

THERMOFORMABLE MULTILAYERED POLYESTER SHEET

This application claims the benefit of U.S. Provisional Application 60/041,015, filed March 19, 1997 (Our Case 8CT-5680 PA).

Field of the Invention

This invention relates to a polyester composite sheet which may be thermoformed into a variety of articles such as bathroom sinks and tubs.

Background of the Invention

5 Filled crystalline resin blends are often difficult to form into profiles or sheet. Crystalline resin has poor melt strength and high shrinkage upon cooling. This makes it difficult to obtain thick sections with good dimensional tolerances. Typically, extruded crystalline resins may also exhibit a very rough surface.

10 U.S. patent 5,441,997 describes polyester molding compositions which have ceramic like qualities, can be molded into relatively thin sections, and have good impact strength. The composition is directed to a polybutylene terephthalate and/or polyethylene terephthalate and an aromatic polycarbonate with inorganic fillers selected from the group consisting of
15 barium sulfate, strontium sulfate, zirconium oxide and zinc sulfate. If desired, a styrene rubber impact modifier is described as added to the

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composition as well as a fibrous glass reinforcing filler. Although these compositions are suited for many applications where ceramic like qualities are desired, it is desirable to have even more improved and more economical molded structures.

5 U.S. patent 5,510,398 to Clark, et al describes the use of the non-dispersing pigments to impart to a polyester thermoplastic composition a granite, fleck-like or speckled surface appearance to an extruded sheet which provides a separate, visibly distinct and identifiable color at numerous sites across the surface of the material wherever the pigment material is visible.

10 Potential non-dispersing pigments which are useful provided the aspect ratio is suitable include titanium whiskers and other natural fibers as well as ground thermosetting resin, thermoplastic or rubber materials. When added to a filled polyester material, the resulting decorative polyester composition typically has chemical resistant properties. U.S. patent 5,304,592 to Ghahary

15 relates to a simulated mineral article which comprises a plastic particulate of thermoplastic and thermosetting resin material within a thermoplastic matrix.

It is desired to obtain further enhancements to polyester materials, especially decorative filled type chemically resistant polyesters, which enhancements include better thermoformability in large parts, greater

20 stiffness, better impact resistance, and higher heat resistance. Hence, it is desirable to provide polyester materials having enhanced structural properties without detracting from the decorative surface and chemical resistant properties. Additionally, it is desirable to provide economically decorative and chemically resistant polyester materials that exhibit reduced

25 shrinkage and warpage with thick sections during molding operations.

U.S. patent 4,737,414 to Hirt et al describes a multilayer composite wherein a layer comprising an aromatic polyetherimide is adjacent to a layer

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comprising an aromatic polyester. A tie layer of a copolyestercarbonate is described.

Summary of the Invention

The compositions of the present invention provide for an economical polyester material having enhanced melt strength and elasticity without
5 undesirably affecting the desirable decorative surface and chemical resistant properties.

According to the present invention, there is provided a thermoplastic composite comprising an extruded thermoformable self-supporting sheet having an outer decorative chemically resistant and renewable filled polyester
10 layer and an adjacent inner supporting thermoplastic layer for enhancing desirable mechanical properties of the composite.

The decorative outer polyester layer comprises a colorant, an inorganic filler, an effective amount of a stabilizer, a UV stabilizer, and optionally polycarbonate, and/or an impact modifier.

15 For enhancing the mechanical properties of the overall composite, the adjacent inner thermoplastic layer comprises a heat deformable layer having mechanical properties such as impact resistance and melt strength which desirably exceed these properties as possessed by the outer polyester layer.

Also, there is provided a process for preparing a decorative article
20 comprising extruding a multilayered sheet by feeding at least two different resin compositions to an extruder, extruding said at least two resin compositions into the multilayered self-supporting coextruded sheet, and thermoforming at least a portion of said coextruded sheet into a decorative article wherein at least one exterior surface of the article comprises one resin
25 and an adjacent layer comprises the other resin. One resin comprises the

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decorative layer and the other layer comprises the supporting layer as previously set forth.

Description of the Preferred Embodiments

The thermoplastic composite comprises an extruded thermoformable self-supporting sheet having an outer decorative chemically resistant filled polyester layer and an adjacent thermoplastic support layer for enhancing desirable mechanical properties of the composite. Both layers are formed from extrudable resin compositions. It is contemplated that a compatibilizing or adhering layer may be included intermediate to the decorative layer and the support layer. It is also contemplated that the support layer may be a laminate or multilayered structure including a regrind layer of unused or scrap resin material that are desirable to be recycled. It is also contemplated another polyester layer may be utilized adjacent the support layer so that the entire exterior of the sheet, both top and bottom, are formed from a decorative polyester type material.

It is also contemplated that the layer immediately adjacent the outer decorative layer be another layer of filled polyester material. Preferably this second polyester layer is of a colored polyester material having a color which is in contrast to the outer decorative layer. By removing a portion of the outer layer by mechanical or other means, the color of the adjacent layer will be revealed. Hence, a decorative design may be imparted to the sheet material using an adjacent layer which contrasts with the outer layer, and removing the outer layer in a pattern.

The following discussion relating the preparation of a multilayered composite makes reference to coextrusion of multiple layers using a plurality of extruders. Each layer is desirably formed from a single extruder with multiple layers formed by using a number of extruders corresponding to the

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number of layers desired and a suitable die assembly so as to yield the appropriate number of layers.

According to the coextrusion process, a plurality of standard extrusion machines may be utilized. Typically the extruder has a housing having a central opening with a helical screw mounted for rotation along an axis interior to a barrel portion. A motor drives the screw through a gear reducer. At one end of the opening, a hopper is utilized for feeding material to be extruded into the rear portion of the screw. Helical threads mounted on the screw are positioned for moving material from the rear portion of the screw to a forward portion. As the material or feedstock is conveyed along the screw, the feedstock is heated by frictional forces caused by rotation of the screw. It is also contemplated that an external heating source such as an electrical resistant heaters may be provided to heat the feedstock.

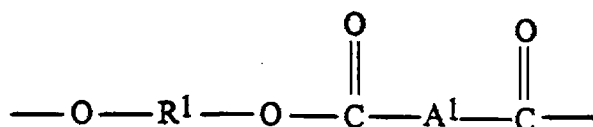
For forming a multilayered coextruded sheet, feedstock in melted form is fed from a respective extruder to a die assembly. Coextrusion systems for forming multilayer film or sheets of thermoplastic materials are generally known, as shown for example in DuBois and Pribble's "Plastics Mold Engineering Handbook", Fifth Edition, 1995, pages 524 to 529. As described, several streams of polymer melt from respective extruders are fed to a die having a feedblock for combining the thermoplastic layers upstream of a die expansion chamber which is generally of the coathanger-type, also referred to as "fishtail"-type. From the point of combining the melt streams, the die is used to form the combined melt streams into a sheet where the layers have been spread to make a multilayered product. The thickness of each layer in the final sheet is proportional to the thickness of its particular feed-block.

Other structures provide a die cavity for the reception of a separate manifold so that the combining of the layers upon exiting the manifold takes place within the die itself and is close as possible to the entrance to the

expansion chamber. The manifold comprises a plurality of slotted, layer distribution passages opening into the expansion chamber, the passages comprising mutually spaced apart openings lying parallel to the slotted die opening.

5 The resulting multilayered extruded sheet may be formed into a desired shaped final article by thermoforming techniques known in the art. Thermoforming comprises simultaneously heating and forming the extruded sheet into the desired shape. Once the desired shape has been obtained, the formed article is cooled below its thermoplastic temperature and removed
10 from the mold. In vacuum molding, the extruded sheet is placed over a concave mold and heated such as by an infra-red heater. Vacuum is applied to draw the extruded sheet into place against the mold cavity. The above may be modified by combining positive air pressure on top of the extruded sheet with vacuum from the underside to increase the molding force. In matched
15 or compression molding, matched male and female molds or dies are employed and the extruded sheet is formed between the mechanically compressed molds. Molds are typically made from a metal having high thermal conductivity such as aluminum. Thermoforming methods and tools are described in detail in DuBois and Pribble's "Plastics Mold Engineering
20 Handbook", Fifth Edition, 1995, pages 468 to 498.

The outer decorative chemically resistant filled layer is a polyester material. Polyesters include those comprising structural units of the following formula:



25 wherein each R^1 is independently a divalent aliphatic, alicyclic or aromatic hydrocarbon or polyoxyalkylene radical, or mixtures thereof and each A^1

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is independently a divalent aliphatic, alicyclic or aromatic radical, or mixtures thereof. Examples of suitable polyesters containing the structure of the above formula are poly(alkylene dicarboxylates), liquid crystalline polyesters, and polyester copolymers. It is also possible to use a branched polyester in which a branching agent, for example, a glycol having three or more hydroxyl groups or a trifunctional or multifunctional carboxylic acid has been incorporated. Furthermore, it is sometimes desirable to have various concentrations of acid and hydroxyl end groups on the polyester, depending on the ultimate end-use of the composition.

The R^1 radical may be, for example, a C_{2-10} alkylene radical, a C_{6-12} alicyclic radical, a C_{6-20} aromatic radical or a polyoxyalkylene radical in which the alkylene groups contain about 2-6 and most often 2 or 4 carbon atoms. The A^1 radical in the above formula is most often p- or m-phenylene, a cycloaliphatic or a mixture thereof. This class of polyester includes the poly(alkylene terephthalates). Such polyesters are known in the art as illustrated by the following patents, which are incorporated herein by reference.

2,465,319	2,720,502	2,727,881	2,822,348
3,047,539	3,671,487	3,953,394	4,128,526

Examples of aromatic dicarboxylic acids represented by the dicarboxylated residue A^1 are isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, 4,4' bisbenzoic acid and mixtures thereof. Acids containing fused rings can also be present, such as in 1,4- 1,5- or 2,6- naphthalenedicarboxylic acids. The preferred dicarboxylic acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid or mixtures thereof.

The most preferred polyesters are poly(ethylene terephthalate) ("PET"), and poly(1,4-butylene terephthalate), ("PBT"), poly(ethylene naphthanoate)

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("PEN"), poly(butylene naphthanoate), ("PBN") and (polypropylene terephthalate) ("PPT"), and mixtures thereof.

Also contemplated herein are the above polyesters with minor amounts, e.g., from about 0.5 to about 5 percent by weight, of units derived
5 from aliphatic acid and/or aliphatic polyols to form copolyesters. The aliphatic polyols include glycols, such as poly(ethylene glycol) or poly(butylene glycol). Such polyesters can be made following the teachings of, for example, U.S. Pat. Nos. 2,465,319 and 3,047,539.

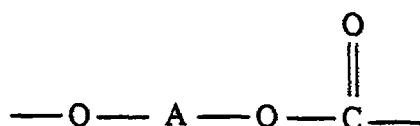
The preferred poly(1,4-butylene terephthalate) resin used in this
10 invention is one obtained by polymerizing a glycol component at least 70 mol %, preferably at least 80 mol %, of which consists of tetramethylene glycol and an acid or ester component at least 70 mol %, preferably at least 80 mol %, of which consists of terephthalic acid, and polyester-forming derivatives therefore.

15 The preferred polyesters used herein have an intrinsic viscosity of from about 0.4 to about 2.0 dl/g as measured in a 60:40 phenol/tetrachloroethane mixture or similar solvent at 23°-30° C. Preferably the intrinsic viscosity is 1.1 to 1.4 dl/g.

Preferably, the polyester composition includes a decorative
20 component. Typical decorative components include colorants in the form of dyes and fillers. One such decorative colorant is described in U.S. patent 5,510,398 to Clark et al. A speckled surface is achieved through a non-dispersing pigment as opposed to a filler because the non-dispersing pigment does not appreciably add to the base color of the resin. Rather, the non-
25 dispersing pigment provides a separate, visibly distinct and identifiable color at numerous sites across the surface of the material wherever the pigment material is visible. In other words, the speckle is visible in the filled polymer matrix as a distinct region of contrasting color.

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The preferred polyester composition is a blend with a polycarbonate resin. Polycarbonate resins useful in preparing the blends of the present invention are preferably aromatic polycarbonate resins. Typically these polycarbonates are prepared by reacting a dihydric phenol with a carbonate precursor, such as phosgene, a haloformate or a carbonate ester. Carbonate polymers may be typified as possessing recurring structural units of the formula



wherein A is a divalent aromatic radical of the dihydric phenol employed in the polymer producing reaction. The dihydric phenols which may be employed to provide such aromatic carbonate polymers are mononuclear or polynuclear aromatic compounds, containing as functional groups two hydroxy radicals, each of which is attached directly to a carbon atom of an aromatic nucleus. Typical dihydric phenols are: 2,2-bis(4-hydroxyphenyl) propane; hydroquinone; resorcinol; 2,2-bis(4-hydroxyphenyl) pentane; 2,4'-(dihydroxydiphenyl) methane; bis(2-hydroxyphenyl) methane; bis(4-hydroxyphenyl) methane; 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; fluorenone bisphenol, 1,1-bis(4-hydroxyphenyl) ethane; 3,3-bis(4-hydroxyphenyl) pentane; 2,2-dihydroxydiphenyl; 2,6-dihydroxynaphthalene; bis(4-hydroxydiphenyl)sulfone; bis(3,5-diethyl-4-hydroxyphenyl)sulfone; 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane; 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane; 2,4'-dihydroxydiphenyl sulfone; 5'-chloro-2,4'-dihydroxydiphenyl sulfone; bis-(4-hydroxyphenyl)diphenyl sulfone; 4,4'-dihydroxydiphenyl ether; 4,4'-dihydroxy-3,3'-dichlorodiphenyl ether; 4,4-dihydroxy-2,5-dihydroxydiphenyl ether; and the like.

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Other dihydric phenols which are also suitable for use in the preparation of the above polycarbonates are disclosed in U.S. Pat Nos. 2,999,835; 3,038,365; 3,334,154; and 4,131,575.

These aromatic polycarbonates can be manufactured by known processes, such as, for example and as mentioned above, by reacting a dihydric phenol with a carbonate precursor, such as phosgene, in accordance with methods set forth in the above-cited literature and in U.S. Pat. No. 4,123,436, or by transesterification processes such as are disclosed in U.S. Pat. No. 3,153,008, as well as other processes known to those skilled in the art.

It is also possible to employ two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the polycarbonate mixtures of the invention. Polyarylates and polyester-carbonate resins or their blends can also be employed. Branched polycarbonates are also useful, such as are described in U.S. Pat. No. 4,001,184. Also, there can be utilized blends of linear polycarbonate and a branched polycarbonate. Moreover, blends of any of the above materials may be employed in the practice of this invention to provide the aromatic polycarbonate.

In any event, the preferred aromatic carbonate for use in the practice in the present invention is a homopolymer, e.g., a homopolymer derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) and phosgene, commercially available under the trade designation LEXAN Registered TM from General Electric Company.

The instant polycarbonates are preferably high molecular weight aromatic carbonate polymers having an intrinsic viscosity, as determined in chloroform at 25° C of from about 0.3 to about 1.5 dl/gm, preferably from

about 0.45 to about 1.0 dl/gm. These polycarbonates may be branched or unbranched and generally will have a weight average molecular weight of from about 10,000 to about 200,000, preferably from about 20,000 to about 100,000 as measured by gel permeation chromatography.

It is further preferred to employ an inorganic filler to the thermoplastic resin to impart additional beneficial properties such as thermal stability, increased density, and texture. Inorganic fillers provide a ceramic-like feel to articles thermoformed from resin composition. Preferred inorganic fillers which are employed in the present thermoplastic compositions include: zinc oxide, barium sulfate, zirconium silicate, strontium sulfate, as well as mixtures of the above. The preferred form of barium sulfate will have a particle size of 0.1-20 microns. The barium sulfate may be derived from a natural or a synthetic source.

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The molding compositions may include from 20 - 85% by weight, preferably 30 - 75% by weight or most preferably 30 - 45% by weight of total composition of an inorganic filler component. For certain applications where a ceramic like product is desired, more than 50%, or more preferably 60 - 85% by weight of the total composition of filler component should be employed. The filler material is chosen to enhance the decorative properties and the renewable properties of the resin sheet. The metal sulfate salts as well as their hydrates are preferred mineral fillers. Preferred metal sulfate salts are the Group IA and Group IIA metal sulfates with barium, calcium and magnesium sulfates being preferred. Barium sulfate which is non-toxic and insoluble in dilute acids is especially preferred. Barium sulfate may be in the form of the naturally occurring barytes or as synthetically derived barium sulfate using well known synthetic techniques. The particle size may vary from 0.5 to 50 microns, preferably from 1 to 15 microns and most preferably 8 microns.

The composition desirably contains impact modifiers such as a rubbery impact modifier. Preferably such impact modifiers are utilized in an amount less than about 30, and preferably less than about 20 percent, more preferably less than about 15 percent by weight based on the total weight of the composition.

The preferred thermoforming additives for thermoforming have a linear or radial (branched) A-B-A block structure. They include styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS). A diblock polymer of the type styrene-ethylene/propylene (SEP) is also included. The most preferred thermoforming additive is of the A-B-A block structure of the type styrene-ethylene/butylene styrene (S-EB-S).

The filled polyester molding composition includes a polyester resin, an inorganic filler material, a polycarbonate resin; and an effective amount of a styrenic modifier which may include random, block, and radial block

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copolymers. A particularly useful class of modifiers comprises the AB (diblock) and ABA (triblock) copolymers alkenylaromatic compounds, especially those comprising styrene blocks. The conjugated diene blocks may be unsaturated, partially or entirely hydrogenated, whereupon they may be represented as ethylene-propylene blocks or the like and have properties similar to those of olefin block copolymers. Examples of triblock copolymers of this type are polystyrene-polybutadiene-polystyrene (SBS), hydrogenated polystyrene-polybutadiene-polystyrene (SEBS), polystyrene-polyisoprene-polystyrene (SIS), poly (a-methylstyrene)-polybutadiene-poly(a-methylstyrene) and poly(a-methylstyrene)-polyisoprene-poly(a-methylstyrene). Particularly preferred triblock copolymers are available commercially as CARIFLEZ®, Kraton D®, and KRATON G® from Shell.

Typical impact modifiers are derived from one or more monomers selected from the group consisting of olefins, vinyl aromatic monomers, acrylic and alkylacrylic acids and their ester derivatives as well as conjugated dienes. Impact modifiers include the rubbery high-molecular weight materials including natural and synthetic polymeric materials showing elasticity at room temperature. They include both homopolymers and copolymers, including random, block, radial block, graft and core-shell copolymers as well as combinations thereof. Suitable modifiers include core-shell polymers built up from a rubber-like core on which one or more shells have been grafted. The core typically consists substantially of an acrylate rubber or a butadiene rubber. One or more shells typically are grafted on the core. The shell preferably comprises a vinylaromatic compound and/or a vinylcyanide and/or an alkyl(meth)acrylate. The core and/or the shell(s) often comprise multi-functional compounds which may act as a cross-linking agent and/or as a grafting agent. These polymers are usually prepared in several stages.

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Olefin-containing copolymers such as olefin acrylates and olefin diene terpolymers can also be used as impact modifiers in the present compositions. An example of an olefin acrylate copolymer impact modifier is ethylene ethylacrylate. Other higher olefin monomers can be employed in copolymers with alkyl acrylates, for example, propylene and n-butyl acrylate. The olefin diene terpolymers are well known in the art and generally fall into the EPDM (ethylene propylene diene) family of terpolymers. Polyolefins such as polyethylene, polyethylene copolymers with alpha olefins are also of use in these compositions. Polyolefin copolymers with glycidyl acrylates or methacrylates may be especially effective in the impact modification of polyester containing blends.

Styrene-containing polymers can also be used as impact modifiers. Examples of such polymers are acrylonitrile-butadiene-styrene (ABS), acrylonitrile-butadiene-alpha-methylstyrene, styrene-butadiene, styrene butadiene styrene (SBS), styrene ethylene butylene styrene (SEBS), methacrylate-butadiene-styrene (MBS), and other high impact styrene-containing polymers.

Impact modifiers are typically based on a high molecular weight styrene-diene rubber. A preferred class of rubber materials are copolymers, including random, block and graft copolymers of vinyl aromatic compounds and conjugated dienes. Exemplary of these materials there may be given hydrogenated, partially hydrogenated, or non-hydrogenated block copolymers of the A-B-A and A-B type wherein A is polystyrene and B is an elastomeric diene, e.g. polybutadiene, polyisoprene, radial teleblock copolymer of styrene and a Y conjugated diene, acrylic resin modified styrene-butadiene resins and the like; and graft copolymers obtained by graft-copolymerization of a monomer or monomer mix containing a styrenic compound as the main component to a rubber-like polymer. The rubber-like

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polymer used in the graft copolymer are as already described herein including polybutadiene, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, ethylene-propylene copolymer, ethylene butylene copolymer, polyacrylate and the like. The styrenic compounds includes
5 styrene, methylstyrene, dimethylstyrene, isopropylstyrene, α -methylstyrene, ethylvinyltoluene and the like.

Procedures for the preparation of these polymers are found in U.S. Patent Nos. 4,196,116; 3,299,174 and 3,333,024, all of which are incorporated by reference.

10 An effective amount of a block copolymer of the A-B-A may be utilized as impact modifier. In accordance with the principles of the present invention, the A-B-A type ingredient is present an amount sufficient for enhancing the thermo-formability of articles produced from the resin. A is a polymerized mono-alkenyl aromatic hydrocarbon block and B is polymerized
15 conjugated diene hydrocarbon block.

In the above type, blocks A typically constituting 3-50 weight percent of the copolymer and the unsaturation of block B having been reduced by hydrogenation. The filled polyester molding composition of the present invention comprises from 5-40 parts by weight, and preferably 10-30 parts by
20 weight of the block copolymer.

With respect to the hydrogenated block copolymers of the A-B-A type, they are made by means known in the art and they are commercially available.

These materials are described in U.S. Pat. No. 3,421,323 to Jones,
25 which is hereby incorporated by reference.

Prior to hydrogenation, the end blocks of these copolymers comprise homopolymers or copolymers preferably prepared from alkenyl aromatic hydrocarbons and particularly vinyl aromatic hydrocarbons wherein the

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aromatic moiety may be either monocyclic or polycyclic. Typical monomers include styrene, alpha methyl styrene, vinyl xylene, ethyl vinyl xylene, vinyl naphthalene and the like or mixtures thereof. The end blocks may be the same or different. The center block may be derived from, for example, polyisoprene
5 or polybutadiene.

The ratio of the copolymers and the average molecular weights can vary broadly although the molecular weight of center block should be greater than that of the combined terminal blocks. Typically, terminal blocks A have average molecular weights of 4,000-115,000 and center block B e.g., a
10 polybutadiene block with an average molecular weight of 20,000-450,000. Still more preferably, the terminal blocks have average molecular weights of 8,000-60,000 while the polybutadiene polymer blocks has an average molecular weight between 50,000 and 300,000. The terminal blocks may comprise 2-50% by weight, or more preferably, 5-30% by weight of the total block polymer.
15 The preferred copolymers will be those formed from a copolymer having a polybutadiene center block wherein 35-55%, or more preferably, 40-50% of the butadiene carbon atoms are vinyl side chains.

Block copolymers such as Kraton G-GXT-0650, Kraton G-GXT-0772 and Kraton G-GXT-0782 are available from Shell Chemical Company, Polymers
20 Division.

Block copolymers of the A-B-A type may also be considered with respect to the formula A'-B'-A' block copolymers.

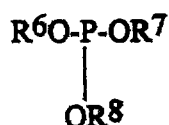
The ratio of the co-monomers may vary broadly. Typically, the the molecular weight center block is greater than that of the combined terminal
25 blocks. Preferably, with the above limitation, the molecular weight of the terminal blocks each will range from about 2000 to about 100,000 while that of the center block will range from about 25,000 to about 1,000,000.

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The impact modifier is desirable present in an amount from 0 to 40 percent by weight, preferable from 4 to 15 percent, for deep drawing sheets, a higher level on the order from 20 to 40 percent is preferred.

In the thermoplastic compositions which contain a polyester and a polycarbonate resin, it is preferable to use a stabilizer material. Typically, such stabilizers are used at a level of 0.01-10 weight percent and preferably at a level of from 0.05-2 weight percent.

The preferred stabilizers include an effective amount of an acidic phosphate salt; an acid, alkyl, aryl or mixed phosphite having at least one hydrogen or alkyl group; a Group IB or Group IIB metal phosphate salt; a phosphorous oxo acid, a metal acid pyrophosphate or a mixture thereof. The suitability of a particular compound for use as a stabilizer and the determination of how much is to be used as a stabilizer may be readily determined by preparing a mixture of the polyester component, the polycarbonate and the filler with and without the particular compound and determining the effect on melt viscosity or color stability or the formation of interpolymer. The acidic phosphate salts include sodium dihydrogen phosphate, mono zinc phosphate, potassium hydrogen phosphate, calcium hydrogen phosphate and the like. The phosphites may be of the formula:

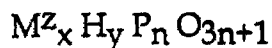


where R^6 , R^7 and R^8 are independently selected from the group consisting of hydrogen, alkyl and aryl with the proviso that at least one of R^6 , R^7 and R^8 is hydrogen or alkyl.

The phosphate salts of a Group IB or Group IIB metal include zinc phosphate, copper phosphate and the like. The phosphorous oxo acids include phosphorous acid, phosphoric acid, polyphosphoric acid or hypophosphorous acid.

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The polyacid pyrophosphates of the formula:



wherein M is a metal, x is a number ranging from 1 to 12 and y is a number ranging 1 to 12, n is a number from 2 to 10, z is a number from 1 to 5
5 and the sum of (xz)+y is equal to n+2.

These compounds include $Na_3HP_2O_7$; $K_2H_2P_2O_7$; $Na_4P_2O_7$; $KNaH_2P_2O_7$ and $Na_2H_2P_2O_7$. The particle size of the polyacid pyrophosphate should be less than 75 microns, preferably less than 50 microns and most preferably less than 20 microns.

10 The preferred polyester layer comprises a decorative component, polycarbonate, an organic filler, a reinforcing material, and a stabilizer. The polyester material preferably comprises Enduran™ 7322 available from the GE Plastics component of General Electric Company is a preferred polyester resin material for the outer layer.

15 A preferred composition includes the following: polyester from about 10 to about 40 percent by weight, preferably the polyester comprising polybutylene terephthalate in an amount from about 7 to about 25 percent and polyethylene terephthalate from about 3 to about 10 percent, aromatic polycarbonate from about 10 to about 25 percent, stabilizer from about 0.01
20 to about 10 percent, impact modifier from 4 to about 15 percent, barium sulfate from about 30 to about 40 percent, with pigment or dyes being present in an effective amount to generate the desired surface effect and when combined with additional ingredients being present in an amount less than about 5 percent.

25 An adjacent thermoplastic support layer comprises a heat deformable material having mechanical properties such as impact resistance and melt strength which desirably exceed such properties of the decorative polyester layer so as to enhance the mechanical properties of the composite. Suitable

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thermoplastic organic polymers for the inner layer includes acrylonitrile-butadiene-styrene (ABS), polycarbonate, polycarbonate/ABS blend, a copolycarbonate-polyester, acrylic-styrene-acrylonitrile (ASA), acrylonitrile-(ethylene-polypropylene diamine modified)-styrene (AES), phenylene ether
5 resins, blends of polyphenylene ether/polyamide (NORYL GTX® from General Electric Company), blends of polycarbonate/polybutylene terephthalate and impact modifier (XENOY® resin from General Electric Company) blends of polycarbonate/PET/PBT, polyamides, phenylene sulfide resins,), poly(vinyl chloride) PVC, polymethylmethacrylate (PMMA), and
10 High-impact Polystyrene (HIPS)

A preferred composition for the support layer comprises an ABS type polymer. In general, ABS type polymers contain two or more polymeric parts of different compositions which are bonded chemically. The polymer is preferably prepared by polymerizing a conjugated diene, such as butadiene
15 or a conjugated diene with a monomer copolymerizable therewith, such as styrene, to provide a polymeric backbone. After formation of the backbone, at least one grafting monomer, and preferably two, are polymerized in the presence of the prepolymerized backbone to obtain the graft polymer. These resins are prepared by methods well known in the art.

20 The backbone polymer, as mentioned, is preferably a conjugated diene polymer such as polybutadiene, polyisoprene, or a copolymer, such as butadiene-styrene, butadiene-acrylonitrile, or the like. Examples of dienes that may be used are butadiene, isoprene, 1,3-hepta-diene, methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-pentadiene; 1,3- and 2,4-
25 hexadienes, chloro and bromo substituted butadienes such as dichlorobutadiene, bromobutadiene, debromobutadiene, mixtures thereof, and the like. A preferred conjugated diene is butadiene.

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One monomer or group of monomers that may be polymerized in the presence of the prepolymerized backbone are monovinylaromatic hydrocarbons. Examples of the monovinylaromatic compounds and alkyl-, cycloalkyl-, aryl-, alkaryl-, aralkyl-, alkoxy-, aryloxy-, and other substituted vinylaromatic compounds include styrene, 3-methylstyrene; 3,5-
5 diethylstyrene, 4-n-propylstyrene, alpha -methylstyrene, alpha -methyl vinyltoluene, alpha -chlorostyrene, alpha -bromostyrene, dichlorostyrene, dibromostyrene, tetra-chlorostyrene, mixtures thereof, and the like. The preferred monovinylaromatic hydrocarbons used are styrene and/or alpha-
10 methylstyrene.

A second group of monomers that may be polymerized in the presence of the prepolymerized backbone are acrylic monomers such as acrylonitrile, substituted acrylonitrile and/or acrylic acid esters, exemplified by acrylonitrile, and alkyl acrylates such as methyl methacrylate. Examples of
15 such monomers include acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha -chloroacrylonitrile, beta -chloroacrylonitrile, alpha -bromoacrylonitrile, and beta -bromoacrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, propyl acrylate, isopropyl acrylate, and mixtures thereof. The preferred acrylic monomer is acrylonitrile and the preferred
20 acrylic acid esters are ethyl acrylate and methyl methacrylate.

In the preparation of the graft polymer, the conjugated diolefin polymer or copolymer exemplified by a 1,3-butadiene polymer or copolymer comprises about 50% by weight of the total graft polymer composition. The monomers polymerized in the presence of the backbone, exemplified by
25 styrene and acrylonitrile, comprise from about 40 to about 95% by weight of the total graft polymer composition.

The second group of grafting monomers, exemplified by acrylonitrile, ethyl acrylate or methyl methacrylate, of the graft polymer composition,

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preferably comprise from about 10% to about 40% by weight of the total graft copolymer composition. The monovinylaromatic hydrocarbon exemplified by styrene comprise from about 30 to about 70% by weight of the total graft polymer composition.

5 In preparing the polymer, it is normal to have a certain percentage of the polymerizing monomers that are grafted on the backbone combine with each other and occur as free copolymer. If styrene is utilized as one of the grafting monomers and acrylonitrile as the second grafting monomer, a certain portion of the composition will copolymerize as free styrene-
10 acrylonitrile copolymer. In the case where alpha -methylstyrene (or other monomer) is substituted for the styrene in the composition used in preparing the graft polymer, a certain percentage of the composition may be an alpha -methylstyrene-acrylonitrile copolymer. Also, there are occasions where a copolymer, such as alpha -methylstyrene-acrylonitrile, is added to the graft
15 polymer copolymer blend. When the graft as polymer-copolymer blend is referred to herein, it is meant optionally to include at least one copolymer blended with the graft polymer composition and which may contain up to 90% of free copolymer.

Optionally, the elastomeric backbone may be an acrylate rubber, such
20 as one based on n-butyl acrylate, ethylacrylate, 2-ethylhexylacrylate, and the like. Additionally, minor amounts of a diene may be copolymerized in the acrylate rubber backbone to yield improved grafting with the matrix polymer.

The preferred ABS material for the support layer comprises Cycolac® GPX3800 and Cycolac® LSA resin available from the GE Plastics component
25 of General Electric Company.

Additional material for the support layer include polycarbonate and polycarbonate blends. The polycarbonate is as before described with Lexan® resin available from GE Plastics component of General Electric Company a

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preferred polycarbonate. Resin blends of polycarbonate may also be used. Preferred polycarbonate resin blends include Xenoy®1731, a polycarbonate poly (butylene terphthalate) blend, Cycloy®MC8002 and MC8100 blends of polycarbonate and ABS.

5 Typical polyphenylene ether resin is a poly(2,6-dimethyl-1,4-phenylene)ether resin having an intrinsic viscosity of from about 0.3 dl/g to about 0.60 dl/g in chloroform. The polyphenylene ether resins useful herein are well known in the art and may be prepared from a number of catalytic and non-catalytic processes from corresponding phenols or reactive derivatives
10 thereof. Examples of polyphenylene ethers and methods for their production are disclosed in U.S. Pat. Nos. 3,306,874; 3,306,875; 3,257,357 and 3,257,358, all incorporated herein by reference.

Typical polyamides suitable for the present invention may be obtained by polymerizing a monoamino monocarboxylic acid or a lactam thereof
15 having at least 2 carbon atoms between the amino and carboxylic acid group; or by polymerizing substantially equimolar proportions of a diamine which contains at least 2 carbon atoms between the amino groups and a dicarboxylic acid; or by polymerizing a monoaminocarboxylic acid or a lactam thereof as defined above together with substantially equimolecular proportions of a
20 diamine and a dicarboxylic acid. The dicarboxylic acid may be used in the form of a functional derivative thereof, for example an ester.

Multilayer structures of ENDURAN® 7322 resin with other resins offer lower cost alternatives to monolayer ENDURAN® 7322 resin while maintaining the surface appearance of a ENDURAN® 7322 resin layer by
25 substituting a portion of the ENDURAN® 7322 resin layer with lower cost resins. Performance properties such as stiffness, heat resistance, impact resistance and/or flammability in the structures are improved by incorporating materials which enhance these properties relative to the

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performance of monolayer ENDURAN® 7322 resin. Processing advantages in thermoforming are also realized by incorporating materials with greater melt strength than the monolayer structure so that larger parts may be thermoformed.

5 Multilayer structures of ENDURAN® 7322 can be combined with various other resins to create systems with reduced cost and/or improved performance. These other resins include ABS (CYCOLAC® GPX3800 resin, CYCOLAC® LSA resin), PC/PBT blends (XENOY® resin), polycarbonate (LEXAN® resin), PC/ABS blends (CYCOLOY® MC8002 resin, CYCOLOY®
10 MC8100 resin), PPO® resin based blends (NORYL® resin), poly(vinyl chloride) PVC, and High-impact Polystyrene (HIPS). These resins may also contain reinforcing fillers (such as glass fibers) which increase stiffness of the structure.

 These structures may be produced by coextrusion and may consist of
15 one or more different materials in addition to the ENDURAN® 7322 layer. Layers may include regrind material. Sheet produced by coextrusion may be then thermoformed to fabricate parts. Sheet or fabricated parts maintain the surface qualities (appearance, feel, etc.) of monolayer ENDURAN® 7322 products and may also be used with special color effects used with
20 ENDURAN® 7322 monolayer sheet.

 Thermoforming of the sheet is performed by placing the sheet over a concave mold and heated such as by an infra-red heater. Vacuum is applied to draw the extruded sheet into place against the mold cavity. Combinations of ENDURAN® 7322 with CYCOLAC® GPX3800, CYCOLAC® LSA, and
25 CYCOLOY® MC8002 have been co-extruded and thermoformed on a 12" x 12" tool with 1" depth. All three combinations have produced good quality sheet with good adhesion and material compatibility. Thermoformed parts

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retained adhesion of layers and surface quality. Other combinations are being extruded and thermoformed.

Multilayer structures can be used either as surfacing materials (for countertops or wall coverings) in the form of coextruded sheet, or in any thermoforming application involving ENDURAN® 7322 resin such as sinks or tubs.

Preferred thickness for the outer decorative layer is from about 0.002 inch (2 mils) to about .250 inch (0.250 mils) with preferred thicknesses of the backing thermoplastic layer being from about 0.050 inch (50 mils) to about .500 inch (500 mils).

Preferred multilayered structures include the following as set forth below:

Enduran™ resin/Cycolac® resin for thermoforming sinks and other articles.

A two layered structure having a total thickness of 200 to 400 mils, preferably 300 mils, with the outer cap layer being 15 to 40 percent of the total thickness.

Enduran™ resin/Cycolac® resin for surfacing applications such as counters and wall.

A two layered structure having a total thickness of 90 to 125 mils, with the outer cap layer being 15 to 30 percent of the total thickness.

Enduran™ resin/ Enduran™ resin for decorative surfacing applications such as counters and wall where a pattern is developed by removal of a portion of the outer layer to expose an adjacent layer.

A two layered structure having a total thickness of 90 to 125 mils, with the outer cap layer being 15 to 30 percent of the total thickness.

A two layer structure comprises Enduran™ resin/ Cycolac® resin and regrind mixture. The outer cap layer is about 33% of the total thickness. The

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total thickness is 90 mils. The Cycolac® resin and regrind mixture contains 50% by weight regrind.

A three layer structure comprises is Enduran™ resin/Cycolac® resin and regrind mixture/Cycolac® resin. The outer cap layer is about 33% of the total thickness. The total thickness is 90 mils. The Cycolac® resin and regrind mixture contains 50% by weight regrind. The bottom layer of Cycolac® resin is 33% of the total thickness. As referred to in these examples, the regrind layer comprises polyester resin and acrylonitrile-butadiene-styrene resin which remain after processing in the form of scrap and excess material. The scrap material is ground and incorporated into the multilayered structure as a separate layer or as part of an acrylonitrile-butadiene-styrene resin layer.

A most preferred two layer structure comprises a co-extruded layer of Enduran™ 7322 resin, Table 1, adjacent a layer of Cycolac® 29344A resin, Table 2. Enduran™ resin and Cycolac® resin are available from the GE Plastics component of General Electric Company.

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Table 1 - Enduran™ resin wt% of ingredient based on total wt%

Valox® 315 resin - poly(butylene terephthalate) - General Electric Company	17.45
Lexan® 131 resin - polycarbonate - General Electric Company	27.25
poly(ethylene terephthalate)	9.8
Kraton G 1651 SEBS a styren-ethylene butylene-styrene block copolymer - Shell Chemical Co.	7.5
BaSO ₄	37.0
PETS - tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))methane	0.2
TINUVIN 234 - UV absorber (Tinuvin 234, a benzotriazole	0.3
PEP-Q - tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylenediphosphonite (Sandostab P-EPZ phosphonite	0.3
Irgafos 168	0.1
MZP Mono zinc phosphate dihydrate (Zn(H ₂ PO ₄) ₂ H ₂ O)	0.1

Table 2 - Cycolac® resin wt% of ingredient based on total wt%

360 HRG - High Rubber Graft ABS	60
570 SAN - styrene-acrylonitrile	40
Pluronic F-88 -	0.2
Wingstay® L antioxidant stabilizer	0.15
Ultranox® 626 stabilizer - GE Specialty Chemicals	0.2
silicone fluid	0.10
Santicizer	0.40

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The desired thickness of the co-extruded sheet is somewhat dependent upon the use of the sheet. Generally, an overall thickness of from 0.02 to 0.50 inch is preferred with the thickness of the Enduran resin layer being from about 5 to about 85 percent of the total thickness. Some of the preferred thickness for different type of uses are set forth in the Table 3.

Table 3 - Thickness of Enduran resin/Cyclac resin co-extruded layers

	Total Sheet Thickness	% Enduran
Shower Wall Surrounds	0.065	20%
Kitchen/bathroom Counters	0.090	40%
Shower Trays	0.220	20%
Lavatory Tops	0.210	20%
Standard size Bathtubs	0.250	30%
Large Jacuzzi Bathtubs	0.285	30%

For a co-extruded two layer sheet, it is highly desirable that the layers be compatible so that the layers adhere. It is desirable to avoid ingredients in one layer that might react with the ingredients in the other layer. The above layers are compatible and are characterized by the absence of reactive materials such as some metal oxides such as magnesium oxide.

To achieve sound damping, it is contemplated that a foam layer may be adjacent the support or inner layer. Typically, the foam layer has a 10 to 50% density reduction for lower cost, weight reduction and sound damping. The foam may be foamed in place. See U.S. 5,486,407 to Noell et. al. It is also contemplated that the inner support layer may be adhered to a cellulosic based material such as a particleboard, fiberboard, chipboard or plywood. It is also contemplated that abrasive resistant coatings such as described in U.S. 5,446,767 may be utilized in conjunction with the present invention.

Thermoforming methods may be utilized as set forth in U.S. 5,601,679 to Mulcahy et al. A co-extruded sheet may be vacuum formed. Typically, the

vacuum former and surrounding metal framework are preheated to minimize chill of the sheet. The sheet is placed on a vacuum box and mounted on the bottom side of the former or platten. Clamp frames are activated for mechanically holding the sheet in place. A suitable heat shield, such as
5 aluminum foil, may be utilized for avoiding heating the surface at selected locations such as other than a sink portion. The sheet is then exposed to the thermo-forming ovens. Top and bottom heaters may be used. During heating, the sheet begins to sag. Once the sheet reaches its proper forming temperature, the assembly is shuttled to a vacuum forming box where sink is
10 vacuum formed in a box. The box has a plurality openings in a mold form for drawing the sheet into mold during the forming operation. After cooling, the resulting thermoformed sheet is removed.

The following specific examples illustrate the present invention. The Examples set forth in Table 4 are for comparison purposes, with Formulations 4 and 6 illustrating results employing the preferred rheology modifiers of the present invention.

TABLE 4

[illegible]

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Table 4 contains comparative studies of various rheology modifiers in unfilled systems. Regardless of the modifier used, the melt elongation of the resulting formulation is well above 555%. Hence, these systems do not differentiate between the rheology modifiers used.

5 Table 5 is directed to the comparison of rheology modifiers in filled systems.

TABLE 5

ADDITIVES	1	2	3	4	5	6	7	8	9	10	11
HEOM 007	0	0	15.0	10.0	7.50	5.0	10.0	15.0	0	0	0
MBS-EXL 3691	0	0	0	5.0	7.5	10.0	10.0	5.0	0	0	0
Kraton G1651	7.5	7.5	0	0	0	0	0	0	10.0	15.0	20.0
PET Linear IV = 0.56	9.8	9.8	8.46	8.46	8.46	8.46	7.56	7.56	9.36	8.46	7.56
LEXAN 131 Linear PC	0	27.2	0	0	0	0	0	0	0	0	0
PC Branched TMTC Based	27.2	0	23.4	23.4	23.4	23.4	20.9	20.9	25.9	23.4	20.92
VALOX 315 PBT	17.5	17.5	15.1	15.1	15.1	15.1	13.5	13.5	16.7	15.1	13.5
BaSO ₄	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Stabilizer Package	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
TEST RESULTS											
Melt Elasticity (% Elongation)	334	375	170	133	127	99	94	150	280	309	270
Original Thickness (inch)	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Part Thickness (After Thermoforming)	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.03	-
	3	6	3	1	1	0	6	5	6	3	

10 Clearly, the melt elongation drops substantially when moving from unfilled to filled systems. Formulations 1, 2, 9, 10, 11 have the highest melt elongation and all of them are modified with Kraton G1651. To those skilled in the art, the rheology modification of unfilled PC/PBT for enhanced blow molding and/or thermoforming is achieved by using core shell modifiers in
 15 single phase or dual phase modification. In the barium sulfate filled formulations delineated above, formulations 3 through 8 have the lowest melt elongation, despite the fact that core shell modifiers (HEOM, MBS) are being used. Another key test result of this study is the vertical wall thickness after thermoforming. Vertical walls in thermoformed part are the most susceptible

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to thinning. Part thinning is an important measure of material distribution throughout a given part. Again, formulations 3 through 8 have the lowest thickness retention, while those with Kraton G1651 have the highest. Consequently, taking into account melt elongation and vertical wall thickness,

5 Kraton G1651 containing formulations outperform those containing HEOM and/or MBS. In Table 5, the influence of high molecular weight acrylic polymer is assessed. According to Ref. 11, these additives improve the melt strength of unfilled PB/PBT blends.

TABLE 6

10

ADDITIVES	1	2	3	4	5	6	7
PC Branched TMTC	23.43	0	0	0	0	0	20.92
PC Branched RL694-111-THPE	0	23.43	0	0	20.92	0	0
LEXAN 131 Linear PC	0	0	23.43	20.92	0	22.42	0
K400 Acrylic Imp. Mod.	0	0	0	5.00	5.00	2.00	5.00
PET Linear IV=0.56	8.46	8.46	8.46	7.56	7.56	8.10	7.56
VALOX 315 Linear PBT	15.06	15.06	15.06	13.47	13.47	14.43	13.47
Kraton G1651	15.0	15.0	15.0	15.0	15.0	15.0	15.0
BaSO ₄	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Stabilizer Package	1.05	1.05	1.05	1.05	1.05	1.05	1.05
TEST RESULTS							
Melt Elasticity (% Elongation)	246	267	309	323	379	353	299
Part Original Thickness (inch)	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Part Thickness (After Thermoforming)	0.030	0.029	0.038	0.016	0.015	0.021	0.011

The addition of the high molecular weight acrylic polymer clearly improves the melt elongation as in formulations 4 through 7 compared to

15 formulation 3. However, they do have a deleterious effect on thickness retention; thus, are detrimental to the thermoforming and/or blowmolding of filled PC/PBT blends. The preferred compositions have a melt elasticity as % elongation of greater than about 300.

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Table 7

ADDITIVES	1	2	3	4	5	6	7
LEXAN 131 Linear PC	23.2	23.2	23.2	23.2	23.2	23.2	23.2
VALOX 315 Linear PBT	15.25	15.25	15.25	15.25	15.25	15.25	15.25
PET Linear IV=0.56	8.50	8.50	8.50	8.50	8.50	8.50	8.50
BaSO ₄	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Stabilizer Package	1.05	1.05	1.05	1.05	1.05	1.05	1.05
Kraton G1651 (SEBS, High MW)	15.0						
Vector 2518 (SBS, Med MW)		15.0					
Vector 8508D (SBS, Low MW)			15.0				
Kraton G1702 (SEP, High MW)				15.0			
Kraton D1102 (SBS, MedLow MW)					15.0		
Kraton D1118 (SBS, Med MW)						15.0	
Kraton D1184 (SBS, High MW, radial)							15.0
<u>TEST RESULTS</u>							
Melt Elasticity (% Elongation)	>555	>555	183	>555	262	214	>555
Unnotched Izod impact (ft-lb/in)	43	16	14	35	17	17	31
Biaxial impact (ft-lb)	15.7	7.3	6.7	7.1	4.1	6.8	8.6

In Table 7, it is shown that A-B-A type impact modifiers desirable have a high molecular weight in order to provide a high melt elasticity. In addition, the type of rubbery block affects the impact of the final product, which is also important to its function as a useful thermoformed article.

Although those skilled in the art have relied on branched polymers (crystalline and/or amorphous) to improve thermoformability and blowmoldability, that assertion is not universal in the filled systems we are evaluating. Formulations 1 and 2 contain branched polycarbonate; however,

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their melt elongation is lower than that of a formulation which contains a linear but high molecular weight polycarbonate. Moreover, the thickness retention of vertical walls of thermoformed parts containing branched polycarbonate is not as good as the one with linear high molecular weight polycarbonate. We would rather advance the dual concept of high molecular weight and branched as being beneficial to thermoforming and/or blowmolding.

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What is claimed is:

1. A thermoplastic composite comprising an extruded thermoformable self-supporting sheet having an outer decorative chemically resistant and renewable filled polyester layer and an adjacent inner supporting thermoplastic layer for enhancing desirable mechanical properties of the composite.
2. A thermoplastic composite according to claim 1 wherein said decorative outer polyester layer comprises a colorant, an inorganic filler, an effective amount of a stabilizer, and optionally polycarbonate, and an impact modifier.
3. A thermoplastic composite according to claim 2 wherein the adjacent inner thermoplastic layer comprises a heat deformable layer having mechanical properties such as impact resistance and melt strength which desirably exceed these properties as possessed by the outer polyester layer.
4. A thermoplastic composite according to claim 3 wherein the adjacent inner thermoplastic layer comprises acrylonitrile-butadiene-styrene, polycarbonate, polycarbonate/ acrylonitrile-butadiene-styrene blend, copolycarbonate-polyester, acrylic-styrene-acrylonitrile, acrylonitrile-(ethylene-polypylene diamine modified)-styrene, phenylene ether resins, blends of polyphenylene ether/polyamide, blends of polycarbonate/polybutylene terephthalate and impact modifier, blends of polycarbonate/PET/PBT, polyamides, phenylene sulfide resins, poly(vinyl chloride), polymethylmethacrylate (PMMA), and high-impact polystyrene.
5. A thermoplastic composite according to claim 4 wherein said outer polyester layer comprises an inert mineral filler.
6. A thermoplastic composite according to claim 5 wherein said outer polyester layer comprises an inert mineral filler comprising barium sulfate.



7. A thermoplastic composite according to claim 6 wherein said outer polyester layer comprises from about 10 to about 40 percent by weight poly(butylene terephthalate) or poly(ethylene terephthalate), aromatic polycarbonate from about 10 to about 25 percent, stabilizer from about 0.01 to about 10 percent, impact modifier from 4 to about 15 percent, barium sulfate from about 30 to about 40 percent, and additional ingredients including pigment or dyes present in an effective amount less than 5 percent.
8. A thermoplastic composite according to claim 7 wherein said outer polyester layer and said adjacent inner are extruded and have an overall thickness from 0.02 inch to 0.5 inch wherein the thickness of said polyester layer is from about 5 to about 85 percent of the overall thickness.
9. A thermoplastic composite according to claim 6 wherein said outer polyester layer comprises a thermoformed material comprising a two layered structure having a total thickness of 200 to 400 mils with an outer layer comprising polyester material and being 15 to 40 percent of the total thickness.
10. A thermoplastic composite according to claim 6 wherein multilayered material comprises a sheet having a two layered structure having a total thickness of 90 to 125 mils wherein said outer polyester layer comprises about 15 to 30 percent of the total thickness and said inner layer comprises an acrylonitrile-butadiene-styrene resin.
11. A thermoplastic composite according to claim 6 comprising at least a two layer polyester outer layer for having a decorative surface, said inner layer having different color than said outer layer, said pattern being developed by removal of a portion of the outer layer to expose said adjacent layer, said two layered structure having a total thickness of 90 to 125 mils wherein said outer layer is 15 to 30 percent of the total thickness and said inner layer comprises an acrylonitrile-butadiene-styrene resin.



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12. A thermoplastic composite according to claim 6 comprising at least two layers, said outer layer comprises polyester and said inner layer comprises a mixture comprising an acrylonitrile-butadiene-styrene resin and a regrind mixture, said outer layer is about 33% of the total thickness.
13. A thermoplastic composite according to claim 1 comprising a three layer structure comprising an outer polyester layer, and adjacent layers comprising an acrylonitrile-butadiene-styrene resin and a regrind layer, said regrind layer comprising a mixture of polyester and an acrylonitrile-butadiene-styrene resin.
14. A process for preparing a decorative article comprising extruding a multilayered sheet by feeding at least two different resin compositions to an extruder, extruding said at least two resin compositions into the multilayered self-supporting coextruded sheet, and thermoforming at least a portion of said coextruded sheet into a decorative article wherein at least one exterior surface of the article comprises one resin and an adjacent layer comprises the other resin, said resin forming said exterior decorative surface comprising a chemically resistant filled polyester layer and an adjacent inner supporting thermoplastic layer for enhancing desirable mechanical properties of the composite.
15. A process for preparing a decorative article according to claim 14 wherein said decorative outer polyester layer comprises a colorant, an inorganic filler, an effective amount of a stabilizer, and optionally polycarbonate, an impact modifier, or a UV stabilizer, and mixtures thereof.
16. A process for preparing a decorative article according to claim 14 wherein the adjacent inner thermoplastic layer comprises a heat deformable layer having mechanical properties such as impact resistance and melt strength which desirably exceed these properties as possessed by the outer polyester layer.



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17. A process for preparing a decorative article according to claim 14 wherein the adjacent inner thermoplastic layer comprises acrylonitrile-butadiene-styrene, polycarbonate, polycarbonate/ acrylonitrile-butadiene-styrene blend, copolycarbonate-polyester, acrylic-styrene-acrylonitrile, acrylonitrile-(ethylene-polypylene diamine modified)-styrene, phenylene ether resins, blends of polyphenylene ether/polyamide, blends of polycarbonate/polybutylene terephthalate and impact modifier, blends of polycarbonate/PET/PBT, polyamides, phenylene sulfide resins, poly(vinyl chloride), and high-impact polystyrene.
18. A process for preparing a decorative article according to claim 14 wherein the adjacent said polyester is selected from the group consisting of poly(ethylene terephthalate) ("PET"), and poly(1,4-butylene terephthalate), ("PBT"), poly(ethylene naphthanoate) ("PEN"), poly(butylene naphthanoate), ("PBN") and (polypropylene terephthalate) ("PPT"), and mixtures thereof.

