Thermoplastic Composites – Products, Processes and Applications

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SUMMARY: The segment of materials known as continuous fiber reinforced thermoplastic composites (CFRTP) occupy a unique processing methodology vastly different than traditional thermoplastics (injection molding, blow molding, thermoforming) and thermosets (SMC molding, filament winding, pultrusion, infusion). This uniqueness hinders the commercial development of applications using CFRTP. For CFRTP to flourish as a valid material segment, fast and efficient transformation processes will need to be developed and industrialized.

KEYWORDS: Thermoplastic composite, continuous fiber reinforcement, diaphragm forming, thermoform stamping,

INTRODUCTION

This paper serves to identify commercially availability of the following.

1.) Thermoplastic composite materials technologies
    a. Melt impregnation
    b. Powder impregnation
    c. Low viscosity reactive thermoplastics
    d. Commingled fibers
2.) Transformation processes
    a. Vacuum bag molding / vacuum infusion
    b. Diaphragm forming
    c. Thermoform stamping
    d. Pultrusion and filament winding
3.) Commercial applications for the above processes
4.) Conclusion

THERMOPLASTIC COMPOSITE MATERIAL TECHNOLOGIES

Melt Impregnation

Melt impregnation is a well established and documented impregnation technique that has roots in the process of making long fiber reinforced thermoplastic injection molding compound. Imperial Chemical Industries (ICI) developed a strong patent position throughout the 1980's (1).

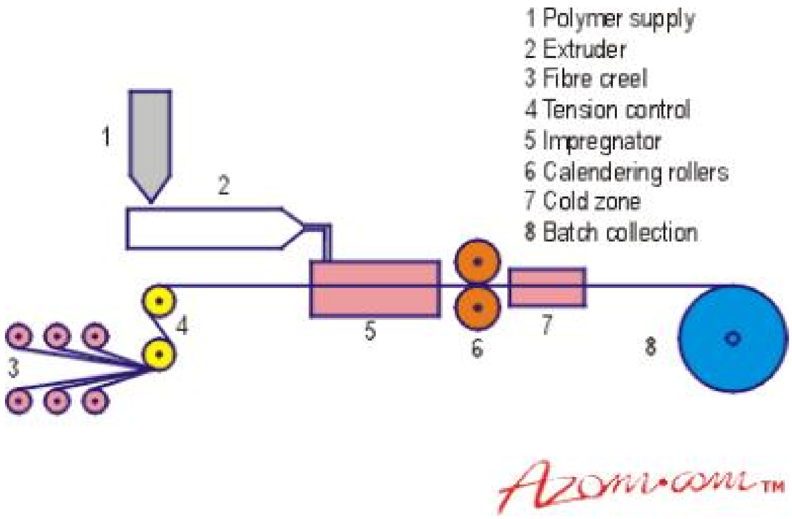


Fig. 1 Schematic of melt impregnation

The key technological component of the process is the impregnation die. Generally speaking, the impregnation die contains a "bath" of molten polymer. In the bath, the fiber roving is guided over and under a series of bars to spread the roving, and provide shearing forces on the roving. These basic actions act to wet out the individual fiber filaments in the fiber roving. Bates (2) reports on the quality of fiber wet out as a function of roving inlet tension, pull speed, number and diameter of cylindrical pins, temperature of polymer, outlet die diameter and pulling tension. He concludes that

A unique impregnation die was studied by Weustink and van Keulen (3) for thermoplastic filament winding. It was concluded that by using conical, co rotating impregnation bars the fiberglass roving "spread" better resulting in better impregnation at high line speeds.

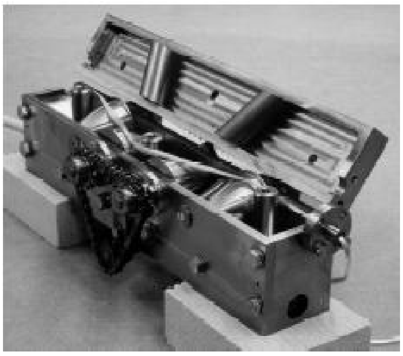


Fig. 2 The die system used by Weustink

Two relatively new melt impregnation techniques have been patented. US Patent 6186769 by Hawley identifies a "pushtrusion" process whereby the polymer processing pressure is used to impregnate and move the glass roving through the die system. US Patent 6709995 by Dyksterhouse expands on his two previous patents 6656316 and 5911932. This technology is predicated on heating the fiberglass roving well above the melt temperature of the polymer.

Again, the main commercial application of the melt impregnation technology is in the manufacture of long fiber injection molding compound; however, there is good interest in thermoplastic pultrusion and filament winding where recyclability, zero emissions, part toughness, and post forming are encouraging attributes.

Powder Impregnation

Powder Impregnation is a widely accepted technology to make thermoplastic prepreg or semipreg. Prepreg is considered fully consolidated; while semipreg needs to be processed for full consolidation. Although there are variants of this process (4), electrostatic powder coating (EPC) appears to be the primary technology. In EPC, the polymer is finely ground and charged oppositely than that of the fiber. The fiber is then run through a "fluidized bath" whereby particles of polymer are attracted into the fiber. From here, the fiber can be wire coated to encapsulate the powdered polymer and fiber, or the fiber / powder can be put through hot rollers to partially or fully impregnate the fiber. Yet another approach would be to use an additional binder to hold the powder in place. The benefit of this is that the fiber is soft and flexible. Several companies employ these types of processes – **Baycomp** (Canada), **Hexcel Applied Fiber Systems** (US), **Cytec** (US), **Sulzer** (Switzerland).

Low Viscosity Reactive Thermoplastics

Two new encouraging emerging technologies are gaining commercial momentum in the CFRTP segment. **Fulcrum™** is based on a thermoplastic urethane (TPU) polymer. The key to this impregnation technology is the reversal of the polymerization process in the melt stage that results in extremely low melt viscosity; hence easy wet out of the reinforcing fibers. These materials are referred to as depolymerizable repolymerizable thermoplastics (DRTP) When cooling, the molecular weight increases to that of a typical thermoplastic. The Fulcrum technology is specifically designed for thermoplastic pultrusion where toughness, recyclability and post forming are desired attributes.

The second technology is from Cyclics Corporation. **Cyclics®** is a cyclic polybutylene terephalate (CPBT) based polymer that when polymerized becomes PBT – a very useful and effective engineering thermoplastic. The CPBT oligomers when processed at low temperatures (180 – 200ºC) have a very low melt viscosity; hence making it very easy to wet out fiber reinforcement. Catalyst is required to start the polymerization reaction. Catalysts have been designed to be very slow or very fast. This flexibility lends itself to a wide range of processes and applications from reaction injection molding type processes to vacuum infusion of very large parts.

One interesting aspect of this technology is that once fully reacted, the molded part can be demolded instantly. The crystalline melt point of PBT is 225ºC – well above the processing temperature of the CPBT.

Commingled Fibers

NASA was one pioneer in the technique of commingling reinforcing fibers with thermoplastic fibers as a route for post impregnation during processing. This solution allowed flexibility in product forms. Commingled fiber yarns or rovings can be used as-is, or can be knitted, woven or braided into a higher performing composite product. These advanced forms drape and conform easily to form complex parts (5).

The concept of commingling was taken to new levels when Saint-Gobain Vetrotex introduced the **Twintex®** product. Twintex is commingled E glass with thermoplastic fibers. Polypropylene (PP) is the first commercial thermoplastic used as it is lightweight and inexpensive. Twintex is made at the bushing level during the glass fiberization step. Due to the industrial nature of the process, it is a very economical, high production process.

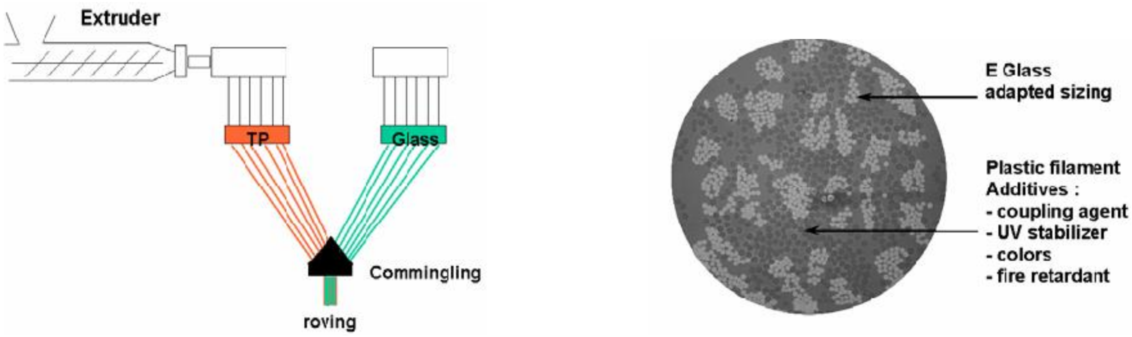
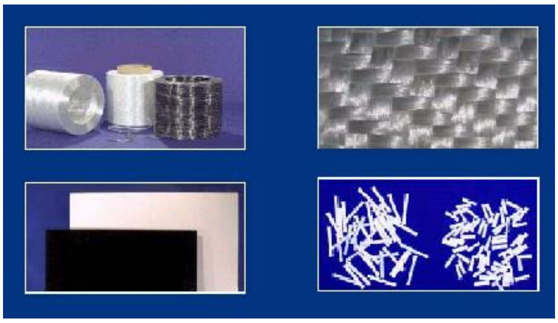


Fig. 3 In-line commingling and an actual cross section of commingled roving

This high volume industrial process has helped the CFRTP market segment expand greatly as price points are competitive with alternative material solutions like wood, metal and thermoset composites. The technology is flexible in terms of product forms and applications. Direct **roving** can be pultruded or filament wound. It can be woven into a compliant **fabric** and vacuum bag molded, diaphragm formed or laminated into a preconsolidated sheet. The preconsolidated **sheet** can be used as-is for flat panel applications, or it can be used as a semi finished good for thermoform stamping or compression molded. Lastly, the roving can be readily converted into long glass **molding compound** for injection molding. The data below shows the range of performance from this one core technology.



Material	Strength (MPa)	Modulus (MPa)
20% IM compound	61	3,650
40% IM compound	86	5,870
Balanced Fabric	240	13,000
Unbalanced Fabric	400	24,000
Unidirectional	700	38,000

Fig. 4 Product various product forms and tensile data for these forms

TRANSFORMATION PROCESSES

The transformation of these materials into molded articles is a critical area for future growth of commercial applications. Simply stated, there is a lack of accepted technology in the market to support growth. Below, several commercial processes will be discussed.

Vacuum Bag Molding

Vacuum bag molding of CFRTP has roots in thermoset infusion. Compliant CFRTP materials are laid in a mold, a bag is placed over the tool, vacuum is drawn, then the tool is heated until the product is fully melted and cooled.

Vacuum bag molding is suitable for applications where 5 – 15 parts per day are required. Extremely large structures, and variable wall thicknesses are achievable.

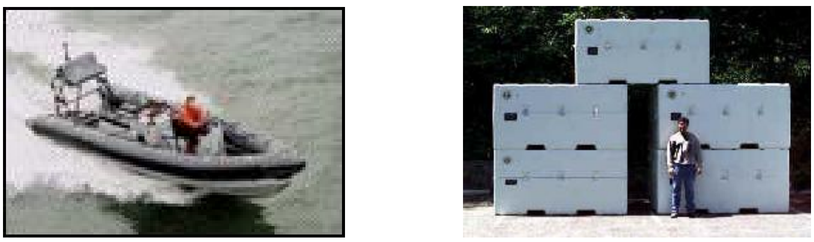


Fig 5 Rigid inflatable boat made by Halmatic (UK), and military shipping containers molded by Integrated Technologies (USA)

Diaphragm Forming

There is good potential for diaphragm forming to become industrial process for the transformation of CFRTP raw materials. The schematic below shows a double diaphragm process. This process is much like traditional thermoforming, but with electrometric diaphragms. The CFRTP material (fabric or sheet) is placed in between the diaphragms. The diaphragms are then clamped; **not** the CFRTP material. This allows the material to conform to the mold while the diaphragms act to constrain the material from wrinkling or folding. Once the diaphragms are clamped, vacuum and heat are applied to melt and remove voids (and to consolidate if unconsolidated raw materials are used). The diaphragms are moved over the tool where vacuum and pressure are used to form the part in a one sided cold tool. Parts are then demolded.

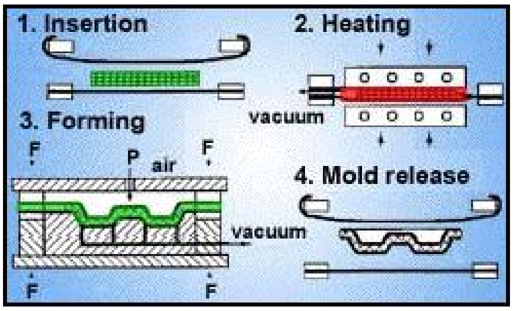


Fig 6 Double diaphragm forming schematic, and a decorative canoe seat made by a diaphragm forming process (photo courtesy of **Diaphorm, Inc**. (US)).

The diaphragm forming process is characterized as a medium series production process for applications requiring 50 – 200 parts per day. The process results in constant thickness, and parts need trimming. Single diaphragm forming is very amenable to variety of decorative surface films, and is very competitive in cost to compression molding (6).

Thermoform Stamping

Stamping of CFRTP sheets is fairly well established in the industry, but not on a large scale, high volume basis. Most processes are captive to the specific processor. Thermoform stamping is characterized by using non shear edge matched tooling that can be matched metal, or metal / rubber. One advantage of rubber is quasi hydrostatic pressure on near vertical walls due to the compression of the rubber. One disadvantage is poor surface aspect on the part due to the lack of a highly polished surface. The CFRTP product is heated, then shuttled to the pressing area by a specialized clamping frame. Pressing requirements can be as low as 50 pounds per square inch of part.

Unlike diaphragm forming where the diaphragms constrain the fabric from wrinkling or folding, the thermoform stamping process uses a clamp frame that allows the CFRTP product to "displace" (versus "flow") as the fabric is drawn (pushed) into the tool. The specific clamping points, and amount of tension on the physical displacement are keys to having the CFRTP product conform to the tool surface with predictable and consistent fiber orientation.

The subject of stamping CFRTP materials is covered in great detail at the National Research Council of Canada (7,8).

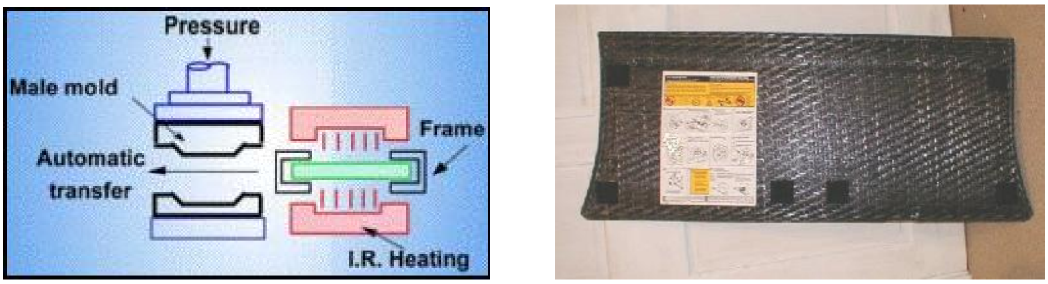


Fig 7 A schematic for the thermoform stamping process and a Saturn Vue load floor made by stamping a sandwich panel of CFRTP skins onto a PP honeycomb core.

Pultrusion and Filament Winding

Progress has been made in the area of thermoplastic pultrusion and filament winding especially with the use of commingled fibers and DRTP where the ease of impregnation leads to fast line speeds.

Pictured below is a filament wound water storage tank, and a thermoplastic composite fence profile. Both applications exploit the toughness and durability characteristics of CFRTP.

Fig 8 Filament wound CFRTP pressure vessel and a pultruded fence profile.

CONCLUSION

The benefits of CFRTP materials are numerous and clear – no VOC, readily recyclable, toughness, durability, post forming, eliminating of painting, can be welded… Absent is a clear and distinct process base to transform CFRTP materials into useful articles. The applications and processes above are just a beginning.

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