COMPOSITES 2006 Convention and Trade Show
American Composites Manufacturers Association
October 18-20, 2006
St. Louis, MO USA

Unsaturated Polyester Urethane Hybrid Technology - Fast Track to Advanced Composites

By

Ron Verleg
Emilien Hummer

Abstract

Over the last 20 years the automotive and aviation industries have shown increasing interest in advanced composites as a light weight construction material. However, the production speed of current advanced composites is seen as bottleneck for the exponential use of advanced composites in these key industries. Unsaturated polyester urethane hybrid technology has the potential to overcome this drawback. That's because hybrid technology results in advanced composites with properties equal to epoxy based materials but with much faster production speed and the capability to use cheaper production methods. In this paper unsaturated polyester urethane hybrid technology, its properties in advanced composites and faster production capabilities are explained in more details.

Introduction

Over the last 50 years acceptance of Fiber Reinforced Plastics (FRP) as an alternative construction material to wood, concrete or metals has grown. Due to continuous developments in reinforcing agents and grades of resin, FRP gradually entered the civil and industrial applications, like boats, cars, windmill blades, appliance housings, electrical boxes, trays, storage tanks, pipes and many more. The main drivers for accepting FRP products were light weight coupled with high stiffness, ease of processing and freedom of design.

Due to an increased understanding in the interaction between fibers and resin systems and the relation with laminate properties, over the last 20 years, FRP has become the material of choice in highly demanding applications in the automotive, aviation and aerospace industries. In these applications, the specific properties of FRP can be engineered into the part. With developments in new processing techniques, reinforcing fibers can be positioned in such a way that they optimally absorb the stresses. Optimized fiber orientation, enables lower weight, thinner walled, stronger and stiffener products to be made. Because of their high performance nature these types of FRP are referred as advanced composites, which are defined as materials consisting of a polymer matrix reinforced with high-strength continuous fibers.

Future predictions in consumption of advanced composites in the automotive and aviation industries will result in strong growth in these structural materials. However the growth predictions can only be realized when cheaper and faster methods of production are developed.

During the 1990s, unsaturated polyester urethane hybrid technology was introduced to the market as a highly promising system. They were able to close the gap between standard unsaturated polyester resins and epoxy resins from property point of view and even outperform them in processing. DSM Composite Resins recent studies have shown that this new resin technology results in the faster and cheaper production of advanced composites.

Unsaturated polyester urethane hybrids

In the 1980s AMOCO Chemical Company[1] published the principle of unsaturated polyester urethane hybrid (UPUH) in several papers. The hybrid system combines the chemistry, processing and cured resin properties of unsaturated polyester (UP) and polyurethane (PU) technologies. It results in a resin system that can be processed with unsaturated polyester and/or polyurethane application techniques to produce cured resin properties that are superior to its original constituents. Cured hybrid products have the stiffness and temperature resistance of unsaturated polyester resins combined with the flexibility and toughness of polyurethanes.

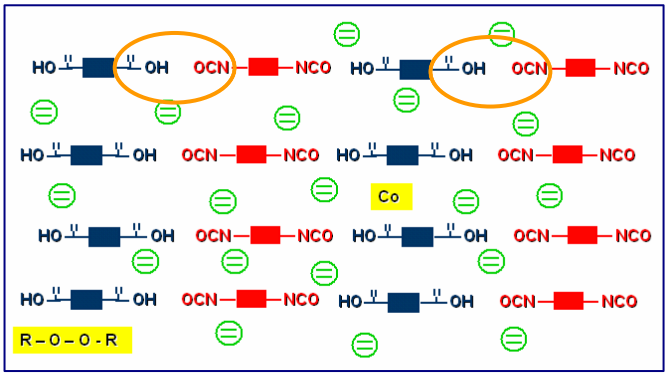


Figure 1a: Overview of the reactive system

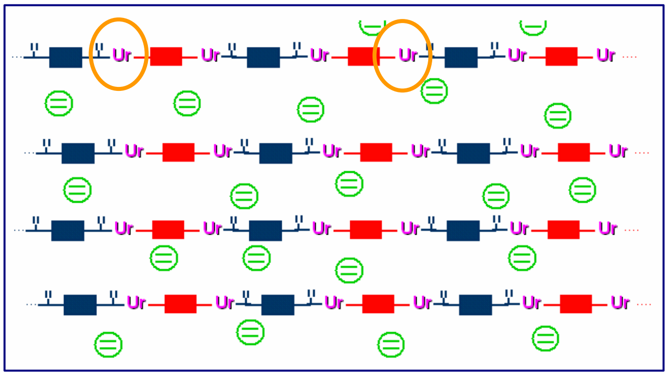


Figure 1b: Polyurethane reaction

The hybrid system consists of two main components, viz. an unsaturated polyester polyol dissolved in styrene, and a polymeric isocyanate resin (polymeric MDI = pMDI). When mixing both components together in the presence of a radical initiation system two curing reaction start: The hydroxyl groups of the unsaturated polyester polyol react with the isocyanate groups of pMDI leading to an `in-situ' development of a high molecular weight polymer. Such a chain extension reaction involves the formation of urethane bonds. The second curing reaction concerns the radical polymerization between unsaturations of the polyester polyol and styrene forming a three-dimensional network (see Fig. 1).

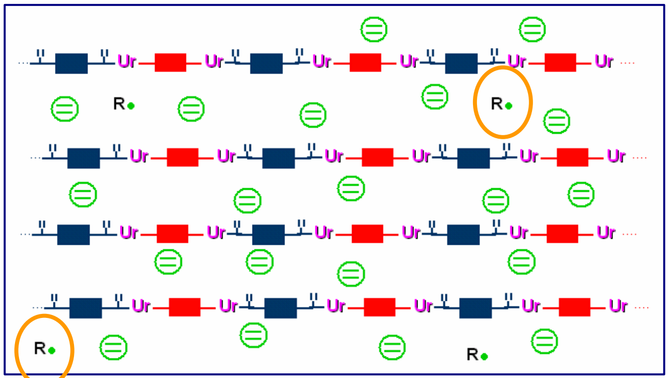


Figure 1c: Free radicals formation

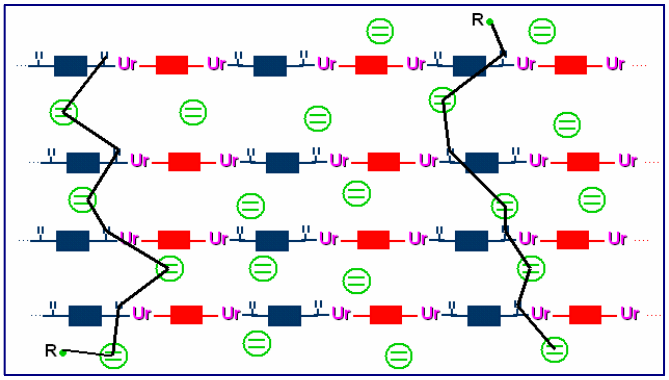


Figure 1d: Styrene-polyester crosslinking

In the early 1990s DSM Resins[2] introduced and commercialized an extended hybrid product line with different polyester polyol resin grades. Table 2 summarizes the liquid and cured resin properties of unsaturated polyester urethane hybrids based on different polyol backbones and compares the characteristics with standard unsaturated polyester and polyurethane systems. Hybrid resins based on unsaturated polyester resins (ISO and BPA) show a big increase in flexibility and toughness, given by the polyurethane component, while maintaining the stiffness and thermal resistance of unsaturated polyester resins. The hybrid based on UP BPA increases the elongation at break from 3 to 8% and impact strength from 10 to 40 kJ/m^2 compared to standard BPA UP, while the HDT value does not changed. Cured hybrid based on vinyl ester resin demonstrates a surprisingly high thermal stability without loosing its flexibility and toughness. Its heat deflection temperature rises from 284°F/(140°C) to 410°F/(210°C) while the elongation at break stays close to 3%.

Despite the promising future for hybrid systems anticipated more than a decade ago, the market development never achieved its forecasted growth. But now hybrid systems are getting a second chance. Due to the increasing interest in advanced composites in the automotive and aerospace industries, production methods have to be optimized in order to produce parts more cost-effectively. Hybrid technology is able to meet this requirement from industry to delivered advanced composites with fast processing characteristics.

UPUH Technology

At the start of this decade, DSM Composite Resins evaluated UPUH technology as alternative matrix material to epoxy resins for advanced composites. Two parameters were studied: (1) the mechanical performance of fiber-reinforced systems and (2) the processing performance of UPUH in resin transfer molding and pultrusion. This paper presents the results of both investigations.

Experimental

The experimental part describes the materials used for the different experiments. Next to the unsaturated polyester urethane hybrid system (UPUH), standard unsaturated polyester (UP) vinyl ester (VE), vinyl ester urethane (VEU) and two grades of epoxy resins are evaluated in different tests. The first grade is a 2-pot RTM cycloalifatic amine cured epoxy resin (CAA-EBPA) and the second grade is an aviation certified, high temperature resistant, one-pot epoxy resin (OERS).

In the production of thin fiber reinforced thermosetting products, the curing of the resin will progress under isothermic conditions. Therefore two methods to measure the development of isothermic viscosity in time as well as the isothermic cure behavior of different resins using is described.

Unidirectional fiber reinforced specimens are made in pultrusion for determining flexural properties, adhesion of the cured resin matrix on the fibers with inter laminar shear strength (ILSS) and the glass transition temperature using dynamic mechanical analysis (DMA).

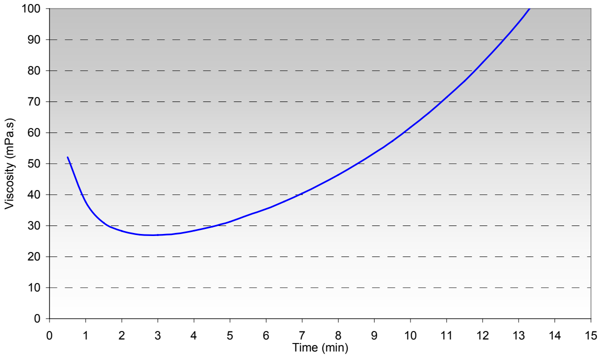
The effect of water on the mechanical properties and fiber/matrix interface is determined after saturating the unidirectional pultrudates with water for 100 hrs at 212°F/(100°C).

In the pultrusion experiments, the effect of the resin matrix on the performance of pultrudates is assessed. In this evaluation, different grades of UP and VE, UPUH and epoxy resins are used. The adhesion of UPUH and 2-pot RTM epoxy resin to different kinds of glass and carbon fibers were examined.

Development of viscosity in time under isothermic conditions

Physica MCR300 is an ideal equipment to follow the viscosity in time of a curing resin under isothermic conditions. Due to the presence of the polyurethane component in the UPUH resins, the viscosity will start to increase immediately after mixing both components. This development of the viscosity has to be determined since it will give an indication about the maximum injection time. After a certain moment the viscosity reaches a value that does not allow a fast permeation through the reinforcement package and good impregnation of the fibers. Fig 2. shows a typical curve of an isothermic viscosity development in time of UPUH. Initially the viscosity development in time drops due to heating up of the cold mixture to test temperature. After a few minutes at test temperature the increase in viscosity is seen.

Figure 2: Typical curve of isothermic viscosity development in time of a curing unsaturated polyester urethane hybrid system.



Procedure

The thermostat of the MCR 300 Physica was set at desired test temperature. The components of the resins were mixed in the right order and quantities. The mixture was poured into the Physica cup and the spindle was positioned. The test then began.

Dielectric cure measurements

The change in dielectric cure properties during the cure of thermosetting resins can be used to determine the cure characteristics under isothermic conditions. In the liquid phase resins have high ionic conductivity resulting in a high dielectric constant. Movements of low molecular weight and ionic components present in the liquid resin in an electrical field cause this ionic conductivity. When the resin starts to cure, the viscosity increases and the movement of components reduces. The ionic conductivity and dielectric constant of resin reduces during the cure. When the resin is cured the components no longer move and the ionic conductivity and electric constant reach a minimum level. DSM Composite Resins has developed their own dielectric cure-meter (DCM) to follow the cure of resins in time.

Procedure

The DCM equipment is designed for use of insulating foils between the electrodes and the test material. The electrodes are incorporated in the surface of the top and bottom part of the mould. The diameter of the circular mould is 30 mm and it has a thickness of 0.5 mm. The temperature of the mould of the DCM is set at test temperature. 2 Grams of catalyzed resin is poured on thin foil and covered with another foil. The foil sample is then placed in the press of the DCM equipment. The measurement of dielectric properties starts when the pres is closed. The following parameters are followed in time during the dielectric cure measurement:

ε_1: Dielectric constant or storage factor
ε_2: Loss factor of dielectric material
$\varepsilon = \varepsilon_1 - i\varepsilon_2$
Φ: Phase angle
Z: Impedance

Fig. 3 shows a typical ε_2-curve of the dielectric cure measurement of a curing unsaturated polyester urethane hybrid resin. The curve of ε_2 is used for evaluating the gel time (or injection time) and cure time of the resin. The injection time is defined as the intersection point of the tangents of the initial slope and the 2nd parts of the ε_2 –curve. The cure time is defined as the intersection point of the slope of the 2nd parts and the final part of the ε_2 –curve.

Figure 3: Typical response of dielectric cure measurement of a curing unsaturated polyester urethane hybrid system.

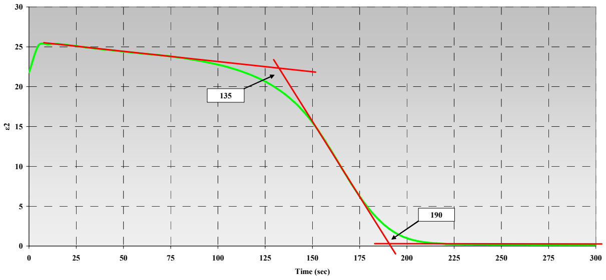


Table 3 summarizes the test conditions of UPUH and 2-pot RTM epoxy system (CAA-EPBA) to determine the isothermic curing behavior in the DCM equipment. The results of DCM evaluation have been used to compare the curing behaviors between grades of thermosetting resins at three different temperatures 122°F/(50°C), 158°F/(70°C) and 194°F/(90°C).

Mechanical performance of unidirectional fiber reinforced composites

The mechanical performance of composites based on hybrid resins was evaluated on unidirectional pultrudates produced with different types of fiber reinforcements.

The mechanical performance of the composites was determined by measuring its flexural properties. The strength of the fiber/matrix was evaluated using inter-laminar shear characteristics.

The hydrolytic resistance of the composite and its fiber/matrix interface was also determined by measuring the ILSS values after exposure to boiling water (212°F /100°C) for 100 hrs. The results of the evaluations with hybrid resins were compared with other thermosetting system, such as unsaturated polyester, vinyl ester and epoxy resins.

Table 4 shows the processing characteristics of unidirectional glass fiber reinforced pultrudates based on different kinds of unsaturated polyester, vinyl ester and hybrid resins.

Table 5 shows two types of thermosetting resins evaluated in unidirectional glass fiber reinforced composites using three different types of glass rovings each with their own glass sizing. The results of the UPUH are compared with the (CAA-EBPA).

Table 6 shows the process conditions for the production of carbon reinforced pultrudates based on UPUH and a special grade of epoxy resin. The grade is an aviation-certified one-component epoxy resin consisting of a glass transition temperature above 400°F/(200°C.)

Tests

Thermal resistance

Glass transition temperatures (Tg) of the resin systems evaluated in this study were determined on 40 x 10 x 3 mm samples, obtained from the unidirectional fiber reinforced pultrudates, using dynamic mechanical analysis according to ISO 537. Dynamic mechanical analysis of cured samples as function of temperature was measured using Rheometic RDA 2. The samples were exposed to oscillating loading with a frequency of 1 Hz and strain of 0.1% and heated to 527°F/(275°C) with a ramp of 5°C/min. The glass transition temperature was determined using the offset point of the loss modulus curve (G´), see Fig.14.

Mechanical performance

The test specimen for determining mechanical properties of unidirectional fiber reinforced pultrudates and biaxial fiber reinforced RTM plates were cut according to the dimensions written in ISO 178 for flexural properties and ISO 14130 for inter laminar shear strengths (ILSS). In order to measure the flexural properties, the test specimens were subjected to three-point bending test at room temperature with a support span of 16 times the thickness of the specimen and 5 mm/min crosshead speed. The properties were measured perpendicular to the fiber direction (0°) for the unidirectional pultrudates and perpendicular to the flow directional for the biaxial RTM plates. From the test results performed on 5 specimens the flexural strength and flexural modulus were determined.

For ILSS, test specimens were subjected to a three-point bending test at room temperature with a support span of 5 times the thickness of the specimen and 1.3 mm/min crosshead speed.

Water boiling test

In order to determine the effect of water on the flexural properties, ILSS and Tg values of unidirectional fiber reinforced pultrudates, specimens were immersed in water at 212°F/(100°C) for 100 hrs. Absorption tests learned that after 100 hrs in boiling water the specimens were saturated with water. After the water-boiling test, the exposed samples were stored under water at room temperature prior to testing. The flexural properties and ILSS were determined at room temperature on fully saturated samples.

Pultrusion production

The pultrudates were produced on a PULSTAR 804 pultrusion equipment using 15 x 900 x 3 mm pultrusion die and two heating zones.

RTM production

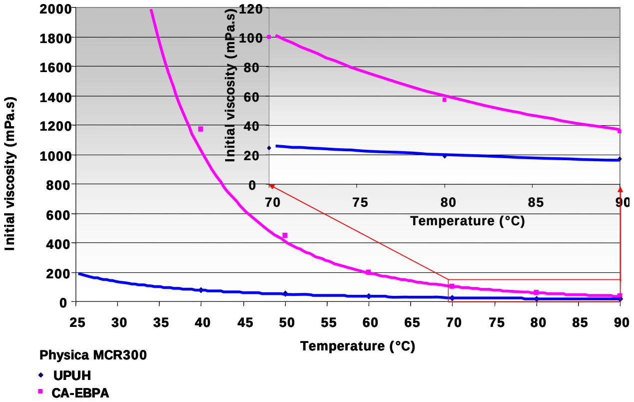
Biaxial glass fiber reinforced RTM plates were produced using a Fritzmeier injection mold (910 x 465 x mm) installed in a clamp force unit. The resins were injected using a 2-component injection machine.

Results and discussion

Initial viscosity measurements

Fig. 4 presents the initial viscosity of the unsaturated polyester urethane hybrid (UPUH) as a function of the operational temperature. Comparing the results with the 2-pot RTM epoxy system (CAA-EPBA) shows the favorable performance of UPUH system expressed in very low initial viscosities at slightly elevated temperature. Moreover the viscosity of the UPUH system does little depend on processing temperature. Between 158 and 194°F (70°C and 90°C) the UPUH system has a relative constant viscosity around 20 mPa.s, while the epoxy system drops its initial viscosity in this temperature range by a factor 3 from 100 to 35 mPa.s.

Figure 4: Initial viscosity of UPUH and CAA-EBPA as function of temperature



<u>Development of viscosity in time</u>

Since one of the curing chemistry of the UPUH contains a polyurethane polymerization, the viscosity of the hybrid mixture will start after mixing the components. In Fig. 5 the development of the viscosity in time as function of three operation temperatures (150°F/(70°C), 176°F/(80°C) and 194°F/(90°C)) is summarized. All three curves show a reduction of the viscosity after mixing and exposing to operation temperature. After 3 minutes at operating temperature, the viscosity starts in increase due to the polyurethane reaction. Within DSM Composite Resins, the maximum injection time is defined as the moment the development of viscosity reaches 100 mPa.s at operation temperature. In Table 1 so-defined the maximum injection time form the UPUH system as a function of the process temperature is presented.

Figure 5: Development of viscosity in time of UPUH as function of temperature

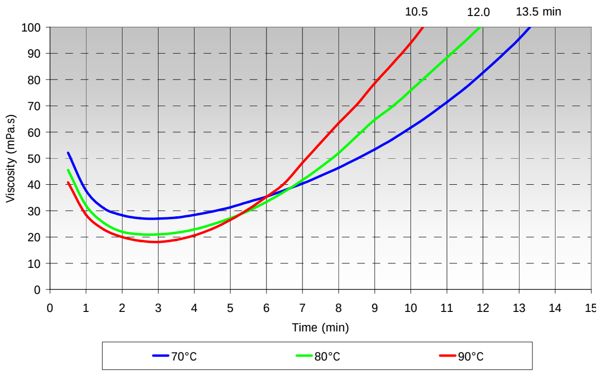


Table 1: Maximum injection time UPUH as function of operation temperature

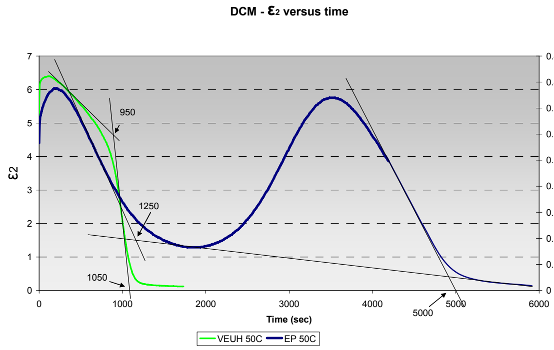
Operation temperature, °F/(°C)	Maximum time of injection, min
150/(70)	13.5
176/(80)	12.0
194/(90)	10.5

<u>Reactivity measurements using DCM</u>

The dielectric curemeter is an ideal equipment to give information about cure characteristics of thermosetting resins under isothermic conditions. The cure characteristics of 2-pot RTM epoxy (CAA-EBPA) system resulted in a completely different cure behavior than the UPUH system (See fig. 6).

The difference in cure behavior can be attributed the curing chemistry of amine hardened epoxy resins. Initially a chain extension reaction occurs between primary amine groups with epoxy groups resulting in linear secondary polyamine chains. This first polymerization lead to a viscosity increase until the mixtures reaches its Tgel value and freezes the polymerization reaction. This point is seen as the first gel point. Later on the epoxy cross-linking reaction starts between the amide groups and remaining epoxy groups resulting in a 3-dimensional network. Also this reaction proceeds till the Tg value is reached and the polymerization freezes in.

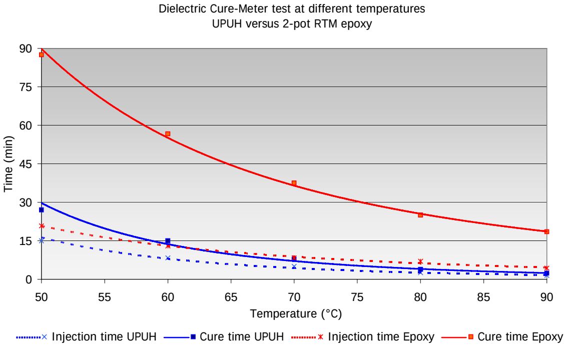
Figure 6: Comparison of curing behavior of UPUH and CAA-EBPA system using dielectric curemeter



This cure behavior of epoxy resins is the reason for the long molding times of epoxy system. Moreover since the epoxy polymerization is a step-wise reaction, it does not have its temperature resistance performance. Therefore epoxy systems have to be postcured under supporting conditions above design temperature for several hrs to reach its maximum thermal resistance performance.

The UPUH shows a different curing profile in dielectric cure measurements. Initially the UPUH mixture stays liquid for a relatively long time since the radical polymerization in inhibited. There is a small increase in viscosity due to the urethane reaction. When the radical polymerization kicks in, a 3-dimensional network develops very quickly, resulting in a stiff thermosetting material. Therefore UPUH based composite can be demolded in a significantly shorter demolding time than epoxy resins. Moreover, the UPUH based composite can be postcured "in-situ" in a short period of time.

Figure 7: Comparison of cure characteristics between UPUH and CAA-EBPA as function of temperature.



In Fig. 7, the result in interpretation of dielectric cure curves of CAA-EBPA and UPUH systems at different operation temperatures is summarized. It is clearly seen that UPUH has a similar dependence of injection time versus temperature as the 2-pot epoxy system. However there is a significant difference in cure time. The cure time of UPUH is a faster than 2-pot RTM epoxy system by a factor of 5.

<u>Mechanical performance of unidirectional fiber reinforced composites</u>

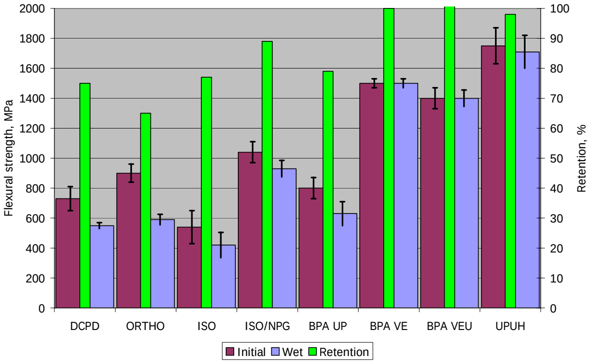
Influence of resin matrix in glass fiber reinforced pultrudate

3-mm Thick unidirectional fiber reinforced pultruded strips are ideally suited for determining the performance of the fiber/matrix combination. Next to the flexural properties, the interlaminate shear strength (ILSS) of the pultruded strips indicates the strength of the fiber/matrix interface. Exposing the strips to boiling water for 100 hrs, results in fully saturated composite materials. Since the strips are saturated it can be assumed that water is present in the matrix and fiber/matrix interface. Determining the retention of ILSS of water saturated pultrudates, will give information about the hydrolysis resistance of the interface.

In Table 7 the results of flexural properties and ILSS values are summarized for glass fiber reinforced pultruded strips with different types of unsaturated polyester and vinyl ester resin. The performances of these systems are compared with the properties of UPUH.

In Fig 8 and 9 the retention of flexural strength and ILSS of the different pultrudates are shown. Both the flexural strengths increase when using cured resin matrices with higher mechanical properties. The unsaturated polyester resins demonstrate the lowest performance between 500 – 1000 MPa. The vinyl ester and vinyl ester urethane resins have flexural strengths around 1400 to 1500 MPa. The UPUH system shows the best performance in flexural strength with values above 1700 MPa.

Figure 8: Flexural strength of glass fiber reinforced pultruded strips and retention after water saturation



As well as higher mechanical performance, the superior flexural properties can also be attributed to better adhesion characteristics of the cured resin matrix to the glass fiber. This can be found back in inter laminar shear properties. Unsaturated polyester resins show figures between 20 and 40 MPa, while vinyl ester and vinyl ester urethanes are between 50 and 60 MPa. The UPUH shows the best adhesion performance with values above 65 MPa.

Th
e

Figure 9
and rete

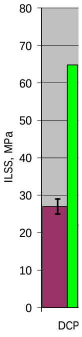
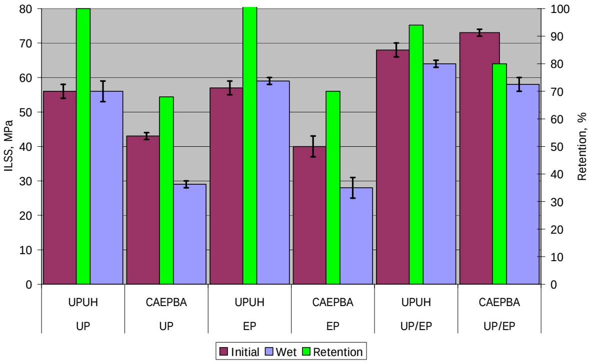


Figure 11: Influence of glass sizing on ILSS of glass fiber reinforced pultruded strips based on UPUH and CAA-EBPA and retention values after water saturation.



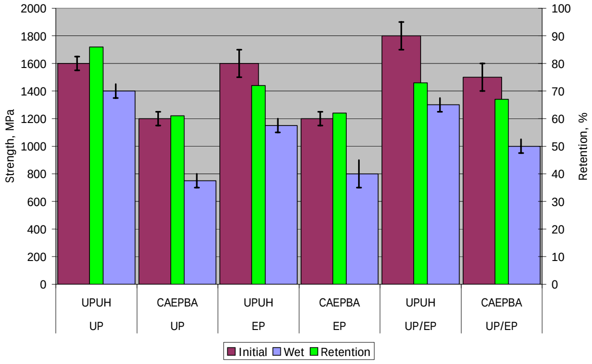
strength of the fiber/matrix interface bonding can also be found back in the hydrolysis resistance of the interface. The vinyl ester and vinyl ester urethanes, as well as the hybrid system, show virtually no loss in flexural strength and ILSS after 100 hrs exposure to boiling water. Unsaturated polyester resins demonstrate a reduction of 20 to 30%.

Influence of glass sizing on glass fiber reinforced pultruded strips based on an unsaturated polyester urethane hybrid and 2-pot RTM epoxy resin

Cured UPUH matrix shows very good adhesion properties to glass fibers. In order to determine whether the glass sizing is playing a role in the adhesion performance, unidirectional fiber reinforced pultruded strips based on glass rovings, with different sizings were evaluated for mechanical performance. Three grades of glass roving were used containing a sizing composed for unsaturated polyester resins, a sizing composed for epoxy resins and a universal sizing composed for unsaturated polyester as well as for epoxy resins.

Moreover the level of adhesion of UPUH on glass rovings was evaluated by comparing the results with pultruded strips based on 2-pot RTM cyclo-alifatic cured epoxy resin (CAA-EBPA).

Figure 10: Influence of glass sizing on flexural strength of glass fiber reinforced pultruded strips based on UPUH and CAA-EBPA and retention values after water saturation.



The hydrolytic strength of the fiber/matrix interface of all samples was determined by exposing the pultrudates to boiling water for 100 hrs. Table 8 summarizes all the results and retentions of flexural properties and ILSS of initial and wet samples. In Fig, 10 and 11 the results and retentions of flexural properties and ILSS are visualized. The UPUH system demonstrates more universal behavior with respect to different types of sizings compared to the CAA-EPBA resin. In all cases UPUH shows an equal or better adhesion of the glass fibers. The hydrolytic resistance of the glass fiber/matrix interface of UPUH is significantly better than for the epoxy system. In all cases, UPUH retains more than 90% of its initial values, while the epoxy system retains just 70 – 80%.

Influence of resin matrix in carbon fiber reinforced pultrudate.

In the advanced composite segment, carbon fibers are the main reinforcement material. In order to determine the interaction between UPUH and carbon fibers, carbon reinforced pultrudates were production according to the conditions mentioned in Table 9. Besides pultrudate based on unsaturated polyester and vinyl ester resins, similar strips were made using an aviation-certified, high temperature resistance one-pot epoxy resin system (OERS).

An interesting aspect of the pultrusion production of the carbon reinforced strips is the big difference in processing speed. As presented in Table 9, the OERS requires die temperature of between 428 – 464°F/(220 - 240°C) in order to get a proper cured material. UPUH can be produced at lower process temperatures and even higher production speeds. The speeds of UPUH mentioned in Table 9 are even not even maximum rates.

Another interesting aspect was the state-of-cure of the OERS. Although producing at 464°F/(240°C), the Tg value of the cured system was only 257°F/(125°C). It required another 2 hrs at 356°F/(180°C) additionally to reach the maximum Tg value for the OERS of 205°F/(401°C). Having this information on hand it was decided the postcure the OERS and UPUH according to their recommended instructies to obtain the best performance.

Carbon reinforced pultruded strips based on UPUH also show mechanical properties superior to unsaturated polyester and vinyl ester resins and equal to high performance epoxy systems (see Table 9, Fig. 12 and 13).

Figure 12: Influence of resin matrix on flexural strength of carbon fiber reinforced pultruded strips and retention values after water saturation.

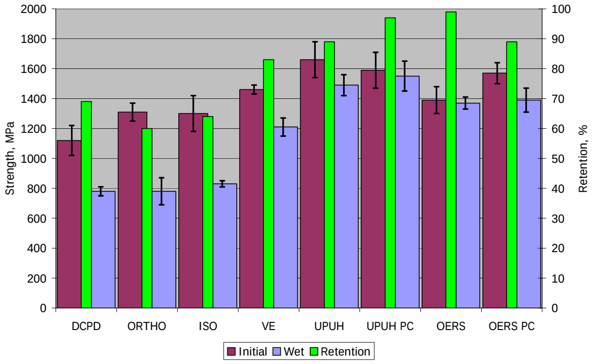
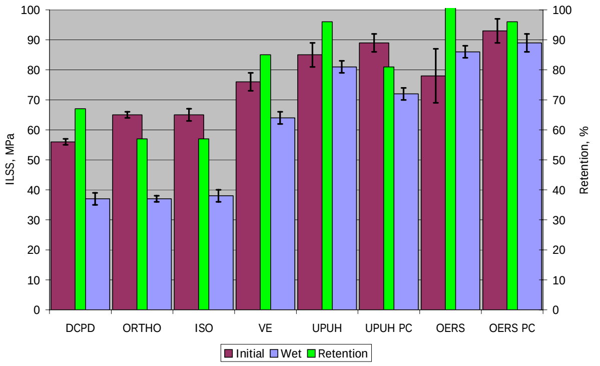


Figure 13: Influence of resin matrix on ILSS of carbon fiber reinforced pultruded strips and retention values after water saturation.



Non-postcured UPUH and one-pot epoxy system (OERS) show equal adhesion performances to carbon fibers expressed in the ILSS values. The ILSS value of OERS increases after exposure for 100 hrs boiling water. This can be attributed to additional epoxy polymerization. The increase of Tg value of non-postcured OERS from 257 – 270°F/(125 to 132°C) supports this fact.

Postcuring the carbon reinforced pultrudates based on UPUH shows a slight increase in ILSS following the trend seen in postcuring the OERS based pultrduates. Exposure to boiling water boiling water has a bigger effect on the postcured pultruded strips based on UPUH than the OERS.

Effect of water on thermal resistance performance of carbon reinforced pultrudates based on high temperature resistant OERS and UHUH.

Water has a huge effect on the thermal performance of carbon reinforced pultrudates. When exposed to boiling water, it penetrates into the composite matrix until it is saturated. Besides filling the free volume in the cured resin matrix, it also fills the space in the cured matrix/fiber interface. The effect of water in the matrix/fiber interface can be found back in the ILSS values. Water present in the free volume of the cured matrix is seen in the reduction of the Tg value of the pultrudate.

Figure 14a: Storage modulus curves from DMA of dry and water-saturated carbon reinforced pultrudates based on UPUH without addition post-cure.

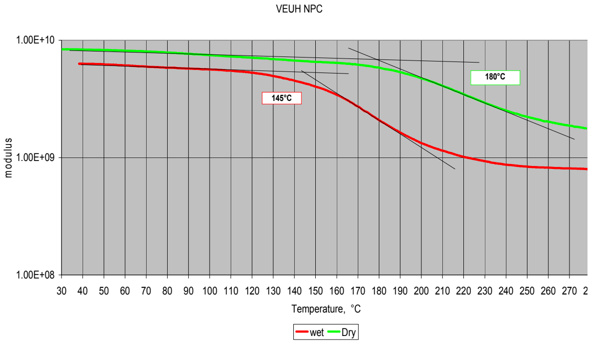


Figure 14b: Storage modulus curves from DMA of dry and water-saturated carbon reinforced pultrudates based on UPUH post-cured for 2 hrs at 392°F/(200°C).

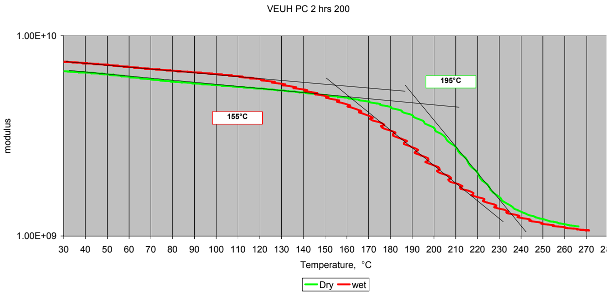


Fig. 14a and b shows the development of storage modulus as a function of temperature of dry and water-saturated carbon fiber reinforced pultrudate based on UPUH, (post cured and non post cured), obtained from DMA. Fig 14c and d present the same storage modulus curves of dry and wet pultrudates based on OERS. In Table 9 summarizes the results of the Tg interpretation on the storage modulus curve. Non-postcured carbon reinforced strips based on UPUH show a reduction in Tg value of 63°F/(35°C) from 356 to 293°F/(180 to 145°C). Postcuring the strips for 2 hrs at 392°F/(200°C) increases the Tg value from 356°F/(180°C) to 383°F/(195°C). Following water exposure, the Tg value drops from 383°F/(195°C) to 311°F/ (155°C).

Post-cured carbon reinforced pultruded strip based on OERS, gives a drop of 131°F/(55°C) when fully saturated with water.

Figure 14c: Storage modulus curves from DMA of dry and water-saturated carbon reinforced pultrudates based on OERS without post-cure

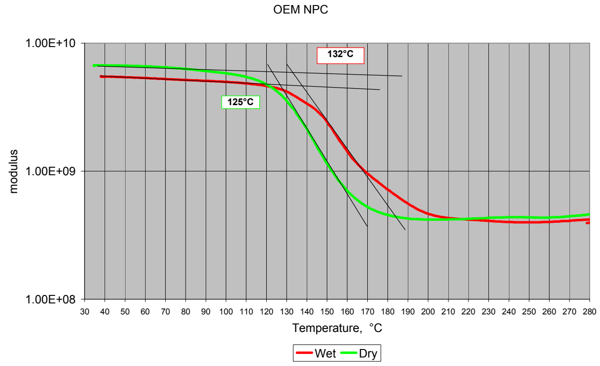
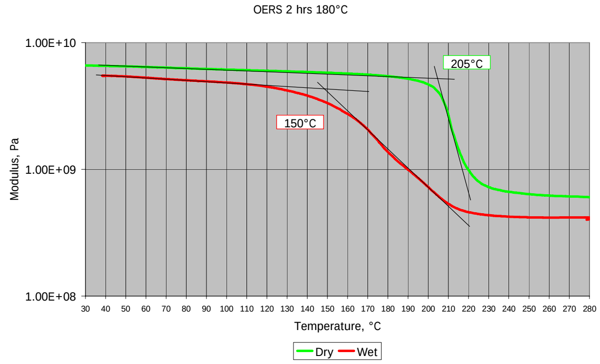


Figure 14d: Storage modulus curves from DMA of dry and water-saturated carbon reinforced pultrudates based on OERS post-cured for 2 hrs at 356°F/(180°C)



Mechanical performance biaxial glass fiber reinforced composites

Comparison between vinyl ester urethane hybrid and 2-pot RTM epoxy system

Biaxial glass reinforced RTM flat plates based on UPUH system were produced using a 2-pot injection machine in a 2-mm thick steel RTM mold at two mold temperatures. Different amounts of peroxides were used to determine the influence of gel – and cure time on the mechanical properties of the RTM plates. The results of flexural strength and ILSS of UPUH based RTM plates were compared to the epoxy system processed at 150°F/(70°C.)

Table 10 and Fig. 15/16 summarize the results of flexural strength and ILSS of UPUH based and CAA-EBPA based biaxial RTM plates. Overall it can be concluded that no difference is seen in mechanical properties between the different cure conditions of the UPUH system. Moreover, UPUH reaches the mechanical performance of biaxial glass fiber reinforced RTM plates based on epoxy resin, and can therefore be used as alternative resin matrix in advanced composites.

Figure 15: Flexural strength of biaxial glass fiber reinforced RTM plates based on UPUH and CAA-EPBA

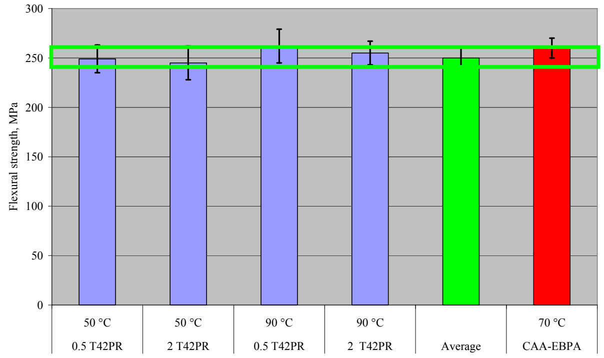
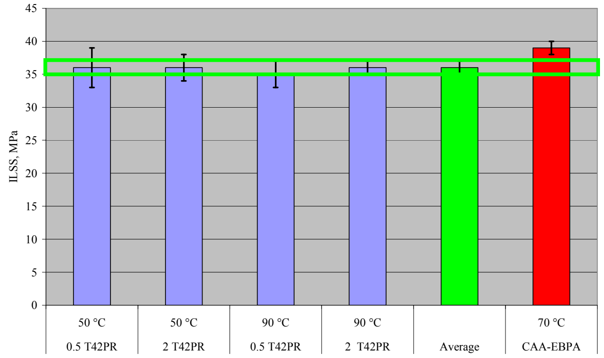


Figure 16: ILSS of biaxial glass fiber reinforced RTM plates based on UPUH and CAA-EPBA



Conclusions

The initial viscosity at elevated temperature of unsaturated polyester urethane hybrid systems is significantly lower than RTM epoxy systems

The development of viscosity at elevated temperature in time allows a maximum injection time of 10 to 14 minutes depending on the mold temperature.

The cure characteristics of unsaturated polyester urethane hybrids is ideally suited for RTM applications at elevated temperatures. The system gives a long injection time and a very fast demolding time. The button-to-button production speed of unsaturated polyester urethane hybrids can be reduced by a factor 3 to 5 compared to epoxy systems

Unsaturated polyester urethane hybrid can be processed at lower operating temperature than comparable performance epoxy system. Moreover the hybrid still increases the speed of pulling by at least a factor of 10.

Unsaturated polyester urethane hybrids show an optimal compatibility with all kinds of glass and carbon fibers, which are treated with different kinds of sizings optimized for specific thermosetting resin matrices. Mechanical properties of cured fiber reinforced pultrudates based on unsaturated polyester urethane hybrid show values that outperform unsaturated polyester and vinyl ester resin, and which meet the performance of epoxy systems.

Mechanical performance of composites based on unsaturated polyester urethane hybrid systems are equal to 2-pot RTM epoxy systems. The hydrolytic stability of the composite material exposed to boiling water of unsaturated polyester urethane hybrid is significantly better than epoxy systems. While the hybrid shows hardly any drop in performance, the epoxy systems drop between 20 – 40% of its original mechanical properties.

Mechanical performance of carbon reinforced pultrudates based on unsaturated polyester urethane hybrid can compete with an aviation certified, high temperature resistant, one-pot epoxy system.

The hydrolytic stability after exposure to boiling water of both resins is comparable, although the influence of post-curing has to be investigated in more detail.

The glass transition temperature and the drop from the initial value of fully saturated carbon reinforced pultrudates based on unsaturated polyester urethanes and the one-pot epoxy system is comparable.

Authors

Ron Verleg
Ron Verleg is expertise manager and business development Daron hybrid technology for the business unit composite resins of DSM Resins. He has a bachelor degree in chemical technology and master degree in Organic Chemistry. He has worked with DSM Resins for more than 18 years in all kinds of fields of composite technology.

Emilien Hummer
Emilien Hummer is application engineer for the Competence Center Closed Mold of DSM Composite Resins. He holds a bachelor degree in polymer and composite technology and provides processing and modeling support for resin transfer molding (RTM) with Daron Hybrid Technology.

Table 2: Liquid properties and cured non-reinforced resin properties of unsaturated polyester resins, unsaturated polyester urethane hybrids and polyurethanes.

	ISO		BPA UP		VE		PU
Property		Hybrid		Hybrid		Hybrid	
Viscosity	400	400	500	350	250	225	
Volume shrinkage, vol%			7.5	5.6			
Tensile strength, MPa	75	95	70	90	90	70	60
Tensile modulus, GPa	3.2	3.4	3.4	3.1	3.4	3.4	2.0
Elongation at break, %	4	7.5	3	8	3	2.5	12
Impact strength, kJ/m^2	10	30	9	40	15	15	
HDT, F	203	221	248	248	284	410	149
HDT, °C	95	105	120	120	140	210	65

ISO UP = Isophthalic acid unsaturated polyester resin
BPA UP = Bisphenolic unsaturated polyester resin
VE = Vinylester resin
HDT: Heat deflection temperature

Table 3: Cure conditions of three resins evaluated in DCM tests.

Type of resin	Peroxide. (%)	Polymeric MDI, (phr)	Cycloaliphatic amine, (phr)	Test temperature °F/(°C)
VEUH	1.0	35		122, 158, 194 (50, 70, 90)
CAA-EBPA			24	

Table 4: Processing conditions unidirectional glass reinforced pultrudate

	Unsaturated polyester					Vinyl ester	
Type of resin	DCPD	ORTHO	ISO	ISO/NPG	BPA	BPA	UPUH
Resin	100	100	100	100	100	100	100
Internal release agent	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tert-Butyl peroxy-2-ethylhexaoate, 90%	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tert-Butyl Peroxybenzoate	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Polymeric isocyanate							34
Die temperature							
Zone 1, °F/(°C)	275/(135)						
Zone 2, °F/(°C)	302/(150)						
Type of glass rovings	Acid resistant (4800 tex)						
Amount of glass rovings	15						

Table 5: Processing conditions unidirectional glass reinforced pultrudates

	UPUH	CAA-EBPA
Type of resin		
Resin	100	100
Internal release agent	0.5	0.5
Tert-Butyl peroxy-2-ethylhexaoate, 90%	0.5	
Tert-Butyl Peroxybenzoate	1.0	
Polymeric isocyanate	34	
Cyclo-alifatic amine		24
Die temperature		
Zone 1, °F/(°C)	275/(135)	302/(150)
Zone 2, °F/(°C)	302/(150)	356/(180)
Type of glass rovings	Standard glass UP sizing (2400 tex) Standard glass EP sizing (2400 tex) Standard glass UP/EP sizing (2400 tex)	
Amount of glass rovings	30	

Table 6: Processing conditions unidirectional carbon reinforced pultrudates

	UPUH	OERS
Resin	100	100
Internal release agent	0.5	0.5
Tert-Butyl peroxy-2-ethylhexaoate, 90%	0.5	
Tert-Butyl Peroxybenzoate	1.0	
Polymeric isocyanate	34	
Cyclo-alifatic amine		
Die temperature		
Zone 1, °F/(°C)	275/(135)	428/(220)
Zone 2, °F/(°C)	302/(150)	464/(240)
Type of carbon rovings	Carbon roving, 48K	
Amount of glass rovings	15	

Table 7: Mechanical performance unidirectional glass fiber reinforced pultrudates based on acid resistant glass and different unsaturated polyester, vinyl ester and UPUH matrices.

Type of resin	DCPD	ORTHO	ISO	ISO/ NPG	BPA UP	BPA VE	BPA VEU	UPUH
Die temperature Zone 1, °F/°C Zone 2, °F/°C	275/(135) 302/(150)							
Speed of pulling, cm/min	100							
Glass content, vol%	63	63	64	65	65	64	64	63
Flexural strength, Initial, MPa Wet, MPa Retention, %	730 ± 79 547 ± 18 75	894 ± 60 585 ± 35 65	541 ± 106 418 ± 85 77	1041 ± 74 930 ± 54 89	799 ± 67 629 ± 84 79	1506 ± 33 1507 ± 27 100	1365 ± 67 1402 ± 54 1003	1737 ± 116 1706 ± 113 98
Flexural modules, Initial, GPa Wet, GPa Retention, %	48 ± 1 45 ± 1 93	48 ± 1 45 ± 1 95	43 ± 1 45 ± 1 103	49 ± 1 48 ± 1 96	48 ± 1 45 ± 2 94	51 ± 1 50 ± 2 98	52 ± 1 51 ± 1 98	53 ± 1 52 ± 1 98
Outer fiber strain, % Initial Wet Retention	3.5 ± 1.2 1.8 ± 0.2 52	2.3 ± 0.6 2.4 ± 1.2 101	3.7 ± 1.3 2.2 ± 0.8 59	2.4 ± 0.1 2.2 ± 0.1 90	2.6 ± 0.9 2.4 ± 0.5 91	3.2 ± 0.1 3.2 ± 0.1 102	2.9 ± 0.1 3.0 ± 0.1 105	3.5 ± 0.5 3.8 ± 0.4 107
ILSS, Initial, MPa Wet, MPa Retention, %	27 ± 2 22 ± 1 81	25 ± 5 25 ± 1 100	25 ± 5 18 ± 4 73	37 ± 1 35 ± 1 94	32 ± 1 28 ± 1 88	57 ± 1 58 ± 1 101	52 ± 2 50 ± 1 96	67 ± 2 65 ± 2 98

Table 8: Mechanical performance unidirectional glass fiber reinforced pultrudates based on glass rovings treated with different kinds of sizing and comparison between UPUH matrices with epoxy resins.

Glass fiber sizing	UP		EP		UP/EP	
Type of resin	UPUH	CAA-EPBA	UPUH	CAA-EPBA	UPUH	CAA-EPBA
Die temperature						
Zone 1, °F/(°C)	275/(135)	302/(150)	275/(135)	302/(150)	275/(135)	302/(150)
Zone 2, °F/(°C)	302/(150)	356/(180)	302/(150)	356/(180)	302/(150)	356/(180)
Speed of pulling, cm/min	100	30	100	30	100	30
Glass content, vol%					80	79
Flexural strength,						
Initial, MPa	1600 ± 50	1200 ± 50	1600 ± 100	1200 ± 50	1800 ± 100	1500 ± 100
Wet, MPa	1400 ± 50	750 ± 50	1150 ± 50	800 ± 100	1300 ± 50	1000 ± 50
Retention, %	86	61	72	62	73	67
Flexural modules,						
Initial, GPa	47.3 ± 0.3	45.7 ± 0.2	57 ± 1	45 ± 2	50.3 ± 0.6	48 ± 1
Wet, GPa	46.8 ± 0.4	39.3 ± 0.3	56.9 ± 0.3	38 ± 3	49 ± 1	46 ± 1
Retention, %	98	86	99	85	98	95
Outer fiber strain, %						
Initial	3.6 ± 0.1	2.6 ± 0.1	3.7 ± 0.1	3.0 ± 0.1	3.7 ± 0.1	3.3 ± 0.1
Wet	3.6 ± 0.4	2.1 ±0.1	4.3 ± 0.0	2.2 ± 0.3	3.7 ± 0.3	3.3 ± 0.3
Retention	102	74	118	76	100	100
ILSS,						
Initial, MPa	56 ± 2	43 ± 1	57 ± 2	40 ± 3	68 ± 2	73 ± 1
Wet, MPa	56 ± 3	29 ± 1	59 ± 1	28 ± 3	64 ± 1	58 ± 2
Retention, %	100	68	104	70	94	80

Table 9: Mechanical performance unidirectional carbon fiber reinforced pultrudates based on different kinds of glass and comparison of vinyl ester and vinyl ester urethane hybrid matrices with epoxy resins.

Type of resin	DCPD	ORTHO	ISO	VE	UPUH		OERS	
Carbon fiber	48 K Carbon roving							
Die temperature								
Zone 1, °F/(°C)	275/(135)						428/(220)	
Zone 2, °F/(°C)	302/(150)						484/(240)	
Speed of pulling, cm/min	100	100	100	100	100		30	
Heat treatment						2 hrs 200		2 hrs 180°C
Carbon content, vol% (calc)	75	75	75	75	75	75	75	75
Flexural strength,								
Initial, MPa	1120 ± 100	1310 ± 60	1300 ± 120	1460 ± 30	1660 ± 120	1590 ± 120	1390 ± 90	1570 ± 70
Wet, MPa	780 ± 30	780 ± 90	830 ± 20	1210 ± 60	1490 ± 70	1550 ± 100	1370 ± 40	1390 ± 80
Retention, %	69	60	64	83	89	97	99	89
Flexural modulus,								
Initial, Mpa	99 ± 2	100 ± 2	100 ± 3	103 ± 1	104 ± 2	98 ± 2	102 ± 2	100 ± 2
Wet, Mpa	83 ± 1	81 ± 1	89 ± 2	101 ± 1	103 ± 1	99 ± 3	98 ± 1	86 ± 4
Retention, %	84	81	88	98	99	101	96	86
Outerfiber strain, %								
Initial	1.5 ± 0.2	1.6 ± 0.1	1.7 ± 0.1	1.8 ± 0.1	1.9 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	2.0 ± 0.1
Wet	1.5 ± 0.1	1.5 ± 0.3	1.2 ± 0.2	1.6 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	2.1 ± 0.1	2.0 ± 0.1
Retention	101	92	67	88	94	100	105	98
ILSS								
Initial, MPa	56 ± 1	65 ± 1	65 ± 2	76 ± 3	85 ± 4	89 ± 3	78 ± 9	93 ± 4
Wet, MPa	37 ± 2	37 ± 1	38 ± 2	64 ± 2	81 ± 2	72 ± 2	86 ± 2	89 ± 3
Retention, %	67	57	57	85	96	81	114	96
Tg (offset G')								
Initial, °F/(°C)					356/(180)	383/(195)	257/(125)	401/(205)
Wet, °F/(°C)	NT	NT	NT	NT	293/(145)	311/(155)	270/(132)	302/(150)
Delta dry-wet, °F/(°C)					95/(35)	104/(40)	-45/(- 7)	131/(55)

Table 10: Mechanical performance biaxial glass fiber reinforced RTM plates based on UPUH and CAA-EPBA

Trígonox 42 PR	Mold Temperature, °F/(°C)	Flexural strength, MPa	ILSS, MPa
0.5	122/(50)	249 ± 14	36 ± 3
2.0	122/(50)	245 ± 17	36 ± 2
0.5	194/(90)	262 ± 17	35 ± 2
2.0	194/(90)	255 ± 12	36 ± 1
Average		250 ± 10	36 ± 1
Epoxy system	158/(70)	260 ± 10	39 ± 1

---

[1] [1] Edwards, H.R.; High Performance Urethane modified Unsaturated Polyesters; BPF Brighton Conference, Paper 10, pp. 37 – 45 (1982)

[2] Koning, de A.; Koster, R.J.; New developments in hybrid resins; Composites, No 3, May-June 1993