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Title: MOLDING OF REINFORCED THERMOPLASTIC COMPOSITES

Abstract: The invention provides for the formation of composites, in particular, laminates from a wet-laid fibrous nonwoven molding compound (1) prepared from a white water slurry (3), or from a dried mat formed from the wet-laid compound. The composites so formed possess increased tensile strength and impact resistance, and are well suited to structural and reinforcing applications.
MOLDING OF REINFORCED THERMOPLASTIC COMPOSITES

TECHNICAL FIELD AND INDUSTRIAL
APPLICABILITY OF THE INVENTION

The present invention relates to methods for manufacturing reinforced thermoplastic composites. In particular, the invention provides methods for fabricating reinforced composite articles from a fibrous, non-woven molding compound or mat made from a mixture comprising reinforcing fibers and a particulate thermoplastic polymer, without the use of a conventional resin binder. The fibrous compound or mat formed from such a wet-laid process provides composites having improved resilience and impact resistance, which are suitable for a multitude of structural and non-structural applications.

BACKGROUND OF THE INVENTION

In recent years, fiber-reinforced composites have become increasingly important as solutions in the search for strong, yet lightweight alternatives to metals as strengthening components in materials where load-bearing ability, impact resistance and other physical strength characteristics are important. Traditional reinforcing elements such as metal fibers or structures carry inherent drawbacks, including the weight they add to the finished products containing them, and their tendency to corrode under certain environmental conditions. Glass fibers or fiber-containing materials were therefore developed as an alternative that could provide the desired strength properties while minimizing the deterioration problems associated with the use of metal reinforcements.

Composite laminates, which are used to make structural reinforcements, construction materials and formed parts may be reinforced using a mat formed from glass fibers. These fibrous mats may be woven or non-woven, and may be formed by several methods.

One method of forming non-woven fibrous mats involves air laying or blowing of fibers onto a collection surface followed by application of a molten or liquid binder polymer, then drying or cooling to form a fibrous mat laden with the polymer. One deficiency of this air laid process is that it is difficult to control the rate and uniformity of deposition of the fibers. In another method, non-woven mats are wet-laid from a slurry of fibers and a binder polymer that is prepared in a medium such as water.
Forming a fibrous mat from a slurry of a solid polymer, binder, fiber reinforcing material and other ingredients is disclosed, for example, in published European Patent Applications 0,148,760 and 0,148,761, Wessling et al., U.S. Pat. No. 4,426,470 issued Jan. 17, 1984 and Gatward et al., U.S. Pat. No. 3,716,449 issued Feb.13, 1973. In general, the fibrous mats so formed contain a uniform distribution of fiber, polymer and binder.

Whether non-woven fibrous mats are made by a dry-laid process or by a wet-laid process from a slurry, the use of a binder polymer has been required as a means of holding the chopped fibers together during the forming process and after the mat is dried. While the use of a polymer, such as a binder polymer, in conjunction with glass fibers should desirably contribute certain properties to the mat, the binder provides an added manufacturing expense, it may be incompatible with the impregnating polymer used in subsequent molding, and may lower the performance of the laminates made from the impregnating polymer and binder.

Several problems have been determined in conjunction with molding of composite laminates, generally, and, in particular, in the handling of polymer systems made with thermally sensitive polymers such as polyvinyl chloride (PVC) or PVC-blends. For example, the composite molding process typically requires prolonged exposure at the molding temperature. This may be particularly true in the manufacture of composites from one or more layers of a reinforcing material by applying heat and pressure to form a compacted layer or laminate. In these processes, sufficient heat and pressure must be applied to allow impregnation of the polymer between the fibers in each layer of the laminate. However, at high molding temperatures, degradation of the polymer will often result. Degradation of a polymer generally occurs upon exposure to temperature over time because each polymer system has an associated finite level of inherent stability, and, as a result, each exposure to a time-temperature combination reduces the residual stability of the system. This degradation is cumulative, and eventually will lead to decreased wet-out or contact between the fibers and the polymer, or a change in the molecular weight of the polymer, either of which results in a laminate that is poorly formed and lacking in strength and durability. To prevent excessive heat exposure, therefore, it has traditionally been necessary to shorten the time required for molding, or to lower the molding temperature. However, lowering the molding temperature may be ineffective if there is any appreciable amount of water in the
molding composition, since at the lower temperature the water may not vaporize sufficiently. At the lower temperatures, good consolidation of the laminate may also not be obtained.

Moreover, the effects of time and temperature are additive, and, accordingly, each polymer system has its own intrinsic processing window within which certain time-temperature combinations can advantageously be used in handling of the polymer. This processing window can be maintained or extended to some degree with the use of thermal or oxidative stabilizers. It is therefore desirable to develop a process that least reduces the amount of inherent stability within a polymer system during the process of manufacturing a final part. Such a process should conserve the residual stability during manufacture, up to and including the formation of the final part.

In addition to the above-mentioned drawbacks, current molding technology often results in shearing of the fiber material, and, as a result, the composite formed includes shorter fibers. For example, the current injection molding technology for combining reinforcement and polymer results in a compound that has the length of the reinforcing fibers reduced by attrition, and there is an accompanying reduction in properties, such as strength, impact resistance and heat distortion temperature, in the laminates produced.

The conventional methods for molding composite polymer systems are therefore deficient in that they rely on the use of a binder which degrades the interface with the reinforcing material. Additionally, the process itself often results in a significant decrease in the inherent stability of the polymer system as the polymer is degraded. Moreover, the molding process used for laminates often results in a degradation of the fiber length. Accordingly, there is a recognized need for a process of making composites, and products thereof, that would prevent these effects. Moreover, a need exists for a more efficient process for making moldable reinforcements using chopped glass fibers that provides enhanced performance characteristics to the composite articles molded therefrom. These needs are fulfilled by the invention described below.

SUMMARY OF THE INVENTION

The present invention provides a process for manufacturing fiber-reinforced composites using wet-laid, nonwoven fibrous molding compound or mat, and the products thereof. These wet-laid compound or mat products are formed by an efficient
aqueous process that combines a particulate polymer with a fiber reinforcement, and eliminates the need for adding a binder resin.

In one aspect, the invention is a method of forming a fiber-reinforced composite comprising:

a) preparing a non-woven, fibrous, wet-laid compound by:
   i) mixing a suspension comprising a reinforcement material and at least one particulate thermoplastic polymer, in the absence of a binder, in an aqueous medium to form a white water slurry;
   ii) dewatering the white water slurry to form a wet-laid compound impregnated with particulate thermoplastic polymer; and

b) molding the wet-laid compound to form a fiber-reinforced composite.

The invention further comprises a process for molding a fiber-reinforced composite from a wet-laid compound comprising a reinforcement material and a particulate thermoplastic polymer, comprising heating the wet-laid compound, under low pressure, to a temperature at which water vaporizes from the compound before the particulate thermoplastic polymer fuses, thereby allowing water to escape, and subsequently applying molding pressure to consolidate the wet-laid compound into a composite article.

In another aspect, the invention further includes a method for improving fiber length retention during continuous manufacture of a reinforced composite article comprising:

a) providing one or more layers of a dried wet-laid mat impregnated with at least one particulate thermoplastic polymer; and

b) molding the one or more layers of dried wet-laid mat in a continuous laminating process to form a fiber-reinforced composite.

The invention additionally comprises a composite article comprising one or more layers of a non-woven, fibrous, wet-laid compound comprising a filamentized long-fiber reinforcement and a thermally stabilized particulate polymer, and excluding a binder; wherein said layers have been consolidated by the application of heat and pressure to form a fiber-reinforced composite article.

The invention further includes a roofing shake comprised of a molded material formed from one or more layers of a wet-laid compound or mat comprising a fiber reinforcement and a particulate thermoplastic polymer in the absence of a binder;
wherein the shake comprises a butt end and a headlap portion having an exposed portion, such that the butt end smoothly tapers into the headlap portion at the termination point of the exposed portion.

The invention also includes a materials system for manufacturing fiber-reinforced composites comprising a long-fiber reinforcement, a particulate, thermally stable particulate polymer and water, and excluding a binder.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a schematic representation of methods of producing molded products according to the invention.

Figure 2 is a representation of a process of forming a wet-laid, fibrous, nonwoven mat according to the present invention.

Figure 3 is a representation of a batch compression molding process for molding composites using layers of a wet-laid mat according to the invention.

Figure 4 is a schematic diagram of a double belt press molding process for molding composite laminates according to the invention.

Figure 5 is a two-dimensional drawing of an artificial shake formed by a composite lamination process according to the present invention.

Figure 6 is a three-dimensional profile of an artificial shake formed by a composite lamination process according to the present invention.

**DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS OF THE INVENTION**

The present invention provides a process for the manufacture of reinforced composites from a materials system that is formed from an aqueous white water slurry. The term "materials system", as used herein, includes a solid material comprising a fiber reinforcement material and a particulate polymer that is derived from a white water slurry, and which comprises an average moisture content of from 0 up to about 30% by weight. The materials system may be in the form of a wet-laid compound, which is a moldable semi-solid formed by dewatering the white water slurry, the resulting product having a water content of from about 2% by weight to about 30% by weight. The wet-laid compound may be formed into an intermediate molding material for use in a molding process, or it may be directly molded, as is. Alternatively, the wet-laid
compound may be dried to form a wet-laid mat having a moisture content of less than about 2% by weight, which may also be formed into intermediate products for further processing, or used directly in molding operations. Molded products from the wet-laid compound or mat made according to the invention have comparable or improved physical properties compared to molded products made with wet-laid mat derived from processes that require the use of a binder during the wet-mat lay-up process. The manufacturing process of the present invention may be used in the production of reinforcement products for various molding uses, such as glass mat thermoplastic (GMT), bulk molding compound (BMC), reinforced polymer films, or impregnated continuous glass strand, roving, yarn, mat or fabric.

The aqueous white water slurry of the invention is comprised of fiber reinforcements and a particulate polymer, while excluding a binder or other added resin such as would be used in traditional white water systems to bind the fiber reinforcements together. As used herein, the term “white water slurry” includes an aqueous slurry comprising a dispersion of one or more types of fiber reinforcements, one or more types of particulate polymers, and one or more other optional additives as may be desired to impart certain characteristics to the whitewater. The term “binder”, as used herein, means a resin in liquid or molten form which is applied to, or incorporated with, a fiber reinforcement material to provide adhesion between the fibers thereof. As used herein, the term “in the absence of a binder” means that no binder is added to the slurry or the materials formed therefrom at any point during manufacture.

The fiber reinforcements useful in the invention include dispersible materials, non-dispersible materials and combinations of the two forms. Preferred dispersible reinforcements include materials such as wet-used-chopped strands of glass, aramids, carbon, polyvinyl alcohol (PVA), hemp, jute, organic materials, mineral fibers and rayon. Preferred non-dispersible reinforcement materials include dry-used-chopped strands and glass fibers designed for processes such as SMC molding, BMC molding and continuous panel fabrication; chopped and continuous reinforcements such as aramid, carbon, glass, wollastonite, jute; mica, flake glass, glass and carbon spheres, mats, organic materials, mineral fibers, and fabrics.

The preferred fiber reinforcement materials may be selected from filamentized organic and inorganic materials such as glass fibers, carbon fibers, metal fibers, cellulose fibers, polymer fibers such as polyamide and polyolefin fibers, and any
combination thereof. Such fibers may be in the form of rovings, strands or individual fibers that have been chopped or otherwise segmented into lengths varying from about 0.125 to 2.0 inch (about 3.2 to about 50.8 mm), designated herein as "long fibers", and segments having a length of from about 0.03125 to 0.125 inch (about 0.79 to 3.2 mm), designated herein as "short fibers", and mixtures thereof. Suitably, the fibers of the reinforcement material may be of a diameter of from about 3 microns to about 90 microns. The fibers may be used in the form of strands comprised of from about 50 to about 4000 fibers. Preferably, the reinforcement material is a chopped long fiber glass prepared by chopping rovings comprising from about 200 to 4000 fibers, each having a diameter of from about 3 microns to about 25 microns, which may be used in wet or dry form.

The fibers of the reinforcement material are preferably surface treated with chemical sizing or coupling agents known in the art. Preferred sizings are selected so as to aid in dispersion without negatively affecting the dispersion properties of the white water slurry. Preferably the sizing composition is selected so as to aid in the dispersion of the reinforcement in the white water slurry. For example, a preferred sizing for a continuous glass roving reinforcement will allow for use of a wet roving that is, having about 2 to about 19% by weight water. The preferred sizing should also be compatible with the particulate thermoplastic polymer such that the properties of the thermoplastic polymer in the white water slurry are optimized. The sizings are preferably water-based and may comprise one or more cross-linking agents, such as silanes, film-formers, surfactants, lubricants or other conventional additives. For example, where the fiber reinforcement is wet-used-chopped strand (WUCS), it may be purchased as a pre-sized product. Examples of such materials are wet-used chopped strand products sized with proprietary sizings 786, 9501 or 9502, which are commercially available under these designations from Owens Corning Inc.

When a particulate polymer such as polyvinyl chloride (PVC) is used in the white water slurry, a compatible sizing for the glass fiber reinforcement may comprise an amino silane such as: "A-1126", which is a modified aminooorganosilane; "A-1120", which is N-beta-(aminoethyl)-gamma-(amino)propyltrimethoxysilane; "A-1102", which is gamma-(amino)propyltriethoxysilane; or "A-1100", which is a gamma-(amino)-propyltriethoxysilane; all of which are available from the Crompton Corporation. Preferably, the fiber reinforcement for use in the invention may be a sized glass reinforcement, which may be
used wet, in continuous strand or chopped form. Typical water content for wet chopped
strands ranges from about 10% to about 25% by weight. For continuous roving it ranges
from about 2% to about 15% by weight. Most preferably, such a fiber reinforcement is
used in wet, chopped form. An example of such a material is wet chopped strand of
approximately 1.25 inch (31.75 mm) length and about 16 microns in diameter, which is
commercially available from Owens Corning Inc. The wet chopped strand may be used
unsized or sized with a compatible sizing.

The fiber reinforcement generally comprises from about 0.02% by weight to
about 3% by weight of the white water slurry. Preferably, the amount of the fiber
reinforcement comprises from about 0.03% by weight to about 0.1% by weight of the
slurry before it is dewatered.

The white water system of the present invention includes at least one particulate
polymer, in the form of particles, granules or microspheres. A single polymer or blends
of polymers may be used. Suitable particulate polymers may be either thermoplastic or
thermosetting, and are typically in solid form at the temperature at which the white
water is formulated. Suitably, the particulate polymer should also be heat fusible. The
term “heat fusible”, as used herein, means that the polymer particles are capable of
deformation under heat to conform to the surfaces of the filaments of the reinforcement
material without melting, thereby joining the particles and the filaments to form a
unitary structure. In this respect, the particulate polymer of the present invention
functions differently from the binder resins that are conventionally used in the
preparation of wet-laid materials, because such binder resins melt and flow readily to
form an amorphous solid structure, with the polymer having accumulated a significant
heat history in the process. The heat fusible particulate polymer of the present invention
is also desirably a hydrophobic, water insoluble polymer. The particulate polymer to be
used in the invention should also be thermally stable. The term “thermally stable”, as
used herein, means that the polymer has a relatively high degree of inherent stability.
Thermally stable polymers according to the invention include polymers that may be
processed or combined with a suitable thermal stabilizer. Examples of such stabilizers
include, but are not limited to, organometallic compounds such as alkyltin derivatives or
mixed metal salts such as Ba/Zn carboxylates. Preferably, the stabilizers should be
organometallic materials. Most preferably, the particulate polymer is a thermoplastic
polymer, which may additionally be stabilized with butyltin thermal stabilizers.
Suitable particulate thermoplastic polymers may, for example, be selected from suspension-polymerizable polymers. The term “suspension-polymerizable”, as used herein, means that such polymers are formed from monomers contained in a suspension, and the polymer so formed may then be separated from the suspension before use. Suspension polymerization typically occurs in the presence of an initiator, which may be selected from any compatible, conventionally known initiators, depending on the particular monomer or blend of monomers in use. Suspension polymerizable polymers such as polyvinylchloride (PVC) and acrylonitrile-butadiene-styrene (ABS) are among the preferred. Additionally, suitable particulate polymers may be selected from addition and condensation polymers such as, for example, polyolefins, polystyrenes, phenolics, epoxies, butadienes, acrylonitriles, and acrylics. A blend of polymers may also be used. The particulate polymer or blend of polymers may also include a heat stabilizer, which retards degradation of the particulate polymer.

Typically, the particle size of the polymer may be larger than the filament diameter of the reinforcement material. The average polymer particle size may range from about 10 microns to about 500 microns. Preferably, the average particle size may be from about 75 microns to about 200 microns. The particle size may be selected to optimize the performance of the polymer in the product, while minimizing waste. Where the particle size is too small, a large amount of the particulate polymer may be filtered out with the aqueous fraction when the whitewater slurry is dewatered. Conversely, where the particle size is too large, the particles do not become fully integrated between the filaments of the reinforcement material during dewatering; instead the particles accumulate on the surface of the product and block airflow during the consolidation step.

The particulate polymer for use in the invention should be of a molecular weight that provides improved impact resistance in composites made according to the invention. Preferably, for example, the inherent viscosity, which may be correlated to molecular weight, of the PVC particulate polymer is from about 0.5 to about 1.2, most preferably from about 0.50 to 0.95. It has been found, for example, that a particulate polyvinyl chloride having an inherent viscosity of either about 0.52 or 0.92 produces a composite with excellent impact resistance and good heat distortion properties.

The particulate polymer used in the processes of this invention may, for example, be prepared as a dilute aqueous suspension containing monomeric molecules
to be polymerized. The suspension may also contain an initiator, and, depending upon
the polymer being formed, a heat stabilizer. The heat stabilizer may be added at the time
of polymerization, or at any other convenient time during the process of manufacturing
the polymer.

A preferred particulate thermoplastic polymer is a suspension-polymerized rigid
polyvinyl chloride (PVC) resin in dry, powdered form, which additionally contains a
heat stabilizer. Examples of such preferred resins are those stabilized with a butyltin
thermal stabilizer and having a particle size of about 125 microns and an inherent
viscosity of either about 0.52 or about 0.92. Such polymers are manufactured, for
example, by Oxyvinyls Inc.

The particulate polymer is generally added to the white water in an amount
ranging from about 20 to about 90 percent by weight of the total solids (based on the
combined dry weight of the weight of fibers and polymer).

Any suitable additive recognized as useful for contributing desired physical,
chemical or mechanical properties to the fibrous compound or mat, or to the composites
formed therefrom, may be included in the white water. Examples of additives that may
be added to the white water include dispersants, surfactants such as amine oxides,
polyethoxylated derivatives of amide condensation products of fatty acids and
polyethylene polyamines, antioxidants, antifoaming agents, foaming agents,
bactericides, radiation absorbers, thickeners, softeners, hardeners, UV stabilizers or
colorants.

Preparation of Wet-Laid Fibrous Nonwoven Compound or Mat

The process of the present invention may be used to prepare a wet-laid
compound that may be molded directly after dewatering a white water slurry without
subsequent drying, or a mat that that is formed by drying the compound after the
dewatering step. Figure 1 represents the process alternatives that are afforded by
practice of the invention. The white water slurry may be dewatered to form a wet-laid
compound having a water content ranging from about 10% by weight to about 30% by
weight of the compound. This compound may be used to form intermediate products
that can be used in subsequent molding processes, including, but not limited to, bulk
molding compound (BMC) or sheet molding compound (SMC). Optionally, the
compound may be further processed by drying to form a mat. The mat may, itself, be
processed into intermediate products that can be subsequently molded, or it may be molded directly into the composite products desired for specific end-use applications.

The process of forming and dewatering the white water slurry is described in U.S. Patent No. 6,093,359. As shown in Figure 2, which represents this process, wet or dry chopped reinforcing fibers, preferably glass, are combined with water in a mixing tank 2 and agitated. The particulate polymer may be added to the mixing tank 2 with the chopped fibers or after beginning agitation of the fiber-water mixture. The resulting combined aqueous suspension, which is usually referred to as a white water slurry 3, may then be processed into a wet-laid, sheet-like compound using conventionally known equipment such as cylinder or Fourdrinier machines, or other machinery such as the Stevens Former, Roto Former, Inver Former, inclined Delta Former and the VertiFormer machines. According to Figure 2, the white water slurry 3, after it leaves the mixing tank 2, is pumped into a headbox 4, from which it is allowed to flow onto a porous moving screen 6 that is over a series of regularly spaced supports 5. The moving screen 6 transports deposited material from the white water slurry 3 away from the headbox and towards a suitable conveyer apparatus 7, which maintains the movement of the formed product throughout the continuous system. It should be noted that, where the manufacture of the wet-laid compound is not performed as a continuous operation, the moving screen 6 or any other porous surface used need not be combined with a moving belt, rather individual batches of white water slurry 3 may be poured through an immobilized screen (not shown).

Referring again to Figure 2, as the white water slurry 3 is deposited on the surface of the moving screen 6, excess water is drained through the porous moving screen 6. The porosity of the surface allows the aqueous component of the white water slurry 3, which is predominantly water, to seep through the pores of the moving screen 6, thereby providing for dewatering of the white water slurry 3 as it is carried over the surface of the moving screen 6. The dewatering process may be aided by applying a vacuum suction from any conventional vacuum source (not shown) to the undersurface of the screen or porous surface that exerts sufficient vacuum to remove moisture from the white water slurry 3 as it is transported along the moving screen 6. The slurry is thereby dewatered sufficiently to form a compacted, sheet-like compound 1. At this point the compound may be removed and diverted to a molding operation, or it may be further processed by drying to form a mat.
To form the mat, the compound 1 is moved onto a conveyor belt 7, which may be a moving belt or other means conventionally used for moving a continuously formed product in a sheet-like configuration. Preferably the conveyor belt 7 is a moving belt that is in continuous flow communication with the dewatering apparatus on the input side, and with the post-treatment equipment such as driers, ovens, winders or the like on the output side. Such apparatus may be linked to the other equipment in a continuous system in order to control the rate of movement of the materials through each stage of the process, and thereby control the rate of formation of the product, as well as characteristics of the product, such as thickness of the mat. In the embodiment represented by Figure 2, the conveyor belt 7 receives the wet-laid compound 1, and transports it into a drier apparatus 8. In this regard, the mat is dried either by air-drying or by exposure to heat. The drier apparatus is preferably an oven, which is set at a temperature high enough to permit fusion of the polymer particles to the filaments of the reinforcement material. For example, the mat may be passed through one or more ovens in a series if the mat is produced in a continuous process, or it may be exposed to a fixed temperature in a single oven for a period of time sufficient to reduce the moisture level to the desired content. An added effect of heating the compound 1 is to accomplish further moisture removal to form a substantially dry mat 1a. The term “substantially dry”, as used herein, means that sufficient water has been removed from the mat to provide a moisture content that is about 2% by weight or less, based on the weight of dry mat. Preferably, the moisture content of the dry mat is less than about 1% by weight, based on the weight of dry mat. Where an oven is used, however, the operating temperature should not be so high as to cause deterioration of the particulate thermoplastic polymer component of the mat 1a, which would affect the heat history of the polymer and result in its reduced physical performance during the molding process. Suitably, the oven temperature is from about 200°C (392°F) to about 250°C (482°F), preferably from about 215°C (419°F) to about 227°C (441°F), depending on the basis weight of the product, the line speed, and the shape and the capability of the oven. The temperature of the compound is monitored by means of thermocouples placed beneath the conveyor belt 7 as it moves through the drier apparatus 8. The rate of movement of the belt is adjusted to permit sufficient exposure at a temperature of from about 171°C to about 199°C (340°F to 390°F) to achieve fusion of the particulate polymer and the reinforcement.
The dried mat 1a, after exiting the drier apparatus 8, is then wound, via a puller means (not shown), into packages 9 for storage or shipment. Where a puller means is used, such an apparatus may be used to control the rate of movement of the product during the dewatering and drying stages of the manufacturing operation, as is achieved by the conveyor belt 7.

In an alternative embodiment (not shown), the dewatered compound 1 is not passed through a drier apparatus such as an oven. Rather, the compound 1 may be directly introduced into a molding process for manufacturing composites. The compound 1 formed according to the invention may be incorporated into any suitable molding process. Examples of such processes include, but are not limited to, compression molding methods using a batch compression molding machine or continuous belt laminator, injection molding and pulltrusion operations.

Additionally, other processing steps may optionally be included in the mat-forming process. For example, it may be desirable to further process the mat 1a, such as by densifying it, before it is moved through the drier apparatus. The step of densifying is performed by pressing it with a flat press or by sending it through calendering rolls (not shown). Densification after drying of the mat 1a is particularly useful for increasing the tensile and tear strength of the mat. Another optional step is to apply materials or ingredients onto the surface of the dewatered compound before, during, or after drying. For example, additives such as pigments or surface active materials may be applied to the dewatered compound 1 as it is moved along the conveyor belt 7, thereby permitting impregnation of the compound 1 before it is exposed to the drying process to form the mat 1a.

The process of making a wet-laid mat according to the present invention is advantageous in that it requires a reduced number of processing steps in comparison to conventional wet lay-up processes. For example, the steps of preparing a liquid binder, such as by melting or dissolution in a solvent before combining it with the reinforcement material is eliminated. Additionally, there is no need for a separate processing step in which a liquid binder is applied to a laid and dewatered mat. Because this step is eliminated, the need for additional apparatus used to apply the liquid binder, such as sprayers, pad or rollers, is also eliminated. Even more significantly, the process dramatically increases the available options in terms of molding and performance, compared to previous methods using equal reinforcement content. Properties such as
impact, flexural and tensile strengths are increased dramatically compared to conventionally reinforced molded composites. The wet-laid mats of the invention may be used to make reinforced molding compounds. The wet-laid mat may also be used in the manufacture of a wide range of laminated composite articles such as roofing materials, automobile part and structural materials such as fencing.

The dried, wet-laid mat 1a formed according to the process of the invention suitably includes from about 10% by weight to about 80% by weight of reinforcing fibers, based on the total weight of dried mat. Preferably, the thermoplastic polymer component comprises from about 20% by weight to about 90% by weight, based on the total weight of the dried mat.

Molding of Fiber-Reinforced Composites

Molding of the wet-laid compound or mat to form composites according to the present invention may be achieved by a number of methods, including single batch processes such as compression molding, or continuous processes such as double belt lamination or pultrusion molding.

As described herein, the white water slurry of the invention may be processed into wet-laid compound that can be molded directly after dewatering, while wet and before it has been dried. Alternatively, the compound may be dried to form a mat and then molded. As yet another alternative, either the dewatered compound or the dried mat may be re-wetted and subsequently dewatered, to form compound suitable for molding, or optionally further processed by drying to form a mat, which can be immediately molded, or molded after it has been dried, packaged and stored. As such, this embodiment of the invention allows for recycling of unused portions of compound or mat into the molding process, thereby minimizing the waste that would otherwise be generated from discarding these materials.

Regardless of the molding method that is used, the operating conditions should be selected in order to facilitate exposure of the material being molded to an optimal temperature and pressure throughout to form a composite without excessive exposure to heat or pressure. Excessive heat may cause degradation of the particulate thermoplastic polymer, while high pressures may result in breakage of the reinforcing fibers. Accordingly, to some degree, the weight and chemical composition of the material, as well as the molding time, must be considered. Preferably, the wet-laid compound or mat formed according to the present invention, with PVC as the particulate polymer, may be
molded at a temperature in the range of from about 360°F to about 390°F (182°C to 199°C), and a pressure of from about 150 psi (pounds per square inch) (1034 kPa) to about 450 psi (3102 kPa). The molding time required to achieve penetration of heat throughout the material may vary depending on its thickness.

In one aspect of the invention, a fibrous, dewatered, wet-laid compound may be wet-molded, directly after the dewatering step, without undergoing a subsequent drying step to reduce the moisture content of the mat. Typically, the water content of the undried, wet-laid compound at the end of the dewatering step is from about 10% by weight to about 30% by weight, preferably from about 20% by weight to about 25% by weight. Before molding, the residual moisture level of the compound may be determined by drying a small quantity, calculating the percentage water, on a weight per weight basis, based on the loss in weight from the wet sample. Alternatively, measuring devices or any other known means may be used to determine the water content of the dewatered, undried compound.

In another aspect of the present invention, substantially dry, wet-laid mat may be molded to form composite laminates. Figure 3 depicts a batch compression molding process in which, dewatered, dried, wet-laid mat 1a formed according to the invention is weighed and cut or otherwise divided to form one or more layers that may be superimposed one over the other to form a charge 100. The charge 100 is then placed into the form of a tool 10, which has been preheated to a suitable molding temperature. As used herein, “suitable molding temperature” means that range of temperatures appropriate for molding a selected resin material, at either ambient or elevated pressure. The range of suitable molding temperatures will vary depending on the type of resin material that forms the resinous matrix that is to be molded into a composite. For example, where the wet-laid compound or mat of the present invention includes a particulate PVC resin, these materials may be processed into composites at temperatures ranging from about 340°F to about 390°F (about 171°C to about 199°C).

The form of the tool 10 may be comprised of opposing inner surfaces 11 of opposing platen 12, each inner surface configured to fit intimately to the opposing inner surface in the absence of any intervening material, such that when an intervening material such as the charge 100 is placed between these inner surfaces 11, the charge 100 may be evenly compressed and cooled during molding to consolidate it into a composite laminate of the desired shape, size and surface configuration. The form of
the tool 10 may be designed to shape the layers into flat, curved or other shapes. Suitably, the charge 100 may be placed in the tool 10 while the form is cold or at ambient temperature. Alternatively, the charge 100 may be preheated to molding temperature, and placed in the tool 10 which has been maintained at temperature greater than ambient temperature, but less than or equal to the molding temperature. Alternatively, the charge 100 may be preheated to a suitable molding temperature, placed in a tool kept at an elevated temperature that is below the molding temperature appropriate to the resin material being molded, as defined above, after which molding pressure is applied. For example, where the method above uses PVC resin, the mold temperature will be kept between about 150°C to about 250°C (about 66°C to about 121°C).

In another embodiment (not shown), the undried, dewatered compound formed according to the present invention may be placed in a cold tool and thereafter molded between heated platens, despite having a proportionately high water content in comparison to typical dried, wet-laid mat used in molding operations. Where the charge is prepared from a wet-laid compound, the platen of the tool containing the charge may be compressed slightly at low pressure, for example at about 5 psi (34 kPa) of pressure, to allow evaporation of water from the charge, then a higher pressure is applied to achieve the desired consolidation. During the actual molding at the higher pressure, a pre-selected amount of pressure may be applied to the material to be molded over a period of time, thereby permitting intermingling of the components of the molding material to form a composite. Heat may also be applied, at a temperature sufficient to promote flowability of the resin component of the molding material. Preferably, the compression-molding machine is set to apply a pressure of from about 150 psi (1034 kPa) to about 450 psi (3102 kPa). For example, the pressure may be set at 200 psi (1379 kPa). Pressure may be applied for a desired period of time that may vary depending on the thickness or number of layers of the charge material and the nature of the components thereof.

Preferably, in this embodiment, the platen and the inner surfaces thereof are pre-heated to a temperature sufficient to permit the vaporization of water from the charge as it is being molded. Because the vaporization of water is possible along the temperature gradient established by the heating of the charge in the molding machine, formation of a fully dried, consolidated laminate is possible even though the charge material comprised
of undried mat contains a relatively high proportion of water; on the order of from about 20% to about 30% by weight water, as opposed to less than 1% by weight water in dried mat. Moreover, it is believed that the vaporization of water from the wet charge results in steam permeating the material, thereby facilitating an even distribution of heat throughout the material as the laminate is being formed. Suitably, the inner surfaces of the compression molding machine may be heated to a temperature of about 360°F (182°C), which allows the desired heating and vaporization effects to occur under low molding pressure conditions. The time required for the vaporization of water from the wet charge and consolidating to form a finished composite may be estimated according to the following formula:

\[ K \times A \times t \times (T_p - 212°F) = M_w \times L_h \]

such that

\[ t = \frac{M_w \times L_h}{K \times A \times (T_p - 212°F)} \]

where \( K \) is the thermal conductivity of the charge in Btu/hr. /sq.ft./°F; \( M_w \) is the mass of water present in the charge material, in pounds; \( L_h \) is the latent heat of water in Btu/pound; \( A \) is the surface area exposed to heat, as measured in square feet; \( T_p \) is the temperature of the mold or platen; and \( t \) is the time required to vaporize the water in the compound, measured in hours. Using this model to calculate molding time in minutes for a sample in which a charge containing 0.25 pounds (0.011 g) of water is placed in a 12 foot x 12 foot (3.66 meter x 3.66 meter) flat plate mold that has been heated to 360°F (182°C), the time required to vaporize the water may be estimated as:

\[ t = 540 \times 1.8 \times 0.25 / (1.13 \times 142 \times 12 \times 2) = 0.063 \text{ hr} = 3.75 \text{ minutes} \]

In a preferred embodiment according to the present invention, the charge may be compressed for a period of from about 1 minute to about 5 minutes. For example, a molding time of about 1 minute may be used.

After the molding process is complete, the temperature of the mold may be reduced gradually, while maintaining pressure, until the inner surface temperature is about 200°F (−93°C). The resulting finished laminate may then be removed from the tool and cooled to room temperature.

In yet another embodiment of the present invention, previously dried mat formed according to the invention may be re-wetted, then molded according to a process as described herein. This aspect of the invention is particularly useful in the manufacture of shaped articles that require cutting or trimming the pre-formed mat to form a charge.
that will fit the desired shape of the mold tool. When such a charge is cut from the
dried, fibrous, wet-laid mat of the present invention, the discarded trimmed portions may
be rewetted and formed again into a molding compound, which may then be molded in
wet or dry form. For example, the discarded portions may be re-suspended in an
aqueous suspension to form a white water slurry via the previously described process,
and the resulting wet-laid compound can then be used in a wet-molding step, as
described above.

Preferably, when the molding operation of the invention utilizes a dry, wet-laid
mat, the mat may be molded in single ply, multiple plies or in combination with one or
more plies of other conventionally known materials suitable for use in composites. Such
added materials may include functional layers, in particular non-fiber containing layers,
wear overlayers, decorative layers, permeation barrier layers, tie layers that are bondable
with an adhesive layer and impact-modifying layers. For example, a functional layer,
which contributes to the flexibility of the resulting product, may be combined with one
or more layers of wet-laid compound or mat to form a multi-layered composite.
Suitable materials that may comprise the one or more functional layers may be selected
from vinyl polymers, including polyvinyl derivatives, acrylic polymers and styrenic
polymers, olefin polymers, and combinations thereof. Alternatively, an impact-
modifying layer such as asphalt or an asphalt-based may be combined with one or more
layers of wet-laid compound or mat formed according to the invention.

In an alternative process, a dried wet-laid mat may be molded in a continuous
molding process to form laminates. Such a continuous manufacture may be achieved
using an apparatus such as a continuous belt laminator. Suitable machines for
performing the continuous process should be capable of rapid throughput under
controlled temperature and pressure conditions. Such machines may be selected from a
double belt press, roll press, rotocure press, gliding press, roller bed press or fluid or air
cushion press. Preferably, a double belt press is used in the continuous manufacturing
process of the present invention. As shown in Figure 4, one or more layers of wet-laid
mat formed according to the process described herein may be integrated to form a
composite laminate using a double belt press 20. In this embodiment, one or more layers
of dried, wet-laid mat 1 may be unwound from rolled stock 21 or input from stacked
sections of mat (not shown), thus being combined to form a continuous charge 100.
Alternatively, one or more layers of wet-laid mat may be manually layered to form a
charge. In other embodiments, the charge 100 may comprise one or more layers of other materials, selected from functional layers, wear overlayers, decorative layers, permeation barrier layers or impact-modifying layers as previously described herein.

Before molding, the charge 100 may optionally be passed through one or more pairs of entry rollers 21 for pre-molding by applying slight pressure that is sufficient to compress the fiber pack of the charge 100, but not sufficient to break the individual fibers. For example, a pressure of up to about 5 psi (34 kPa) may be used. The size of the gap between the entry rollers 21 may, for example, be calibrated to provide sufficient pressure on the charge 100, depending on its thickness, to generate a partially consolidated material that can then be compacted to form a laminate.

The charge 100 is next drawn through a continuous laminator, which is preferably in the form of a double belt press 20. The double belt press 20 is a flat bed press comprised of two endless belts 27, usually made of steel, which run one above the other around two pairs of upper and lower drums 22 to form a thermally controlled compression zone between them. Within this compression zone, the charge 100 is compressed under heat and elevated temperature to form a laminate. After exiting the entry rollers, the charge 100 is then passed through the thermally controlled compression zone of the double belt press 20. The belts of the double belt press 20 are maintained at a temperature sufficient to heat the layers of the charge to permit fusing and compaction of the reinforcement and particulate polymer, which, in turn eliminates air voids from between the filaments and polymer particles in the wet-laid mat.

As the incoming charge 100 is then drawn through the entrance of the thermally controlled compression zone of the double belt press 20, it is seized between the upper and lower belts, and is “sandwiched” between the belts as it moves through the thermally controlled compression zone. The charge 100 is drawn through the machine continuously at constant speed while it is exposed to a fixed pressure, or is drawn through a machine with a constant controlled gap between the belts 27, through which pressure is vertically applied at a 90° angle to the horizontal direction of movement of the charge 100. The amount of pressure applied may vary from about 10 psi (69 kPa) to about 450 psi (3102 kPa), and is preferably from about 150 psi (1034 kPa) to about 250 psi (1724 kPa). The temperature in the thermally controlled compression zone is maintained at a range of from about 320°F (about 160°C), and is preferably maintained within the range of from about 340°F (about
171°C to about 188°C). The actual contact time between the heated surfaces in the thermally controlled compression zone is on the order of about 30 to about 300 seconds.

The composite laminate 23 so formed then exits the double belt press 20 and is drawn over one or more cooling rolls 24. Before cooling, the laminate 23 may optionally be embossed to provide a decorative or textured surface. The means for embossing may be selected from those conventionally known in the art, such as by passing over textured rolls or stamping. The cooled laminate 23 may then be cut using any suitable cutting means 25 and stacked into sheets 26 or otherwise packaged (not shown) according to the desired application.

The composites formed according to the present invention may be manufactured in any form conventionally attainable by molding means known in the art for the manufacture of molded composite products from a wet-laid compound or mat. For example, the wet-laid mat of the invention may be molded into articles such as roofing shingles, shakes or tiles, structural panels for use in construction, cladding, artificial fencing, decking, truck and automobile parts for manufacture or repair purposes; and miscellaneous parts such as appliance lids, conveyor belts, counter tops, entry doors, garage doors, hurricane shutters, satellite dishes, concrete forms, railroad ties, seating, ready-to-assemble furniture, and laminate flooring. The wet-laid compound may be prepared and stored as a bulk molding compound (BMC), in preparation for use in conventional molding operations.

For example, an artificial shake may be manufactured as a composite laminate using the wet-laid mat of the present invention. The shakes so formed are highly resistant to weathering and physical abuse from hail or other elemental hazards. A preferred embodiment of an artificial shake formed according to the invention is represented by Figure 5. According to Figure 5, the shake 13 may be a generally rectangular member, when taken in planar view, having a length greater than its width; and further comprising a butt end 14 which extends upwardly, and preferably more than half the length to a point 15, the area between the butt end 14 and the point 15 defining the exposed portion of the shake 13. The butt end 14 smoothly tapers into a headlap portion 16 at the termination of the exposed portion at 15. The exposed portion may be molded to achieve a textured configuration that simulates wood or slate or other specialty roofing materials. The backside of the shake is preferably flat, such that the shake 13, when viewed in profile, as in Figure 6, assumes the shape of an elongated
wedge 17, wherein the butt end 14 forms the thicker end of the wedge, and the headlap portion 16 forms the thinner, elongated end of the wedge. The artificial shakes formed according to the present invention exhibit increased stiffness in relation to shakes previously known in the prior art, because of the increased rigidity contributed by the particulate thermoplastic polymer contained in the glass mat GMT product. Accordingly, whereas typical designs for artificial shakes have included ribs and other structural configurations on the backsides of such shakes to provide the desired rigidity, such configurations are not required for the manufacture of the shakes according to the present invention. In fact, it is preferable that ribs be excluded from the backsides of the shakes because their inclusion produces points of weakness corresponding to the points of attachment of the rib elements. These points of weakness cause the shake to be more prone to impact damage at the site of each such rib.

The composites, and, in particular, laminates formed according to the present invention provide certain improvements over laminates formed from wet-laid, binder-added mat formed according to the prior art. Such improvements include increased rigidity and impact resistance of the laminate product, as well as increased fiber length retention in the finished product. In particular, a continuous molding process such as the double belt laminating process, when utilized to process laminates from the fibrous, nonwoven mat of the present invention, results in increased retention of fiber length when the mat is subjected to a molding process. In such a process, the improvement in retained average fiber length may be about 1.5x or higher. As a result of this improvement, mechanical properties of the resulting laminates, such as flexural modulus and coefficient of thermal expansion, are enhanced. In addition, these properties may also be affected by the proportion of reinforcing fiber material.

In this regard, exemplary laminates formed according to the continuous double belt molding process described herein, wherein the reinforcing fiber material is glass present in an amount from 0 to about 35% by weight, may demonstrate a weight average fiber length of from about 10 mm to about 32 mm. The tensile strength of such laminates may range from about 12 kpsi (82.73 mPa) to about 30 kpsi (206.82 mPa), while the flexural strength may range from about 17 kpsi (117.20 mPa) to about 40 kpsi (275.76 mPa), and the impact strength, as measured by the notched Izod test, may range from about 3 ft-lbs/in (13.35 N.m/m) /to about 15 ft-lbs/in (66.72 N.m/m). These
composite laminates also show heat distortion temperatures ranging from about 75°F to about 185°F (~167°C to ~365°F).

EXAMPLES

Example I -- Compression Molded Composites from a Dried, Wet-Laid PVC/Glass Mat Thermoplastic (GMT) Product

A white water slurry containing about 3080 g of wet-used chopped glass strand (WUCS) reinforcement (Owens Corning type E glass), 8450 g of polyvinyl chloride (PVC) powder and 1.8 x 10^6 g water was prepared in a mixing tank. The resulting slurry had a solids content of about 1% by weight. The slurry was further diluted with water at a ratio of about 1:14 to form the white water, which was then pumped from the tank into a headbox, from which it was deposited onto a moving screen by gravity feed and vacuum suction. The excess aqueous medium was drained as the material was carried along the moving screen and the deposited solid material formed into a sheet of wet-laid compound. The compound was subsequently sent into an oven where the remaining moisture was removed and the compound was dried at a temperature of 430°F (~221°C) to form a mat. The mat was then cut into several evenly-sized (12-inch x 12-inch) (304.8 mm x 304.8 mm) portions to form a charge weighing approximately 436 g.

A standard compression molding press (Pasadena electrically heated press, 210-ton (190.49 metric ton) capacity) was pre-heated to a temperature of 360°F (182°C). The weighed charge was placed in an unheated tool. The tool was then placed in the press and molding pressure of about 150 psi (1034 kPa) applied. The tool was then removed and the laminate de-molded and further cooled under ambient conditions.

A sample of a composite laminate was made using a dried, wet-laid mat comprised of particulate polyvinyl chloride (PVC) and chopped glass fibers that had been prepared according to Example 1, above. The laminate thus obtained (designated as Sample A) was tested to determine its physical and mechanical properties. Comparative evaluations were performed using laminate products made using conventional processes. One of these comparative samples was "FIBERLOC POLYMER COMPOSITES® 81530", available from the The Geon Co., which was made of short glass fiber compounded together with polyvinyl chloride and injection molded. Other comparative samples included "AZDEL® C300 and AZDEL® C401", which comprised 30% by weight, and 40% by weight, respectively, of long glass fiber
and compounded polypropylene. Both these products are commercially available from Azdel, Inc. (The AZDEL® C401 included a higher weight proportion of glass, however the glass volume percent was comparable to that of the samples of the invention because the specific density of polypropylene is less than the density of the PVC used in the laminate made according to the invention). Additional comparative samples were prepared using rigid vinyl molding compound that contained no reinforcing fibers, southern pine wood, which is representative of wood used to make roofing products such as shakes, and a standard industrial aluminum alloy having the designation “7075-T6”.

The mechanical, thermal and physical properties evaluated included tensile strength (ASTM D638), which is a measure of the strength required to pull apart the sample in thousands of pounds per square inch (kpsi); tensile modulus (ASTM D638), which is a measure of the stiffness of the composite in millions of pounds per square inch (mpsi); flexural strength (ASTM D790), which is the strength required for bending on deformation (in kpsi); flexural modulus (ASTM D790), which is a measure of resistance to deformation (in mpsi); and flex elongation (ASTM D790), which is a percentage measure of how much the composite will bend before breaking. Notched Izod impact strength (ASTM D256) was also determined for 0.125 inch (3.2 mm) by 0.50 inch (12.7 mm) notched samples. The thermal performance of the each sample was assessed in terms of the coefficient of linear thermal expansion (CTE) according to standardized method ASTM D696, and the heat distortion temperature, according to standardized method ASTM D648. As physical characteristics, the density, which is a measure of how lightweight the molded sample was, was reported as weight per cubic centimeter of composite. The proportion of glass fiber, as a percentage by weight of the molded product, was also determined. Comparative results for each sample are reported in Table 1, below.
<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>UNITS</th>
<th>SAMPLE A</th>
<th>FIBERLOC 81530</th>
<th>RIGID VINYL MOLDING COMPOUND</th>
<th>AZDEL C300</th>
<th>AZDEL C401</th>
<th>SOUTHERN PINE (WOOD)</th>
<th>AL ALLOY 7075-76</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Content</td>
<td>Wt.%</td>
<td>30</td>
<td>30</td>
<td>0</td>
<td>30</td>
<td>40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>1.61</td>
<td>1.64</td>
<td>1.33</td>
<td>1.13</td>
<td>1.24</td>
<td>0.6</td>
<td>2.8</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>kpsi</td>
<td>21</td>
<td>15</td>
<td>6.3</td>
<td>8</td>
<td>13</td>
<td>5.7</td>
<td>68.6</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>kpsi</td>
<td>1400</td>
<td>1400</td>
<td>340</td>
<td>600</td>
<td>800</td>
<td>1600</td>
<td>10,000</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>kpsi</td>
<td>30</td>
<td>22</td>
<td>10.3</td>
<td>13</td>
<td>20</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>kpsi</td>
<td>1400</td>
<td>1350</td>
<td>360</td>
<td>600</td>
<td>750</td>
<td>1900</td>
<td>10,300</td>
</tr>
<tr>
<td>Flex Elongation</td>
<td>%</td>
<td>3</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Heat Distortion Temp.</td>
<td>°F (°C)</td>
<td>293 (145)</td>
<td>173 (78)</td>
<td>164 (73)</td>
<td>280 (138)</td>
<td>310 (154)</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>CTE</td>
<td>ppm/°F</td>
<td>13</td>
<td>10</td>
<td>35</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>12.5</td>
</tr>
<tr>
<td>Notched Izod Impact</td>
<td>ft-lbs/in.</td>
<td>6</td>
<td>1.6</td>
<td>7.4</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Energy at Max. Load</td>
<td>ft-lbs</td>
<td>4</td>
<td>na</td>
<td>na</td>
<td>6</td>
<td>7</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Total Energy</td>
<td>ft-lbs</td>
<td>8</td>
<td>na</td>
<td>na</td>
<td>12</td>
<td>14</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

na = data not available
The results in Table 1 show that a composite laminate made according to the present invention shows better strength properties than other composite materials made using a comparable reinforcement, but not prepared using a particulate thermoplastic polymer in a white water process, as is achieved by the present invention. The product of the invention also demonstrated better strength and heat resistance properties in comparison to a rigid vinyl molding compound made of PVC in the absence of glass fibers. The composite of the invention also was observed to be superior in performance when compared to wood materials that have been conventionally used for structural products such as roofing materials.

Example II—Compression Molded Composite from a Wet-Laid PVC/Glass Compound

A sample was prepared as in Example 1, but before the material was sent to an oven to remove the remaining moisture and form a mat, it was removed from the machine while wet, having a water content of about 25% by weight. The wet compound was molded in a standard molding press that had been preheated to about 360°F (~182°C). The charge was placed in an unheated tool, the tool was placed in the press and an initial pressure of about 5 psi (34 kPa) applied. The tool was then allowed to heat for 5 minutes past the last visual evidence of water being evaporated from the tool.

At that point, the pressure was increased to 200 psi (1379 kPa) and held for 1 minute. While maintaining pressure, the temperature of the tool was then allowed to cool below 200°F (~93°C). The tool was then removed and the finished laminate de-molded and further cooled under ambient conditions. No visible porosity was observed in the part. Void analysis, as measured by optical techniques, confirmed less than 1 percent porosity. This was similar to the porosity observed after molding laminates with dried mat as in Example 1.

Example III -- Continuous Molded Composite Laminate

Samples of laminates made from a dry, wet-laid mat according to the process described in Example 1 were prepared. A charge made from 6 layers of mat was molded using a continuous double belt press. The resulting sample was designated Sample B. Another sample, Sample C, was prepared using 16 layers of the wet-laid mat, and molded on a compression-molding machine at approximately 300 psi (2068
kPa). A third sample, D, having similar composition to Sample C was compression molded at approximately 1400 psi (9652 kPa). A commercially available short fiber reinforced composite prepared from compounded pellets of short-fiber reinforced vinyl compound was injection molded to form comparative sample E, which reflects the current commercial technology. The thickness of this sample was about the same as Samples B and C.

Each sample was tested to determine how the physical properties were affected by type of molding process used. The laminate of sample A was too thin to undergo the standard test for heat distortion temperature that was applied to the other specimens, and therefore the test was not performed for that sample. The sample laminates were also evaluated to ascertain the retention of fiber length after molding. Plaques of each sample were heated to burn off the non-glass component of the consolidated material, leaving the fiber segments. Approximately 400 individual fiber segments were selected and measured to determine the average length, based on a length-weighted average, according to the formula

$$\frac{n_i l_i}{n_i}$$

in which $n_i$ represents the number of fibers and $l_i$ represents the length of the fibers.

The results are included in Table 2.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MOLDING DETAILS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molding Method</td>
<td>Double Belt</td>
<td>Compression</td>
<td>Compression</td>
<td>Injection</td>
</tr>
<tr>
<td>Molding Pressure</td>
<td>300 psi</td>
<td>300 psi</td>
<td>1400 psi</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>PHYSICAL PROPERTIES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.62</td>
<td>1.60</td>
<td>1.62</td>
<td>1.64</td>
</tr>
<tr>
<td>Flex Modulus (kpsi)</td>
<td>1350</td>
<td>1180</td>
<td>1110</td>
<td>1350</td>
</tr>
<tr>
<td>Flex Strength (kpsi)</td>
<td>30.54</td>
<td>30.65</td>
<td>23.32</td>
<td>22.00</td>
</tr>
<tr>
<td>Heat Distortion Temp.</td>
<td>N/A</td>
<td>282°F (139°C)</td>
<td>185°F (85°C)</td>
<td>172°F (78°C)</td>
</tr>
<tr>
<td><strong>FIBER LENGTH DATA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Fiber Length (mm)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Final Fiber Length (mm)</td>
<td>16</td>
<td>15</td>
<td>4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The results showed that, after molding, the average lengths of the fiber segments in the samples molded via the continuous double belt press or via a batch compression
molding process at lower pressure were greater than the fiber lengths for samples that had been compression-molded at higher pressure. The invention also demonstrated much better fiber length retention after molding than the sample that had been injection-molded from compounded pellets.

The results also showed that improvements in physical properties such as flex strength and heat distortion temperature are a result of fiber length retention during the molding or lamination operation. The data also suggests that excessive molding pressure is a factor that may contribute to fiber length degradation, and a resulting decline in physical properties.

Example IV -- Effect of PVC Resin Molecular Weight on Laminate Properties

The effects of resin molecular weight on the physical properties of laminates formed according to the invention were evaluated. Laminate plaques F-I were prepared using dried wet-laid mat of the invention. Each laminate comprised a particulate PVC, with the different samples each having an inherent viscosity ranging from 0.52 to 1.02. Each sample was molded at a temperature between 340°F - 390°F (~171°C to ~199°C) and a pressure of about 420 psi (2896 kPa). The samples were evaluated, using the standard methods herein described, to determine the resulting physical and mechanical properties. The results are shown in Table 3.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Inherent Viscosity (IV)</td>
<td>0.52</td>
<td>0.72</td>
<td>0.92</td>
<td>1.02</td>
</tr>
<tr>
<td>Plaque Glass Content (% wt.)</td>
<td>29.0</td>
<td>29.2</td>
<td>28.7</td>
<td>28.5</td>
</tr>
<tr>
<td>Plaque Thickness (inches)</td>
<td>0.131</td>
<td>0.132</td>
<td>0.132</td>
<td>0.124</td>
</tr>
<tr>
<td>Specific Gravity (inches)</td>
<td>1.608</td>
<td>1.606</td>
<td>1.608</td>
<td>1.598</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FLEX PROPERTIES</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flex Modulus (kpsi)</td>
<td>1132</td>
<td>1086</td>
<td>1128</td>
<td>1085</td>
</tr>
<tr>
<td>Flex Strength (kpsi)</td>
<td>32.55</td>
<td>32.10</td>
<td>32.06</td>
<td>31.11</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>3.5</td>
<td>3.7</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Energy To Yield (in-lb)</td>
<td>9.0</td>
<td>9.8</td>
<td>8.9</td>
<td>8.6</td>
</tr>
<tr>
<td>Heat Distortion Temperature</td>
<td>146°C</td>
<td>152°C</td>
<td>165°C</td>
<td>173°C</td>
</tr>
<tr>
<td></td>
<td>295°F</td>
<td>360°F</td>
<td>329°F</td>
<td>343°F</td>
</tr>
<tr>
<td>Vhit,Mean Failure Energy (MFE) (in-lb/mil)</td>
<td>116</td>
<td>158</td>
<td>154</td>
<td>126</td>
</tr>
<tr>
<td>Normalized MFE (in-lb/mil)</td>
<td>0.9</td>
<td>1.2</td>
<td>1.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

According to this data, very good results were achieved in a low-pressure (420 psi) (2896 kPa) molding process using a particulate PVC having a relatively low...
inherent viscosity (0.52), which provided a cost-effective manufacturing option. Excellent results were also obtained using a particulate PVC of higher inherent viscosity (0.92). The higher inherent viscosity, which relates to higher molecular weight of the PVC, also produced an unexpected increase in heat distortion temperature of about 45°F (25°C).

It is believed that applicants’ invention includes many other embodiments which are not herein specifically described, accordingly this disclosure should not be read as being limited to the foregoing examples or preferred embodiments.
WHAT IS CLAIMED IS:

1. A method of forming a fiber-reinforced composite comprising:
   a) preparing a non-woven, fibrous, wet-laid compound (1) by:
      i) mixing a suspension comprising a reinforcement material and at
         least one particulate thermoplastic polymer, in the absence of a binder, in
         an aqueous medium to form a white water slurry (3);
      ii) dewatering the white water slurry to form a wet-laid compound
          impregnated with particulate thermoplastic polymer; and
       b) molding the wet-laid compound to form a fiber-reinforced composite.

2. The method of claim 1, further comprising drying (8) the wet-laid compound,
   after dewatering and before molding, to form a mat.

3. The method of claim 2, further comprising re-wetting dried mat, before molding,
   to form a wet-laid compound.

4. The method of claim 3, wherein the rewetted mat is one or more discarded
   trimmed portions of dried mat generated during a composite molding process.

5. The method of claim 2, wherein one or more functional layers are molded
   together with the one or more layers of wet-laid mat.

6. The method of claim 1, wherein the step of molding the wet-laid compound (1)
   further comprises heating the wet-laid compound impregnated with particulate
   thermoplastic polymer to a temperature that is above the boiling point of water, such that
   water vaporizes from the wet-laid compound before the particulate thermoplastic
   polymer fuses, and fusing the particulate thermoplastic polymer.

7. The method of claim 6, wherein the particulate thermoplastic polymer is
   polyvinyl chloride.

8. The method of claim 6, wherein the molding comprises placing the wet-laid
   compound in a mold that is heated to a temperature of from about 340°F (171°C) to
   about 390°F (199°C).

9. The method of claim 1, wherein the step of molding the wet-laid compound (1)
   is performed in a continuous molding process.

10. The method of claim 9, wherein the continuous molding process is a double belt
    press molding process (20).

11. The method of claim 1, wherein the step of molding the wet-laid compound (1)
    is a batch molding process.
12. A product formed by the process of claim 1.
13. A process for molding a fiber-reinforced composite from a wet-laid compound (1) comprising a particulate polymer and a reinforcement material, comprising heating the wet-laid compound, under low pressure, to a temperature at which water vaporizes from the wet reinforcement, but before the particulate thermoplastic polymer fuses, thereby allowing water to escape, and subsequently applying molding pressure to allow the wet-laid compound to consolidate into a part.
14. The process of claim 13, wherein the heating takes place in a mold (10) that is heated to a temperature of from about 340°F to about 390°F (about 171°C to about 199 °C).
15. The method of claim 14, wherein the molding pressure is applied by compression molding performed at a pressure of from about 150 psi (1034 kPa) to about 450 psi (3102 kPa).
16. The method of claim 15, wherein the compression molding is performed at a mold closure rate of from about 0.1 mm/sec to about 10 mm/sec.
17. The method of claim 13, wherein one or more layers of the wet-laid compound (1) are heated together, and molding pressure applied to form a laminate.
18. The method of claim 13, wherein the molding pressure is applied by a continuous double-belt press laminating process (20).
20. The method of claim 13, wherein one or more functional layers are heated together with one or more layers of the wet-laid compound (1), and molding pressure applied to combination of functional layers and layers of wet-laid compound to form a laminate.
21. A method for improving fiber length retention during continuous manufacture of a reinforced composite article comprising:
a) providing one or more layers of a wet-laid mat impregnated with at least one particulate thermoplastic polymer; and
b) molding the one or more layers of wet-laid mat in a continuous laminating process to form a fiber-reinforced composite.
22. The method of claim 21, wherein the improvement in retained average fiber length in the molded composite is on the order of 1.5 times or higher, when compared to the fiber length in composites compression-molded from long-fiber pellets.
23. The method of claim 21, wherein the molding is performed by a double belt press molding process (20).

24. The method of claim 21, wherein the molding is performed at a temperature of from about 340°F to about 390°F (about 171°C to about 199°C), and a pressure of from about 150 psi (1034 kPa) to about 450 psi (3102 kPa).

25. A method of molding a composite laminate from a dried, wet-laid mat, comprising:
   a) forming a charge (100) comprising one or more layers of dried, wet-laid mat;
   b) heating the charge to the molding temperature of the dried wet-laid mat;
   c) placing the heated charge into a tool (10) maintained at a temperature below the molding temperature of the dried, wet-laid mat; and
   d) applying molding pressure to form a composite laminate.

26. The method of claim 25, wherein the dried, wet-laid mat comprises a particulate PVC polymer and a fiber reinforcement; the molding temperature is from about 320°F to about 390°F (about 160°C to about 199°C); the temperature of the tool is from about 150°F to about 250°F (about 66°C to about 121°C); and the molding pressure is from about 150 psi (1034 kPa) to about 450 psi (3102 kPa).

27. A composite laminate formed according to the method of claim 21, having a length-weighted average fiber length of from about 10 mm to about 32 mm.

28. The composite laminate of claim 27, wherein the particulate thermoplastic polymer is polyvinyl chloride and the reinforcing material is long glass fibers ranging from about 0.125 inch (3.2 mm) to about 2 inches (50.8 mm) in length.

29. The composite laminate of claim 27, having a heat distortion temperature of the laminate of from about 75°C to about 185°C (about 167°F to about 365°F).

30. The composite laminate of claim 27, having a tensile strength of from about 12 kpsi (82.73 mPa) to about 30 kpsi (206.82 mPa).

31. The composite laminate of claim 27, having a flexural strength of from about 17 kpsi (117.20 mPa) to about 40 kpsi (275.76 mPa).

32. The composite laminate of claim 27, having a notched Izod impact strength of from about 3 ft-lbs/in (13.35 N.m/m) to about 15 ft-lbs/in (66.72 N.m/m).

33. A composite article comprising one or more layers of a non-woven, fibrous, wet-laid compound or mat comprising a filamentized long-fiber reinforcement and a
thermally stabilized particulate polymer, in the absence of a binder; wherein said layers
have been consolidated by the application of heat and pressure to form a fiber-reinforced
composite article.
34. The composite article of claim 33, which is in the form of a laminate.
35. The composite article of claim 34, which is in the form a roofing tile, shake,
shingle or cladding.
36. The composite article of claim 33, which is in the form of a part for use in truck
or automobile manufacture or repair.
37. The composite article of claim 33, which is in the form of a railroad tie.
38. The composite article of claim 33, which is in the form of a structural panel for
use in construction.
39. The composite article of claim 33, which is in the form of fencing.
40. The composite article of claim 33, which is in the form of an appliance part, a
conveyor belt, a counter top, an entry door, a garage door, a hurricane shutter, a satellite
dish, a concrete form or ready-to-assemble furniture.
41. The composite article of claim 33, which is in the form of laminate flooring.
42. A roofing shake comprised of a molded material formed from one or more layers
of wet-laid compound or mat comprising a fiber reinforcement and a particulate
thermoplastic polymer, and excluding a binder; wherein the shake comprises a butt end
and a headlap portion having an exposed portion, such that the butt end smoothly tapers
into the headlap portion at the termination point of the exposed portion.
43. A roofing shake according to claim 42, further comprising a planar lower
surface, such that the entire lower surface, when placed against a roofing surface, is
flush with the roofing surface.
44. A materials system for use in molding fiber-reinforced composites, comprising a
long fiber reinforcement, a particulate polymer and water, and excluding a binder.
45. The materials system of claim 44, wherein the particulate polymer is a
thermoplastic polymer.
46. The materials system of claim 45, wherein the particulate polymer is a stabilized
polyvinyl chloride.
47. The materials system of claim 44, wherein the long fiber reinforcement is
selected from the group consisting of glass fibers, carbon fibers, metal fibers, cellulose
fibers, polymer fibers and combinations thereof.
48. The materials system of claim 47, wherein the long fiber reinforcement is glass fibers.
FIG. 1

WHITE WATER SLURRY

DEWATERING

WET-LAID COMPOUND

DRYING

WET-LAID MAT

MOLDING

INTERMEDIATE PRODUCTS

MOLDING

FINAL MOLDED PRODUCTS