

ALTERNATIVE REACTIVE MONOMER CHEMISTRIES IN RESINS FOR PULTRUSION PROCESSING

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ABSTRACT

Vinyl toluene (VT), under the family of methyl styrenes, is a reactive monomer that embodies alternative molecular chemistry to traditional styrene monomer. While present in the market for a substantial period of time, this family of monomers has not been widely utilized in reactive polymer resins or low-profile resins (LP) supplied into pultrusion applications. Recent restrictive changes in ground level ozone non-attainment criteria, workplace exposure concerns and toxicity classification of styrene monomer (SM), coupled with the entry of additional vinyl toluene producers into the market, should present new incentives and opportunities for resin producers to supply products utilizing this alternate styrene free technology into the pultrusion market.

This paper will provide comparative results focused on process efficiency and pultruded product properties obtained utilizing isopolyester resin in alternate monomer, vinyl toluene, versus the same properties obtained utilizing commercial isopolyester in styrene monomer. The paper will further investigate the properties obtained when only the low-profile resin utilizes alternate monomer, vinyl toluene.

1. INTRODUCTION

Styrene monomer traditionally finds widespread use in the composites industry primarily due to its world scale production and its low-cost commodity market position. Styrene monomer is produced essentially for downstream use in the manufacture of polystyrene, engineering thermoplastics and synthetic rubber. The composites industry utilizes a very small fraction of the global styrene monomer supply. While styrene monomer provides a readily available, low cost, reactive monomer for composites, it does have its challenges in meeting the performance demands and evolving environmental and toxicity issues facing today's composite fabricator. Among others, these challenges include slow reactivity at elevated temperatures, high exotherm on polymerization, and a less than desirable shrink profile. Additionally, styrene monomer is classified as a HAP with a high vapor pressure and a low flash point. It also presents undesirable environmental, exposure and toxicity issues.

1.1 Purpose audience and scope

This paper is intended to investigate the use of resins and low-profile resins supplied in alternate monomer, vinyl toluene, as a potential solution to process restrictions and product property limitations of resins and low-profile resins provided in styrene monomer systems which are currently in widespread use in pultrusion applications.

The results contained herein should be of value to resin producers and pultrusion fabricators interested in potentially enhanced product performance in addition to increased process efficiency.

The scope of this work was intentionally limited to a relatively simple product profile. Resin mix preparations, peroxide types and quantities, die temps were held constant. The variables were strictly monomer types incorporated into the resins and low-profile resins along with line speed. It was our intention to illustrate the viability of alternate monomers in providing increased production efficiency while yielding a superior performance styrene monomer free pultruded product.

1.2 Background

There are extensive examples of methyl styrenes, vinyl toluene, being utilized in resins for molding compound, usually BMC. The primary drivers for using vinyl toluene in this market are its superior performance in terms of its speed of cure at elevated temperatures without increased exotherm and its minimal shrinkage during polymerization. In fact, BMC resins in vinyl toluene have shown gel and cure times at more than double the speed of the same resins in styrene monomerⁱ. The shrinkage comparison is best illustrated by the differences in shrinkage of the homo-polymers, Poly-vinyl-toluene shrinks 26% less than Polystyreneⁱⁱ. The high dielectric constant and dielectric strength retention of product molded with resins in VT has provided superior performance in BMC fabricated product in electrical applications for many years. These enhanced properties of resins using methyl styrenes, vinyl toluene, are desirable across many composite fabrication techniques, in this case pultrusion.

Another significant driver for looking at alternate monomers in our industry is the perennial desire to mitigate the EH&S issues associated with styrene monomer. Under the Clean Air ACT (CAA) styrene is a HAP and therefore subject to Maximum Achievable Control Technology (MACT)ⁱⁱⁱ. As a result of the findings by the National Toxicology program (NTP), styrene monomer is listed on the Federal Register as “reasonably anticipated to be a human carcinogen”^{iv}. Further, the state of California under Proposition 65 has listed styrene monomer as a substance known to the state to cause cancer.

Table 1. Monomer Properties

Property – Units	Vinyl Toluene (VT)	Styrene Monomer (SM)
Vapor press @ 20°C mmHg	1.1	4.5
Vapor press @ 100°C mmHg	83	190
Flash Point TCC °C	52,8	34.4
Vol Shrink on Polymer %	12.6	17
Dielectric constant	2.57	2.41

HAP	No	Yes
RoC listed	No	Yes
CA. Prop 65	No	Yes

2. EXPERIMENTATION

2.1 Resin/Resin Mix Preparation

Resins and low-profiles were prepared according to Table 2. Viscosities were held constant and NV within 3%. Resin mixes were prepared according to Table 3.

Table 2 Resins;

Material	Polymer	Monomer
1 - Control iso Resin	Commercial Iso Polyester	Styrene (SM)
2 - Iso Resin 2	Iso Polyester	Styrene (SM)
3 - Iso Resin 3	Iso Polyester	Vinyl Toluene (VT)
4 - Control Low-profile Resin	Polystyrene	Styrene (SM)
5 – Low-profile Resin	Polystyrene	Vinyl Toluene (VT)

Table 3 Resin Mixes

Material	Specification	Parts/Hundred %
Resin	Selected from 1-3 above	58.7
Resin	Selected from 4 or 5 above	14.7
Pigment/Filler	Microdol H	22
Release 1&2	Zn St./M Wiz Pul 24	1.5/.071
UV absorber	Tinuvin P	.15
Peroxides	Perk 16/Trig C/Trig 21	0.37/0.22/0.15
Adjust	Monomer	1.5

2.2 Product Set up

3mm x 100mm strip profile was set up according to Table 4

Table 4 3x100 set up

Material	Specification	No. per Profile
MAT	450g x 100mm	2
VEIL	CEREX x 100mm	2
PLAIN	4800 TEX	50
SPUN	2400 TEX	2

3 x 100 Profiles were run on commercial pultrusion equipment. Die length was 1m with 2 heating zones set at 120°C and 160°C

Trial strips were run utilizing the following resin mixes at the indicated pull speeds:

- Run 1 – Control, Commercial Iso SM/Commercial LP SM – Speed @ 0.5m/min.
- Run 2 – Iso resin in styrene monomer/LP in Vinyl Toluene – Speed @ 0.5m/min.
- Run 3 – Iso resin in Vinyl Toluene/LP in Vinyl Toluene – Speed @ 0.5m/min
- Run 3A – Iso resin in Vinyl Toluene/LP in Vinyl Toluene – Speed @ 1.0m/min
- Run 3B – Iso resin in Vinyl Toluene/LP in Vinyl Toluene – Speed @ 1.5m/min

2.3 Product Mechanical testing

Physical testing was carried out by an independent certified laboratory;

Intertek ITS Testing Services Ltd.

The Wilton Center, Redcar, TS10 4RF U.K.

Using the following test methods by ASTM International^v

- Tensile Modulus, Strength & Elongation at Break (ASTM D638 -14).
- Flexural Modulus & Strength (ASTM D790 15e2)
- Compression Modulus & Strength (ASTM D695 -15)

- Short Beam Strength (ASTM D2344-16)

3. RESULTS

The intention of this work was to investigate the viability of utilizing vinyl toluene as an alternate monomer in pultrusion applications by comparing the physical and mechanical properties of product produced utilizing iso-resins and low-profile resins supplied in vinyl toluene verses a traditional control iso-resin and low-profile resin supplied in styrene monomer. We further investigated the effect on properties obtained by replacing only the low-profile resin with one utilizing vinyl toluene. Additionally, since resins supplied in vinyl toluene typically cure much faster at elevated temperatures than resins supplied in styrene monomer, we obtained mechanical properties on product where we ran the line speed at 2 times and 3 times the speed that we ran the control resin. This rate change effectively tripled the production rate while the cure time in the die was reduced from 2 minutes down to 40 seconds.

The following tables contain the physical and mechanical properties observed from the various pultrusion runs as outlined in experimental

Table 5: Laminate Density and Volume

Material	Specific Gravity g/cc	Volume mm ³	Weight mg
Run 1 Control Iso-SM/LP-SM	1.782	308.11	549.1
Run 2 Iso-SM/LP-VT	1.770	309.43	547.7
Run 3 Iso-VT/LP-VT	1.740	310.25	539.8

Lower specific gravity indicates less shrink. Laminates with VT measured up to 2.4% lower specific gravity. Pultruded product with VT showed 0.7% less post cured post die shrinkage.

Table 6 Tensile Modulus, Strength and elongation at Break (ASTM D638-14)

Run Number	Materials Polymer-Monomer	Line Speed M/min	Young's Modulus GPa	Tensile stress @ break MPa	Tensile strain @ break %
1- Control	Iso-SM/LP-SM	0.5	26.7	398	1.7

2	Iso-SM/LP-VT	0.5	27.8	444	1.8
3	Iso-VT/LP-VT	0.5	39.8	450	1.7
3A	Iso-VT/LP-VT	1.0	30.2	442	1.8
3B	Iso-VT/LP-VT	1.5	29.9	438	1.8

Tensile results show properties maintained across the sample range including those where the rate is increased 3 times that of the control.

Table 7: Flexural Modulus and strength (ASTM D790-15e2)

Run Number	Materials Polymer-Monomer	Speed M/min	Flexural Modulus GPa	Flexural Strength MPa	Strain @ Max load %
1-Control	Iso-SM/LP-SM	0.5	13.2	372	3.2
2	Iso-SM/LP-VT	0.5	15.6	391	2.9
3	Iso-VT/LP-VT	0.5	14.8	396	3.2
3A	Iso-VT/LP-VT	1.0	13.7	391	3.4
3B	Iso-VT/LP-VT	1.5	14.7	384	3.1

We can see that flexural properties are maintained or marginally enhanced across the sample range, similar to the tensile results, even when the production rate for the product profiles utilizing VT is tripled.

Table 8: Compression Modulus and Strength (ASTM D695-15)

Run Number	Polymer - Monomer	Speed M/min.	Modulus of Elasticity GPa	Compressive Strength MPa	Strain @ Failure %
1 Control	Iso-SM/LP-SM	0.5	28.4	400	1.5
2	Iso-SM/LP-VT	0.5	27.6	518	2.0
3	Iso-VT/LP-VT	0.5	27.9	466	1.8

3A	Iso-VT/LP-VT	1.0	26.3	477	2.0
3B	Iso-VT/LP-VY	1.5	26.0	482	1.7

In all samples where VT is utilized the compression strength of the laminates is enhanced as is the strain at failure. The modulus of elasticity variation consistently falls within normal sample deviation. Again, we observe that compression properties are maintained at increased production rates. All samples failed in typical brittle manner.

Table 9: Short Beam Strength (ASTM D2344-16)

Run Number	Polymer - Monomer	Speed M/min	Short Beam Strength (MPa)	Maximum load (N)	Failure Type
1- Control	Iso-SM/LP-SM	0.5	32.3	805	Interlaminar
2	Iso-SM/LP-VT	0.5	39.0	964	Tension
3	Iso-VT/LP-VT	0.5	40.4	1009	Tension
3A	Iso-VT/LP-VT	1.0	36.4	903	Tension
3B	Iso-VT/LP-VT	1.5	38.1	949	Tension

The short beam strength analysis showed significant improvement in all finished product where VT was utilized. It is interesting to note that there was measurable increase in strength even when only the LP in VT is substituted into the system. Although there is no apparent reason for the differing failure types it is well known that VT typically exhibits superior wetting of glass and fillers and generally provides better flow in BMC applications. Again, we notice that the product profiles containing VT outperformed the control even at the double and triple production rates.

Table 10; Laminate Strength to Weight Ratio S:W = Shear strength/Specific Gravity

Run Number	Polymer - Monomer	Speed M/min	Specific Gravity	Short Beam Strength (MPa)	Strength/Weight Ratio and improvement vs control
1 - Control	Iso-SM/LP-SM	0.5	1.782	32.3	18.13, +0.00%

2	Iso-SM/LP-VT	0.5	1.770	39.0	22.03, +21.5%
3	Iso-VT/LP-VT	0.5	1.740	40.4	23.22, +28.1%
3A	Iso-VT/LP-VT	1.0	1.740	36.4	20.92, +15.4%
3B	Iso-VT/LP-VT	1.5	1.740	38.1	21.90, +20.8%

A very important characteristic of FRP products is the strength to weight ratio. In table 9 we observed the improvement in Short Beam strength performance of the pultruded products containing VT. The superior strength (MPa) combined with lower density of the VT containing pultruded product profiles provides an improvement in strength to weight ratios (S:W) ranging from 15 – 28% in table 10.

3. CONCLUSIONS

The results of this work have provided conclusive evidence that vinyl toluene is a viable alternative monomer for pultrusion applications. Vinyl toluene can be readily incorporated into typical iso polyester systems. It is fully compatible and can be supplied either as a partial replacement for styrene monomer or full replacement to provide a styrene monomer free option. Since vinyl toluene is compatible with most resins currently in use, facilitating a changeover working with the resin companies, would be relatively straightforward.

During our study, we have seen significant product property enhancements, most notably;

- Higher strength product – Increased Strength to Weight ratio product
- Less shrinkage of the product – dimensional stability and less post die stress
- Lower density product – more product/kg of resin

Equally important, this study shows that due to the fast reaction rate of vinyl toluene, measurable process efficiency is certainly possible. During the study, we observed triple the normal pull rate without significant degradation of the product properties. In fact, in all cases the mechanical properties of the high pull rate product exceeded those of the control. Also observed was greater consistency of short beam strength and maximum load results on the vinyl toluene containing samples versus the control samples. On average, they showed more than 50% reduction in standard deviation values. Vinyl toluene is a non-HAP, low VOC, styrene replacement monomer that is not subject to the restrictive environmental and health and safety regulations that styrene monomer is.

This study was designed to prove the viability of an alternate monomer option, specifically vinyl toluene for pultrusion applications. The results are encouraging in the initial analysis. Subsequent work will focus on additional resin chemistries, vinyl esters and urethane acrylates, as well as

optimizing conditions to provide more product property enhancements and provide further process efficiency.

4. REFERENCES

- i - Dow Chemical USA Organic Chemicals Department Building 1710 Midland MI. 4864
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