

Characterization of Pultruded Polyurethane Composites: Environmental Exposure and Component Assembly Testing

by

Michael Connolly
John King
Trent Shidaker and
Aaron Duncan
*Huntsman Polyurethanes
Auburn Hills, MI*

Abstract

Polyurethane-based composites have become an accepted alternative in the pultrusion industry, especially for applications requiring high strength and durability. Pultruded composites based on two-component polyurethanes are now widely known to exhibit superior strength and toughness compared to traditional pultrusion resins, allowing manufacturers to cost-effectively produce lighter, stronger and more damage tolerant profiles. However, verifying that a particular material meets the physical property requirements for an application is only one step in ensuring that material is fit for the purpose. Evaluation of pultruded profiles in 'real world' tests such as long term environmental exposure and performance in secondary processing and assembly operations is critical to ensure component functionality is maintained over its life-cycle. This paper will report on physical property changes due to environmental exposure for pultruded polyurethane (PU), vinyl ester (VE), unsaturated polyester (UPE) and unsaturated polyester-urethane hybrid (UPE-PU) composites. Environmental tests include UV exposure and immersion in water, salt water, hydrocarbon fluids and strong acid solutions. In addition, impact, screw pull-out and bearing strength performance of composites based on each resin system will be compared to evaluate durability and functionality in component assembly.

Introduction

While not yet common place, polyurethane resins have become more widely used as composite matrix ma-

terials in the past decade, especially for pultrusion processing. The growth in polyurethane use has been driven by the outstanding composite properties and potential for high pultrusion line speeds that have been reported using these matrices (Ref. 1-6). High transverse strength, interlaminar shear strength and damage resistance exhibited by polyurethane composites create the potential for simplifying the reinforcement lay-up and reducing profile thickness.

Because they tend to perform well under such conditions, composites are used in many applications in which they are exposed to aggressive, potentially degrading environments. Therefore, evaluation of pultruded profiles in such environments is critical to ensure functionality is maintained over time. As with environmental exposure, performance of a component in 'real world' tests of cutting, machining, drilling, bonding and mechanical assembly is important to prove viability in an application.

Polyurethane pultrusion technology is under development or has been commercialized in applications ranging from structural channels to tubes and beams to electrical components to window lineals and stiffeners to sporting goods. In each case, the pultruded profiles undergo some form of secondary operations before end use. For processes such as cutting and assembly, the toughness and durability of polyurethane composites can pay significant dividends in reduced scrap, ease of assembly, decreased labor or reduced assembly cost.

Previous reports on polyurethane composites have focused on basic property evaluation and pultrusion processing methodology for PU resins. This paper will discuss changes in physical properties due to environmental and chemical exposure for unsaturated polyester (UPE), vinyl ester (VE), unsaturated polyester-urethane (UPE-PU) hybrid and polyurethane (PU) resin-based profiles with identical fiberglass reinforcement. Performance in tests mimicking secondary assembly operations (*i.e.*, screw pull-out and bearing strength) will also be described for each resin system. With this information in hand, composite design engineers, pultruders and end users will better understand how PU pultrusion technology can enable differentiated pultruded products through composite redesign and improved safety factors.

Environmental Exposure

Water Absorption

Many long term performance measures are linked to a material's propensity to absorb moisture, especially for those materials that are sensitive to hydrolysis. High water absorption can result in significant swelling stresses and subsequent fiber-matrix debonding, resulting in loss of composite strength and stiffness and providing opportunity for more water ingress and hydrolytic polymer degradation. As a first step in a larger program to study environmental effects, water absorption was meas-

ured for the VE, UPE, UPE-PU hybrid and PU composites of identical reinforcement lay-up: 2.54-mm thick with two 300-g/m² (1.0-oz/ft²) continuous filament mats (CFM) and rovings with standard multi-resin compatible sizing for a total glass content of ~68 wt %. The PU profiles exhibited substantially lower water absorption (0.35 wt%) than the identically constructed competitive composites: 36 %, 42 % and 53 % lower, respectively, than the UPE-PU hybrid, VE and UPE profiles.

It has been observed that PU resins tend to wet fiberglass reinforcements well; hence, the void content of pultruded PU composites is typically very low (less than 1 %). In addition, the interfacial fiber-matrix bond strength of PU to fiberglass – with appropriately matched sizing – has been reported by Agrawal and Drzal (Ref. 7) to be quite high. These factors – low void content and high interfacial strength – are key drivers affecting water absorption and subsequent long term behavior.

Sea Water Immersion

In applications such as grating for off-shore oil platforms, sheet pile for sea walls and structural components for marine docks, profiles are obviously exposed to sea water. Compared to fresh or distilled water, sea water tends to be a more aggressive environment since the metal salts can catalytically promote hydrolysis. Many factors could be chosen to judge long term performance. Since these exposure tests were limited to twelve weeks duration, a sensitive material characteristic was needed to differentiate the various composites. This study focused on the change of transverse flexural strength after exposure as this factor is strongly dependent on resin type. A preliminary study of exposure of VE, UPE, hybrid and PU profiles to artificial sea water following ASTM C581 protocols is shown in Figure 1. Not only do PU profiles display higher initial strength than the competitive resins, but they retain more strength over time than the VE, UPE and hybrid profiles. These general-purpose competitive resins all contain ester linkages in the polymer backbone which can hydrolyze over time, decreasing resin strength. The polyurethane resin used in this study does not contain ester chain linkages. In addition to hydrolysis, the salt water can diffuse into voids in the composites potentially causing resin-fiber delamination and additional strength and stiffness reduction.

Acid Immersion

Pultruded composites are commonly used in chemical process environments and may potentially be exposed to strong acids which can degrade the matrix and potentially the reinforcement. While E-glass-based composites without a surfacing veil are not typically exposed to strong acids, such composites over their life-cycle could be exposed to acid rain or electric fields which can generate nitric acid in the presence of nitrogen, ozone and water. Hence, testing for acid resistance should be evaluated before field use.

Again, following ASTM C381 methodology, composite profiles of each resin system were immersed in strong acid (hydrochloric and nitric acids) for a period of twelve weeks. Figure 2 displays the effect of HCl exposure on the transverse flex strength of each type of pultrusion. As with salt water exposure, the PU profiles maintained higher strength throughout the test compared to the VE, UPE and UPE-urethane hybrid samples. The PU and hybrid composites exhibit an exponential loss of strength over the test cycle with a strength reduction of 40-50 % over the 12 week test. Both the VE and UPE profiles show evidence of a rapid initial loss of strength followed by a monotonic strength reduction totaling 65-75 %.

Specimens exposed to nitric acid (data not shown) exhibited similar behavior with some variations. The VE and UPE profiles performed better in nitric acid than in HCl, losing 55-60% of their strength while the hybrid samples performed slightly worse (50-55 % loss). The PU profiles displayed a monotonic loss in strength over the whole period, eventually losing 60-65% of the original strength. Clearly, the hybrid and PU resins containing urethane linkages in the polymer backbone are more sensitive to nitric acid-promoted hydrolysis than the VE and UPE resins containing only ester linkages while the sensitivity is reversed for HCl promoted hydrolysis.

Hydrocarbon and Other Chemical Immersion

Because of their previously described toughness and strength, PU-based composites are being investigated for a range of military and civilian transport applications. VE, UPE, UPE-urethane hybrid and PU profiles of identical construction were evaluated in accordance with MIL-PRF-C62419A specifications. In Figure 3, the longitudinal and transverse flexural strengths of composites based on each resin are shown after four weeks immersion in fluids commonly found transportation applications.

Motor oil, brake fluid and ethylene glycol-based antifreeze were found to have no measureable effect on either the longitudinal or flexural strength for all four resin systems. Immersion in the 10% methanol/water solution, on the other hand, resulted in ~10% reduction of the longitudinal strength for all four resins. Only the UPE profiles exhibited a small loss in transverse strength in the 10% methanol solution.

For gasoline, the longitudinal strength of the VE, UPE and PU profiles were unaffected. For the UPE-urethane hybrid resin, however, the longitudinal strength was severely reduced (~40%) after four weeks immersion in gasoline. The transverse strength of the VE composites was unaffected by gasoline immersion while the transverse strength of the UPE, hybrid and PU profiles were perhaps marginally reduced.

UV Exposure

Many pultrusion applications involve outdoor use with potential for long-term exposure to ultra-violet (UV) light. As with hydrolysis, UV radiation can cause polymer breakdown and reduction in strength. In addition, UV degradation leads to discoloration which is usually assumed to indicate property reduction. VE, UPE, hybrid and PU profiles with identical reinforcement (2.54 mm thick with two layers of 230-g/m² CFM, ~72 wt % fiberglass) were exposed to UV and humid environments in a QUV chamber for 1000 hours. None of the resins contained UV stabilizing additives. In Figure 4, the color shift and glass 'blooming' are displayed for each type of composite over the 1000 hour QUV test cycle while the change in transverse strength is shown in Figure 5. Although there is some scatter in the data, it is clear that the PU and hybrid resins exhibit better strength retention (10-15 % loss) versus the UPE (15-20 %) and the VE (25-30 %). Interestingly, the VE composite displays the smallest color change while the PU and hybrid UPE-PU exhibit greater yellowing, indicating that color shift is not necessarily a telling factor in strength degradation. The hybrid and PU profiles appear to have a rapid color change initially at 250 hours, but little change afterwards while the VE and UPE composites exhibit a monotonic color change over the 1000 hour test.

The hybrid and PU profiles contain impurities in the isocyanate portion of the resin, making them very susceptible to discoloration. Since the pure polyurethane resin contains more than 50% by volume isocyanate, the base resin color is darker than the competitive resins. While it is difficult to discern in this photograph, the VE, UPE and hybrid profiles display more fiber 'blooming' than the PU composite. The improved wet-out of the PU profiles will yield a thicker layer of resin at the composite surface, reducing the amount of resin that degrades and falls off the composite during UV exposure. With appropriate UV stabilizers, color shift, 'blooming' and strength loss for all resin systems can be reduced.

Impact Performance

In Figure 6, Dynatup instrumented impact curves are compared for identical composites based on the VE, UPE, UPE-PU hybrid and PU resin systems. The fiberglass lay-up is identical for all resins. The profile is 4.06-mm (0.160-inch) thick and contains three 300-g/m² continuous filament mats (CFM) along with glass rovings for a total glass content of ~68 wt %. In this type of experiment, the area under the curve indicates the total energy absorption during dart or 'tup' penetration while the area up to the maximum load reveals the impact energy tolerated by the composite before catastrophic failure. As has been reported previously for thinner profiles (Ref. 6), the PU composite displays superior toughness relative to the VE, UPE and UPE-urethane hybrid resin profiles. For 4.06 mm thick profiles, the total energy ab-

sorption for PU profile was found to be 20 %, 31 % and 39 % higher than the hybrid, VE and UPE resin profiles, respectively (see TABLE 1). The more critical energy-to-maximum load was found to be 32 %, 36 % and 118 % higher for PU profiles compare to hybrid, VE and UPE profiles, respectively. A similar trend can also be observed in TABLE 1 for thinner 3.175-mm and 2.54-mm profiles containing only two continuous filament mats.

Upon examining the data further, the 2.54-mm PU profile is found to have more or similar tolerance to initial damage than the thicker 3.175- and 4.06-mm VE and UPE profiles and the 3.175-mm hybrid profile. Despite the change in thickness and reinforcement schedule, the 2.54-mm PU samples have higher energy-to-max load. It is clear that PU composites have a clear advantage to the end user for uses requiring both high stiffness and toughness.

Secondary Operations

Screw Pull-Out

Fenestration (window lineals, stiffeners,...) and architectural moldings are the fastest growing segments in the pultrusion industry. These relatively small, but complex profiles pass through several secondary operations (cutting, machining, sanding,...) before assembly into the final product. These types of components are often assembled with screws – either directly into the composite or into a wood or plastic backing plate. Such backing plates usually are necessary because the UPE or VE resins used typically in fenestration and similar applications have a tendency to crack and fail when the loads are applied directly to the composite. Evaluating screw retention in pultruded composites based on the various resins would yield valuable insight into the utility of each resin in such applications.

The results of an initial study of screw pull-out force are displayed in Figure 7. As with mechanical properties and damage tolerance, PU profiles exhibited significantly higher performance than the competitive resins for profiles of identical fiberglass construction. Using a modification of ASTM C1037, the force to remove a #10 self-tapping screw was measured. For 2.54-mm thick profiles with two layers of 300-g/m² CFM, the maximum pull-out force for PU profiles was found to be 31 % higher than for a hybrid UPE-urethane composite and 43% and 79% higher than VE and UPE composites, respectively. When considering the force to initial crack formation, the difference is even more pronounced. The resistance to initial cracking of the PU composite was measured to be 48 %, 99 % and 171 % higher, respectively, than the UPE-PU hybrid, VE and UPE profiles. For 4.06-mm profiles with three layers of 300-g/m² CFM, the pull-out force is double that of 2.54-mm, but the differences between the PU and competitive resins are almost identical. It is important to note that the

force-to-crack for 2.54-mm PU profiles is 30% higher than for 4.06-mm UPE and only 16% lower than 4.06-mm VE.

Once an initial crack is formed, a screw can easily work free over time with repeated loading. With such pronounced differences between PU profiles and the competitive materials, an opportunity may exist to re-engineer attachment methods and lower assembly costs, perhaps eliminating plastic, wood or metal backing plates that are common in profile assembly. Additional benefits of using PU profiles which are mechanically assembled could include reduced labor costs, reduced warranty replacement and repairs, lower assembly scrap and improved product quality.

Bearing Strength

Pultruded composites have become common-place in structural applications including as waste-water treatment, cooling towers and radiofrequency-transparent towers. Such structures are assembled typically with mechanical fasteners and bolts perhaps combined with structural adhesives. The ASTM D953 bearing strength test has been used widely to evaluate the ability of polymer composites to withstand the localized loading associated with mechanically assembled composite structures.

While lap-shear testing of adhesive bond strength is on-going, Figure 8 displays the bearing strength of identical composites based on each of the four resin systems. As has been observed previously with other strength tests, the PU composites possess the highest bearing strength of the four resin systems in both the longitudinal and transverse directions. The hybrid and PU profiles exhibit bearing strengths 14% and 40% higher in the longitudinal direction compared to the VE and UPE profiles, respectively. In the transverse direction, the PU profiles have 16% higher bearing strength than the VE and hybrid profiles and 43% higher than the UPE composite.

Conclusions

Polyurethane-based composites have become an accepted alternative in the pultrusion industry. PU pultruded profiles have proven to exhibit superior strength and toughness compared to VE, UPE and hybrid UPE-urethane resins. PU profiles have been found to exhibit promising preliminary results in environmental exposure tests and evaluation of assembly methods. These characteristics provide the design engineer, pultruder and end-user with broad latitude in PU composite design, process and fabrication at competitive costs, opening new opportunities in new markets – perhaps in some where composites have not been cost or performance competitive before the development of PU pultrusion resins.

Many composites are ‘over-engineered’ to account for property loss over time and to maintain a sufficient

‘safety factor’ for end-use. Because of the outstanding performance of PU profiles, it may be possible to re-engineer the reinforcements used and, hence, fabricate lighter weight and potentially less-expensive composites with PU compared to commonly used UPE and VE. With judicious design, it is feasible to produce PU profiles that are not only tougher, stronger and lighter than competitive composites, but will remain so over time. Additionally, the strength and toughness of PU pultrusions could translate into easier component assembly, reduced scrap, reduced warranty costs and greater customer satisfaction.

All information contained herein is provided "as is" without any warranties, express or implied, and under no circumstances shall the authors or Huntsman be liable for any damages of any nature whatsoever resulting from the use or reliance upon such information. Nothing contained in this publication should be construed as a license under any intellectual property right of any entity, or as a suggestion, recommendation, or authorization to take any action that would infringe any patent. The term "Huntsman" is used herein for convenience only, and refers to Huntsman LLC, its direct and indirect affiliates, and their employees, officers, and directors.

References

1. Joshi, R.R., Varas, L.L., Padsalgikar, A.D., “Polyurethanes in Pultrusion: Styrene Free Alternative Systems”, *International Composites Expo 1999-SPI*, (Society for the Plastics Industry), April 1999.
2. Coffee, H.D., Perry, M.J., “Processing Techniques for Reinforced Thermosetting Urethane Composites,” *Proceedings of Composites 2001-CFA*, (Composites Fabricators Association), October 2001.
3. Vaughn, J.G., Lackey, E., Coffee, H.D., Barksby, N., Lambach, J.L., “Pultrusion of Fast-Gel Thermoset Polyurethanes: Processing Considerations and Mechanical Properties,” *Proceedings of Composites 2003-CFA*, (Composites Fabricators Association), October 2003.
4. Sumerak, J.E., “Pultrusion Gets Tough: Polyurethane Resin Offers New Growth,” *Composites Fabrication*, (American Composites Manufacturers Association), February 2004.
5. Connolly, M., King, J.P., Shidaker, T.A., Duncan, A.C., “Pultruding Polyurethane Composite Profiles: Practical Guidelines for Injection Box Design, Component Metering Equipment and Processing,” *Proceedings of Composites 2005-ACMA*,

(American Composites Manufacturers Association), Sept. 2005.

6. Connolly, M., King, J.P., Shidaker, T.A., Duncan, A.C., "Processing and Characterization of Pultruded Polyurethane Composites," Proceedings of the 8th World Pultrusion Conference, (European Pultruders Technical Association), March 2005.
7. Agrawal, R.K., Drzal, L.T., "Adhesion Mechanisms of Polyurethanes to Glass Surfaces: III. Investigation of Possible Physico-Chemical Interactions at the Interphase," J. Adhesion, vol. 55, p. 221, 1996.

Biography:

Michael Connolly, Ph.D. is Product Manager—Urethane Composites for Huntsman Polyurethanes in Auburn Hills, MI. Michael has been employed in polyurethane product development for 10 years at Huntsman and has 17 years experience in a range of polymer materials development roles. He received his doctoral degree in Polymer Science and Engineering from the University of Massachusetts-Amherst in 1989.

John King is a Senior Development Engineer for Huntsman Polyurethanes based in Auburn Hills, MI supporting pultrusion and polyurethane composite development. John has served as a mechanical engineer in polyurethane composites for 5 years and for 26 years in numerous other engineering design and development roles.

Trent Shidaker is Development Manager for Polyurethane Composite and Rigid Foam development for Huntsman Polyurethanes in Auburn Hills, MI. Trent has been employed as manager or project leader in polyurethane foam and composite development at Huntsman for 10 years.

Aaron Duncan is a Development Engineer at Huntsman Polyurethanes in Auburn Hills, MI supporting polyurethane pultrusion development. Aaron has worked in adhesive, coatings, elastomer and composite development at Huntsman for 4 years.

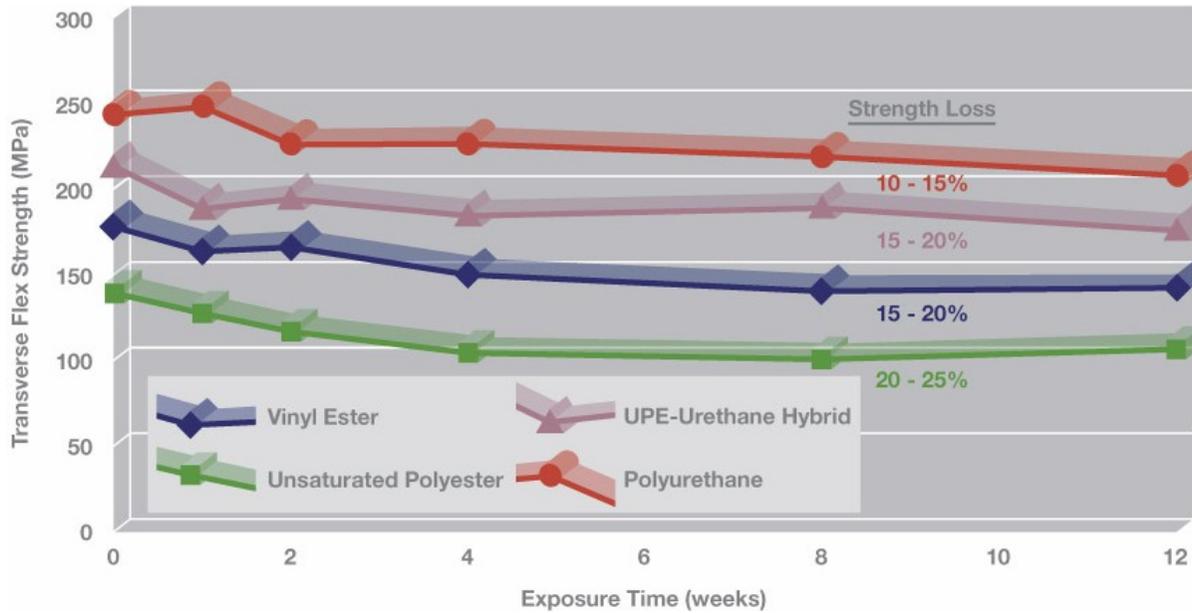


Figure 1 – Effect of Salt Water Exposure on Transverse Flexural Strength of Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (2.54 mm thick, 2 x 300 g/m² CFM, ~68 wt % fiberglass)

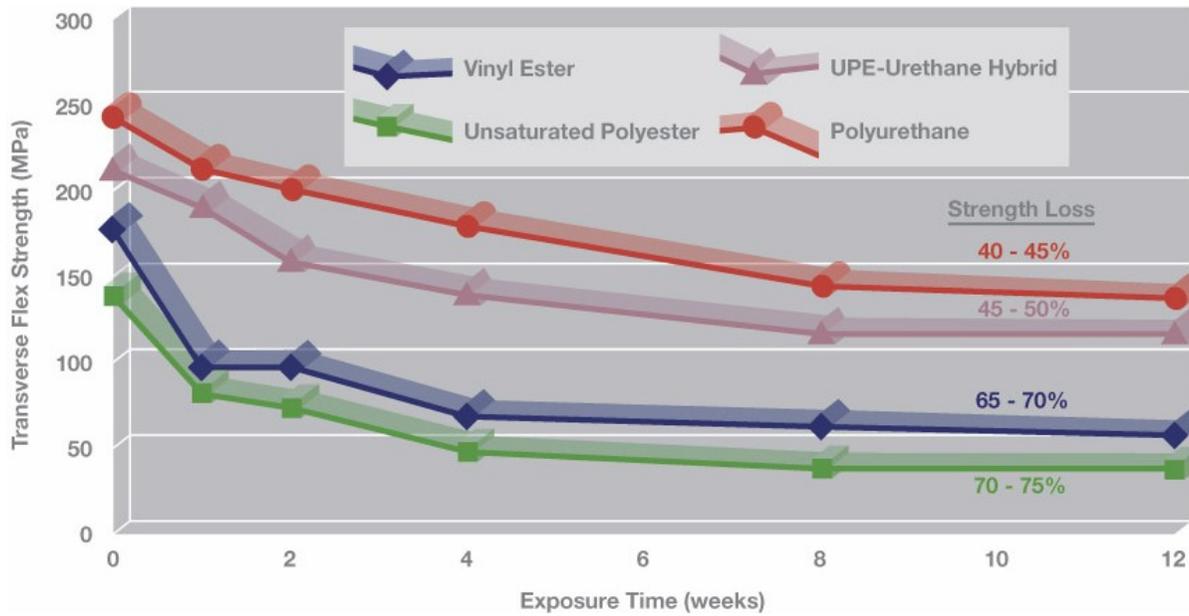


Figure 2 – Effect of HCl Exposure on Transverse Flexural Strength of Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (2.54 mm thick, 2 x 300 g/m² CFM, ~68 wt % fiberglass)

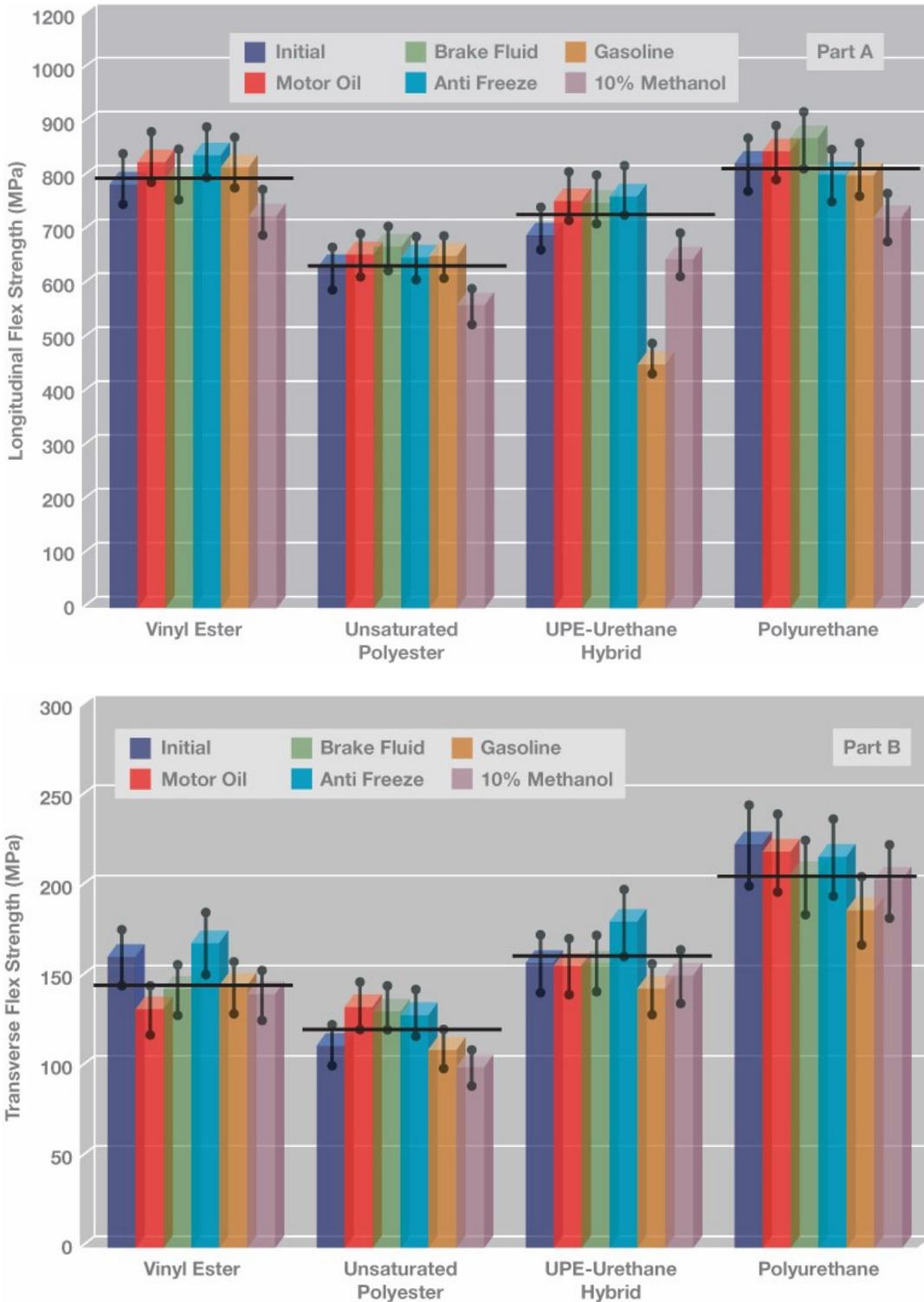


Figure 3 – Effect of Four (4) Weeks of Chemical Immersion on Longitudinal (Part A) and Transverse (Part B) Flexural Strength of Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (2.54 mm thick, 2 x 230 g/m² CFM, ~72 wt % fiberglass)

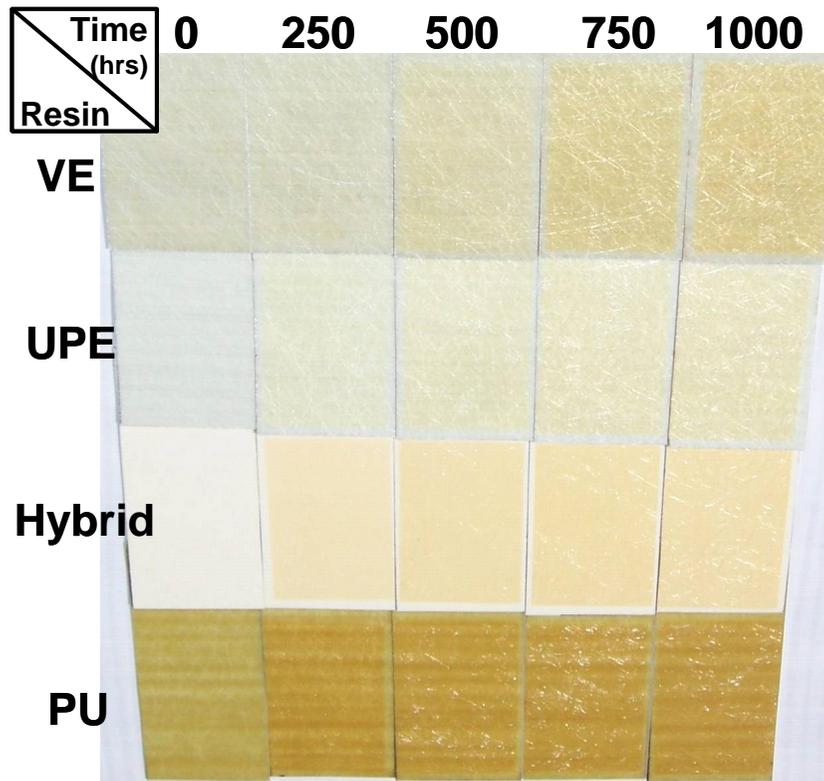


Figure 4 – Color Change after QUV Exposure for Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (2.54 mm thick, 2 x 230 g/m² CFM, ~72 wt % fiberglass)

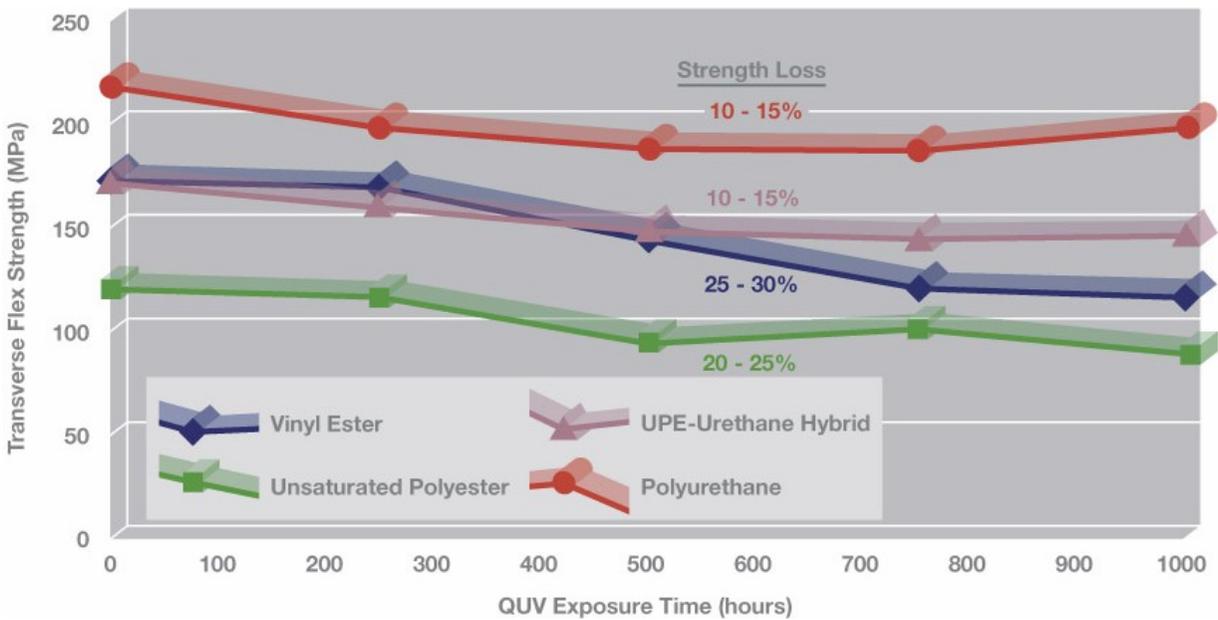


Figure 5 – Effect of QUV Exposure on Transverse Flexural Strength of Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (2.54 mm thick, 2 x 230 g/m² CFM, ~72 wt % fiberglass)

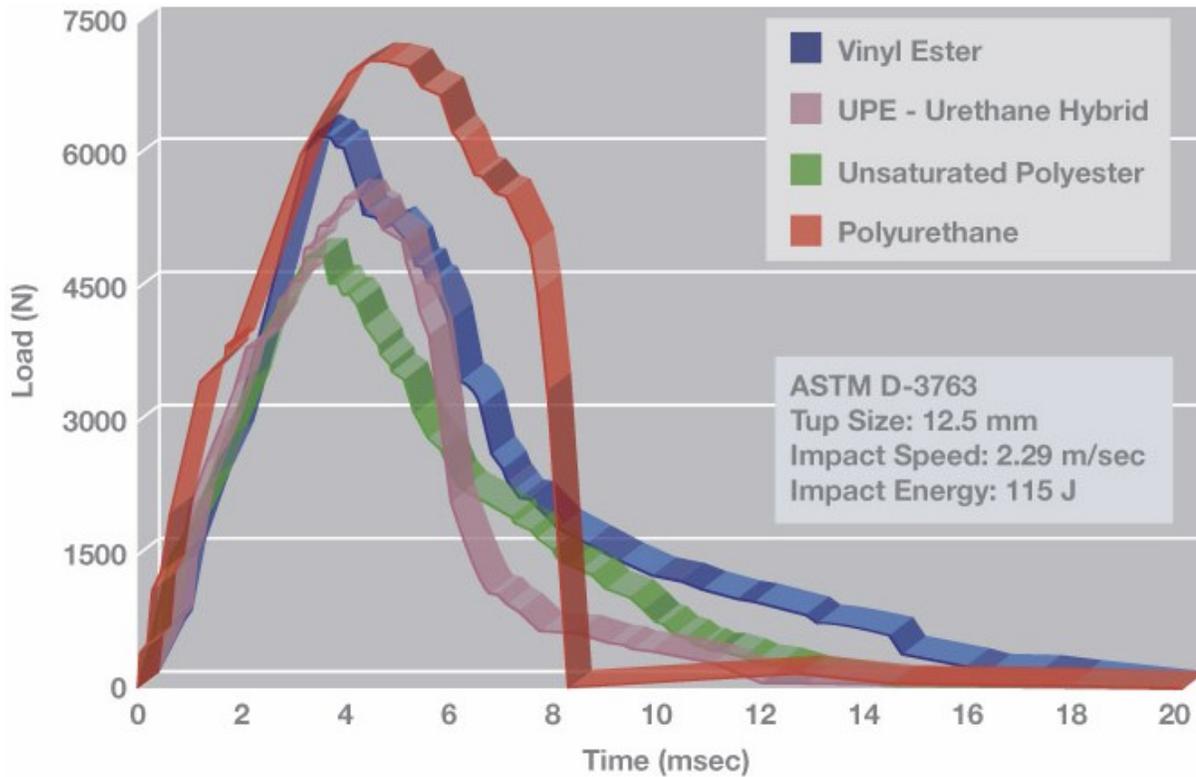


Figure 6 – Dynatup Instrumented Impact Behavior of Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (4.06 mm thick, 3 x 300 g/m² CFM, ~68 wt % fiberglass – average of four impact curves)

TABLE 1 DYNATUP INSTRUMENTED IMPACT RESULTS (ASTM D3763, 12.5 mm Tup, 2.29 m/sec)										
	RESIN									
	Vinyl Ester		Unsaturated Polyester		UPE-Urethane Hybrid			Polyurethane		
Thickness (mm)	2.54	4.06	2.54	4.06	2.54	3.175	4.06	2.54	3.175	4.06
# of CFM (300 g/m ²)	2	3	2	3	2	2	3	2	2	3
Max Load (N)	3260	6553	3047	4910	3496	4295	5603	4088	5108	7209
Energy to Max Load (J)	18.2	25.9	11.4	20.7	18.8	23.5	31.9	24.8	28.2	46.5
Total Energy (J)	29.3	73.2	27.7	53.1	32.0	35.5	53.6	38.4	51.2	75.8

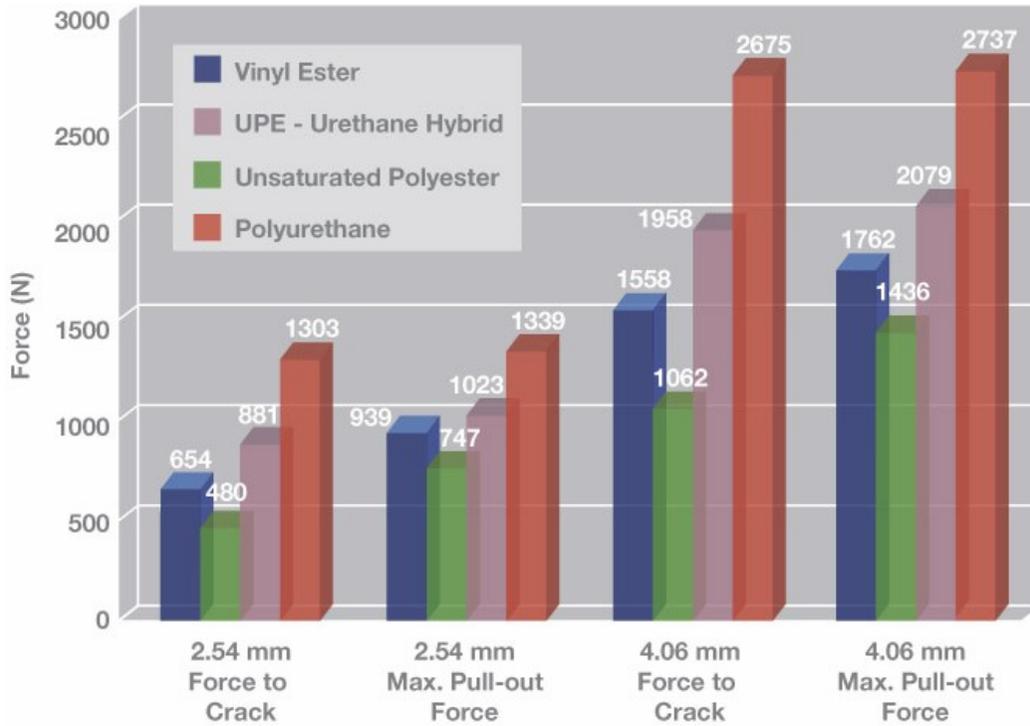


Figure 7 – Screw Pull-Out Force for Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (modified ASTM D1037, #10 self-tapping screw, 2.54 mm thick with 2 x 300 g/m² CFM and 4.06 mm thick with 3 x 300 g/m² CFM)

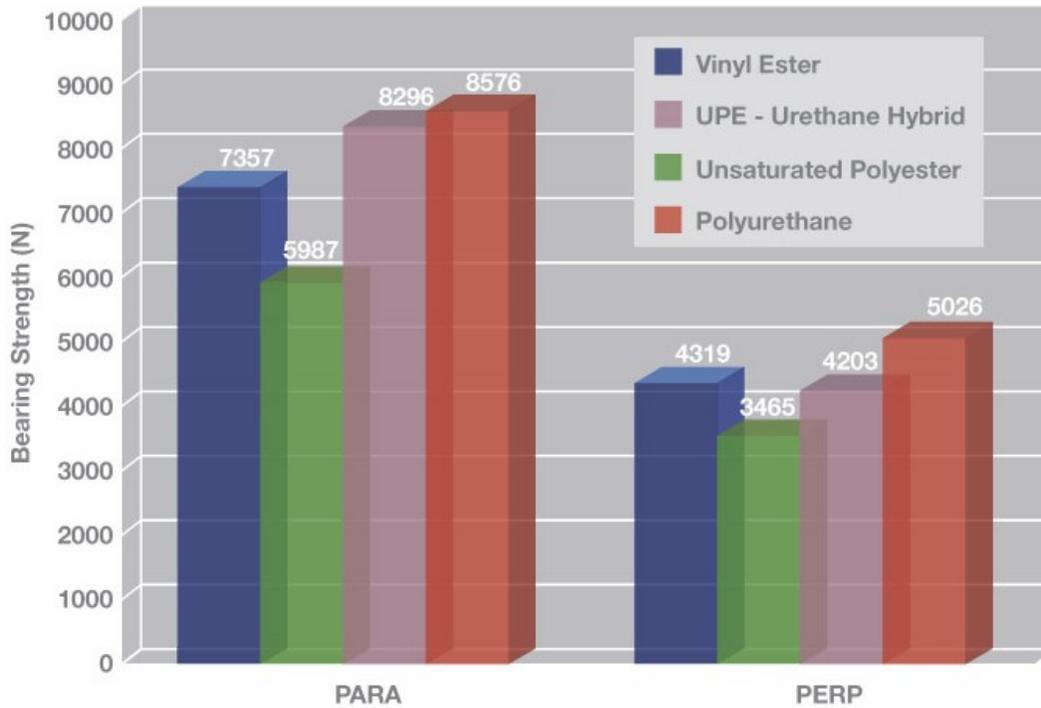


Figure 8 – Bearing Strength for Vinyl Ester, Unsaturated Polyester, Unsaturated Polyester-Urethane Hybrid and Polyurethane Pultruded Profiles (ASTM D953, 4.06 mm thick, 3 x 300 g/m² CFM, ~68 wt % fiberglass)