



REDUCING USE OF STYRENE MONOMER IN UNSATURATED POLYESTER RESINS

University of Massachusetts Lowell

Toxics Use Reduction Institute

Academic Research Program

Reducing use of styrene monomer in unsaturated polyester resins

Richard A. Poillucci
and
Assistant Professor Christopher J. Hansen

Department of Mechanical Engineering
University of Massachusetts Lowell

The Toxics Use Reduction Institute
Academic Research Program

June 2013

Project Manager: Pam Eliason



All rights to this report belong to the Toxics Use Reduction Institute. The material may be duplicated with permission by contacting the Institute.

The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, 600 Suffolk Street, Suite 501 Wannalancit Mills, Lowell, MA 01854

Academic Research Program

The Academic Research program is a project of the Toxics Use Reduction Institute (TURI). The program connects the research capabilities of the University of Massachusetts with the emerging needs of Massachusetts manufacturers and the Commonwealth, to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies and, in some cases, evaluate and/or adopt processes and technologies resulting from research. Past projects supported by this program have focused on finding alternatives to the use of toxic chemicals in various plastics applications. These projects are described in more detail on TURI's website (www.turi.org and click on Research, Academic Research Program).

Notice: *This report has been reviewed by the Institute and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Toxics Use Reduction Institute, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.*

Table of Contents

ABSTRACT	i
1. INTRODUCTION	1
2. Background	1
2.1 Styrene Monomer and Health Hazards in Composites Manufacturing	1
2.2 Styrene Use in Unsaturated Polyester Resins.....	2
2.3 Existing Efforts to Increase Safety	3
2.4 Styrene Use in Massachusetts Industry.....	4
3. EXPERIMENTAL METHODS	5
3.1 Approach	5
3.2 Solubility of Monomers and Polyester	5
3.3 Viscosity Characterization	6
3.4 Manufacturing of Polyester	6
3.5 Screening Alternative Chemistries via Microfluidics for Mechanical Characterization	7
4. RESULTS AND DISCUSSION	8
4.1 Identification of Candidate Monomers	8
4.2 Solubility Results	10
4.3 Curing Results	10
4.4 Manufactured Polyester	11
4.5 Microfluidic Verification Results	11
5. SUMMARY AND CONCLUSIONS.....	12
6. Acknowledgements.....	13
7. References.....	13
Appendix A. GHS Data and Key for Chemicals Considered	15

ABSTRACT

Unsaturated polyester resins are ubiquitous in the manufacture of economical fiberglass composites ranging from marine and automotive transportation to off-the-shelf consumer products. These resins typically contain 35-50 volume percent styrene monomer. Styrene is classified as a suspected carcinogen, neurotoxin, and respiratory tract irritant and poses a health hazard for employees who are exposed to either vapors or physical contact with the styrene monomer. Specific to Massachusetts, styrene is a toxic covered by the Toxics Use Reduction Act (TURA) and is consistently the highest volume toxic chemical used within the state. The aim of this study is to reduce and replace styrene monomer within unsaturated polyester resins with alternate monomers that are substantially less hazardous to human health. The alternative monomers are selected based on reduced health risk, low cost, and low mixture viscosity, while retaining the ability to react with the polyester resin. Over 30 compounds are screened for suitably low toxicity and human health hazards, from which 7 compounds were experimentally characterized. Of these chemicals, trimethylolpropane diallyl ether (TMPDE) displayed the greatest promise in curing fully at room temperature. Additional monomer candidates that warrant further experimental study have been identified. Finally, a microfluidic device designed to rapidly screen a range of monomer-resin compositions was designed and the mixing of binary blends over a range of intermediate compositions is demonstrated.

1. INTRODUCTION

Unsaturated polyester resins find common use within fiberglass composites manufacturing for applications that include marine structures (e.g., boat hulls), automotive repair (e.g., body filler), fiberglass construction products (e.g., showers, bathtubs), and renewable energy (e.g., wind turbine blades). The widespread application of these resins is based on a commodity pricing structure for unsaturated polyester resins that offers an economical route to fiber-reinforced composite materials. Underpinning the economics of the resins, however, is the dilution of polyesters with 35-50 volume percent styrene monomer. While inexpensive, styrene monomer is classified as a suspected carcinogen, neurotoxin, and respiratory tract irritant by the IARC (International Agency for Research on Cancer) [1]. Composites manufacturing employees who work with styrenated polyester resins are frequently exposed to vapors and possible physical contact with styrene, thereby exposing workers to the risks associated with styrene contact. The aim of this study is to reduce or replace styrene monomer with alternate allyl- and vinyl-based reactive monomer diluents that are substantially less toxic to human health. This hazard reduction-based approach will result in reduced potential for worker exposure to harmful vapors during the manufacturing process.

2. Background

2.1 Styrene Monomer and Health Hazards in Composites Manufacturing

Styrene monomer, shown in Figure 1, is a molecule comprised of a benzene ring and a vinyl functional group. Styrene is volatile, has a high vapor pressure at room temperature, and has a low flash point of 31°C. Due to this volatility, active ventilation strategies are required in manufacturing settings in order to remain below the 15 minute exposure ceiling concentration of 100 ppm set by National Institute for Occupational Safety and Health (NIOSH) and an Immediately Dangerous to Life or Health (IDLH) concentration of 700 ppm. The Occupational Safety & Health Administration (OSHA) has set permissible exposure limit of 100 parts per a million (ppm) time weighted average and a 200 ppm ceiling [2].

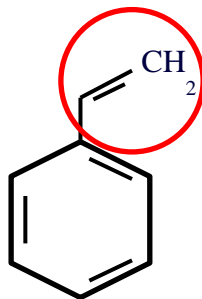


Figure 1. Styrene molecule, with the vinyl functional group circled.

Styrene monomer has multiple associated human health hazards, such as respiratory and skin irritation [3]. Styrene also attacks the central nervous system if exposure persists over a long period of time, leading to possible headaches and depression [4]. The greatest industry concern focuses its carcinogenic potential [1].

In spite of these known adverse health effects, styrene is almost the exclusive reactive monomer of choice for unsaturated polyester resins due to cost, availability, processing viscosity, and mechanical property considerations. Styrene is inexpensive and available in bulk quantities (worldwide annual production is approximately 25 million tons), such that styrene dilution of polyesters reduces the cost to below half that of higher performance epoxies [5]. Styrene is an excellent diluent to achieve proper processing viscosity for polyester resins. Simple adjustment of the styrene fraction permits wet lay-up with woven textiles, as well as spray-up using a spray gun nozzle and a fiber chopper. Finally, styrenated polyester resins can be cured at room temperature and exhibit mechanical properties that outperform those observed for alternate monomer diluents [5].

2.2 Styrene Use in Unsaturated Polyester Resins

Unsaturated polyester resins form a backbone polymer matrix chemistry for the composites manufacturing industry. Figure 2 displays a generic unsaturated polyester resin radical polymerization reaction. The polymerization reaction is initiated via a peroxide, typically methyl ethyl ketone peroxide (MEKP). The resulting radical reacts with the vinyl functional group on a styrene molecule, whereby the radical will propagate to react with either additional styrene or a neighboring polyester chain. The resulting cross-linked matrix offers good mechanical performance and acceptable resistance to environmental degradation.

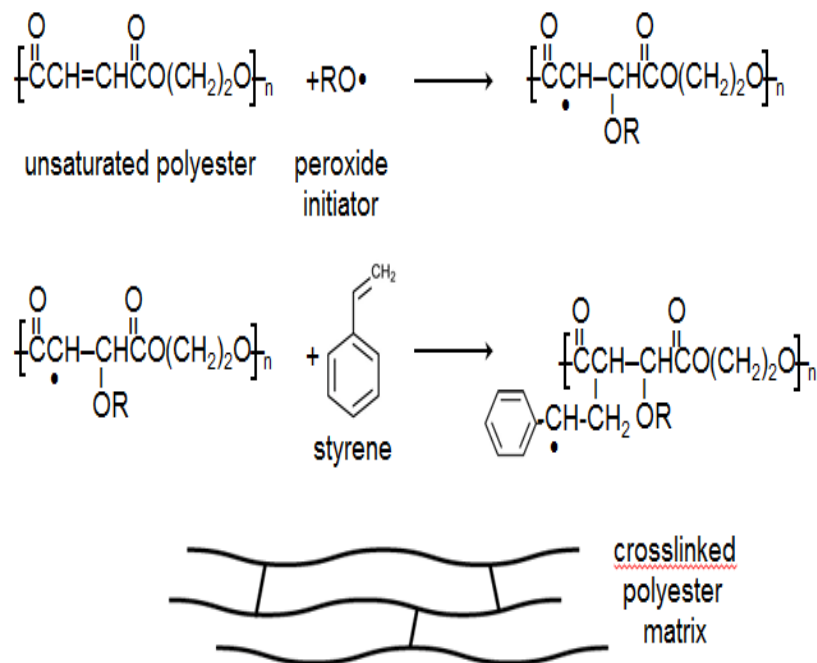


Figure 2. Polymerization reactions within a polyester resin.

Industrial polyester resins are typically manufactured in large batch reactors from phthalic anhydride and maleic anhydride and a hydroxyl component, such as propylene glycol or ethylene glycol. The polyester resin formulation incorporates the styrene component immediately after the condensation reaction to prevent crystallization of the polymer component. Hence, it is extremely difficult to purchase a commercial polyester without added monomer [5]. A typical polyester resin system contains a polyester base composed of maleic anhydride and propylene glycol (50-65 wt %), which is then diluted with styrene (35-50 wt%), and the polymerization process is initiated by addition of methyl ethyl ketone peroxide (MEKP) (1-2 wt %).

Viscosity of the polyester resin is of critical importance to the manufacturing of composites. A resin with a high viscosity may clog the nozzle during a spray-up procedure, as well as potentially result in inhomogeneous distribution of the cured matrix. Moreover, elevated viscosity can prevent proper wet out of the reinforcement fiber. However, a resin with an excessively low viscosity may migrate from the initial application location due to gravitational forces and results in resin-starved regions of the product.

2.3 Existing Efforts to Increase Safety

Efforts to address the health hazards associated with styrene usage in polyester resins broadly falls into two categories: engineering controls and hazard reduction. In an engineering controls approach, styrene is still incorporated into resins but human exposure is minimized by reduction of the ambient vapor levels. A widely used approach is active ventilation of manufacturing space to keep vapor levels below the exposure limits discussed previously. An alternative approach is to reduce monomer volatilization by creating formulations that contain paraffin waxes, which form a surface barrier to suppress emissions. However, the wax layer interferes with surface adhesion to other parts if not removed prior to bonding [6, 7]. The ambient concentration of styrene vapor can be reduced in composite “spray-up” by using spray guns that monitor the amount of resin sprayed. This feedback assists employees to spray sufficient rather than excessive quantities of resin, thereby reducing styrene volatilization [8].

The second approach seeks to eliminate exposure to styrene by using non-toxic chemistries in polyester resins. To date, however, many of the commercialized formulations with styrene-replacement chemicals chosen possess human health hazards similar to styrene. Vinyl toluene, for instance, has been used to replace styrene [5]; though it is not a known carcinogen, vinyl toluene is strongly irritating to both workers’ skin and respiratory tracts [9]. The organization Minnesota Technical Assistance Program (MNTAP) has investigated current commercially available styrene-free resins, including one manufactured by NOVOC LLC. Though the resin formulation is proprietary, MNTAP reports that employees working with the non-styrenated resin were exposed to 250-300% greater acetone vapors while styrene vapor exposure decreased by 17-55%. Performance, however, was 15-25% lower relative to standard styrenated resins on a wide range of metrics, including flexural modulus [8].

Table 1 displays the health effects associated with alternative monomers that are presently used as styrene replacements within non-styrenated polyester resins.

Table 1. Styrene monomer substitutes in commercial unsaturated polyester resin formulations.

Substitute Monomer	Health Effects
Vinyl Toluene [5, 9]	Affects central nervous system Respiratory irritant Skin irritant
Alpha-methylstyrene [10, 11]	Animal carcinogen Respiratory irritant Skin irritant
Diallyl phthalate [5, 12]	Possible organ toxicity Harmful if inhaled Skin sensitizer

2.4 Styrene Use in Massachusetts Industry

Styrene is the highest volume toxic chemical reported under the Toxics Use Reduction Act (TURA) within the Commonwealth of Massachusetts. In 2010, the most recently reported data in the TURA database (<http://turadata.turi.org/>), approximately 291 million pounds of styrene monomer was used by 11 separate Massachusetts companies. However, as noted in Keenan *et al.* [13], many users of unsaturated polyester resins are small companies (<10 workers or less than 10,000 lb. usage per year), and thus are exempt from TURA reporting requirements. The companies that are required to report usage can be separated into two general categories: manufacturers of the raw resins distributed to other manufacturers, and manufacturers that fabricate consumer products from the raw resins.

The research detailed in this report aims to develop promising compositions that could be implemented by batch resin manufacturers (e.g., Nexeo Solutions LLC, Advance Coatings Co, and ITW Devcon Plexus). The impact of such an upstream change will be to eliminate the possibility of styrene exposure at the level of both the resin manufacturer and the downstream manufacturer. Moreover, resins are distributed beyond the state border of Massachusetts and will impact a wider manufacturing base. As will be noted later in this report, resin manufacturers represent a key leverage point in moving the market towards safer resin formulations. A majority of material “release” reported under TURA occurs at the level of polyester resin end use where worker exposure to styrene vapors is most likely (e.g., E Parrella Co, Mustang Motorcycle Products LLC, Swimex Inc). The manufacturing description provided by Swimex Inc to the TURA database highlights the nature of close and intimate contact with styrene monomer-based resins during manual lay-up and open mold procedures, in which large quantities of vapors are often released. The end goal to eliminate styrene monomer from within polyester resins will aid in similar manufacturing situations throughout Massachusetts to protect the health of manufacturing workers.

3. EXPERIMENTAL METHODS

3.1 Approach

The experimental approach to identify suitable styrene alternatives is schematically shown in Figure 3.

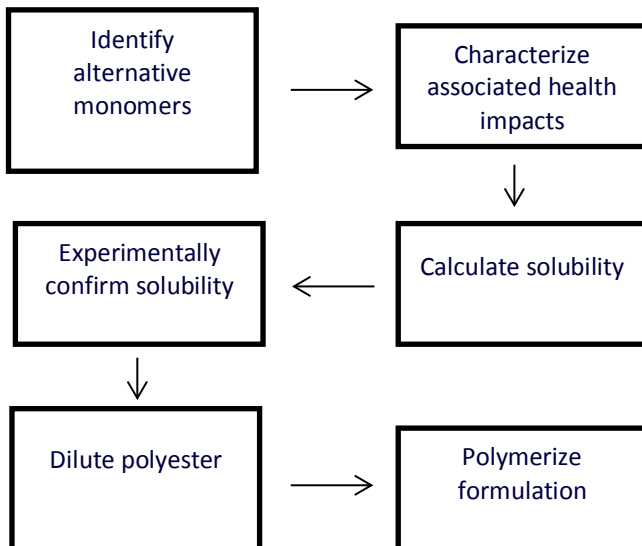


Figure 3. Experimental approach to styrene reduction within unsaturated polyester resins.

Initial identification of alternative monomers to replace styrene focused on those materials that possess similar chemical functional groups, low cost, and low mixture viscosity to permit satisfactory processing. Next, these chemicals are screened for their human health impacts with data and approaches described in the OSHA guidance on globally harmonized system (GHS) [14] and the Green Screen method [15]. The solubility of monomers with suitably low hazards is theoretically calculated and those chemicals predicted to be soluble in unsaturated polyesters are experimentally mixed to verify miscibility. For fully miscible compositions, the formulation is subsequently polymerized. Finally, a microfluidic device is fabricated and used as a rapid screening technique to create a range of polyester-monomer compositions, from which the best composition will be determined based on mechanical performance as determined by dynamic mechanical analysis (DMA).

3.2 Solubility of Monomers and Polyester

All alternative chemicals to styrene monomer must be appropriately soluble within the polyester. The solubility of the alternate monomers is first predicted via Hansen solubility parameter calculations. The monomer solubility parameters are estimated via the Hansen solubility method that calculates the solubility contribution due to dispersion bonds, polar bonds, and hydrogen bonds according to Equations 2 through 4, respectively. F_{di} is the force due to dispersion bonds, F_{pi} is the force due to polar bonds, and E_{hi} is the energy due to hydrogen bonds. V is the molar volume, which is calculated based on the molar weight and density of the respective chemical. Equation 5 calculates the total solubility of the chemical from the individual components [16].

$$\delta_d = \frac{\sum F_{di}}{V} \quad (2)$$

$$\delta_p = \sqrt{\frac{\sum F_{pi}^2}{V}} \quad (3)$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \quad (4)$$

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (5)$$

If the overall solubility parameter difference ($\Delta\delta$) between a chemical and the polyester of interest is ≤ 5 $(\text{MJ}/\text{m}^3)^{1/2}$, the two components are predicted to likely be miscible. Smaller values of $\Delta\delta$ correspond with an improved likelihood that the chemical and the polyester will be soluble [16].

The calculated solubility parameter and the experimental solubility parameter can differ significantly, so promising candidates are subsequently experimentally tested. This approach is performed by mixing a small portion of polyester with a monomer diluent of 30 to 50 volume percent in a 20 mL scintillation vial. Compositions that do not readily mix at room temperature are sonicated for 2 hours to promote dispersion. In the event that the sample still does not mix, the specimen is sonicated for an additional 2 hours at 60 °C.

3.3 Viscosity Characterization

The allyl- and vinyl-based candidate monomers are mixed into an unsaturated polyester resin obtained from Poliver S.p.A. (Italy) from 35 to 50 wt% to observe the solution viscosity. The diluent composition for each monomer choice is varied between pure candidate monomer to pure styrene monomer in steps of approximately 25% in order to obtain a working viscosity near 500 cP, which is standard for industry resins. Candidate compositions are first narrowed based on simple visual observations of viscosity. Mixtures with sufficiently low viscosity are subsequently measured under stress-controlled conditions on a rheometer (TA Ares G2) fitted with a cone and plate geometry.

3.4 Manufacturing of Polyester

A sample of a solid, non-diluted polyester was provided by Poliver, but did not mix as expected based on typical phthalic anhydride and maleic anhydride-based resins. No other commercial non-styrenated polyester sources were identified, so polyester resin was synthesized in the laboratory. Maleic anhydride is chosen for its typical use in industry, reactivity, and ultimate mechanical properties. Propylene glycol was selected for the hydroxyl component, as ethylene glycol is more hazardous than propylene glycol due to the greater reactivity of the primary hydroxyl groups in polyethylene glycol relative to the secondary hydroxyl groups in polypropylene glycol. As an added benefit, propylene glycol can be derived from biological sources, such as corn-starch [17]. The polyester resin is synthesized from a stoichiometric mixture of equivalent molar quantities of propylene glycol and maleic anhydride within a round bottom flask. The flask is heated in silicone oil to heat the reaction to 150 to 180°C. The water evolved by the reaction is removed via a water-chilled condenser schematically shown in Figure 4. The water vapor from the reaction migrates to the water

evaporation tube, where it condenses to a liquid. The water removal process is maintained for 12+ hours to drive the condensation reaction polymers to higher molecular weight.

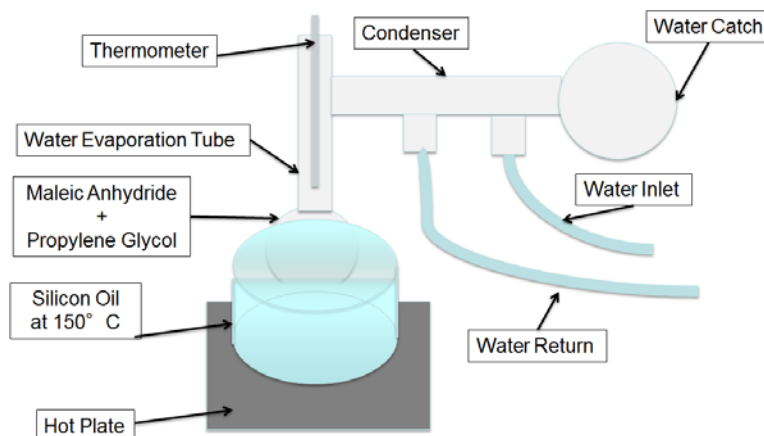


Fig. 4. Experimental setup for manufacturing polyester.

After the chemicals are sufficiently reacted to produce long-chain polyesters, the polyester and unreacted monomers are suspended by adding sufficient acetone to solubilize the material within the flask. The solution is poured from the flask into a crystallization dish, then diluted with methanol to induce precipitation of the polyester while retaining the unreacted monomers within the supernatant. The supernatant is removed by pipette and the purification step is repeated for a total of three times. The resulting purified polyester is crystallized on the container bottom, from where it is recovered for further study and dilution with alternatives to styrene monomer.

3.5 Screening Alternative Chemistries via Microfluidics for Mechanical Characterization

Chemistries identified as promising candidates in the initial stages of this work will exhibit a range of mechanical properties as the monomer-to-polyester compositions are varied. A chemical gradient microfluidic device is designed to rapidly obtain multiple compositions of monomer and polyester within microfluidic channels. Specifically, composition A and composition B are displaced from syringes via a syringe pump set to a constant flow rate through a microfluidic device similar to the schematic seen in Figure 5. The fluids flow and diffusively mix under laminar conditions to result in a range of predictable polyester resin compositions, which subsequently fill cavities that correspond to specimen dimensions for DMA.

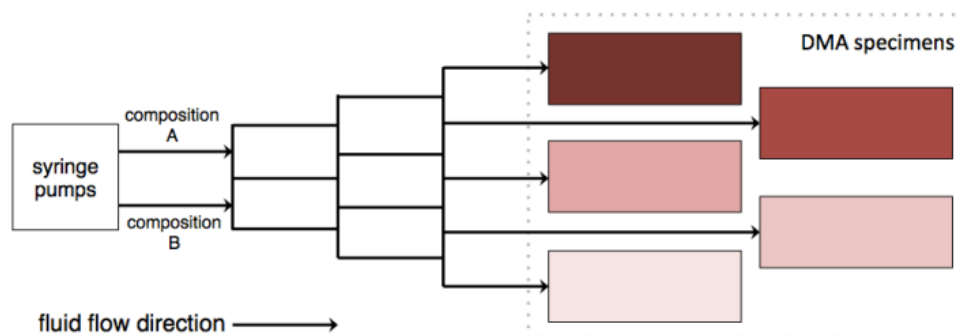


Fig. 5. Schematic of microfluidic device to create a gradient of DMA specimen compositions.

The microfluidic channels are 500 μm in width and are fabricated by CNC (computer numerical control) micro-milling from a 5 mm thick plate of acrylic. The patterned plate is then bonded to a neat acrylic block via application of acetonitrile and pressure to the interface of the acrylic blocks, thereby encapsulating the microfluidic network. In order to verify the chemical ratios mixed within each channel, visualization tests are performed by flowing water dyed red with rhodamine 6G (0.01 wt%) or yellow-green with fluorescein (0.01 wt%) (Sigma-Aldrich).

4. RESULTS AND DISCUSSION

4.1 Identification of Candidate Monomers

Candidate chemicals were identified by consideration of their toxicity, cost, and viscosity (μ). The ideal candidate would exhibit no toxicity and similar cost and viscosity to styrene as processed. The list of initial candidates is provided in Table 2. The reader should note all pricing was obtained from Sigma-Aldrich and that prices for bulk quantities required at the industrial scale are anticipated to be lower. While many of the chemicals are not present in commercially available formulations, trimethylolpropane diallyl ether is sold by Perstorp as a means to replace or reduce styrene within formulations [19].

Table 2. Styrene and Alternate Substitutes

Chemical	Toxicity	Cost (L^{-1})	μ (cP)	Reason for Selection
Styrene	Possible Carcinogen	\$34	0.675	Viscosity and price
Limonene oil	Skin and respiratory tract irritant[18]	\$12	0.925	Viscosity, price, and source material
Vinyl neodecanoate	Likely Non-Toxic[18]	\$43	1.1	Viscosity, functional group
Vinyl laurate	Likely Non-Toxic[18]	\$59	0.945	Viscosity, functional group
Trimethylolpropane diallyl ether	Possible organ toxicity and skin and respiratory tract irritant[18]	\$140	20 [19]	Sold by Perstorp resins [19]

Chemical	Toxicity	Cost (L ⁻¹)	μ (cP)	Reason for Selection
Isobornyl methacrylate	Possible organ toxicity and skin and respiratory tract irritant[18]	\$144	11 [20]	Functional group
Trimethylcyclohexyl methacrylate	Possible organ toxicity and skin and respiratory tract irritant[18]	\$144	----	Functional group
Dicyclopentadienyl methacrylate	Skin irritant[21]	----	8 [22]	Functional group
Pentaerythritol tetraacrylate	Skin and respiratory tract irritant	\$304	600-1000 [23]	Functional group

The candidate chemicals are subsequently screened with data and approaches used in the OSHA guidance on the globally harmonized system (GHS) [14] and the Green Screen method [15] to determine their human health impacts. The information sources are wide-ranging, from suppliers such as Sigma Aldrich to governmental regulators such as the European Chemical Agency. The GHS results for the chemicals in Table 3 are provided in Table 4. An expanded selection of chemicals screened during this project and an accompanying key are provided in Appendix A.

Table 4. GHS table of chemical hazards associated with monomer candidates.

	CAS #	Group I Human						Group II and II* Human								EcoTox		Fate		Physical	
		C	M	R	D	E	AT	ST		N		SNS	SNR	IrS	IrE	AA	CA	P	B	Rx	F
								single	repeat	single	repeat										
Styrene	100-42-5	Susp					M	H	M					H	H						M
Limonene Oil	5989-27-5	L	L		L	L			L			H		H	H	VH	L	V L	L	L	M
Vinyl Neodecanoate	51000-52-3													L	L						L
Vinyl Laurate	2146-71-6					L								L	L		L		L		L
Trimethylolpropane diallyl ether	682-09-7						M							H	H						
Isobornyl methacrylate	7534-94-3						M							H	H						
Trimethylcyclohexyl methacrylate	7779-31-9						M							H	H						
Dicyclopentadienyl Methacrylate	51178-59-7																				
Pentaerythritol tetraacrylate	4986-89-4											H		H	H						

As shown in Table 4, most monomers exhibit the health hazards of high skin and eye irritation due to their reactive nature. Although the health hazards are not completely eliminated, the chemicals compare favorably when measured against the hazards associated with styrene. The reader should also note the significant data gaps that exist in hazards information (illustrated by empty cells in Table 4). For example, no classifying tests on dicyclopentadienyl methacrylate have been reported to date. Finally, though limonene oil is listed as a low carcinogen, this corresponds to no known carcinogen effects associated with this chemical.

4.2 Solubility Results

Styrene was mixed with the Poliver non-styrenated polyester resin and was found to be fully miscible. Though the chemical composition of the Poliver polyester was unknown due to its proprietary composition, monomers with solubilities similar to styrene are expected to be soluble within the Poliver polyester. A summary of experimental results is provided in Table 5.

Table 5. Solubility calculations and mixing results for reactive monomers.

Monomer	Calculated Solubility (MJ/m ³) ^{1/2}	Mixing State
Styrene	17.68	Mixed
Limonene	15.27	No mixing
Vinyl neodecanoate	16.66	No mixing
Trimethylolpropane eiallyl ether	19.25	Mixed
Trimethylolpropane diallyl ether + 1 wt% acetone	N/A	Mixed
Isobornyl methacrylate	15.91	No mixing
Trimethylcyclohexyl methacrylate	16.20	No mixing
Dicyclopentadienyl methacrylate	15.86	No mixing
Pentaerythritol tetraacrylate	19.40	No mixing

Monomers with solubility parameters within 5 (MJ/m³)^{1/2} of styrene's value (i.e., 17.7 (MJ/m³)^{1/2}) were subsequently mixed with the Poliver resin in the laboratory to verify their solubility. Trimethylolpropane diallyl ether (TMPDE) was soluble [24]. Though the TMPDE is fully miscible with the polyester, it possessed an extremely high viscosity. A common method used to modulate the resin viscosity is to add acetone or methanol [8]. Here, the addition of <1 wt% acetone to the TMPDE-Poliver mixture lowered the resin viscosity substantially. The polyester-monomer formulations ultimately required the addition of styrene (25% to 50% of monomer solution) in order to provide the appropriate mixing and curing, which will be discussed in the following section.

4.3 Curing Results

The polymerization of miscible solutions listed in Table 5, composed of 50 wt% monomer and 50 wt% polyester and initiated with the addition of 2 wt% methyl ethyl ketone peroxide (MEKP), are summarized in Table 6 below. Compositions that had monomer fractions that exceeded 50% styrene were considered to be

insufficiently useful for styrene reduction and were not further pursued. Similarly, monomers that are immiscible were not further pursued due to their chemical incompatibility. The control specimen with pure styrene monomer cured at room temperature. The trimethylolpropane diallyl ether mixtures with and without acetone did not cure at room temperature, but polymerized under elevated temperature conditions at 70°C. However, an oxygen inhibition layer which results in a tacky surface was observed in the resulting cured resin. In addition, the partially immiscible compositions exhibited polymerization restricted to the styrene-rich fraction.

Table 6. Polymerization results of 50 wt% liquid monomer solution to 50 wt% solid polyester.

Monomer	Percent Styrene in solution %	Temp. (°C)	Cure State
Styrene	100%	21	Cured
Limonene	75%	21	Partially immiscible, only styrene fraction cured
Vinyl neodecanoate	75%	21	Partially immiscible, only styrene fraction cured
Trimethylolpropane diallyl ether	45%	21	Not cured
Trimethylolpropane diallyl ether + acetone	45%	21	Not cured
Trimethylolpropane diallyl ether + acetone	45%	70	Cured with an oxygen inhibited layer
Trimethylolpropane diallyl ether	45%	70	Cured with an oxygen inhibited layer

4.4 Manufactured Polyester

The stoichiometric reaction between maleic anhydride and propylene glycol using the experimental set up seen in Figure 4 produced polyester resin. The expected crystallization of polymer that remained following purification steps did not occur, but rather a gelled polymer matrix was formed. The authors posit that the ester in the acetone caused partial crosslinking of the polyester. Future success in polyester crystallization is expected if an alternative chemical to acetone is used in future polyester manufacturing.

4.5 Microfluidic Verification Results

A microfluidic device was successfully fabricated to assess mixing conditions for fluid flows. The diffusive mixing was observed via input water compositions dyed yellow and red (Figure 6) that subsequently split and recombine. The fluid compositions within the five channels at the end of the device shown in Figure 6 increase linearly in red dye content from 0% (bottom) to 100% (top).



Fig 6. Fluorescein- (left) and rhodamine-dyed (right) water inputs flow at 0.05 mL/min and diffusively mix.

The dyed water flow rates had to be maintained below approximately 1 mL/min in order to achieve full diffusive mixing within this microfluidic geometry. Above this flow rate, the parallel streams have insufficient time to fully diffuse within each generation of channels prior to bifurcation at the channel end for each generation of the network. The interdiffusion of the inlet fluids within a channel is governed by Equation 1, which relates the horizontal width of the fully formed gradient, X , to the diffusion coefficient D and the experimental mixing time T [25]:

$$X = \sqrt{2DT} \quad (1)$$

As the channel width linearly increases, the flow rate must be reduced quadratically in order to increase the residence time of the diffusing species. Similarly, polyester resin mixtures demonstrate analogous behavior, though the concomitant decrease in diffusion with increased viscosity requires further reduction in flow rates. Flow rates were varied from 0.05 mL/min to 0.20 mL/min in increments of 0.05 mL/min. The best diffusive mixing was observed at 0.05 mL/min. In order to increase throughput, narrower channels or increased temperatures (which lead to reduced viscosities and increased diffusivities) will be required.

5. SUMMARY AND CONCLUSIONS

Alternative monomers to styrene have been identified for use in polyester resins based on reduced toxicity, cost, and processing viscosity. The identified monomers were mixed into a commercially available non-styrenated polyester. Though the monomers demonstrated limited chemical compatibility, styrene content was reduced by 50% with the use of trimethylolpropane diallyl ether. A rapid screening gradient network microfluidic device was fabricated and successfully demonstrated the generation of five distinct composition outputs from two input solutions.. Recommendations for future work center on the use of a polyester synthesized in-house with which additional monomers can be mixed. Additional monomers that have passed the GHS screening should be tested for miscibility and polymerization potential. Promoters, commonly used in industry, could be tested as a means to further the polymerization of non-styrenated compositions. Finally, many industrial users of unsaturated polyester resins express a desire to know which, if any, existing non-styrenated resins would be suitable for their operations in Massachusetts. Hence, a database of resin

formulations, their GHS health data, and their associated mechanical properties should be assembled and shared with Massachusetts companies.

6. Acknowledgements

We gratefully acknowledge funding for this work from the Toxics Use Reduction Institute (TURI) and the assistance of Pam Eliason, Mary Butow, and all members of the TURI staff for their experience and insight in matters of chemical toxicity and safety. We also acknowledge the technical assistance from Prof. Daniel Schmidt, Prof. Meg Sobkowicz-Kline, and Xun Chen in the UMass Lowell Plastics Engineering department in alternative monomer chemistries and synthesis of polyester resin. We would also like to acknowledge Sartomer and Poliver, which donated their respective monomer and polyester materials for this research.

7. References

- [1] IARC, IARC MONOGRAPHS ON THE EVALUATION OF CARCINOGENIC RISKS TO HUMANS. 2002. p. 437-545.
- [2] OSHA. *Styrene*. [cited 2013 June 25]; Available from: http://www.osha.gov/dts/chemicalsampling/data/CH_268200.html.
- [3] ECHA. *Styrene*. [cited 2013 May 21]; Available from: http://apps.echa.europa.eu/registered/data/dossiers/DISS-828de07e-8908-129c-e044-00144fd73934/AGGR-15696e02-e935-4857-9990-2ba0494ebe9d_DISS-828de07e-8908-129c-e044-00144fd73934.html.
- [4] OSHA. *Styrene*. 2012 02/27/2012 [cited 2013 May 21]; Available from: <http://www.osha.gov/SLTC/styrene/>.
- [5] Doyle, E.N., *The Development and Use of Polyester Products*. 1969, McGraw-Hill Education.
- [6] Walewski, L.M., Inhibiting styrene emissions in unsaturated polyester resins. 1985, Ashland Inc.: United States.
- [7] Fink, J.K., *Reactive Polymers Fundamentals and Applications - A Concise Guide to Industrial Polymers*. 2005, William Andrew Publishing/Plastics Design Library.
- [8] Agency, M.P.C., *Green Chemistry: Composites project using styrene-free resin*. 2012.
- [9] OSHA. *Vinyl Toluene*. 2007 07/23/2007 [cited 2013 May 21]; Available from: http://www.osha.gov/dts/chemicalsampling/data/CH_275700.html.
- [10] Dalsin, P.D., et al., Polyester resin-based high index ophthalmic lenses having improved optical uniformity and/or tintability. 1997, Signet Armorlite Inc. Wells Fargo Business Credit Inc.: United States.
- [11] Medicine, N.L.o. *ALPHA-METHYL STYRENE (Cas: 98-83-9)*. 06/24/2005 [cited 2013 May 21]; Available from: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+196>.
- [12] Aldrich, S. *Diallyl phthalate*. [cited 2013; Available from: <http://www.sigmaaldrich.com/catalog/product/aldrich/269379?lang=en®ion=US>.
- [13] C. Keenan, E.H., *Styrene Use in Massachusetts*. 1993, Massachusetts Toxics Use Reduction Institute.
- [14] OSHA. *A Guide to The Globally Harmonized System of Classification and Labelling of Chemicals (GHS)*. 2012 [cited 2013 May 22,]; Available from: <http://www.osha.gov/dsg/hazcom/ghs.html>.

- [15] Clean Production Action. *GreenScreen for Safer Chemicals*. 2012 [cited 2013 May 22,]; Available from: <http://www.cleanproduction.org/Greenscreen.php>.
- [16] Krevelen†, D.W.v. and K.t. Nijenhuis, *Properties of Polymers - Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions* (4th, Completely Revised Edition). 2009: Elsevier. 189-227.
- [17] McAlvin, J.E.P.D., *Green Composites Through the Use of Styrene-Free Resins and Unsaturated Polyesters Derived from Renewable and Recycled Raw Materials*. 2011.
- [18] ECHA. *European Chemicals Agency*. Available from: <http://echa.europa.eu/>.
- [19] Perstorp, Trimethylolpropane Diallyl Ether 90. 2008.
- [20] Sartomer, SR423A ISOBORNYL METHACRYLATE
- [21] Sartomer, CD535 DICYCLOPENTADIENYL METHACRYLATE MSDS.
- [22] Sartomer, CD535 DICYCLOPENTADIENYL METHACRYLATE.
- [23] Chemical, H.G. *PENTAERYTHRITOL TRIACRYLATE (PETA)*. [cited 2013 June 25]; Available from: <http://www.union-pigment.com/china/radiation-curable-3524.html>.
- [24] Akiyama, M., A. Matsumura, and S. Shigematsu, *Unsaturated polyester resin coating composition*. 1988, Nippon Gohsei Kagaku Kogyo Kabushiki Kaisha: United States.
- [25] Dertinger, S.K.W., et al., *Generation of Gradients Having Complex Shapes Using Microfluidic Networks*. *Analytical Chemistry*, 2001. **73**(6): p. 1240-1246.

Appendix A. GHS Data and Key for Chemicals Considered

	Group I Human					Group II and II* Human								EcoTox		Fate		Physical		
	C	M	R	D	E	AT	ST		N		SNS*	SNR*	IrS	IrE	AA	CA	P	B	Rx	F
							single	repeat	single	repeat										
Styrene	Susp					M(3)	H(2)	M(3)					H(2)	H(2)						M(3)
Butyl Vinyl Ether						M(3)			L(4)		M(3)	M(3)	M(3)	M(3)		M(2)	vH(1)			vH(1)
Ethyl Vinyl Ether							M(3)				M(3)	M(3)	M(3)	H(2)					M(3)	vH(1)
N- Vinyl-Pyrrolidone	H(2)					M(3)	M(3)													L(4)
Vinyl Laurate						L(4)							L(4)	L(4)		L(4)		L(4)		L(4)
Vinyl Neodecanoate													L(4)	L(4)						L(4)
Limonene Oil	L(4)	L(4)		L(4)		L(4)		L(4)			H(2)		H(2)	H(2)	VH(1)	L(4)	VL(5)	L(4)	L(4)	M(3)
Trimethylolpropane diallyl ether							M(3)						H(2)	H(2)						
Trimethylolpropane allyl ether							M(3)						H(2)	H(2)						
3-allyloxy-1,2 prepenediol							M(3)						H(2)	H(2)						
Pentaerythritol allyl ether													H(2)			H410				
Methanol						H(2)	VH(1)						M(3)	M(3)						H(2)
Acetone									L(4)				M(3)	H(2)						H(2)
ε-Caprolactone							M(3)						H(2)	vH(1)						
Vinyl Toluene						L(4)							H(2)	H(2)	H(2)					M(3)
4,4'-diphenylmethane diisocyanate (XDI)	susp						H(2)				H(2)	H(2)	H(2)	H(2)						

	Group I Human					Group II and II* Human								EcoTox		Fate		Physical		
	C	M	R	D	E	AT	ST		N		SNS*	SNR*	IrS	IrE	AA	CA	P	B	Rx	F
							single	repeat	single	repeat										
Paraphenylene diisocyanate (PPDI)						M(3)							H(2)	VH(1)						
1,5 - naphthalene diisocyanate						M(3)	M(3)				M(3)	M(3)	H(2)	H(2)	H(2)					
<u>1,3-bis(1-isocyanato-1-methylethyl)benzene</u>						VH(1)						H(2)	H(2)							
isophorone diisocyanate IPDI						VH(1)	M(3)				H(2)	H(2)	H(2)	H(2)	H(2)					
hydroxyethyl methacrylate											H(2)		H(2)							
Methacrylic acid monoester with 1,2-propandiol											H(2)		H(2)							
2-hydroxyethyl acrylate						M(3)					H(2)		VH(1)							
Hydroxypropyl Acrylate (HPA)						H(2)					H(2)		VH(1)							
Di(ethylene glycol) dimethacrylate						H(2)					H(2)		VH(1)							
Pentaerythritol triacrylate											H(2)		H(2)	H(2)						
Pentaerythritol tetraacrylate											H(2)		H(2)	H(2)						
1,4-Butanediol diacrylate						M(3)					H(2)		VH(1)							
Trimethylolpropane triacrylate											H(2)		H(2)	H(2)						
1,6-Hexanediol diacrylate											H(2)		H(2)	H(2)						

	Group I Human					Group II and II* Human								EcoTox		Fate		Physical		
	C	M	R	D	E	AT	ST		N		SNS*	SNR*	IrS	IrE	AA	CA	P	B	Rx	F
							single	repeat	single	repeat										
oxybis(methyl-2,1-ethanediyl) diacrylate											H(2)		H(2)	VH(1)						
3,3,5-Trimethylcyclohexyl methacrylate							M(3)						H(2)	H(2)						
Isobornyl methacrylate							M(3)						H(2)	H(2)						
DICYCLOPENTADIENYL METHACRYLATE																				
Ethoxylated bisphenol A diacrylate							M(3)				H(2)		H(2)	H(2)						
4,4'-methylenedi-o-toluidine	h(2)						M(3)				H(2)				H(2)	VH(1)				
Dicyclopentenyl methacrylate							M(3)						H(2)	H(2)						
Maleic anhydride						M(3)					H(2)	H(2)	VH(1)							
p-Toluenesulfonic acid monohydrate							M(3)						H(2)	H(2)						
Potassium Octoate (Potassium 2-ethylhexanoate)			M(3)										H(2)	vh(1)		M(3)				
zinc Octoate (Zinc 2-ethylhexanoate)			M(3)			M(3)	M(3)				H(2)		H(2)	H(2)						M(3)
Zirconium Octoate			M(3)			M(3)	M(3)						H(2)	H(2)		M(3)				
Cobalt Naphthenate Pastilles	M(3)					M(3)					H(2)		H(2)	H(2)						
Cobalt 2-ethylhexanoate (Cobalt Octoate)						M(3)					H(2)		H(2)	H(2)						M(3)
Copper Naphthenate						M(3)										VH(1)				M(3)
VINYLNORBORNENE						L(4)														
Bicyclo[2.2.1]hepta-2,5-diene		M(3)							M(3)											H(2)
3-Bromopropene (Allyl bromide)	H(2)	H(2)				H(2)							VH(1)		VH(1)					H(2)
Allyloxy(polyethylene oxide), acetate (6-9 EO)													H(2)	H(2)						

Key: Hazard Benchmark Acronyms

C	Carcinogenicity
M	Mutagenicity and Genotoxicity
R	Reproductive Toxicity
D	Developmental Toxicity
E	Endocrine Activity
AT	Acute Mammalian Toxicity
ST	Systemic/Organ Toxicity
N	Neurotoxicity
SnS	Sensitization- Skin
SnR	Sensitization- Respiratory
IrS	Skin Irritation/Corrosivity
IrE	Eye Irritation/Corrosivity
AA	Acute Aquatic Toxicity
CA	Chronic Aquatic Toxicity
P	Persistence
B	Bioaccumulation
Rx	Reactivity
F	Flammability
single	Single exposure
repeat	Repeated exposure