RUBBER MODIFIED STYRENE COPOLYMERS AND THEIR USE IN FORMING ORIENTED ARTICLES

Inventors: John Chi Hee Kwok, Moon Township, PA (US); Robert D. Roberts, Northampton, MA (US)

Correspondence Address:
Suzanne Kikel/NOVA Chemicals Inc.
400 Frankfort Road
Monaca, PA 15061 (US)

Appl. No.: 11/525,418

Filed: Sep. 22, 2006

Related U.S. Application Data

Continuation-in-part of application No. 11/034,084, filed on Jan. 12, 2005.

Publication Classification

Int. Cl. C08L 53/00 (2006.01)
U.S. Cl. .......................................................... 525/88

ABSTRACT

An oriented, i.e. uniaxial or biaxial, thermoplastic article, e.g. extruded sheet, blown film, and cast film, comprising a first component comprising a continuous phase and a dispersed phase, wherein A) the continuous phase contains a polymer composition resulting from the polymerization of a monomer mixture containing a styrenic monomer and an alkyl (meth)acrylate monomer in the presence of the dispersed phase; and B) the dispersed phase contains one or more block copolymers selected from di-block and tri-block copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, wherein the oriented thermoplastic article has a thickness ranging from 0.02 mm to 0.50 mm, a tensile strength ranging from 15 Mpa to 70 Mpa as measured by ASTM D 882, an impact value ranging between 0.05 ft. lb/mil to 1.0 ft. lb/mil as measured by ASTM D 3763, and a haze value less than 10% as measured by ASTM D 1003.
RUBBER MODIFIED STYRENE COPOLYMERS AND THEIR USE IN FORMING ORIENTED ARTICLES

RELATED CASE

This is a Continuation-In-Part of Non-Provisional U.S. Ser. No. 11/034,084 filed on Jan. 12, 2005, which was published on Jul. 13, 2006 as U.S. Publication No. 2006/0155063 A1, pertaining to rubber modified styrene copolymers and their use in disposable card applications.

BACKGROUND OF THE INVENTION

The present invention is directed to rubber modified styrene copolymers and their use in making thermoplastic articles. More particularly, the present invention relates to oriented, i.e., uniaxially oriented and biaxially oriented, thermoplastic articles, e.g., extruded sheets, cast films, and blown films, and compositions comprising said rubber modified styrene copolymers, e.g., rubber modified styrene methyl methacrylate copolymers, and which thermoplastic articles may be used to form multi-layer structures.

1. Field of the Invention

It is known to provide rubber modified styrene copolymers, for example, rubber modified styrene methyl methacrylate copolymers. U.S. Pat. No. 4,772,667 to Biletech et al. discloses a thermoplastic polymer that includes a styrene monomer, an acrylate, a methacrylate and a block copolymer.

U.S. Pat. No. 5,290,862 to Blasius discloses a polymer alloy that contains from 30 to 83 weight percent of a brittle polymer, from 3 to 50 weight percent of a rubbery polymer, and from 15 to 67 weight percent of a ductile polymer, provided that the ductile polymer and the rubbery polymer are at least compatible.

U.S. Pat. No. 5,891,962 to Otsuzuki et al. discloses a transparent, rubber-modified styrene resin that contains 70 to 96 parts by weight of a copolymer formed of 20 to 70 wt. % of styrene monomer units and 30 to 80 wt. % of alkyl (meth)acrylate monomer units and 4 to 30 parts by weight of a rubbery copolymer. The rubbery copolymer is dispersed in the copolymer as particles and the copolymer and the rubbery polymer have substantially the same refractive index.

Henceforth, the above described thermoplastic polymer compositions have not been used in sheet or film applications because they do not provide the required clarity, stiffness, impact strength, resilience and flexural durability properties.

It would be desirable to provide a low cost thermoplastic sheet or film material that provides sufficient stiffness, resilience and flexural durability properties.

Monovinyl and vinyl aromatic-based resins, such as for example, styrene based resins, i.e. polystyrene-based resins, are well known and widely employed for producing foams and oriented articles for use in food packaging, toys, small appliances, compact discs, and audio/video cassette casings. Processes used to manufacture such articles involve extrusion, injection molding, blow molding, and thermoforming applications.

Oriented film or sheet may also be made from styrene polymers. Examples of oriented articles, e.g., films, sheets, or tubes are disclosed in U.S. Pat. Nos. 4,386,125; 5,322,664; 5,756,577; and 6,107,411.

U.S. Pat. No. 4,386,125 issuing to Asahi Kasei Kogyo Kabushika Kaisha, discloses a transparent film, sheet, or tube of a block copolymer or a block copolymer composition having excellent low-temperature shrinkage of not less than 15% in terms of a heat shrinkage factor at 80°C in at least one direction and good mechanical properties. The block copolymer has a melt flow of 0.001 through 70 grams/10 min. and comprises an aromatic vinyl hydrocarbon polymer block having a number average molecular weight of 10,000 through 70,000 and a polymer block composed mainly of a conjugated diene, and a residual group of a coupling agent or a poly functional initiator such as an organo polyliothium compound.

U.S. Pat. No. 5,322,664 discloses a method and apparatus for making a clear single layer polystyrene non-foam film for use as a label on containers. A blend of general purpose polystyrene and styrene-butadiene or styrene butyl acrylate is extruded from an annular extruder die orifice to form a frustoconical tube which is stretched before cooling air is applied to form a clear film that has machine direction orientation and cross direction orientation that can be used as a shrinkable label on containers. During the extrusion stage, the polystyrene has flow rates of about 8-10 (grams/10 min. condition G) and VICAT softening temperatures of about 220 to 225°F.

U.S. Pat. No. 5,756,577 was issued on May 26, 1998 to Villarreal et al. and was assigned to Group Cydsa, S.A. de C.V. This patent claims a heat shrinkable thermoplastic film or sheet comprising a block copolymer of styrene-butadiene, wherein the amount of polymerized butadiene units in the copolymer constitutes from about 1 to about 50% by weight of the composition. The film or sheet has a tensile strength of about 372 kg/cm² in the machine direction and about 255 kg/cm² in the transverse direction, and a shrinkage value at 130°C of about 44% for the machine direction and about 0% for the transverse direction.

U.S. Pat. No. 6,107,411 was issued on Aug. 22, 2000 to Toyoda et al. and was assigned to Denki Kagaku Kogyo Kabushiki Kaisha. This patent disclosed a block copolymer consisting essentially of a vinyl aromatic hydrocarbon and a conjugated diene, which is excellent in transparency, stiffness, impact resistance, and spontaneous shrinkage resistance; a composition comprising such a block copolymer, and heat shrinkable films prepared by orienting them. The block copolymer satisfies certain conditions such as a specific weight ratio of the vinyl aromatic hydrocarbon to the conjugated diene in the block copolymer, a specific molecular weight of the block copolymer, a specific storage modulus, a specific block proportion of the vinyl aromatic hydrocarbon polymer, and a specific proportion of chains consisting of repeating units of the vinyl aromatic hydrocarbon.

A process for making an extruded oriented sheet is well known in the art and is discussed further herein below. It is also known to those skilled in the art that the control of the film or sheet thickness, the temperature of the film, and the draw ratios are important parameters that define the film properties. Generally, materials having high melt strength
and retaining their orientation are considered better film or sheet forming materials than those having lower melt strength and not retaining their orientations.

SUMMARY OF THE INVENTION

A) the continuous phase comprises a polymer composition resulting from the polymerization of a monomer mixture comprising (i) from about 25 parts by weight to 75 parts by weight of a styrenic monomer and (ii) from about 25 parts by weight to 75 parts by weight of an alkyl (meth)acrylate monomer, wherein the alkyl group is a C₁ to C₄ linear, branched or cyclic alkyl group, in the presence of the dispersed phase; and

B) the dispersed phase comprises from about 2 parts by weight to about 50 parts by weight of one or more block copolymers selected from the group consisting of diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, for a total of 100 parts by weight of the combination of A) and B),

wherein said oriented thermoplastic article is selected from the group consisting of sheet and film, and has a thickness ranging from about 0.02 mm to about 0.50 mm, a tensile strength ranging from about 15 Mpa to about 70 Mpa as measured by ASTM D882, an impact value ranging from about 0.05 ft. lb/mil to about 1.0 ft. lb/mil as measured by ASTM D3763; and a Haze value less than 10% as measured by ASTM D1003.

The invention also provides a process for preparing an oriented, i.e. uniaxial or biaxial, thermoplastic article, the steps comprising:

A) forming a thermoplastic composition comprising a continuous phase and a dispersed phase, wherein

A) the continuous phase comprises a polymer composition resulting from the polymerization of a monomer mixture comprising (i) from about 25 to 75 parts by weight of a styrenic monomer and (ii) from about 25 to 75 parts by weight of an alkyl (meth)acrylate monomer, wherein the alkyl group is a C₁ to C₄ linear, branched or cyclic alkyl group, in the presence of the dispersed phase; and

B) the dispersed phase comprises from about 2 to about 50 parts by weight of one or more block copolymers selected from the group consisting of diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, for a total of 100 parts by weight of the combination of A) and B);

maintaining said thermoplastic composition in a molten state while mixing said composition; and

extruding said composition in a molten state to form said article; and

subjecting said article to an orientation process to form said oriented thermoplastic article;

wherein said oriented thermoplastic article is selected from the group consisting of sheet and film and has a thickness ranging from about 0.5 mm to about 0.02 mm, a tensile strength ranging from about 15 Mpa to about 70 Mpa as measured by ASTM D 882; an impact value ranging from about 0.05 ft. lb/mil to about 1.0 ft. lb/mil as measured by ASTM D 3763; and a Haze value less than 10% as measured by ASTM D 1003.

The oriented article may be a uniaxially or a biaxially extruded sheet, cast film, or blown film.

These and other object of the present invention will be better appreciated and understood by those skilled in the art from the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties, which the present invention desires to obtain. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

As used herein, the terms "(meth)acrylic" and "(meth)acrylate" are meant to include both acrylic and methacrylic acid derivatives, such as the corresponding alkyl esters often referred to as acrylates and (meth)acrylates, which the term "(meth)acrylate" is meant to encompass.

As used herein, the term "polymer" is meant to encompass, without limitation, homopolymers, copolymers and graft copolymers.

Unless otherwise specified, all molecular weight values are determined using gel permeation chromatography
(GPC) using appropriate polystyrene standards. Unless otherwise indicated, the molecular weight values indicated herein are weight average molecular weights (Mw).

[0037] In making the thermoplastic sheet and film of the invention, a particular thermoplastic composition is used. The thermoplastic composition is characterized as having a continuous phase and a dispersed phase. The continuous phase contains a polymer composition resulting from the polymerization of a monomer mixture containing styrenic and alkyl (meth)acrylate monomers in the presence of the dispersed phase.

[0038] The styrenic monomers are present in the monomer mixture at a level of at least 25, in some cases at least 30 and in other cases at least 35 parts by weight based on the combined weight of the monomer mixture and the dispersed phase. Also, the styrenic monomers are present in the monomer mixture at a level of up to 75, in some cases up to 70, in other cases up to 65, in some instances up to 60, in other instances up to 55 and in particular situations up to 50 parts by weight based on the combined weight of the monomer mixture and dispersed phase. The amount of styrenic monomer is determined based on the physical properties desired in the resulting thermoplastic sheet or film. The amount of styrenic monomer in the monomer mixture can be any value recited above or can range between any of the values recited above.

[0039] The alkyl (meth)acrylate monomers are present in the monomer mixture at a level of at least 25, in some cases at least 30 and in other cases at least 35 parts by weight based on the combined weight of the monomer mixture and dispersed phase. Also, the alkyl (meth)acrylate monomers are present in the monomer mixture at a level of up to 75, in some cases up to 70, in other cases up to 65, in some instances up to 60, in other instances up to 55 and in particular situations up to 50 parts by weight based on the combined weight of the monomer mixture and dispersed phase. The amount and type of alkyl (meth)acrylate monomers is determined based on the physical properties desired in the resulting thermoplastic sheet or film. The alkyl group in the alkyl (meth)acrylate monomers can be a C1 to C12, in some cases a C1 to C4, and in other cases a C1 to C4 linear, branched or cyclic alkyl group. The amount and type of alkyl (meth)acrylate monomers in the monomer mixture can be any value recited above or can range between any of the values recited above.

[0040] In an embodiment of the invention, the styrenic monomer is selected from styrene, p-methyl styrene, tertiary butyl styrene, dimethyl styrene, nuclear brominated or chlorinated derivatives thereof and combinations thereof.

[0041] In another embodiment of the invention, the alkyl (meth)acrylate monomers include methylmethacrylate and optionally butyl acrylate.

[0042] In an embodiment of the invention, the monomer mixture includes one or more chain transfer agents. Any chain transfer agent that effectively controls the molecular weight of the styrene/alkyl (meth)acrylate copolymers can be used in the invention. Non-limiting examples of suitable chain transfer agents include alkyl mercaptans according to the structure R—SH, where R represents a C1 to C12 linear, branched or cyclic alkyl or alkenyl group; mercaptoacids according to the structure RSH—COO, where R is as defined above and X is H, a metal ion, N+H4 or a cationic amine salt; dimers or cross-dimers of α-methylstyrene, methyl methacrylate, hydroxy ethylacrylate, benzyl methacrylate, allyl methacrylate, methacrylonitrile, glycidyl methacrylate, methacrylic acid, tert-butyl methacrylate, isocyanatoethyl methacrylate, meta-isopropenyl-α,α-dimethyl isocyanate, α-sulfopropylalkyl methacrylates and alkali salts thereof. Suitable dimers that can be used in the invention are disclosed, for example, in U.S. Patent Application Publication No. 2004/0176527, the relevant portions of which are herein incorporated herein by reference.

[0043] When used, the one or more chain transfer agents may be present in the monomer mixture at a level of from at least 0.001 wt. %, in some cases at least 0.01 wt. % and in other cases at least 0.1 wt. % and to up to 10 wt. %, in some cases up to 7.5 wt. % and in other cases up to 5 wt. % of the monomer mixture. The amount of chain transfer agent can be any value or can range between any of the values recited above.

[0044] The dispersed phase is present in the thermoplastic composition at a level of at least 2 parts by weight, in some cases at least 3 parts by weight, in other cases at least 5 parts by weight, and in some situations at least 10 parts by weight based on the combined weight of the monomer mixture and dispersed phase. Also, the dispersed phase is present in the thermoplastic composition at a level of up to 50 parts by weight, in some cases up to 45 parts by weight, in other cases up to 40 parts by weight, in some instances up to 35 parts by weight, in other instances up to 30 parts by weight, and in particular situations up to 25 parts by weight based on the combined weight of the monomer mixture and dispersed phase. The amount of dispersed phase is determined based on the physical properties desired in the resulting thermoplastic sheet. The amount of dispersed phase in the thermoplastic composition can be any value recited above or can range between any of the values recited above.

[0045] The dispersed phase desirably contains one or more block copolymers, which may be rubbery block copolymers. Desirably, the block copolymers include one or more diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene and partially hydrogenated styrene-isoprene-styrene. Examples of suitable block copolymers include, but are not limited to, the STEREON® block copolymers available from the Firestone Tire and Rubber Company, Akron Ohio; the ASAPRENETM block copolymers available from Asahi Kasei Chemicals Corporation, Tokyo Japan; the KRATON® block copolymers available from Kraton Polymers, Houston, Tex.; and the VECTOR® block copolymers available from Dexco Polymers L.P., Houston, Tex.

[0046] In an embodiment of the invention, the block copolymer is a linear or radial block copolymer.

[0047] In an embodiment of the invention, the block copolymer has a weight average molecular weight of at least 50,000 and in some cases not less than about 75,000, and can be up to 500,000, in some cases up to 400,000 and in other cases up to 300,000. The weight average molecular weight of the block copolymer can be any value or can range between any of the values recited above.

[0048] In another embodiment of the invention, the block copolymer is a triblock styrene-butadiene-styrene or sty-
rene-isoprene-styrene copolymer having a weight average molecular weight of from about 175,000 to about 275,000.

[0049] In a further embodiment of the invention, at least some of the polymers in the continuous phase are grafted onto the block copolymer in the dispersed phase.

[0050] In an embodiment of the invention, the dispersed phase is present as discrete particles dispersed within the continuous phase. Further to this embodiment, the volume average particle size of the dispersed phase in the continuous phase is at least about 0.1 μm, in some cases at least 0.2 μm and in other cases at least 0.25 μm. Also, the volume average particle size of the dispersed phase in the continuous phase can be up to about 2 μm, in some cases up to 1.5 μm and in other cases up to 1 μm. The particle size of the dispersed phase in the continuous phase can be any value recited above and can range between any of the values recited above.

[0051] In another embodiment of the invention, the aspect ratio of the dispersed particles is from at least about 1, in some cases at least about 1.5 and in other cases at least about 2 and can be up to about 5, in some cases up to about 4 and in other cases at least up to about 3. When the aspect ratio of the dispersed particles is too large, the resulting thermoplastic sheet is hazy and not clear or transparent. The aspect ratio of the dispersed discrete particles can be any value or range between any of the values recited above. As a non-limiting example, the aspect ratio can be measured by scanning electron microscopy or light scattering.

[0052] The particle size and aspect ratio of the dispersed phase can be determined using low angle light scattering. As a non-limiting example, a Model LA-910 Laser Diffraction Particle Size Analyzer available from Horiba Ltd., Kyoto, Japan can be used. As a non-limiting example, a rubber-modified polystyrene sample can be dispersed in methyl ethyl ketone. The suspended rubber particles can then be placed in a glass cell and subjected to light scattering. The scattered light from the particles in the cell can be passed through a condenser lens and converted into electric signals by detectors located around the sample cell. As a non-limiting example, a He—Ne laser and/or a tungsten lamp can be used to supply light with a shorter wavelength. Particle size distribution can be calculated based on Mie scattering theory from the angular measurement of the scattered light.

[0053] The thermoplastic composition is formed by dispersing the dispersed phase in a monomer mixture containing styrenic and alkyl (meth)acrylate monomers, deaerating or sparging with nitrogen, while mixing and adding a suitable free radical polymerization initiator at a suitable temperature to effect free radical polymerization. In an embodiment of the invention, at least some of the monomer mixture reacts with unsaturated groups in the dispersed phase to provide grafting to the dispersed phase. Methods for polymerizing the monomer mixture and dispersed phase are known in the art. Examples of such methods are disclosed in, as non-limiting examples, U.S. Pat. No. 4,772,667 to Biletch et al., and U.S. Pat. No. 5,891,962 to Otsuzuki et al., the relevant portions of which are herein incorporated by reference. Desirably, the manufacturing conditions are adapted to provide thermoplastic compositions, thermoplastic sheets and thermoplastic items having the properties described herein.

[0054] Any suitable polymerization initiator can be used in the invention. Non-limiting examples of suitable polymerization initiators include dibenzoyl peroxide, di-tert-butyl peroxide, dicumyl peroxide, dicumyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl perpivalate, tert-butyl peroxysuccinate, or butyl peroxycarbonate and also azo compounds, e.g., 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2,3-dimethylbutyronitrile), 2',1'-azobis-(1-cyclohexanenitrile), as well as combinations of any of the above.

[0055] In the invention, the difference between the refractive index of the continuous phase and the dispersed phase is not more than 0.01 and in some cases not more than 0.001.

[0056] In the invention, the adjuvants include pigments or colorants or both. The pigments and/or colorants can be included in the thermoplastic composition and are included as part of the resulting thermoplastic sheet. As non-limiting examples, the pigments and/or colorants can include titanium dioxide. The pigments and/or colorants when added to the thermoplastic composition will generally result in an opaque sheet. A clear or transparent sheet can be defined as having a Haze value of 10% or less, and it is known to those skilled in the art that Haze values generally do not apply to an opaque sheet.

[0057] As used herein, “pigments and/or colorants” refer to any suitable inorganic or organic pigment or organic dyestuff. Suitable pigments and/or colorants are those that do not adversely impact the desirable physical properties of the thermoplastic sheet. Non-limiting examples of inorganic pigments include titanium dioxide, iron oxide, zinc chromate, cadmium sulfides, chromium oxides and sodium aluminum silicate complexes. Non-limiting examples of organic type pigments include azo and diazo pigments, carbon black, phthalocyanines, quinacridone pigments, perylene pigments, isosindolinone, anthraquinones, thioindigo and solvent dyes.

[0058] The adjuvants can include one or more additives selected from lubricants, fillers, light stabilizers, heat stabilizers, surface-active agents, and combinations thereof. These additives, when added to the thermoplastic composition will generally result in an opaque sheet.

[0059] Suitable fillers are those that do not adversely impact, and in some cases enhance, the desirable physical properties of the thermoplastic sheet. Suitable fillers include, but are not limited to, calcium carbonate in ground and precipitated form, barium sulfate, talc, glass, clays such as kaolin and montmorillonites, mica, and combinations thereof.

[0060] Suitable lubricants include, but are not limited to, ester waxes such as the glycerol types, the polymeric complex esters, the oxidized polyethylene type ester waxes and the like, metallic stearates such as barium, calcium, magnesium, zinc and aluminum stearate, and/or combinations thereof.

[0061] Generally, any conventional ultra-violet light (UV) stabilizer known in the art can be utilized in the present invention. Non-limiting examples of suitable UV stabilizers include 2-hydroxy-4-(octoxy)-benzophenone, 2-hydroxy-4-(octyl oxy)-phenyl phenyl-methanone, 2-(2'-hydroxy-3,5-di-tert-butylphenyl)benzotriazole, and the family of UV stabilizers available under the tradename TINUVIN® from Ciba Specialty Chemicals Co., Tarrytown, N.Y.

[0062] Heat stabilizers that can be used in the invention include, but are not limited to, hindered phenols, non-
limiting examples being the IRGANOX® stabilizers and antioxidants available from Ciba Specialty Chemicals.

[0061] When any or all of the indicated adjuvants are used in the present invention, they can be used at a level of at least 0.01 weight percent, in some cases at least 0.1 weight percent and in other cases at least 0.5 and up to 10 weight percent, in some cases up to 7.5 weight percent, in other cases up to 5 weight percent, and in some situations up to 2.5 weight percent of the thermoplastic composition and/or the thermoplastic sheet of the invention. The amount, type and combination of adjuvants used will depend on the particular properties desired in the thermoplastic sheet. The amount of any single adjuvant or any combination of adjuvants can be any value recited above and can range between any of the values recited above.

[0064] Thorough mixing and dispersion of the additive in the thermoplastic composition is important, but otherwise processing conditions are similar to those typically employed in the art.

[0065] The present thermoplastic sheet is prepared by working the above-described thermoplastic composition to form the thermoplastic sheet. Desirably, the thermoplastic composition, along with any desired adjuvants and/or other polymers are combined, may be mixed on a heated mill roll or other compounding equipment, and the mixture cooled, granulated and extruded into a sheet. The formulation may be admixed in extruders, such as single-screw or double-screw extruders, compounded and extruded into pellets, which may be then re-fabricated. The extruder may also be used to extrude the composition as pipe, sheet, film or profile.

[0066] The thermoplastic composition can be extruded at a temperature that allows for formation of a sheet with the desired physical properties. In an embodiment of the invention, the thermoplastic composition is extruded at from at least about 400°F. (204°C), in some cases at least about 450°F. (232°C) and up to about 550°F. (288°C), in some cases up to about 600°F. (300°C). The extrusion temperature can be any temperature or range between any of the temperatures indicated above.

[0067] Sheets may be uniaxially or biaxially oriented either during or after extrusion or after casting or blowing processes by reheating and stretching. The processes and techniques for uniaxially and biaxially orienting sheets are well known to those skilled in the art.

[0068] Granules of the thermoplastic composition may be molded or extruded into appropriate parisons which are then treated by conventional molding and blowing techniques into bottles or other containers, which containers may be stretch oriented uniaxially or biaxially, or may be left unoriented. It is known in the art for such containers to have closures that allow them to be sealed or capped. The processes and techniques for uniaxially and biaxially orienting containers are also well known to those skilled in the art.

[0069] The thermoplastic sheet has a melt flow of from at least about 1.0 g/10 minutes, in some cases at least about 2.5 g/10 minutes, and in other cases at least about 3 g/10 minutes, and up to about 10 g/10 minutes, in some cases up to 4.5 g/10 minutes, and in other cases up to 4 g/10 minutes measured according to ASTM D 1238. The melt flow of the thermoplastic sheet can be any value, or can range between any of the values recited above.

[0070] A clear sheet is desired and/or required. For clear sheets, the thermoplastic sheet has a haze value of from at least about 0.01% and can be up to about 10%, in some cases up to 7.5%, in other cases up to 5% and in some situations up to 4%, and in other cases from 5% up to 10%. The haze value of a sheet sample is measured using a Color Quest® XE-Touch reflectance/transmittance spectrophotometer equipped with Universal® color quality control software, available from Hunter Associates Laboratory, Inc., Reston, Va. The haze value of the thermoplastic sheet can be any value, or can range between any of the values recited above.

[0071] The tensile strength (tensile break) of the thermoplastic sheet can be at least about 3,500 psi, in some cases at least about 4,000 psi and in other cases at least about 5,000 psi and can be up to about 10,000 psi, in some cases up to 9,000 psi, in other cases up to 8,000 psi and in some situations up to 7,000 psi measured according to ASTM D-638. The tensile strength of the thermoplastic sheet can be any value, or can range between any of the values recited above.

[0072] The flexural modulus tensile of the thermoplastic sheet can be at least about 100,000 psi, in some cases at least about 200,000 psi and in other cases at least about 300,000 psi and can be up to about 700,000 psi, in some cases up to 600,000 psi, in other cases up to 500,000 psi and in some situations up to 400,000 psi measured according to ASTM D-790. The tensile strength of the thermoplastic sheet can be any value, or can range between any of the values recited above.

Uniaxial and Biaxial Oriented Thermoplastic Articles

[0073] The rubber modified styrenic copolymer composition described herein for a thermoplastic sheet as disclosed in U.S. Published Application No. 2006/0155063 A1, published on Jul. 13, 2006 (U.S. Ser. No. 11/034,084, filed Jan. 12, 2005), can be used in the preparation of oriented articles, e.g. blown film, cast film and extruded sheet that are uniaxially or biaxially oriented. In addition to other applications, these oriented thermoplastic articles made from the rubber modified styrenic copolymer composition of the invention may be used as a shrink wrap label where food contact is not necessarily a requirement. Additional applications for the oriented thermoplastics articles include cookie trays, envelope windows, and flexible packaging.

[0074] Regardless of the type of applications the oriented thermoplastic articles are used for, the above teachings and/or components of the rubber modified styrenic copolymer compositions used in forming the extruded sheets for the disposable card applications generally apply to the rubber modified styrenic copolymer compositions used in forming the uniaxial and biaxial oriented thermoplastic articles of this invention, for example, extruded sheet, cast film and blown film, for potential use as labels on shrink wrap.

[0075] As stated herein above, the processes and techniques for producing a uniaxial or biaxial oriented sheet and film are well known to those skilled in the art. General processes and techniques for forming a uniaxial and biaxial oriented sheet or film are disclosed in U.S. Pat. No. 6,433,
For the manufacture of an oriented extruded sheet, the polymer resin granules are fed into an extruder where the resin is heated to a molten state having a polymer melt temperature ranging between about 210°C and 270°C, preferably about 260°C, and then extruded through a sheet T-die and onto a roll stack. The roll stack is operated such that the temperature of the material is above its Tg (glass transition temperature). The roll stack imparts a high degree of orientation (>100%) in the machine direction (MD). As the sheet comes off the roll stack the sides of the sheet are engaged by a series of clamps that are attached to a continuous chain. The clamps pull the sheet through a “tenter frame” which is a long oven. The oven has several heating zones in which the temperature of the material is maintained about its Tg. As the sheet is carried through the tenter oven, the continuous chain of clamps begins to diverge thereby imparting a high degree of orientation (>100%) in the transverse direction (TD). In order for the temperature of the material to remain above its Tg, the temperature in each heating zone is set above the Tg of the polymer. For the rubber modified styrene copolymer composition of the invention which contains a polystyrene component and which has a Tg of about 105°C, the temperature in each heating zone will typically be set at about 105°C to about 110°C.

Depending on the final application of the sheet, the amount of orientation imparted in the machine direction (MD) and in the transverse direction (TD) will vary. For many applications, the stretch ratios for MD and TD are usually the same or balanced, e.g. MD=TD=2:1. That is, a cookie tray will typically require a 2:1 draw ratio in both the MD and TD, while an envelope window will require a draw ratio of 7:1 in the MD and TD. However, if a hinge is associated with the part, the sheet may require an unbalanced biaxial orientation in the MD and TD orientation, e.g. MD=2:1 draw ratio while TD=1:3:1 draw ratio. A sheet containing a styrenic component similar to that of the rubber modified styrene copolymer composition of the invention and having a 2:1 draw ratio in both the MD and TD may have shrink tension of about 150 to about 200 pounds per square inch (psi) as measured according to ASTM D 2838.

This pulling or orientation in the machine direction and transverse direction may be done simultaneously or sequentially. When a sheet made of the rubber modified styrene copolymer composition of the invention is biaxially oriented using the process described above, generally it is done sequentially where the sheet is first pulled in the machine direction and then pulled in the transverse direction. It is apparent that a uniaxially oriented sheet is one that has been pulled or orientated in either the machine direction or in the transverse direction. Typically, for a uniaxially oriented sheet, the sheet is pulled in the machine direction.

Cast and blown film may be oriented into uniaxially or biaxially oriented film by subjected the film to a tenter frame in a similar manner as that of the extruded sheet, with similar stretch and draw ratios.

Other additives may be added to the rubber modified styrene copolymer composition of the invention used to form the oriented articles. Further examples of suitable additives are softening agents; plasticizers, such as cumarone-indene resin, a terpene resin, and oils in an amount of about 2 parts by weight or less based on 100 parts by weight of the polymer; pigments; anti-blocking agents; slip agents; lubricants; coloring agents; antioxidants; ultraviolet light absorbers; fillers; anti-static agents; impact modifiers. Pigment can be white or any other color. The white pigment can be produced by the presence of titanium oxide, zinc oxide, magnesium oxide, cadmium oxide, zinc chloride, calcium carbonate, magnesium carbonate, etc., or any combination thereof in the amount of 0.1 to 20% in weight, depending on the white pigment to be used. Carbon black, phthalocyanine blue, Congo red, titanium yellow or any other coloring agent known to the printing industry may be used to produce the colored pigment.

Examples of anti-blocking agents, slip agents or lubricants are silicone oils, liquid paraffin, synthetic paraffin, mineral oils, petrolatum, petroleum wax, polyethylene wax, hydrogenated polybutene, higher fatty acids and the metal salts thereof, linear fatty alcohols, glycerine, sorbitol, propylene glycol, fatty acid esters of monohydrate or polyhydroxy alcohols, phthalate, hydrogenated castor oil, beeswax, acetylated monoglyceride, hydrogenated sperm oil, ethylenedinitro fatty acid esters, and higher fatty amides. The organic anti-blocking agents can be added in amounts that will fluctuate from 0.1 to 2% in weight.

Examples of anti-static agents are glycerine fatty acid, esters, sorbitan fatty acid esters, propylene glycol fatty acid esters, stearil citrate, pentaerythritol fatty acid esters, polyglycerine fatty acid esters, and polyoxystyrene glycerine fatty acid esters. An anti-static agent may range from 0.01 to 2% in weight. Lubricants may range from 0.1 to 2% in weight. A flame retardant will range from 0.01 to 2% in weight; ultra-violet light absorbers will range from 0.1 to 2% in weight. The above compositions are expressed as percent of the total weight of the polymer blend.

The oriented film and sheet of the invention can be used in any of the well-known food packaging processes, such as in the preparation of yogurt cups, cake domes, cookie trays, envelope windows, CD jewel box shrink film packaging, trays of all sizes and shapes for general food packaging and vending cups. The food packaging process typically involves the polymer film or sheet having a thickness of a few millimeters (typically between 0.2 mm and 0.6 mm). The extruded oriented film or sheet is fed to one or more heating ovens where its temperature is increased above the glass-transition temperature of resin.

Once the desired temperature is reached, the sheet and film are formed into the desired shape by known processes such as plug-assisted thermoforming where a plug pushes the sheet or film into a mold of the desired shape. Air pressure and/or vacuum can also be employed to mold the desired shape. During the orientation processing of the film or sheet, the molecules are aligned in both the MD and TD directions. Molecular alignment has long been known to significantly increase the overall toughness of the resin. Thus, when a formed article or part is made from the extruded oriented film or sheet of the invention, the formed article or part retains the “toughness” characteristic imparted to the film or sheet during the orientation process.

The rubber modified styrene copolymer composition of the oriented articles will generally have a mean melt
strength at 210°C. of not less than 12.5 cN, and a melt flow at condition G of less than 2.5 grams/10 minutes.

Preferably, the oriented article of the invention comprised of the rubber modified styrenic copolymer composition of the invention has a thickness ranging from about 0.02 mm to about 0.50 mm; a tensile strength ranging from about 15 Mpa to about 70 Mpa as measured by ASTM D 882, an Impact value ranging from about 0.05 ft. lb/mil to about 1.0 ft. lb/mil as measured by ASTM D 3763, and a Haze value less than 10% as measured by ASTM D 1003.

The present invention will further be described by reference to the following examples. The following examples are merely illustrative of the invention and are not intended to be limiting. Unless otherwise indicated, all percentages are by weight.

EXAMPLES

The test methods used to evaluate the uniaxial and biaxial sheets comprised of the rubber modified styrenic copolymer composition of the invention were:

- Tensile Strength (Tensile Break)—ASTM D-882
- Impact Strength (Dynatup Instrumentation)—ASTM D-3763
- Haze—ASTM D-1003 (Samples were measured using a Color Quest® XE-Touch reflectance/transmittance spectrophotometer equipped with Universal Software® color quality control software, available from Hunter Associates Laboratory, Inc., Reston, Va.)

<table>
<thead>
<tr>
<th></th>
<th>Example 1 (Comp.)</th>
<th>Example 2 MD</th>
<th>Example 3 MDO &amp; TDO</th>
<th>Example 4 (Comp.)</th>
<th>Example 5 MDO</th>
<th>Example 6 MDO &amp; TDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (Mpa)</td>
<td>43.2 MD</td>
<td>55.3 MD</td>
<td>49.7 MD</td>
<td>38.8 MD</td>
<td>68.0 MD</td>
<td>52.4 MD</td>
</tr>
<tr>
<td>Impact (Dynatup)</td>
<td>27.3 TD</td>
<td>15.6 TD</td>
<td>45.8 TD</td>
<td>33.6 TD</td>
<td>32.4 TD</td>
<td>54.1 TD</td>
</tr>
<tr>
<td>Ft. lb./mil</td>
<td>0.08 TE</td>
<td>0.07 TE</td>
<td>0.10 TE</td>
<td>0.07 TE</td>
<td>0.13 TE</td>
<td>0.12 TE</td>
</tr>
<tr>
<td>Haze Value (%)</td>
<td>8.0</td>
<td>9.0</td>
<td>10.0</td>
<td>7.0</td>
<td>7.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

TE = Total Energy (normalized)
EML = Energy at Maximum Load (normalized)

Examples 1-6

Examples 1 through 6 pertain to extruded sheets comprised of the rubber modified styrenic copolymer composition of the invention. Examples 1 and 4 are comparative samples in that they were not subjected to an orientation process. Examples 2 and 5, which are inventive samples, were subjected to a uniaxial oriented process in the machine direction (MD) only; and Examples 3 and 6, which are also inventive samples, were subjected to a biaxial oriented process, i.e. in the machine direction (MD) and the transverse direction (TD).

These extruded sheets were prepared by the method that was discussed hereinafore, i.e. a thermoplastic composition in granulate form was fed into an extruder where the resin was heated to a molten state having a polymer melt temperature of about 230°C., and then extruded through a sheet T-die and onto a roll stack. The roll stack was operated such that the temperature of the material was above its Tg (glass transition temperature). For the uniaxially oriented sheet, the roll stack imparted a high degree of orientation (>100%) in the machine direction (MD) only.

For the biaxially oriented sheets, as the sheets came off the roll stack the sides of the sheets were engaged by the tenter clamps and conveyed through the several heating zones of the tenter frame. The tenter clamps imparted a high degree of orientation (>100%) in the transverse direction (TD) to the sheets.

The granules were prepared by polymerizing 47 wt. % styrene, 33.5 wt. % methyl methacrylate and 5 wt. % butyl acrylate in the presence of 14.5 wt. % styrene-butadiene block copolymer with an average styrene content of 39.75 wt. % using tert butyl peroxycarbonate as initiator. The resulting product was clear. The thermoplastic composition was then extruded to form sheets ranging in thickness from 2.9 mils to 18.8 mils.

The physical properties for Examples 1 through 6 are shown in Table 1. The extruded sheets of Examples 1 through 6 were also tested as indicated in Table 1 in both the machine direction (MD) and the transverse direction (TD).

The data for the properties shown in Table 1 illustrate that the Examples which have been oriented i.e. Examples 2, 3, 5, and 6 have higher impact and tensile strength values compared Examples 1 and 4, that were not subjected to an orientation process. Also, the results for the properties of Examples 1-3 and Examples 4-6 were due to slightly different processing conditions. That is, in order to produce lower Haze values of Examples 4-6, the melt temperature on the extruder used for the cast material was reduced about 20 degrees compared to that used for Examples 1-3. Additionally, for Examples 4-6, slight process temperature changes were made in both the machine orientation equipment (about a 5-10 degree reduction), and the transverse orientation oven (about a 5 degree increase), as well as a reduction in the line speed. As Table 1 illustrates, these changes in processing conditions decreased Haze and improved some of the other properties for Examples 4-6 compared to Examples 1-3.

The present invention has been described with reference to specific details of particular embodiments
thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

We claim:

1. An oriented thermoplastic article, comprising a first component comprising a continuous phase and a dispersed phase, wherein:

A) the continuous phase comprises a polymer composition resulting from the polymerization of a monomer mixture comprising (i) from about 25 parts by weight to 75 parts by weight of a styrenic monomer and (ii) from about 25 parts by weight to 75 parts by weight of an alkyl (meth)acrylate monomer, wherein the alkyl group is a C₁ to C₁₂ linear, branched or cyclic alkyl group, in the presence of the dispersed phase; and

B) the dispersed phase comprises from about 2 parts by weight to about 50 parts by weight of one or more block copolymers selected from the group consisting of diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, for a total of 100 parts by weight of the combination of A) and B), and

wherein said oriented thermoplastic article has a thickness ranging from about 0.02 mm to about 0.50 mm, a tensile strength ranging from about 15 Mpa to about 70 Mpa as measured by ASTM D 882, an impact value ranging from about 0.05 ft. lb./mil to about 1.0 ft. lb./mil as measured by ASTM D 3763, and a Haze value less than 10% as measured by ASTM D 1003.

2. The oriented thermoplastic article of claim 1 wherein said oriented thermoplastic article is an uniaxially oriented thermoplastic article.

3. The oriented thermoplastic article of claim 2 wherein said uniaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.

4. The oriented thermoplastic article of claim 1 wherein said oriented thermoplastic article is a biaxially oriented thermoplastic article.

5. The oriented thermoplastic article of claim 4 wherein said biaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.

6. The oriented thermoplastic article of claim 1 wherein the dispersed phase B) is present as discrete particles dispersed within the continuous phase A).

7. The oriented thermoplastic article of claim 1 wherein the volume average particle size of the dispersed phase B) is from about 0.1 µm to about 2 µm.

8. The oriented thermoplastic article of claim 1 wherein the difference between the refractive index of the continuous phase A) and the dispersed phase B) is not more than 0.01.

9. The oriented thermoplastic article of claim 1 wherein the styrenic monomer is selected from the group consisting of styrene, p-methyl styrene, tertiarly butyl styrene, dimethyl styrene, nuclear brominated or chlorinated derivatives thereof and combinations thereof.

10. The oriented thermoplastic article of claim 1 wherein the alkyl (meth)acrylate monomer comprises methylmethacrylate and optionally butyl acrylate.

11. The oriented thermoplastic article of claim 1 wherein the block copolymer has a weight average molecular weight of not less than about 75,000.

12. The oriented thermoplastic article of claim 1 wherein the block copolymer is a linear or radial block copolymer.

13. The oriented thermoplastic article of claim 1 wherein the block copolymer is a triblock styrene-butadiene-styrene or styrene-isoprene-styrene copolymer having a weight average molecular weight of from about 175,000 to about 275,000.

14. The oriented thermoplastic article of claim 1 wherein at least some of the polymers in A) are grafted onto the block copolymer in B).

15. The oriented thermoplastic article of claim 1 further comprising a printed layer over at least a portion of a surface of the thermoplastic sheet.

16. The oriented thermoplastic article of claim 1 wherein the monomer mixture further comprises a chain transfer agent.

17. A multi-layer structure comprising at least two layers and wherein at least one layer of said multi-layer structure is comprised of the oriented thermoplastic article of claim 1.

18. A multi-layer structure of claim 17 wherein at least the other layer of said multi-layer structure is comprised of a rubber modified polystyrene composition.

19. A multi-layer structure of claim 17 wherein at least the other layer of said multi-layer structure is comprised of a polyethylene composition.

20. A multi-layer structure of claim 17 wherein at least the other layer of said multi-layer structure is comprised of an ethylvinyl acetate composition.

21. A process for preparing an oriented thermoplastic article, comprising:

forming a thermoplastic composition comprising a continuous phase and a dispersed phase, wherein

A) the continuous phase comprises a polymer composition resulting from the polymerization of a monomer mixture comprising (i) from about 25 to 75 parts by weight of a styrenic monomer and (ii) from about 25 to 75 parts by weight of an alkyl (meth)acrylate monomer, wherein the alkyl group is a C₁ to C₁₂ linear, branched or cyclic alkyl group, in the presence of the dispersed phase; and

B) the dispersed phase comprises from about 2 to about 50 parts by weight of one or more block copolymers selected from the group consisting of diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, for a total of 100 parts by weight of the combination of A) and B);

maintaining said thermoplastic composition in a molten state while mixing said composition; and

forming said oriented thermoplastic article; and

wherein said oriented thermoplastic article has a thickness ranging from about 0.02 mm to about 0.50 mm, a tensile strength ranging from about 15 Mpa to about 70 Mpa as measured by ASTM D 882, an impact value ranging from about 0.05 ft. lb./mil to about 1.0 ft. lb./mil as measured by ASTM D 3763, and a Haze value less than 10% as measured by ASTM D 1003.
22. The process of claim 21 wherein said oriented thermoplastic article is an uniaxially oriented thermoplastic article.

23. The process of claim 22 wherein said uniaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.

24. The process of claim 21 wherein said oriented thermoplastic article is a biaxially oriented thermoplastic article.

25. The process of claim 24 wherein said biaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.

26. The process of claim 21 wherein the dispersed phase B) is present as discrete particles dispersed within the continuous phase A).

27. The process of claim 21 wherein the volume average particle size of the dispersed phase B) is from about 0.1 μm to about 2 μm.

28. The process of claim 21 wherein the difference between the refractive index of the continuous phase A) and the dispersed phase B) is not more than 0.01.

29. The process of claim 21 wherein the styrenic monomer is selected from the group consisting of styrene, p-methyl styrene, tert-butyl styrene, dimethyl styrene, nuclear brominated or chlorinated derivatives thereof and combinations thereof.

30. The process of claim 21 wherein the alkyl (meth)acrylate monomer comprises methylenacrylate and optionally butyl acrylate.

31. The process of claim 21 wherein the block copolymer has a weight average molecular weight of not less than about 75,000.

32. The process of claim 21 wherein the block copolymer is a linear or radial block copolymer.

33. The process of claim 21 wherein the block copolymer is a triblock styrene-butadiene-styrene or styrene-isoprene-styrene copolymer having a weight average molecular weight of from about 175,000 to about 275,000.

34. The process of claim 21 wherein at least some of the polymers in A) are grafted onto the block copolymer in B).

35. The process of claim 21 wherein the monomer mixture further comprises a chain transfer agent.

36. A thermoplastic composition for an oriented thermoplastic article comprising a first component comprising a continuous phase and a dispersed phase, where:

   A) the continuous phase comprises a polymer composition resulting from the polymerization of a monomer mixture comprising (i) from about 25 parts by weight to 75 parts by weight of a styrenic monomer and (ii) from about 25 parts by weight to 75 parts by weight of an alkyl (meth)acrylate monomer, wherein the alkyl group is a C₁₄ linear, branched or cyclic alkyl group, in the presence of the dispersed phase; and

   B) the dispersed phase comprises from about 2 parts by weight to about 50 parts by weight of one or more block copolymers selected from the group consisting of diblock and triblock copolymers of styrene-butadiene, styrene-butadiene-styrene, styrene-isoprene, styrene-isoprene-styrene, partially hydrogenated styrene-isoprene-styrene, for a total of 100 parts by weight of the combination of A) and B), and

wherein said first component ranges in an amount of about 0.1 to about 100% by weight, based on the weight of the thermoplastic composition.

37. A thermoplastic composition of claim 36, wherein said composition further comprises about 70% by weight of the first component, and about 30% by weight of a rubber modified polystyrene.

38. A thermoplastic composition of claim 36, wherein said composition further comprises about 70% by weight of the first component, about 15% by weight of a rubber modified polystyrene, and about 15% by weight of a tie component.

39. A thermoplastic composition of claim 36, wherein said composition further comprises about 40% by weight of the first component, about 40% by weight of a rubber modified polystyrene, and about 20% by weight of a tie component.

40. A thermoplastic composition of claim 36, wherein said composition further comprises about 70% by weight of the first component, and about 30% by weight of a tie component.

41. A thermoplastic composition of claim 36 wherein said thermoplastic composition is an uniaxially oriented thermoplastic article.

42. A thermoplastic composition of claim 41 wherein said uniaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.

43. A thermoplastic composition of claim 41 wherein said thermoplastic article is a biaxially oriented thermoplastic article.

44. A thermoplastic composition of claim 43 wherein said biaxially oriented thermoplastic article is selected from the group consisting of extruded sheet, blown film, and cast film.