

# **DEVELOPMENT IN THERMOFORMING THERMOPLASTIC COMPOSITES**

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## **ABSTRACT**

Today many thermoplastic resins have entered the foray of composite materials in applications such as aerospace, vehicle and recreational applications. The advantages of thermoplastics are well known and include storage and shelf life, short processing cycles, recyclability and sustainability. In combination with reinforcing materials, synergies in strength, modulus, impact resistance and other properties, thermoplastics can be tailored for a wide range of applications. In this paper, the current state of the composite market, current commercial materials, and various production process used in industry are reviewed. A focus is made on the thermoforming process which is an under-utilized, yet highly efficient manufacturing method, practical for composite applications with limited deformation requirements. A thermoforming technique of layering commingled glass-polypropylene woven fibers with various surface layers is introduced in order to demonstrate this manufacturability.

## **Introduction**

Composite materials are found in thousands of applications across many industries from aerospace, to automotive, to recreation, to packaging. Starting in the 1940s, with the advent of thermoset plastic materials, the fiberglass reinforced plastics (FRP) industry began to develop composites [1]. Today, many thermoplastic-based materials have also been developed to address a wide range of applications. Nielsen [2] listed many advantages of composite materials including strength and modulus, impact resistance, corrosion resistance, chemical resistance, improved mechanical damping and increased heat distortion temperature. Essentially, the advantage of a composite material is the ability to combine the desired properties of its building blocks. To date, the driving force in development of composites has been enhanced strength-to-weight ratios in the aircraft industry [1], but now cost advantages are also becoming a major factor, particularly in automotive applications [3]. There is even a burgeoning industry to incorporate sustainable materials into composite structures [4].

The use of the thermoforming process for smaller scale, higher volume applications is now being considered as it has been proven to be a highly efficient manufacturing method for polymer-based products. A thermoforming technique of layering commingled glass-polypropylene woven fibers with various surface layers is introduced in order to demonstrate manufacturability and the ability create composite materials with synergistic properties. The mechanical properties of twelve composite laminations were compared versus single-ply homogeneous components to present the usefulness and limitations of the process.

## **Markets Served by Composite Polymer Materials**

According to JEC Magazine [5], through 2012 there was a rebound in the American composites market of approximately 15% to 210 million pounds. This represented 35% of the global composites industry that was valued at over \$100 billion and currently employs

approximately 550,000 professionals worldwide [6]. The major domestic market segments were further broken down in Figure 1.

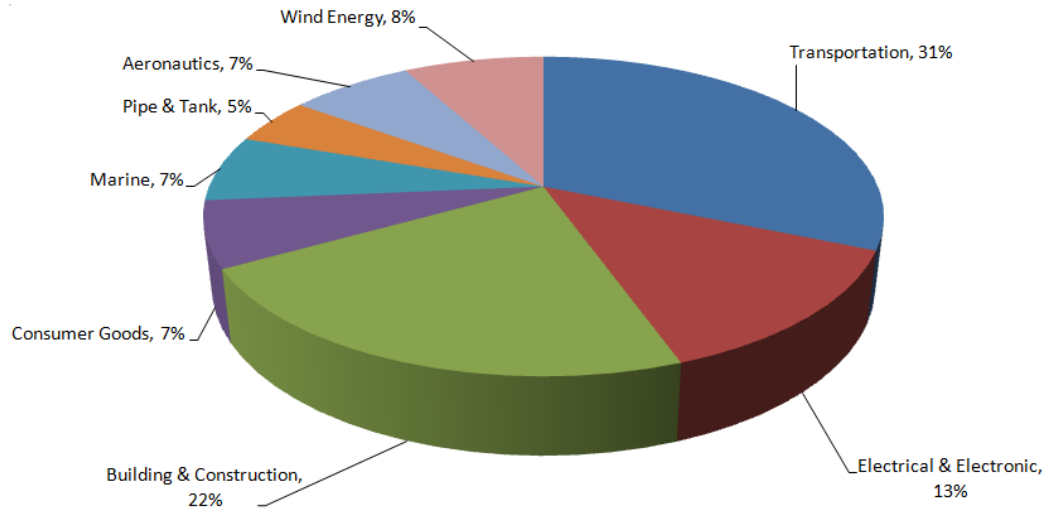


Figure 1 - US composites market by volume (2012) [5].

The largest market sector today is the transportation industry. Costs to produce final assembled modules of composites in several automotive applications have proven advantageous, particularly in structural and semi-structural components when compared to other various materials technologies [7]. In the aircraft industry, significant portions of structural fuselage and airfoil components are now made from composites, primarily due to their high strength-to-weight ratios. For example, Boeing's 787 Dreamliner and Airbus' A350 XWB are built with 50% and 52% advanced composites, respectively [8].

### Current Thermoplastic Composite Materials

Today, thermoplastic composites are still a niche market, occupying only 10% of the composites markets [9]. Thermoplastics are typically 500 to 1000 times more viscous than thermoset resins which tends to hinder the infusion of polymer into the reinforcing substrate [9]. They also necessitate higher pressures, and so require more robust and elaborate tooling and

equipment than competing thermoset resins [9]. In addition, thermoplastic composites require significantly more energy input to heat and cool the polymer. In applications, thermoplastics also have very different maximum service temperatures than thermosets. Table 1 shows the thermoplastic polymers most commonly used for thermoplastic composites along with their corresponding glass transition temperatures,  $T_g$ , melt temperatures,  $T_m$ , and processing temperatures,  $T_{process}$  [9].

Polymer	Morphology	$T_g$ (°C)	$T_m$ (°C)	$T_{process}$ (°C)	Cost (Relative)
PBT	Semi-crystalline	56	223	250	\$\$
PA-6	Semi-crystalline	48	219	245	\$
PA-12	Semi-crystalline	52	176	224	\$
PP	Semi-crystalline	-20	176	190	\$
PEEK	Semi-crystalline	143	343	390	\$\$\$
PEI	Amorphous	217	---	330	\$\$
PPS	Semi-crystalline	89	307	325	\$
PEKK	Semi-crystalline	156	306	340	\$\$

**Table 1. Common thermoplastics used in composites [9,10]**

One benefit of thermoplastic matrices is that they are relatively flexible compared to thermoset matrices. This flexibility improves impact resistance and reduces damage in the thermoplastic-based composites. Thermoplastic polymers currently are the only matrix materials that allow the new intermediate modulus, high-strength, high-strain, carbon fibers to be used to their full potential in composite design [11]. Designs engineered with unidirectional reinforcing materials have optimized this property.

Another advantage of thermoplastics is that they mitigate many end-of-life issues that have become critical for the automotive industry [12]. This is due to the fact that at the end of product life, an advanced thermoplastic composite component may be ground to a pellet-size processable material, whereas most thermoset composite materials can only be

ground and used as filler [9]. Processing methods of thermoplastics also have a lower environmental impact than typical thermoset processing, where the chemical reactions in fabrication commonly emit volatile organic compounds (VOCs). For example, environmental regulations regarding styrene emissions of unsaturated polyester can significantly affect the total cost of processing [9].

### **Glass Mat Thermoplastic Composites**

The most common class of thermoplastic composites is glass mat thermoplastic (GMT) materials that have been in production for decades [9]. Matrix polymers utilized have included polypropylene (PP), polyvinyl chloride (PVC), polycarbonate (PC), polyamide (PA), polyphenylene sulfide (PPS) and polyesters such as PBT and PET. Due to its low cost, the majority of products in this category are made with PP, which holds more than 95% market share [13]. Traditional GMT composites contain milled short fibers (less than 6 mm) whereas the category termed long-fiber-reinforced thermoplastics (LFRTs) contains reinforcement fiber with lengths up to 10 mm and longer. Both types commonly contain fiber loadings of 30-50% by weight [14]. Chopped long-glass fibers provide superior fill-in thin sections such as ribs and bosses. Unidirectional, very-long glass fibers offer extremely high stiffness and strength along one axis. The glass fibers are commonly formed in an interlocking network of reinforcement. In the typical fabrication process, the blanks are passed through an indexing infrared (IR) or convection oven then moved manually or robotically to a nearby press and for compression molding [7].

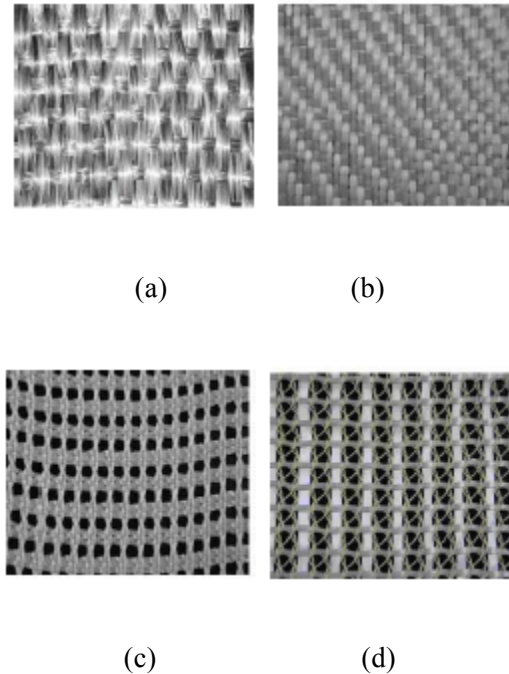
### **Lightweight Reinforced Thermoplastic Composites**

Lightweight reinforced thermoplastic (LWRT) composites are a development of GMT materials with added key features of higher stiffness-to-weight ratio, impact resistance, higher flexural modulus, higher damping, higher thermal insulation when compared to short fiber

composites with the same fiber percentage [7, 14]. These materials are commonly produced with glass and polypropylene fiber fleeces [7]. The proportion of the various fibers (20-60% glass) and the way the fleece is needled allows numerous mechanical properties to be tailored to suit the application. In processing, during the heating stage, the PP fibers melt and form the matrix material, forming a composite with individual reinforcing fibers but no fiber bundles [7]. Then in a subsequent stamping stage, engineered tooling designed to not to press down as deeply in selected areas, allows local stiffening, similar to a sandwich composite. In areas where higher tensile strength is desired, such as stress concentration points, the blank can be more fully pressed and the material consolidated. Since LWRT composites are typically stamped at very low pressure, this process allows very large parts to be created or multiple parts produced in a multi-cavity or family mold [7].

### **Textile-Reinforced Advanced GMT Composites**

Textile-reinforced advanced GMT composites further outperform earlier materials because of highly engineered mat structures. These sheet-formed laminates have been found to have improved performance in higher stiffness applications, longer fatigue life, higher impact resistance across a range of temperature conditions, and have proven superior in managing loads at higher strain rates [7]. This category of composites commonly uses a combination of traditional glass mats and one or more layers of textile reinforcements. The textile layers are formed from continuous fibers woven using glass, aramid, thermoplastic polyester, or carbon. Figure 2 shows some of the reinforcing weaves in use today in the automotive industry including plain weave, (Figure 2a), twill weave, (Figure 2b) and two specialty weaves, (Figures 2c and 2d).



**Figure 2. Common thermoplastic weaves: (a) plain weave, (b) twill weave, (c) multi-axial weave and (d) plain weave with fill [7]**

With this technology, properties can be tailored for specific applications. Mechanical characteristics can be modified by varying the ratio of fibers in the warp and weft directions. Secondly, the order of placement of the fabric layers in the lamination plan can be varied to affect physical properties. When the fabrics are used on the surface, the lamination will generally display a higher flexural modulus. If better surface conditions are required for aesthetics, chopped, non-woven mat is preferable for the top layers [7].

### **Commingled Thermoplastic Composites**

The fiber commingling process is a method of producing a pre-impregnated thermoplastic-based material for manufacturing. Here, fine reinforcing fibers and fine polymer fibers are blended to produce a multi-component thread. Alternatively, the glass fibers may be coated with polymer in a precursor stage of thread production. Cohesion of a polymer, such as polypropylene to high surface energy glass fibers, is achievable with the use of compatibilizers, which are often copolymer additives to the resin melt. The "hybrid-yarn" thread produced is then

woven into various textile forms. In downstream fabrication processes, the application of sufficient heat and pressure cause the polymer to flow between both the fibers of the threads and between adjacent threads such that upon cooling, a solidified three-dimensional form is manufactured [9].

The main advantage of the commingling process is that the textile pre-form weave is now quite drape-able over projected mold shapes, and is significantly lower in cost than many alternatives, when considering the additional strength to weight ratios that are possible. Disadvantages can include higher processing pressures relative to thermoset options and longer times in the heating phase relative other thermoplastic options such as injection molding. Quality issues associated with using woven reinforcing substrates include excessive fiber movement, as the commingled yarns can undergo much de-bulking during the melting process.

Twintex ®, a trade name of Fiber Glass Industries of Amsterdam New York refers to a commingled fabric of glass and polypropylene fibers. The fiber volume fraction of this material is typically 60 percent by weight and the material is commonly hand-laid and processed by a vacuum bag method and presses under heat at 50°C<sup>and</sup> higher depending on cycle/cure time. The polypropylene component of the weave, with its low melt makes it relatively easy to form. In the recommended process, hand lay-up and thermoforming under a vacuum membrane is performed at 90°C for twelve hours [15]. Herein, a process is presented, utilizing a sheet-fed, two-stage industrial thermoforming machine, demonstrating 120-180 second cycle times are practical.

### **Composite Forming Techniques**

The manufacture of composites has primarily centered on methods to create laminations of thermoset polymers within female molds or over male molds by manual wet-layup techniques. These methods are commonly augmented by vacuum assists to even resin reinforcement consistencies, followed by autoclaving to assist curing.



Other processes include pultrusion, compression or matched die molding, resin transfer molding and thermoforming. Pultrusion is a common method of producing composite profiles (including hollow profiles), rubber hose, pipe, building panels, and electrical insulators [16]. This is a continuous process where spool-fed fibers are impregnated with resin by drawing through a bath, or in a spray chamber, then passed through a die and cured. Compression molding is a matched die molding technique. The equipment is a press (usually hydraulically-driven) utilizing pressures that can range up to several hundred tons. The process can be used to shape condensation polymer-based composites such as acrylic, urea, and phenolics. Systems of this type are often used for the final formation of pre-preg materials such as sheet molding compound (SMC) or bulk molding compound (BMC). These materials, made of resin, initiator, and reinforcement components, are sold in ready to form sheets, logs or ropes. Parts as large as car bodies have been made in this manner [16]. In resin transfer molding (RTM) and reaction-injection molding (RIM), a mold is loaded with reinforcing material. Reinforcements are often stitched or bonded to tolerate the pressure of injection and retain the proper shape. After the mold is closed, resin is injected into it. The pressure of injection forces the resin to flow through and wet the reinforcement. Often a vacuum is applied to remove trapped air. These techniques have been used to make relatively large parts, such as the body panels for the Pontiac Fiero [17].

### **Thermoforming of Thermoplastic Composites**

Advantages of the thermoforming process for composites are the same as with homogenous materials: low cycle time, low cost of tooling, speed to market, and relatively clean in comparison to competing processes. A disadvantage of thermoforming for highly reinforced laminations arises due to the fact that it is a stretch forming process. The ability of a material to form is subject to its ductility relative to the desired geometry. Depth of draw, radius of curvature, stress concentrations and surface friction are variables to be considered along with material properties. With composites, consideration must also be given to the adhesion of any

layers in lamination prior to the application of the forming force. The lamination plan, clamping and venting is critical, such that when forming force is applied, delamination does not occur.

Process factors affecting the performance and quality of final product, according to Gunel [18], are heating period and rate, mold temperature, forming rate and cooling rate. These factors are often published based on trial testing by material manufacturers. Operating conditions have a great influence, so pre-production trials to fully characterize grades of material are encouraged.

Computer numerical simulations using finite element analysis (FEA) software can now evaluate deformation to a great detail based on several mathematical models. They have been proven to be useful for both part designers and tool makers in the development of a thermoformed product, particularly in identifying stress concentrations, formation problems and thickness, which is the foundation of many critical features.

### **Experimental: Thermoforming Composite Laminations with Commingled Twintex®**

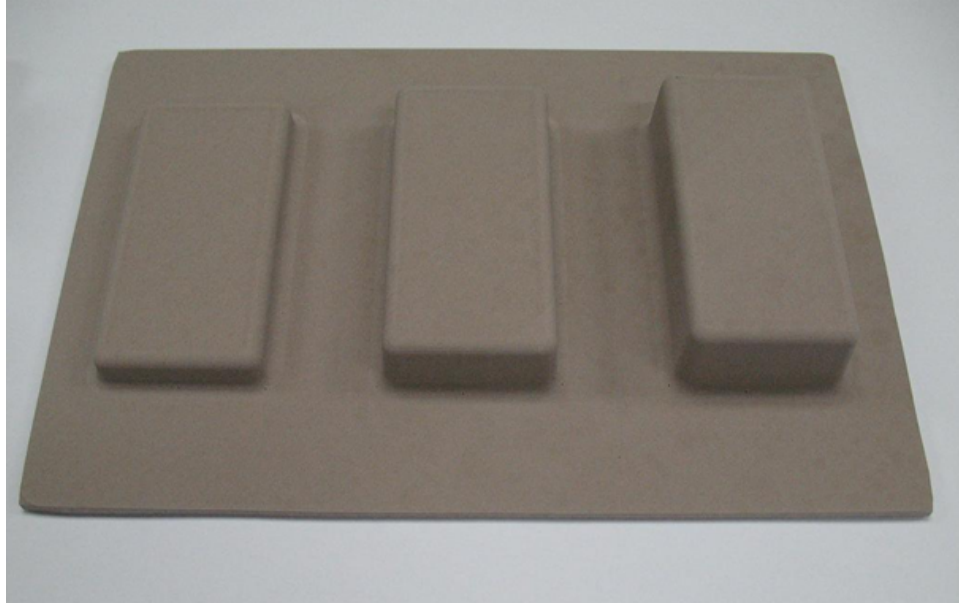
In order to validate the two-stage thermoforming process as a viable, efficient manufacturing process for composite laminates several factors were considered. To begin, the thermoforming process requires thermoplastic materials which heat quickly, become relatively soft for deformation, and cool quickly making the process efficient. In general, reinforced materials have not found a home with this process because they are generally not highly elastic. Recognizing that fact, there are many applications that are not extremely demanding in deformation that could still benefit from the economics of the process.

A search of available reinforcing thermoplastics led to a product called Twintex®, which was originally developed by Saint-Gobain S.A., who sold it to Owens Corning (OCV Reinforcements), who have since sold the rights to Fiber Glass Industries (FGI) of Amsterdam New York. For this research, FGI provided two lots of material for testing and evaluation in the thermoforming process: TPP60N22P, a plain weave 745 GSM (22 ounce/yard) commingled E-glass and polypropylene product; and TPP60N44T a heavier 1492 GSM (44 ounce/yard) twill

weave of the same fibers. When combined in lamination with surface layers with selected characteristics, the additional strength rigidity and impact performance afforded by the reinforcement enhance the laminated material's structural performance and expand the window of applications. The selection of surface materials was somewhat limited, but four commodity materials and two engineering polymers were procured for evaluation. Polyvinyl Chloride (PVC) was selected due to its wide usage in the thermoforming industry and its good characteristics for weatherability. Polyethylene terephthalate (PET) was selected for its good stretch characteristics and the fact that it is a preferred substitution to PVC due to biological concerns. High density polyethylene (HDPE) was selected as a good laminate due to its known chemical resistance. Polypropylene (PP) was tested as a laminate as it should be wholly compatible with the commingled glass-PP weave. This product, displaying cohesive bonding, should result in an economically produced, high strength material. The last products sampled, provided by Topas Advanced Polymers of Florence, KY, were a single-ply cyclic olefin copolymer (COC) Topas 8007 and a multilayer sheet with outer layers of Polyethylene Terephthalate Glycol (PETG) and an inner layer of the Topas 8007 COC. The advantage of COC has been seen in outstanding moisture and biological resistance. The layered film was created to enhance processability [19].

Owing to the lack of elasticity with Twintex®, the manufacturer has recommended the process of manual formation and autoclaving [15]. It is the objective of this experiment to demonstrate that this material can be utilized with the simple two-stage stretch-vacuum process. The guidelines of the manufacturer were adhered to in regards to minimum radius of curvature, with radii less than 5mm and draft angles less than three degrees. To deform the laminations, a simple three-dimensional male mold was produced with three levels of protrusion in order to evaluate the stretch potential of the reinforcement. Another design feature of the protrusions was the rectangular shape which afforded a better evaluation of anisotropy in the 0-90 degree woven materials. This was particularly important with the unbalanced TPP60N44T twill weave. It also

provided the opportunity to evaluate the performance in the stress-concentration points at the upper level corners, as per Figure 3.



**Figure 3. Thermoforming mold as machined for lamination trials**

The lamination plan was comprised of the surface layer and the reinforcing layer. Essentially, the surface layer was the vacuum retaining layer, which would pull the reinforcing layer down to the mold in the second (vacuum) stage. According to the manufacturer of the reinforcement, this simple technique has not been utilized in industry [20]. To evaluate the viability of this process, sections were cut to 500 mm wide, 750 mm long sections to accommodate the clamp size on the sheet fed thermoforming machine. Figure 4 shows the material as clamped in the machine prior to heating. Figure 5 shows the material under heat in the oven section of the machine, and Figure 6 shows the product post-forming and prior to off-line trimming.



Figure 4. Clamped laminates prior to heating



Figure 5. Laminates in oven approaching forming heat.





**Figure 6. PVC-TPP60N22P lamination post-forming, prior to trim.**

Edges were taped in order to hold the laminates together during mounting. In a continuous process, this could be accomplished by needling, or tacking together with thread. This would entail using two feed rolls, and a needling station prior to the oven section.

During the heating stage it was found that in order to achieve an optimum deformation cycle time of 120 seconds, an average 190 degree Celsius heat was required for the TPP60N22P laminations. For the TPP60N44T laminations the time had to be extended to 180 seconds for the same process temperature.

## **Results**

The initial observation was that deformation of the laminations was limited due to the inelasticity of the reinforcing layers. As anticipated, formabilities of the laminations were found to be quite limited. Table 2 displays the max depth of deformation per half width (radius) of separation of the initial upper contact surface. Cavity formation percentage was calculated as a

percentage of the actual strain length versus the lineal mold cavity length in the same plane of deformation.

**Table 2. Deformation Results for Various Laminations at 23.6 Pa**

Material	Max. Deformation (mm/mm):	Cavity Form %:
PVC-22P	0.193	7.8%
COC-22P	0.171	5.7%
PCP-22P	0.221	4.5%
PETG-22P	0.236	4.9%
PP-22P	0.274	10.9%
HDPE-22P	0.189	2.6%
PVC-44T LONGITUDINAL	0.193	4.8%
PVC-44T TRANSVERSE	0.238	4.8%
PCP-44T LONGITUDINAL	0.132	4.9%
PETG-44T LONGITUDINAL	0.136	5.4%
PP-44T LONGITUDINAL	0.158	6.1%
HDPE-44T LONGITUDINAL	0.168	3.7%

Deformation depth and cavity formation percentage was seen to be directly related to the vacuum generation of the equipment and the cooling rate of the material. The results listed in Table 2 are based on the maximum vacuum capability of the sheet fed thermoformer utilized, at 23.6 Pascal as measured at the vacuum box. The lack of deformation can be attributed the high strength and modulus of the reinforcing threads at measured at in uniaxial tension tests 377 MPa and 20.7 GPa respectively, which is 7.6 to 12.7 times greater than that of the surface layers.

Second, performance of the process varied greatly due to the cohesion and adhesion of the laminates. Some of the materials exhibited pull-through of the surface layer into the reinforced matrix creating an exceptional mechanical bond. Several tests of composite strength in these regards were performed to ASTM Standards, the most useful being T-peel testing performed to ASTM D1876-08 [21] that quantified the adhesion strength. The PVC- TPP60N22P

laminations displayed a low 11.47 N/m peel strength, whereas COC- TPP60N22P showed a 111.2 N/m peel strength. The PP- TPP60N22P showed a high 2270 N/m peel strength due to the cohesive nature of its bond. The PVC surface layer specimens did not adhere well and often delaminated in trimming and handling. The semi-crystalline, HDPE and PP laminations exhibited much greater warp when cooled off the mold. These materials had excellent adhesion and cohesion properties and thus were deemed successful composite products. The PET products exhibited little warp and had good adhesive qualities, whereas the COC materials also had little warp and clearly showed outstanding stiffness and strength

Other tests regarding flexural and impact resistance showed the synergies of combining reinforcement with surface layers. Generally, the mechanical properties increased significantly. For example, the PET- TPP60N22P, tensile strength increased 136%, modulus increased 102% and impact resistance increased to 85.6 kJ/m<sup>2</sup> from 3.48 kJ/m<sup>2</sup> versus the single-ply material. Contact the author for complete comparative mechanical results.

## **Conclusions**

Further development of the thermoforming process is warranted due to the successful lamination of commingled woven reinforcing fabrics with various surface layers. Tailoring these laminations to desired properties in applications is the primary feature, followed by the efficiency and economy of the process versus competing materials and processes. In many cases the physical properties are enhanced dramatically compared to that of the sub-components. The disadvantages found have been primarily based on low thermoformability of the reinforcement due to the lack of elasticity and the lack of compatibility in adhesion as found in the PVC- TPP60N22P laminations.

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