission factor in this study, is given as an insert in Figure 4. The results for total mass of styrene emitted and emission factor derived from the profiles are provided in Table 3. Total mass of styrene emitted from the panels was derived by integrating the mass emitted as a function of time (mg m^{-3} min) and multiplying by the flow rate of air into the chamber (m^3 min^{-1}). The total styrene mass emitted and emission factors for the five test temperatures are illustrated as Figure 5. Figure 6 depicts the styrene emission profiles for each test temperature between 48 and 264 hours of the experiment.

Table 3. Styrene emission parameters at varied test temperatures

Temperature (°C)	Total Styrene (mg)	Emission Factor (10^{-3} mg m^{-2} hr^{-1})
10	2.11	9.10 (± 0.1)
23	5.98	15.1 (± 0.7)
30	9.77	17.3 (± 0.5)
40	13.73	21.7 (± 0.2)
50	17.87	25.2 (± 0.1)

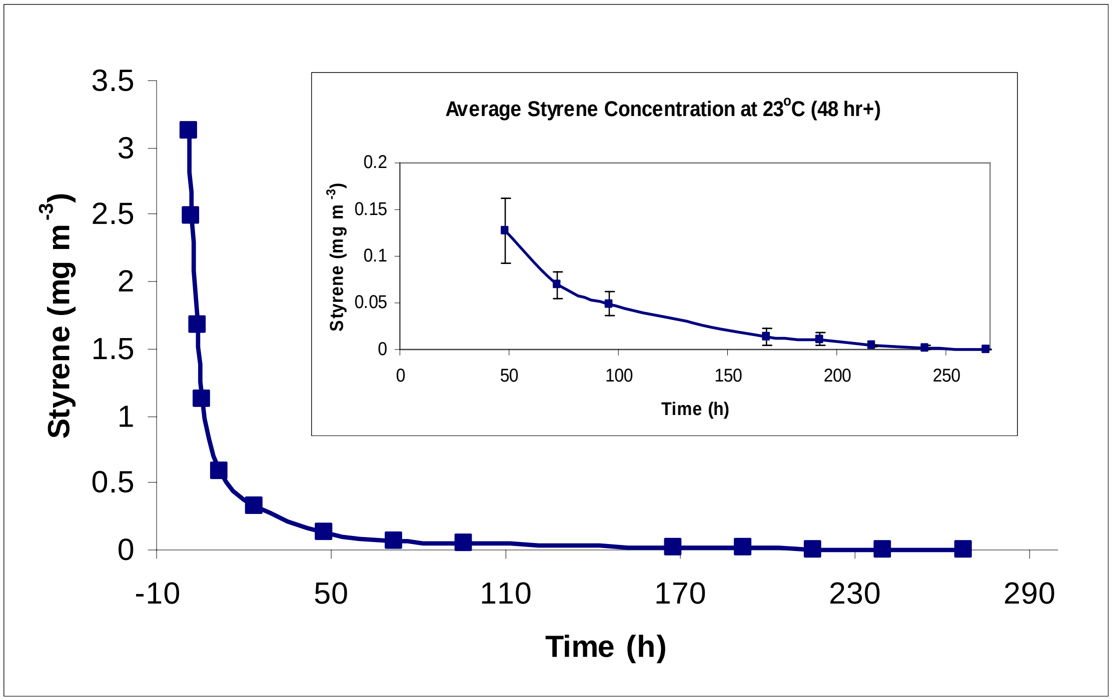


Figure 4. Styrene emission profile at 23°C

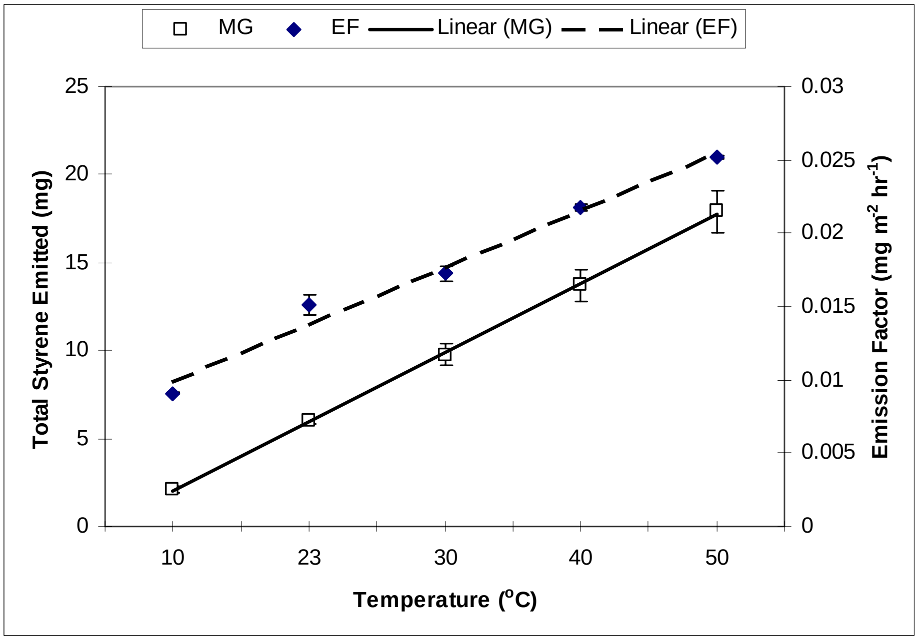


Figure 5.Mass of styrene emitted (MG) and emission factor (EF) over temperature range

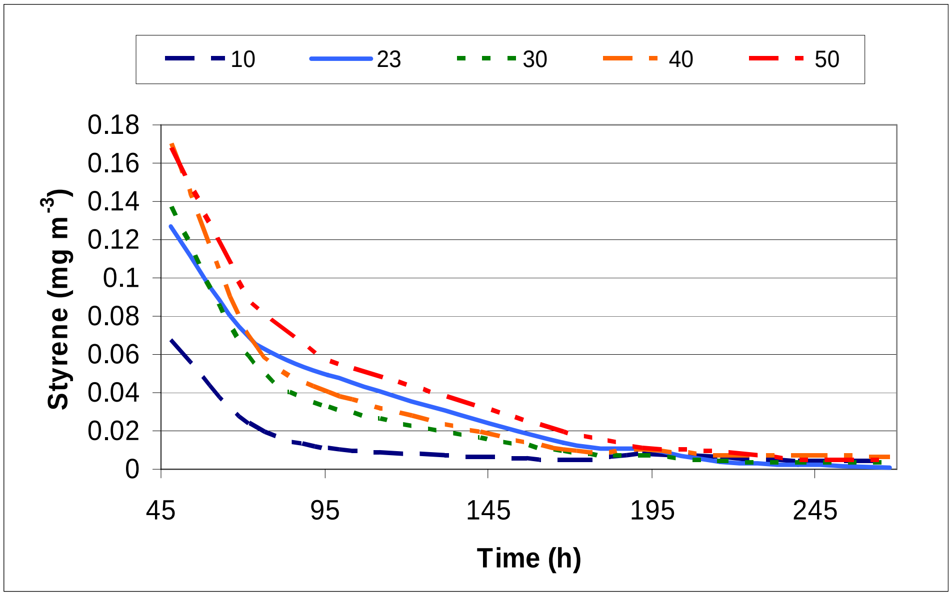


Figure 6. Styrene Emission Profiles Over Temperature Range (48 – 264 hrs)

The maximum initial concentration of styrene measured in the chamber air increased with increased temperature (Table 4). In the first 48 hours, the styrene concentration profile is predominantly representative of an evaporative emission process, while after 48 hours the emissions are expected to become more diffusion driven. The total mass of styrene emitted and emission factor both increased with increasing temperature. The emission factor increases nearly linearly between 10°C and 50°C (R^2 = 0.997), while the total mass of styrene emitted appears to increase linearly (R^2 = 0.993) over the temperature range as well (Table 3 and Figure 5).

At 48 hours after test initiation, the average styrene concentrations for all three test temperatures were less than 0.20 mg m^{-3} (Table 4). Chamber air styrene concentrations converged for all test temperatures at approximately 192 hours (Figure 6). While large amounts of VERTCM at elevated temperature may contribute to odor complaints in indoor environments in the initial emission stage, styrene concentrations in the chamber air at ≥ 48 hours are below the Agency for Toxic Substances and Disease Registry's (ATSDR) Minimal Risk Level (MRL) of 0.25 mg m^{-3} for continuous nonoccupational inhalation exposures to styrene below which no appreciable increased risk is expected (ATSDR, 1992).

Table 4. Chamber styrene concentration data

Temperature (°C)	Chamber Concentration at 1 hour (mg m^{-3})	Chamber Concentration at 48 hours (mg m^{-3})	48 Hr. Parts Per Million (ppm)
10	0.74 ± 0.1	0.068 ± 0.007	0.015
23	3.13 ± 0.6	0.127 ± 0.014	0.029
30	8.85 ± 0.7	0.137 ± 0.023	0.033
40	14.4 ± 0.7	0.166 ± 0.020	0.041
50	22.4 ± 1.4	0.168 ± 0.032	0.043

Preliminary analysis of the VERTCM emission properties using high surface area loading (2.67 m^2 m^{-3}) at the highest emission factor (0.025 mg m^{-2} hr^{-1}) and a conservative air exchange rate (1 ACH) indicates that indoor air concentrations of styrene emitted from VERTCM would not likely exceed ATSDR chronic exposure guidelines (0.25 mg m^{-3}). This suggests that, with limited material loading (exposed surface area) and sufficient air exchange rate, after the initial evaporative emissions of styrene have ceased, it is possible that inhalation exposures to styrene emitted from like VERTCM composites in enclosed spaces can be controlled to below the most conservative current regulatory guidelines for chronic inhalation exposure to styrene.

As observed in Table 5, the styrene emission factor (EF) between the Hodgson *et al*. (1993) data for Carpet 4 and this study correlate well, despite large differences in environmental test chamber (ETC) volume, average air velocity over the surface of the material, and loading factor of material into the chamber (all of which should be independent of the diffusive emission properties of VOCs from a dry building material). There is some difference in the total mass of styrene emitted (MG) between Carpet 4 and VERTCM, and significant differences in EF and MG between Carpet 1 (1a and 1b are duplicate samples) compared to Carpet 4 and VERTCM. There may be physical parameters present which could explain these differences.

Table 5. Comparison of Hodgson (Carpet) and VERTCM experimental and styrene emission parameters (23°C, 50% RH, 1 ACH)

Sample Type	ETC volume (m^3)	Air Velocity ($cm\ s^{-1}$)	Loading Factor ($m^2\ m^{-3}$)	MG (mg)	EF ($10^{-3}\ mg\ m^{-2}\ hr^{-1}$)
Carpet 1a	20.0	5 - 10	0.44	2.20	2.0 ± 0.2
Carpet 1b	20.0	5 - 10	0.44	3.41	3.5 ± 0.2
Carpet 4	20.0	5 - 10	0.44	25.9	16.1 ± 0.6
VERTCM	0.176	40 - 65	2.33	14.6	15.1 ± 0.7

According to Hodgson *et al*. (1993), the source of styrene from Carpets 1 and 4 was the styrene-butadiene rubber (SBR) latex adhesive on the carpet backing (Van Ert *et al.*, 1987). No explanation for the differences in mass of styrene emitted and styrene emission factor was given between Carpets 1 and 4 in the 20 m^3 chamber experiments. It could be that other carpet properties affected styrene emissions between Carpets 1 and 4 (construction, fiber type, fiber treatment, etc.). Large differences were observed in the emission factors and profiles for styrene in this study and preliminary studies of VERTCM with Kevlar™ fibers as described below. While these differences could be explained by differences in experimental and analytical procedures, material physical properties may be influencing the diffusion and emission process of volatiles from dry building materials.

In a preliminary study conducted by the investigator, emission profiles from panels of VERTCM containing woven Kevlar™ fibers were constructed using small environmental test chamber (ETC) methodology. Panels of uncoated, room-temperature cured VERTCM manufactured at the UAB School of Engineering, Department of Materials Science and Engineering measuring approximately 24 x 15 x 0.3 cm were placed upright in a small ETC and monitored for approximately five days to determine total mass of styrene emitted and emission factor at 23°C and 35°C. The total styrene amount emitted was 6.37 mg at 23°C and 7.39 mg at 35°C. The highest styrene concentration measured in the chamber was 1.4 mg m^{-3} at the lowest temperature and 1.6 mg m^{-3} at the highest temperature. The average emission factor was determined to be 0.66 mg m^{-2} hr^{-1} at 23°C and 0.91 mg m^{-2} hr^{-1} at 35°C.

In the preliminary study of Kevlar™ VERTCM, the emission factor for styrene was determined to be much greater than that described in this study. Analysis of the porosity and density of the Kevlar™ VERTCM and E-glass VERTCM showed the Kevlar™ VERTCM to be less dense and more porous than the E-glass VERTCM (Table 6). Unfortunately, little was known about the original material properties (initial styrene content of the resin, etc.) of the Kevlar™ VERTCM panels other than that they were manufactured three years prior to emission testing.

Table 6. Emission factor, density and porosity (obtained at a pressure of 0.54 psi Hg) characteristics of two different types of vinyl ester resin

Material	Emission Factor (10^{-3} mg m^{-2} hr^{-1})	Density (g cm^{-3})	Total Pore Area (m^{2} g^{-1})	Average Pore Diameter (µm)
E-Glass VERTCM	15.1	1.93	10.4	0.01
Kevlar™ VERTCM	660	1.37	18.3	0.04

There may be other limitations which explain the differences in emission factors for VERTCM between the Kevlar™ and E-glass experiments. Two different chambers were used (although chamber size and configuration should have no influence on the calculated results) and a third-party laboratory was used to analyze the charcoal tube samples in the Kevlar™ experiment (although the laboratory used was an American Industrial Hygiene Association IHLAP certified laboratory). As well, the tested Kevlar™ panels did not have sealed edges in the chamber, which may have facilitated diffusion and emission of styrene along the orientation of the fiber strands.

A recent study by Zhang *et al.* (2007) demonstrated that density and porosity may be important material factors in volatile emissions processes. In that study, a dry board that was more dense and had a larger percentage of micropores and mesopores (as opposed to larger macropores) had a higher formaldehyde partition coefficient (K) than a dry board with similar initial formaldehyde concentration and a larger percentage of macropores. Pore size has an effect on the bonding potential of a volatile to a substrate. If material density and porosity have a significant effect on the diffusion and emission of volatiles from dry building materials, then these two physical parameters, and possibly other unidentified physical parameters, may have to be considered in the application of emission models currently proposed for predicting volatile emissions from dry building materials.

One limitation of the analyses performed here is that the materials tested were research quality materials and not products made for consumer consumption, even though these materials are of similar composition and production to many of those found in the marketplace. La Scala *et al.* (2006) state that most commercial resins used at the time of their study had styrene contents in the 50% range, so these results may underestimate typical styrene emission concentrations for some materials, although the industry trend over the past few years has been to decrease the styrene content of the vinyl ester resins. Initial styrene concentration in the resin and cured panel (Co) is an important input variable into the mass transfer models used to predict indoor air VOC concentrations and influences the emitted mass and emission factor (EF) in chamber studies (increased Co typically increases EF); however, the models assume that all volatile compounds in the material are eventually emitted. In this study, only a fraction of the initial concentration of styrene in the panel was emitted, even at the highest test temperatures. This was also shown by Xiong and Zhang (2010).

Because of the potential differences in styrene content, material density and porosity, and changes in emission factor and emission rate over a temperature range, until further analysis verifies continuity among materials and validates existing physical-based mass transfer models, it would be prudent to test individual finished materials intended for consumer applications using environmental test chamber methodology for the prediction of volatile concentrations in indoor air, especially when characterizing potential human exposures.

Conclusions

Total mass of styrene emitted and styrene emission factor increased with increasing temperature in the chamber. The emission factor (EF) for styrene emitted from VERTCM at 23°C correlated well with one EF derived for styrene from a carpet backing adhesive sample in a previous study, but did not correlate well with the EF derived for another carpet backing adhesive sample, or with an EF for styrene from a carpet adhesive in another study. Given these chamber data for styrene emission from a thermoset composite resin, the mass transfer models and other physical-based emission models constructed at 23°C can be validated against the data derived here. Also, these models can be modified and improved to scale over a temperature range such that volatile emissions from dry building materials can be better anticipated, modeled and controlled.

Additional potential confounders such as density and porosity of the material, which may account for differences in emission factor of styrene reported in the literature, need to be considered. Ultimately, a functional model that can be scaled not only to the amount of exposed material, room size and air exchange rate, but also for other material properties and conditions over a temperature range, will be useful for controlling indoor air quality complaints and perhaps protecting humans from unhealthy levels of volatile organic compounds in indoor environments.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 1992. Toxicological Profile for Styrene. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

American Society for Testing and Materials. 1997. ASTM Designation: D 5116-97. 2006. ASTM Designation: D 5116-06. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.

Colombo A., De Bartoli M., Pecchio E., Schauenburg H., Schlitt H., Vissers H. 1990. Chamber testing of organic emission from building and furnishing materials. The Science of the Total Environment, 91:237-249.

Deng Q., Yang X., Zhang J. 2009. Study on a new correlation between diffusion coefficient and temperature in porous building materials. Atmospheric Environment, 43(12):2080-2083.

Greenguard Environmental Institute (GEI). 2006. Laboratory Qualifications and Proficiency Requirements. Greenguard Product Certification Program. GG Publications, Inc.

Guo H., Murray F., Lee S.C., Wilkinson S. 2004. Evaluation of emissions of total volatile organic compounds from carpets in an environmental chamber. Building and Environment, 39:179-187.

Hodgson, A.T. Wooley, J.D. Daisey, J.M. 1993. Emissions of volatile organic compounds from new carpets measured in a large-scale environmental test chamber. Journal of Air and Waste Management, 43:316-324.

International Agency for Research on Cancer (IARC). 2002. IARC Monographs Volumes 1-88. Styrene [100-42-5]; 60(82).

Johnson A.C., Morata T.C., Lindblad A.C., Nylen, et al. 2006. Audiological findings in workers exposed to styrene alone or in concert with noise. Noise Health, 8(30):45-57.

La Scala U.C., Orlicki J., Jain R., et al. 2006. Emission modeling of styrene from vinyl ester resins. Clean Technology Environmental Policy. DOI 10.1007/s10098-006-0076-1.

Matthews T.G. 1987. Environmental chamber test methodology for characterizing organic vapors from solid emission sources. Atmospheric Environment, 21(2); 321-329.

Van Ert M.D., Clayton J.W., Crabb C.L., Walsh D.W. 1987. Identification and characterization of 4-phenylcyclohexene – an emission product from new carpeting. USEPA-OTS report.

Wallace L., Pellizzari E., Leaderer B., et al. 1987. Emissions of volatile organic compounds from building materials and consumer products. Atmospheric Environment, 21(2):385-393.

Wirten L. 2006. Influence of moisture and substrate on the emission of volatile organic compounds from wall structures. Doctoral Dissertation. Helsinki University of Technology; Espoo, Finland.

Xiong J., Zhang Y. 2010. Impact of Temperature on the initial emittable concentration of formaldehyde in building materials: experimental observation. Indoor Air 20: 523-529.

Zhang Y., Luo X., Wang X., Qian K., Zhao R. 2007. Influence of temperature on formaldehyde emission parameters of dry building materials. Atmospheric Environment, 41:3203-3216.

Ziaee S., Palmese G.R. 1999. Effects of temperature on cure kinetics and mechanical properties of vinyl ester resins. Journal of Polymer Science, 37:725-744.

CHAPTER 3

VALIDATION AND LIMITATIONS OF A MASS TRANSFER VOC EMISSION MODEL FOR A DRY BUILDING MATERIAL

Abstract

Volatile organic compound (VOC) emission from building materials into air has been quantified, characterized and modeled. Internal diffusion of VOC through a material based on Fick's law of diffusion is the basis for mass transfer modeling of diffusive emission used to estimate VOC concentrations in air over time. Current mass transfer models have been shown to appropriately estimate air VOC concentrations at approximately room temperature, while other research has shown that temperature has a profound effect on the diffusion coefficient, D, of VOC in a material. Here, a mass transfer model is operated at 23°C and 40°C using input parameters applicable for each temperature. The model estimates are validated against environmental test chamber data for styrene emission from a vinyl ester resin thermoset composite material. The model correlates well with the 23°C chamber data, but underestimates chamber data by as much as 10^{-4} at 264 hours for the 40°C modeling. This suggests that the model requires adjustment for predicting VOC air concentrations at temperatures other than 23°C.

Keywords: Modeling; VOC; mass transfer; diffusion coefficient; styrene, environmental test chamber

Introduction

Emission of semi-volatile and volatile organic compounds (VOCs) from building materials into indoor air has been well documented (Wallace *et al*. 1987, Clausen *et al*. 1991, Bartekova *et al*. 2005). Consequently, several researchers have attempted to model the rate of emission of VOCs from these materials in order to determine resultant indoor air VOC concentrations, which could be used to estimate the potential for adverse human health effects. Some early models were based on empirical data obtained from emission profiles using environmental test chamber (ETC) methods and measured VOC concentrations in indoor air.

One limitation with empirical models is that they are not easily scaled up using ETC data for modeling VOC concentrations in enclosed spaces. More recent physical models, also known as mass transfer models based on heat transfer mechanics, allow for estimation of volatile-material emissions incorporating variations in room volume, air exchange rate, loading (amount) of building material in the enclosed space, and variations in other material and VOC properties. One of the earliest models was developed by Little *et al*. (1994). Little's model was validated using ETC emission data from samples of new carpet obtained by Hodgson *et al*. (1993). While Little's modeled results correlated well with predicted air VOC concentrations obtained from the ETC data, it neglected the effect of mass transfer resistance (h) at the material-air interface. Xu and Zhang (2003) proposed a revision to Little's mass transfer model to incorporate mass transfer resistance.

While Xu and Zhang's corrections improved Little's model in the evaporative phase, the model used by Little was shown to accurately predict VOC emission from a dry building material where emission is primarily diffusion driven, as VOCs diffuse through and out of the material into air. Diffusive emissions from building materials contribute to prolonged air-VOC concentrations and are more likely to contribute to human inhalation exposures in indoor air over a longer period. Chronic exposures to poor indoor air quality, such as that caused by VOCs emitted from building material, have been linked to a variety of adverse health effects in humans and contribute to air quality phenomenon such as Sick Building Syndrome (Tichenor, 2006).

Despite recent advances in modeling diffusion-driven emission of VOC from building material, there are still limitations to applying the models to a variety of materials and environmental conditions. The existing mass transfer models have been developed from a limited set of quantified emission data, including Little's model based on VOC emission from new carpet samples. Significantly, the models to date have been constructed around emission data obtained at approximately 23°C and approximately 50% relative humidity (RH). While the mass transfer models are scalable for physical parameters (room size, air exchange rate, etc.), they are not equipped to incorporate other influencing parameters such as change in temperature and humidity.

As diffusion of VOC through and out of a building material has been shown to be primarily temperature dependant, it is apparent how incorporating this parameter into the model would be important for predicting resultant indoor air VOC concentrations (Zhang *et al*. 2007). While humidity may have a role in influencing emission parameters, especially in the early evaporative phase of a dry material or on emission from a wet building material (paint, caulk, adhesive, etc.), humidity appears to have a negligible effect on diffusive emission of VOC over the longer term (Wirten, 2006). Therefore, variation in temperature is the more important parameter for estimating diffusive VOC emission from a dry building material.

The characterization and modeling of styrene emission from a cured vinyl ester resin thermoset composite material (VERTCM) has not been reported in the literature and models have neglected the effects of temperature on predicting diffusive emissions. This paper attempts to validate Little's mass transfer model for predicting diffusive emission of styrene, a VOC, from a dry building material (VERTCM), and to address some additional limitations in practical applications of mass transfer models advanced in the literature to date.

Materials and Methods

Theory

VOC emission rates from building materials are dependent on a variety of factors, including manufacturing composition and process, product installation and use, environmental conditions such as temperature, humidity and airflow, and other factors, including time. It is well know that emission quantities and rates can change with time. Emissions are usually greater in the early stages with "wet" building materials (e.g. paint, caulk, adhesive, etc.) or with "dry" building materials (e.g. oriented strand board, vinyl floor tile, etc.) when evaporative emissions occur shortly after manufacture or installation. Evaporative emissions are surface driven and are typically large because of the rapid flux of VOC concentrated at the material-air interface into the surrounding airspace.

Initially the flux of VOC from the material is high, particularly because evaporative emission drives an abundance of VOC from on or near the material surface. Over time, the emissions become more linear and stable, as VOC diffuses through void space over a specified thickness of material at a near steady state. Like heat, the VOC migrates from an area of higher concentration (material) to an area of lower concentration (room air) in an attempt to reach equilibrium. This phenomenon is based on Fick's law for diffusion (Eq.1), and involves conductive heat transfer theory described using mass transfer terms, thus the nomenclature used of a physical or mass transfer model (Rohsenow and Hartnett, 1973),

$$\frac{W}{A} = -D\left(\frac{\partial C}{\partial y}\right) \qquad (1)$$

where W is mass of vapor transported (mg), A is exposed surface area (m^2), D is the coefficient of diffusion ($m^2\ s^{-1}$) and dC/dy represents the concentration gradient.

While evaporative emissions are typically greater than diffusive emissions in the early stages, of particular concern to human health are emissions driven from dry building materials by internal diffusion and which occur over the longer term (days, weeks, months), contributing to poor indoor air quality. Several researchers identified internal diffusion of a VOC though the material as the driving force for material-air emission (Clausen *et al*. 1993, Meininghaus *et al*. 2000). Consequently, it is important to identify and quantify those physical and environmental parameters that affect internal diffusion forces. It is widely accepted that temperature and concentration of VOC are the most important parameters affecting diffusive emission.

Both chamber studies and mathematical modeling have been utilized to characterize VOC emissions from building materials. Chamber studies have the advantage of accurately quantifying VOC emission factors and emission rates, as well as total mass of VOC emitted. While chamber studies are useful in verifying modeled data *post hoc*, they are time consuming and come with other practical limitations. Modeling offers an inexpensive and presumably straightforward alternative to chamber studies for predicting indoor air contaminant levels for a range of conditions and over a specified time, and has been steadily advanced in the literature. Chamber data can be used to validate model estimates.

Empirical or Statistical Models

Models derived from chamber data are limited in that environmental conditions (temperature, humidity, airflow, etc.) as well as ventilation rate (ACH) and loading factors (the amount of material per volume of chamber space) can affect VOC emission rates and therefore limit models to specific conditions obtained for the chamber data. This semi-empirical nature of models built on chamber data limits their usefulness when applied to actual conditions encountered in a variety of settings. Statistical models summarized by Zhang and Shaw include: Constant Emission Factor model; First-Order Decay model; Double Exponential model; Second Order Decay model; n^{th} Order Decay model (Zhang and Shaw, 1997).

Physical or Mass Transfer Models

Mass transfer models are typically categorized as either interfacial (evaporative) or internal (diffusive). Fick’s law of diffusion is used to describe both the diffusion of heat through a material or mass across a boundary or through a medium. Because of its application to both heat and mass transfer, Fick’s law of diffusion formed the basis for development of a mass transfer model proposed by Little *et al* (1994).

Little transformed a linear, one-dimensional conductive heat transfer model described by Carslaw and Jaeger (1959) into an analgous mass transfer model. By rewriting the temperature terms into mass terms and adjusting the equation for equilibrium partitioning, Little was able to develop a functional model by combining the appropriate boundary conditions into a single equation (Eq.2),

$$\left(\frac{V}{A*Kv}\right)\frac{\partial C}{\partial t}\Big|_{x=L} + D\frac{\partial C}{\partial x}\Big|_{x=L} + \left(\frac{Q}{A*Kv}\right)C\Big|_{x=L} = 0 \tag{2}$$

where the first term represents the accumulation of VOC in the chamber air, the second term represents the mass flux of VOC diffusing out of the exposed material surface, the third term represents the VOC leaving the chamber, and the required model input parameters are:

<u>Material-Volatile Properties</u>

D – Diffusion coefficient of the VOC in the material (m^2 s^{-1})

Kv – Partition coefficient between the material and air (dimensionless)

Co – The initial concentration of the VOC in the material (ug m^{-3})

L – the thickness of the material (m)

A – the exposed surface area of the material (m^2)

Chamber Properties

V – interior volume of environmental test chamber (m^3)

Q – volumetric flow rate of air through the chamber ($m^3\ s^{-1}$)

Model Calculated Values

$$h = Q \big/ [A \times D \times K_v] \tag{3}$$

$$k = V \big/ K_v \times A \tag{4}$$

The concentration of VOC in the material slab as a function of distance from the base of the slab and time $C_{(x,t)}$ can be determined from the solution

$$C_{(x,t)} = 2Co \sum_{n=1}^{\infty} \left\{ \frac{\exp(-Dq_n^2 t)(h - q_n^2)\cos(q_n L)}{\left[L(h - kq_n^2)^2 + q_n^2 (L + k) + h\right]\cos(q_n L)} \right\} \tag{5}$$

Using the parameters described above and where the q_n s are the positive roots of

$$q_n \tan(q_n L) = h - kq_n^2 \tag{6}$$

the various terms in Equation (6) can be substituted into Equation (5) to predict the concentration of VOC in the chamber air (y) at any particular point in time (t) by

$$y_t = \frac{C_{(x,t_i)}}{Kv} \tag{7}$$

A schematic of the physical functions for development and application of the model is presented as Figure 1, where y represents the concentration of VOC in air (mg m^{-3}) at any given time (t).

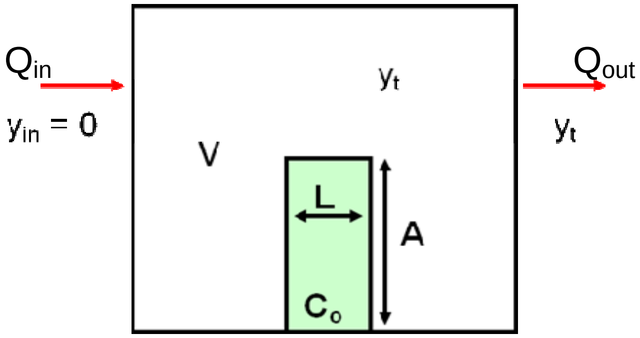


Figure 1. Representation of the model material-physical input parameters.

Several assumptions are made for development and application of the diffusion-based model. First, the concentration of the VOC is assumed to be evenly distributed throughout a homogenous material of finite thickness. Second, diffusion is one-dimensional (axial), neglecting radial diffusion. Third, the internal diffusion coefficient, D, and material-air partition coefficient, Kv, are independent of concentration where equilibrium is assumed to exist between VOC concentration at the material surface interface with the air.

The model forwarded by Little was shown to correlate well with diffusive VOC emissions as determined from ETC data obtained from new carpet samples at 23°C (Little *et al*. 1994). As described above, key model input parameters other than chamber conditions and panel dimensions are the diffusion coefficient (D), partition coefficient (Kv) and initial concentration (Co) of the volatile in the material being tested. These parameters can be measured directly, calculated or estimated from chamber emission data.

Building Material

The building material used to validate the model consists of a glass-reinforced vinyl ester resin thermoset composite material (VERTCM). The VERTCM consisted of eight layers of woven E-90 glass fiber infused with a Derakane® vinyl ester resin containing 38% styrene by weight. Styrene, a toxic and possibly carcinogenic volatile organic compound (VOC) has been measured in indoor air quality studies and could contribute to human inhalation exposures (ATSDR, 1992). Thermoset composite materials containing styrene form a rigid material that can withstand high stresses and temperatures, and are being developed for military, transportation and civilian uses. Important material parameter inputs into the model are summarized here, however details of the components and production of the VERTCM used in this study are described elsewhere (Chapter 2).

Environmental Test Chamber Experiment

The environmental test chamber (ETC) used in this research was a LH-6 Laboratory Humidity Chamber (Associated Environmental Systems, Inc., Ayer, MA) modified to meet the definition of an ETC for use in emission studies (Chapter 2). Panel emission tests for model validation were conducted at 23°C and 40°C (±1°C) with an air exchange rate of 1 (±5%) air changes per hour (ACH). The tests were conducted within an absolute humidity ratio range of 0.005 (40°C) to 0.010 (23°C) grams of water per grams of dry air (15 – 50% relative humidity range). For each test, four VERTCM panels with sealed panel edges were suspended upright in the chamber, with both faces of the panels exposed to the chamber air (Table 1, where loading factor is the exposed material surface area per volume of chamber air, or $m^2\ m^{-3}$).

Table 1. Chamber test material properties

Temperature ($\pm 1^oC$)	**Panel Thickness L (m)**	**Panel Exposed Surface Area A (m^2)**	**Loading Factor (m^{-1})**
23	0.006	0.41	2.33
40	0.006	0.33	1.88

Interior chamber air was sampled in triplicate at 1, 2, 4, 6, and 12 hours the first day, as well as at each subsequent 24 hour period on days 2, 3, 4, 5, 8, 9, 10, 11 and 12, for a total of 14 sample points over 264 hours. Three 12-liter samples of chamber air were collected onto SKC 226-01 (Lot 2000) charcoal sorbent tubes using SKC AirChek XR5000 personal sampling pumps pre-calibrated to 1.0 ± 0.05 liter per minute. Chamber air analysis for styrene was conducted using gas chromatography with flame ionization detection (Agilent Technologies 6850, Atlanta, GA) against a six-point calibration with a minimum correlation of $R^2 = 0.997$.

The average of the data from the three samples was used to determine total mass of styrene emitted and the emission profiles generated at 23°C and 40°C, which were then used in the validation of the model. For these materials, emission ≥ 48 hours was chosen as representative of diffusion-driven emissions where styrene migrates through and out of the material, which is the primary process relevant to longer term indoor air quality concerns (Deng and Kim, 2003).

Determination of Material-Volatile Parameters Co, Ce, Kv and D

Determination of initial concentration (Co). The initial concentration (Co) of a VOC in a building material is not only an important model parameter, but also is required in this study for the determination of the partition coefficient, Kv. The term Co is representative of the total mass of VOC contained in the original amount of material post manufacture but pre-emission. There are a number of ways to obtain this parameter for a variety of materials. Zhang *et al*. (2007) determined Co for formaldehyde in dry building materials using an extraction method. They desorbed formaldehyde from chopped material using heated toluene with a water extraction to measure total formaldehyde. One potential disadvantage of this method is that some VOC could be lost during the material chopping process. Cryogenic milling with fluidized bed desorption has been suggested to mitigate VOC loss (Cox *et al*. 2001).

Little *et al*. (1994) proposed that Co might be determined from chamber emission data, but this procedure would assume that all VOC initially present in the material would be available for emission, which is not always the case. Some VOC might be trapped inside the material, or, as in the case of styrene in thermoset composite material, is bound by strong electron forces. A comparison between emission data obtained for this material and Co data, obtained as described below, demonstrates that relying on emission data to determine Co would have been inappropriate for the estimation of initial styrene content of the material.

For this study, Co was determined by dissolving a known mass of panel in methylene chloride. Four new samples of VERTCM were weighed and placed separately in 4 ml scintillation vials with Teflon™ caps containing 4 ml of laboratory grade methylene chloride. The vials were refrigerated at <0°C and agitated daily on a vortex mixer until the resin appeared to be dissolved and fabric separation could be visually observed. After approximately one week, a sample of the methylene chloride solution was removed from the vials and injected into the gas chromatograph for determination of styrene concentration using flame ionization detection against a four-point calibration curve with a minimum correlation of $R^2 = 0.998$.

After analysis, the contents of each vial were poured onto a glass plate and allowed to evaporate in a laboratory hood. After drying, the panel sample was weighed again and placed back into the scintillation vial containing 4 ml of fresh methylene chloride. The procedure was repeated, and the total concentration of styrene from the double-digestion and analysis was correlated to mass loss of resin in the panel samples to estimate the original concentration (Co) of styrene in the panels. The four concentrations (mg m^{-3}) of styrene were averaged to produce a final estimate of Co in the VERTCM panels used to derive Kv for model validation.

Determination of emittable concentration (Ce). Xiong and Zhang (2010) recently demonstrated that the initial concentration (Co) of VOC in the material and the emittable concentration (Ce) are not always equivalent. The term Ce only approaches Co when the material conditions (i.e. porosity, tortuosity, chemical reaction, physical constraints, etc.) allow for nearly complete diffusion of a VOC through and out of the material. It is much more realistic that some VOC in the material will be trapped and will be unavailable for emission.

This fraction of emittable VOC (Ce) in a building material is an important input parameter into the model, as it supplants Co when only a fracton of the total VOC in the material is available for emission. For this experiment, the fraction of emittable VOC from the material was established as the total mass of styrene emitted from the VERTCM over the 12-day test period at 23°C and 40°C. This mass fraction was adjusted to the volume of the four panels at each test temperature to calculate Ce (mg m^{-3} VERTCM).

Determination of partition coefficient (Kv). Partition coefficient, Kv, was determined experimentally based on the determination of Kv described by Hodgson *et al*. (1993). A sample of new panel of known dimension and mass was placed in a 125 ml Erlenmeyer flask (air volume 143 - 148 ml) and sealed with heavy duty aluminum foil and non-VOC emitting metal tape. Three replicate samples were prepared and conditioned at 23°C and 40°C allowing the flask headspace to reach an equilibrium concentration of styrene (approximately 24 hours based on observation in the laboratory). After equilibration, air samples from inside the flask were collected in a glass syringe and a known volume of sample air was manually injected into the gas chromatograph for determination of styrene concentration using flame ionization detection against a six-point calibration curve with a minimum correlation of $R^2 = 0.997$.

The experiment was replicated for consistency and the air styrene concentrations for the three flasks were averaged to estimate a final equilibrium air concentration of styrene. This equilibrium concentration was then applied to the equilibrium assumption equation (Eq. 7) defined previously using the initial styrene concentration in the material (Co) determined previously, in order to derive Kv for model validation.

Determination of diffusion coefficient (D). There are several ways for determining the diffusion coefficient, D, of a VOC through any thickness of material. Some researchers have developed values for D using regression analysis based on chamber estimations of the partition coefficient values (Little *et al*. 1994). Diffusion coefficient can also be determined experimentally in the laboratory (Bodalal *et al*. 2000, Cox *et al*. 2001). Seo *et al*. (2005) discussed how D could be estimated based on experimentally derived values for the density and porosity of the material and the calculated diffusion of a volatile in air. The latter method was used to derive D for this model validation, incorporating mercury vapor intrusion porosity data (pressure = 0.54 psi) provided by Micromeritics Analytical Services of Norcross, GA, on two samples of similar VERTCM panel. Using Seo's method, pore size distribution data (Figures 2 and 3) were used to determine the porosity (%) of the material in the mesopore range of 2 to 50 nm (IUPAC, 1985).

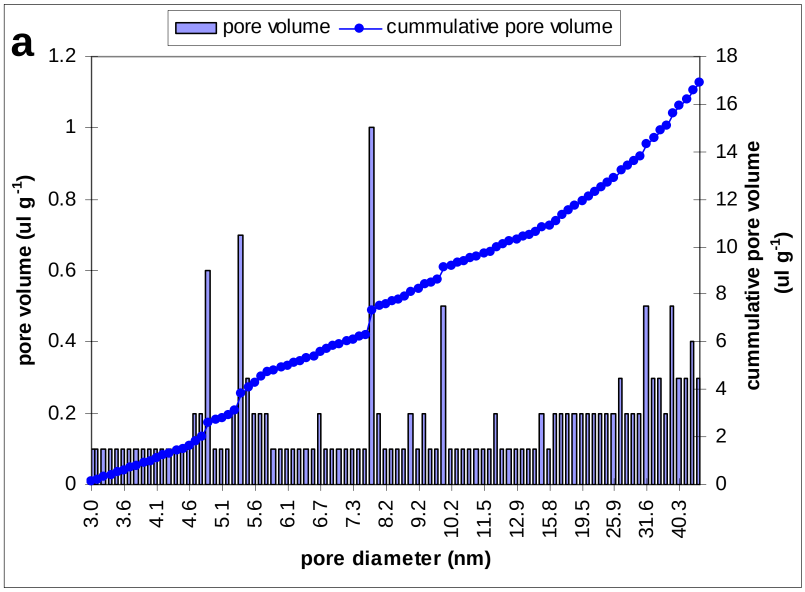


Figure 2. Pore size distributions for VERTCM sample #1 (a).

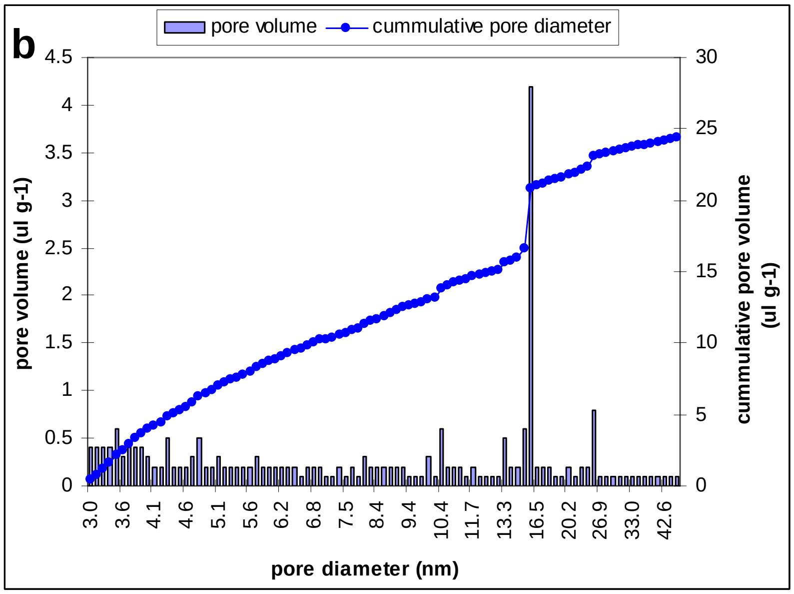


Figure 3. Pore size distributions for VERTCM sample #2 (b).

According to Seo, the effective diffusion coefficient, De, of a volatile compound in a dry building material is a function of,

$$\frac{1}{D_m} = \frac{1}{D_a} + \frac{1}{D_k} \tag{8}$$

where Dm is the molecular diffusion coefficient, Da is the diffusion coefficient of the volatile in air, and Dk is the Knudsen diffusion coefficient ($m^2\ s^{-1}$). The term Da can be calculated using Equation (9) by Lyman *et al*. (1990) and Dk is defined by Equation (10) from Seo *et al*. (2005),

$$D_a = \frac{10^{-3}(T)^{1.75}\sqrt{M_r}}{P\left(V_a{}^{1/3} + V_b{}^{1/3}\right)^2} \tag{9}$$

$$D_k = 0.97r\sqrt{\left(\frac{T}{M}\right)} \tag{10}$$

where T is temperature ($^{\mathbf{o}}$K), Mr is the molecular ratio of the volatile and air, P is atmospheric pressure (1 atm), V is the molecular volume (m^3) of the volatile ($V_{\mathbf{b}}$) and air ($V_{\mathbf{a}}$), r is the average pore size radius (nm) of the material in the mesopore range, and M is the molecular weight of the VOC.

Equation 10 aligns with the assertion by Blondeau *et al*. (2003) and others that D is inversely proportional to the molecular weight of the molecule. Once Da and Dk are determined and Dm solved, the effective diffusion coefficient D can be estimated from porosimetry data of the material by,

$$D = D_m\left(\frac{\varepsilon}{\tau}\right) = D_p\left(\frac{1}{\tau}\right) \tag{11}$$

where ε is the voidage fraction (%) based on the pore size distribution over the mesopore range, and τ is the pore tortuosity factor. The term $D_{\mathbf{p}}$ represents the diffusive porosity of the VOC in the material. The tortuosity factor for this experiment was estimated from the literature based on porosity and density analysis of building materials and using the relation Equation (12) by Blondeau *et al*. (2003),

$$\tau = -0.0112\varepsilon + 2.2271 \tag{12}$$

where ε is the voidage fraction (%) and τ is the unitless pore tortuosity factor.

Results and Discussion

Initial Concentration, Co

An initial concentration of styrene in the panel, Co, used to calculate Kv, was estimated at 3.33 x 10^8 mg styrene per m^{-3} of material, the observed concentration (Table 2). The expected concentration of styrene in the material was calculated based on the styrene concentration in the resin (38%), the approximate mass of the resin used per panel, and the average mass of each panel used in each experiment. The ratio of observed to expected styrene concentration (O/E) was 1.06, or 106%, which was determined as an acceptable approximation of the initial concentration Co.

Table 2. Replicate sample determination of original styrene concentration, Co

Vial #	**Styrene (g)**	**Mass loss (g)**	**Styrene/Mass Loss (mg g^{-1})**	**Styrene/Material (mg m^{-3})**
1	0.00203	0.0537	37.87	70,467,345
2	0.00619	0.0552	112.12	208,628,315
3	0.00611	0.0177	345.14	642,213,912
4	0.00787	0.0357	220.46	410,208,968
			Average	**33,2879,635**

Emittable Concentration, Ce

The fraction of emittable VOC (Ce) from the material was established as the total mass of styrene emitted from the VERTCM over the 12-day test period at 23°C and 40°C, as listed in Table 3.

Table 3. Styrene emission parameters at varied test temperatures

Temperature (^oC)	**Total Styrene (mg)**	**VERTCM ($x10^{-4}$ m^3)**	**Ce (mg m^3)**
23	5.98	9.35	6,396
40	13.73	9.99	13,744

Partition Coefficient, Kv

Partition coefficient was determined by first establishing the average equilibrium concentration in a known volume of air around a known volume of material (Table 4). By replicate analysis, it was observed that equilibrium could be reached at each test temperature by ramping the three vials sequentially from 23°C to 40°C without any negative effect, thus the material volume (m^3) unity between tests in Table 4.

Table 4. Average equilibrium air styrene concentrations and air-material concentrations

Vial #	**23°C**	**40°C**
1	2562	5542
2	3029	5663
3	2514	5657
Avg. Air (mg m^{-3})	**2702**	**5621**
SD (±)	284	67.9
Material (m^3)	6.25×10^{-6}	6.25×10^{-6}
y (mg m^{-3})	**63,019**	**131,924**

Partition coefficient was determined by dividing the original concentration of styrene in the material, 3.33×10^8 mg styrene per m^{-3} of material, by the air-material styrene concentrations in Table 4 using the air-material equilibrium assumption Equation (13) to derive Kv (Table 5).

$$Kv = \frac{C|_{x=L}}{y} \tag{13}$$

Table 5. Equilibrium air concentrations and calculation of Kv at 23°C and 40°C.

Temperature (^oC)	**Equilibrium Air Concentration (y)**	**Kv = Co/y**
23	63,019 (±10%)	5282 (±1241)
40	131,924 (±9%)	2523 (±567)

Diffusion Coefficient, D

Average VERTCM panel density and porosity data are given in Table 6. Calculated parameters for Da, Dk, Dm and De are provided in Table 7.

Table 6. VERTCM panel density and porosity values.

VERTCM panels	**1 (a)**	**2 (b)**	**Avg.**
Density (g ml^{-1})	1.85	1.89	1.87
Porosity (%)	4.5	3.3	3.9
Mesopore Radius (nm)	5.39	5.71	5.55

Table 7. Calculated values for diffusion coefficient (D)

Temp. (^oC)	**23**	**40**
Da (10^{-6} m^2 s^{-1})	7.36	8.11
Dk (10^3 m^2 s^{-1})	8.81	9.06
Dm (10^{-6} m^2 s^{-1})	7.35	8.11
D (10^{-7} m^2 s^{-1})	1.33	1.46

Model Validation

Parameters utilized in the model validation are listed in Table 8.

Table 8. Estimated model input parameters

Temp. (^oC)	**Q (L m^{-1})**	**V (m^3)**	**L (m)**	**A (m^2)**	**Ce (10^6 mg m^{-3})**	**Kv (unitless)**	**De (10^{-7} m^2 s^{-1})**
23	2.92	0.175	0.003	0.41	6.4	5282	1.33
40	2.92	0.175	0.003	0.33	13.7	2523	1.46

These terms were input into the model for validation at 23°C and 40°C with a root period of π/L = 1047 (m^{-1}). The series equation (Eq. 5) converges rapidly at the onset, indicating that diffusion in the VERTCM is rapid. The results of the chamber data versus the modeled data are represented in Figures 4 through 7.

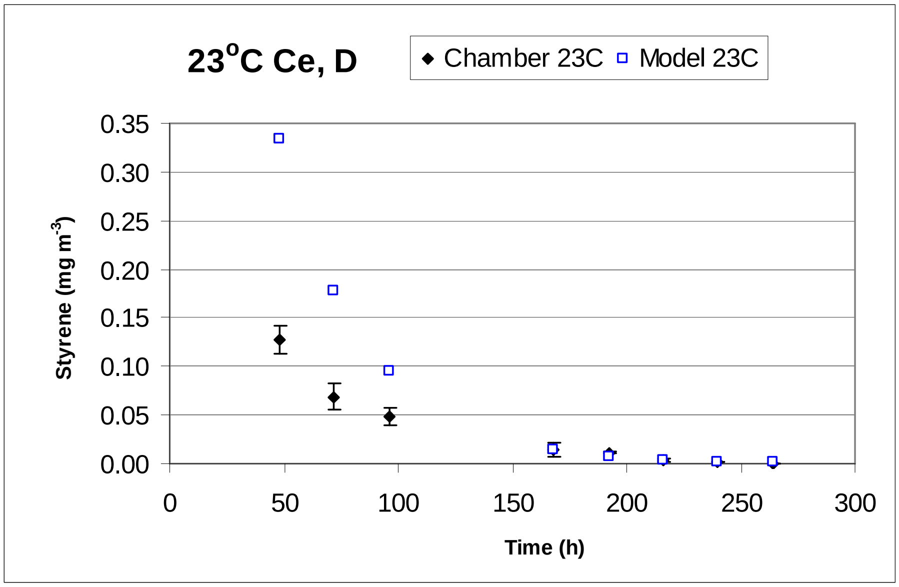


Figure 4. Chamber (with error estimation) and modeled results at 23°C.

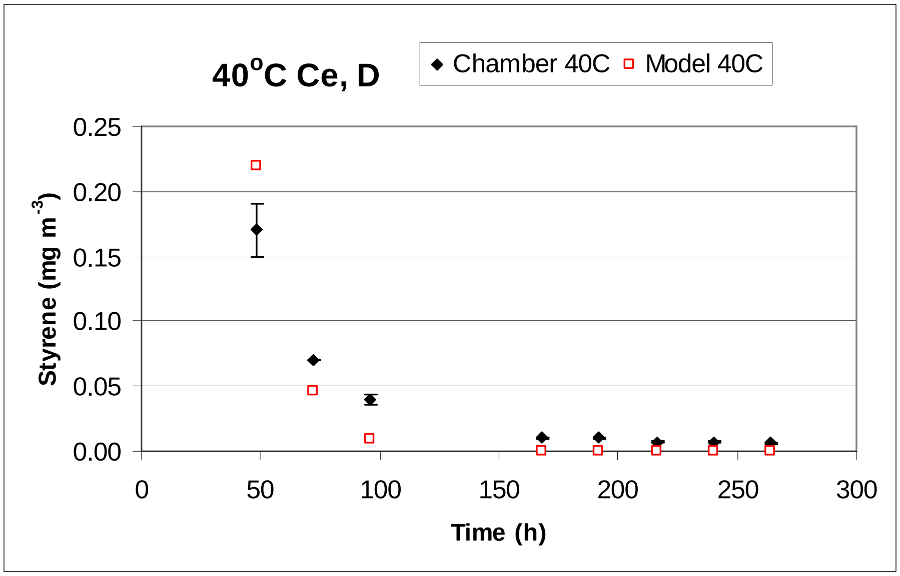


Figure 5. Chamber (with error estimation) and modeled results at 40°C.

Figures 4 and 5 show the model predicted values overestimate air styrene concentrations at 23°C in the first week, and underestimate air styrene concentrations at 40°C at time >48 hours. Data resolution diminishes during the second week. In order to demonstrate how modeled results correlate with chamber results in the second week, log styrene concentrations are provided as Figures 5 and 6.

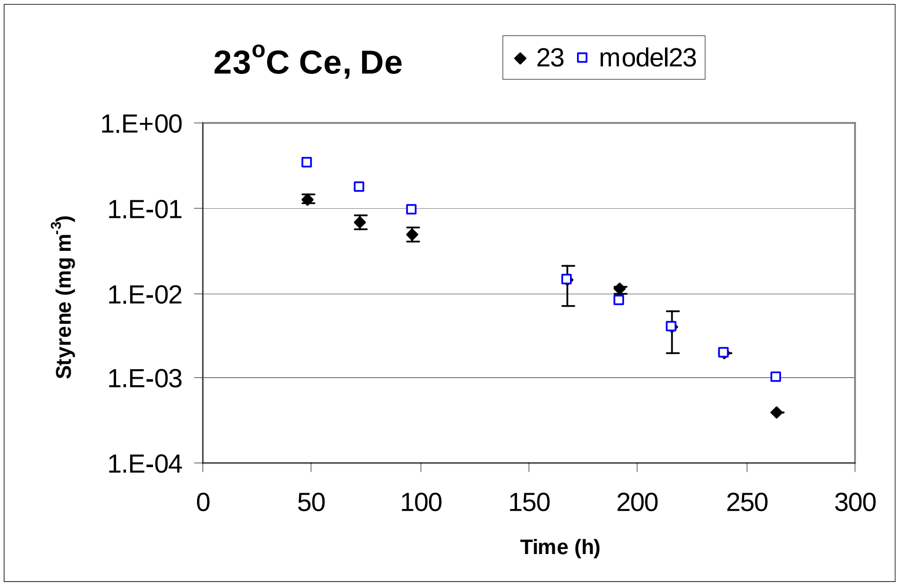


Figure 6. Chamber and modeled results at 23°C (log concentration).

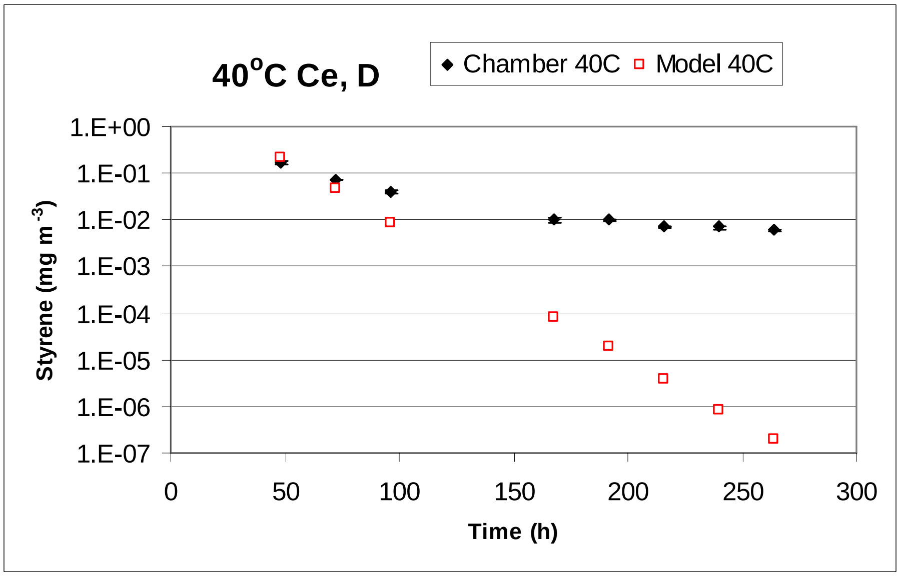


Figure 7. Chamber and modeled results at 40°C (log concentration).

Experimental chamber data for styrene emission from the VERTCM tested here correlate well with the model in the diffusive emission stage (≥48 hr) at 23°C (Table 9). Chamber versus modeled results at 40°C show that the model does not correlate well in the diffusive phase at a temperature greater than 23°C (Figure 7).

At 40°C, the log transform of the styrene concentration scale shows the modeled concentration data underpredicts the chamber data by a factor of more than 10^{-4} at the conclusion of the experiment (Figure 7), indicating a need for adjustment to the model for temperatures ≠23°C . Table 9 lists the Model:Chamber ratio and demonstrates how the model deviates rapidly from the chamber results as time progresses.

Table 9. Fit of modeled to chamber data over a temperature range.

Hr	**Chamber 23°C**	**Model 23°C**	**Model/Chamber Ratio**
48	0.127	0.334	2.63
72	0.069	0.178	2.58
96	0.049	0.095	1.94
168	0.014	0.014	1.00
192	0.011	0.008	0.73
216	0.004	0.003	0.75
240	0.002	0.002	1.00
264	0.0004	0.0009	2.25
Hr	**Chamber 40°C**	**Model 40°C**	**Model/Chamber Ratio**
48	0.17	0.22	1.29
72	0.07	0.046	0.66
96	0.04	0.009	0.23
168	0.01	0.00008	0.008
192	0.01	0.00002	0.002
216	0.007	0.000004	0.0006
240	0.007	0.0000008	0.0001
264	0.006	0.0000002	0.00003

As discussed previously, the model did not correlate well for either test temperature in the evaporative emission phase (<48 hr) as it neglects mass transfer resistance at the material-air interface. This latter limitation in the model was described previously and can be corrected.

Of interest is that the one-dimensional model developed by Little appears to function well for the two-sided panel experiment performed here. The VERTCM panels used here were placed upright in the chamber instead of flat on the chamber floor as was the carpet experiment conducted by Hodgson *et al*. (1993) and on which the model was based. The panels averaged 0.6 cm thickness, and the model functioned well as long as the input parameter for L was set at 0.3 cm, or half of the total panel thickness. Therefore, the assumption of one-dimensional diffusion holds up in the model even when one-dimensional diffusion occurs in opposite directions simultaneously toward parallel, exposed panel surfaces.

Conclusions

This validation of the mass transfer model developed by Little *et al*. (1994), which is based on heat transfer dynamics and was derived for multiple VOC from new carpet samples, demonstrates that the theory on which the model is based is suitable for predicting volatile emission from a dry building material after evaporative emission has ceased. While the model is suitable for diffusive volatile emission over the long-term, it does have some limitations which should be addressed.

The first correction would be to adjust the model to incorporate the effect of mass transfer resistance in the evaporative emission phase; however, this term does not affect the diffusive emission process studied here, and has been accomplished by other researchers using Little's model. Another limitation is that Little's model is based on experimental data collected at 23°C and 50% RH. While the model can be scaled based on characteristics of the dry building material (i.e. exposed material surface area, material thickness, etc.) and environment (i.e. room size, ventilation rate, etc.), it cannot be scaled over a temperature range. Further work would include an adjustment to scale the model over a temperature range, and further to validate this adjustment for a variety of building materials and volatile compounds. Additionally, application of the model demonstrates that certain material-volatile parameters such as D, Kv, Co and Ce need to be readily obtainable either experimentally or reliably estimated by other methods (i.e. porosity characteristics, etc.).

The biggest challenge to further development and refinement of the model, other than temperature variation, appears to be establishing what fraction (Ce) of the initial VOC concentration, Co, is available for emission. Further investigation into how the parameters of material density and porosity play into this factor needs attention, as density and porosity parameters are obtainable through laboratory analysis and can be used in the derivation of the diffusion coefficient, D, as well.

The mass transfer model developed by Little, or others based on the theory of heat transfer, could be improved to provide a straightforward and accurate method for predicting VOC emissions and exposures in the pre-construction design phase or post-construction remediation phase of building and transportation manufacturing, provided the required input data are accurate and readily available. More research is required to determine if the fraction of emittable VOC (Ce) to original VOC concentration (Co) is consistent across multiple VOCs and materials of different porosity and density.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 1992. Toxicological Profile for Styrene. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Bartekova A., Huelman P, Lungu C. 2005. The potential exposure of residents to emissions from building materials used in a new composite panel house, Proceedings of The Air & Waste Management Association's 98th Annual Conference & Exhibition Proceedings, Minneapolis, Minnesota, June 2005, ISBN 0-923204-88-1.

Blondeau P., Tiffonnet A.L., Damian A., et al. 2003. Assessment of Contaminant Diffusivities in Builidng Materials from Porosimetry Tests. Indoor Air; 13: 302-310.

Bodalal A., Zhang J.S., Plett E.G. 2000. A method for measuring internal diffusion and equilibrium partition coefficients of volatile organic compounds for building materials. Building and Environment, 35: 101-110.

Carslaw, H.S. and Jaeger J.C. 1959. Conduction of Heat in Solids, 2nd Ed. Oxford: Clarendon Press.

Clausen P.A., Wolkoff P., Holst E., Nielsen P.A. 1991. Long-term emission of volatile organic compounds from waterborne paints – methods of comparison. Indoor Air, 4:562-576.

Clausen P.A., Laursen E., Wolkoff E., Rasmusen E., Nielsen P.A. 1993. Emission of volatile organic compounds from a vinyl floor covering. ASTM STP 1205, Niren L. Nagda, Ed. American Society for Testing and Materials, PA, pp 3-13.

Cox S., Zhao D., Little J. 2001. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. Atmospheric Environment, 35:3823-3830.

Deng B., Kim C.N. 2003. A unified conjugate mass transfer model of VOC emission. Korean Journal of Chemical Engineering, 20(4):685-692.

Hodgson, A.T. Wooley, J.D. Daisey, J.M. 1993. Emissions of volatile organic compounds from new carpets measured in a large-scale environmental test chamber. Journal of Air and Waste Management, 43:316-324.

Little J.C., Hodgson A.T., Gadgil A.J. 1994. Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment, 28(2):227-234.

Lyman W.J, Reehl W.F., Rosenblatt D.H. 1990. Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington D.C., 960 pp., 17-4.

Meininghaus R., Gunnarsen, L., Knudsen, H. N. 2000. Diffusion and sorption of volatile organic compounds in building materials - impact on indoor air quality. Environmental Science & Technology, 34:15, 3101-3108.

Rohsenow, W. M. and Hartnett, J. P. Eds. 1973. Handbook of Heat Transfer, McGraw-Hill, NY. p. 1-5.

Seo J., Kato S., Ataka Y., Zhu, Q. 2005. Evaluation of Effective Diffusion Coefficient in Various Building Materials and Absorbents by Mercury Intrusion Porosimetry. Indoor Air, The 10th International Conference on Indoor Air Quality and Climate, Sep. 4 – Sep. 9, 2005.

Tichenor, B. 2006. Criteria for Evaluating Programs that Assess Materials/Products to Determine Impacts on Indoor Air Quality: Contractor Report (final) submitted to USEPA; Macon, NC.

Wallace L., Pellizzari E., Leaderer B., Zelon H., Sheldon L. 1987. Emissions of volatile organic compounds from building materials and consumer products. Atmospheric Environment, 21(2):385-393.

Wirten L. 2006. Influence of moisture and substrate on the emission of volatile organic compounds from wall structures. Doctoral Dissertation. Helsinki University of Technology; Espoo, Finland.

Xiong J., Zhang Y. 2010. Impact of Temperature on the initial emittable concentration of formaldehyde in building materials: experimental observation. Indoor Air; 20: 523-529.

Xu Y, Zhang Y. 2003. A general model for analyzing single surface VOC emission characteristics from building materials and its application. Atmospheric Environment, 38:113-119.

Zhang J. S. and Shaw C. Y. 1997. Modeling of Volatile Organic Compound (VOC) Emissions from Building Materials/Furnishings - a literature review. National Research Council Canada, Report No. IRC-IR-755, December 1997. 24 pp.

Zhang Y., Luo X., Wang X., Qian K., Zhao R. 2007. Influence of temperature on formaldehyde emission parameters of dry building materials. Atmospheric Environment, 41:3203-3216.

CHAPTER 4

APPLICATION OF A MASS TRANSFER MODEL TO PREDICT STYRENE EMISSION FROM A THERMOSET COMPOSITE BUILDING MATERIAL OVER A TEMPERATURE RANGE

Abstract

Accurate models to predict volatile organic compound (VOC) concentrations in indoor air would be useful in the design and remediation of building and transportation infrastructure in the interest of protecting human health. The so-called mass transfer models, based on the theory and mechanics of heat transfer, offer the most promise for predicting indoor air VOC concentrations for a variety of VOCs and materials. However, mass transfer models developed to date do not factor in the critical influence of temperature on the diffusion of VOC from a material. This paper models styrene emission from a dry building material (VERTCM) and validates modeled concentrations against data obtained in an environmental test chamber over a range of temperatures. Results show that the modeled data fit the chamber data at 23°C, but underestimate chamber data by as much as 10^{-6} at the highest temperature tested (50°C). Emperical adjustments to the model show that, for VERTCM, the modeled data can be made to fit the chamber data to within a factor of no more than 2.8.

Keywords: Modeling; VOC; mass transfer; diffusion coefficient; styrene, environmental test chamber

Introduction

Emission of and exposure to volatile organic compounds (VOCs) associated with building materials has been a subject of significant study. Emission of VOC is especially important in enclosed spaces such as homes, buildings and vehicles because humans typically spend a significant portion of their time in these environments. Intermediate and chronic exposures to low levels of indoor air VOC can contribute to chronic symptoms and disease expression among exposed individuals. Being able to anticipate, recognize and control these exposures can become a time-consuming and expensive process, especially if numerous samples are required to be collected in the field to identify the VOC or other contributing contaminant.

Consequently, there has been an effort to model the potential for exposure to VOCs and other air contaminants in enclosed spaces. Modeling is a useful tool to estimate exposures and implement controls without the need for extensive room air sampling or occupant monitoring. Some exposure models consider the generation rates of contaminant and develop exposure profiles based on indoor conditions such as room size, air exchange and flow dynamics, sink/source effects and rates of emission from the source. Other models have been developed to describe the VOC emission rate functions and factors of building material constituents, validated with chamber sampling data under controlled conditions.

According to Zhang and Shaw (1997), there are two major categories of models to describe evaporative and/or diffusive emission of VOCs from building materials: (1) empirical or statistical models; and (2) physical or mass transfer models, sometimes referred to as computational fluid dynamics (CFD) models.

Empirical Models

La Scala *et al*. (2006) modeled styrene emissions from a viscous vinyl ester resin. They found that the mass and emission rate of styrene increased with increasing styrene content of the resin and exposed resin surface area, and that emissions increased exponentially with increase in temperature. They also found that the lower styrene content resins in a range of 20 to 50% styrene by weight reached the diffusive emission phase earlier with respect to time. Their model, however, was developed to predict styrene emissions from an uncured resin during the manufacturing phase, as emission from cured resin consumer products is not currently regulated.

Dunn (1987) investigated empirical modeling using VOC emissions from latex caulk. He compared a thin film model with a deep source model and proposed the possibility of scaling results between combinations of material surface area and chamber volume ratios (A:V) and air exchange rate (ACH). These models required the assumption of a pure source, a limitation for many manufactured materials, and the computational analysis was cumbersome.

Colombo, A. *et al*. (1990) fit an empirical model to chamber data for VOC emissions from particle board, gypsum board and plywood. They proposed that quasi-static emission rates could be modeled from chamber data by considering the physical phenomenon of concentration, concentration gradient and the rate parameters of emission. He described the limitations of double-exponential empirical modeling from least square fitting of emission rate relative to time and suggests that chamber data for VOC emissions are best used to quantify emissions because of these limitations.

Empirical models are developed for estimating evaporative emissions from wet building materials, (e.g. paint, caulk, adhesive, etc.) and/or diffusive emissions from dry building materials (e.g. formaldehyde emitted from oriented strand board, styrene from butadiene-styrene carpet backing, etc.). One major limitation of the empirical models such as the first-order decay model obtained from chamber data is that they are difficult to scale up and modify around dynamic building conditions. In order to surpass this obstacle, several researchers began working with physical based models based on the theory of heat transfer to predict VOC emissions from dry building materials.

Physical Models

Mass transfer or physical models offer an advantage to predicting VOC emissions for materials of known physical parameters at various environmental conditions. Sparks *et al*. (1996) concluded that a mass transfer model provided a better estimate of gas-phase VOC emissions than a first-order empirical decay model. Their model, however, correlated the mass transfer coefficient by a single Reynold's number (Re), which is unrealistic in dynamic environments. Yang, *et al*. (1998) compared an empirical first-order decay model and subsequent application of a physical computational fluid dynamics (CFD) model to describe the effect of incomplete mixing on predicted estimates, with promising results. Huang, *et al*. (2002) developed a numerical model and compared it with a CFD model and experimental results. They found the CFD model agreed more accurately with chamber VOC concentrations than the numerical model.

Little, *et al*. (1994) were among the first to propose and develop a simple, physical model to predict VOC emissions using a few physical parameters (Chapter 3).

This model is based on heat transfer theory and mechanics, utilizing certain simplifying assumptions requiring validation. Little's model, built around the concept of internal diffusion and using Fick's law of diffusion, has become the basis on which following models have been developed. Cox, *et al*. (2001) applied and validated Little's model parameters for VOC emissions from vinyl flooring. Little's model, like Clausen's (1993), lacked incorporation of mass transfer resistance at the material-air interface, which caused an underestimation of predicted emissions in the early evaporative phase. Xu and Zhang (2003) used an improved mass transfer model based on Little's research to correct for this physical phenomenon. This improvement lowers the initial mass loss estimation to more closely fit the experimental data and reduces the overestimation of VOC concentration in the first 48 hours.

Huang and Haghighat (2002) used a physical model to predict the small chamber air concentration based on the mass transfer coefficient (h), partition coefficient (Kv), mass diffusion coefficient in the material (D) and VOC initial concentration in the material (C_o). Their computational fluid dynamics (CFD) model was validated using chamber emission data, finding good correlation between the data but noting a discrepancy between experimental and predicted results in the initial stages, which was attributed to instability and incomplete mixing in the early stages of the tests. Using chamber concentration and emission data (total emissions and emission rate), the mass diffusion coefficient (D), convective mass transfer coefficient (h), partition coefficient (Kv) and material thickness (L), Zhang and Xu (2003) were able to generate dimensionless mass transfer numbers which they describe, given material surface geometry and environmental conditions (excluding temperature change), can be correlated to different contaminants, materials, and air flow velocities.

Additional Considerations

Previous characterization and modeling of VOC emissions from dry building material has yielded insight into the driving forces behind volatile emission rates and the parameters needed to predict resultant indoor air volatile concentrations. Conditions which have been shown to affect diffusion and emission of VOCs from a building material are: VOC concentration in the material; VOC concentration gradient; air exchange rate; and, the rate of internal diffusion, or D. Virtually all of the data generated for model development and validation, however, has occurred within a very narrow range of experimental temperature. In fact, most of the models to date have been developed and validated using only two to three datasets generated at approximately 23^{o}C and 50% RH. Only recently have researchers studied the effect of temperature on VOC diffusion (D) through and partitioning (Kv) from dry building materials.

As material-VOC emission modeling using mass transfer theory advances, new methods and information describing the chemical-physical relationships and their effects on the function and reliability of the proposed models are being elucidated. Zhang *et al.* (2007) developed the C-history method, using computational fluid dynamics (CFD) principles, to correlate the partition coefficient (Kv) of formaldehyde from various density dry building materials over a temperature range (18, 30, 40 and 50^{o}C) given the known or estimated parameters of diffusion coefficient (D), initial formaldehyde concentration in the material (Co) and the chamber air concentrations over time. It was determined that both the partition coefficient (Kv) and the diffusion coefficient (D) are significantly affected by temperature change, with D increasing on the order of 5 times between the lower and upper temperatures.

Deng (2009) studied the effect of material porosity and test temperature on the diffusion coefficient (D) using Zhang's *et al*. (2007) experimental data, correlating changes in D relative to varied temperature. Xiong and Zhang (2010) demonstrated that the effective material-volatile concentration (Ce) was not equivalent to the original material-volatile concentration (Co) as only a fraction of original VOC in the material is available to diffuse out into air, and that this distinction between terms was important to model accuracy.

Materials and Methods

VERTCM Materials

Vinyl ester resin thermoset composite material (VERTCM) panels were prepared at the UAB School of Engineering's Department of Materials Science and Engineering laboratory. Squares of E-90 course weave glass fiber (E-glass) measuring approximately 1.44 m^2 were cut to size and a Derakane® resin mixture containing 38% styrene by weight was applied by hand pouring and spreading with a plastic trowel until the fiber was completely covered and saturated. This process was repeated until eight layers of fiber formed the panel, with the resin amount equal to approximately twice the fabric weight (each fiber layer weighed approximately 350 grams). After layup, the panels were sealed under vacuum to cure overnight.

The following day, the cured panels were uncovered and cut on a wet saw to form test panels with a final cured panel thickness of 0.60 (± 0.01) cm and panel width ranging between approximately 19.2 to 26.0 (± 0.01) cm. After cutting, all four edges of the test panels were sealed with a non-VOC emitting metallic tape (Figure 1). The VERTCM panels were wrapped in two layers of heavy-duty aluminum foil, double-bagged in plastic (4 millimeter) sheeting, marked with identification numbers, and stored at -80°C.

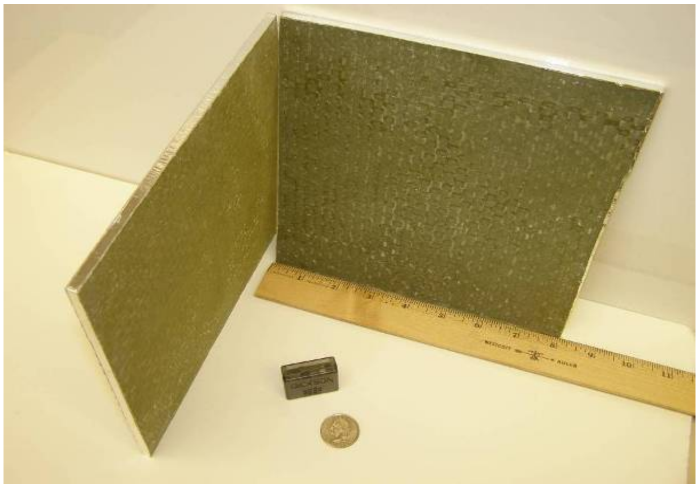


Figure 1. E-Glass VERTCM panels used for chamber emission data

Environmental Test Chamber (ETC)

The environmental test chamber (ETC) used in this research consisted of a LH-6 Laboratory Humidity Chamber (Associated Environmental Systems, Inc., Ayer, MA) modified to meet the definition of an ETC for use in emission studies. The chamber has an internal volume of 175.5 liters ($V = 0.176\ m^3$) and is temperature (0 – 90°C ± 1°C) and humidity (10 – 98%RH, ± 5%) controlled. The interior consists of stainless steel walls with a retrofitted door of anodized aluminum. Ports for inlet air (split inlet) are located on one side of the chamber, and air sampling ports are located on the top of the chamber. Chamber air is well mixed (2 internal fans with diffuser and split inlet air supply). In order to meet the requirements of an ETC, performance verification tests were conducted to ensure that the chamber to be used met these definitions (Chapter 2).

VERTCM Panel Testing

Previous research has shown styrene and other VOC emissions to be temperature dependent (La Scala *et al.*, 2006; Zhang *et al.*, 2007). Therefore, panel emission tests were conducted at 10°C, 23°C, 30°C, 40°C and 50°C (±1°C) with an air exchange rate of 1 (±5%) air changes per hour (ACH). All tests were conducted within a humidity ratio range of 0.004 (10°C) to 0.014 (30°C) grams of water per grams of dry air (10-50% RH). Chamber inlet flow, temperature and humidity were monitored and recorded for the duration of each test (Dickson TK120, Addison, IL). The air velocity over the face of the panels was measured with a hot-wire anemometer (TSI 8386, Shoreview, MN). The total average velocity of five measurements over each panel face ranged from 0.40 m s^{-1} to 0.65 m s^{-1}. Table 1 contains the various panel properties for each sample run, including test temperatures, humidity, exposed panel surface areas and the loading factor (exposed material surface area per volume of chamber air, or m^2 m^{-3}).

Table 1. Panel surface area and loading factor

Temperature (°C)	Panels (#)	Exposed Panel Surface Area (m^2)	Loading Factor (m^{-1})
10	4	0.32	1.82
23	4	0.41	2.33
30	4	0.33	1.88
40	4	0.33	1.88
50	4	0.32	1.82

The experiment start time began immediately upon closing the chamber door. Interior chamber air was sampled at 1, 2, 4, 6, and 12 hours the first day, as well as at 24 hour intervals on days 2, 3, 4, 5, 8, 9, 10, 11 and 12, for a total of 14 sample points over 264 hours. Three simultaneous 12 liter samples of chamber air were collected on SKC 226-01 (Lot 2000) charcoal sorbent tubes using SKC AirChek XR5000 personal sampling pumps pre-calibrated to 1.0 ± 0.05 liter per minute. The air flow and sampling train are illustrated in Figure 2.

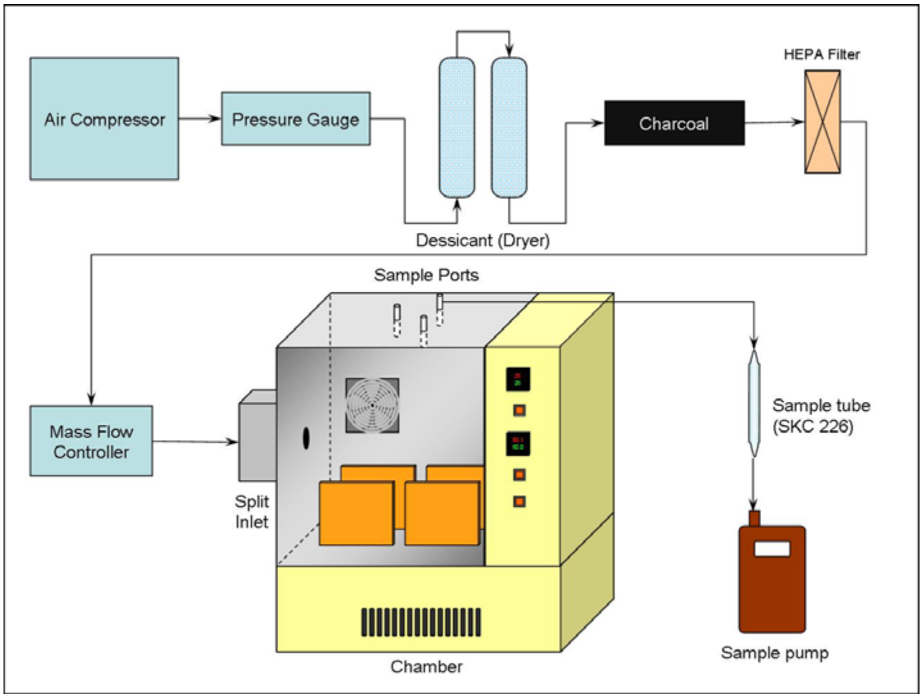


Figure 2. Air flow and sampling diagram for small test chamber experiment

Chamber air analysis for styrene was conducted using gas chromatography with flame ionization detection (Agilent Technologies 6850, Atlanta, GA). Desorbed samples were analyzed by 1.0 µl syringe injections onto a splitless inlet at 250°C. Chromatograph peaks were quantified with a flame ionization detector at 250°C against a 6-point calibration curve with a minimum correlation of $R^2 = 0.997$ and a limit of quantification

(LOQ) of 0.1 µg. No significant peaks other than the desorbent carbon disulfide (CS_2), an internal standard of 4-Chlorobenzotrifluoride (4-CBTF) and styrene were observed over a total method run time of approximately 5 minutes. Styrene eluted at approximately 1.90 minutes.

Determination of EF

Emission factor (EF) was derived from the chamber concentration data using the following equation,

$$EF(t_i) = \frac{\left(\frac{\Delta C_i}{\Delta t_i} + NC_i \right)}{L} \tag{1}$$

where $EF(t_i)$ is the emission factor over the time interval t_{i+1}-t_i (mg m^{-2} h^{-1}), $\Delta C_i/\Delta t_i$ is the slope of the time-concentration curve over the time interval t_{i+1}-t_i, N is the air change rate (h^{-1}), C_i is chamber concentration at time t_i (mg m^{-3}), and L is the loading factor (m^2 m^{-3}).

Emission factor is not a constant and varies over the emission profile. Determination of the emission factor during the latter stages of the emission profile, where the slope of the profile becomes quasi-static, allows for the determination of potential indoor air concentrations given a known material exposed surface area and room air exchange rate at a specific point in time.

The Little Model

Little *et al.* (1994) proposed a physical model based on heat transfer mechanics. Where heat is transferred across space by a temperature gradient from higher temperatures to lower temperatures, eventually reaching an equilibrium state, the same basic principle can be applied to modeling gas transfer through space, or in the case of diffusion, the migration of a VOC contaminant through void space in a building material. In this example, the same methods for describing heat transfer through a solid material was proposed by Little *et al*. (1994) to model gaseous diffusion of VOC through and out of a solid material,

$$\left(\frac{V}{A*Kv}\right)\frac{\partial C}{\partial t}+D\frac{\partial C}{\partial x}+\left(\frac{Q}{A*Kv}\right)C_x \;=0 \qquad (2)$$

where the first term represents the accumulation of VOC in the chamber air, the second term represents the mass flux of VOC diffusing out of the exposed material surface, the third term represents the VOC leaving the chamber, and application of the model is dependent on the following known, estimated and/or calculated parameters:

<u>Material-Volatile Properties</u>

D – Diffusion coefficient of the VOC in the material ($m^2\ s^{-1}$)
Kv – Partition coefficient between the material and air (dimensionless)
Co – The initial concentration of the VOC in the material (ug m^{-3})
L – the thickness of the material (m)
A – the exposed surface area of the material (m^2)

<u>Chamber Properties</u>

V – interior volume of environmental test chamber (m^3)
Q – volumetric flow rate of air through the chamber ($m^3\ s^{-1}$)

Model Calculated Values

$$h = Q \Big/ \left[A \times D \times K_v\right] \tag{3}$$

$$k = V \Big/ K_v \times A \tag{4}$$

A schematic of the physical functions for development and application of the model is presented as Figure 3, where y represents the concentration (mg m^{-3}) of VOC in air at any given time (t).

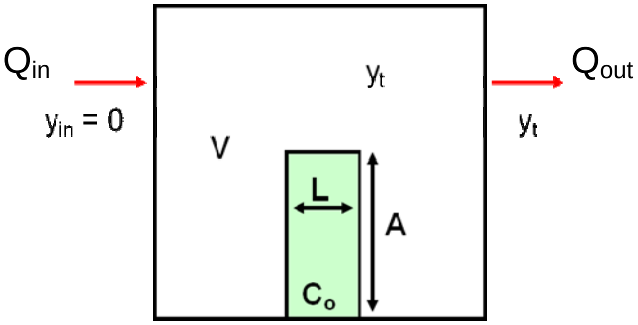


Figure 3. Representation of the model material-physical input parameters.

The key assumption to the development and application of the model is that the VOC concentration in the surface of the material slab ($C|_{x=L}$) is in equilibrium with the chamber air (y), or,

$$Kv = \frac{C|_{x=L}}{y} \tag{5}$$

Where Kv is the unitless partition coefficient. Using an analogous heat transfer solution written using mass transfer terms and adjusted for equilibrium partitioning, the concentration of VOC in the material slab as a function of distance from the base of the slab and time $C_{(x,t)}$ can be determined from Equation (6).

$$C_{(x,t)} = 2Co\sum_{n=1}^{\infty}\left\{\frac{\exp(-Dq_n^2 t)(h-q_n^2)\cos(q_n x)}{\left[L(h-kq_n^2)^2+q_n^2(L+k)+h\right]\cos\left(q_n L\right)}\right\} \tag{6}$$

Using the parameters described above and where the q_n s are the positive roots of

$$q_n \tan(q_n L) = h - kq_n^2 \tag{7}$$

the various terms in Equation (7) can be solved and substituted into Equation (6) to predict the concentration of volatile in the chamber air (y) at any particular point in time (t).

The model makes several assumptions about the material and emissions in the model design. First, the model assumes that the VOC is uniformly distributed throughout the material and diffuses one-dimensionally out of a single uniform layer of the material. Second, the parameters of diffusivity (D) and partitioning (Kv) are assumed to be independent of the concentration of volatile in the material and the chamber air, and resistance to diffusion between the material surface and the well-mixed air of the chamber is minimal. Application of the model against experimental results supports these assumptions, and while in some tests small discrepancies have been observed in the early stages of the emission profile due to early-stage mass transfer resistance for some materials, this resistance can be corrected for and has no significant effect on the estimation of later stage (diffusive) emissions from a dry building material.

As described above, key model input parameters other than chamber conditions and panel dimensions are the diffusion coefficient (D), partition coefficient (Kv) and initial concentration (Co) of the volatile in the material being tested. These parameters can be either measured directly or estimated from chamber emission data. The concept of emittable concentration (Ce) is also considered.

Determination of Material-Volatile Parameters Co, Ce, Kv and D

Determination of initial concentration (Co). The initial concentration (Co) of a VOC in a building material as determined in this experiment was necessary to estimate partition coefficient, Kv. The term Co is representative of the total mass of VOC contained in the original amount of material post manufacture but pre-emission. There are a number of ways to obtain this parameter for a variety of materials. Zhang and Xu (2003) determined Co for formaldehyde in dry building materials using an extraction method. Little *et al.* (1994) proposed that Co could be determined from chamber emission data, but this would assume that all VOC initially present in the material would be available for emission, which is not always the case.

For this experiment, Co was determined by dissolving a known mass of panel in methylene chloride. After approximately one week, a sample of the methylene chloride solution was analyzed by gas chromatography (GC) for determination of styrene concentration using flame ionization detection against a four-point calibration curve with a minimum correlation of $R^2 = 0.998$. Replicate data were averaged and correlated to mass loss of resin in the panel samples to estimate the original concentration (Co) of styrene in the VERTCM (Chapter 3).

Determination of emittable concentration (Ce). Xiong and Zhang (2010) recently demonstrated that the initial concentration (Co) of volatile in the material and the emittable concentration (Ce) are not always equivalent. The term Ce only approaches Co when the material conditions (i.e. porosity, tortuosity, chemical reaction, physical constraints, etc.) allow for nearly complete diffusion of a VOC through and out of the material. It is much more realistic that some volatile in the material will be trapped and will be unavailable for emission. This fraction of emittable volatile in a building material is an important input parameter into the model. For this experiment, the fraction of emittable volatile from the material was established as the total mass of styrene emitted from the VERTCM over the 12-day test period at 23°C, 30°C, 40°C and 50°C, and correlated to panel volume at each temperature to calculate Ce.

Determination of partition coefficient (Kv). Partition coefficient, Kv, was determined experimentally and was based on the determination for Kv described by Hodgson *et al*. (1993). Analysis was conducted by gas chromatograph for determination of styrene concentration using flame ionization detection against a six-point calibration curve with a minimum correlation of $R^2 = 0.997$. The experiment was replicated for consistency and three air styrene concentrations for each of the test temperatures were averaged to estimate a final equilibrium air concentration of styrene. This equilibrium concentration was then applied to equation (5) defined previously using the initial styrene concentration in the material (Co) determined experimentally here in order to derive Kv for model validation.

Determination of diffusion coefficient (D). There are several ways for determining the diffusion coefficient, D. Seo *et al*. (2005) determined D based on experimentally derived values for the density and porosity of the material and the calculated diffusion of a volatile in air. Here, Seo's method was used to derive D for this model validation, incorporating mercury vapor intrusion porosity data (obtained at a pressure of 0.54 psi) provided by Micromeritics Analytical Services of Norcross, GA, on two samples of similar VERTCM panel (Figure 4).

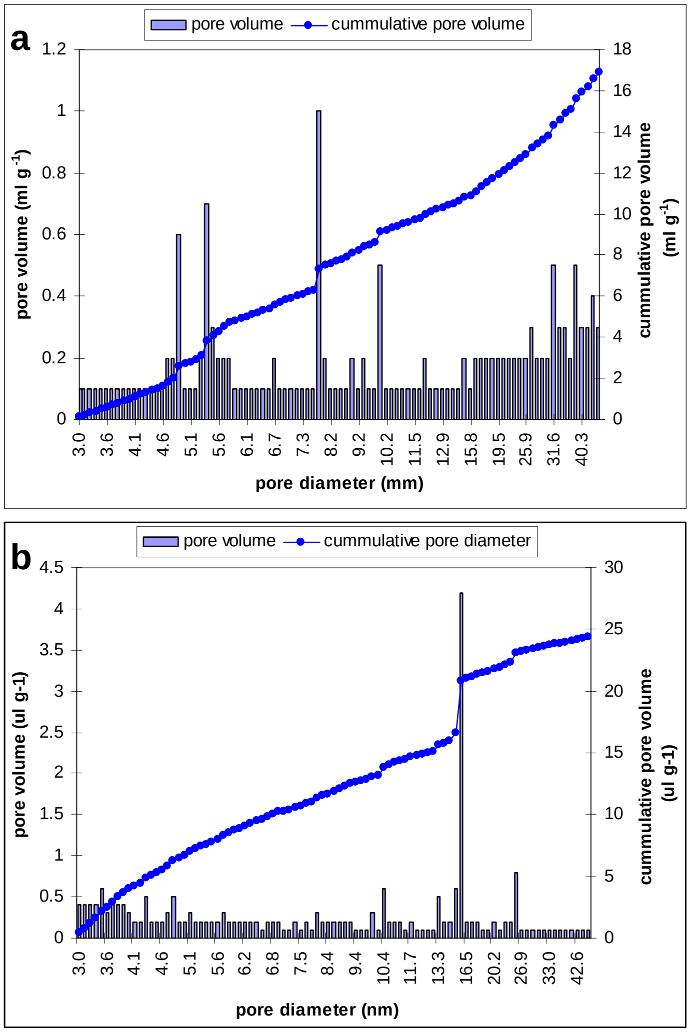


Figure 4. Pore size distributions for VERTCM sample #1 (a) and #2 (b).

According to Seo *et al*. (2005), the effective diffusion coefficient, D, of a volatile compound in a dry building material is a function of,

$$\frac{1}{D_m} = \frac{1}{D_a} + \frac{1}{D_k} \tag{8}$$

where Dm is the molecular diffusion coefficient, Da is the diffusion coefficient of the volatile in air, and Dk is the Knudsen diffusion coefficient (m^2 s^{-1}). Da can be calculated using Equation (9) from Lyman *et al*. (1990), and Dk is defined by Equation (10) from Seo *et al*. (2005),

$$D_a = \frac{10^{-3}(T)^{1.75}\sqrt{M_r}}{P\left(V_a^{\ 1/3} + V_b^{\ 1/3}\right)^2} \tag{9}$$

$$D_k = 0.97r\sqrt{\left(\frac{T}{M}\right)} \tag{10}$$

where T is temperature ($^{\mathbf{o}}$K), Mr is the molecular ratio of the volatile and air, P is atmospheric pressure (1 atm), V is the molecular volume (m^3) of the volatile ($V_{\mathbf{b}}$) and air ($V_{\mathbf{a}}$), r is the average pore size radius (nm) of the material in the mesopore range, and M is the molecular weight of the VOC. Once Da and Dk are determined and Dm solved, the effective diffusion coefficient D (m^2 s^{-1}) can be estimated from porosimetry data of the material by,

$$D = D_m \left(\frac{\varepsilon}{\tau} \right) \tag{11}$$

where ε is the voidage fraction (%) based on the pore size distribution over the mesopore range (2-50 nm), and τ is the unitless pore tortuosity factor. The tortuosity factor for this experiment was estimated from the literature based on porosity and density analysis of building materials and using the relation Equation (12) by Blondeau *et al*. (2003),

$$\tau = -0.0112\varepsilon + 2.2271 \tag{12}$$

where ε is the voidage fraction (%) and τ is the unitless pore tortuosity factor.

Results and Discussion

Emission Factor, EF

Total mass of styrene emitted and emission factor (a rate function of emission) increased with increasing temperature (Table 2), demonstrating the effect temperature has on volatile emissions from a material.

Table 2. Styrene emission parameters at varied test temperatures

Temperature (^{o}C)	Total Styrene (mg)	Emission Factor (10^{-3} mg m^{-2} hr^{-1})	
10	2.11	9.10	(± 0.1)
23	5.98	15.1	(± 0.7)
30	9.77	17.3	(± 0.5)
40	13.73	21.7	(± 0.2)
50	17.87	25.2	(± 0.1)

Initial Concentration, Co

Initial concentration of styrene in the panel, Co, used to calculate Kv, was estimated at 3.33 x 10^8 mg styrene per m^{-3} of material (Table 3).

Table 3. Replicate sample determination of original styrene concentration, Co

Vial (#)	Styrene (g)	Mass loss (g)	Styrene/Mass Loss (mg g^{-1})	Styrene/Material (kg m^{-3})
1	0.00203	0.0537	37.87 (±0.10)	70.5 (±2.3)
2	0.00619	0.0552	112.1 (±0.20)	208.6 (±7.3)
3	0.00611	0.0177	345.1 (±0.19)	642.2 (±21.8)
4	0.00787	0.0357	220.5 (±0.16)	410.2 (±13.8)
			Average	332.9 (±45.0)

Emittable Concentration, Ce

The fraction of emittable volatile (Ce) from the material was established as the total mass of styrene emitted from the VERTCM over the 12-day test period at 10°C, 23°C, 30°C, 40°C and 50°C, as listed in Table 4.

Table 4. Styrene emitted fraction at varied test temperatures

Temperature (°C)	Total Styrene (mg)	VERTCM (x10^{-4} m^3)	Ce (mg m^{-3})
10	2.11	9.11	2,316 (±11%)
23	5.98	9.35	6,396 (±11%)
30	9.77	9.23	10,585 (±11%)
40	13.73	9.99	13,744 (±10%)
50	17.87	9.51	18,791 (±10%)

Partition Coefficient, Kv

Partition coefficient was determined by first establishing the average equilibrium concentration in a known volume of air around a known volume of material (Table 5). By replicate analysis, it was observed that equilibrium could be reached at each test temperature by ramping the three vials sequentially from 10°C to 50°C without any negative effect, thus the material volume (m^3) unity between tests in Table 5.

Table 5. Average equilibrium air styrene concentrations and air-material concentrations

Vial	10°C	23°C	30°C	40°C	50°C
1	690	2562	3886	5542	7204
2	1136	3029	3971	5663	7601
3	664	2514	3646	5657	7135
Avg. Air (mg m^{-3})	830	2702	3834	5621	7313
SD (±)	265	284	168	67.9	252
Material (kg m^{-3})	19.2 (±2.1)	63.0 (±6.3)	89.6 (±9.9)	131.9 (±11.8)	171.2 (±15.4)

Partition coefficient was determined by dividing the original concentration of styrene in the material, 3.33×10^8 mg styrene per m^{-3} of material, by the air-material styrene concentrations in Table 5 using the model air-material equilibrium assumption Equation (13) to derive Kv (Table 6).

$$Kv = \frac{C\big|_{x=L}}{y} \tag{13}$$

Table 6. VERTCM partition coefficient calculations for 10 to 50°C.

Temperature (°C)	Equilibrium Air Concentration (y)	Kv = Co/y
10	19,163	17,371 (±4,247)
23	63,019	5,282 (±1,241)
30	89,558	3,717 (±913)
40	131,924	2,523 (±567)
50	171,209	1,944 (±438)

Based on the calculations in Table 6, a function of partition coefficient relative to temperature was developed, as illustrated in Figure 5.

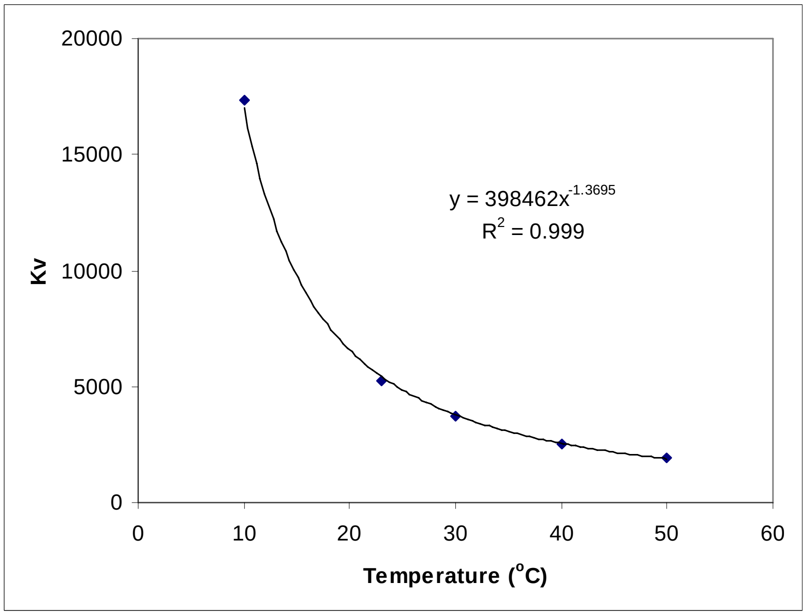


Figure 5. Function of Kv to a range of 10°C to 50°C for VERTCM

Diffusion Coefficient, D

Calculation of the molecular diffusion coefficient (Dm) and subsequent calculation of the effective diffusion coefficient (D) as described by Seo *et al.*(2005) above and, based on the input parameters for ε and τ listed in Table 7 below, yielded the following relationship for Da and D illustrated as Figure 6.

Table 7. VERTCM panel density and porosity values.

VERTCM panels	1 (a)	2 (b)	Avg.
Density (g ml^{-1})	1.85	1.89	1.87
Porosity (%)	4.5	3.3	3.9
Mesopore Radius (nm)	5.39	5.71	5.55

Table 8. Calculated values for diffusion coefficient (D)

Temp. (^oC)	10	23	30	40	50
Da (10^{-6} m^2 s^{-1})	6.79	7.36	7.66	8.11	8.57
Dk (10^3 m^2 s^{-1})	8.62	8.81	8.92	9.06	9.21
Dm (10^{-6} m^2 s^{-1})	6.80	7.35	7.66	8.11	8.57
D (10^{-7} m^2 s^{-1})	1.23	1.33	1.38	1.46	1.55

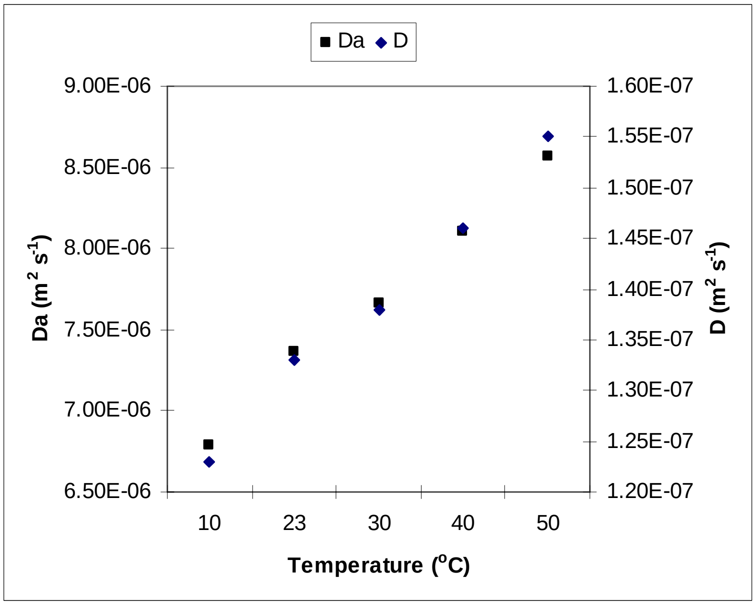


Figure 6. Relationship of Da with D for VERTCM by Seo *et al*. (2005)

Model Validation

Based on the methods described above, the parameters for the model utilized here were determined experimentally or calculated from the literature (Tables 9 and 10).

Table 9. Static model input parameters

Q (L m^{-1})	V (m^3)	L (m)	ε (%)	τ (ratio)
2.92	0.175	0.006	5.51	2.17

Table 10. Variable (by T°C) estimated model input parameters

Temp. (°C)	Ce (x10^6 mg m^{-3})	Kv (unitless)	Da (x10^{-6} m^2 s^{-1})	D (x10^{-7} m^2 s^{-1})
23	4.85	5282	7.36	1.33
30	9.87	3717	7.66	1.38
40	13.8	2523	8.11	1.46
50	18.5	1944	8.57	1.55

These terms were input into the model to validate the model at 23°C, 30°C, 40°C and 50°C. The results of the chamber data against the modeled data are represented in Figures 7, 8, 9, and 10. The □ model values (ex. "model23") represent model estimates based on total emitted fraction (Ce) of styrene and estimates of D of 10^{-7} m^2 s^{-1}, while the ▲ model values (ex. "23D-11") represent model estimates based on the emitted fraction (Ce,df) during the diffusive phase (48-264 hours) with estimates of D of 10^{-11} m^2 s^{-1}.

The model was not validated against the 10°C chamber data, and no attempt was made at this time to adjust the model to fit the 10°C chamber data. This analysis was omitted because the model slightly overpredicted the chamber data for 10°C by 0.05 mg m^{-3}, or an equivalent of approximately 0.5 ppm at 10°C. Since the model was slightly protective of health by overpredicting the expected air styrene concentration, and only so by a very small amount, model validation by chamber data focused only on conditions where increased temperature would be expected to increase air styrene concentrations (i.e. ≥23°C).

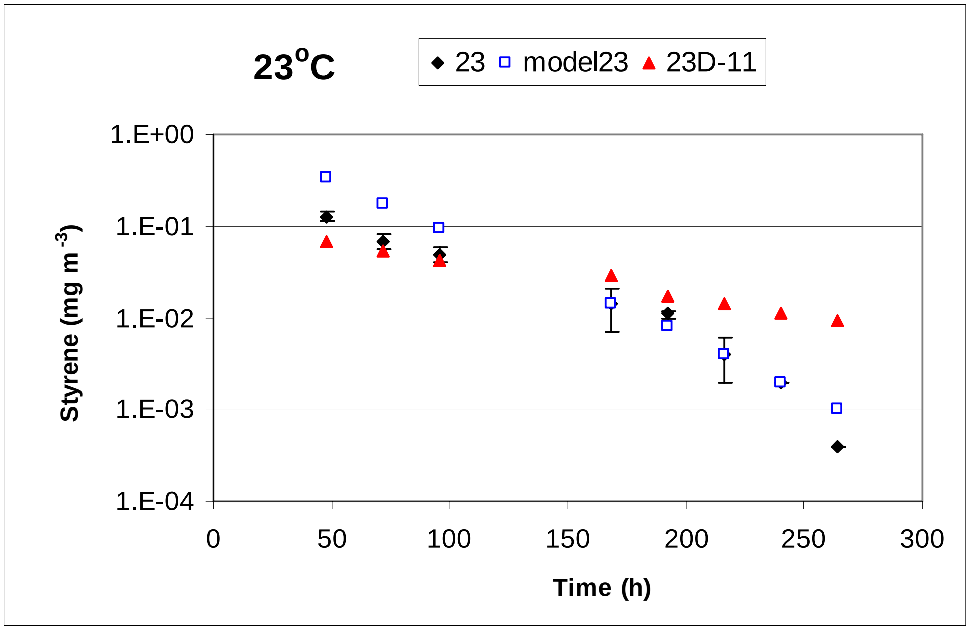


Figure 7. 23°C modeled results compared to chamber data at 23°C

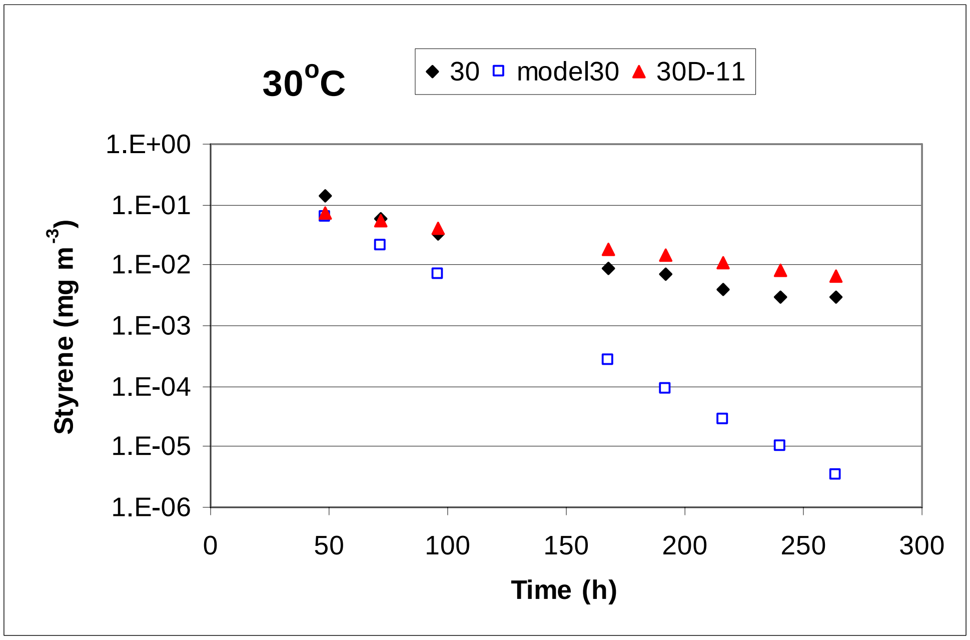


Figure 8. 30°C modeled results compared to chamber data at 30°C

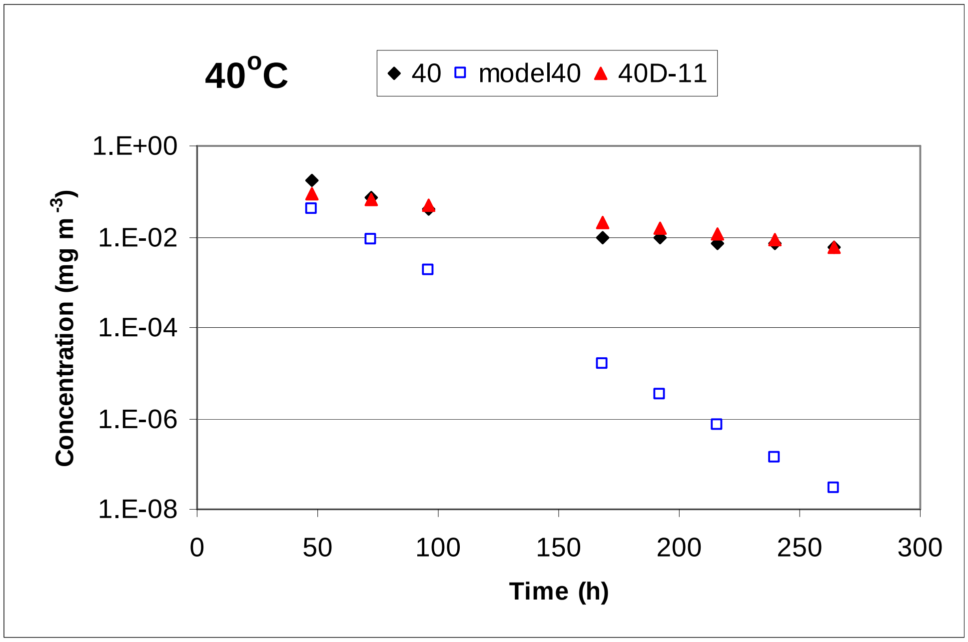


Figure 9. 40°C modeled results compared to chamber data at 40°C

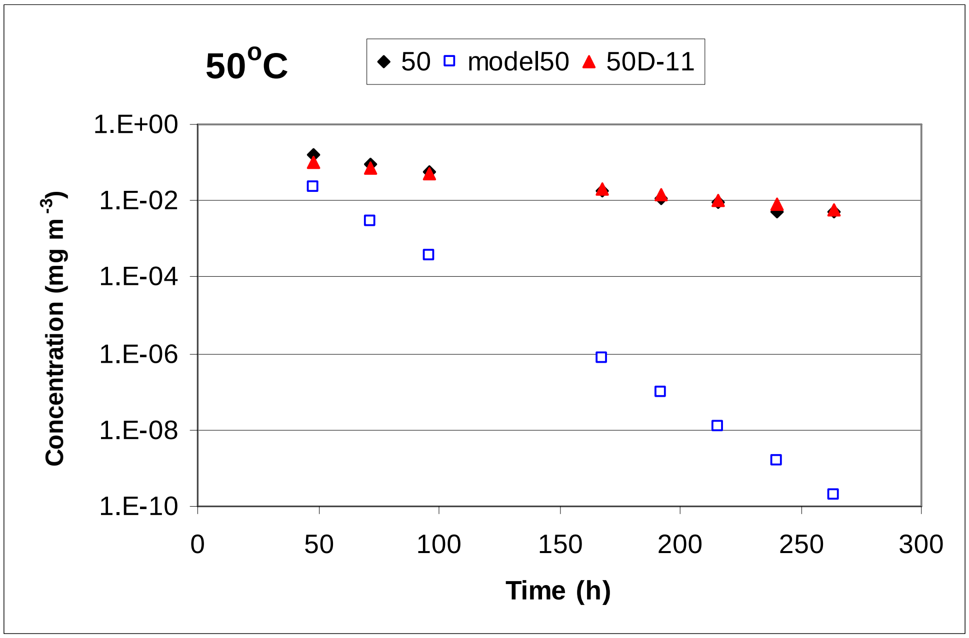


Figure 10. 50°C modeled results compared to chamber data at 50°C

Application of the estimated or measured parameters of Ce, Kv and D to the model resulted in a good correlation of modeled results compared to chamber data at 23°C. The ratio of predicted to measured concentration data was within a range of 0.73 to

2.63 for time ≥48 hours. Of interest is that the model correlated well with the 23°C chamber data when the effective diffusion coefficient (D) and estimated total emittable concentration (total styrene mass emitted 0-264 hours) were used. This principle did not hold up as well when temperature-relevant D and Ce were applied to temperatures >23°C.

Application of temperature-dependent parameters (Table 10) for Ce, Kv and D at temperatures >23°C (30°C, 40°C, 50°C) did not result in a good correlation between modeled results when compared to chamber data. In fact, at the end of the modeled test period, the model under-predicted the measured chamber data by orders of magnitude, with an approximate two orders of magnitude decrease in the final predicted concentration at the at the end of each test per 10°C increase in temperature (Figures 7, 8, 9 & 10).

Sensitivity analysis of the modeled results showed that this exponential decrease in modeled concentration was primarily due to the diffusion coefficient (D) and not Kv or Ce. Increasing the Ce by a factor of 10 increased the modeled concentration by an order of magnitude but did not change the slope of the log concentration gradient. This is in keeping with statements in the literature that contaminant concentration, diffusion coefficient and air change rate are the three driving forces behind VOC air concentrations. It also confirms that diffusion is rapid for these materials (increased rate of diffusion accelerates decrease in emitted concentration), as evidenced by the rapid convergence of the series equation (Eq. 6) in application of the model.

Additional analysis of the model was performed to see what adjustments would provide a better fit of the modeled data to chamber data. It was discovered that lowering the coefficient of diffusion (D) by a factor of 10^{-4} provided a better fit of the modeled data than using the un-adjusted D (Figures 7, 8, 9 and 10). Using a De x10^{-4} provided an even better fit of the model to chamber data when only the diffusive portion (≥ 48 hours) of the mass of styrene emitted at each temperature, or Ce,df, was used instead of the Ce mass estimated from chamber data and listed in Table 11. This adjustment moved the modeled data in closer proximity to the chamber data, while still slightly over-predicting the styrene air concentration, especially in the second week, which would ultimately serve to be protective of human health.

Table 11. Styrene emitted mass over test (Ce) and ≥ 48 hours (Ce,df).

Temperature (^{o}C)	Total Mass (mg)	Emitted Mass (mg)	VERTCM (x10^{-4} m^3)	Ce (mg m^3)	Ce,df (mg m^3)
10	2.11	0.89	9.11	2,316	977
23	5.98	2.13	9.35	6,396	2,278
30	9.77	2.12	9.23	10,585	2,297
40	13.73	2.56	9.99	13,744	2,563
50	17.87	2.94	9.51	18,791	3,091

It was found that by using the Ce mass in the diffusive phase (i.e. Ce,df), as well as lowering D by a factor of 10^{-4}, provided the best fit of the modeled data to the chamber data for temperatures >23°C. Ultimately, inputting the temperature-specific values of Ce, Kv and D and making the adjustments described above significantly improved the model's ability to predict styrene air concentrations at temperatures >23°C. These adjustments improved the mass transfer model function from underpredicting styrene air concentrations on the order of 10^{-3} to 10^{-6}, to slightly overpredicting the styrene air concentrations by no more than a factor of 2.8x (Table 12).

Table 12. Fit of modeled to chamber data over a temperature range.

Hr	**23C**	**Model23C**	**23D-11**	**Model:Chamber Ratio Using D, Ce**	**Model:Chamber Ratio Using Dx10^{-4}, Ce,df**
48	0.127	0.254	0.0672	2.00	0.53
72	0.069	0.135	0.0531	1.97	0.77
96	0.049	0.072	0.0425	1.47	0.87
168	0.014	0.011	0.0291	0.79	2.08
192	0.011	0.006	0.0176	0.55	1.60
216	0.004	0.003	0.0141	0.75	3.53
240	0.002	0.002	0.0113	1.00	5.65
264	0.0004	0.0009	0.0091	2.50	22.8
Hr	**30C**	**Model30C**	**30D-11**	**D, Ce**	**Dx10^{-4}, Ce,df**
48	0.137	0.062	0.0705	0.453	0.515
72	0.059	0.021	0.0563	0.356	0.954
96	0.032	7.00 E-03	0.0412	0.219	1.29
168	0.009	2.65 E-04	0.0187	0.029	2.08
192	0.007	8.90 E-05	0.0144	0.013	2.06
216	0.004	2.79 E-05	0.0111	0.007	2.78
240	0.003	1.00 E-05	8.53 E-03	0.003	2.84
264	0.003	3.37 E-06	6.56 E-03	0.001	2.19
Hr	**40C**	**Model40C**	**40D-11**	**D, Ce**	**Dx10^{-4}, Ce,df**
48	0.17	0.0412	0.0878	0.242	0.516
72	0.07	8.54 E-03	0.0649	0.122	0.927
96	0.04	1.77 E-03	0.0483	0.044	1.21
168	0.01	1.58 E-05	0.02	0.002	2.00
192	0.01	3.28 E-06	0.0149	3.28 E-04	1.49
216	0.007	6.79 E-07	0.0111	9.70 E-05	1.59
240	0.007	1.41 E-07	8.26 E-03	2.01 E-05	1.18
264	0.006	2.92 E-08	6.15 E-03	4.87 E-06	1.03
Hr	**50C**	**Model50C**	**50D-11**	**D, Ce**	**Dx10^{-4}, Ce,df**
48	0.168	0.0234	0.103	0.139	0.613
72	0.088	2.98 E-03	0.0743	0.034	0.844
96	0.056	3.81 E-04	0.0538	0.007	0.961
168	0.019	7.89 E-07	0.0204	4.15 E-05	1.07
192	0.011	1.01 E-07	0.0148	9.18 E-06	1.35
216	0.009	1.28 E-08	0.0107	1.42 E-06	1.19
240	0.005	1.64 E-09	7.76 E-03	3.28 E-07	1.55
264	0.005	2.09 E-10	5.62 E-03	4.18 E-08	1.124

Model Adjustment for Temperature Range

For practical application of the model to predict air styrene concentrations for this VERTCM at temperatures > 23°C, a sensitivity analysis was performed to gauge which model parameter adjustment provided a better fit of modeled results with the chamber data. It was discovered that decreasing the value for the diffusion coefficient (D) by a factor of 10^{-4} improved the ratio of predicted to measured results significantly (Table 12). Further, if the concentration of styrene emitted only over the diffusive range (48-264 h) is applied to the initial concentration input parameter (Co) in the model, the fit is even better. An exponential formula (Eq. 14) was derived from the regression of the Ce,df to Ce ratio over the temperature range and this relationship can be used to estimate the diffusive fraction of styrene for this material at temperatures >23°C which can then be used to predict air styrene concentration for this material over a temperature range (Figure 11).

$$\frac{Ce, df}{Ce} = 0.3247^{e-0.0136(T)} \tag{14}$$

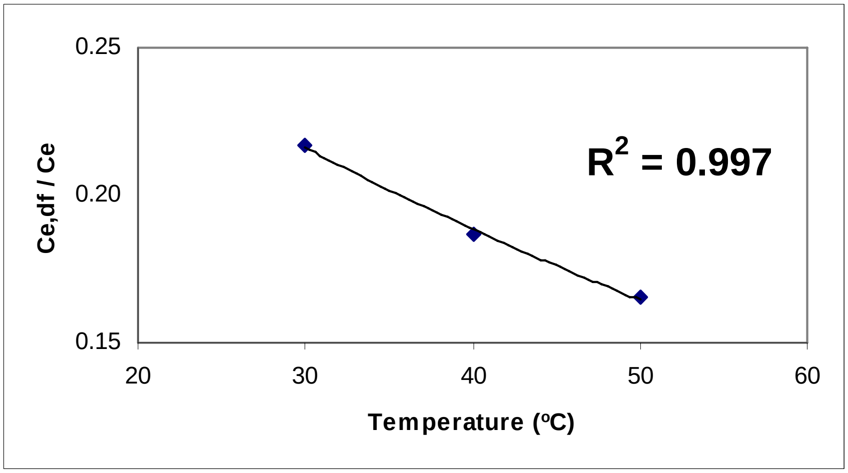


Figure 11.Styrene diffusive fraction (Ce,df) to emittable fraction (Ce) as a function of temperature.

Model application to VERTCM at T>23°C

The following steps outline application of temperature dependent material-volatile input parameters to accurately predict air styrene concentrations for the VERTCM studied here.

First, the temperature of interest is identified. Next, the temperature (°C) is applied to Equation (14) to derive the Ce,df:Ce ratio. The emitted fraction of styrene Ce can be either experimentally derived (such as by gravimetric analysis in a microbalance or chamber data at T°C) or estimated from the data reported here. The temperature-dependent emittable fraction of styrene during the diffusive phase can then be solved by

$$C_{e,df} = (y)C_e \tag{15}$$

The temperature-dependent partition coefficient Kv can be determined experimentally as described here and estimating Co based on the amount and styrene content of the materials used to form the VERTCM by,

$$Kv = \frac{C\big|_{x=L}}{y} \tag{13}$$

Finally, the effective diffusion coefficient (D) can be determined from laboratory experiment as described here, or can be estimated using Equations (8), (9) and (10) along with mercury vapor intrusion porosimetry data and finally adjusting the D by a factor of 10^{-4}.

Conclusions

Currently, it is not clear why reducing the diffusion coefficient, De, by four orders of magnitude provides a better fit for the modeled data at temperatures >23°C. It could be that the estimate of D used here is too large for application in this model, although Xiong and Zhang (2010) applied material mercury intruding porosimetry analysis to derive a D of 3.95 x 10^{-8} m^2 s^{-1} for formaldehyde in particle board with good correlation to experimental analysis. Bodalal *et al*. (2000) derived an inverse correlation for D with VOC molecular weight. For styrene with a molecular weight of 104.2, the expected D was shown to range from approximately 2 x10^{-11} m^2 s^{-1} for vinyl floor tile to 8 x10^{-11} m^2 s^{-1} for carpet. Zhang and Xu (2003) estimated for styrene at 23°C a D of 4.1 x 10^{-12} m^2 s^{-1} based on an analysis of chamber data from Hodgson's carpet VOC emission data and on which Little derived the mass transfer model used here. Additionally, there is no explanation for why an adjusted D is required for temperatures >23°C yet an un-adjusted D functions better at 23°C. Samples of VERTCM panel used here have been sent to Tsinghua University in Beijing, China for confirmation analysis of D and Kv, and the experimental results are forthcoming.

Also, it was interesting to find that using the emittable fraction of styrene during the diffusive phase only (Ce,df) and not the emittable fraction that included the evaporative phase (i.e. total Ce) provided a better fit of modeled data to chamber data, but only at temperatures >23°C. Again, this adjustment did not work as well for the 23°C data, and there is no forthright explanation as to why this adjustment is required to make modeled data fit chamber data at temperatures >23°C. Ultimately, estimation and application of the temperature-dependent parameters derived in this study should provide an acceptable estimate of styrene air concentrations from like VERTCM over a range of temperatures.

A useful model to predict air VOC concentrations based on a handful of material and VOC properties would be extremely beneficial for protecting human health in indoor environments. Mass transfer models appear to offer the most advantage and functional ability than other models, especially when multiple VOCs and materials are present, and where environments are dynamic (i.e. temperature, air exchange rate, etc.). Experimental analysis has shown, however, that not all material-VOC relationships behave consistently, especially when material composition or environmental temperature may be variable. Only additional analysis across materials, VOCs and temperatures will elucidate whether or not the mass transfer models can predict in the future indoor air VOC concentrations with accuracy and precision.

References

Blondeau P., Tiffonnet A.L., Damian A., et al. 2003. Assessment of Contaminant Diffusivities in Builidng Materials from Porosimetry Tests. Indoor Air; 13: 302-310.

Bodalal A., Zhang J.S., Plett E.G. 2000. A method for measuring internal diffusion and equilibrium partition coefficients of volatile organic compounds for building materials. Building and Environment, 35 (2000) 101-110.

Clausen P.A., Laursen E., Wolkoff E., Rasmusen E., Nielsen P.A. 1993. Emission of volatile organic compounds from a vinyl floor covering. ASTM STP 1205, Niren L. Nagda, Ed. American Society for Testing and Materials, PA, pp 3-13.

Colombo A., De Bartoli M., Pecchio E., Schauenburg H., Schlitt H., Vissers H. 1990. Chamber testing of organic emission from building and furnishing materials. The Science of the Total Environment, 91:237-249.

Cox S., Zhao D., Little J. 2001. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. Atmospheric Environment, 35:3823-3830.

Deng B., Kim C.N. 2003. A unified conjugate mass transfer model of VOC emission. Korean Journal of Chemical Engineering, 20(4):685-692.

Dunn J. 1987. Models and statistical methods for gaseous emission testing of finite sources in well-mixed chambers. Atmospheric Environment, 21(2):425-430.

Hodgson, A.T. Wooley, J.D. Daisey, J.M. 1993. Emissions of volatile organic compounds from new carpets measured in a large-scale environmental test chamber. Journal of Air and Waste Management, 43:316-324.

Haghighat F., Huang H., Lee C.S. 2005. Modeling approaches for indoor air VOC emissions from dry building materials – a review. ASHRAE Transactions 111, 635-645.

Huang H., Haghighat F. 2002 . Modeling of volatile organic compounds emission from dry building material. Building and Environment, 37(12): pp 1127-1138.

La Scala U.C., Orlicki J., Jain R., Palmese G., Vaidya U., Sands J.M. 2006. Emission modeling of styrene from vinyl ester resins. Clean Technology Environmental Policy. DOI 10.1007/s10098-006-0076-1.

Little J.C., Hodgson A.T., Gadgil A.J. 1994. Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment, 28(2):227-234.

Lyman W.J, Reehl W.F., Rosenblatt D.H. 1990. Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington D.C. 960 pp., 17-4.

Seo J., Kato S., Ataka Y., Zhu, Q. 2005. Evaluation of Effective Diffusion Coefficient in Various Building Materials and Absorbents by Mercury Intrusion Porosimetry. Indoor Air, The 10th International Conference on Indoor Air Quality and Climate, Sep. 4 – Sep. 9, 2005.

Sparks, L.E. Tichenor, B.A. Chang J. Guo, Z. 1996. Gas-phase mass transfer model for predicting volatile organic compound (VOC) emission rates from indoor pollutant sources. Indoor Air, 6(1), 31-40.

Xiong J., Zhang Y. 2010. Impact of Temperature on the initial emittable concentration of formaldehyde in building materials: experimental observation. Indoor Air; 20:523-529.

Xu Y, Zhang Y. 2003. A general model for analyzing single surface VOC emission from building materials and its application. Atmospheric Environment, 38:113-119.

Yang X., Chen Q., Zhang J.S. 1998. Impact of early stage incomplete mixing on estimating VOC emissions in small test chambers. Indoor Air, 8:180-189.

Zhang J. S. and Shaw C. Y. Modeling of Volatile Organic Compound (VOC) Emissions from Building Materials/Furnishings - a literature review. National Research Council Canada, Report No. IRC-IR-755, December 1997. 24 pp.

Zhang Y, Xu Y. 2003. Characteristics and correlations of VOC emissions from building materials. International Journal of Heat and Mass Transfer, 46:4877-4883.

Zhang Y., Luo X., Wang X., Qian K., Zhao R. Influence of temperature on formaldehyde emission parameters of dry building materials. Atmospheric Environment, 2007, 41:3203-3216.

CHAPTER 5

SUMMARY

Styrene Emission from VERTCM

As the United States moves toward its goal of energy independence, one component of that goal will consist of energy-efficient transportation. Advanced composite materials are lighter and stronger than metals typically used in transportation (e.g. steel, aluminum), and are expected to replace metal in many forms of transportation and institutional design (wall partitions, seating, ceilings, stairs, etc.). In transit applications, these lightweight composite materials promote efficiency by reducing the costs of fuel consumption, replacing heavier metal components in truck and car cabins, bus, train, ship and airplane hulls, and in other components. As an example, Boeing's new Dreamliner 787, which is more than 60% composite material, can carry more cargo for longer distances on an equivalent amount of fuel, reducing carbon emissions (www.boeing.com). In the interest of smart community design, composite materials are anticipated to increase in demand because of their strength, light weight, formable structure and resistance to corrosion and degradation.

One challenge with composite materials is keeping them cost effective. Some composite materials require heat and/or pressure for curing, which increases cost as well as carbon emissions, a concern for climate change scientists. Some composites, such as vinyl ester resin thermoset composite material (VERTCM), can be room-temperature cured and are advantageous in that they can be effectively used for the formation of large structures such as train and airplane hulls without additional energy input. TCMs are the preferred composite in aeronautical applications because they do not deform at extreme temperatures. VERTCMs typically use styrene as a diluent and strengthener in the resin molding process. Because styrene is classified as a Hazardous Air Pollutant (HAP) by the USEPA, many composite manufacturers are moving toward lower styrene resins or other diluents and strengtheners (such as plant-based resins) that may not be as cost effective or resistant to damage and deterioration as the styrene-based VERTCMs.

Additionally, Ziaee and Palmese (1999) have shown that as much as 50% of styrene monomer in VERTCM remains unreacted after cure, with the potential to emit from the composite long after manufacture. Therefore, the interior air of enclosed spaces could present a health hazard to workers (drivers, pilots, etc.) and occupants. Preliminary research indicates that while some styrene monomer may remain unreacted with the potential to emit from the material, it is not likely that all unreacted styrene is available for emission because of the limited availability of connected pore space within any given material (Xiong and Zhang, 2010). Also, the diffusion and partitioning of styrene out of a composite is rate-limited, so that the emissions may be less than that which would present a potential health hazard.

Given the concerns and implications described above, it is important to the billion-dollar-per-year composite industry and the protection of human health to answer the following question: Does the potential for unreacted styrene emitted from vinyl ester resin composite material represent a substantial concern to worker and public health, thereby justifying styrene's removal and/or replacement with potentially more expensive and less effective diluents and strengtheners?

VERTCM Emission Factors Applied to Two Exposure Scenarios

The emission factors (EF) for VERTCM were determined from the chamber profiles of air styrene concentrations over a range of temperatures (Chapter 2) by the following equation.

$$EF(t_i) = \frac{\left(\frac{\Delta C_i}{\Delta t_i} + NC_i \right)}{L} \tag{1}$$

where: $EF(t_i)$ = emission factor at time t_i (mg m^{-2} h^{-1})

$\Delta C_i/\Delta t_i$ = the slope of the time-concentration curve at time t_i

C_i = chamber concentration at time t_i (mg m^{-3})

N = air change rate (h^{-1})

L = loading factor (m^2 m^{-3})

The emission rate (ER) of styrene from VERTCM can also be determined from the EF, by

$$ER = EF(A) \tag{2}$$

where: ER = emission rate (mg h^{-1})

EF = emission factor (mg m^{-2} h^{-1})

A = source area (m^2)

The resultant concentration, C (mg m^{-3}), of VOC in air is derived by Equation (3),

$$C = \frac{EFxA}{Q} = \frac{ER}{Q} \tag{3}$$

where A is exposed material surface area (m^2) and Q is air flow (m^3 h^{-1}), which is equivalent to air exchange rate per hour (ACH) when adjusted for volume (m^3).

Determination of the emission factor during the latter stages of the emission profile, where the slope of the profile becomes quasi-static, allows for the determination of potential indoor air concentrations given a known material exposed surface area and room air exchange rate at a specific point in time. The time for VOC concentrations to reach undetectable levels (i.e. y = 0) can also be estimated by extending the emission profile based on the slope of the line. Integrating the mass emitted as a function of time (mg m^{-3} min) and multiplying it with flow rate (m^3 min^{-1}) allows the total mass (mg) of VOC emitted from the material to be calculated (Eq. 4 and Table 1).

$$Mass = \int_{t=0}^{T} C(t)dt \tag{4}$$

Table 1. Emission parameters of VERTCM over a temperature range.

Temp (°C)	Mass (mg)	Slope (10^{-5})	EF (mg $m^{-2}hr^{-1}$)
10	2.11	1.46	0.009
23	5.98	3.45	0.015
30	9.77	3.84	0.017
40	13.73	4.34	0.022
50	17.87	4.74	0.025

The purpose of this exercise is to determine the emission characteristics of styrene from a VERTCM, and to model the emissions to estimate the potential for the material to contribute to human inhalation health hazards. Using conservative parameters (i.e. high emission factor, low air exchange rate), the emission factor was used to estimate elevated styrene inhalation exposures in indoor/enclosed spaces for simulated truck and airplane interiors.

For the truck scenario, an interior cabin volume of 12 m^3 (V = 2 m x 2 m x 3 m) with 32 m^2 exposed VERTCM was assumed. Multiplying the emission factor (EF) determined previously for VERTCM at 50°C (EF = 0.025 mg $m^{-2}hr^{-1}$) with the exposed surface area (A) gives the emission rate (ER). Assuming a conservative air exchange rate (Q/V ≈ air changes per hour or ACH) of 1.0 ACH, the potential exposure (C mg m^3) can be calculated by dividing ER by Q (Eq. 3).

For the airplane exposure scenario, parameters for interior volume (V m^3) and exposed material surface area (A m^2) were based on dimensions of Boeing's 787 Dreamliner, a new production transport aircraft utilizing approximately 60% composite material (Figure 1). It should be noted that the Boeing 787 Dreamliner described in this study and used to estimate the styrene emission factor for estimating inhalation exposures is not constructed from VERTCM but from an advanced carbon composite. An air exchange rate (Q m^3 h^{-1}) was based on 50% of the lower bound of the recommended 20-30 ACH for commercial aircraft with 50% recycling of air (Hunt and Space, 2011). Emission factor was set for an elevated operating temperature of 30°C (EF = 0.017 mg m^{-2} h^{-1}).

Figure 1. Boeing 787 Dreamliner (see Appendix C)

Modeled air-styrene concentrations (C) from the VERTCM composite for a hypothetical truck cabin and airplane fuselage (Table 2) indicate that inhalation exposures should not exceed the lowest available nonoccupational exposure limit under extreme conditions (ATSDR, 1998).

Table 2. Exposure model input and output parameters

Type	V (m^3)	A (m^2)	EF ($mg\ m^{-2}\ h^{-1}$)	ER ($mg\ h^{-1}$)	ACH (h^{-1})	Q ($m^3\ hr^{-1}$)	C ($mg\ m^{-3}$)	ATSDR ($mg\ m^{-3}$)
Truck	12	32	0.017	0.54	1	12	0.05	0.25
Airplane	876	410	0.025	10.5	10	8,760	0.001	0.25

(V = interior volume, A = exposed material surface area, Q = air flow rate through interior, C = predicted indoor air styrene concentration, and ATSDR = Agency for Toxic Substances and Disease Registry Minimal Risk Level for nonoccupational chronic exposures to inhaled styrene.)

Additionally, at 48 hours after test initiation, the average styrene concentration for all five test temperatures dropped to below 0.20 mg m^{-3} (Table 3). This is representative of indoor air styrene concentrations of between 0.015 ppm and 0.045 ppm between 10°C and 50°C. These concentrations are all below the Agency for Toxic Substances and Disease Registry's (ATSDR, 2008) Minimal Risk Level (MRL) of 0.25 mg m^{-3} for continuous, year-round, daily inhalation exposures to styrene below which no appreciable increased risk is expected. This suggests that, with limited material loading (exposed surface area) and sufficient air exchange rate, after the initial evaporative emissions of styrene have ceased, it is possible that inhalation exposures to styrene emitted from like VERTCM composites in enclosed spaces can be controlled to below the most conservative current regulatory guidelines for chronic exposures.

Table 3. Chamber styrene concentration data

Temperature (°C)	Chamber Concentration at 1 hour (mg m^{-3})	Chamber Concentration at 48 hours (mg m^{-3})	48 Hr. Parts Per Million (ppm)
10	0.74 ± 0.1	0.068 ± 0.007	0.015
23	3.13 ± 0.6	0.127 ± 0.014	0.029
30	8.85 ± 0.7	0.137 ± 0.023	0.033
40	14.4 ± 0.7	0.166 ± 0.020	0.041
50	22.4 ± 1.4	0.168 ± 0.032	0.043

Study Limitations

One limitation to the analyses performed here is that the materials tested were research quality materials and not products made for consumer consumption, even though these materials are of similar composition and production to those found in the marketplace. Also, model validation was conducted using parameters estimated from data derived in the laboratory, without the benefit of third-party validation of the estimates prior to completion of this document. While the estimates are similar to some reported in the literature, and while the mass transfer model performed well at the temperature for which it was designed (23°C), it would be beneficial to have confirmation of these laboratory findings.

Project Significance and Conclusions

The following conclusions can be drawn from this study.

1. Styrene emits from VERTCM post cure.
2. Styrene mass emitted and emission factor increase with increasing temperature.
3. Only a fraction (Ce) of styrene originally present (Co) in the VERTCM is available to emit.
4. An existing mass transfer model appropriately predicts diffusive (>48 h) air styrene concentrations emitted from VERTCM at 23°C using the parameters measured or estimated independently the laboratory.
5. The mass transfer model significantly underestimates diffusive air styrene concentrations when compared to chamber data for temperatures >23°C.
6. The mass transfer model can be empirically adjusted to appropriately fit diffusive air styrene concentrations emitted from similar VERTCM by corrections to the diffusion coefficient (D) and emitted fraction during the diffusive stage of emissions (i.e. Ce,df).
7. The emission data obtained here can be used in the validation and development of physical models for predicting VOC emissions from dry building materials at various temperatures for the anticipation, evaluation and control of IAQ investigations.

This project is significant in that the materials being tested are novel, emit styrene, and are expected to play a larger role in commercial applications in the future. There are no data in the literature pertaining to the use of a small environmental test chamber to measure styrene emissions from VERTCM. There is evidence that styrene emissions from some types of VERTCM can result in indoor air styrene concentrations that exceed exposure guidelines (Chapter 2).

Emission of styrene takes on new importance in light of recent statements about the concerns to human health from styrene exposures. In October 2010, the State of Washington included styrene on a list of 59 chemicals of concern (COC) in products and manufacturing with negative implications for children's health. In November 2010, the USEPA reported they would begin screening 134 chemicals for potential contributions to endocrine disruption in humans in 2011; styrene is included on this list. On June 10, 2011, the U.S. National Institute for Environmental Health Sciences added styrene to a list of 240 known or possible human carcinogens, joining the World Health Organization's International Agency for Research on Cancer (IARC, 2002) in assessment of styrene's carcinogenic potential.

There is a need to know what potential for human exposures to styrene is created when using VERTCM in an indoor or enclosed environment. Not only does this research contribute to the advancement of public health and the scientific literature, but also can serve to stimulate future work, especially as the effects of temperature on the diffusivity and partitioning of volatile organic compounds from building materials, as well as the effects of material density and porosity on availability of VOC to emit from a material, are currently being characterized and modeled.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2008. ATSDR HazDat, Air Comparison Values in ppb (for VOC Compounds Only). February 12, 2008. Page 2 of 3.

Hunt E.H., Space D.R. The Airplane Cabin Environment. Issues Pertaining to Flight Attendant Comfort. [Accessed June 2011.] Available at: http://www.boeing.com/commercial/cabinair/ventilation.pdf

International Agency for Research on Cancer (IARC). 2002. IARC Monographs Volumes 1-88. Styrene [100-42-5]; 60(82).

Xiong J., Zhang Y. 2010. Impact of Temperature on the initial emittable concentration of formaldehyde in building materials: experimental observation. Indoor Air; 20: 523-529.

Ziaee S., Palmese G.R. 1999. Effects of temperature on cure kinetics and mechanical properties of vinyl ester resins. Journal of Polymer Science; 37:725-744.

APPENDIX A

MICROMERITICS VERTCM DENSITY AND POROSITY DATA

MICROMERITICS
ANALYTICAL *The Particle Testing Authority*
SERVICES

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
Bar Code:
File: C:\...\05MAY\10-2465B.SMP

Analysis Gas: Nitrogen
Reported: 5/26/2010 9:44:40AM
Sample Mass: 11.6292 g
Temperature: 22.51 °C
Number of Purges: 10

Analysis Start: 5/26/2010 9:09:41AM
Analysis End: 5/26/2010 9:35:42AM
Equilib. Rate: 0.005 psig/min
Expansion Volume: 74.2450 cm³
Cell Volume: 38.1050 cm³

Density and Volume Table

Cycle#	Volume (cm³)	Volume Deviation (cm³)	Density (g/cm³)	Density Deviation (g/cm³)	Elapsed Time (mm:ss)	Temperature (°C)
1	6.1665	0.0013	1.8859	-0.0004	9:18	22.50
2	6.1644	-0.0008	1.8865	0.0002	11:05	22.51
3	6.1636	-0.0016	1.8867	0.0005	12:53	22.48
4	6.1662	0.0010	1.8860	-0.0003	14:36	22.52
5	6.1656	0.0004	1.8862	-0.0001	16:25	22.51
6	6.1647	-0.0005	1.8864	0.0001	18:12	22.54
7	6.1652	0.0000	1.8863	0.0000	20:00	22.50
8	6.1634	-0.0018	1.8868	0.0005	21:47	22.54
9	6.1673	0.0021	1.8856	-0.0006	23:35	22.50
10	6.1651	-0.0001	1.8863	0.0000	25:24	22.53

Summary Data	Average	Standard Deviation
Volume:	6.1652 cm³	0.0012 cm³
Density:	1.8863 g/cm³	0.0004 g/cm³

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2465.SMP

LP Analysis Time: 5/26/2010 12:01:19PM
HP Analysis Time: 5/26/2010 2:17:00PM
Report Time: 5/26/2010 2:17:00PM

Sample Weight: 3.6440 g
Correction Type: None
Show Neg. Int: No

Summary Report

Penetrometer parameters

Penetrometer:	705 - (02) 15 Bulb, 0.392 Stem, Powder		
Pen. Constant:	11.117 µL/pF	Pen. Weight:	73.0411 g
Stem Volume:	0.3920 mL	Max. Head Pressure:	4.4500 psia
Pen. Volume:	14.2463 mL	Assembly Weight:	242.8272 g

Hg Parameters

Adv. Contact Angle:	130.000 degrees	Rec. Contact Angle:	130.000 degrees
Hg Surface Tension:	485.000 dynes/cm	Hg Density:	13.5335 g/mL

Low Pressure:

Evacuation Pressure:	50 µmHg
Evacuation Time:	5 mins
Mercury Filling Pressure:	0.54 psia
Equilibration Time:	10 secs

High Pressure:

Equilibration Time:	10 secs

No Blank Correction

Intrusion Data Summary

Total Intrusion Volume = 0.0354 mL/g
Total Pore Area = 13.411 m²/g
Median Pore Diameter (Volume) = 0.0160 µm
Median Pore Diameter (Area) = 0.0050 µm
Average Pore Diameter (4V/A) = 0.0106 µm
Bulk Density at 0.54 psia = 1.8498 g/mL
Apparent (skeletal) Density = 1.9793 g/mL
Porosity = 6.5429 %
Stem Volume Used = 33 %

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2465.SMP

LP Analysis Time: 5/26/2010 12:01:19PM
HP Analysis Time: 5/26/2010 2:17:00PM
Report Time: 5/26/2010 2:17:01PM

Sample Weight: 3.6440 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
0.54	333.9105	0.0000	0.0000	0.000	0.000
0.77	234.5124	0.0038	0.0038	0.000	0.000
1.02	177.5552	0.0045	0.0007	0.000	0.000
2.01	89.9706	0.0056	0.0010	0.000	0.000
3.00	60.2082	0.0059	0.0003	0.000	0.000
4.01	45.1556	0.0062	0.0003	0.000	0.000
5.50	32.8757	0.0065	0.0003	0.000	0.000
6.99	25.8563	0.0068	0.0003	0.000	0.000
8.49	21.2991	0.0070	0.0002	0.000	0.000
10.49	17.2456	0.0072	0.0002	0.000	0.000
12.97	13.9411	0.0074	0.0002	0.000	0.000
15.97	11.3271	0.0076	0.0002	0.000	0.000
20.00	9.0422	0.0080	0.0004	0.001	0.000
22.99	7.8657	0.0083	0.0003	0.001	0.000
25.00	7.2354	0.0085	0.0002	0.001	0.000
29.96	6.0376	0.0093	0.0008	0.001	0.000
36.33	4.9777	0.0093	0.0000	0.001	0.000
46.82	3.8629	0.0094	0.0001	0.001	0.000
57.10	3.1676	0.0095	0.0001	0.001	0.000
71.54	2.5281	0.0095	0.0001	0.002	0.000
86.72	2.0856	0.0096	0.0000	0.002	0.000
111.82	1.6175	0.0096	0.0001	0.002	0.000
137.03	1.3198	0.0097	0.0001	0.002	0.000
172.61	1.0478	0.0098	0.0001	0.002	0.000
217.28	0.8324	0.0098	0.0001	0.002	0.000
266.43	0.6788	0.0099	0.0000	0.003	0.000
327.32	0.5526	0.0099	0.0000	0.003	0.000
417.63	0.4331	0.0099	0.0001	0.003	0.000
517.40	0.3496	0.0100	0.0000	0.004	0.000
636.48	0.2842	0.0100	0.0000	0.004	0.000
696.90	0.2595	0.0101	0.0000	0.005	0.000
796.96	0.2269	0.0101	0.0000	0.005	0.001
987.83	0.1831	0.0102	0.0001	0.006	0.001
1196.13	0.1512	0.0102	0.0000	0.007	0.001
1297.32	0.1394	0.0103	0.0001	0.009	0.002
1396.99	0.1295	0.0103	0.0000	0.010	0.001
1496.99	0.1208	0.0103	0.0000	0.011	0.001
1596.68	0.1133	0.0104	0.0000	0.012	0.001
1696.72	0.1066	0.0104	0.0000	0.014	0.001
1894.52	0.0955	0.0105	0.0001	0.016	0.003
2044.96	0.0884	0.0105	0.0000	0.018	0.002

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2465.SMP

LP Analysis Time: 5/26/2010 12:01:19PM
HP Analysis Time: 5/26/2010 2:17:00PM
Report Time: 5/26/2010 2:17:01PM

Sample Weight: 3.6440 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (μm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
2195.34	0.0824	0.0106	0.0001	0.021	0.003
2344.48	0.0771	0.0106	0.0000	0.023	0.002
2494.29	0.0725	0.0107	0.0001	0.026	0.003
2645.08	0.0684	0.0107	0.0001	0.029	0.003
2694.35	0.0671	0.0107	0.0000	0.030	0.001
2843.33	0.0636	0.0108	0.0001	0.033	0.003
2993.61	0.0604	0.0108	0.0001	0.037	0.003
3243.99	0.0558	0.0109	0.0001	0.042	0.005
3493.76	0.0518	0.0110	0.0001	0.048	0.006
3742.55	0.0483	0.0111	0.0001	0.055	0.007
3992.33	0.0453	0.0112	0.0001	0.062	0.006
4240.84	0.0426	0.0112	0.0001	0.070	0.008
4486.94	0.0403	0.0113	0.0001	0.078	0.008
4725.38	0.0383	0.0114	0.0001	0.085	0.008
4982.35	0.0363	0.0115	0.0001	0.096	0.010
5282.57	0.0342	0.0116	0.0001	0.107	0.011
5483.48	0.0330	0.0117	0.0001	0.115	0.009
5731.70	0.0316	0.0118	0.0001	0.126	0.011
5982.72	0.0302	0.0119	0.0001	0.138	0.012
6229.50	0.0290	0.0119	0.0001	0.149	0.011
6479.17	0.0279	0.0120	0.0001	0.165	0.015
6728.15	0.0269	0.0121	0.0001	0.179	0.014
6978.37	0.0259	0.0129	0.0008	0.298	0.119
7477.78	0.0242	0.0131	0.0002	0.323	0.026
7976.57	0.0227	0.0132	0.0002	0.350	0.026
8475.09	0.0213	0.0134	0.0001	0.376	0.026
8974.13	0.0202	0.0136	0.0002	0.411	0.036
9271.71	0.0195	0.0137	0.0001	0.435	0.023
9570.01	0.0189	0.0138	0.0001	0.461	0.027
10022.97	0.0180	0.0140	0.0002	0.506	0.044
10469.78	0.0173	0.0143	0.0002	0.562	0.056
10974.08	0.0165	0.0145	0.0002	0.620	0.058
11470.37	0.0158	0.0187	0.0042	1.655	1.035
11969.81	0.0151	0.0193	0.0006	1.813	0.158
12573.63	0.0144	0.0195	0.0002	1.866	0.053
13073.84	0.0138	0.0197	0.0002	1.915	0.049
13623.26	0.0133	0.0202	0.0005	2.073	0.158
13969.70	0.0129	0.0203	0.0001	2.104	0.031
14307.43	0.0126	0.0204	0.0001	2.141	0.038
14565.99	0.0124	0.0205	0.0001	2.178	0.037
14970.35	0.0121	0.0207	0.0001	2.224	0.046

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2465.SMP

LP Analysis Time: 5/26/2010 12:01:19PM
HP Analysis Time: 5/26/2010 2:17:00PM
Report Time: 5/26/2010 2:17:01PM

Sample Weight: 3.6440 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (μm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m^2/g)	Incremental Pore Area (m^2/g)
15420.15	0.0117	0.0208	0.0002	2.277	0.053
15764.44	0.0115	0.0210	0.0001	2.323	0.046
16168.53	0.0112	0.0211	0.0002	2.378	0.056
16614.60	0.0109	0.0213	0.0002	2.442	0.064
16966.74	0.0107	0.0215	0.0002	2.507	0.065
17314.95	0.0104	0.0221	0.0006	2.727	0.220
17666.92	0.0102	0.0222	0.0001	2.778	0.051
18066.34	0.0100	0.0225	0.0003	2.906	0.128
18416.26	0.0098	0.0226	0.0001	2.957	0.051
18760.05	0.0096	0.0228	0.0001	3.012	0.055
19159.72	0.0094	0.0229	0.0001	3.074	0.062
19759.85	0.0092	0.0231	0.0002	3.162	0.088
20267.18	0.0089	0.0233	0.0002	3.242	0.080
20771.03	0.0087	0.0235	0.0002	3.328	0.086
21176.59	0.0085	0.0237	0.0002	3.402	0.074
21630.28	0.0084	0.0238	0.0002	3.487	0.085
22030.87	0.0082	0.0240	0.0002	3.572	0.084
22632.60	0.0080	0.0243	0.0003	3.716	0.144
23183.86	0.0078	0.0244	0.0001	3.746	0.030
23735.36	0.0076	0.0246	0.0002	3.873	0.126
24086.73	0.0075	0.0247	0.0001	3.948	0.075
24636.56	0.0073	0.0249	0.0002	4.052	0.103
25036.39	0.0072	0.0251	0.0001	4.130	0.079
25437.98	0.0071	0.0252	0.0001	4.210	0.080
25887.72	0.0070	0.0254	0.0002	4.300	0.090
26438.72	0.0068	0.0256	0.0002	4.407	0.107
26937.98	0.0067	0.0257	0.0002	4.514	0.107
27387.78	0.0066	0.0259	0.0001	4.594	0.080
27788.96	0.0065	0.0260	0.0002	4.688	0.094
28239.65	0.0064	0.0262	0.0002	4.784	0.096
28990.19	0.0062	0.0264	0.0002	4.933	0.149
29489.96	0.0061	0.0266	0.0002	5.040	0.107
29990.32	0.0060	0.0268	0.0002	5.150	0.110
30439.42	0.0059	0.0269	0.0002	5.261	0.111
30887.64	0.0059	0.0271	0.0002	5.366	0.106
31287.48	0.0058	0.0274	0.0003	5.584	0.218
31776.03	0.0057	0.0274	0.0000	5.602	0.018
32319.92	0.0056	0.0276	0.0002	5.763	0.161
32870.18	0.0055	0.0278	0.0002	5.892	0.129
33459.98	0.0054	0.0280	0.0002	6.047	0.155
33958.87	0.0053	0.0282	0.0002	6.181	0.134

Sample: UAB Composite #1
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2465.SMP

LP Analysis Time: 5/26/2010 12:01:19PM
HP Analysis Time: 5/26/2010 2:17:00PM
Report Time: 5/26/2010 2:17:01PM

Sample Weight: 3.6440 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
34596.50	0.0052	0.0284	0.0002	6.309	0.128
35441.57	0.0051	0.0286	0.0003	6.505	0.196
36146.13	0.0050	0.0289	0.0002	6.682	0.177
36945.23	0.0049	0.0291	0.0002	6.858	0.176
37592.70	0.0048	0.0295	0.0005	7.236	0.379
38393.62	0.0047	0.0298	0.0003	7.449	0.212
39142.97	0.0046	0.0300	0.0002	7.647	0.198
39944.93	0.0045	0.0303	0.0002	7.858	0.211
40440.91	0.0045	0.0304	0.0002	8.012	0.155
40940.77	0.0044	0.0306	0.0002	8.196	0.183
42445.24	0.0043	0.0311	0.0005	8.636	0.440
43291.39	0.0042	0.0314	0.0002	8.857	0.221
43941.61	0.0041	0.0316	0.0002	9.064	0.207
44943.51	0.0040	0.0318	0.0003	9.328	0.264
46445.92	0.0039	0.0322	0.0004	9.693	0.366
47946.19	0.0038	0.0326	0.0004	10.066	0.373
49443.53	0.0037	0.0329	0.0004	10.463	0.397
50142.97	0.0036	0.0332	0.0003	10.740	0.276
52944.57	0.0034	0.0337	0.0006	11.387	0.647
54442.97	0.0033	0.0341	0.0004	11.832	0.445
55934.69	0.0032	0.0345	0.0004	12.280	0.448
57919.00	0.0031	0.0349	0.0004	12.832	0.552
59896.55	0.0030	0.0354	0.0004	13.411	0.578

MICROMERITICS
ANALYTICAL *The Particle Testing*
SERVICES *Authority*

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
Bar Code:
File: C:\...\05MAY\10-2466.SMP

Analysis Gas: Nitrogen
Reported: 5/26/2010 10:43:08AM
Sample Mass: 10.1226 g
Temperature: 22.55 °C
Number of Purges: 10

Analysis Start: 5/26/2010 10:08:39AM
Analysis End: 5/26/2010 10:35:27AM
Equilib. Rate: 0.005 psig/min
Expansion Volume: 74.2450 cm^3
Cell Volume: 38.1050 cm^3

Density and Volume Table

Cycle#	Volume (cm^3)	Volume Deviation (cm^3)	Density (g/cm^3)	Density Deviation (g/cm^3)	Elapsed Time (mm:ss)	Temperature (°C)
1	5.2419	0.0030	1.9311	-0.0011	9:36	22.52
2	5.2379	-0.0011	1.9326	0.0004	11:26	22.54
3	5.2392	0.0003	1.9321	-0.0001	13:16	22.55
4	5.2404	0.0014	1.9317	-0.0005	15:06	22.57
5	5.2389	0.0000	1.9322	0.0000	16:56	22.55
6	5.2392	0.0002	1.9321	-0.0001	18:48	22.55
7	5.2377	-0.0013	1.9327	0.0005	20:39	22.57
8	5.2401	0.0011	1.9318	-0.0004	22:27	22.57
9	5.2370	-0.0020	1.9329	0.0007	24:18	22.54
10	5.2374	-0.0016	1.9328	0.0006	26:11	22.58

Summary Data	Average	Standard Deviation
Volume:	5.2390 cm^3	0.0015 cm^3
Density:	1.9322 g/cm^3	0.0005 g/cm^3

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2466A.SMP

LP Analysis Time:	5/26/2010 3:16:33PM	Sample Weight:	6.7394 g
HP Analysis Time:	5/26/2010 5:37:01PM	Correction Type:	None
Report Time:	5/26/2010 5:37:01PM	Show Neg. Int:	No

Summary Report

Penetrometer parameters

Penetrometer: 307 - (02) 15 Bulb, 0.392 Stem, Powder

Pen. Constant:	10.898 µL/pF	Pen. Weight:	82.4518 g
Stem Volume:	0.3920 mL	Max. Head Pressure:	4.4500 psia
Pen. Volume:	14.3586 mL	Assembly Weight:	235.4033 g

Hg Parameters

Adv. Contact Angle:	130.000 degrees	Rec. Contact Angle:	130.000 degrees
Hg Surface Tension:	485.000 dynes/cm	Hg Density:	13.5335 g/mL

Low Pressure:

Evacuation Pressure:	50 µmHg
Evacuation Time:	5 mins
Mercury Filling Pressure:	0.54 psia
Equilibration Time:	10 secs

High Pressure:

Equilibration Time:	10 secs

No Blank Correction

Intrusion Data Summary

Total Intrusion Volume = 0.0236 mL/g
Total Pore Area = 10.444 m²/g
Median Pore Diameter (Volume) = 0.0106 µm
Median Pore Diameter (Area) = 0.0048 µm
Average Pore Diameter (4V/A) = 0.0090 µm
Bulk Density at 0.54 psia = 1.8958 g/mL
Apparent (skeletal) Density = 1.9846 g/mL
Porosity = 4.4729 %
Stem Volume Used = 41 %

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2466A.SMP

LP Analysis Time: 5/26/2010 3:16:33PM
HP Analysis Time: 5/26/2010 5:37:01PM
Report Time: 5/26/2010 5:37:01PM

Sample Weight: 6.7394 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
0.54	332.7116	0.0000	0.0000	0.000	0.000
0.77	234.2463	0.0010	0.0010	0.000	0.000
1.02	177.6184	0.0015	0.0005	0.000	0.000
2.01	90.0571	0.0024	0.0009	0.000	0.000
3.01	60.0960	0.0030	0.0005	0.000	0.000
4.01	45.1518	0.0032	0.0002	0.000	0.000
5.50	32.8627	0.0035	0.0003	0.000	0.000
7.00	25.8468	0.0037	0.0002	0.000	0.000
8.49	21.2979	0.0038	0.0002	0.000	0.000
10.48	17.2512	0.0040	0.0001	0.000	0.000
12.98	13.9384	0.0041	0.0001	0.000	0.000
15.97	11.3264	0.0043	0.0001	0.000	0.000
20.01	9.0408	0.0044	0.0001	0.000	0.000
23.00	7.8648	0.0045	0.0001	0.000	0.000
25.00	7.2359	0.0045	0.0001	0.000	0.000
29.96	6.0368	0.0047	0.0001	0.000	0.000
36.07	5.0141	0.0047	0.0000	0.001	0.000
46.30	3.9060	0.0048	0.0001	0.001	0.000
56.70	3.1897	0.0048	0.0001	0.001	0.000
71.61	2.5258	0.0049	0.0001	0.001	0.000
86.53	2.0901	0.0050	0.0001	0.001	0.000
111.26	1.6256	0.0050	0.0001	0.001	0.000
136.63	1.3237	0.0051	0.0001	0.001	0.000
172.02	1.0514	0.0052	0.0001	0.001	0.000
216.33	0.8361	0.0052	0.0001	0.002	0.000
265.73	0.6806	0.0053	0.0000	0.002	0.000
326.51	0.5539	0.0053	0.0000	0.002	0.000
416.39	0.4344	0.0054	0.0000	0.003	0.000
516.28	0.3503	0.0054	0.0000	0.003	0.000
636.49	0.2842	0.0054	0.0000	0.003	0.001
696.28	0.2598	0.0055	0.0000	0.004	0.000
796.45	0.2271	0.0055	0.0000	0.004	0.000
987.56	0.1831	0.0055	0.0001	0.005	0.001
1196.93	0.1511	0.0056	0.0001	0.006	0.001
1296.30	0.1395	0.0056	0.0000	0.007	0.001
1396.97	0.1295	0.0056	0.0000	0.008	0.001
1496.47	0.1209	0.0057	0.0000	0.009	0.001
1596.97	0.1133	0.0057	0.0000	0.010	0.001
1695.61	0.1067	0.0057	0.0000	0.011	0.001
1896.32	0.0954	0.0058	0.0000	0.013	0.002
2045.15	0.0884	0.0058	0.0000	0.015	0.002

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2466A.SMP

LP Analysis Time: 5/26/2010 3:16:33PM
HP Analysis Time: 5/26/2010 5:37:01PM
Report Time: 5/26/2010 5:37:01PM

Sample Weight: 6.7394 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
2195.64	0.0824	0.0059	0.0000	0.017	0.002
2345.65	0.0771	0.0059	0.0000	0.019	0.002
2495.84	0.0725	0.0059	0.0000	0.021	0.002
2644.09	0.0684	0.0060	0.0000	0.023	0.002
2693.02	0.0672	0.0060	0.0000	0.025	0.001
2845.23	0.0636	0.0060	0.0000	0.027	0.003
2995.14	0.0604	0.0061	0.0000	0.030	0.002
3245.20	0.0557	0.0062	0.0001	0.034	0.005
3493.92	0.0518	0.0062	0.0001	0.039	0.005
3742.46	0.0483	0.0063	0.0001	0.044	0.005
3992.73	0.0453	0.0063	0.0001	0.050	0.006
4241.75	0.0426	0.0064	0.0001	0.057	0.006
4484.84	0.0403	0.0065	0.0001	0.066	0.009
4723.44	0.0383	0.0066	0.0001	0.075	0.009
4988.38	0.0363	0.0067	0.0001	0.084	0.010
5284.84	0.0342	0.0068	0.0001	0.095	0.011
5480.74	0.0330	0.0069	0.0001	0.104	0.009
5730.10	0.0316	0.0069	0.0001	0.114	0.010
5980.81	0.0302	0.0070	0.0001	0.124	0.010
6229.83	0.0290	0.0071	0.0001	0.135	0.011
6476.62	0.0279	0.0072	0.0001	0.147	0.012
6731.25	0.0269	0.0073	0.0001	0.160	0.012
6976.43	0.0259	0.0074	0.0001	0.172	0.013
7474.91	0.0242	0.0075	0.0001	0.195	0.023
7975.08	0.0227	0.0077	0.0001	0.221	0.026
8474.34	0.0213	0.0078	0.0002	0.250	0.029
8972.35	0.0202	0.0080	0.0002	0.279	0.029
9270.68	0.0195	0.0086	0.0006	0.403	0.124
9574.18	0.0189	0.0086	0.0001	0.417	0.014
10023.26	0.0180	0.0088	0.0001	0.445	0.028
10470.83	0.0173	0.0089	0.0001	0.477	0.032
10975.13	0.0165	0.0091	0.0002	0.514	0.037
11472.75	0.0158	0.0098	0.0007	0.688	0.174
11973.34	0.0151	0.0100	0.0003	0.756	0.068
12572.77	0.0144	0.0102	0.0002	0.803	0.048
13072.87	0.0138	0.0104	0.0002	0.851	0.047
13622.15	0.0133	0.0105	0.0002	0.902	0.051
13967.77	0.0129	0.0107	0.0001	0.936	0.034
14308.82	0.0126	0.0108	0.0001	0.978	0.043
14565.09	0.0124	0.0109	0.0001	1.014	0.036
14971.22	0.0121	0.0110	0.0001	1.058	0.044

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2466A.SMP

LP Analysis Time: 5/26/2010 3:16:33PM
HP Analysis Time: 5/26/2010 5:37:01PM
Report Time: 5/26/2010 5:37:01PM

Sample Weight: 6.7394 g
Correction Type: None
Show Neg. Int: No

Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m^2/g)	Incremental Pore Area (m^2/g)
15419.31	0.0117	0.0112	0.0001	1.108	0.049
15764.72	0.0115	0.0113	0.0001	1.152	0.044
16167.47	0.0112	0.0115	0.0001	1.200	0.048
16613.90	0.0109	0.0116	0.0002	1.256	0.056
16968.62	0.0107	0.0117	0.0001	1.304	0.048
17317.07	0.0104	0.0119	0.0001	1.353	0.049
17663.39	0.0102	0.0120	0.0001	1.403	0.050
18066.26	0.0100	0.0121	0.0001	1.461	0.058
18411.65	0.0098	0.0123	0.0001	1.515	0.054
18762.44	0.0096	0.0124	0.0001	1.565	0.051
19163.13	0.0094	0.0125	0.0001	1.626	0.060
19759.33	0.0092	0.0136	0.0010	2.061	0.435
20264.85	0.0089	0.0138	0.0002	2.154	0.093
20775.22	0.0087	0.0139	0.0001	2.218	0.064
21176.71	0.0085	0.0140	0.0001	2.271	0.053
21629.53	0.0084	0.0142	0.0001	2.335	0.064
22030.78	0.0082	0.0143	0.0001	2.382	0.047
22632.99	0.0080	0.0144	0.0002	2.467	0.085
23184.58	0.0078	0.0146	0.0001	2.541	0.074
23736.35	0.0076	0.0147	0.0002	2.619	0.078
24085.65	0.0075	0.0148	0.0001	2.677	0.059
24637.50	0.0073	0.0150	0.0001	2.755	0.078
25036.71	0.0072	0.0154	0.0005	3.010	0.255
25437.10	0.0071	0.0156	0.0001	3.072	0.062
25887.39	0.0070	0.0157	0.0001	3.139	0.067
26439.16	0.0068	0.0158	0.0001	3.219	0.080
26939.28	0.0067	0.0159	0.0001	3.294	0.075
27389.39	0.0066	0.0161	0.0001	3.364	0.070
27789.37	0.0065	0.0162	0.0001	3.429	0.065
28239.85	0.0064	0.0163	0.0001	3.495	0.066
28989.79	0.0062	0.0164	0.0002	3.608	0.113
29489.87	0.0061	0.0166	0.0001	3.689	0.081
29989.93	0.0060	0.0167	0.0001	3.773	0.084
30439.85	0.0059	0.0168	0.0001	3.852	0.079
30889.11	0.0059	0.0169	0.0001	3.932	0.079
31288.71	0.0058	0.0170	0.0001	4.008	0.076
31784.46	0.0057	0.0172	0.0001	4.097	0.089
32324.01	0.0056	0.0173	0.0001	4.193	0.095
32872.98	0.0055	0.0175	0.0002	4.303	0.110
33463.11	0.0054	0.0176	0.0001	4.412	0.109
33955.38	0.0053	0.0178	0.0002	4.586	0.174

Sample: UAB Composite #2
Operator: CB
Submitter: University of Alabama
File: C:\9500\DATA\2010\05MAY\10-2466A.SMP

LP Analysis Time: 5/26/2010 3:16:33PM
HP Analysis Time: 5/26/2010 5:37:01PM
Report Time: 5/26/2010 5:37:01PM

Sample Weight: 6.7394 g
Correction Type: None
Show Neg. Int: No

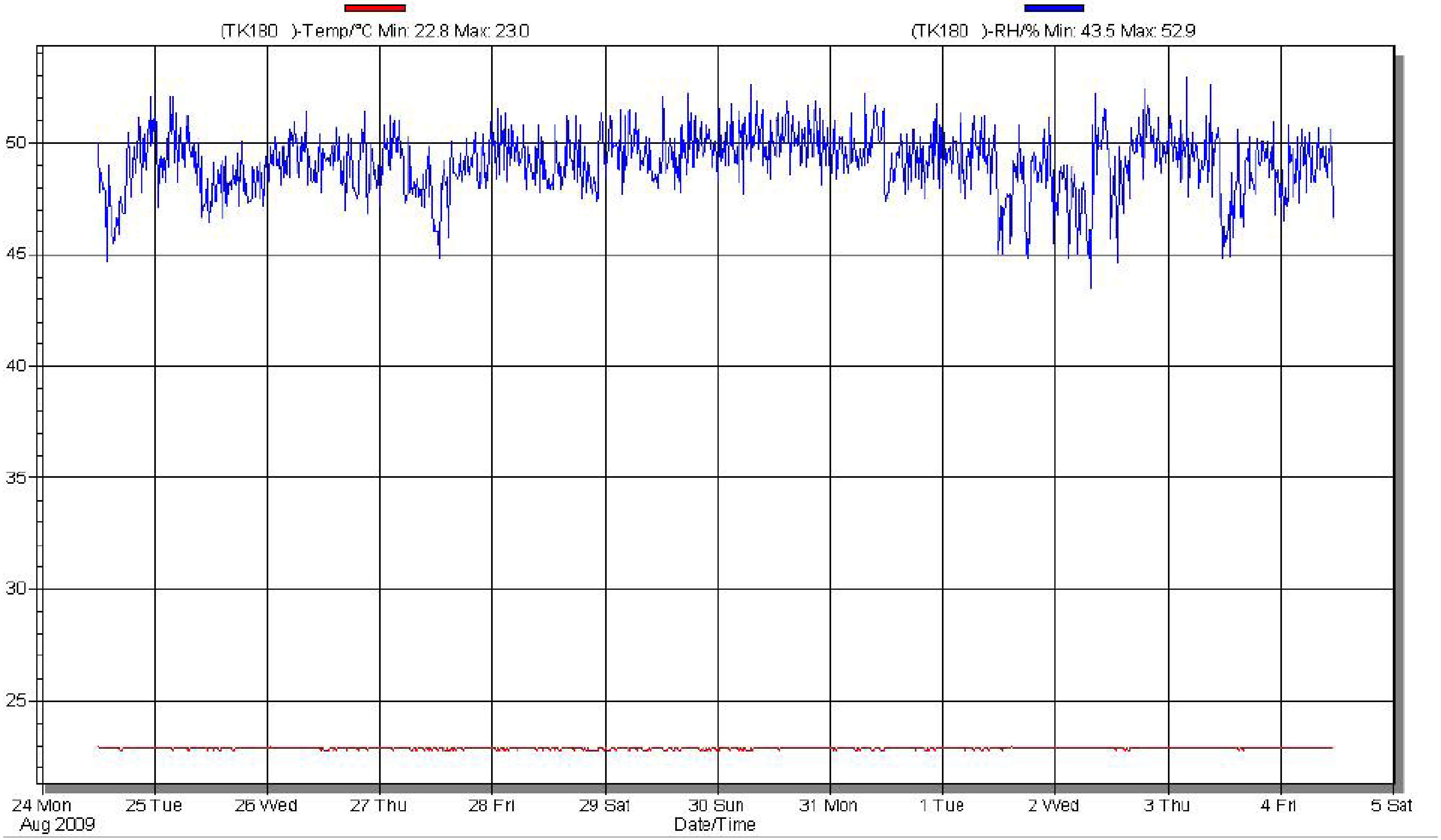
Tabular Report

Pressure (psia)	Pore Diameter (µm)	Cumulative Pore Volume (mL/g)	Incremental Pore Volume (mL/g)	Cumulative Pore Area (m²/g)	Incremental Pore Area (m²/g)
34601.55	0.0052	0.0180	0.0002	4.706	0.119
35446.94	0.0051	0.0182	0.0002	4.861	0.155
36143.79	0.0050	0.0184	0.0002	4.987	0.127
36944.62	0.0049	0.0185	0.0002	5.132	0.145
37595.50	0.0048	0.0187	0.0002	5.264	0.132
38395.48	0.0047	0.0189	0.0002	5.418	0.154
39146.44	0.0046	0.0191	0.0002	5.572	0.154
39947.72	0.0045	0.0192	0.0002	5.731	0.159
40446.09	0.0045	0.0194	0.0002	5.865	0.134
40943.27	0.0044	0.0196	0.0002	6.027	0.162
42444.74	0.0043	0.0199	0.0003	6.302	0.274
43293.02	0.0042	0.0201	0.0002	6.520	0.219
43943.30	0.0041	0.0203	0.0002	6.687	0.166
44942.24	0.0040	0.0205	0.0002	6.903	0.216
46447.34	0.0039	0.0210	0.0005	7.430	0.527
47947.04	0.0038	0.0214	0.0003	7.780	0.350
49445.70	0.0037	0.0216	0.0003	8.094	0.314
50144.84	0.0036	0.0218	0.0002	8.280	0.186
52945.56	0.0034	0.0223	0.0005	8.839	0.559
54442.17	0.0033	0.0226	0.0003	9.185	0.346
55938.77	0.0032	0.0229	0.0003	9.551	0.366
57924.00	0.0031	0.0232	0.0004	9.991	0.441
59897.02	0.0030	0.0236	0.0003	10.444	0.453

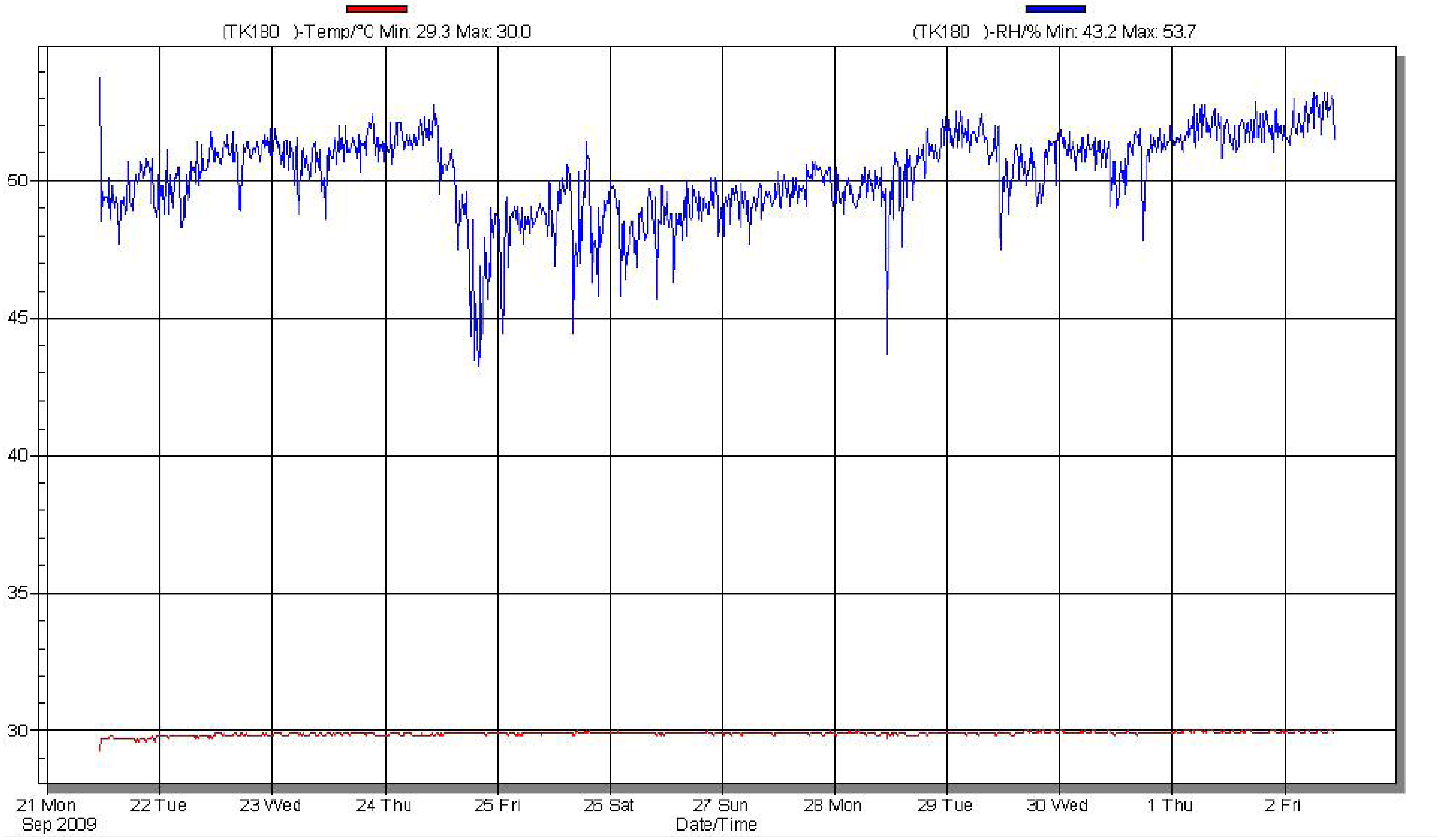
APPENDIX B

TEMPERATURE AND HUMIDITY GRAPHS

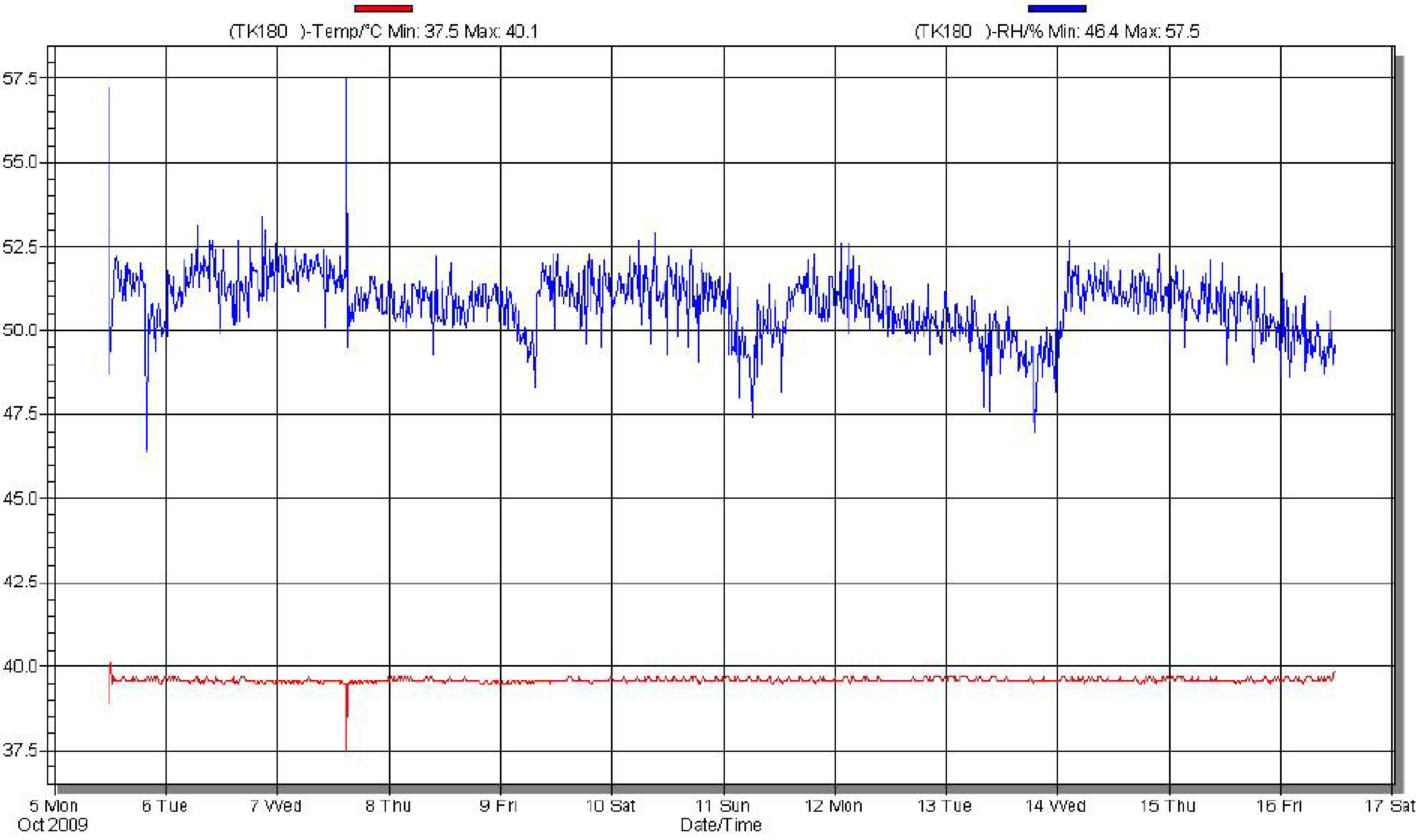
Downloaded Data - Friday, September 04, 2009



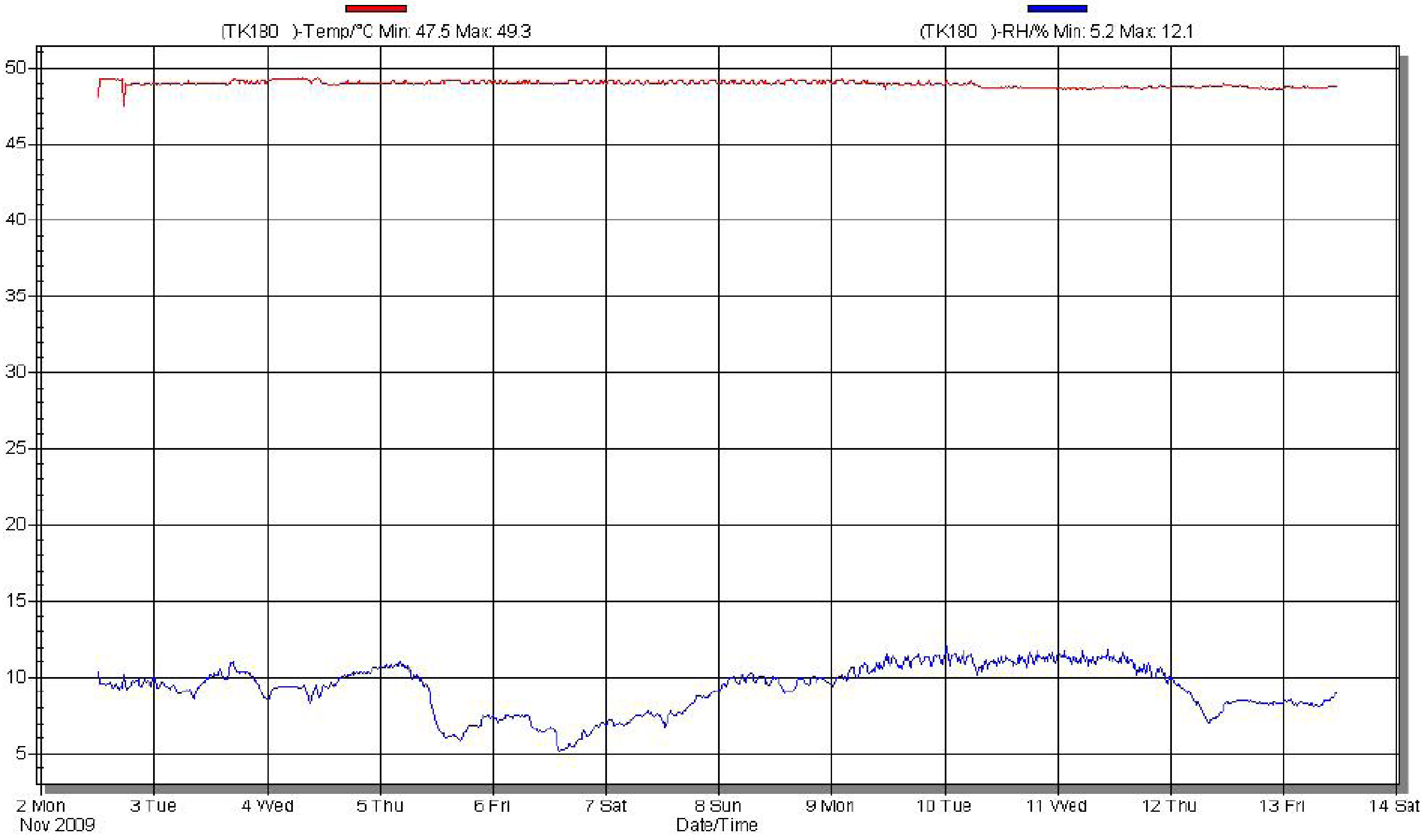
Downloaded Data - Friday, October 02, 2009



Downloaded Data - Friday, October 16, 2009



Downloaded Data - Friday, November 13, 2009



APPENDIX C

STATEMENT ON VERTCM

Statement on VERTCM and other styrene-containing resins

According to the EPRI Center for Materials Production (2000), composite technology began to replace heavier metal in military applications as far back as the 1960s, and has since branched out into a broader market of consumer products (ex. transportation). As far as composites are concerned, reinforced plastics and advanced composites are the two primary resin-based composite products currently produced. Of the reinforced plastics, fiber reinforced plastics (FRP) are common, with 65% consisting of glass fiber reinforced with polyester or vinyl ester resin in an open mold process, and 35% consisting of high volume manufactured composites or advanced (carbon or aramid fiber) composite.

There are generally two types of composites abundant in consumer applications: thermoplastics and thermoset composites. Thermoplastics can be melted or re-formed under high temperature or pressure, whereas thermosets undergo chemical crosslinking which is irreversible, giving them a preferred quality in aerospace and nautical applications. As of 2000, the proportion of thermoset composites in use consisted of: polyester (80-85%); epoxy (7-8%); vinyl ester (3-4%); and phenolic resins (1-2%). Glass fiber (such as E-glass) constitutes 90% of composite reinforcement material, with other fibers, powders and fillers constituting the other 10% (EPRI, 2000). Like the material in this study, vinyl ester resin thermoset composite material (VERTCM) is used in storage tanks, pipes and ducts, utility poles, aircraft fuselages, boats and other marine applications. In fact, styrene emission from VERTCM is a current issue for the next generation of battleships like the DDx, as well as ground tanks and truck trailers where this composite is replacing metal components (Vaidya, 2011).

The processing and forming of thermoset resin includes open mold (boats, bathtubs) filament winding, pultrusion (pulling), resin transfer molding (RTM) and Vacuum Infusion Processing (VIP), the latter capturing 90% of the volatile organic compounds (VOCs) released from unreacted styrene in the material. Styrene acts as both a diluent during molding and as a strengthener during the cure process, and is the most frequently used monomer in polystyrene and co-polymers (polyester, polyurethane, poly-methylmethacrylate, and polyvinyl actetate). Styrene is also thought to form benzaldehyde by oxidation reactions after cure. Because of the high potential for un-reacted VOCs to emit from VERTCM, much research has been conducted to attempt to limit or reduce not only the amount of styrene available to emit, but also the process by which the composite is made to reduce emissions as well (Schubel *et al*. 2006).

Open mold composite systems have successfully reduced styrene emissions by adding vapor suppressing additives or substituting non-styrene diluents, including eco-friendly fatty acids and other plant-based materials. One limitation is that these substitutes are more expensive and may result in reduced composite performance specifications (La Scala *et al*. 2004). A closed mold process can capture a majority of VOC, including the vacuum assisted resin transfer method (VARTM) process which was used in this study, not to infuse the e-glass with the resin, but rather to ensure uniform material thickness and surface structure.

In gel coat spraying, styrene content of the resin as well as spraying equipment and procedures all affected styrene emission during the production process, with 60% of VOC released during spray-up and 40% of the VOC released during cure. Techniques used for reducing styrene emission up to 50% included change in orifice size (increasing) led to lower styrene emission as compared to increasing spray pressure (Saamanen and Skrifvars, 2002).

VERTCM Manufacture

VERTCM panels were prepared in the UAB School of Engineering's Department of Materials Science and Engineering laboratory using the materials and methodology established by the Department for the production of VERTCM. It should be noted that the Boeing 787 Dreamliner described in this study and used to estimate the styrene emission factor for estimating inhalation exposures is not constructed from VERTCM but from an advanced carbon composite; the VERTCM styrene emissions evaluated here were based on the physical dimensions of the Boeing 787 Dreamliner for comparative purposes only, but has direct application to the next generation of military transport.

Squares of E-90 course weave glass fiber (E-glass) measuring approximately 120 cm x 120 cm were cut to size and set aside for layup. Fiber panel layup consisted of cleaning the glass layup area with acetone and applying three coats of a releasing interface (Freekote 700-NC, Henkel Corp.) with a lint-free cloth. The resin used consisted of Derakane® 510A-40 (Ashland Chemical) containing 38% styrene by weight mixed with promoter (Trigonox 239, AkzoNobel Polymer Chemicals), accelerator (Cobalt Nap-all, Ashland Chemical) and inhibitor (Acetylacetone +99%, Sigma-A) in ratios to every gram of resin of 0.015, 0.002 and 0.001, respectively. To form the panels, one layer of E-glass was placed onto the work area on top of a Teflon panel and the resin mixture applied by hand pouring and spreading with a plastic trowel until the fiber was completely covered and saturated. This process was repeated until eight layers of fiber formed the panel, with the resin amount equal to approximately twice the fabric weight.

Each fiber layer weighed approximately 350 grams. After layup, the panels were topped with Teflon and breather cloth and sealed under vacuum to allow for overnight curing at room temperature.

The following day, the cured panels were removed from the work area and cut on a wet saw to form test panels suitable for upright placement in the environmental chamber (Figure 1). The final cured panel thickness measured approximately 0.55 cm and panel width ranged from 19.2 to 26.0 cm. After cutting, all four edges of the test panels were sealed with a non-VOC emitting metallic tape. Individual panels were immediately wrapped in two layers of heavy-duty aluminum foil, double-bagged in sealed 4 MIL polyethylene sheeting, marked with identification numbers, and stored at -80°C.

References

EPRI Center for Materials Production (2000) Industry Segment Profile: Composites. Job # 1000135. Columbus, OH. 37 pp.

La Scala J., Sands J.M., Palmese G. (2004). Clearing the air: Army composites research reduces harmful emissions. The AMPTIAC Quarterly; 8(4), 118-125.

Schubel P.J., Parsons A.J., Lester E.H. et al. (2006) Characterization of thermoset laminates for cosmetic automotive applications: Part II – cure and residual volatile assessment. Composites: Part A 37:1747-1756

Saamanen A. and Skrifvars M. (2002) The effect of spraying and rolling process factors on styrene emission during the application of unsaturated polyester resins. AIHA Journal 63: 4, 474-481.

Vaidya, Uday. 2011. UAB Dept. of Materials Science Engineering. Personal communication.