Abstract

Unsaturated polyesters and vinyl esters have been the workhorse resins in the pultrusion industry for a quarter century or more. In efforts to expand their markets and differentiate their products, however, pultruders are continually seeking out new materials and processes, which can mitigate some of the limitations of traditional resins such as brittleness or slow reactivity. During the past three years polyurethane resins, which exhibit superior strength and damage-tolerance relative to traditional polyester and vinyl ester pultrusion resins, have been successfully commercialized. Such advantages do not come without new challenges as polyurethane resins require their own unique material handling and processing methods. There is a perception in the pultrusion industry that these requirements present an insurmountable barrier for practical application of polyurethane resins. This paper aims to address this perception by providing a practical discussion of injection box design, material handling, component metering equipment, die design, and process conditions used for pultruding polyurethane profiles. Using the guidelines presented in this paper, manufacturers can be confident of running a robust pultrusion process with continuous line operation.

Introduction

Polyurethane resins have drawn considerable interest as composite matrix materials in the past six years, especially for pultrusion processing (Ref. 1-8). This interest stems from the outstanding composite properties and potential for high pultrusion line speeds that can be achieved using polyurethane matrices. Several resin suppliers and pultrusion manufacturers have reported transverse profile strengths twice that of unsaturated isophthalic polyester resins and excellent damage tolerance (impact, machining and fasteners). In some cases, line speeds in excess of 2-meters/minute (79-inches/minute) have also been reported. The high transverse strength, interlaminar shear strength and damage resistance exhibited by polyurethane composites create additional potential for simplifying the reinforcement layup, reducing profile thickness and perhaps making unidirectional profiles in place of mat-reinforced parts.

Despite these advantages, there appears to be a perception within the pultrusion industry that polyurethane resins are difficult to process and expensive to use. As with any other new resin technology, there are unique material handling and process characteristics for urethane resins that must be mastered to optimize profile production. Over the past six years, a substantial body of knowledge has been developed that addresses these cost and processing concerns. This paper will present data on neat resin properties, neat resin and urethane composite properties and discuss a cost model for taking advantage of these properties by redesigning the profile geometry and reinforcement construction. Guidelines for component metering equipment, injection box design and process conditions will be outlined which will provide pultruders with a starting point to produce polyurethane pultrusion profiles. A schematic of a typical polyurethane pultrusion set-up is shown in Figure 1.

Material Properties

Several previous studies (Ref. 3, 6-8) have reported on the excellent physical properties that can be attained with polyurethane resin based pultrusion profiles. Properties of the neat polyurethane resin used in the current study are shown in Table 1. With a general knowledge of neat resin properties, one will recognize that the strength, impact resistance and strain-at-break are reasonably good compared to other resins of similar modulus and glass transition temperature, however, not spectacularly so.

The true value of using polyurethane resins is much more apparent after evaluating composite properties. The flexural properties of a profile pultruded from an unsaturated isophthalic polyester (UPE) and a polyurethane (PU) resin are compared in Figure 2. The reinforcement lay-up is identical for both resins. The profile is 2.41-mm (0.095-inch) thick and contains two 230-g/m² (0.75-oz/ft²) continuous strand mats (CSM) and rovings for a total glass content of 65 wt%. Since the flexural modulus of the composite is dominated by the reinforcement, little difference is observed between the UPE and PU. However, the flexural strength and strain-at-break are 88% and 66% higher parallel to the fibers, respectively, and 120% and 100% higher perpendicular to the fibers, respectively, for the PU composite versus the UPE. The explanation of this significant property improvement is multifaceted. Polyurethane resins exhibit
excellent wetting efficiency and adhesion to the glass reinforcement. Combining these effects with a moderately tough resin, a nearly optimal synergy of stiffness and toughness between the PU resin and the glass reinforcement is created. Since standard, multi-resin compatible rovings and CSM was used in this study, there is potential for even higher performing polyurethane composites with optimized glass sizing technology.

Polyurethane resins have been under development for use in a wide range of applications. Considering their high strength compared to UPE composites, PU-based pultrusion profiles can be fabricated with all rovings while maintaining transverse strength and increasing longitudinal stiffness, greatly simplifying the guiding system. Analogously, PU profiles could also be manufactured with thinner walls at constant stiffness compared to UPE based profiles. To further understand the value of the high strength of PU composites, the corner strength of an L-profile (15.2-cm x 2.54-cm, 6-inch x 1-inch) of varying thickness was evaluated (Figure 3). In this experiment, the L-profile was clamped in the tensile testing equipment and the corner strength (load per unit width) was evaluated for specimens approximately 25.4-mm (1-inch) wide by constraining the short leg of the profile under a 6.35-mm (0.25-inch) diameter bar and pulling up on the long leg of the L-profile.

As with the flat sections discussed above, the standard UPE profile at 2.41-mm (0.095-inch) contained two 230-g/m² (0.75-oz/ft²) continuous strand mats and rovings for a total glass content of 65 wt%. As shown in Figure 3, the load-to-fracture for the all-roving PU profile versus the CSM reinforced UPE profile increased by 18% at 2.41-mm thickness. At 2.03-mm (0.080-inch) thickness, the unidirectional PU profile exhibits similar corner strength to the standard UPE samples. However, the 1.65-mm (0.065-inch) unidirectional PU sections displayed much lower strength than expected. Based on the trend observed with the 2.41 and 2.03 mm profiles, a corner strength of approximately 4 kg/cm would be expected for the 1.65 mm profile. Upon closer examination, it was determined that the developmental 1.65-mm die was improperly engineered. The standard 2.41-mm and prototype 2.03-mm dies were designed with a smooth 3.175-mm (0.125-inch) radius inside corner. However, the 1.65-mm die was merely beveled at a 45° angle, creating a local stress concentration and premature failure during testing as might be expected in this situation. Despite this design flaw, the 1.65-mm PU profile with two mats exhibited a 52% increase in corner strength compared to the standard 2.41-mm UPE profile. This experiment reveals a great potential for PU resins in production of thinner and potentially lighter weight, lower cost pultrusion profiles.

Cost Analysis
The outstanding material performance of polyurethane profiles described in the previous section does, however, come at a cost premium relative to common isophthalic unsaturated polyester resins considering resin cost alone. In the current climate of severe price volatility in resin costs, PU resins are typically 40-60% more expensive than UPE resins and are similarly priced to many vinyl esters (VE). While the cost of PU resin is typically greater than UPE resin, the toughness, damage tolerance and strength of polyurethane resins bring potential to simplify and reduce the cost of the reinforcement layup in pultrusion profiles by replacing mat with rovings. Further, converting mat to rovings in the design will increase profile stiffness and liberate the potential to reduce the overall composite geometry. These two design elements together can actually offer a cost reduction for PU versus UPE.

Using the physical property assets of PU composites to their full potential, a cost analysis (Figure 4) revealed potential for significant cost and weight savings in an I-beam section. Such a beam 3.3-mm (0.130-inch) thick may contain three 300-g/m² (1-oz/ft²) continuous strand mats (CSM) and have a total glass content of 59 wt%. However, under the constant thickness assumption in this model, it is not possible to attain cost equivalence between PU and UPE profiles even when using only two 230-g/m² (0.75-oz/ft²) mats and filling the remaining profile space with rovings. However, a significant increase in the bending stiffness (+22%) of the beam will be obtained due to the extra rovings.

On the other hand, both weight (-13%) and cost savings (-7%) may be achieved at equivalent beam stiffness by reducing the number and weight of mats AND the wall thickness (2.76-mm, 0.109-inch). Depending on design intent, structural components may be fabricated to take advantage of either the higher stiffness at constant cross-section or lower weight and cost with reduced wall thickness. Experiments are in progress to prove the viability of this model, specifically whether beams pultruded with a polyurethane matrix have sufficient transverse, bearing and buckling strength at reduced wall thickness compared to UPE matrix profiles. The results of these new experiments will be the subject of a future publication.

Metering Equipment
Polyurethane resins are two-component systems comprised of a polyol and an isocyanate, typically based on a modified polymeric MDI (diphenylmethane diisocyanate). The polyol is a fully formulated blend of base resin, catalyst, internal mold release (IMR) and other additives. This blend does not usually include filler, colorant or UV stabilizers, for example.

To process this system, a two-component metering unit is required for production runs due to the limited pot-life of the mixed resin (15-22 minutes depending on ambient temperature and mix quality). The metering unit dispenses mixed resin into a closed injection box or injection die. However, limited open-bath runs are possible even for relatively large parts provided the bath vol-
volume is kept to a minimum and fresh resin is regularly added.

The required metering unit is comprised of several subsystems which are commercially available including: metering pumps or cylinders, resin tanks, a mixhead and transfer hoses, mixing elements and a solvent flush system. Complete metering systems with a broad range of technical sophistication can be purchased from several commercial suppliers. It is feasible to operate such turn-key systems directly from the pultrusion machine controller, allowing real-time component metering control and almost completely automated resin processing.

**Pumps/Cylinders**

Components may be metered either by air-driven cylinders or by electrically driven pumps. Single-acting cylinders can be used, but double-acting cylinders are preferred as they provide minimal flow fluctuations when the cylinder reverses direction. Cylinder pumps are rugged, reliable and can be either fixed or a more versatile variable ratio setup which allows for processing with and without fillers. An air pressure regulator must be installed to control the flow rate from the pump.

Electrically-driven gear or progressive-cavity pumps can also be used, providing a smooth continuous resin flow with little pressure fluctuation. Electric motor(s) control either both pumps (fixed ratio) or each component individually (variable ratio). Component ratio and flow rate are controlled by the motor speed which is critical to maintaining optimum mixing. Gear pumps are not suitable for use with abrasive fillers (generally in the polyol side). Progressive cavity pumps can be used with fillers but are generally more expensive than gear pumps. A typical arrangement would use a gear pump for the isocyanate and progressive cavity pump for the polyol.

Pumps must be sized according to the largest product to be run and linespeed requirements. The volume of resin per length of product times the linespeed will determine the lowest total resin volume output for which the pumps should be sized. However, very large pumps may be difficult to control for very small resin throughput.

**Resin Tanks**

One tank each is required for the isocyanate and polyol to provide resin supply during pump operation. The tanks are usually installed to provide gravity or pressure feed for the pumps and should be sized to minimize the need for refilling during operation. Both tanks should be sealed to minimize exposure to humid atmosphere and have a desiccant filter installed to provide dry makeup air. An agitator is required in the polyol tank to ensure the IMR and filler, if any, remain homogenized. The hose from the isocyanate tank to the pump should be polyethylene lined for maximum life. An inline strainer on the isocyanate feed is also suggested to prevent debris, if any, from entering the pump. For the highest level of process control, both the polyol and isocyanate tanks may be jacketed to maintain constant component temperature, but this stringent action is not required.

**Mixhead**

The mixhead controls the on-off flow of resin, combining the polyol and isocyanate streams to begin the mixing process. In simplest form, the mixhead consists of two ball valves with one handle and a body in which the streams combine. More sophisticated mixheads can be pneumatically or electrically operated. Check valves at the entrance to the mixhead valves will prevent backflow into the resin hoses in the case of pressure differentials between the two components. It is also feasible, but somewhat costly, to set up a mixhead with a third stream to add colorant or other liquid additives directly on-line. This approach would prevent contamination of the polyol tank and allow for rapid changeover of profile color. Component mix ratios must be adjusted accordingly to compensate for any additive.

**Mixing Elements**

Typically, static mixtubes are connected to the outlet of the mixhead to thoroughly mix the two components before introduction into the injection box. The size of the mixtube and number of elements should be sized to provide good mixing without creating high backpressure. Sizing parameters are dependent on flow rate requirements, isocyanate to polyol ratio, component viscosity and component compatibility. Three 0.375-inch O.D. mixtubes attached in series with 24 mix elements in each tube will provide good mixing for most resin combinations.

**Solvent Flush System**

It is necessary to flush the mixhead, mixtubes and injection box during shutdown of a pultrusion run to prevent resin from curing in place. The flush solvent is typically introduced into the mixhead through a three-way ball valve. Resin is initially purged out of the mixhead and mixtubes with air followed by thorough flushing with solvent. Typically a two-gallon paint pot pressurized with air works well as a solvent container. The solvent should have a high flashpoint to minimize the hazard of passing it through a hot die. Propylene carbonate is a satisfactory flush solvent to remove uncured polyurethane resin. Pressure regulators should be installed to control air pressure in the solvent pot and for flushing and the mixhead.

**Injection Box Design**

Injection processing for pultrusion has been practiced in development and production for more than a decade. The approach reported by Gauchel & Lehman (ref. 9) using a ‘tear-drop’ injection die is probably the best known. Resin injection can be performed internally within the die, typically by modifying it with a weir surrounding the profile, or within an injection box added on to the die in place of a typical wet-bath. Each has its advantages. Development work is best suited for an injection box approach as it can be fabricated rapidly and inexpensively from high density polyethylene (HDPE).
Steel or anodized aluminum will be more robust for the heavy use of a production environment. The configuration of the wet-out chamber for closed injection processes is considered to be highly proprietary to pultruders. However, there are several ‘rules-of-thumb’ that are known in the public domain.

The most critical design parameter is limiting ‘dead spots’ in the injection zone, especially for fast reacting resins such as polyurethanes, where the resin can accumulate and possibly cure. The entire volume of the injection box or die must be replenished 3-5 times before the gel time to ensure long runs can be made without gelation. Mathematically, this can be expressed as follows:

\[
V_i = \frac{(A_x)(l_x)(t_{gel})(\phi_g)}{(3 \text{ to } 5)}
\]

where

- \(V_i\) = injection box volume
- \(A_x\) = profile cross-sectional area
- \(l_x\) = line speed
- \(t_{gel}\) = resin gel time
- \(\phi_g\) = glass volume fraction

For example, for a profile with 3.23-cm² (0.5-in²) cross-section at 50 volume % (68 wt %) glass, a 500-ml injection box will turn over five times in 20-minutes at 0.77-m/min (30.5-in/min). As this line speed is usually achieved easily, long production runs should not present problems in this case.

Profiles can be fabricated with polyurethane resin either using either rovings alone or a combination of mat and rovings. Each requires a different approach to injection box design, particularly in constraining the reinforcement into the correct location and preventing leakage of resin from the injection box.

For unidirectional profiles, especially those thicker than 2.5-mm (0.098-inch), rovings should be fed through the back plate of the injection box through a series of tapered slots conforming to the shape of the finished profile. High resin percolation along the length of rovings presents a challenge in eliminating resin leakage. To seal the back plate, the slots should compress the rovings to 10-15 % less than their thickness in the finished profile. Rovings should be guided into the die at an angle to aid resin turn-over in the box and keep the rovings at the surface of the profile. Entrance angles of 3-5 degrees should work satisfactorily.

For mat reinforced profiles, uniform roving distribution is the key to producing pultruded profiles free of sink marks and scaling. The mat and roving should be guided through a slot (again with 10-15% compression) in a form as close as possible to the profile shape. Carding systems developed for open-bath processing can often be used to guide dry reinforcements into the injection box. Once rovings enter the box, tension will prevent them from redistributing. Upstream carding has a significant impact on both the distribution and tension on both rovings and mat within the injection box.

In the case of both unidirectional and mat reinforced profiles, optimum wet-out is achieved through a combination of pressure and residence time in the injection box. For a 30.5-cm (12-inch) long box running at 1.8-m/min (72-in/min), the residence time of the reinforcement in the box is only 10 seconds. Obviously, substantial pressure is required to wet the reinforcement in such a short time. With a well-sealed box, injection pressures of 7-10 Bar (105-150 psi) are achievable although 3-5 Bar (45-75 psi) is more common. The mixed polyurethane resin typically is injected through two or more ports to smooth out pressure and velocity gradients in the box or weir. The location and number of ports has a great impact on wetting efficiency.

**Die Design**

There are no special die design requirements for pultruding polyurethane resins compared to styrene-based resins. A typical die has a 3.2-mm (0.125-inch) inlet radius and has parallel walls along the full 0.9-1.0 meter (36-39 inch) length. Dies designed with an inlet taper may be used, but must have cooling on the entire tapered section to prevent die lock. Certain dies may have an exit taper. Such dies can be used as well, but may limit line speed if the gel zone shifts into the exit taper region, degrading surface quality. Polyurethane resins shrink considerably less than styrene resins, typically 2.0-2.5 % for the base resin and approximately 1.0% or less for the composite. Although there have been limited studies directly comparing layups, pull forces for PU pultrusion have been found to be similar to UPE and VE despite the low shrinkage.

**Recommended Process Conditions**

There is some perception within the pultrusion industry that polyurethane resins are difficult to process and are prone to die lock. With a well formulated PU resin system and appropriate process conditions, polyurethanes exhibit quite robust and reproducible processing. High quality PU pultrusion profiles have been run continuously for over 48-hours at 60-inches/minute using a standard resin having a 20-minute gel time. This run was not terminated due to gelation in the injection box or die lock, but simply because sufficient profile had been produced. Using a well-designed closed injection box and dosing resin with a metering pump, runs of indefinite time are feasible. Short runs of 30-60 minutes are also possible in an open bath with minimized dead spots and good resin mixing. In contrast to die lock issues found in epoxy pultrusion, line purges up to 5-minutes in length have been performed without restart problems during PU runs when required to address saw or reinforcement concerns.

As shown schematically in Figure 1, the die should be set up with cooling at the entrance (~10-cm, 4-inches) to prevent heat from diffusing into the injection box,
causing die lock. Production runs typically use two subsequent heating zones with Zone 1 at 160-177°C (320-350°F) and Zone 2 at 190-199°C (375-390°F). At steady state conditions, Zone 2 will remain heated by the resin exotherm. Normally, Zone 3 is unheated and allowed to cool by ambient conditions or it may be actively cooled. At line speeds over 1.5-m/min (6-ft/min), active cooling of the die may be necessary to keep the profile exit temperature below 120°C (250°F) and limit possible warpage. Profile cooling with water after exiting the die is also useful to prevent damage by the pullers. For profiles thicker than 6.2-mm (0.25-inch) at high line speeds (> 1.5-m/min, 6-ft/min), it may be necessary to heat Zone 3 and/or lengthen the die to ensure cure in the core of the profile. In this circumstance, line speed limitations result from heat transfer both into and out of the profile, not from resin conversion. Line speeds up to 1.8-m/min (85-in/min) have been run with unidirectional profiles while maintaining good surface quality and low pull forces. It is feasible to run similar line speeds with mat reinforced profiles using the appropriate injection box design and good reinforcement guidance as well as sufficient heater wattage and resin pump capacity.

Material Handling

As noted earlier, the polyol component should be mixed vigorously before use and continually during use. Care should be taken to limit exposure to air as the polyol is somewhat hygroscopic. Since CO₂ will be generated when MDI reacts with H₂O, the absorbed moisture can lead to resin foaming upon mixing with the isocyanate. Similarly, any additive such as CaCO₃ filler or colorants should contain minimal moisture. However, it is not required to dry the additives or reinforcements since a limited amount of moisture can be tolerated without degrading processing or profile quality.

The MDI should remain in enclosed containers except during transfer operations. With prolonged exposure, MDI will react with H₂O in air foaming the PU resin, solidifying some MDI in the tank and perhaps clogging the equipment filters. Reaction with moisture in the air is not an issue for short term exposure (up to several hours time) for typical material transfer operations. Small amounts of unused MDI can be decontaminated with a mixture of water, surfactant and ammonia according to the MSDS. Alternately, the MDI can be reacted with residual polyol in a well-ventilated area. Care should be taken to limit resin volumes to prevent excessive exotherm generation.

EHS Matters

All resins used in the composite industry present environmental, health and safety (EHS) hazards of one kind or another. Styrene is currently under study by the US Environmental Protection Agency (EPA) and could be listed as a carcinogen, although that scenario is unlikely. Epoxy curatives, especially aromatic amines, may induce dermal sensitivities over time, some are carcinogenic and many exhibit strong odors.

The two-component polyurethane resin systems described in this paper are compliant with the EPA’s Maximum Achievable Controls Technology (MACT) rules and do not use styrene or generate volatile organic compounds (VOC). For polyurethane resins, the polyol component presents relatively few EHS hazards other than the acidic nature of the IMR which is premixed into the blend. The fully formulated polyol can be easily handled with simple personal protective equipment (PPE) such as nitrile or butyl gloves and safety glasses.

The liquid isocyanate component (a polymeric MDI variant) on the other hand can lead potentially to long-term occupational exposure issues (allergic-type respiratory or dermal sensitivities) if improperly processed, handled and stored. However, the required PPE, training for use, handling and storage and monitoring of worker exposure are all well-known and easy to implement. Compared to toluene diisocyanate (TDI) and aliphatic isocyanates which are volatile and hazardous at ambient conditions, MDI has a very low vapor pressure (<0.0006-mm Hg at 25°C) and is a limited respiratory hazard near 25°C unless formed into an aerosol. Nitrile, butyl or neoprene gloves and safety glasses are the recommended PPE. Latex gloves do not provide sufficient protection. Ventilation is not necessary for normal transfer operations of MDI at ambient conditions.

At the exit of a pultrusion die, Joshi et al. (Ref. 5) observed locally elevated concentrations of MDI vapor which increased as a function of line speed. Very small amounts (PPB levels) of MDI volatilize off the pultruded profile due to incomplete conversion. With minimal ventilation, Joshi et al. (Ref. 5) also found exposure of pultrusion line operators was well below OSHA and ACGIH MDI exposure limits. Based on this study, ventilation controls such as a canopy hood are recommended at the die exit and over all large volumes of mixed resin and atmospheric (or hygiene) monitoring should be done to ensure the ventilation controls are sufficient to keep local MDI concentrations below OSHA limits.

Conclusions

Development of pultrusion profiles based on polyurethane resins has advanced in the past six years to full commercialization. PU composites have proven to exhibit superior strength and toughness compared to UPE and VE resins. To take full advantage of these properties, PU resins must be processed using methods that are new or at least not widely known and understood in the pultrusion industry. Using the guidelines outlined in this paper, most pultruders should be able to produce moderately complex profiles with polyurethane resins. Processing, guide system and injection box design optimization by the pultruder will lead to full utilization of the potential of the polyurethane resin.
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References

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Aaron Duncan is a Development Engineer at Huntsman Corporation in Auburn Hills, MI supporting polyurethane pultrusion development. Aaron has worked in adhesive, coatings, elastomer and composite development at Huntsman for 3 years.
TABLE 1 – Physical Properties of Neat Polyurethane Pultrusion Resin

<table>
<thead>
<tr>
<th>Property</th>
<th>SI Units</th>
<th>English Units</th>
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<tbody>
<tr>
<td>Tensile Modulus (ASTM D638)</td>
<td>2925 MPa</td>
<td>424,100 psi</td>
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<tr>
<td>Tensile Strength (ASTM D638)</td>
<td>71 MPa</td>
<td>10,300 psi</td>
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<td>Tensile Strain-to-Failure (ASTM D638)</td>
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<td>5.9 %</td>
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<tr>
<td>Notch Izod Impact (ASTM D256)</td>
<td>43.3 J/m</td>
<td>0.81 ft-lb/in</td>
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<tr>
<td>Glass Transition Temperature (DMA)</td>
<td>135-140 °C</td>
<td>275-284 °F</td>
</tr>
</tbody>
</table>

Figure 1 - Schematic of a Typical Polyurethane Pultrusion Set-up
Figure 2 - Comparison of Flexural Properties of Unsaturated Polyester and Polyurethane Pultruded Properties

Figure 3 - Comparison of Corner Strength of Pultruded Unsaturated Polyester and Polyurethane L-Profiles with Various Glass Construction
Figure 4 - Comparison of Cost, Weight and Stiffness of Unsaturated Polyester and Polyurethane I-Beams with Various Glass Lay-Ups