Disclosed herein is a golf ball comprising a core, a cover and a velocity-reduced layer disposed therebetween, wherein the velocity-reduced layer reduces the coefficient of restitution of the ball by at least 0.005, and wherein the velocity-reduced layer has a loss tangent in the range of 0.01 to 100 at frequency less than 100 Hz.

Related U.S. Application Data

Continuation-in-part of application No. 10/741,987, filed on Dec. 19, 2003.
Continuation-in-part of application No. 10/759,494, filed on Jan. 16, 2004.
GOLF BALL WITH VELOCITY REDUCED LAYER
CROSS-REFERENCE TO RELATED APPLICATIONS

This non-provisional patent application is a continuation-in-part of co-pending application entitled “Multi-layer Golf Ball” bearing Ser. No. 10/194,291; a continuation-in-part of co-pending application entitled “Golf Ball Comprising a Plasticized Polyurethane” bearing Ser. No. 10/741,987; a continuation-in-part of co-pending application entitled “Golf Ball with Vapor Barrier Layer and Method of Making Same” bearing Ser. No. 10/755,638; and a continuation-in-part of co-pending application entitled “Golf Ball with Vapor Barrier Layer and Method of Making Same” bearing Ser. No. 10/759,494. The disclosures of the parent cases are incorporated by reference in their entireties.

FIELD OF THE INVENTION

The present invention relates to golf balls, and more particularly, to a golf ball having a velocity-reduced layer.

BACKGROUND OF THE INVENTION

Golf balls can generally be divided into two classes: solid and wound. Solid golf balls include single-layer, dual-layer (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by tensioned elastomeric thread, and a cover. Solid balls have traditionally been considered longer and more durable than wound balls, but lack the particular “feel” that is provided by the wound construction and typically preferred by accomplished golfers.

By altering ball construction and composition, manufacturers can vary a wide range of playing characteristics, such as resilience, durability, spin, and “feel,” each of which can be optimized for various playing abilities. One golf ball component, in particular, that many manufacturers are continually looking to improve is the center or core. The core is the “engine” that influences how far the golf ball will travel when hit by a club head. Generally, golf ball cores and/or centers are constructed with a polybutadiene-based polymer composition. Compositions of this type are constantly being altered in an effort to provide a targeted or desired coefficient of restitution (“COR”), while at the same time often targeting a lower compression which, in turn, can lower the golf ball spin rate and/or provide better “feel.”

As recently reported in the press, due to the recent advances in golf ball compositions and dimple designs, some of the high performance golf balls may eventually exceed the maximum distance of 317 yards×3yds, when impacted by a standard driver at 160 feet per second and at 10° angle as set forth by the United States Golf Association (USGA). (See “Golf Ball’s Historic Flight, New Product Is Hailed for Distance, Accuracy,” by L. Shapiro, The Washington Post at pp. D1, D4, Mar. 22, 2001). As disclosed in U.S. Pat. No. 5,209,485, to reduce the distance that a golf ball would travel, inefficient dimple patterns and low resilient polymeric compositions are suggested. Low resilient compositions include a blend of a commonly used diene rubber, such as high cis-polybutadiene, and a low resilient halogenated butyl rubber. Inefficient dimple patterns include an octahedral pattern with a dimple free equator and a dimple coverage of less than 50%. As disclosed in the ’485 patent, the resulting ball travels about 50 yards less than comparative balls and has a coefficient of restitution of about 0.200 less than the coefficient of restitution of comparative balls. The ’485 patent theorizes that about 40% of the reduction in distance is attributable to the inefficient design, and about 60% is attributable to the low resilient ball composition. However, the art does not suggest a way to fine-tune the distance of high performance golf balls to adhere to the USGA limit.

However, there remains a need in the art to fine tune the distance that a golf ball would travel without affecting the other desired qualities, such as resilience, durability, spin, and “feel” of the golf ball.

SUMMARY OF THE INVENTION

The present invention is directed to a high performance golf ball that has a selectively reduced CoR with controlled weight, compression and spin rates.

Golf balls in accordance with the present invention comprise a core, a cover and a velocity-reduced layer disposed therebetween, wherein the velocity-reduced layer reduces the coefficient of restitution of the ball by at least 0.005, and wherein the velocity-reduced layer has a loss tangent in the range of 0.01 to 100 at frequency less than 100 Hz.

DETAILED DESCRIPTION OF THE INVENTION

The distance that a golf ball would travel upon impact by a golf club is a function of the coefficient of restitution (CoR) and the aerodynamic characteristics of the ball, among other things. The CoR is defined as the ratio of the relative velocity of two colliding objects after the collision to the relative velocity of the two colliding objects prior to the collision. For golf balls, the CoR has been approximated as a ratio of the velocity of the golf ball after impact to the velocity of the golf ball prior to impact, and it varies from 0 to 1.0. A CoR value of 1.0 is equivalent to a perfectly elastic collision, and a CoR value of 0.0 is equivalent to a perfectly inelastic collision. The CoR is related to the initial velocity of the ball, which must not exceed 250±5 ft/s, which the maximum limit set forth by the USGA. Hence, the CoR of golf balls are maximized and controlled, so that the initial velocity of the ball does not exceed the USGA limit.

The CoR of the golf ball is affected by a number of factors including the composition the core and the composition of the cover. The core may be single layer core or multi-layer core. It may also be solid or fluid filled. It may also be wound or foamed, or it may contain fillers. On the other hand, the cover may also be single layer cover or multi-layer cover. The cover may be thin or thick. The cover may have a high hardness or low hardness to control the spin and feel of the ball. The cover may comprise a thermoplastic or a thermoset material, or both. Compositions and dimensions of the cover and the core have been fully discussed in the art, such as U.S. Pat. Nos. 6,419,535, 6,152,834, 5,919, 100, 5,885,172, 5,783,293, 5,692,974, and PCT publication
In accordance with one aspect of the present invention, the inventive golf ball comprises a velocity-reduced layer, positioned preferably between the core and the cover. It may also be a part of the core or a part of the cover. Preferably, it is sized and dimensioned so that the reduction in CoR is incremental and selective. Additionally, it is preferred that the velocity-reduced layer reduces the CoR of the ball by at least 0.005 less than the CoR of a golf ball without such velocity-reduced layer, when the volume of the velocity-reduced layer would be occupied by the core.

A preferred material for the velocity-reduced layer is a visco-elastic polymer. Visco-elastic polymer is a polymer that exhibits properties of both liquids, i.e., viscous flow, and solids, i.e., elasticity. Visco-elasticity depends on temperature, time duration or frequency of the applied force, e.g., shear forces or impact forces, and strain. A well-known visco-elasticity in the relevant temperature range, and therefore is also suitable for the velocity-reduced layer. Polyurea, which has properties similar to polyurethane, is another suitable polymer.

Generally the visco-elasticity is expressed as a damping coefficient, which indicates whether the material will bounce back or return the energy to the system. For example, a visco-elastic polymer with a high damping coefficient attenuates more of the force applied to it and has a low resilience. As stated above, the attenuated force is converted into a small amount of heat. The damping coefficient can also be expressed as a loss tangent (tan δ), which is a dimensionless term and is a measure of the ratio of energy loss to energy stored in a cyclic deformation, i.e., tan δ=G"/G' Higher value of the damping coefficient corresponds to higher absorption of the impact force for materials that are damping in nature. Exemplary properties of a visco-elastic polymer, i.e., Sorbothane® polyurethane, are listed below:

<table>
<thead>
<tr>
<th>Durometer Hardness</th>
<th>30 Shore 00 (c ≤ 5 Shore A)</th>
<th>50 Shore 00 (10-15 Shore A)</th>
<th>70 Shore 00 (20 Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resilience (Rebound Height Test)</td>
<td>16%</td>
<td>18%</td>
<td>25%</td>
</tr>
<tr>
<td>ASTM D2632 92</td>
<td>Tangent of Delta at 5 Hertz</td>
<td>0.30</td>
<td>0.56</td>
</tr>
<tr>
<td>Tangent of Delta at 15 Hertz</td>
<td>0.38</td>
<td>0.58</td>
<td>0.60</td>
</tr>
<tr>
<td>Tangent of Delta at 50 Hertz</td>
<td>0.45</td>
<td>0.57</td>
<td>0.59</td>
</tr>
<tr>
<td>Tangent of Delta at 50 Hertz</td>
<td>0.35</td>
<td>0.50</td>
<td>0.55</td>
</tr>
</tbody>
</table>

example of a visco-elastic material is Silly Putty® (see U.S. Pat. No. 2,541,851), which is a dimethyl silicone treated with a compound of boron and then heated. Silly Putty® behaves like an elastic solid in reaction to a short-time stress, e.g., bouncing like a ball, and behaves like a viscous liquid in reaction to long-duration lower stress, e.g., flowing like a liquid if left on a table top. These visco-elastic properties also vary depending on the temperature of the polymer.

Another desirable property of visco-elastic polymer is that it converts some of the mechanical energy from the impact force to a small amount of heat, thereby partially dissipating the energy that would otherwise be available to propel the golf ball. Hence, visco-elastic polymer is a preferred material in accordance with the present invention. More preferably, suitable visco-elastic polymers should exhibit visco-elasticity in the range of ambient temperatures from about 40°F to about 120°F.

An example of a suitable visco-elastic polymer is a thermoset, polyether-based, polyurethane material, commercially available as Sorbothane® from Sorbothane, Inc., in Kent, Ohio. This thermoset polyurethane is available with very low hardness, e.g., less than 20 on a Shore A durometer scale (or about 70 on Shore 00 scale), and more preferably less than 40 Shore A. A typical characteristic of this material is that it has low resilience in a rebound test, in accordance with ASTM D2632 92 which has been modified to account for the tackiness of the polymer, and therefore would have a low CoR value when incorporated on to a golf ball. Additionally, thermoplastic polyurethane also exhibits the loss tangent values are typically expressed at a particular frequency, since a popular usage of visco-elastic polymer is to absorb and attenuate vibration energy. In terms of its application to golf ball design, the most applicable tangent of delta values would be the ones at the lower frequency.

While there is no known direct correlation between the resilience of a polymeric compound, which is related to CoR, and its loss tangent, it is observed that a material with a low resilience would typically have a high loss tangent or damping coefficient at a given frequency and % strain at a certain temperature value. Hence, polymeric compounds with low resilience are also suitable for the velocity-reduced layer, some of which may also have visco-elastic properties in the preferred temperature range. Dynamic mechanical measurements on plastics can be conducted under ASTM D4092-89 and D4065-95 standards.

In accordance with one aspect of the present invention, the velocity-reduced layer preferably comprises a visco-elastic material with a low tangent value at room temperature (or in their segmental motion relaxation including its glass transition temperature) from about 0.01 to about 100 at a frequency less than 100 Hz and at about 23°C, and more preferably from about 0.05 to about 10 and most preferably from about 0.1 to about 10. In accordance with another aspect of the invention, suitable materials for the velocity-reduced layer include polymers with low resilience, such as those in the material CoR range of about 0.3 to about 0.7, and more preferably from about 0.4 to about 0.65 and
most preferably from about 0.45 to about 0.6. As used herein material CoR is the measured resilience or CoR of a solid sphere made from said material.

In accordance with another aspect of the present invention, the velocity-reduced layer preferably comprises thermoplastic or thermostet resins that have a loss tangent at −20° C. from about 0.05 to 0.50. Suitable thermoplastic resins include, but are not limited to, polyamide, polypyrethene, polyester, polyolefin, polystyrene and ionomer resins, and thermostetting resins include but are not limited to, epoxy, polyurethane, polyimide, polyurea and phenol resins. Two or more of these resins can be used in combination. Fillers, colorants, dispersants, anti-aging agents, high density fillers and other additives can be added to the resins. Such resins are disclosed in U.S. Pat. No. 6,843,734 B2 as outermost cover materials used to increase the ball’s spin rate. These materials or polymers are usable herein as a velocity reducing intermediate layer. The ‘734 patent is incorporated herein by reference in its entirety.

Other suitable materials for velocity-reduced layer include those disclosed in U.S. Pat. No. 6,578,836 B2, specifically from col. 2, line 58 to col. 4, line 6. Additionally, materials used to dampen vibrations in vehicles can also be used as the velocity-reducing layer. See, e.g., U.S. Pat. No. 6,719,108 B2. The ‘836 and ‘108 patents are incorporated herein in their entireties.

Exemplary suitable velocity reduced materials disclosed in the ‘836 patent include dicene type rubber and hydrogenated forms thereof such as NR, IR, epoxidized natural rubber, SBR, BR (high cis BR and low cis BR), acrylonitrile-butadiene rubber (NBR), hydrogenated NBR, hydrogenated SBR; olefin type rubber such as ethylene-propylene rubber (EPDM, EPM), maleic acid modified ethylene-propylene rubber (M-EPDM), butyl rubber (IR), a copolymer of isobutylene and aromatic vinyl or dicene type monomer, acrylic rubber (ACM); halogen containing rubber such as Br-IR, Cl-IR, bromide of a isobutylene paramethyl styrene copolymer (Br-IPMS), chloroprene rubber (CR), hydride rubber (CHR), chloro-fluorosulfonated polyethylene (CSM), chlorinated polyethylene (CM), maleic acid modified chlorinated polyethylene (CM-C); silicone rubber such as methylvinyl silicone rubber, dimethyl silicone rubber, methylphenyl vinyl silicone rubber; sulfur containing rubber such as polysulfide rubber; fluoro rubber such as vinylidene fluoride type rubber, fluorine containing vinyl ether type rubber, tetrafluoroethylene-propylene type rubber, fluorine containing silicone type rubber, fluorine containing phosphazene type rubber; urethane rubber, epichlorohydrin rubber, and the like. These rubber compositions may be composed of only one kind or a mixture of two or more kinds of these components. Further, an ordinary vulcanizing agent or a cross-linking agent, a vulcanization accelerator or a cross-linking accelerator, various kinds of oil, an antioxidant, a filler, a softener and various types of other compounding agents generally mixed in the rubber can be mixed with the rubber composition.

Exemplary suitable thermoplastic resins include polyolefin type resin, polyamide type resin, polyester type resin, polycarbonate type resin, polynitrile type resin, poly-methacrylate type resin, polyvinyl type resin, cellulose type resin, fluorine type resin, imide type resin, and the like.

Suitable polyolefin resins include isotactic polypropylene, syndiotactic polypropylene, ethylene-propylene copolymer resin, and the like. Suitable polyamide resins include Nylon 6 (N6), Nylon 66 (N66), Nylon 46 (N46), Nylon 11 (N11), Nylon 12 (N12), Nylon 610 (N610), Nylon 612 (N612), Nylon 6/66 Copolymer (N6/66), Nylon Jun. 66, 19610 Copolymer (N6/66/10), Nylon MXD 6 (MXD 6), Nylon 6T, Nylon 6/6T Copolymer, Nylon 66/PP Copolymer, Nylon 66/PPS Copolymer, a polyamide elastomer, and the like. Suitable polyester resins include polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyethylene terephthalate (PET), a polyester elastomer, a PET/PEI copolymer, polyarylate (PAR), polybutylene terephthalate (PBN), liquid crystal polyester, a polyoxy-alicyclic diimide diacid/polybutylene terephthalate copolymer, and the like. Suitable polyester resins include polycetal (POM), polybenzyl oxides (PPO), polyethylene (PFPE), polyether ketone (PEEK), and the like. Suitable polyamide resins include polycaprolactone (PCL), polyethyleneimide, an acrylonitrile/styrene copolymer (AS), a methacrylonitrile/styrene copolymer, a methacrylonitrile/styrene/butadiene copolymer, and the like. As specific examples of the polyurethane resin, followings are enumerated: polyfunctional methacrylate (PMMA), polyethyl methacrylate, and the like. Suitable polyvinyl resins include vinyl acetate (EVA), polyvinyl alcohol (PVA), a vinyl alcohol/ethylene copolymer (EVOH), polyvinylidene chloride (PVDC), polyvinyl chloride (PV), a vinyl chloride/vinylidene chloride copolymer, a vinylidene chloride/methyl acrylate copolymer, and the like. Suitable cellulose resins include cellulose acetate, cellulose acetate butyrate, and the like. Suitable fluorine resins include polyvinylidene fluoride (PVDF), polyfluorohydrocarbons (PVDF), tetrafluoroethylene/ethylene copolymer (ETFE), and the like. Suitable imide resins include aromatic polyimide (PI) and the like.

In one embodiment, the velocity reduced layer is a rubbery, elastomeric material having a hardness from 10 Shore A to 50 Shore D, wherein the loss tangent at 23° C. is at least is less than 100, preferably less than 10 and most preferably less than 5. In another embodiment, the velocity reduced layer is a thermostatic rigid materials having a hardness range of 30 to 80 Shore D wherein the loss tangent at 23° C. is at least is less than 100, preferably less than 10 and most preferably less than 5.

In accordance with another aspect of the present invention, plasticizers are blended with polyurethane to provide higher flexibility, lower hardness and lower rebound resulting in increased energy absorption. Specifically, the increased energy absorption property of plasticized polyurethane is particularly suitable for the velocity-reduced layer of the present invention. Plasticized polyurethane is fully disclosed in commonly owned U.S. Pat. No. 6,849,675, which is incorporated herein by reference in its entirety. Plasticized polyurethane is the combination of polyurethane and plasticizer(s). Polyurethane is formed by conventional methods, such as forming a pre-polymer comprising a polyol and an isocyanate, followed by a curing agent. Plasticizer can be added at a variety of points prior to, during, or after formation of the urethane or blends thereof. Plasticized polyurethane may be thermostatic or thermosetting. Preferably, the amount of plasticizer in polyurethane is about 1 to 30 parts per hundred parts of dry polyurethane weight (phr), and more preferably from about 5 phr to about 25 phr.
[0026] The plasticizer is preferably selected from the group consisting of alkyl adipates, alkyl phthalates, alkyl azelates, alkyl benzoates, alkyl citrates, soy and linseed oils, and mixtures thereof. The preferred plasticizer is dialkyl phthalate. Alternatively, the plasticizer comprises \( C_{2-C_{10}} \) dialkyl adipates, \( C_{3-C_{10}} \) dialkyl phthalates, or acetyl tributyl citrate; or the plasticizer comprises dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisopropyl adipate, dibutyl adipate, bis(2-ethylhexyl) adipate, acetyl tributyl citrate, or a mixture thereof.

[0027] In one embodiment, the plasticized polyurethane composition comprises a foamed polyurethane compound produced by the reaction of a polyol and toluene diisocyanate, an amount of a non-halogen containing foaming agent sufficient to produce foam from the polyurethane compound, and a non-halogen containing plasticizer selected from the group consisting of phthalate plasticizers and phosphate ester plasticizers. If the plasticized polyurethane is a non-halogen foaming agent, preferably the non-halogen containing foaming agent is water or a non-halogen containing gas. More preferably, the non-halogen containing foaming agent is water. Most preferably, the non-halogen containing plasticizer is a phosphate ester.

[0028] In another embodiment, the phosphate ester comprises 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, mixed dodecyl and tetradeccyl diphenyl phosphate, trioctyl phosphate, tributyl phosphate, butylphenyl diphenyl phosphate, isopropylated triphenyl phosphate, or a mixture thereof. Preferably, the phosphate ester comprises 2-ethylhexyl diphenyl phosphate and isodecyl diphenyl phosphate. The phthalate plasticizer may comprise diisononyl phthalate, dihexyl phthalate, diheptyl phthalate, butyl octyl phthalate, linear dialkyl phthalate wherein the alkyl groups are independently carbon chains having from seven to eleven carbon atoms, and butyl cyclohexyl phthalate. Alternatively, the non-halogen containing plasticizer is an alkyl aryl phthalate.

[0029] In an alternative embodiment, the alkyl aryl phthalate comprises butyl benzyl phthalate, alkyl benzyl phthalate wherein said alkyl group has a carbon chain having from seven to nine carbon atoms, and texanol benzyl phthalate. Ideally, the composition further comprises synthetic poly-isoprene, natural polyisoprene, polybutadiene, butyl rubber, polynorbornene, ethylene-propylene diene monomer rubber, or styrene-butadiene rubber, combined with high levels of oils, plasticizers, fillers, and mixtures thereof.

[0030] The plasticizer may also comprise phthalic acid esters; aliphatic dibasic acid esters; trimellitate esters; fatty acid esters; benzoic esters; aliphatic phosphates; aromatic phosphates; halogenated aliphatic phosphates; and mixtures thereof. In a preferred embodiment, the plasticizer comprises a hydrophobic plasticizer. If so, the hydrophobic plasticizer comprises aromatic esters selected from the group consisting of dibutyl phthalate, dioctyl phthalate, dioctyl adipate, bis(2-ethylhexyl) phthalate, dicyclohexyl phthalate, butyl lauryl phthalate, diisooctyl phthalate, butyl-cocotaulkyl phthalate, diisoceryl phthalate, dilauryl phthalate, diisodecyl phthalate, butylbenzyl phthalate, octydle-canoyl phthalate, dimethylglycol phthalate, ethylphthevaly ethylene glycolate, methylphthevaly ethylene glycolate, butylphthevaly ethylene glycolate, dimonyl phthalate, dioctyl phthalate, octyldecyl phthalate, ditridecyl phthalate, dica

[0031] Alternatively, the hydrophobic plasticizer may comprise aliphatic esters selected from the group consisting of mono- di-, or polymer of higher fatty acid having 8 or more carbons with di-, tri-, or polyhydric alcohol, glycerin monostearate, glycerin 12-hydroxy stearate, glycerin distearate, diglycerin monostearate, tetracyglycerin monostearate, glycerin monolaurate, diglycerin monolaurate, tetracyglycerin monolaurate, polypropylene adipate, diisodecyl adipate, bis(2-methylhexyl) adipate, dicapryl adipate, disoctyl adipate, octyldecanoyl adipate, isocetylphthaleoyl adipate, dibutyl fumarate, dioctylfumarate, triethyl citrate, acetyltrithyl citrate, tributyl citrate, and acetyltributyl citrate.

[0032] Still alternatively, the hydrophobic plasticizer may comprise phosphate esters selected from the group consisting of tricresyl phosphate, phenylidicresyl phosphate, xyleylidicresyl phosphate, cresylidixylenyl phosphate, triphenyl phosphate, tributyl phosphate, trichloroethyl phosphate, triethyl phosphate, tributyl phosphate, trichloroethyl phosphate, trioctyl phosphate, and arylalky phosphate. The hydrophobic plasticizer may also include epoxy compounds selected from the group consisting of butylepoxy stearate, octylepoxy stearate, epoxibutyl oleate, epoxidized butyl oleate, epoxidized soybean oil, epoxidized linseed oil, epoxidized alkyl oil, and epoxidized alkyl oil alcohols ester; and mixtures thereof.

[0033] In still another embodiment, the plasticizer is selected from the group consisting of alkyl adipates, alkyl phthalates, alkyl azelates, alkyl benzoates, alkyl citrates, similar soy and linseed oils, \( C_{2-C_{10}} \) dialkyl adipates, \( C_{2-C_{10}} \) dialkyl phthalates, acetyl tributyl citrate, dibutyl phthalate, bis(2-ethylhexyl) phthalate, diisopropyl adipate, dibutyl adipate, bis(2-ethylhexyl) adipate, acetyl tributyl citrate, phthalates, adipates, sebacates, azelates, trimellitates, glutarates, benzoates, alkyl alcohols, phosphates, and mixtures thereof.

[0034] In accordance with another aspect of the invention, suitable polymers for the velocity-reduced layer include the latex disclosed in U.S. application publication no. 2001/0005699, which is not incorporated by reference. The disclosed polymers include elastomer latex that preferably has a flexural modulus of less than 10,000 psi and more preferably less than 3,000 psi. A preferred elastomer latex is a thermosetting latex, such as low ammonia natural latex, pre-vulcanized natural latex, elastomer adhesives, synthetic latexes, acrylic esters, alkyl resins, or mixtures thereof. Latex possesses high tensile strength, good elasticity, low flexural modulus and a strong ability to form strong, coherent films or thin layers. Using the preferred latex, the velocity-reduced layer can be as thin as about 0.0005 inch to about 0.01 inch. The hardness of such latex is typically less than 90 Shore A or less. Such layer absorbs some of the impact force from the club and thereby reducing the force propelling the ball. This reference also discloses other suitable visco-elastic polymers, which may be solid, semi-solid, gel, or gel like, and exhibit changing viscosity in response to shear forces, tensile forces and/or compressive strain. The disclosed visco-elastic polymers include polydimethyl siloxane, dimethyl cyclosiloxane, hydroxy-terminated polydimethyl siloxane, uncured polybutadiene, polybutadiene lightly cured with low levels of peroxide, zinc
oxide and less than 10 phr of zinc diacrylate or another α,ν-unsaturated carboxylic acid, polyvinyl alcohol, acrylic plastisol, acrylic organosol, hydrocarbon based gel, sulfonated ionomer, butyl rubber ionomer, ionized cross-linked polyanacrylamide gel, microporous fast-response gel, thermoelementiser elastomer gel, or blends thereof. Additionally, ionomers, metallocene polymers, polycarbonate/polyester blends, polyvinylidene fluoride (PVDF) such as Kynar®, fluororubber such as Viton®, thermoplastic urethane including silicone-urethane and urea can be incorporated into the latex.

[0035] In accordance with another aspect of the invention, suitable polymers for the velocity-reduced layer include polystyrene rubber disclosed in U.S. application publication no. 2003/0069082, which is incorporated by reference. Polystyrene rubber dissipates the impact energy from the pole club to attenuate the rebound energy available for ball propulsion. Polystyrene rubber typically is available in three forms: (i) a millable, extrudable solid elastomer that exhibits thermoplastic properties, (ii) a dispersion of high molecular weight polymer in solvents, or (iii) a liquid polymer.

[0036] The chemical compositions and the reactions necessary to produce polystyrene rubber are well known and are fully described in U.S. Pat. Nos. 2,195,380, 2,466,963 and 3,243,403 among others. The disclosures of these patents are incorporated herein by reference in their entireties. In general, polystyrene rubbers are synthetic polymers prepared by reacting polyfunctional organic compounds with alkali metal or alkaline earth metal sulfide solutions to provide high molecular weight polymers having the recurring unit, RSS, wherein R is typically a divalent organic radical and S is a disulfide linkage through which the organic radicals are interconnected. To improve the properties of the polystyrene polymers, a mixture of difunctional and trifunctional organic compounds is typically used. The trifunctional compound is present at a relatively small amount to produce a slightly cross-linked structure. The organic radicals typically include aliphatic halides, e.g., alkylene chlorides, such as ethylene dichloride and its homologues, or oxygen-containing aliphatic dichloride such as bis-beta-chloroethyl ether and beta-beta-chloroethyl formal.

[0037] Examples of suitable liquid polystyrene rubbers include those prepared from bis-beta-chloroethyl formal and are essentially composed of recurring (S.CH₂.CH₂.O.CH₂.O.CH₂.CH₂.S) groups and have free mercapto terminals through which the liquid may be cured. Typically, a small percentage of trichloropropane is mixed with the bis-beta-chloroethyl formal to provide the cross-linking. Suitable curing agents include an oxidizing agent, such as zinc peroxide, lead peroxide or the curing agents disclosed in the '963 patent. Other non-toxic curing agents are disclosed in U.S. Pat. No. 3,046,248, which is incorporated herein by reference. Modifying agents, such as cure-retarding agents, cure accelerating agents, pigments, fillers may be incorporated into the composition. By selecting the proper curing agents and modifying agents, cures at room temperature can be achieved. On the other hand, cures at elevated temperature can be used to reduce the overall curing time. Cures may also be accelerated in the presence of acid, and retarded under alkaline conditions, when dibutyl tin oxide is used as a curing agent. On the other hand, when other curing agents are used, cures may be retarded under acidic conditions and accelerated under alkaline conditions.

Typically, the liquid base polymer and the curing agent(s) are mixed just prior to use. It is also possible to premix the liquid base polymer and the curing agent(s) under anhydrous conditions, and immediately before use water is added to the premixed condition to cure the polymer.

[0038] Liquid polysulfide polymers are also available in a single component or a one-part stable, hygroscopic liquid polymer that cures when it contacts moisture in atmospheric air without the need of curing agent(s) or water. Examples of such one-part liquid polymer include a liquid polychlorylene polysulfide polymer. Dispersed in such liquid are a dormant curing agent that is activated by the presence of moisture, and a water-soluble deliquescent accelerating agent adapted to attract and absorb moisture from the surrounding. Such one-part curable polymer is disclosed in U.S. Pat. No. 3,225,017, and the disclosure of this patent is hereby incorporated by reference in its entirety. The one-part curable polymer may be initially dried to remove moisture. Alternatively, the deliquescent accelerating agent may also be a desiccating agent to dry the polymer. Alternatively, a single additive can be desiccating, deliquescent, dormant curing and accelerating agent dispersed to dry the polymer and to cure the polymer when exposed to moisture. Suitable curing agents for the one-part curable polymers include organic oxidizing agents, such as dinitro benzene, and inorganic oxides, such as alkali metal and alkali metal salt peroxide (e.g., sodium peroxide, sodium pyrophosphate peroxide, sodium carbonate peroxide and sodium perborate), the alkali earth metal peroxides (e.g., calcium peroxide and barium peroxide), and other metal peroxides such as zinc peroxide and manganese dioxide and oxidizing agents (e.g. ammonium dichromate).

[0039] Another example of a curable liquid polysulfide polymer at room temperature by atmospheric moisture with or without additional curing agents or catalysts is an isocyanate-terminated polysulfide polymer, disclosed in U.S. Pat. No. 3,386,963. Another example of an isocyanate-terminated liquid polysulfide polymer is disclosed in U.S. Pat. No. 6,322,650 B1. Another example of a liquid polysulfide polymer curable at room temperature relatively quickly (less than 1 hour at about 70-75°F) is disclosed in U.S. Pat. No. 3,637,574. These references are incorporated herein by reference.

[0040] In the solid form, polysulfide rubber is a cured or vulcanized rubber capable of flow under pressure and elevated temperature with substantial recovery of its pre-flow physical properties upon cooling. As the solid polymer is heated to a flowable state, the polysulfide rubber can be extruded or it can be cast into a mold to form a layer for the golf ball.

[0041] Examples of solid, extrudable and castable polysulfide rubbers are disclosed in U.S. Pat. Nos. 4,263,078, 4,165,425 and 4,190,625 among others. The '625 patent discloses a thermoplastic, elastomeric polysulfide rubber that can be extruded or cast. This polysulfide rubber is a hydroxyl terminated rubber cured by a zinc oxide. It also has sulfur linkages averaging about at least 1.8 sulfur atoms per linkage unit and is catalyzed by an alkali metal hydroxide. The catalytic agent induces softening on heating and helps the elastomer to regain its pre-heating properties upon cooling. The extrusion of this polysulfide rubber is accomplished using standard equipment suitable for extruding other solid thermoplastic elastomers.
In another example, the solid polysulfide rubber is cured with lower alkyl tin oxide, such as di-n-butyl tin oxide, and used in hot applied processes as disclosed in the '425 patent. This particular polysulfide rubber is thiol terminated and cured with the lower alkyl tin oxide at temperatures between 100°C and 300°C to become a solid thermoplastic elastomer that can be softened by heating and then cast or injection molded into a velocity-reduced layer.

Another suitable solid polysulfide rubber is based on a thiol terminated liquid polysulfide polymer cured with zinc oxide and a sulfur containing compound selected from 2-mercapto-benzothiazol, zinc lower alkyl dithiocarbamate and alkyl thiram polysulfides at temperatures from about 200°F to about 390°F. Agents, which improve the flowing properties of the composition, such as copolymers of styrene and alkylenes, organic or inorganic reinforcing fibrous materials, phenolic resins, coumarone-indene resins, antioxidants, heat stabilizers, polyalkylene polymers, factice, terpene resins, terpene resins esters, benzothiazyl disulfide or diphenyl guanidine, can also be added to the composition. Advantageously, this polysulfide rubber possesses a good ability to wet the substrate and forms good bonds with such substrate when cooked.

Polysulfide rubber is also available dissolved in a solvent, such as aliphatic and aromatic hydrocarbons, esters, ketones and alcohols, among others. Solvents are typically used to reduce the viscosity of liquid polysulfide to apply the polysulfide as a thin film of velocity-reduced layer on the golf ball. The solvent is allowed to evaporate or otherwise flashed before the cover is encased on the core sub-assembly. The advantages of a solvent-based polysulfide rubber are that velocity-reduced layer can be formed by dipping or spraying and that no precise mixing of the multiple components is required.

In accordance with another aspect of the invention, suitable polymers for the velocity-reduced layer include butyl rubber disclosed in U.S. application publication no. 2003/0069085, which is incorporated herein by reference. Butyl rubber is another preferred material with an ability to dissipate the impact energy from golf clubs to attenuate the rebound energy available for ball propulsion. For instance, the resilience of butyl rubber as measured on a Bashore resiliometer is in the range of 18% to 25%, as compared to cis-polybutadiene rubber, which is in the range of 85%-90% when they are cross-linked using appropriate cross-linking agents. Butyl rubber (IR) is an elastomeric copolymer of isobutylene and isoprene. Detailed discussions of butyl rubber are provided in U.S. Pat. Nos. 3,642,728, 2,356,128 and 3,099,644. The disclosures of these references are incorporated herein by reference in their entirety. Butyl rubber is an amorphous, non-polar polymer with good oxidative and thermal stability, good permanent flexibility and high moisture and gas resistance. Generally, butyl rubber includes copolymers of about 70% to 99.5% by weight of an isoprene, which has about 4 to 7 carbon atoms, e.g., isobutylene, and about 0.5% to 30% by weight of a conjugated multiolen, which has about 4 to 14 carbon atoms, e.g., isoprene. The resulting copolymer contains about 85% to about 99.8% by weight of combined isoprene and 0.2% to 15% of combined multiolen. Commercially available butyl rubbers, such as those manufactured by ExxonMobil Chemical Company, typically have about 1 to 2.5 mole percent of isoprene. Butyl rubbers generally have molecular weight of about 20,000 to about 500,000. Suitable butyl rubber is also available from United Coatings under the tradenname Elastron™ 858. Elastrom 858 is a butyl rubber coating applied as a solution in a volatile hydrocarbon solvent, which is typically sprayed or dipped on to an object or a surface, and contains lead peroxide as a crosslinking agent.

Butyl rubbers are also available in halogenated form. Halogenated butyl rubbers may be prepared by halogenating butyl rubber in a solution containing inert C3-C5 hydrocarbon solvent, such as pentane, hexane or heptane, and contacting this solution with a halogen gas for a pre-determined amount of time, whereby halogenated butyl rubber and a hydrogen halide are formed. The halogenated butyl rubber copolymer may contain up to one halogen atom per double bond. Halogenated butyl rubbers or halobutyl rubbers include bromobutyl rubber, which may contain up to 3% reactive bromine, and chlorobutyl rubber, which may contain up to 3% reactive chlorine. Halogenated butyl rubbers are also available from ExxonMobil Chemical.

Butyl rubber is also available in sulfonated form, such as those disclosed in the '726 patent and in U.S. Pat. No. 4,229,337. Generally, butyl rubber having a viscosity average molecular weight in the range of about 5,000 to 85,000 and a mole percent unsaturation of about 3% to about 4% may be sulfonated with a sulfating agent comprising a sulfur trioxide (SO3) donor in combination with a Lewis base containing oxygen, nitrogen or phosphorus. The Lewis base serves as a complexing agent for the SO3 donor. SO3 donor includes compound containing available SO3, such as chlorosulfonic acid, fluorosulfonic acid, sulfuric acid and oleum.

Other suitable velocity-reduced polymers include the elastomers that combine butyl rubbers with the environmental and aging resistance of ethylene propylene diene monomer rubbers (EPDM), commercially available as Exxon™ from ExxonMobil Chemical. More specifically, these elastomers are brominated polymers derived from a copolymer of isobutylene (IH) and p-methylstyrene (PMS). Bromination selectively occurs on the PMS methyl group to provide a reactive benzyl bromine functionality. Another suitable velocity-reduced polymer is copolymer of isobutylene and isoprene with a styrene block copolymer branching agent to improve manufacturing processability.

Another suitable polymer is polyisobutylene. Polyisobutylene is a homopolymer, which is produced by cationic polymerization methods. Commercially available grades of polyisobutylene, under the tradenname Vistanex™ also from ExxonMobil Chemical, are highly paraffinic hydrocarbon polymers composed on long straight chain molecules containing only chain-end olefinic bonds. An advantage of such elastomer is the combination of low rebound energy and chemical inertness to resist chemical or oxidative attacks. Polyisobutylene is available as a viscous liquid or semisolids, and can be dissolved in certain hydrocarbon solvents.

Halogenated butyl rubber can be blended with a second rubber, preferably a double bond-vulcanizable rubber, in a specific mixing ratio in a two-step kneading process and then cured to form a rubber blend that has high adhesion to diene rubbers. This rubber blend is discussed in U.S. Pat. No. 6,342,567 B2. The '567 patent is hereby incorporated herein by reference. Alternatively, a brominated isobutylene/
p-methylstyrene, discussed above, can be used in place of the halogenated rubber. Other suitable polymers include thermoplastic elastomer blends that may be dynamically vulcanized and comprise a butyl rubber or a halogenated butyl rubber, such as those discussed in U.S. Pat. Nos. 6,062,283, 6,334,919 B1 and 6,346,571 B1. These references are incorporated herein by reference. Alternatively, butyl rubber may be blended with a vinylidene chloride polymer, i.e., saran, as disclosed in U.S. Pat. No. 4,239,799. The ’799 patent is also incorporated herein by reference.

Butyl rubbers can be cured by a number of curing agents. Preferred curing agents for golf ball usage include sulphur for butyl rubber, and a peroxide curing agent, preferably zinc oxide, for halogenated butyl rubbers. Other suitable curing agents may include antimony oxide, lead oxide or lead peroxide. Lead based curing agents may be used when appropriate safety precautions are implemented. Butyl rubbers are commercially available in various grades from viscous liquid to solids with varying the degree of unsaturation and molecular weights.

Butyl rubber and halogenated butyl rubber can be processed by milling, calendering, extruding, injection molding and compression molding, among other techniques. These processing techniques can produce a semi-cured sheets or half-sheaves of the velocity-reduced polymer, which can be wrapped around a core or a core subassembly. The velocity-reduced layer can be fully cured by exposure to heat at elevated temperatures typically in the range of about 250°F to 450°F.

In accordance with another aspect of the invention, another suitable velocity-reduced polymer is poly(vinyl chloride) or PVC. Poly(vinyl chloride) is a vinyl polymer produced by polymerizing vinyl chloride. Additionally, any number of fillers, additives, fibers and flakes, such as mica, micaceous ion oxide, metal, ceramic, graphite, aluminum or more preferably leafing aluminum, can be incorporated into the velocity-reduced layer. Alternatively, the velocity-reduced layer may comprise a foamed polymer, such as the foamed plasticized polyurethane, discussed above.

In a preferred embodiment, a golf ball in accordance with the present invention has a diameter of about 1.68 inches and weighs about 1.62 ounces. The ball comprises a core and a cover with a velocity-reduced layer disposed therebetween. The velocity-reduced layer comprises any of the suitable polymers described above, or a blend thereof, and has a thickness of at least 0.003 inch (or less if latex is used, as discussed above), and preferably from about 0.003 inch to about 0.040 inch, more preferably from about 0.005 inch to about 0.030 inch and most preferably from about 0.005 inch to about 0.020 inch.

For example, a golf ball with a single-layer solid core of 1.59 inch in diameter and made from a conventional high resilience core of high cis-polybutadiene rubber with ZDA reactive co-agent and peroxide cross-linking agent with a single layer ionomer cover has a compression of about 90 and a CoR of about 0.810. When a velocity-reduced layer of about 0.020 inch thick made from the suitable polymers disclosed herein is incorporated between the core and the cover, and the core is reduced to about 1.55 inch, the resulting CoR is no greater than 0.805 and preferably no greater than 0.800.

The velocity-reduced layer may have any hardness, but preferably has a durometer measurement from about 5 on Shore C scale to about 80 on Shore D scale, more preferably from about 10 Shore C to about 95 Shore C. The golf ball in accordance with the invention has CoR in the range from about 0.500 to about 0.845, more preferably from about 0.600 to about 0.825 and most preferably from about 0.650 to about 0.810.

In the case of ionomers, the loss tangent at 23 deg. C is less than 1, preferably less than 0.1, and more preferably in the range of 0.01 to 0.09. In the case of rigid thermoplastic materials, the loss tangent at 23 deg. C is less than 1, preferably less than 0.1 and more preferably in the range of 0.01 to 0.09.

Hardness is preferably measured pursuant to ASTM D-2240 in either button or slab form on the Shore D scale. More specifically, Shore D scale measures the indentation hardness of a polymer. The higher Shore D value indicates higher hardness of the polymer. Compression is measured by applying a spring-loaded force to the golf ball center, golf ball core or the golf ball to be examined, with a manual instrument (an “Atti gauge”) manufactured by the Atti Engineering Company of Union City, N.J. This machine, equipped with a Federal Dial Gauge, Model DB1-C, employs a calibrated spring under a known load. The sphere to be tested is forced a distance of 0.2 inch (5 mm) against this spring. If the spring, in turn, compresses 0.2 inch, the compression is rated at 100; if the spring compresses 0.1 inch, the compression value is rated as 0. Thus more compressible, softer materials will have lower Atti gauge values than harder, less compressible materials. Compression measured with this instrument is also referred to as PGA compression. The approximate relationship that exists between Atti or PGA compression and Riechle compression can be expressed as:

\[
\text{Atti or PGA compression} = (160 - \text{Riechle Compression})
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According to other aspects of the present invention, the velocity-reduced materials discussed above can be used in the core and/or the cover, either alone or in combination with other polymers. Also, more than one velocity reduced layers can be provided on a single ball. Furthermore, the velocity reduced layer(s) can be castable or non-castable, thermoplastic or thermoset.

Other than in the operating examples, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages such as those for amounts of materials and others in the specification may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. 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 set 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 value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Furthermore, when numerical ranges of varying scope are set forth herein, it is contemplated that any combination of these values inclusive of the recited values may be used.

[0062] While various descriptions of the present invention are described above, it is understood that the various features of the embodiments of the present invention shown herein can be used singly or in combination thereof. For example, the dimple depth may be the same for all the dimples. Alternatively, the dimple depth may vary throughout the golf ball. The dimple depth may also be shallow to raise the trajectory of the ball's flight, or deep to lower the ball's trajectory. This invention is also not to be limited to the specifically preferred embodiments depicted therein.

What is claimed is:

1. A golf ball comprising a core, a cover and a velocity-reduced layer disposed therebetween, wherein the velocity-reduced layer reduces the coefficient of restitution of the ball by at least 0.005, and wherein the velocity-reduced layer has a loss tangent in the range of 0.01 to 100 at frequency of about 100 Hz.

2. The golf ball of claim 1, wherein the velocity-reduced layer comprises a polyurethane or polyurea having a material hardness of less than 40 Shore A.

3. The golf ball of claim 1, wherein the velocity-reduced layer comprises a polyurethane or polyurea having a material hardness less than about 20 Shore A.

4. The golf ball of claim 1, wherein the loss tangent is in the range of 0.05 to 50.

5. The golf ball of claim 4, wherein the loss tangent is in the range of 0.1 to 10.

6. The golf ball of claim 1, wherein the material coefficient of restitution is in the range of 0.3 to 0.7.

7. The golf ball of claim 6, wherein the material coefficient of restitution is in the range of 0.4 to 0.65.

8. The golf ball of claim 7, wherein the material coefficient of restitution is in the range of 0.45 to 0.6.

9. The golf ball of claim 1, wherein the velocity-reduced layer comprises plasticized polyurethane.

10. The golf ball of claim 9, wherein the plasticized polyurethane is foambale.

11. The golf ball of claim 1, wherein the velocity-reduced layer comprises latex.

12. The golf ball of claim 11, wherein the latex has a flexural modulus of less than 10,000 psi.

13. The golf ball of claim 12, wherein the latex has a flexural modulus of less than 3,000 psi.

14. The golf ball of claim 11, wherein the latex has a material hardness of less than 90 Shore A.

15. A golf ball comprising a core, a cover and a velocity-reduced layer disposed therebetween, wherein the velocity-reduced layer reduces the coefficient of restitution of the ball by at least 0.005, and wherein the velocity-reduced layer comprises a rubbery elastomeric material having a hardness from 10 Shore A to 50 Shore D wherein the loss tangent at 23° C and a frequency of about 100 Hz is less than 100.

16. The golf ball of claim 15 wherein the loss tangent is less than 10.

17. The golf ball of claim 15, wherein the loss tangent is less than 5.

18. A golf ball comprising a core, a cover and a velocity-reduced layer disposed therebetween, wherein the velocity-reduced layer reduces the coefficient of restitution of the ball by at least 0.005, and wherein the velocity-reduced layer comprises a thermoplastic rigid materials having a hardness from 30 to 80 Shore D, wherein the loss tangent at 23° C and a frequency of about 100 Hz is less than 100.

19. The golf ball of claim 18, wherein the loss tangent is less than 10.

20. The golf ball of claim 18, wherein the loss tangent is less than 5.

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