

**COMPOSITE MOLDED ARTICLE AND METHOD OF MAKING A
COMPOSITE MOLDED ARTICLE**

This application is being filed on 23 January 2004 as a PCT International
5 Patent application in the name of VEC Technology, Inc., a U.S. national
corporation, applicant for the designation of all countries except the US, and Robert
P. McCollum, a U.S. citizen, Shiraz Sidi, a Canadian citizen, Jeffrey J. O'Hara and
Richard Eugene Clark, U.S. citizens, applicants for the designation of the US only.

10 **Field of the Invention**

The invention relates to a composite molded article having a smooth
attractive surface. More particularly, the invention relates to combining materials in
a mold to result in a composite article having a finished surface. The invention also
relates to a method for making composite molded articles comprising a reinforced
15 thermosetting material having a thermoplastic exterior layer, the method having
improved efficiency and reduced emissions of hazardous air pollutants.

Background of the Invention

The invention relates to a composite molded article. The invention further
20 relates to a shaped and layered reinforced composite article. The article is in the
form of a laminated material having improved physical properties affecting the
structural integrity and cosmetic appearance of the article. The invention also relates
to the manufacture of composite molded articles using closed mold processing.
More particularly, the invention relates to an improved method for making a
25 thermoset article having a fiber reinforced structure and an attractive thermoplastic
exterior layer having improved attributes including weatherability, strength and
resistance to cracking, marring and non-aqueous solvents.

Composite structures comprising a fibrous reinforcement material
impregnated with a cured, thermoset resin are known for manufacturing useful, non-
30 metal articles for consumer and industrial purposes. These include articles such as
spas, tubs, recreational vehicles, auto body panels and marine components such as
boat decks and hulls, for example. Fiber reinforced composite articles are known for
their strength and durability. In addition to having desirable structural
characteristics, the articles may have a decorative or visually attractive surface. The
35 decorative surface may be a visually exposed layer formed on the exterior, the
interior, or on a portion thereof, or the entire surface of a useful article to provide a
smooth, attractive appearance. The visually exposed layer may be polished, shiny or
matte, transparent, white or colored. Materials selected for the exterior decorative

surface of the composite require a combination of desirable properties including outdoor weatherability, impact resistance, attractive cosmetic qualities and ease of processing.

Conventional methods for making fiber reinforced composite structures involve manually shaping the reinforcing fiber to a mold surface and then impregnating the fiber with an appropriate curable, thermoset resin. Typically, a gel coat of clear or pigmented thermoset resin is applied to the surface of the mold before forming a final laminate structure. The gel coat results in a cosmetically attractive exterior surface for the finished article and protects the fiber composite from attack by ultra violet radiation from the sun. However, layers made from gel coat materials can under adverse circumstances, develop crazing, cracks and color fading over time. Cracks can range from surface or cosmetic hairline cracks to cracks that extend from the surface of the gel coat into the laminate resulting in potential structural defects. Even hairline cracks need to be repaired to prevent greater structural damage from developing. Repairs can be expensive and the original color of the gel coat is virtually impossible to match.

Gel coats are typically applied to the mold surface in liquid form. The thickened liquid gel coat material is placed on the mold surface in a layer about 0.3 mm to about 0.8 mm thick. The gel coat material contains volatile organic components (VOCs) such as styrene monomer that is released to the ambient environment. Many of these volatile components are classified as hazardous air pollutants that are harmful to human health and the environment. Stricter government regulation continually lowers emission standards. Further, VOCs are often flammable resulting in a fire hazard. Elaborate precautions and expensive equipment is required to minimize the release of and exposure to these volatile substances.

An alternative to a thermoset resin gel coat is a thermoplastic layer on the exterior surface of the composite. Thermoplastic layers tend to have better weatherability and more flexibility than thermoset plastics and have less tendency to form cracks. The sheet may be shaped by thermoforming methods and then reinforced with fiberglass composite backing. Chapman et al., U.S. Patent 5,875,732 disclose a boat hull construction comprising ultra high molecular weight (UMHW) polyethylene having KEVLAR® and fiberglass-resin reinforcement. The thermoplastic UMHW polyethylene hull is shaped in a thermoforming step and the reinforcement applied to the inner surface of the hull using a vacuum bag molding technique. Vacuum bag molding processes involve conventional lay-up of resin and filler materials on an open mold followed by covering the lay-up materials with a

plastic layer that enables a vacuum to be drawn to force the plastic against the reinforcement.

Russell, U.S. Patent 4,178,406 discloses a method for making a fiberglass-reinforced article wherein a preformed thermoplastic film is placed in a holding
5 fixture, a fibrous reinforcement material and curable thermoset resin layer are applied to the film and finally, a second preformed thermoplastic film is applied to the reinforcing layer. The composite is then subjected, in a thermoforming process, to a vacuum to form the shaped article. The film is in the form of a sheet having an average thickness of 40 mils (about 1 mm). Such thin materials can be difficult to
10 handle and are easily wrinkled resulting in an unsightly appearance and uneven bonding between the film and the reinforcing layer.

Rigid, thermo-formable panels comprising an acrylic film laminated to a thermo-formable substrate provide improved handling properties. Representative panels are described in Rutledge, U.S. Patent 4,221,836; Goldworthy, U.S. Patent
15 4,498,941 and Hicks et al., U.S. Patent 5,069,851. The rigid panels can be shaped by thermoforming methods well known in the art and reinforced with a composite thermoset resin and fiberglass backing. Combining the fiberglass reinforced polyester resin with the individual thermoformed product is generally performed manually outside the thermoforming mold in a slow, labor intensive process. Such a
20 method results in undesirable emission of hazardous air pollutants during application.

Boat hulls, components of motor or recreational vehicles, tubs, tub surrounds and spas having a gel coat finish, due to their wear in normal use and/or exposure to sun, tend to lose their glossy appearance, develop a chalky surface and may develop
25 "orange peel" micro-cracks that can ultimately result in structural failure of the composite construction.

For these and other reasons, there is a continuing need to improve the useful lifetime, aesthetic properties and structural integrity of shaped and layered reinforced, composite molded constructions. There is also a need to improve the
30 production rate of shaped laminated composite articles, to reduce labor costs and to control the emission of hazardous air pollutants.

Summary of the Invention

The invention provides shaped and layered composite articles comprising a
35 layer of a thermoplastic acrylic polymer having a thickness up to about 2.5 mm, or greater than about 1 mm to about 2.5 mm, a layer of a thermoplastic polymer having a thickness of 0.5 to 15 mm, and a third layer of fiber reinforcement composite. The range of thickness for the first and second thermoplastic layers may or may not

overlap. For example, the thickness of the first layer may be up to about 2.5 mm and the thickness of the second layer from about 3.0 mm to about 15 mm. The term "composite" refers generally to a combination of one or more materials differing in form or composition on a macro-scale. The constituents retain their identities in the sense that they do not dissolve or merge completely into one another, although they act in concert. Normally the components can be physically identified and exhibit an interface between one another.

The composite article may also include a member comprising rigid polyurethane foam. The polyurethane foam member functions to provide stiffening for the construction or floatation in the case of marine articles. The composite article may have a second fiber reinforcement composite layer enclosing the rigid polyurethane foam reinforcement.

The acrylic polymer layer provides a cosmetically attractive appearance to the structure and resists cracking and accidental marring. The acrylic polymer layer constitutes the surface of the composite article that is normally viewable and is usually the exposed, exterior surface. The surface may have a flat, curved, concave or convex shape. Incorporating colored material, such as a pigment, into the acrylic polymer layer may vary the appearance of the article. Graphic arts methods may be used to incorporate a decorative design into or onto the construction. The composite article is useful for automotive applications, marine articles such as boat hulls and hatches, outdoor recreational vehicles such as ATVs and snowmobiles and, in general, for any structure that is exposed to outdoor environmental conditions, direct sunlight and extreme temperature ranges.

The thermoplastic acrylic polymer layer and the thermoplastic layer may be a laminate in the form of a combined thermoplastic sheet. The thermoplastic sheet may be preformed by conventional thermoforming methods to a desired shape. Non-exclusive possible shapes include components of an auto body such as door, hood, trunk, grill, and tonneau panels, tub, tub surrounds, spas, a boat hull and boat components such as decking, hatches and seats, and components of recreational objects such as ATVs, power water craft, outboard motor cowling, water skis and surf boards. The thermoplastic sheet is shaped so that the acrylic polymer layer is the exterior or normally visible layer of the composite article. The acrylic polymer layer provides a durable surface with an attractive appearance to the exterior of the molded article while the thermoplastic layer provides strength and rigidity to the molded article. The thermoplastic may be ABS, ASA or ABS-acrylic alloy, for example. A thermoplastic alloy is simply a mixture of thermoplastics that results in a melt stable single-phase material because the polymers have some interaction that combines them together. The acrylic polymer may comprise polyacrylate ester,

polymethylmethacrylate ester or thermoplastic chemical derivatives of these polymers. Likewise, the ABS-acrylic alloy may comprise one or more than one of a polyacrylate ester, a polymethylmethacrylate ester and their chemical derivatives.

5 The thermoplastic sheet may have more than two layers. For example, one or more layers of thermoplastic acrylic polymer, acrylic-styrene-acrylonitrile (ASA), or ABS-acrylic alloy may be laminated to the surface of the thermoplastic sheet that will become the interior surface of the molded article. The interior layer constitutes a surface of the construction to which fiber reinforcement composite is usually applied. The thermoplastic sheet would have an exterior layer of a thermoplastic
10 acrylic polymer, a layer of thermoplastic polymer selected from ASA, ABS or ABS-acrylic alloy and an interior layer of acrylic polymer, ASA, or ABS-acrylic alloy. The interior layer of acrylic polymer, ASA, or ABS-acrylic alloy provides an improved bonding surface for the thermoset resin to form a stronger bond between the cured thermoset resin and the thermoplastic sheet.

15 The fiber reinforcement composite comprising fiber reinforcement and thermoset resin is applied to the interior surface of the molded thermoplastic sheet and cured. The fiber reinforcement composite provides strength and rigidity to the construction. The fiber reinforcement may be woven or non-woven synthetic or natural material. Suitable thermoset resins are well known to those skilled in the art and include generally resins capable of undergoing an irreversible, chemical cross
20 linking reaction. The thermoset resin should be adhered to or form a strong adhesive bond with the mating surface of the thermoplastic sheet. The strength of the bond may be enhanced if the interior (bonding) surface of the thermoplastic sheet is acrylic or acrylic alloy.

25 The invention also provides a method with improved efficiency and reduced emissions of hazardous air pollutants for making composite molded articles comprising a thermoplastic sheet with reinforcement. The method involves placing the thermosetting materials, fiber reinforcement and thermoplastic sheet between opposed apart mold halves to form a laminate. The mold halves have
30 complementary mold surfaces. When the two mold halves are assembled with their respective molding surfaces in opposition to one another, a mold plenum is defined within which to fabricate the desired article. The thermoplastic sheet is preformed to a desired shape substantially conforming to the shape of the mold surfaces particularly the exterior mold surface. The thermoplastic sheet and the mold
35 surfaces have complementary shapes so that the thermoplastic sheet can be positioned between the mold halves and allow the mold halves to be brought together to define the mold plenum with little or no modification or distortion of the mold surface. Fibrous reinforcement material is placed on the thermoplastic sheet.

The opposed apart mold halves are brought together to form the mold plenum. Molding fluid is injected into the mold plenum to impregnate the fibrous reinforcement material. The mold plenum is a substantially closed system that prevents escape of volatile organic substances from the molding fluid to the atmosphere. The molding fluid is cured to form a rigid composite molded article. All the thermosetting material is reacted and forms a solid reinforced composite structure leaving little volatile material. The thermoplastic sheet is formed as the external layer of the composite structure.

In another embodiment, first and second mold halves having complementary molding surfaces are assembled with their respective molding surfaces in opposition to one another. When the mold halves are brought together, a mold plenum is formed within which to fabricate a desired article. Fibrous reinforcement material is placed on the mold surface of one of the first or second mold halves. A thermoplastic sheet having a shape substantially conforming to the shape of the mold plenum is placed on the reinforcement material. The mold halves are brought together forming a mold plenum and molding fluid is injected into the mold plenum to impregnate the reinforcement material. The molding fluid is cured to form a rigid composite molded article with the thermoplastic sheet on the exterior of the article structure.

In another embodiment, a thermoplastic sheet is placed between opposed apart mold halves. The mold halves have complementary molding surfaces such that the mold surfaces form a mold plenum when the mold halves are brought together. The thermoplastic sheet may be softened before placing the sheet between the mold halves. Alternatively, the mold surfaces may be heated to a temperature sufficient to soften the thermoplastic sheet. The mold halves are closed together and the thermoplastic sheet is shaped to conform to the shape of the mold surfaces. The mold halves are separated and fibrous reinforcement material is placed on one surface of the shaped thermoplastic sheet. The mold halves are again brought together to form a mold plenum and molding fluid is injected into the mold plenum to impregnate the fibrous material. The molding fluid is cured to form a rigid laminated composite molded article with the thermoplastic sheet on the exterior of the article.

In another embodiment, a thermoplastic sheet is placed between opposed apart mold halves. The mold halves have complementary molding surfaces such that the mold surfaces form a mold plenum when the mold halves are brought together. The thermoplastic sheet may be softened before placing the sheet between the mold halves. The molding surface in contact with the thermoplastic sheet is provided with vacuum ports for applying a vacuum to shape the softened

thermoplastic sheet to the mold surface. This embodiment avoids the need to close the mold halves to shape the thermoplastic sheet. After shaping the thermoplastic sheet, fibrous reinforcement material is placed on the surface of the shaped thermoplastic sheet. The mold halves are brought together to form a mold plenum and molding fluid is injected into the mold plenum to impregnate the fibrous material. The molding fluid is cured to form a rigid laminated composite molded article with the thermoplastic sheet on the exterior of the article.

In still another embodiment, first and second mold halves having complementary molding surfaces are assembled with their respective mold surfaces in opposition to one another. When the mold halves are closed together, a mold plenum is formed within which to fabricate a desired article. A first thermoplastic sheet is preformed to a desired shape to substantially conform to the shape of the mold surfaces. The thermoplastic sheet and the mold surfaces have complementary shapes so that the thermoplastic sheet can be positioned between the mold halves and allow the mold halves to be brought together to define the mold plenum. The first thermoplastic sheet is placed between opposed apart mold surfaces and fibrous reinforcement material is placed on the thermoplastic sheet. A second thermoplastic sheet having a shape complementary to the first thermoplastic sheet is placed in contact with the reinforcement material. A layered structure is formed comprising a first thermoplastic sheet, a reinforcement material and a second thermoplastic sheet. The mold halves are brought together to form the mold plenum. Molding fluid is injected into the mold plenum to impregnate the reinforcement material. The molding fluid is cured to form a rigid composite article having the thermoplastic sheet as an interior surface and an exterior surface.

Composite articles often have very high cosmetic requirements for visible surfaces. The molding surface of a closed mold membrane may have minor flaws that would adversely affect cosmetic appearance. It is desirable that the cosmetic surface of the molded article does not come in direct contact the surface of the mold membrane. The cosmetic surface of such articles may be accommodated in the closed mold by inserting a soft liner between the mold membrane surface and the cosmetic surface of the thermoplastic sheet. Liner material may have single or multiple layers. Examples of suitable soft liner materials include felt or a composite of plastic film laminated to sponge backing, thermoplastic foam or resilient backing material stable under molding conditions. Typically, the liner material is pattern cut to cover the mold membrane and is affixed to the surface of the membrane with adhesive. A soft liner also accommodates slight variations in the dimensions of the shaped thermoplastic sheet that may occur during the thermoforming process. For example, softening and hardening of a thermoplastic may result in some dimensional

shrinkage. If the cooling rate of the thermoformed sheet varies, it may cause slight shrinkage of the sheet that cannot be easily controlled. Shrinkage adversely affects the ability of the sheet to conform closely to the shape of the mold membrane. A soft liner compensates for small differences in the dimensions of the thermoformed sheet and the mold membrane.

The article may further have a cured polyurethane foam reinforcement, having varied geometries, to provide additional rigidity to the construction. If the article is a boat hull, the rigid polyurethane foam may be used to reinforce the transom, deck or seats, for example, as well as the hull. Polyurethane foam also provides buoyancy to marine articles. Certain rigid polyurethane foam reinforcement members are also known in the art as "stringers" or "logs" when used to reinforce a boat hull. The polyurethane foam reinforcement may be in the form of a pre-shaped, rigid foam article that is positioned on the fiber reinforcement layer. The shape of the log generally conforms to the shape of the thermoformed thermoplastic sheet. The conforming shape indexes the position of the log with respect to the shape of the thermoplastic sheet during injection of thermoset resin thereby reducing the likelihood of the log shifting its position after the mold is closed. The rigid foam article may be positioned on the fiber reinforcement layer prior to or after infusing the fiber reinforcement material with thermosetting resin. It is usually more convenient to position the rigid polyurethane foam reinforcement before infusing the thermosetting resin. The rigid polyurethane foam reinforcement may be enclosed with an additional fiber reinforcement composite layer. The additional composite layer helps to retain the rigid polyurethane foam reinforcement in place and further strengthens the construction. The number and placement of the rigid polyurethane foam reinforcement articles is determined by the shape and size of the composite construction.

An appropriately sized thermoplastic sheet is shaped by thermoforming means to obtain a shape that conforms to the mold shape for forming the final composite structure. The thermoplastic sheet material can be warmed in order to ease formation of the structure or shape in the thermoforming step. The thermoforming mold can also be warmed or heated to an appropriate temperature to efficiently introduce the shape into the thermoplastic sheet. A temperature of the mold is carefully selected to match a temperature useful with the thermoplastic sheet. In some instances, the temperature used is greater than the softening point of the thermoplastic sheet. Generally, for thermoplastic sheets, the thermoforming step is conducted at a temperature greater than 150 °F typically from about 250 °F to about 350 °F.

A closed molding apparatus such as multiple insert tooling technology available from RTM Composites, Fenton, MI or the apparatus described in McCollum et al., U.S. Patent 6,143,215 may be adapted to form the composite construction. The apparatus of the '215 patent comprises opposed apart and closed male and female mold halves having complementary molding surfaces. When the two mold halves are assembled with their respective molding surfaces in opposition to one another, a mold plenum is defined within which to fabricate the desired article. The thermoplastic sheet may be preformed to a desired shape substantially conforming to the shape of the mold surfaces, particularly the mold surface for receiving the acrylic side of the thermoplastic sheet. The thermoplastic sheet is formed so that the acrylic polymer layer is the exterior, or "show", layer of the composite structure. The thermoplastic sheet and the mold surfaces have complementary shapes so that the thermoplastic sheet can be positioned between the mold halves and allow the mold halves to be brought together to define the mold plenum with little or no modification or distortion of the mold surface or the thermoplastic shape. In order to prevent accidental marring of the acrylic surface by the mold surface, a soft liner may be placed between the acrylic surface and the mold surface.

Fibrous reinforcement material is placed on the interior surface. If a polyurethane foam log is a component of the construction, it is positioned on the fiber reinforcement material and a second layer fiber reinforcement material is positioned to cover the log and overlap with the first layer of fiber reinforcement material. The opposed apart mold halves are brought together to form the mold plenum. Molding fluid is injected into the mold plenum to impregnate the fibrous reinforcement material. The mold plenum is a substantially closed system that prevents escape of volatile organic substances from the molding fluid to the atmosphere. The molding fluid is cured to form a rigid composite molded article. Substantially all of the thermosetting material undergoes a cross linking reaction and forms a solid reinforced composite structure leaving little volatile material.

The composite constructions of the invention can be made by open or closed molding methods. The process described above illustrates one closed molding method, but other closed molding methods known to those skilled in the art, such as vacuum bag or multiple insert tooling methods, are equally applicable.

Other details and advantages of the invention will become apparent from the following detailed description and the accompanying figures.

Brief Description of the Drawings

FIGURE 1 is a partial cross section of a molding apparatus showing a shaped thermoplastic sheet between male and female mold halves.

5 FIGURE 2 is a partial cross section of a molding apparatus showing a shaped thermoplastic sheet positioned in a female mold half with fiber reinforcement material.

FIGURE 3 is a partial cross section of a molding apparatus showing male and female mold halves closed about a shaped thermoplastic sheet to form a mold plenum.

10 FIGURE 4 is a partial cross section of a molding apparatus showing reinforcement material positioned in a female mold half with fiber reinforcement material.

FIGURE 5 is a partial cross section of a molding apparatus showing a thermoplastic sheet positioned between a male and a female mold half.

15 FIGURE 6 is a partial cross section of a molding apparatus showing a shaped thermoplastic sheet positioned in a female mold half with fiber reinforcement material.

FIGURE 7 is a partial cross section of a closed molding apparatus having a mold plenum showing a shaped thermoplastic sheet with fiber reinforcement material positioned in the plenum.

20 FIGURE 8 is a partial cross section of a molding apparatus showing two shaped thermoplastic sheets with reinforcement material therebetween.

FIGURE 9 is a partial cross section of a closed molding apparatus having a mold plenum showing two shaped thermoplastic sheets with fiber reinforcement material positioned in the plenum.

25 FIGURE 10 is a partial cross section of a mold half with vacuum ports.

FIGURE 11 is a partial cross section of another embodiment of the invention showing a soft liner between the surface of a mold membrane and a cosmetic surface of a thermoplastic sheet.

30 FIGURE 12 is a boat hull having laminated features of the invention.

FIGURE 13 is a cross section of a boat hull construction.

FIGURE 14 is a partial profile of a boat hull construction.

FIGURE 15 is a cross section of another embodiment of the invention.

FIGURE 16 is a cross section of another embodiment of the invention.

35 FIGURE 17 is a cross section of another embodiment of the invention.

FIGURE 18 is a cross section of another embodiment of the invention.

Detailed Description of the Invention

The methods of the invention involve placing a thermoplastic sheet, a fiber reinforcement material and a molding fluid in a mold to form a composite structural unit.

5 The composite material comprises a fiber reinforcement or a filament reinforcement material. Such materials typically comprise a woven or non-woven sheet made up of fiber portions or filament materials. The woven or non-woven material can be formed from the fibers or can be impregnated or combined with other coatings or resins in the woven or non-woven sheet. A variety of natural or
10 synthetic fibers can be used in the reinforcement layer. Natural fibers can include cotton, flax, jute, knaff and other fibers derived from natural sources understood by one of ordinary skill in the art. Similarly, synthetic fibers can include polyolefin fibers, polyester fibers, polyamide fibers, and other such thermoplastic or thermosetting fiber materials. Further, other types of reinforcement fibers can
15 include glass fiber, carbon fiber, or other specialty fibers such as boron fibers, etc.

 The product and process of the invention uses a thermoplastic sheet as an interior or exterior surface layer that provides a decorative or cosmetic appearance to the structure. The thermoplastic layer has the benefit that it is easily included into the laminate thermoset structure, and avoids the problems inherent in gel coat
20 formation. Thermoplastic sheets useful in the invention include sheets having a thickness of about 0.5 mm to 15 mm, a softening point of about 200 °F to 400 °F and are manufactured in the form of large rectangular sheets or in roll form that can be applied to the molding processes of the invention. The thermoplastic sheets must be easily handleable and useful in premold operations and in the molding operations of
25 the invention. The thermoplastic sheet has the benefit that it is easily included in a thermosetting structure, and avoids the problems inherent in a gel coat.

 Thermoplastic sheets useful in the invention include sheets having layer of acrylic film with a thickness up to about 2.5 mm and a layer of ABS or ABS-acrylic alloy with a thickness of about 0.5 mm to about 15 mm. The thermoplastic sheet may
30 have an additional layer comprising a thermoplastic acrylic or ABS-acrylic alloy having a thickness up to about 2.5 mm. Another useful thermoplastic sheet has a layer of thermoplastic acrylic, a layer of ASA and a layer of ABS. Thermoplastic sheets with more than three layers may be used, but are typically not economical. The thermoplastic sheet has a softening point of about 200 °F to about 400 °F.

35 Suitable thermoplastic sheets may be formed by extrusion methods well known to those skilled in the art. A sheet having two layers or more layers is readily made using extrusion technology and is suitable for carrying out the invention. The sheets may be manufactured in the form of large rectangular sheets or in roll form

that can be applied to molding processes suitable for forming constructions of the invention. The thermoplastic sheets must be easily handled and useful in thermoforming operations and in molding operations for forming a composite structure. An important aspect of the thermoplastic sheet is that it can be placed into
5 a thermal forming mold that can achieve the general overall shape of the finishing mold. The thermoformed shape preferably has few or no bubbles, folds, sags, or other distortion of the smooth surface of the exterior acrylic polymer layer. Such surface flaws are to be avoided when forming the final article to provide a smooth uniform surface that, to the eye, has a uniform color density.

10 The thermoplastic sheet may be in the form of cut-sheet stock, roll-fed stock or directly extruded to the thermoforming mold. The thickness of the thermoplastic sheet may range from about 0.5 mm to about 15 mm. Roll-fed stock or direct extrusion thermoforming is generally limited to a sheet thickness less than about 3 mm. One skilled in the art will select sheet thickness based upon finished part
15 requirements. Suitable thermoplastic materials include ABS, PVC, acrylonitrile styrene acrylate copolymers (ASA), acrylate ethylene styrene copolymers (AES), polystyrene, polycarbonates, nylon, polyacrylates, polymethacrylate copolymers, polyethylene polypropylene and thermoplastic sheets that may be a combination of thermoplastic materials such as alloys or laminates. Exemplary two layer
20 thermoplastic materials include sheets having an ABS layer and a layer comprising a polyacrylate, polymethacrylate, or an acrylate/methacrylate copolymer and may include thermoplastic elastomers and elastomer blends. Further, the ABS layer may be alloyed with a polyacrylate, polymethacrylate, or an acrylate/methacrylate copolymer. Exemplary materials include an acrylic sheet sold under the trade
25 designation ACRYLSTEEL M and an acrylic/ABS laminate sheet sold under the trade name ALTAIR PLUS and QUARITE PLUS both commercially available from Aristech Acrylics LLC, Florence KY, LUSTRAN ABS 752 commercially available from Bayer Polymers, Pittsburgh, PA and WEATHER PRO commercially available from Spartech Corp., Clayton, MO. The acrylic portion of the laminate
30 provides a cosmetically attractive exterior surface. Other suitable sheet material include ASA and AES sheet sold under the trade name CENTREX, and polycarbonate sheet sold under the trade name MAKROLON all of which are commercially available from Bayer Corp., Pittsburgh, PA. Thermoplastic polyolefin sheet having product designation HDPE SP, LDPE SP, HIPS SP are commercially
35 available from SPARTECH Corp., Clayton, MO. These sheet materials are supplied in various grades and a person skilled in the art understands how to select a grade appropriate to achieve the desired characteristics of the fabricated article.

In general, the process of the invention involves forming a fiber reinforced thermoplastic article having either an interior or exterior surface layer formed from a thermoplastic sheet having a visible cosmetically attractive layer. An appropriately sized thermoplastic sheet is introduced into a preform thermal forming mold in order to obtain a shape that conforms to the mold shape of the final thermosetting structure. The thermoplastic sheet material can be warmed in order to ease formation of the structure or shape in the premold step. The thermoforming mold can also be warmed or heated to an appropriate temperature to efficiently introduce the shape into the thermoplastic sheet. A temperature for pre-molding is carefully selected to match a temperature useful with the thermoplastic sheet. In some instances, the temperature used is greater than the softening point of the thermoplastic sheet. Generally, for thermoplastic sheets, the premold step is conducted at a temperature from about 250 °F to about 350 °F. The thermoplastic sheet can also be directly introduced into the mold for forming the composite article without pre-forming. If the sheet is not pre-formed, the sheet can be warmed to a temperature above its heat deflection temperature prior to introduction into the mold. Heat deflection temperature may be determined according to ASTM D-648 method and is commonly specified by suppliers of sheet material.

Suitable molding fluids include thermoset resins well known to those skilled in the art and include polyester, vinyl esters, acrylic polymers, polyepoxides, aminoplasts, alkyd resins, polyamides, polyolefins, polyurethanes, vinyl polymers and phenolic resins and mixtures thereof capable of undergoing an irreversible, chemical crosslinking reaction. Non-limiting examples of useful polyester materials include RD-847A polyester resin commercially available from Borden Chemicals of Columbus OH, STYPOL polyester resins commercially available from Cook Composites and Polymers of Port Washington WS, POLYLITE polyester resins with styrene commercially available from Reichold Inc. of Durham, NC. and NEOXIL polyesters commercially available from DSM B.V. of Como, Italy. Various additives may be incorporated into the resin including curing catalysts, viscosity modifying agents, mold release agents, fillers, pigments, opacifiers and the like. Viscosity modifying agents may include Group II metal oxides or hydroxides and crystalline, hydrogen saturated polyesters.

Useful resin includes the following formulations:

	Parts by weight per each 100 parts of resin
Unsaturated polyester resin	100
Unsaturated vinyl resin	0 - 100
styrene	0 - 100
Divalent metal; preferably a Cobalt mixed carboxylate (6% in mineral spirits)	0.1 - 10
Toludine compound	0.1 - 10
Acetyl acetamide compound	0.1 - 10
Mixed silicone wetting agent/deaerator	0.1 - 10
Vegetable Oil	0.1 - 10
Plastic microspheres	0.1 - 10
Inorganic filler, (CaCO ₃ , Al ₂ O ₃ hydrate)	5 - 30
Pigment (Black)	0.1 - 10
Pigment (White)	0.1 - 10
Alkyl catechol compound	0.001 - 0.1

The composite molding apparatus for carrying out the invention is characterized by using replaceable and reusable mold membranes or skins. Replaceable mold membranes provide an inexpensive and easily replaced mold surface for making composite articles having different shapes or simply to replace a worn surface. A molding apparatus for carrying out the invention is described in McCollum et al., U.S. Patent Nos. 5,971,742, 6,143,215 and 6,257,867. In the description that follows, the same reference numeral is used for the same part illustrated throughout the figures showing views and embodiments of the invention.

In part, the molding apparatus comprises of a pair of mold halves in an opposed apart relationship. Fig. 1 shows a first mold half 1 and a second mold half 3 forming a pair of opposed mold halves 1, 3 in cross section. The mold halves are assembled with their respective mold surfaces 5, 7 in opposition to one another to define a mold plenum within which to fabricate the desired composite article. Each mold half includes a rigid housing 9, 11 and a membrane 13, 15 removably mounted to the rigid housing to form a fluid tight chamber 17, 19. The membranes may be made from fiberglass composite, reinforced nylon, sheet metal or other suitable materials that may be conveniently and cheaply fabricated, shaped and reshaped in a manner known to those skilled in the art. The membranes of each mold half may be of the same or different material. Further, the membranes may be flexible, and are

supported during the molding step by a backing fluid 21 to ensure proper dimensioning of the finished article.

Each fluid tight chamber 17, 19 is completely filled with a non-compressible, heat conductive backing fluid 21. The fluid 21 supports the membranes 13, 15 and evenly distributes any injection pressure loading across its entire surface. Since the backing fluid 21 is non-compressible, any force exerted on the membranes 13, 15 will be transferred through the fluid to the walls of the rigid housings 9, 11. Backing fluids include inorganic liquids such as water and organic liquids such as polyglycols and polysilicones. Selection of backing fluid will depend on molding variables such as temperature and pressure. For example, those skilled in the art understand that a backing fluid with a higher vaporization temperature and thermal stability is preferred as the operating temperature of the mold increases.

The mold half 1 may include one or more injection sprues 23 extending through the mold half 1 to provide a pathway through which a desired molding fluid may be injected under pressure into the mold plenum. The opposing mold half may also include one or more sprues. The number and placement of sprues depends upon the configuration and desired characteristics of the article to be molded and the flow characteristics of the molding fluid employed in a manner understood by one skilled in the art.

In accordance with the present invention, a thermoplastic sheet 25 is shaped by thermoforming using a master mold. Thermoforming methods for shaping thermoplastic sheets are well known and are understood by one skilled in the art. Thermoforming conditions such as heating rate, forming temperature and cooling rate may vary with the properties of the particular sheet material being shaped. For example, the sheet may be shaped in a vacuum forming step wherein the sheet is softened by heating, placed on the master mold and then shaped by applying a vacuum to the softened sheet to conform the sheet to the shape of the master mold. The master mold may provide a male or female molding surface. A shape is chosen for the master mold so that the shape of the molded thermoplastic sheet is complementary to the shape of the mold membranes of the injection molding apparatus. The shaped sheet fits within and substantially conforms to the shape of the mold plenum defined by the mold halves. The mold membranes 13, 15 likewise have male and female molding surfaces. The female features of the shaped thermoplastic sheet are complementary to the male features of the mold membranes.

The thermoplastic sheet 25 may have a cosmetically attractive surface 31 and the cosmetically attractive surface 31 is intended to be the exterior surface of finished composite object. The composition of the thermoplastic sheet may be the

same throughout or may be a laminate comprising a film 27 on a rigid support 29. For example, the film 27 may be acrylic and the rigid support 29 may be ABS. As shown in Figures 2 and 3, when the sheet 25 is placed in the mold, the cosmetic surface 31 is proximate the surface of the mold membrane 15 and reinforcement material 33 is placed opposite the cosmetically attractive surface 31. In embodiments described below, the placement of sheet 25 and reinforcement material 33 on the mold membrane may be reversed. The reinforcement material may be proximate the surface of the mold membrane and the sheet positioned on the reinforcement material. The particular arrangement of thermoplastic sheet and reinforcement material in the injection molding apparatus is determined so that the cosmetically attractive surface of the sheet is the exterior or visible surface of the finished composite article.

The thermoplastic sheet 25 may be a single thermoplastic polymer, a blend or alloy of two or more thermoplastic polymers, a laminate of two or more thermoplastic polymers or a laminate having a foam core, such as a polyurethane foam having thermoplastic sheet material affixed to one or both sides of the foam core. A thermoplastic laminate may have a surface comprising a cosmetically attractive film 27 combined with a high impact thermoplastic substrate 29 for strength. Referring to Figures 1-2, the mold halves 1, 3 are positioned in an open, opposed apart relationship for receiving a shaped thermoplastic sheet 25. The shaped thermoplastic sheet 25 is placed between the mold halves 1, 3 so that the shape of the thermoplastic sheet 25 conforms to the shape of the mold membranes 13, 15 to allow the mold halves 1, 3 to be brought together to a closed position. Figure 2 shows the shaped thermoplastic sheet 25 positioned on the mold membrane 15. Fiber reinforcement material 33 is placed on the surface 37 opposite the cosmetically attractive surface 31 of the shaped thermoplastic sheet 7. The fiber reinforcement material 33 may be filamentary woven, non-woven or stitched manmade or natural fiber and may be preformed mat of chopped strand or continuous strand. Suitable fibers include fiberglass, nylon, polyester, hemp, knaff and the like. Referring to Figure 3, the mold halves 1, 3 are brought together to form the mold plenum 35. The fiber reinforcement material 33 may be placed in contact with the thermoplastic sheet 25 before the thermoplastic sheet 25 is placed in contact with the mold membrane 15 without deviating from the inventive concept.

The temperature of the backing fluid 21 may be varied to optimize the cure rate of the particular molding fluid being used. Typically, the temperature of the backing fluid 21 is 80 °F to 200 °F. Further, the temperature of the backing fluid 21 in each mold half 1, 3 may be the same or different and can be selected empirically based on the properties of the sheet material and the molding fluid. After the mold

halves 1, 3 are brought together to form a mold plenum 35, the desired molding fluid is injected into the mold plenum 35 through the injection sprue 23. The injection rate can be varied by varying the temperature of the molding fluid. The temperature of the molding fluid is typically in the range of 70 °F to 150 °F and the injection rate is typically 25 to 50 pounds of molding fluid per minute. The optimal injection rate is easily determined based upon factors well known to those skilled in the art. Once the mold plenum is completely filled with molding fluid the injection ceases.

Whether the plenum is completely filled can be determined by means described in the U.S. patents referred to above. These include visual observation of discharge of excess molding fluid through air bleeds (not shown) or pressure sensors (not shown) within the mold halves to sense pressure changes during injection of molding fluid. A relatively sharp increase of injection pressure indicates that the mold plenum 35 is filled. The temperature of each molding surface 5, 7 can be regulated to provide an optimum cure rate with which to obtain the desired properties of the finished article or to otherwise optimize the molding process. The curing of the molding fluid is typically an exothermic process and curing is allowed to continue until a peak exotherm is observed. The laminated composite molded article is removed from the mold after curing the resin. The article may be removed before the resin is completely cured without departing from the spirit of the invention.

In another embodiment, a pair of mold halves 1, 3 are placed in an opposed apart relationship as described above for the first embodiment. Referring to Figure 4, reinforcement material 33 is placed in contact with the mold surface 7. A shaped thermoplastic sheet 25 is placed between the mold halves 1, 3 and in contact with the reinforcement material 33. The thermoplastic sheet 25 has a shape that conforms to the shape of the mold membranes 5, 7 to allow the mold halves 1, 3 to be brought together to a closed position forming a mold plenum. The thermoplastic sheet 25 may be a laminate comprising a cosmetically attractive film 27 combined with a high impact thermoplastic substrate 29 providing a cosmetically attractive surface 31. The cosmetically attractive film 27 provides the exterior surface of the composite article. The mold halves 1, 3 are brought together to form a mold plenum. Molding fluid is injected into the plenum to impregnate the reinforcement material. The molding fluid is cured and the composite molded article is removed from the mold.

Referring to Figures 5-7, in another embodiment, a thermoplastic sheet 57 is placed between the mold halves 1, 3 and the mold halves 1, 3 are brought together to shape the sheet 57 to conform the shape of the mold membranes 13, 15. The thermoplastic sheet 57 may be softened by heating before placing the sheet between the mold halves 1, 3 to facilitate the shaping step. Alternatively, the temperature of

the backing fluid 21 may be adjusted to a temperature sufficient to soften the thermoplastic sheet 57 as the mold halves are brought together. The method of softening the thermoplastic sheet 57 is affected by variables such as the thickness, flexibility and softening point of the sheet that are readily ascertained by a person of ordinary skill. Generally, thinner, flexible sheets less than about 5 mm thickness may be softened by heat from the backing fluid 21 as the mold halves 1, 3 are brought together. Sheets thicker than about 5 mm may be softened by hot air, infrared heaters, a heated platen or any conventional method before inserting between the mold halves. The mold halves 1, 3 are separated and reinforcement material 33 is placed on the surface 39 of the shaped thermoplastic sheet 57. The mold halves 1, 3 are again brought together to form a mold plenum 35 and molding fluid is injected into the plenum 35. The molding fluid is cured and the composite molded article is removed from the mold.

In another embodiment, a composite molded article is formed having reinforcement material sandwiched between a first and a second thermoplastic sheet. Referring to Figures 8-9, mold halves 1, 3 are arranged in a spaced apart, opposed relationship. A first thermoplastic sheet 41 is placed in mold half 3. The thermoplastic sheet is shaped to substantially conform to the shape of the mold membrane 15. Reinforcement material 33 is placed on the thermoplastic sheet 41. The reinforcement material 33 may be a preform in the shape of the desired article. A second thermoplastic sheet 43 conforming to the shape of the first thermoplastic sheet 41 is placed on the reinforcement material 33. The first and second thermoplastic sheets 41, 43 may be the same or different thermoplastics. For example, if both sides of the finished article can be viewed, it may be desirable for all exterior surfaces to have a cosmetic appearance. Whereas, if only one side of the finished article can be viewed, only the sheet providing the viewed surface need have a cosmetic appearance. The mold halves 1, 3 are closed toward each other so that the thermoplastic sheets 41, 43 and reinforcement material 33 are sandwiched in the mold plenum 35. Molding fluid is injected into the plenum 35, the molding fluid is cured and the composite molded article is removed from the mold.

It may be advantageous to apply vacuum to the thermoplastic sheet after it is placed in the closed mold apparatus. Vacuum may hold the thermoplastic sheet in place on the mold membrane or may assist with thermoforming the thermoplastic sheet to the shape of the mold membrane. As shown in Figure 10, vacuum ports 45 are formed in the mold membrane 15. The ports 45 are associated with vacuum lines 47 that are connected to a vacuum pump (not shown) or other vacuum source. The number and placement of vacuum ports 45 is not critical and may be varied based on their intended use. For example, fewer ports may be required to simply

hold a shaped sheet in place whereas more ports may be required to thermoform the sheet. Also, vacuum ports may be provided in either or both mold membranes 13, 15.

Referring to Figure 11, a compressible, non-abrasive, soft liner 49 may be positioned on the mold membrane 15. A soft liner prevents marring of the cosmetic surface of the thermoplastic sheet from unevenness, burrs or accidental debris on the mold membrane 15 during molding of a composite article. The soft liner 49 may have a thickness of about 3mm to about 25 mm and may be pre-formed to the shape of the mold. However, the soft liner 49 does not require pre-molding preparation if it readily conforms to the shape of the mold membrane 15. The soft liner 49 is pattern cut to fit the mold membrane 15 and bonded to the mold membrane 15 with an adhesive. The liner material may comprise a single material such as wool felt that is commercially available in a variety of suitable grades from USFELT, Sanford, ME. Also, a liner material having multiple layers including a foam rubber layer may be used. The rubber layer may be open or closed cell rubber comprising natural rubber, NEOPRENE, SBR, EDPM, polyethylene, polyurethane, NPVC, and EVA rubber material. A suitable multi-layer material is an open cell foam rubber having a plastic film adhered to one side and is commercially available from Griswold Rubber Co., Moosup, CT. In the case of a multi-layer soft liner, the liner is preferably positioned so that the foam rubber layer is proximate the mold membrane and the plastic film is proximate the cosmetic surface of the thermoplastic sheet. A shaped thermoplastic sheet 51 having a cosmetically attractive surface 31 on at least one side is positioned on the soft liner 49 so that the cosmetically attractive surface 31 contacts the soft liner 49. Reinforcement material (not shown) may be placed on surface 55 of the thermoplastic sheet 51 opposed to the cosmetically attractive surface 31, the mold halves closed together to form a mold plenum and molding fluid injected into the plenum and cured to form the composite article. A soft liner may be used between the cosmetic surface of a thermoplastic sheet and the molding surface of either or both mold membranes 13, 15 without departing from the scope of the invention.

The diverse applications for fiber reinforced composite articles includes structural and decorative parts of land vehicles such as automobiles, trucks, vans and buses, campers and trailers including, for example, truck beds and covers, tonneau covers and hoods, grill covers and body panels; building and construction articles and replacements parts including bathtubs, hot tubs, showers, shower pans and wall surrounds; recreational water craft including boat hulls, decks, hatch covers, masts, seating and consoles; recreational equipment such as golf cart chassis and bodies, canoes and kayaks; playground equipment such as water slides, surf boards, snow

and water skis, sandboxes; and aircraft and aerospace components. In general, composite fiber reinforced structures are suitable replacements for metal in a broad variety of uses where strength and durability are necessary and an attractive or decorative appearance is desirable.

5 One composite construction of the invention is a boat hull. The designs of boat hulls vary in size and shape. A particular design may require rigid polyurethane foam reinforcement (stringers or logs) for strength, rigidity and floatation. The size, shape and number of logs for a particular hull design may differ from those described below. However, a person skilled in boat construction
10 understands the structural criteria for a particular design. The invention is applicable to boat hulls suitable for construction from molded composite materials. Although a boat hull is used to exemplify a construction according to the invention, a person of ordinary skill recognizes that the full scope of the invention is not limited to a particular object or shape and includes a broad range of applications as described
15 above.

A boat hull according to the invention comprises a layer of acrylic polymer film having a thickness up to about 2.5 mm, often greater than 1mm to 2.5 mm, and a layer comprising an ABS or ABS-acrylic alloy thermoplastic having a thickness of about 0.5 to about 15 mm. An additional layer comprising a thermoplastic acrylic
20 polymer, ASA or ABS-acrylic alloy having a thickness up to about 2.5 mm may be included. A layer comprising fiber reinforcement composite is applied to the thermoplastic layer that is the interior layer of the finished construction. Rigid polyurethane foam reinforcement may be included in the construction next to the fiber reinforcement composite layer.

25 Sheet materials are supplied in various grades and a person skilled in the art understands how to select a grade appropriate to achieve the desired characteristics of the finished construction. Sheet materials may be custom made by plastic extrusion methods to provide any number of layers and combination of thermoplastic materials for a particular appearance, structure, strength or molding
30 process.

The construction also comprises fiber reinforcement or a filament reinforcement composite layer. Fiber reinforcement typically comprises a woven or non-woven sheet made up of fiber portions or filament materials. The woven or non-woven material can be formed from the fibers or can be impregnated or
35 combined with other coatings or resins in the woven or non-woven sheet. A variety of natural or synthetic fibers can be used in the reinforcement layer. Natural fibers can include cotton, flax, jute, knaff and other fibers derived from natural sources known to one of ordinary skill in the art. Similarly, synthetic fibers can include

polyolefin fibers, polyester fibers, polyamide fibers, and other such thermoplastic or thermosetting fiber materials. Inorganic fibers can include glass fiber reinforcement materials, carbon fiber reinforcement materials, or other specialty fibers such as boron fibers, etc.

5 The fiber reinforcement is infused with a molding fluid that is subsequently cured to strengthen the thermoplastic shape. Suitable molding fluids include unsaturated thermoset resins well known to those skilled in the art and include polyester, vinyl esters, acrylic polymers, polyepoxides, aminoplasts, alkyd resins, polyamides, polyolefins, polyurethanes, vinyl polymers and phenolic resins and
10 mixtures thereof capable of undergoing an irreversible, chemical crosslinking reaction. Non-limiting examples of useful polyester materials include RD-847A polyester resin commercially available from Borden Chemicals of Columbus OH, STYPOL polyester resins commercially available from Cook Composites and Polymers of Port Washington WS, POLYLITE polyester resins with styrene
15 commercially available from Reichold Inc. of Durham, NC. and NEOXIL polyesters commercially available from DSM B.V. of Como, Italy. The strength of the adhesive bond between the thermoplastic surface and the cured unsaturated thermoset resin may vary with different combinations of thermoplastic and resin. A person skilled in making reinforced composite structures understands how to select
20 materials to optimize bond strength for a particular structure. Various additives may be incorporated into the resin including curing catalysts, viscosity modifying agents, mold release agents, fillers, pigments, opacifiers and the like. Viscosity modifying agents may include Group II metal oxides or hydroxides and crystalline, hydrogen saturated polyesters.

25 The construction may further comprise rigid polyurethane foam reinforcement, often referred to as "logs" or "stringers". Stringers are used to provide structural reinforcement and floatation for composite boat hulls. Stringers may be of any shape and dimension suitable to the design of the boat hull and are formed and cured by conventional methods for shaping polyurethane foam.
30 Typically, the structural foam is a two-part, self-expanding, self-curing foam that has expanded to fill the mold prior to cure. Major components of polyurethane are a diisocyanate and an active hydrogen compound such as a polyol or polyamine. An isocyanate and active hydrogen functional group combine to form urethane bonds. Isocyanate compounds for forming polyurethane foam are commercially available in
35 various grades from BASF Corp., Bayer Group and PPG Industries. Blowing agents for foam formation include "hydrogenated chlorofluorocarbons" (HCFC), water and/or CO₂. Suitable polyol compounds vary greatly in chemical structure to provide a broad range of physical properties. Typical polyol compounds include

polyether polyols, polyvalent alcohols, bisphenol compounds, alkanol amines, polyester polyols, and so forth. Treatises, such as Rigid Urethane Foam Processing from Technomic, Pub. Co., or Urethane Foams: Technology and Application from Noyes Data Corp., are available that describe criteria for selecting components for forming polyurethane foam. Persons skilled in making polyurethane foam understand how to compound polyurethane to obtain desired properties.

A composite construction according to the invention is described with reference to Figures 12-14. Figure 12 is a representation of a boat hull 10 having sides 2, a flange 4, strakes 6, chine 8 and a transom 12. The flange 4 may function as a gunwale or attachment surface for a deck, hull liner or other components of the construction. The side walls 2 are a substantially planar surface and may form an angle with the chine 8 of about 85° to 105°. The transom 12 may have apertures (not shown) for installing mechanical components such as a bilge pump or a stern drive. Figure 13 shows the hull 10 in cross section and as substantially symmetrical with respect to the keel 14. The hull 10 includes side walls 2 forming an angle with a bottom surface 21 comprising an exterior thermoplastic acrylic polymer surface layer 18, a thermoplastic layer 20 having an interior surface 19a, a fiber reinforcement composite layer 22 contiguous with the interior surface 19a and an optional rigid polyurethane foam stringer 16. The stringer 16 is enclosed with a second fiber reinforcement composite layer 24 to retain the stringer 16 in the desired position during the molding process. The stringer 16 may have a shape that conforms to the shape of the thermoplastic layer. The stringer 16 shown in Figure 13 has a protrusion 26 that conforms to the depression 28 on the interior of the hull 10 formed by the strake 6. The protrusion 26 engages the depression 28 to assist retaining the stringer 16 in place during the molding process. The bottom surface 21 may be flat or curved. Figure 14 is an enlargement of a portion of Figure 13 showing the composite construction in greater detail.

Figure 15 shows in cross section of another embodiment of a hull construction having an additional interior layer 70 of thermoplastic material comprising an acrylic polymer, ASA or ABS/acrylic alloy contiguous with the fiber reinforcement layer 76. The construction of Figure 15 comprises an exterior acrylic polymer layer 74, an adjacent thermoplastic layer 72, a thermoplastic interior layer 70 contiguous with the thermoplastic layer 72 and a fiber reinforcement layer 76 contiguous with the interior layer 70. The interior layer 70 provides a bonding surface 78 for the fiber reinforcement layer 76. The construction may include a rigid polyurethane foam stringer 16. The stringer 16 is enclosed within a fiber reinforcement composite layer 24 to retain the stringer 16 in the desired position.

Another embodiment is described with reference to Figures 16-18. Figure 16 is a representation of a bathtub 40 having exterior sides 42, interior sides 43a, a bottom 48 adjacent the interior sides 43a, a concave interior 44 and apertures 46 at one end for plumbing connections. Figure 17 shows the tub 40 in cross section. The tub 40 includes an exterior thermoplastic acrylic polymer layer 52, a thermoplastic layer 54 laminated to the acrylic polymer layer 52, and a fiber reinforcement composite layer 56 contiguous with the thermoplastic layer 54. The acrylic polymer layer 52 has a cosmetically attractive surface 58 that is wholly or partly viewable depending on the installation of the tub 40. The tub 40 illustrates a construction having both concave and convex viewable surfaces. Figure 18 shows the tub 40 in cross section with optional rigid polyurethane foam support 60. The shape and position of the rigid polyurethane supports may vary with tub design as necessary to provide the desired strength and rigidity to the tub. The rigid polyurethane supports 60 are enclosed with a fiber reinforcement composite layer 62 to retain the support 60 in position during the molding process.

Working Examples

Representative examples of making a composite according to the invention follows. An acrylic/ABS sheet having the dimensions 3.8 mm x 1650 mm x 2030 mm and sold under the trade designation DR/GX 3800 commercially available from Spartech Corp., Clayton, MO, is mounted in a rotary style thermoforming apparatus. The acrylic surface is the cosmetic surface, and the sheet is thermoformed so that the acrylic surface is the exterior surface of the finished article. The sheet is positioned in a pre-heating station and heated at temperatures ranging from about 320 °F to about 370 °F. The sheet is heated until a proper forming temperature is achieved as indicated by the sheet beginning to sag. The sheet must be softened to obtain an initial preshape such that the preformed sheet can be placed in the mold without causing gaps, wrinkles or other surface flaws. A shape master mold heated to about 170 °F is brought in contact with the softened sheet and a vacuum is applied. The sheet is formed to the shape of the master mold. The shaped sheet is allowed to cool to room temperature and stiffen.

A closed mold apparatus available from VEC Technology Inc., Greenville, PA is used to make the composite article. The apparatus comprises opposed mold halves, each half having a rigid housing with a membrane attached. The membranes are shaped as male and female mold members so that a mold plenum is formed when the mold halves are brought together. The rigid housing and membrane of each mold half form a fluid tight chamber. The respective fluid chambers are filled with water as a backing fluid. The backing fluid supports the membrane to ensure proper

dimensioning and enables temperature adjustments to regulate the cure rate of molding fluid.

The shape of the thermoplastic sheet conforms to the shape of the mold membranes so that the mold halves can be brought together to form the mold plenum. The temperature of the backing fluid in each mold half is adjusted to 150 °F. The shaped thermoplastic sheet is placed in a mold half. About 17.6 pounds of fiberglass mat, is applied to the exposed surface of the thermoplastic sheet, that is, the surface of the sheet opposite the surface of the sheet in contact with the membrane. The mold halves are brought together to form the mold plenum.

A resin blend for forming a molding fluid is prepared according to the following compositions:

Example 1

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.3
N,N-di-me-p-toludine	0
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0

15

Results:	Gel time	13' 47"
	Gel to Peak	21' 15"
	Peak Exotherm	220.8°F

20

Example 2

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.12
N,N-di-me-p-toludine	0
Di-me-acetyl acetamide	0.15
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.07

5 Results: Gel time 45' 24"
 Gel to Peak 22' 15"
 Peak Exotherm 247.8°F

Example 3

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.1
N,N-di-me-p-toludine	0.1
Di-me-acetyl acetamide	0.15
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.07

Results: Gel time 76' 21"
 Gel to Peak 45' 36"
 Peak Exotherm 186.8°F

5

Example 4

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.2
N,N-di-me-p-toludine	0.2
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.07

Results: Gel time 22' 12"
 Gel to Peak 8' 25"
 Peak Exotherm 327.2°F

10

Example 5

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.1
N,N-di-me-p-toludine	0.2
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.07

Results: Gel time 104' 02"

5

Example 6

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.2
N,N-di-me-p-toludine	0.1
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.07

Results: Gel time 34' 25"

Gel to Peak 20' 22"
 Peak Exotherm 242.1°F

Example 7

5

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.2
N,N-di-me-p-toludine	0.1
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.1

Results: Gel time 35' 23"
 Gel to Peak 21' 37"
 Peak Exotherm 224.2°F

10

Example 8

	Parts by Weight
Vinyl ester resin	100
Cobalt mixed carboxylate (6% in mineral spirits)	0.2
N,N-di-me-p-toludine	0.1
Di-me-acetyl acetamide	0
Mixed silicone wetting agent/deaerator	0.5
Vegetable Oil	0.5
Plastic microspheres	0.5
Al ₂ O ₃ (3H ₂ O)	20
Pigment (Black)	0.2
Pigment (White)	0.75
Styrene	7
t-bu-catechol	0.1

Results: Gel time 91' 35"
 5 Gel to Peak 30' +
 Peak Exotherm Below 110°F

Example 9

	WT.-%
Unsaturated polyester resin	76
Vinyl ester resin	4
Cobalt mixed carboxylate (6% in mineral spirits)	0.2
N,N-di-me-p-toludine	0.6
Di-me-acetyl acetamide	0.15
Mixed silicone wetting agent/deaerator.	0.8
Vegetable Oil	0.4
Plastic microspheres	0.4
CaCO ₃	16.4
Pigment (Black)	0.2
Pigment (White)	0.8
Styrene	0
t-bu-catechol	0.03

5 Molding fluid comprising resin blend, catalyst and about 0.001 pound of a flame retardant is heated in a reservoir to 82 °F. The molding fluid is injected into the mold plenum to impregnate the fiberglass reinforcement material. The injection rate is about 190 inches-sec⁻¹ until full. The molding fluid is allowed to cure for about 60 minutes. A peak exotherm temperature of about 151 °F occurs at about 40 minutes (otherwise as noted). The mold halves are separated and the composite is
 10 allowed to air cool before being removed from the mold. After removing the composite from the mold, excess material may be trimmed from the edges and holes cut as needed to complete fabrication of the finished article.

While certain embodiments of the invention have been disclosed and described herein, it should be appreciated that the invention is susceptible of
 15 modification without departing from the spirit of the invention or the scope of the following claims.

We claim:

1. A method of making a molded article comprising the steps in the order as follows:
 - 5 (a) placing in a spaced apart opposed relationship a first mold half comprising a first shaped mold membrane and a second mold half comprising a second shaped mold membrane wherein the first and second shaped mold membranes define a mold plenum when brought together to mold articles;
 - (b) placing a thermoplastic sheet in the mold plenum wherein the
10 shape of the thermoplastic sheet substantially conforms to the shape of the mold membrane;
 - (c) placing reinforcement material in the form of a woven or nonwoven continuous strand fiberglass sheet in the mold plenum;
 - (d) closing the first and second mold halves such that the
15 thermoplastic sheet and reinforcement material are contacted in the mold plenum;
 - (e) introducing molding fluid under pressure into the mold plenum;
 - and
 - (f) curing the molding fluid.
- 20 2. A method according to claim 1 further comprising the step of placing a shaped protective liner between the thermoplastic sheet and the mold membrane that protects the surface of the surface of the thermoplastic sheet from damage from the mold during molding.
- 25 3. A method of making a molded article comprising the steps:
 - (a) placing in a spaced apart opposed relationship, a first mold half comprising a first mold membrane and a second mold half comprising a
second mold membrane, wherein the first and second mold membranes
define a mold plenum when brought together to mold articles;
 - 30 (b) placing reinforcement material in contact with one of the first or second mold membranes;
 - (c) placing a thermoplastic sheet in contact with the reinforcement material wherein the thermoplastic sheet has a shape substantially
conforming to the shape of the mold plenum;
 - 35 (d) closing the first and second mold halves toward each other such that the thermoplastic sheet and reinforcement material are in contact in the mold plenum;
 - (e) injecting molding fluid under pressure into the mold plenum; and
 - (f) curing the molding fluid.

4. A method of making a molded article comprising the steps:
- (a) placing a thermoplastic sheet into a first mold half wherein the mold half comprises a first shaped mold membrane;
 - (b) placing in a spaced apart opposed relationship the first mold half and sheet and a second mold half comprising a second shaped mold membrane wherein the first and second shaped mold membranes define a mold plenum when brought together to mold articles;
 - (c) closing the first and second mold halves such that the thermoplastic sheet is shaped in the mold plenum;
 - (d) opening the first and second mold halves;
 - (e) placing reinforcement material in contact with a surface of the shaped thermoplastic sheet;
 - (f) closing the first and second mold halves toward each other such that the thermoplastic sheet and reinforcement material are in contact in the mold plenum;
 - (g) injecting molding fluid under pressure into the mold plenum; and
 - (h) curing the molding fluid.
5. A method of making a molded article comprising the steps:
- (a) placing a first thermoplastic sheet having a shape into a first mold half wherein the mold half comprises a first shaped mold membrane and the shape of the thermoplastic sheet substantially conforms to the shape of the mold membrane;
 - (b) placing reinforcement material in contact with a surface of the shaped thermoplastic sheet;
 - (c) placing a second thermoplastic sheet conforming to the shape of the first thermoplastic sheet in contact with the reinforcement material wherein the first thermoplastic sheet, the reinforcement material and the second thermoplastic sheet comprise a laminate;
 - (d) placing in a spaced apart opposed relationship the first mold half and the laminate, with a second mold half comprising a second shaped mold membrane wherein the first and second shaped mold membranes define a mold plenum when brought together to mold articles;
 - (e) closing the first and second mold halves toward each other such that the thermoplastic sheets and reinforcement material are sandwiched in the mold plenum;
 - (f) injecting molding fluid under pressure into the mold plenum; and
 - (g) curing the molding fluid.

6. An article comprising a shaped and layered construction, the structure comprising:
 - (a) an acrylic polymer layer having a thickness up to about 2.5 mm;
 - (b) a thermoplastic layer in direct contact with the acrylic polymer layer having a thickness of about 0.5 mm to about 15 mm; and
 - (c) a third layer comprising a fiber reinforced thermoset composite.
7. An article according to claim 6 wherein the acrylic polymer layer is an exposed, decorative exterior layer of the construction.
8. An article according to claim 7 wherein the third layer is adjacent to the thermoplastic layer.
9. An article according to claim 6 wherein the acrylic polymer layer is about 0.4 mm to about 1 mm and the thermoplastic layer is about 1.5 mm to about 15 mm.
10. A structure according to claim 6 wherein the thermoplastic layer is selected from the group consisting of ABS, ASA or ABS-acrylic alloy.
11. An article according to claim 6 wherein the structure is in the shape of a bathtub, a component of a motor vehicle or recreational equipment or an aircraft or aerospace device.
12. An article according to claim 6 further comprising rigid polyurethane foam reinforcement and the rigid polyurethane foam is enclosed by a fiber reinforcement composite layer.
13. An article according to claim 6 wherein the composite is reinforced with a natural or synthetic fibrous material.
14. An article comprising a shaped and layered construction, the structure comprising:
 - (a) a first acrylic polymer layer having a thickness up to about 2.5 mm;
 - (b) a thermoplastic layer in direct contact with the acrylic polymer layer having a thickness of about 0.5 to about 15 mm;
 - (c) a third layer comprising an acrylic polymer, ASA or ABS-acrylic alloy; and

(d) a fiber reinforcement composite layer contiguous with the third layer.

15 15. An article according to claim 14 wherein the acrylic polymer layer is an exposed, decorative exterior layer of the construction.

10 16. An article according to claim 14 wherein the first acrylic polymer layer is about 0.4 mm to about 1 mm and the thermoplastic layer is about 1.5 mm to about 15 mm.

17. An article according to claim 14 wherein the thermoplastic layer is selected from the group consisting of ABS, ASA or ABS-acrylic alloy.

15 18. An article according to claim 14 wherein the structure is in the shape of a bathroom tub, a component of a motor vehicle or recreational equipment or an aircraft or aerospace device.

20 19. A construction according to claim 14 wherein the composite is reinforced with a natural or synthetic fibrous material.

20. An article according to claim 14 further comprising rigid polyurethane foam reinforcement and the rigid polyurethane foam is enclosed by a fiber reinforcement composite layer.

25 21. An article comprising a shaped and layered construction, the structure comprising:

(a) a first acrylic polymer layer having a thickness up to about 2.5 mm;

30 (b) a thermoplastic ABS or ABS-acrylic alloy layer having a thickness of about 0.5 mm to about 15 mm;

(c) a third layer comprising an acrylic polymer, ASA or ABS-acrylic polymer alloy;

(d) a fourth layer comprising a fiber reinforcement composite contiguous with the third layer; and

35 (e) a structural polymer foam reinforcement.

22. An article according to claim 21 wherein the acrylic polymer layer is an exposed, decorative exterior layer of the construction.

23. An article according to claim 21 wherein the first acrylic polymer layer is about 0.4 mm to about 1 mm and the thermoplastic layer is about 1.5 mm to about 15 mm.

- 5 24. An article according to claim 21 wherein the structure is in the shape of a bathroom tub, a component of a motor vehicle or recreational equipment or an aircraft or aerospace device.