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(54) **Title**: GOLF BALLS CONTAINING IONOMERS AND POLYAMINES OR TERTIARY POLYAMIDES

(57) **Abstract**: Provided herein are compositions comprising an ionomer and a polyamine or a tertiary polyamide. The polyamine and the tertiary polyamide have a molecular weight of greater than 500 Da and do not contain an ester moiety or a primary amine moiety. The polyamine comprises at least three moieties that are tertiary amines or hindered secondary amines, and the polyamide comprises tertiary amide moieties and no secondary or primary amide moieties. The compositions may optionally include a filler. Further provided are articles such as golf balls and films containing these compositions.

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TITLE OF THE INVENTION

GOLF BALLS CONTAINING IONOMERS AND POLYAMINES OR TERTIARY POLYAMIDES

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. Application No. 12/215,674, filed on June 30, 2008, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to compositions comprising ionomers and polyamines or tertiary polyamides and articles such as golf balls and films containing the compositions.

Description of Related Art

Several patents and publications are cited in this description in order to more fully describe the state of the art to which this invention pertains. The entire disclosure of each of these patents and publications is incorporated by reference herein.

Golf balls and golf ball components may be formed from a variety of compositions, which provides a golf ball manufacturer the ability to alter the feel and aerodynamic characteristics of a particular ball.

For example, ionomers are copolymers of alpha olefins, particularly ethylene, and C_{3-8} α,β ethylenically unsaturated carboxylic acid, wherein the acid moieties of the copolymers are at least partially neutralized. U.S. Patent No. 3,264,272 (Rees) teaches methods for making such ionomers from acid copolymers. A process for preparing the acid copolymers on which the ionomers are based is described in U.S. Patent No. 4,351,931.

While ionomer covered golf balls possess virtually cut-proof covers, their spin and feel may be inferior compared to balata covered balls. Polyurethanes and polyureas have also been recognized as useful materials for golf ball covers. Golf ball covers made of these materials have durability comparable to that of covers made from ionomer resins, but have the softer feel of a balata cover. Golf balls with a polyurethane or polyurea cover do not fully match ionomer resin golf balls with respect to the resilience or rebound of the golf ball cover, however. This property is in part a function of the initial velocity of a golf ball after impact with a golf club. Polyurethane and polyurea covers also have inferior moisture barrier properties compared to ionomer covers.

Ethylene acid copolymers neutralized by reaction with diamines are described in U.S. Patent No. 3,471,460. An ionomer neutralized by reaction with a polyamine, preferably a diamine, that contains at least one $R-CH_2-NH_2$ group, and optionally partially neutralized with a base comprising a metal cation, is described in U.S. Patent No. 4,732,944. An ionomer composition comprising an ethylene acid copolymer neutralized by reaction with a "basic metal ion salt" and a compound comprising both an amine and a carboxylic acid in the same molecule is described in U.S. Patent Application Publication No. 2006/0014898. An ionomer composition having greater than about 70 percent of the acid groups neutralized by reaction with a neutralizing component including ammonium salts and/or monoamine salts is described in U.S. Patent No. 7,160,954.

Ionomer compositions neutralized by reaction with various amines are described in *Journal of Applied Polymer Science*, 1991, 42, 621-628. An ionomer composition neutralized by reaction with hexamethylene tetramine (HMT), a tertiary polyamine with molecular weight of 140 Da (Daltons), is reported to have a lower flex modulus than a comparative ionomer not containing HMT.

Japanese Patent No. 3540453 discloses an ionomer composition modified by the addition of $H_2N\text{-}[CH_2RCH_2NHCH_2CH(OH)\ CH_2NH]_n\text{-}CH_2RCH_2NH_2$, wherein, R is a divalent alicycle or an aromatic hydrocarbon group, and $1 \leq n \leq 20$. Japanese Patent Application JP1997-296082 discloses a similar composition wherein a condensed cyclic compound having two or more aminoalkyl groups is also present. Japanese Patent Application JP2005-263868 discloses an ionomer composition modified by a diamine compound wherein weight change begins at ≥150°C, as determined by a gravimetric method according to JIS K7120. An example of the amine is reported as "4 and 4-diamino-hexylmethane", believed to be 4,4'-diaminodicyclohexylmethane.

It is desirable to provide a high performance material to be used in a structural layer of a golf ball, such as a cover, intermediate layer, core or center. In particular it is desirable to provide resins that have a balance of high coefficient of restitution (COR), high flex modulus, low moisture transmission, and good durability. It is also desirable that the compositions have melt properties suitable for injection molding, and in particular for injection molding in thin layers.

SUMMARY OF THE INVENTION

Accordingly, provided herein is a thermoplastic composition comprising:

(a) an E/X/Y ethylene acid copolymer wherein E represents copolymerized units of ethylene, X represents copolymerized units of C_3 to C_8 α,β ethylenically unsaturated carboxylic acid, and Y represents copolymerized units of softening comonomer preferably selected from the group consisting of vinyl acetate, alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms, wherein the amount of X is about 2 to about 30 weight % of the E/X/Y copolymer, and the amount of Y is 0 to about 45 weight % of the E/X/Y copolymer, based on the total weight of the ethylene acid copolymer, wherein at least a portion of the acid moieties of the E/X/Y acid copolymer are neutralized to form an ionomer comprising salts of alkali metal, an alkaline earth metal, and/or transition metal cations;

(b) a polyamine or polyamide having a molecular weight of greater than 500 Da, not containing an ester moiety or a primary amine moiety, wherein the polyamine comprises at least three moieties that are tertiary amines or hindered secondary amines, and wherein the polyamide comprises tertiary amide moieties and no secondary or primary amide moieties; and optionally

(c) a filler.

Also provided are articles prepared from the compositions, such as golf balls. One golf ball comprises a core and a cover and optionally at least one intermediate layer positioned between the core and the cover, wherein the core, the cover or the intermediate layer(s) when present comprises or is prepared from the thermoplastic composition described above.

Further provided is a film prepared from the thermoplastic composition described above.

DETAILED DESCRIPTION OF THE INVENTION

The following definitions apply to the terms as used throughout this specification, unless otherwise limited in specific instances.

The technical and scientific terms used herein have the meanings that are commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including the definitions herein, will control.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” "containing," "characterized by," “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus.

The transitional phrase "consisting of" excludes any element, step, or ingredient not specified in the claim, closing the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. A 'consisting essentially of' claim occupies a middle ground between closed claims that are written in a 'consisting of' format and fully open claims that are drafted in a 'comprising' format. Optional additives as defined herein, at a level that is appropriate for such additives, and minor impurities are not excluded from a composition by the term “consisting essentially of”.

When a composition, a process, a structure, or a portion of a composition, a process, or a structure, is described herein using an open-ended term such as “comprising,” unless otherwise stated the description also includes an embodiment that “consists essentially of” or “consists of” the elements of the composition, the process, the structure, or the portion of the composition, the process, or the structure.

The articles “a” and “an” may be employed in connection with various elements and components of compositions, processes or structures described herein. This is merely for convenience and to give a general sense of the compositions, processes or structures. Such a description includes “one or at least one” of the elements or components. Moreover, as used herein, the singular articles also include a description of a plurality of elements or components, unless it is apparent from a specific context that the plural is excluded.

The term "about" means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such.

The term “or”, as used herein, is inclusive; that is, the phrase “A or B” means “A, B, or both A and B”. Exclusive “or” is designated herein by terms such as “either A or B” and “one of A or B”, for example.

In addition, the ranges set forth herein include their endpoints unless expressly stated otherwise. Further, when an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed. The scope of the invention is not limited to the specific values recited when defining a range.

When materials, methods, or machinery are described herein with the term “known to those of skill in the art”, “conventional” or a synonymous word or phrase, the term signifies that materials, methods, and machinery that are conventional at the time of filing the present application are encompassed by this description. Also encompassed are materials, methods, and machinery that are not presently conventional, but that will have become recognized in the art as suitable for a similar purpose.

Unless stated otherwise, all percentages, parts, ratios, and like amounts, are defined by weight.

As used herein, the term “copolymer” refers to polymers comprising copolymerized units resulting from copolymerization of two or more comonomers. In this connection, a copolymer may be described herein with reference to its constituent comonomers or to the amounts of its constituent comonomers, for example “a copolymer comprising ethylene and 15 weight % of acrylic acid”, or a similar description. Such a description may be considered informal in that it does not refer to the comonomers as copolymerized units; in that it does not include a conventional nomenclature for the copolymer, for example International Union of Pure and Applied Chemistry (IUPAC) nomenclature; in that it does not use product-by-process terminology; or for another reason. As used herein, however, a description of a copolymer with reference to its constituent comonomers or to the amounts of its constituent comonomers means that the copolymer contains copolymerized units (in the specified amounts when specified) of the specified comonomers. It follows as a corollary that a copolymer is not the product of a reaction mixture containing given comonomers in given amounts, unless expressly stated in limited circumstances to be such.

The term “dipolymer” refers to polymers consisting essentially of two monomers, and the term “terpolymer” refers to polymers consisting essentially of three monomers.

Finally, when an article, such as a golf ball, is described as including more than one layer or component that comprises or is prepared from a particular composition, for example “wherein the core or the cover comprises or is prepared from the thermoplastic composition described herein”, that particular composition may be the same or different in each of the layers or components.

Resins having a high flex modulus have previously been prepared using ionomers with relatively high levels of acid comonomer. Using this approach, however, an upper limit of about 90 kpsi in flex modulus has been reached. It is desired, nevertheless, to use resins having a flex modulus greater than 90 kpsi, provided other properties such as COR, moisture transmission, durability and moldability remain acceptable.

It has now surprisingly been discovered that resins having a high coefficient of restitution (COR), high flex modulus, low moisture transmission, and good durability are obtained by blending ionomers with a polyamine containing at least three amine groups. More specifically, these polyamines are tertiary amines or hindered secondary amines or polyamides comprising tertiary amides.

Acid Copolymers

The acid copolymers used to make the compositions described herein are preferably “direct” acid copolymers. “Direct” copolymers are polymers in which the copolymerized monomers are part of the polymer backbone or chain. They may be polymerized by adding all monomers simultaneously. In contrast, in graft copolymers, another comonomer is attached to non-terminal repeat units in an existing polymer chain, often by a subsequent free radical reaction.

The acid copolymers are preferably alpha olefin, particularly ethylene, C_3 to C_8, α,β-ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, copolymers. They may optionally contain a third softening monomer. By “softening”, it is meant that the polymer is made less crystalline and has a lower flex modulus than related polymers not having the “softening” monomer. Suitable “softening” comonomers are monomers selected from alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms, and vinyl acetate.

The ethylene acid copolymers can be described as E/X/Y copolymers where E represents copolymerized units of ethylene, X represents copolymerized units of the α,β ethylenically unsaturated carboxylic acid, and Y represents copolymerized units of a softening comonomer. X is present in 2 to 30 weight % of the polymer, and Y is present in from 0 to 45 weight % of the polymer. That is, the amount of X is 2 to 30 weight %, and the amount of Y is 0 to 45 weight %, based on the total weight of the E/X/Y copolymer. An E/X/Y copolymer wherein Y is 0 weight % of the copolymer may be considered an E/X dipolymer. When Y is present in the E/X/Y copolymer (i.e., an E/X/Y terpolymer), it may be present in an amount from about 0.1 weight % to 45 weight % of the copolymer, preferably from 5 to 35, or from 5 to 25 weight % of the copolymer.

Preferred are copolymers wherein Y is 0% of the copolymer (that is, an E/X dipolymer). Preferred are dipolymers wherein the C_3 to C_8 α,β-ethylenically unsaturated carboxylic acid are acrylic acid or methacrylic acid. Specifically preferred acid copolymers include ethylene/acrylic acid and ethylene/methacrylic acid dipolymers.

When combined with other components as described herein, an ethylene dipolymer consisting essentially of copolymerized comonomers of ethylene and from about 10 to about 24 weight % of copolymerized comonomers of C_3 to C_8 α,β ethylenically unsaturated carboxylic acid is particularly useful for preparing compositions which have a balance of high coefficient of restitution (COR), high flex modulus, low moisture transmission, moldability and good durability. Preferably, the E/X dipolymer may include about 14 to about 22 weight %, more preferably 18 to about 22 weight %, of the copolymerized carboxylic acid.

Of note are a dipolymer comprising ethylene and about 15 weight % of acrylic acid, a dipolymer comprising ethylene and 15.4 weight % of acrylic acid, a dipolymer comprising ethylene and about 18 weight % of acrylic acid, and a dipolymer comprising ethylene and about 21 weight % of acrylic acid. Ethylene/acrylic acid dipolymers are of note because a given weight of acrylic acid will provide more acid moieties than an equal weight of methacrylic acid.

Further of note is a dipolymer comprising ethylene and about 19 weight % of methacrylic acid. Also of note is a dipolymer comprising ethylene and about 15 weight % of methacrylic acid.

More preferably, the dipolymer may include 18 to 20 weight % of copolymerized methacrylic acid, or about 21 weight % of copolymerized acrylic acid.

Ethylene acid dipolymers with high levels of acid can be prepared through the use of "co-solvent technology" as described in U.S. Patent No. 5,028,674 or by employing somewhat higher pressures than those at which copolymers with lower acid levels can be prepared.

The E/X/Y copolymers may have melt index flow rates in the range of about 10 g/10 min to about 400 g/10 min, or greater, measured at 190°C using a 2160 g weight. Preferably, the copolymers have melt index flow rates of about 50 to about 300 g/10 min. Of note is a dipolymer comprising ethylene and 19 weight % of methacrylic acid having a melt index of 250 g/10 min.

Mixtures of acid copolymers are suitable, provided the properties, such as melt index, of the mixture fall within the ranges described above. For example, two or more E/X dipolymers having differing amounts of X and/or differing melt indices may be used. Also, an E/X dipolymer and an E/X/Y terpolymer (wherein Y is present in the copolymer in an amount from 0.1 to 45 weight %, preferably from 0.1 to 35 weight %) may be mixed.

Ionomers

Unmodified, melt processible ionomers can be prepared from acid copolymers described above by methods known in the art of preparing ionomers. By "unmodified", it is meant that the ionomers are not blended with any material that has been added for the purpose of modifying the properties of the unblended ionomer. For example, the polyamines and polyamides described herein are considered modifiers. Unmodified ionomers include partially neutralized acid copolymers, particularly copolymers prepared from copolymerization of ethylene and acrylic acid or methacrylic acid. The unmodified ionomers may be neutralized to any level that does not result in an intractable (i.e., not melt processible) polymer, or one that does not have useful physical properties. Preferably, about 15 to about 90%, more preferably about 30 to about 75% of the acid moieties of the acid copolymer are neutralized to form carboxylate groups. The ionomers further comprise, as counterions, one or more cations. Although any positively charged moiety may be suitable, the ionomers used herein preferably comprise cations of one or more alkali metals, alkaline earth metals, and/or transition metals.

Preferred cations for use in the unmodified ionomers include cations of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, or combinations of two or more of these cations. Of note are sodium, calcium, potassium and lithium cations. Magnesium and zinc are preferred, and zinc is more preferred.

Preferably at least 20 equivalent %, at least 35 equivalent %, at least 50 equivalent %, or at least 75 equivalent % of the cations in the composition are magnesium cations. More preferably at least 20 equivalent %, at least 35 equivalent %, at least 50 equivalent %, or at least 75 equivalent % of the cations in the composition are zinc cations.

Of note is an ionomer made from a dipolymer comprising ethylene and 19 weight % of methacrylic acid neutralized with sufficient ZnO to produce an ionomer having an MI of 4.0. Also of note is an ionomer made from a dipolymer comprising ethylene and 15 weight % of methacrylic acid neutralized with ZnO.

Polyamines or Polyamides

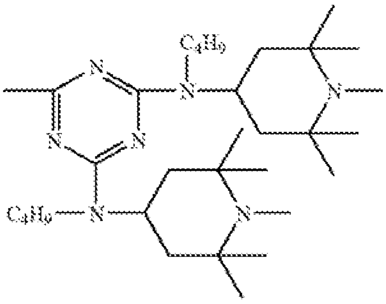
The thermoplastic composition also includes a polyamine compound or a polyamide compound having a molecular weight of greater than 500 Da, not containing an ester moiety or a primary amine moiety, wherein the polyamine comprises comprises at least three moieties that are tertiary amines or hindered secondary amines and wherein the polyamide comprises tertiary amide moieties and no secondary or primary amide moieties.

“Hindered” means that sterically bulky groups are adjacent to the secondary amine, such as tertiary or quaternary carbon atoms. The polyamines may be monomeric, oligomeric or polymeric. Preferred polyamines have molecular weight greater than 1000 Da, or greater than 1500 Da.

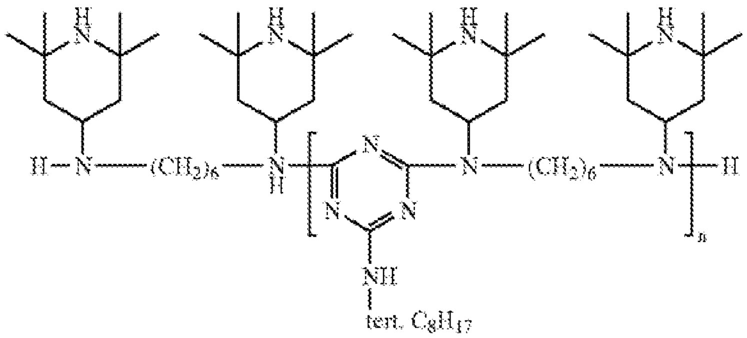
Examples of hindered secondary amine moieties include 2,2,6,6-tetramethylpiperidine and related materials such as 4-amino-2,2,6,6-tetramethylpiperidine. Polyamine derivatives of these monoamines having molecular weights above 500 Da may be prepared by combining by covalent bonding at least three of these secondary amine moieties.

Some Hindered Amine Light Stabilizers (HALS) marketed under the tradename CHIMASSORB by Ciba (CIBA) Specialty Chemicals, Vienna, Austria are examples of suitable polyamines.

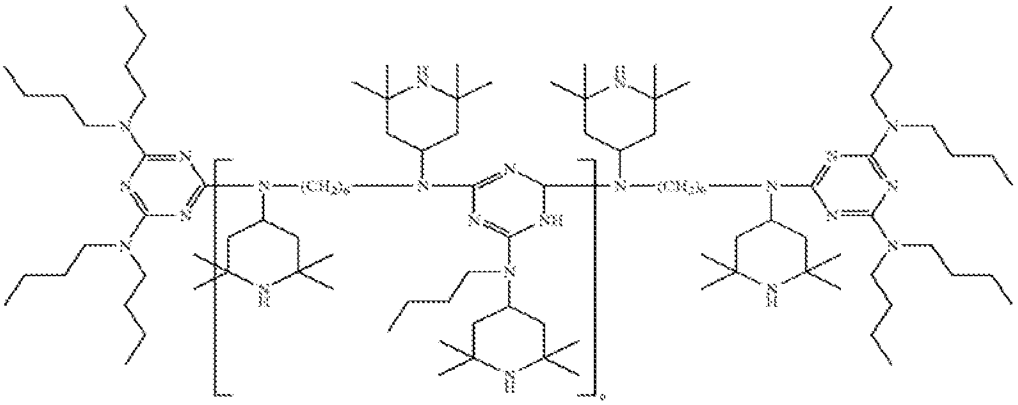
One HALS that may be used is CHIMASSORB 119,having the chemical structure R-NH-$(CH_2)_3$-NR-$(CH_2)_2$-NR-$(CH_2)_3$-NH-R, where R is



In addition, other high molecular weight monomeric HALS may be used, such as CHIMASSORB 944 or CHIMASSORB 2020. CHIMASSORB 944, poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidyl)imino]], has the following chemical structure:



CHIMASSORB 2020 has the following chemical structure:



Polyamides comprising tertiary amides include polyvinylpyrrolidone (PVP) and poly(2-ethyl oxazoline). Tertiary amide moieties are those that do not include an N-H bond. Secondary amides have one N-H bond and primary amides have an NH_2 moiety. Notably, these polyamides can function as Lewis bases.

Polyvinylpyrrolidone, or Povidone, CA number [9003-39-8], Merck Index, 13, 7783, is available commercially from International Specialty Products of Wayne, NJ, as a series of products having average molecular weights of about 10,000 to about 1,300,000

Da or more (e.g about 10,000 Da, about 29,000 Da, about 55,000 Da, about 700,000 Da or about 1,300,000 Da). Copolymers of vinyl pyrrolidone, such as poly(1-vinylpyrrolidone-co-styrene), CA number [25086-29-7], may also be used.

Poly(2-ethyl oxazoline), or N-propionyl substituted linear polyethylenimine, CA number [25805-17-8], is available commercially from International Specialty Products as a series of products having average molecular weights of about 50,000 to about 500,00 Da or more (e.g. about 50, 000 Da, about 200,000 Da or about 500,00 Da). Of note is the material having average molecular weight of about 50,000 Da, which is commercially available under the tradename AQUAZOL 50.

A number of provisos apply to the present description. For example, polyamides containing secondary amide moieties, such as nylons, are not contemplated for use in the thermoplastic composition described herein. In addition, ester moieties and primary amine moieties are not desirable in the polyamine or polyamide. Without being bound by theory, esters or primary amines in the polyamine or polyamide may negatively interact with the ionomer, reducing melt flow.

Combinations of two or more of the suitable polyamine or polyamide additives may be used in the thermoplastic compositions, however. Polyamides may be preferred for use in some of the thermoplastic compositions described herein.

The amount of polyamine or polyamide may be from about 1 to about 40 weight %, preferably about 3 to about 40 weight %, about 5 to about 35 weight %, about 10 to about 30 weight % or about 15 to about 25 weight %, based on the total weight of the thermoplastic composition.

In summary, some preferred thermoplastic compositions comprise an E/X dipolymer comprising 14 to 20 wt% of (meth)acrylic acid, neutralized to form an ionomer comprising zinc cations. The preferred thermoplastic compositions further comprise 15 to 25 wt%, based on the total weight of the thermoplastic composition, of a suitable polyamine or polyamide, and more preferably comprise a polyamine modifier.

Other components

The thermoplastic compositions may optionally comprise small amounts of other materials commonly used and well known in the polymer art. Such materials include conventional additives used in polymeric materials including plasticizers; stabilizers, including viscosity stabilizers and hydrolytic stabilizers; primary and secondary antioxidants, such as for example IRGANOX 1010 (commercially available from CIBA); ultraviolet ray absorbers and stabilizers; anti-static agents; dyes; pigments or other coloring agents; fire-retardants; lubricants; processing aids; slip additives; antiblock agents such as silica or talc; release agents; other components known in the art of golf ball manufacture to be useful but not critical to golf ball performance and/or acceptance, such as inorganic fillers as described below, acid copolymer waxes, such as for example

Honeywell wax AC540, TiO_2, which is used as a whitening agent, optical brighteners, and surfactants; and mixtures or combinations of two or more conventional additives. These additives are described in the *Kirk Othmer Encyclopedia of Chemical Technology*, 5th Edition, John Wiley & Sons (New Jersey, 2004), for example.

These conventional ingredients may be present in the compositions in quantities that are generally from 0.01 to 15 weight %, preferably from 0.01 to 10 weight %, so long as they do not detract from the basic and novel characteristics of the composition and do not significantly adversely affect the performance of the composition or of the golf balls prepared from the composition. In this connection, the weight percentages of such additives are not included in the total weight percentages of the thermoplastic compositions defined herein. Typically, many such additives may be present in from 0.01 to 5 weight %, based on the total weight of the thermoplastic composition.

The optional incorporation of such conventional ingredients into the compositions can be carried out by any known process. This incorporation can be carried out, for example, by dry blending, by extruding a mixture of the various constituents, by the conventional masterbatch technique, or the like. See, again, the *Kirk-Othmer Encyclopedia*.

Filler

Various fillers may be added to compositions to reduce cost, to affect rheological and mixing properties such as density, flex modulus, mold release, and/or melt flow index and the like, to adjust physical properties such as the modulus, tear strength and the like, to increase or decrease weight, and/or to reinforce the material. The amount of filler employed is primarily a function of weight requirements and distribution of the golf ball. The fillers may be used to adjust the properties of a golf ball layer, to reinforce the layer, or for any other purpose.

For example, the compositions of the invention can be reinforced by blending with a wide range of density-adjusting fillers, e.g., ceramics, glass spheres (solid or hollow, and filled or unfilled), and fibers, inorganic particles, and metal particles, such as metal flakes, metallic powders, oxides, and derivatives thereof, as is known to those of skill in the art.

The filler may be chosen to impart additional density to compositions of the previously described components, the selection being dependent upon the type of golf ball desired (i.e., one-piece, two-piece, wound or multilayer), as will be more fully detailed below. The filler may be included in one or more layers of the golf ball. Generally, the filler will be inorganic, having a density from about 4 grams/cubic centimeter (g/cc), or from about 5 g/cc to about 10 g/cc or higher and may be present in amounts between 0 and about 60 weight % based on the total weight of the thermoplastic composition. Examples of useful fillers include metals such as titanium, tungsten, aluminum, bismuth, nickel, molybdenum, iron, steel, lead, copper, brass, boron, boron carbide whiskers, bronze, cobalt, beryllium, zinc, tin; metal oxides including zinc oxide, iron oxide, aluminum oxide, tin oxide, titanium oxide, magnesium oxide, zinc oxide and zirconium oxide; as well as other well known corresponding salts and oxides thereof. Other preferred fillers include barium sulfate, lead silicate, tungsten carbide, limestone (ground calcium/magnesium carbonate), zinc sulfate, calcium carbonate, zinc carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind and ground flash filler, and mixtures of two or more of any suitable fillers. It is preferred that the filler materials be non-reactive or almost non-reactive.

Fillers may be employed in a finely divided form, for example, in a size generally less than about 20 mesh U.S. standard size, preferably from about 100 mesh to about 1000 mesh, except for fibers and flock, which are generally elongated. Flock and fiber sizes are desirably small enough to facilitate processing. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations.

Fillers may also be used to modify the weight of the core or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

Blowing or Foaming Agent(s)

The compositions may be foamed by the addition of at least one physical or chemical blowing or foaming agent. The use of a foamed polymer allows the golf ball designer to adjust the density or mass distribution of the ball to adjust the angular moment of inertia, and, thus, the spin rate and performance of the ball. Foamed materials also offer a potential cost savings due to the reduced use of polymeric material. A description of suitable blowing or foaming agents and methods for their use is included in U.S. Patent Appln. No. 12/215,674, filed on June 30, 2008, to which the present application claims priority.

Other Ionomer Compositions

Any golf ball or golf ball component described herein may comprise or be prepared from an ionomer composition. As used herein, the term “ionomer composition” refers to a composition that comprises an ionomer and that is different from the thermoplastic composition described herein. For example, the ionomer composition may be modified or unmodified, but if modified with a polyamine or polyamide, the polyamine or polyamide has a molecular weight of less than 500 Da; or contains an ester moiety or a primary amine moiety; or does not comprise at least three moieties that are tertiary amines or hindered secondary amines; or comprises secondary or primary amide moieties and no tertiary amide moieties. Moreover, the golf balls or golf ball components described herein may comprise or be prepared from a blend of the thermoplastic compositions described herein with one or more ionomer compositions.

Suitable E/X/Y copolymers for use in the ionomer compositions are as described above with respect to the thermoplastic compositions. Suitable neutralization levels are from 0 to 100%, preferably 50% to 100%, 50% to 100%, 60% to 100%, 70% to 100%, 80% to 100%, 90% to 100%, 95% to 100% or about 100%. In summary, the unmodified ionomers may be neutralized to any level that does not result in an intractable (not melt processible) polymer, or a material that does not have useful physical properties. Suitable counterions for the ionomers are as described above with respect to the thermoplastic composition described herein.

Some preferred ionomer compositions are modified with one or more organic acids or with one or more salts of organic acids. Suitable organic acids include, without limitation, monofunctional organic acids having fewer than 36 carbon atoms, optionally substituted with from one to three substituents independently selected from C_1 to C_8 alkyl groups. The organic acids may be saturated or unsaturated, and, if unsaturated, may include more than one carbon-carbon double bond. The term “mono-functional” refers to acids with one carboxylic acid moiety. The suitable organic acids include C_4 to C_{36} (for example C_{18}), more particularly C_6 to C_{26}, and even more particularly C_6 or C_{12} or C_{18} to C_{22} acids. In some cases, C_{19} to C_{36} acids are preferred.

Specific examples of suitable organic acids include, but are not limited to, caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, isostearic acid, behenic acid, erucic acid, oleic acid, iso-oleic acid, and linoleic acid. Naturally derived organic fatty acids such as palmitic, stearic, oleic, erucic, behenic acids, and mixtures thereof may also be employed.

As is well known in the art, commercial grades of organic acids may include a number of structurally different organic acids of varying lesser amounts. As used herein, unless otherwise specified in limited circumstances, a composition that comprises a named acid may also include other acids that are present in commercial grades of the named acid, at levels that are proportional to their levels in the commercial grade. Furthermore, when the transitional term “consisting essentially of” is applied to compositions that comprise a named acid, other acids that are present in commercial grades of the named acid, at levels that are proportional to their levels in the commercial grade, are not excluded from the composition.

Suitable E/X/Y copolymers for use in ionomer compositions that are modified with organic acids are as described immediately above. Suitable neutralization levels for these modified ionomer compositions are from 0 to 100%, preferably 50% to 100%, 50% to 100%, 60% to 100%, 70% to 100%, 80% to 100%, 90% to 100%, 95% to 100% or about 100%. In summary, the modified ionomers may be neutralized to any level that does not result in an intractable (not melt processible) polymer, or a material that does not have useful physical properties. Suitable counterions for these modified ionomers are as described above with respect to the thermoplastic composition described herein.

Preferred modified ionomer compositions include the ionomer compositions described in U.S. Patent Application Nos. 11/789,831, filed on April 25, 2007; 11/201,893, filed on August 11, 2005; and 09/422,142, filed on October 21, 1999; and in U.S. Patent Nos. 6,953,820 6,653,382; and 6,777,472. Other preferred modified ionomer compositions are described in U.S. Provisional Appln. No. 61/001,454, filed on November 1, 2007; in U.S. Patent Nos. 6,100,321; 6,815;480; and 7,375,151; and in U.S. Patent Appln. Publn. Nos. 2003/0050373 and 2003/0114565.

Finally, the ionomer compositions may further comprise one or more fillers, blowing agents, or other additives as described above with respect to the thermoplastic compositions.

Golf Ball Construction

The thermoplastic compositions described herein may be used in golf balls that have any type of construction. General descriptions of golf balls, golf ball structures, golf ball components, the desirable physical properties of golf balls, the selection of materials for performance criteria, and the principles by which golf balls are typically designed are included in U.S. Patent Appln. No. 12/215,674.

As used herein with respect to golf balls, the term "layer" includes any substantially spherical or spherically symmetrical portion of a golf ball, i.e., a golf ball core or center, an intermediate layer, and/or a golf ball cover. As used herein, the term "inner layer" refers to any golf ball layer beneath the outermost structural layer of the golf ball. As used herein, the terms "layer" and “structural layer” include a cover, but do not include a coating layer, top coat, paint layer, or the like. As used herein, the term "multilayer", when used without specifying a number of layers, refers to a golf ball with at least three structural layers comprising a cover, an intermediate layer and core. The term “component” refers to any constituent part of a golf ball. A component may have any shape.

Preferred one-piece golf balls

Preferred one-piece golf balls are made by injection or compression molding a sphere of desired size from the thermoplastic composition described above or its blends with other ionomer compositions or with non-ionomeric thermoplastic resins. The ionomer compositions and other resins may be modified or unmodified, and may include conventional additives as described above with respect to the thermoplastic compositions. The one-piece ball may include sufficient filler to provide a golf ball having a desired weight or density. Preferably, enough filler is used so that the ball has a density 1.14 gm/cc or a weight of 45 grams. One-piece golf balls may be coated, lacquered, or otherwise finished as described below with respect to covers.

Preferred two-piece golf balls

Two-piece balls include a core or center and a cover. They may be manufactured by well-known techniques wherein covers are injection or compression molded over cores. The core of a two-piece ball may be made by injection or compression molding a solid of desired size and shape. Preferred core shapes are substantially spherical or spherically symmetrical.

The core and the cover are prepared from a thermoplastic composition, for example the thermoplastic composition described herein, or from a thermoset composition. The compositions of the core and the cover may be the same or different. The core and cover compositions are optionally filled with sufficient filler to provide a desired density. Suitable core densities can be, for example, from about 1.14 g/cc to about 1.2 g/cc, depending on the diameter of the core and the thickness and composition of the cover. It may be desirable, for example, to produce a golf ball meeting the weight limit (45 grams or less) and size limit set by the USGA. The amount of filler in the cover may be the same as or different from the amount of filler in the core. Likewise, the density of the cover may be the same as or different from the density of the core.

In particular, the innermost layer of the golf ball is known as the center or core. A solid core is prepared from a composition that is typically injection-molded or compression-molded to form a substantially spherical or spherically symmetrical solid. Any core material known to one of ordinary skill in the art is suitable for use in the golf balls described herein. Suitable core materials include thermoset materials, such as rubber, styrene butadiene, polybutadiene, isoprene, polyisoprene, trans-isoprene, as well as thermoplastic materials such as ionomer resins, ionomer compositions, polyamides or polyesters, and thermoplastic and thermoset polyurethane or polyurea elastomers. Alternatively, the core can be prepared from the thermoplastic compositions described herein.

Preferred thermoplastic cores comprise or are prepared from one or more ionomer compositions. Preferably, these ionomer core compositions are modified E/X/Y copolymers in which the amount of X is 2 to 25 wt%, preferably 5 to 15 wt%, and the amount of Y is 2 to 50 wt%, preferably 5 to 40 wt%. Preferably, the softening monomer, Y, is an alkyl ester of (meth) acrylic acid, and more preferably an alkyl ester of acrylic acid. The melt index of the parent acid copolymer is preferably in the range of 20 to 500 g/10 min, measured at 190°C using a 2160 g weight. About 50 to 100% of the carboxylic acid moieties in the parent acid copolymers are neutralized. Preferred counterions include sodium, zinc, magnesium, and calcium. The melt index of the ionomer is preferably about 0.1 to 5 g/10 min, measured at 190°C using a 2160 g weight.

To form the ionomer core compositions, these ionomers are modified with one or more organic acids or with one or more salts of organic acids. Preferred organic acids include caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, isostearic acid, behenic acid, erucic acid, oleic acid, iso-oleic acid. The modifier(s) are present in an amount of about 5 to 50 wt% or about 10 to 50 wt%, based on the total weight of the ionomer core composition. Preferred counterions and preferred neutralization levels are as set forth above with respect to ionomer compositions. Magnesium is more preferred, however, and more preferably at least about 80% to 100% of the acid moieties of the E/X/Y copolymer and of the organic acid are neutralized.

The core has an average diameter such that the thickness of the cover and any additional layers can be added to the diameter of the core to provide a golf ball of desired size, for example, at least about 1.68 inches in diameter.

The outermost structural layer of a golf ball is known as the cover. The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others.

The covers can be made by any suitable method, including, without limitation, casting, injection molding, reaction injection molding, or compression molding a cover composition. Covers can be made from any conventional golf ball cover material such as ionomer resins, ionomer compositions, balata rubber, thermoset/thermoplastic polyurethanes and the like. Covers may also be prepared from the thermoplastic compositions described herein, or from blends of two or more suitable materials.

The cover typically has a thickness that is adequate to provide sufficient strength, good performance characteristics, and durability. For example, cover layers may be from about 0.005 inch to about 0.35 inch in thickness. In one golf ball, the cover thickness is from about 0.02 inches to about 0.35 inches. The cover preferably has a thickness of about 0.02 inches to about 0.12 inches, preferably about 0.1 inches or less. When the compositions of the invention are used to form the outer cover of a golf ball, the cover may have a thickness of about 0.1 inches or less, preferably about 0.07 inches or less.

The cover of a golf ball, or the surface of a one-piece ball, may be painted, coated, or surface treated for further benefits. For example, the golf ball may be coated with a urethane lacquer or otherwise finished for appearance purposes; however, such a coating, painting and/or finishing generally does not have a significant effect on the performance characteristics of the ball.

Of note is a two-piece golf ball comprising a cover that comprises or is prepared from the thermoplastic composition described herein and a thermoset rubber core. Also of note is a two-piece golf ball comprising a cover that comprises or is prepared from the thermoplastic composition described herein and a thermoplastic core. Further of note is a two-piece ball in which the core comprises or is prepared from the thermoplastic composition described herein.

Preferred wound golf balls

Of note is a wound golf ball comprising a cover that comprises or is prepared from the thermoplastic composition described herein and a thermoset rubber core.

Preferred multilayer golf balls

Multilayer golf balls contain one or more additional layers between the cover and the core or center. These additional layers are also known as mantles or intermediate layers. Suitable covers and centers for multilayer balls are as described above with respect to two-piece golf balls.

Multilayer balls may be manufactured by well-known techniques wherein an injection or compression molded core is covered by one or more intermediate layers or mantles and a cover. The various layers of the golf balls are made by injection or compression molding a sphere or layer of desired size or thickness. Any of the cover, the core, or the intermediate layer(s) may comprise or be prepared from a thermoplastic composition, for example the thermoplastic composition described herein. Alternatively, any of the structural layers may comprise or be prepared from a thermoset composition.

In addition, any of the golf ball components may optionally include sufficient filler to provide a golf ball having a desired density, for example one that meets the size and weight limits set by the USGA. Accordingly, the amount of filler employed in the core and/or mantle(s) can be varied from 0 to about 60 weight % depending on the size (thickness) of the components and the desired distribution of the weight in the ball. Preferably, enough filler is used so that the ball has an overall density of about 1.14 gm/cc. The filler can be used in the core and not in the mantle, in the mantle and not in the core, or in both.

The intermediate layer may comprise or be prepared from ionomer resins, ionomer compositions, the thermoplastic compositions described herein, or non-ionomeric compositions including, but not limited to, polyvinyl chloride, copolymers of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride, polyolefins, such as polyethylene, polypropylene, polybutylene copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst, polyphenylene ether, copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic acid, ethylene acrylic acid, propylene acrylic acid, polyamides such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam).

Other suitable materials include but are not limited to, thermoplastic or thermosetting polyurethanes, thermoplastic block polyesters, for example, a polyester elastomer such as that marketed by DuPont under the trademark HYTREL®, or thermoplastic block polyamides, for example, a polyether amide such as that marketed by Elf Atochem S. A. under the trade name PEBAX, a blend of two or more non-ionomeric thermoplastic elastomers, or a blend of one or more ionomers and one or more non-ionomeric thermoplastic elastomers. Moreover, mixtures of two or more of any of the suitable materials described above, including polyamide/ ionomer blends, polyphenylene ether/ionomer blends, etc., may also be used in the intermediate layer.

At least one intermediate layer may also be a moisture barrier layer, such as the ones described in U.S. Patent 5,820,488. Other suitable materials for use in moisture vapor barrier layers include the ionomer compositions described in U.S. Patent Application Nos. 11/789,831, filed on April 25, 2007; 11/201,893, filed on August 11, 2005; and 09/422,142, filed on October 21, 1999; and in U.S. Patent Nos. 6,953,820 6,653,382; and 6,777,472.

When the intermediate layer comprises or is prepared from an ionomer composition, the ionomer may include so-called "low acid" or "high acid" ionomers, as well as blends of low acid and high acid ionomers. In general, ionomers prepared by neutralizing acid copolymers including up to about 15 percent acid are considered low acid ionomers, while those including greater than about 15 percent acid are considered high acid ionomers.

A low acid ionomer is believed to impart high spin. Thus, in one golf ball, the intermediate layer includes a low acid ionomer in which the acid is present in about 10 to 15 weight percent and which optionally includes a softening comonomer, e.g., iso- or n-butylacrylate, to produce a softer terpolymer. The softening comonomer may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

In another golf ball, the intermediate layer includes at least one high acid ionomer, for low spin rate and maximum distance. In this ionomer, the acrylic or methacrylic acid is present in about 15 to about 35 weight percent, and the ionomer has a high modulus. In one golf ball, the high modulus ionomer includes about 16 percent by weight of a carboxylic acid, preferably from about 17 percent to about 25 percent by weight of a carboxylic acid, more preferably from about 18.5 percent to about 21.5 percent by weight of a carboxylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The additional comonomer may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl alkyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high modulus ionomers include, but are not limited to, high acid ethylene/acrylic acid copolymers, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, and the like.

Preferred for use in intermediate layers are ionomer compositions and their blends with other materials that are suitable for use in intermediate layers. Particularly preferred for use in intermediate layers are the thermoplastic compositions described herein, and their blends with other materials that are suitable for use in intermediate layers.

Turning now to the structure of the multilayer golf ball, the range of thicknesses for the intermediate layer is large because of the vastly different constructions that are possible, i.e., an outer core layer, an inner cover layer, a wound layer, a moisture/vapor barrier layer, and the like. In general, however, suitable intermediate layers, or inner cover layers, may have a thickness of about 0.3 inches or less. Varying combinations of ranges of thickness for the intermediate and outer cover layers may be used in combination with other golf balls described herein.

The ratio of the thickness of the intermediate layer to the outer cover layer is preferably about 10 or less, preferably from about 3 or less. In another golf ball, the ratio of the thickness of the intermediate layer to that of the outer cover layer is about 1 or less. The core and intermediate layer(s) together may be considered to form an “inner ball” preferably having a diameter of about 1.48 inches or greater for a golf ball having a diameter of 1.68 inch.

Finally, in multilayer balls, the core itself may have more than one layer. When the core includes an inner core layer and an outer core layer, the inner core layer may be preferably about 0.9 inches or greater in thickness and the outer core layer preferably has a thickness of about 0.1 inches or greater.

Preferred multilayer golf balls and golf balls of note include, without limitation, those set forth in the following Table.

TABLE: Preferred Multilayer Golf Balls

Golf Ball	Core	Mantle(s)[1]	Cover
ML1	TPC[2]	Any suitable[3]	Any suitable
ML2	Any suitable	TPC	Any suitable
ML3	Any suitable	Any suitable	TPC
ML4	TPC	Any suitable	Ionomer Comp.[4]
ML5	Any suitable	TPC	Ionomer Comp.
ML6	TPC	Any suitable	Polyurethane[5]
ML7	Any suitable	TPC	Polyurethane
ML7	Thermoset	Any suitable	TPC
ML8	Thermoset	TPC	Any suitable
ML9	Ionomer Comp.	TPC	Ionomer Comp.
ML10	Ionomer Comp.	TPC	Polyurethane

Notes for Table:

(1) When the multilayer golf ball has more than one mantle, only one of the mantles need include the component listed in the Table. The materials for the other intermediate layer(s) are selected independently from the suitable materials described herein. In addition, the composition of each mantle may be the same as or different from the composition(s) of the other mantle(s).
(2) “TPC” is an abbreviation for “the thermoplastic composition described herein”.
(3) “Any suitable” means that the material for this component may be selected independently from the suitable materials described herein for use in the specified golf ball component.
(4) “Ionomer Comp.” refers to the ionomer compositions described herein.
(5) The term “polyurethane” refers to thermoset or thermoplastic polyurethanes.

Selection of Materials for Performance Criteria

The properties such as hardness, modulus, compression, resilience, core diameter, intermediate layer thickness and cover layer thickness of the golf balls have been found to affect play characteristics such as spin, initial velocity and feel of the present golf balls. For example, the flexural and/or tensile modulus of the intermediate layer are believed to have an effect on the "feel" of the golf balls. Again, a detailed description of the principles of the selection of materials for performance criteria is included in U.S. Patent Appln. No. 12/215,674.

Initial Velocity and COR

Notably, however, the thermoplastic compositions described herein can provide tailored resiliency as indicated by the coefficient of restitution (COR). Coefficient of restitution is measured by firing a sphere that is 1.50 to 1.68 inches in diameter at an initial velocity of 125 feet/second against a steel plate positioned 3 feet from the point where initial velocity is determined and dividing the velocity of rebound from the plate by the initial velocity. COR may be determined on a sphere prepared from a single composition or a sphere having two or more layers (for example, a finished golf ball).

Of note is the thermoplastic composition that when formed into a sphere of 1.50 to 1.68 inches in diameter exhibits a rebound velocity of greater than 94 ft/sec, or greater than 99 ft/sec, when the sphere is fired at an initial velocity of 125 ft/sec against a steel plate positioned 3 feet from the point where initial velocity is determined.

Examples include a golf ball comprising a core, a cover prepared from an ionomer composition or a polyurethane; and an intermediate layer comprising or prepared from the thermoplastic composition described herein wherein the composition of intermediate layer when formed into a sphere of 1.50 to 1.68 inches in diameter exhibits a rebound velocity of greater than 94 ft/sec, or greater than 99 ft/sec, when the sphere is fired at an initial velocity of 125 ft/sec against a steel plate positioned 3 feet from the point where initial velocity is determined.

The thermoplastic compositions described herein, when formed into such a sphere, may have a coefficient of restitution of greater than about 0.6, preferably greater than about 0.5, more preferably greater than about 0.68, most preferably greater than about 0.7.

These rebound velocities and COR values are for spheres prepared from the thermoplastic composition without filler. Filled compositions may have reduced rebound velocity or COR compared to the unfilled composition, the reduction roughly proportional to the volume % of filler in the composition.

Flexural Modulus

Also notably, it is preferable that the golf balls have an intermediate layer with a flexural modulus of about 500 psi to about 500,000 psi. More preferably, the flexural modulus of the intermediate layer is about 1,000 psi to about 250,000 psi. Most preferably, the flexural modulus of the intermediate layer is about 2,000 psi to about 200,000 psi. The thermoplastic compositions described herein may have flexural modulus greater than 60, 80, 90, 100, 110, or 120 kpsi. Of note is a thermoplastic composition having a flexural modulus of greater than 80 kpsi, or 100 kpsi, measured according to ASTM D-790 B. Accordingly, the thermoplastic compositions described herein are useful for high modulus intermediate layers or cover layers. Examples include a golf ball comprising a core, a cover prepared from an ionomer or a polyurethane; and an intermediate layer comprising or prepared from the thermoplastic composition described herein having a flexural modulus of greater than 80 kpsi, or 100 kpsi, measured according to ASTM D-790 B.

The flexural modulus of the cover layer is preferably about 2,000 psi or greater, and more preferably about 5,000 psi or greater. In one golf ball, the flexural modulus of the cover is from about 10,000 psi to about 150,000 psi. More preferably, the flexural modulus of the cover layer is about 15,000 psi to about 120,000 psi. Most preferably, the flexural modulus of the cover layer is about 18,000 psi to about 110,000 psi. In another golf ball, the flexural modulus of the cover layer is about 100,000 psi or less, preferably about 80,000 or less, and more preferably about 70,000 psi or less. In one golf ball, when the cover layer has a hardness of about 50 Shore D to about 60 Shore D, the cover layer preferably has a flexural modulus of about 55,000 psi to about 65,000 psi.

In one golf ball, the ratio of the flexural modulus of the intermediate layer to the cover layer is about 0.003 to about 50. In another golf ball, the ratio of the flexural modulus of the intermediate layer to the cover layer is about 0.006 to about 4.5. In yet another golf ball, the ratio of the flexural modulus of the intermediate layer to the cover layer is about 0.11 to about 4.5.

In one golf ball, the thermoplastic compositions described herein are used in a golf ball with multiple cover layers having essentially the same hardness, but with differences in their flexural moduli. In this golf ball, the difference between the flexural moduli of the two cover layers is preferably about 5,000 psi or less. In another golf ball, the difference in flexural moduli is about 500 psi or greater. In yet another golf ball, the difference in the flexural moduli between the two cover layers, wherein at least one is reinforced is about 500 psi to about 10,000 psi, preferably from about 500 psi to about 5,000 psi. In one golf ball, the difference in flexural moduli between the two cover layers formed of unreinforced or unmodified materials is about 1,000 psi to about 2,500 psi.

In summary, the selection of compositions with specific resilience, compression, hardness and/or flex modulus will largely depend upon the type of golf ball desired (i.e., one-piece, two-piece, wound, or multi-layered), and in the type of performance desired for the resulting golf ball as detailed above.

The following examples are provided to describe the invention in further detail. These examples, which set forth a preferred mode presently contemplated for carrying out the invention, are intended to illustrate and not to limit the invention.

EXAMPLES

Testing Criteria for Examples

Coefficient of Restitution (COR) is measured by firing an injection-molded neat sphere of the resin the size of a golf ball from an air cannon at a velocity determined by the air pressure. The initial velocity generally employed is 125 feet/second. The sphere strikes a steel plate positioned three feet away from the point where initial velocity is determined, and rebounds through a speed-monitoring device located at the same point as the initial velocity measurement. The return velocity divided by the initial velocity is the

COR. One can also measure COR at several initial velocities, develop a correlation and determine a COR at a specified initial velocity based on the correlation.

In the Examples below, melt index (MI) refers to melt index as determined according to ASTM D1238 at 190°C using a 2160 g weight, with values of MI reported in g/10 minutes.

The Shore D hardness of a material is measured generally in accordance with ASTM D-2240, except the measurements are made on the curved surface of a molded sphere, rather than on a plaque. Shore D hardness of multilayer spheres is measured with all layers present. When a hardness measurement is made on a dimpled sphere, Shore D hardness is measured at a land area of the dimpled sphere.

Flex Modulus is measured according to ASTM D-790 B.

Tensile Strength is measured according to ASTM D-638.

Water vapor transmission rate (WVTR or MVTR) was measured on a PERMATRAN-W Model 700 instrument (available from MOCON, Inc., Minneapolis, MN) operated according to operating instructions at 38.1°C and 100% RH.

Impact Durability is the average number of hits to failure of balls fired by an air cannon of a COR tester at 175 or 135 ft/sec which impact a flat metal plate at a perpendicular angle.

Scuff resistance was determined in the following manner: a D-2 tool steel plate machined to simulate a sharp grooved pitching wedge with square (box) grooves was mounted on a swing arm that swings in a horizontal plane. The simulated club face was oriented for a hit on a golf ball at a 54° angle. The machine was operated at a simulated club head speed of 140 feet per second. Balls were prepared as described below from each of the test compositions. Comparison balls with polyurethane covers were obtained commercially. At least three balls of each composition were tested and each ball was hit once. After testing, the balls were rated according to the following criteria (see Table A). A stereo optical inspection microscope (2x to 10x) or equivalent was used to view the balls. Scuff damage was characterized by the presence of indented lines, lifts or groove bands. Indented lines are visible lines created by permanent displacement of the resin, but without cutting, breaking or discontinuity of the surface. Lifts are scuffs in which the resin is displaced enough that the surface is broken such that a portion of the resin is separated from the bulk of the ball. Severe lifts include flaps, whiskers or strands. Groove bands are bands of resin missing from the bulk of the ball corresponding in dimension to a single groove of the club face. The ratings were assigned numerical values based on the criteria in Table A.

TABLE A

0	No sign of impact or damage

1	1 or more indented lines on ball, but no cuts on the surface
1.5	Cut marks from the clubface are present, but no ridges
2	1 or more ridges
3	1 or more whiskers
3.5	Part of a ridge is missing with/without presence of whiskers
4	1 or more groove bands of material missing from cover
5	1 or more groove bands of material missing and material is sheared down to the bottom surface of dimples.

Compositions were prepared by melt blending the ionomer resins and the modifier employing a Werner & Pfleiderer twin-screw extruder. After blending, the compositions were extruded into the appropriate shapes for mechanical property testing. The materials were injection molded into flex bars and tensile test pieces and then tested for Shore D hardness, room temperature flex modulus, and room temperature tensile properties after aging for a period of at least two weeks at room temperature. The compositions were molded into spheres of about 1.53 to1.54 inch diameter, and the spheres were tested for golf ball properties, such as Atti compression, coefficient of restitution (COR), Shore D Hardness, and drop rebound. The compositions were also molded over commercial thermoset rubber cores to afford balls with diameter of about 1.68 inch. The balls were tested for golf ball properties, such as Atti compression, coefficient of restitution (COR), durability and scuff resistance. For accurate comparison of compression data, the diameter of the balls was corrected to 1.68 inch diameter using accepted methods, such as shimming.

Films were prepared by melting the composition in a twin screw extruder, exiting through a coat-hanger shaped sheet die to make a film of about 76 to about 104 micron thickness.

Ionomeric Materials Used

Code	Composition	Base Resin Melt Index, g/10 min	Neutralizing agent	Neutrn. level, %	Ionomer Melt Index, g/10 min
I-1	E/19MAA		ZnO		4.0
I-2	E/19MAA		NaOH		4.5
I-3	E/19MAA		$Mg(OH)_2$		1.1
I-4	E/8.7MAA		ZnO		5.2
I-5	E/15MAA		ZnO		0.7
I-6	E/19MAA		ZnO		1.3
I-7	E/15MAA		$Mg(OH)_2$		1
I-8	E/19MAA		NaOH		2.6
I-9	E/9MAA/23nBA		$Mg(OH)_2$		1.0
I-10	E/15MAA	220	ZnO		4.2

I-11	E/19MAA	60	$Mg(OH)_2$		2.5
I-12	E/8.5AA/15.5nBA with magnesium stearate		$Mg(OH)_2$	98	1
I-13	E/15MAA	60	LiOH		2.6
I-14	E/15MAA	60	NaOH		0.9
I-15	E/10.5AA/15.5nBA with oleic acid (35 wt%)		$Mg(OH)_2$		1

Other Materials Used

Amine-1: CHIMASSORB 944, available from CIBA.

PVP-1: A polyvinylpyrrolidone, 30,000 Dalton molecular weight, available from International Specialty Products (ISP), Wayne, NJ.

PVP-2: A polyvinylpyrrolidone, 15,000 Dalton molecular weight, available from ISP.

PVP-3: A polyvinylpyrrolidone, 90,000 Dalton molecular weight, available from ISP.

PEO-1: A poly(2-ethyl oxazoline, 50,000 Dalton molecular weight, available from ISP.

AO-1: antioxidant IRGANOX 1010 available from CIBA.

Three samples of each composition were tested. The results are reported as average values in the Tables below. Standard deviations, if reported, appear in parentheses. Comparative Examples using nonmodified ionomers were run with each set of Examples. Some variability in properties for a given composition between tests sets may be expected.

As shown in Tables 1 to 4, addition of a polyamine (Amine-1) to ionomers provides a significant increase in flex modulus and decrease in elongation at break. Addition of Amine-1 has modest, mixed effects on MI. Modification with amines provides increased compression, hardness, and COR, but may have little effect on scuff or durability.

Table 1

Example	C1	1	2	C2	3	4
I-1	100	90	80	0		
I-4	0	0	0	100	95	90
Amine-1	0	10	20	0	5	10
MI	4.0	4.8	4.1	5.2	3.6	4.2
Appearance	clear	white, opaque	white, opaque			
Spheres						
Compression as measured	159	164	171	142	154	157
Hardness, Shore D	66	71	72	55.1	59.7	64.4
COR-125	0.717	0.767	0.794	0.513	0.577	0.668
2-Piece Balls						
Compression	101	104	109	78	84	88

Example	C1	1	2	C2	3	4
COR-125	0.805	0.808	0.813	0.737	0.753	0.772
Impact Durability at 135 ft/sec	112	96	48			
at 175 ft/sec				6	9.2	7.6
Scuff testing	3.2	3.3	3.9	2.8	3.1	3.0
Film						
WVTR (mil·g/m^2·day)	20	26	36			
Tensile and Flex Pieces						
Flex Modulus (kpsi)	62	102	125	24 (3)	43 (4)	62 (4)
Stress at Break (kpsi)	2.57	3	3.35			
Elongation at Break (%)	104	91	87	225	191	114
Tensile Strength (kpsi)	2.67	3.43	4.28	2.10	2.42	2.34
Hardness, Shore D				49.2	57.9	61.0

Table 2

Example	C1	5	6	7	8
I-1	100	80	75	70	40
I-6	0	0	0	0	40
Amine-1	0	20	25	30	20
MI	4.0	3.5	4.0	5.0	1.9
Spheres					
Compression as measured	168	178	178	183	178
Hardness, Shore D	64	71	73	74	72
COR-125	0.699	0.794	0.799	0.799	0.793
2-Piece Balls					
Compression	116	123	125	127	125
COR-125	0.792	0.803	crack	crack	0.804
Impact Durability at 135 ft/sec	89	29	<5	<5	36
Scuff Testing	3	3	3	3	3
Tensile and Flex pieces					
Flex Modulus ASTM D-790 B (kpsi)	61	126	144	154	128
Stress at Break (kpsi)	3.1	4.4	3.6	1.3	4.3
Elongation at Break (%)	83%	47%	4%	1%	32%
Tensile Strength (kpsi)	3.1	3.6	3.6	1.3	3.7

Table 3

Example	C3	9	10	11	12	13	C4
I-1				67.5	45		
I-10	100	90	80				
I-11				22.5	45	80	100
Amine-1		10	20	10	10	20	

Example	C3	9	10	11	12	13	C4
MI	4.2	2.8	3.5	2.5	1.8	0.5	2.5
Spheres							
Compression as measured	164	169	176	177	174	180	172
average hardness, D	64	66	68	68	69	72	67
COR-125	0.668	0.748	0.758	0.769	0.770	0.799	0.770
2-piece Balls							
Compression	115	120	119	125	121	122	118
COR-125	0.787	0.791	0.794	0.798	0.798	0.805	0.796
Impact Durability at 135 fps	101	60	48	70	93	48	138
Scuff Testing	3	3	3	3	3	3	3
Tensile And Flex Pieces							
Flex Modulus (ksi)	59	81	102	104	105	130	90
Stress at Break (ksi)	2.9	3.2	3.6	3.5	3.7	4.4	3.5
Elongation at Break (%)	96%	49%	50%	68%	67%	42%	91%
Tensile Strength (kpsi)	2.9	3.2	3.3	3.5	3.7	4.1	3.5

Table 4

Example	C5	14	15	16
I-6	100	98.20	96.70	95.20
AO-1	0	0.3	0.3	0.3
Amine-1	0	1.5	3.0	4.5
MI		1.2	0.98	1
Spheres				
Specific Gravity, g/cc				
COR-125	0.677	0.687	0.703	0.715
Compression	161	162.3	159.7	159.4
Hardness, Shore D	64.7	66.0	66.7	67.1

Table 5

Example	C6	17	18
I-7	100	96.7	95.2
AO-1	0	0.3	0.3
Amine-1	0	3.0	4.5
MI		0.67	
Spheres			
COR-125	0.703	0.714	0.718
Compression	155.0	154.1	152
Hardness, Shore D	63.3	64.1	64.1

Table 6

Example	C7	19	20	C8	21
I-8	100	96.7	95.2	0	0
I-9	0	0	0	100	96.7
AO-1	0	0.3	0.3	0	0.3
Amine-1	0	3.0	4.5	0	3.0
MI		2			0.86
Spheres					

COR-125	0.753	0.753	0.757	0.642	0.638
Compression	173.0	170.5	168	62.0	89.2
Hardness, Shore D		67.8	67.6		47.2

As summarized in the previous Tables, COR, Shore D, and Compression generally increase with addition of amine to an ionomer. Table 7 shows an example in which the ionomer is also modified with a fatty acid salt.

Table 7

Example	C9	22
I-12	100	96.7
AO-1	0	0.3
Amine-1	0	3.0
MI	0.65	0.79
Spheres		
COR-125	0.805	0.781
Compression	103	112.4
Hardness, Shore D	52	52

The results of experiments designed to show the effect of the addition of polyamides such as polyvinylpyrrolidone or poly(2-ethyl oxazoline) to ionomers are set forth in Tables 8 and 9. A blend of 80:20 I-5:PVP-1 showed increased compression, hardness, and COR compared to the unmodified ionomer (Table 8). Flex modulus increased twofold. A similar increase in flex modulus was observed with a poly(2-ethyl oxazoline)-modified ionomer (Table 9).

Table 8

Example	C10	23	C11	24
I-3	0	0	100	85
I-5	100	80	0	0
PVP-1	0	20	0	15
MI	0.38	0.13	1.1	0.07
Neat Spheres				
Specific Gravity, g/cc	0.968	1.010		
Compression as measured	153	170		
Hardness, Shore D	66	72		
COR-125	0.690	0.735		
2-Piece Balls				
Compression			103.4	93.1
COR-125			0.795	Fail**
Durability at 175 ft/sec			2.2	Fail**
Scuff Test			3.0	2.8
Tensile and Flex Pieces				
Flex Modulus (Kpsi)	49	108	73 (7)	110 (11)

Example	C10	23	C11	24
Hardness, Shore D	65	68	65	68
Tensile at Break (psi)	2700	3200	3273	
Elongation at Break (%)	77	78	97	

Table 9

Example	C12	25	26
I-1	100	95	85
PEO-1	0	5	15
MI	4.0	2.2	2.6
Appearance	clear	white, hazy	white, opaque
2-Piece Balls			
Compression	90.8	98.0	102.7
COR-125	0.783	0.790	0.790
Durability at 175 ft/sec	3.8	2.0	2.0
Scuff Test	3.4	3.0	3.1
Tensile and Flex Pieces			
Flex Modulus (Kpsi)	49(12)	67(10)	99(9)
Hardness, Shore D	63	64	68
Tensile at Break (psi)	2928	3077	3414
Elongation at Break (%)	121	136	113

The data reported in Tables 10 and 11 show the effect of polyvinylpyrolidinone (PVP) loading, molecular weight, and delivery (dry or aqueous solution).

Table 10

Example	C12	27	28	29	30*	31	32
I-1	100	95	85	70	85	85	85
PVP-1	0	5	15	30	15	0	0
PVP-2	0	0	0	0		15	
PVP-3	0	0	0	0	0	0	15
MI	4.0	1.7	0.63	0.2	0.17	0.53	0.26
Appearance		faint yellow, clear	yellow, clear	yellow, hazy	faint orange clear	yellow, clear	white, clear, surface rough
2-Piece Balls							
Compression	90.8	101.2	95.5	102.2	100.9	95.9	95.4
COR-125	0.783	0.793	0.795	Fail**	0.794	Fail**	0.793
Durability at 175 ft/sec	3.8	1.0	3.8	Fail**	1.2	Fail**	2.8
Scuff Test	3.4	3.5	3.3	3.0	3.0	3.2	3.5
Tensile and Flex Pieces							
Flex Modulus (Kpsi)	49(12)	63(8)	118(10)	139(9)	104(9)	97(8)	112(15)
Hardness, Shore D	63	65	68	73	69	69	68
Tensile at Break (psi)	2928	3206	2937			3301	3408

Example	C12	27	28	29	30*	31	32
Elongation at Break (%)	121	129	41			65	52

* passed through the extruder twice

** “failed” balls broke or were misshapen

Table 11

Example	C12	33	34
I-1	100	95	85
PVP-1 (25 aq)	0	5	0
PVP-2 (50 aq)	0	0	15
MI	4.0	1.9	0.83
Appearance		pale yellow, clear	yellow, clear
2-Piece Balls			
Compression	90.8	97.5	97.0
COR-125	0.783	0.791	Fail**
Durability at 175 fps	3.8	2.4	Fail**
Scuff Test	3.4	3.0	3.1
Tensile and Flex Pieces			
Flex Modulus (Kpsi)	49 (12)	77 (9)	124 (11)
Shore D	63	63	68
Tensile at Break (psi)	2928	3057	3174
Elongation at Break (%)	121	117	73

“n aq” means an aqueous solution with n % by weight.

** “failed” balls broke or were misshapen

In Tables 12 and 13, impact durability was measured on 2-piece balls with conventional rubber cores. Compression and scuff resistance were measured on 2-piece balls with cores with nominal diameter of 3.94 cm and weight of 36.3 g prepared from I-15 and barium sulfate.

Table 12

Example	C13	35	36	C14	37
I-13	100	90	80	50	40
I-10	0	0	0	50	40
Amine-1	0	10	20	0	20
MI	2.6	1.3	3.2	3.5	2.4
Neat Spheres					
Compression	169	160	166	170	163
Hardness, Shore D	66.3	66.8	68.0	66.2	69.0
COR-125	0.757	0.756	0.760	0.746	0.760
2-Piece Balls					
Compression	113	112	115	103	113

Example	C13	35	36	C14	37
COR-125	0.836	0.836	0.832	0.837	0.834
Durability at 135 fps	136	102	1	100	31
Scuff Test	3	2.5	crack	3	2.5
Tensile and Flex Pieces					
Flex Modulus (kpsi)	71	84	101	74	102
Shore D	59.3	62.2	64.7	60.1	65.6
Tensile Strength (kpsi)	3.4	3.6	3.6	3.4	3.6
Elongation at Break (%)	103	107	106	103	71
Stress at break (kpsi)	3.4	3.6	3.6	3.4	3.6

The data in Table 12 illustrate that the effect of adding Amine-1 was to increase flex modulus significantly, with little change in COR.

Table 13

Example	C15	38	39	C16	40	41
I-1	50	45	40	0	0	0
I-2	50	45	40	0	0	0
I-10	0	0	0	50	40	0
I-14	0	0	0	50	40	80
Amine-1	0	10	20	0	20	20
MI	4.5	4.3	5.0	2.5	3.0	4.7
Neat Spheres						
Compression	174	157	166	168	162	168
Hardness, Shore D	68.6	69.9	72.5	66.5	68.6	69.4
COR-125	0.795	0.784	0.793	0.758	0.760	0.763
2-Piece Balls						
Compression	112	113	112	110	113	113
COR-125	0.843	0.842	0.842	0.837	0.836	0.839
Durability at 135 fps	99	78	1	136	44	45
Scuff Test	3	2.8	crack	3	2.5	3
Tensile and Flex Pieces						
Flex Modulus (kpsi)	93	104	125	72	100	105
Shore D	63.2	65.6	68.8	60.0	65.7	66.1
Tensile Strength (kpsi)	3.8	3.7	3.8	3.3	3.4	3.3
Elongation at Break (%)	136	94	88	86	85	64
Stress at break (kpsi)	3.8	3.8	4.3	3.3	3.5	3.6

The data in Table 13 illustrate that the effect of adding Amine-1 was to increase flex modulus significantly, with little change in COR.

While certain of the preferred embodiments of this invention have been described and specifically exemplified above, it is not intended that the invention be limited to such embodiments. Various modifications may be made without departing from the scope and spirit of the invention, as set forth in the following claims.

WHAT IS CLAIMED IS:

1. A thermoplastic composition comprising:

(a) an E/X/Y copolymer; wherein E represents copolymerized units of ethylene, X represents copolymerized units of a C_3 to C_8 α,β ethylenically unsaturated carboxylic acid, and Y represents copolymerized units of a softening comonomer; wherein the amount of X is about 2 to about 30 weight % and the amount of Y is 0 to about 45 weight %, based on the total weight of the E/X/Y copolymer; and wherein at least a portion of the acid moieties of the E/X/Y copolymer are neutralized to form an ionomer comprising carboxylate moieties and cations of one or more alkali metals, alkaline earth metals, or transition metals;

(b) a polyamine or a polyamide, in an amount of about 1 to about 40 weight % based on the total weight of the thermoplastic composition, said polyamine or polyamide having a molecular weight of greater than 500 Da;

with the provisos that: the polyamine and polyamide do not contain an ester moiety or a primary amine moiety; that the polyamine comprises at least three moieties that are tertiary amines or hindered secondary amines; and that the polyamide comprises tertiary amide moieties and does not contain secondary amide moieties; and optionally

(c) a filler.

2. The thermoplastic composition of Claim 1 wherein the E/X/Y copolymer is an ethylene acid dipolymer consisting essentially of copolymerized units of ethylene and of C_3 to C_8 α,β ethylenically unsaturated carboxylic acid, and wherein the amount of X is from about 10 to about 24 weight %.

3. The thermoplastic composition of Claim 1 or claim 2 wherein the ionomer of the ethylene dipolymer comprises one or more cations selected from the group consisting of sodium, calcium, potassium, lithium, magnesium and zinc cations.

4. The thermoplastic composition of any of claims 1 to 3 wherein the softening comonomer is selected from the group consisting of vinyl acetate, alkyl acrylate and alkyl methacrylate; wherein the alkyl groups have from 1 to 8 carbon atoms; and wherein the amount of Y is from about 0.1 to about 45 weight %.

5. The thermoplastic composition of any of claims 2 to 4, further comprising an E/X/Y terpolymer; wherein the softening comonomer Y of the E/X/Y terpolymer is selected from the group consisting of vinyl acetate, alkyl acrylate and alkyl methacrylate, wherein the alkyl groups have from 1 to 8 carbon atoms; and

wherein the amount of Y in the E/X/Y terpolymer is 0.1 to 45 weight %, based on the total weight of the E/X/Y terpolymer.

6. The thermoplastic composition of any of claims 1 to 5 wherein (b) the polyamine or the polyamide consists essentially of the polyamine and the polyamine consists essentially of a derivative of 2,2,6,6-tetramethylpiperidine or 4-amino-2,2,6,6-tetramethylpiperidine; or wherein (b) the polyamine or the polyamide consists essentially of the polyamide and the polyamide consists essentially of polyvinylpyrrolidone, a copolymer of vinyl pyrrolidone, or poly(2-ethyl oxazoline).

7. The thermoplastic composition of any of claims 1 to 6 having a flex modulus of greater than 80 kpsi measured according to ASTM D-790 B; or having a rebound velocity of greater than 94 ft/sec, said rebound velocity measured by forming the thermoplastic composition into a sphere having a diameter of 1.50 to 1.68 inches and firing the sphere at an initial velocity of 125 ft/sec against a steel plate positioned 3 feet from the point where initial velocity is determined.

8. The thermoplastic composition of any of claims 2 to 7, wherein the amount of X is from about 14 to about 20 wt%, the ionomer comprises zinc cations, wherein the polyamine or the polyamide consists essentially of the polyamine, and wherein the amount of the polyamine is about 15 to about 25 wt%.

9. An article comprising or prepared from the thermoplastic composition of any of claims 1 to 8.

10. The article of claim 9 wherein the article is a film.

11. The article of Claim 9 wherein the article is a one-piece golf ball or a two-piece golf ball comprising a core and a cover; optionally wherein the cover comprises or is prepared from the thermoplastic composition.

12. The article of Claim 9 wherein the article is a multilayer golf ball comprising a core, a cover and one or more intermediate layers positioned between the core and the cover, wherein the core, the cover or one or more of the intermediate layers comprises or is prepared from the thermoplastic composition.

13. The golf ball of Claim 12 wherein the cover comprises or is prepared from a polyurethane composition; or wherein the cover comprises or is prepared from

the thermoplastic composition; or wherein the cover comprises or is prepared from an ionomer composition; or wherein at least one intermediate layer comprises or is prepared from the thermoplastic composition; or wherein the core comprises or is prepared from an ionomer composition; or wherein the core is a thermoset rubber core.

14. The golf ball of claim 13 wherein the ionomer composition comprises an ionomer derived from an E/X/Y copolymer; wherein E represents copolymerized units of (meth)acrylic acid, and Y represents copolymerized units of an alkyl ester of (meth)acrylic acid, said alkyl group having from 1 to 8 carbon atoms; wherein the amount of X is about 5 to about 15 weight % and the amount of Y is about 5 to about 40 weight %, based on the total weight of the E/X/Y copolymer;
and wherein the ionomer composition further comprises one or more fatty acids selected from the group consisting of caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, isostearic acid, behenic acid, erucic acid, oleic acid, iso-oleic acid, and linoleic acid;
and wherein about 80% to about 100% of the acid moieties of the E/X/Y copolymer and of the organic acid are neutralized to form an ionomer composition comprising carboxylate moieties and cations of magnesium.

15. The golf ball of Claim 12 wherein the cover comprises or is prepared from a polyurethane or an ionomer composition, wherein at least one of the intermediate layers comprises or is prepared from the thermoplastic composition, and wherein the thermoplastic composition has a flex modulus of greater than 80 kpsi measured according to ASTM D-790 B; or wherein the cover comprises or is prepared from a polyurethane or an ionomer composition, and wherein the thermoplastic composition, when formed into a sphere of 1.50 to 1.68 inches in diameter, exhibits a rebound velocity of greater than 94 ft/sec when the sphere is fired at an initial velocity of 125 ft/sec against a steel plate positioned 3 feet from the point where initial velocity is determined.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/048585

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/08 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 241 625 B1 (YOKOTA MASATOSHI [JP]; IWAMI SATOSHI [JP]; OHAMA KEIJI [JP]) 5 June 2001 (2001-06-05) the whole document -----	1-5,7-15
X	US 6 319 154 B1 (YOSHIDA KAZUNARI [JP]; MORIYAMA KEIJI [JP]) 20 November 2001 (2001-11-20) the whole document -----	1-5,7-15
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 22 September 2009	Date of mailing of the international search report 30/09/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Van Golde, Lambertus

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/048585

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No
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