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(57) Abstract

Random thermoplastic ethylene copolymers can be used to increase the elongation to break and toughness of thermoplastic vulcanizates. Polypropylene is a preferred thermoplastic phase. The rubber can be olefinic rubbers. Random thermoplastic ethylene copolymers are different from Ziegler–Natta ethylene copolymers as the compositional heterogeneity of the copolymer is greater with Ziegler–Natta copolymers. This difference results in substantial differences in properties (elongation to break and toughness) between thermoplastic vulcanizates modified with random thermoplastic ethylene and those modified with Ziegler–Natta ethylene copolymers. An increase in elongation to break results in greater extensibility in the articles made from a thermoplastic vulcanizate.

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MODIFICATION OF THERMOPLASTIC VULCANIZATES WITH A THERMOPLASTIC RANDOM COPOLYMER OF ETHYLENE

FIELD OF INVENTION

Thermoplastic random copolymers of ethylene can be used to increase the elongation to break and toughness of thermoplastic vulcanizates made from a thermoplastic polypropylene phase and a crosslinkable rubber. The thermoplastic random copolymers of ethylene are available from several suppliers as polymers from single site catalyst, often referred to as metallocene catalyst polymerized polymers. They differ from other ethylene copolymers in that the comonomer is rather uniformly distributed in substantially all of the polymer chains, while in prior art thermoplastic ethylene copolymers the comonomer was disproportionately increased in a portion of the polymer chains and the comonomer was disproportionately reduced in a portion of the polymer chains resulting in a broad compositional distribution for the polymer.

BACKGROUND OF INVENTION

Thermoplastic vulcanizates from polypropylene and a rubber have gained wide acceptance as a substitute for thermoset rubbers in a variety of applications. It would be desirable for many of these applications to increase the elongation to break of said thermoplastic vulcanizates and to increase the total toughness (as measured by the area under the stress strain curve) when a thermoplastic vulcanizate is measured in a tensile test.

Polyethylene and copolymers of polyethylene are very interesting polymers because they can have both amorphous regions and crystalline regions. Amorphous regions of polyethylene are rubbery at room temperatures having a glass transition temperature well below 0°C. Crystalline regions of polyethylene are more rigid materials having a melting point generally between about 80°C and 135°C depending on the characteristics of the crystals and the density of the polyethylene. The crystalline regions of polyethylene are more dense, i.e., have higher densities than the amorphous region of the polymer.

High density polyethylene has higher relative proportions of crystalline polymer versus amorphous polymer than its low-density counterparts. Generally polymer chain branching and the incorporation of comonomers decrease the crystallinity in polyethylene due to the fact that the crystal structure cannot accommodate many comonomers or large chain branches. The amorphous regions of semi-crystalline polyethylene adds to the toughness of the material as it can undergo elastic and plastic deformation to accommodate stresses or strains thus avoiding fracture of the crystalline regions.

Ethylene-propylene-diene polymers (EPDM) also known as ethylene-propylene-diene-polymethylene rubber with weight ratios of ethylene to propylene of from 25:75 to about 75:25 have sufficient incorporation of both ethylene and propylene in the polymer chain such that these materials are rubbery at room temperature rather than solid. such as polyethylene or polypropylene.

Copolymers from polyethylene have been made in the past with catalysts other than single site catalysts. Various polymerization techniques have been used so that a specified portion of comonomer is present in the copolymer. However. few polymerization catalysts or polymerization systems are known which truly randomly polymerize ethylene with comonomers into a thermoplastic copolymer. Linear low density polyethylene involves the polymerization with an ethylene feed and a second olefin feed. generally 4-8 carbon atoms. keeping a relatively constant feed ratio. The catalysts have several different active sites such that some sites incorporate the second olefin more efficiently than others. The different sites also can result in different polymer chain lengths. This results in a broad molecular weight distribution and a broad compositional distribution in the resulting polymer. Another method of making low-density polyethylene involves using polymerization conditions that encourage branching in the polyethylene chain. said branching disrupting the crystallinity of the polyethylene and causing a reduced amount of crystallinity and consequently a reduced density.

SUMMARY OF INVENTION

Thermoplastic vulcanizates from polypropylene, a rubber, and a thermoplastic random copolymer of ethylene can be prepared by blending a thermoplastic random copolymer of ethylene with the components of a thermoplastic vulcanizate or by mixing a thermoplastic random copolymer of ethylene with a preformed thermoplastic vulcanizate from polypropylene and a rubber. The thermoplastic random copolymers of ethylene are commercially available as a result of the development of single site catalysts including metallocene catalysts. The thermoplastic random copolymers of ethylene currently have rather narrow molecular weight distributions and rather narrow compositional distributions. The average comonomer concentration is from about 5 to about 30 weight percent based on the weight of the ethylene copolymer. As is known to the art, thermoplastic vulcanizates usually comprise from about 15 to about 75 parts of the thermoplastic phase and from about 25 to about 85 parts by weight of the rubber phase. They can further comprise various amounts of curatives, plasticizers, fillers, etc. The thermoplastic random copolymer of ethylene is desirably present in amounts of from about 5 to about 150 parts per 100 parts of polypropylene in the thermoplastic vulcanizate. The rubber can be any hydrocarbon rubber such as butyl rubbers, halobutyl rubbers, halogenated (e.g. brominated) copolymers of paramethyl styrene and isobutylene, EPDM rubber, and natural rubber or diene-based homo or copolymer rubber.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic random copolymer of ethylene used to modify thermoplastic vulcanizates in this invention is different from other ethylene copolymers used in thermoplastic vulcanizates in the past: it is much more random in terms of the incorporation of comonomer(s) in the copolymer. In the past, copolymers with more than 2, 5, or 10 weight percent comonomer were either rubbers or were a physical blend of copolymers low in ethylene repeat units and other copolymers significantly richer in ethylene repeat units, which blend would have a relative weight percent of comonomer and ethylene cited in the product literature. The thermoplastic random copolymer of ethylene used in this invention can have very narrow molecular weight distributions (Mw/Mn) of from about 1.5 or 1.7 to 3.5, more desirably from about 1.8 to about 3.0 and preferably from about 1.5 or 1.9 to 2.8 due to the single site catalyst, also referred to as metallocene catalyst, currently used to prepare such polymers. This disclosure is not limited to thermoplastic random copolymers of ethylene made with metallocene catalysts, but rather uses those commercially available polymers as illustrative of a polymerization method capable of making random copolymers operable in this disclosure. Further, the molecular weight distributions are recited as a method of identifying these polymers, but are not a requirement for operativeness of the copolymer in a thermoplastic vulcanizate.

The thermoplastic random copolymer of ethylene can have varying amounts of one or more comonomers therein. In the examples, the thermoplastic random copolymer of ethylene is often referred to as a plastomer indicating that it has some properties of both a plastic and an elastomer. Desirably the amount of repeat units from one or more comonomers is from about 5, 10, 15 or 20 to about 30 or 35 weight percent of the thermoplastic random copolymer of ethylene. More desirably, the amount of repeat units from said one or more comonomers is from about 10 to about 25 weight percent. The amount of ethylene in said thermoplastic random copolymer of ethylene is desirably from about 65 or 70 to about 80, 85, 90 or 95 weight percent, and more desirably from about 65, 70 or 75 to about 80, 85 or 90 weight percent. The one or more comonomers can be any ethylenically unsaturated compound copolymerizable with ethylene using a single site catalyst. The one or more ethylenically unsaturated monomers desirably have from about 3 or 4 to about 12 carbon atoms, more desirably from about 3 or 4 to about 8 carbon atoms, and are preferably monoolefins with the specified range of carbon atoms. Examples of such comonomers include alkylacrylates such as ethylacrylate, butylacrylate; monoolefins such as propylene or octene, etc.

The thermoplastic random copolymers of ethylene desirably have densities of from about 0.85 or 0.86 to about 0.91. 0.92 or 0.93 grams per cubic centimeter. more desirably from about 0.86 or 0.87 to about 0.90. 0.91 or 0.92 grams per cubic centimeter. As the polymerization systems. e.g.. the single site catalyst polymerization system which includes metallocene catalysts readily incorporate comonomers with the ethylene in the thermoplastic random copolymer of ethylene. the comonomers are randomly distributed within the individual polymer chains and the individual polymer chains are rather uniform in comonomer composition. Due to the uniform distribution of repeat units from the comonomers within the polymer chains and the uniformity of comonomer distribution within the polymer. as opposed to prior art polyethylene copolymers. the thermoplastic random copolymers of ethylene tend to have rather narrow melting temperature ranges by test methods such as dynamic scanning calorimetry (DSC) as compared to prior art ethylene copolymers. This is due to the fact that the thermoplastic random copolymers of ethylene have a very uniform crystalline structure and thus melt within a narrow temperature range. The random copolymers of ethylene vary from most other ethylene copolymers in that the melting peak in the dynamic scanning calorimetry of the random copolymers decreases as the comonomer content increases. The peak represents the largest amount of endothermic crystal melting at a single temperature. Therefore, desirably the random copolymer of ethylene has a peak melting temperature of less than about 120°C. more desirably from about 50 to about 120°C. still more desirably from about 55. 60. or 65 to about 105 or 110°C. and preferably from about 55. 60 or 65 to about 90. 95 or 100°C. Prior art ethylene copolymers melt over a broader temperature range because they have a broader range of copolymer compositions.

The thermoplastic random copolymer of ethylene can be incorporated into the components used to form a thermoplastic vulcanizate (TPV) or blended with a TPV composition prior to vulcanization of the rubber component. or added after said vulcanization. The physical properties of the resulting blend may or may not vary depending upon whether the thermoplastic random copolymer of ethylene was added prior to or subsequent to vulcanization of the rubber phase. The thermoplastic random copolymer of ethylene can be considered a supplement to the polypropylene of the thermoplastic vulcanizate or can be considered to be substituted on a weight basis for the polypropylene in a thermoplastic vulcanizate. When the random copolymer is added prior to vulcanization, it is anticipated that a majority of the thermoplastic random copolymers of ethylene are in the thermoplastic phase of the resulting thermoplastic vulcanizate, although it may be disproportionately present at the interface between the rubber phase and the thermoplastic phase. Since the melting temperature of the crystalline portion of the thermoplastic random copolymer of ethylene is lower than that of the semi-crystalline polypropylene, it is readily melt-blendable with the thermoplastic vulcanizate or the components thereof at the normal processing/mixing temperatures for the thermoplastic vulcanizate.

The thermoplastic random copolymer of ethylene is desirably present in amounts from about 5 to about 150 parts per 100 parts of polypropylene in the thermoplastic vulcanizate, more desirably in amounts from about 10 to about 120 parts per 100 parts of polypropylene, still more desirably from about 10 or 25 to about 100 parts per 100 parts by weight of polypropylene, and preferably from about 25 to about 80 parts by weight per 100 parts by weight of polypropylene. Thus the thermoplastic random copolymer of ethylene may be present in amounts from about 20 to about 60 weight percent of the thermoplastic phase of the thermoplastic vulcanizate. Since the thermoplastic phase of the thermoplastic vulcanizate can be from about 15 to about 75 percent of the blend of the thermoplastic and rubber phase (without fillers, oils, etc.), the percentage of thermoplastic random copolymer of ethylene based upon the total weight of the thermoplastic vulcanizate can range from 1 or 2 to about 40 or 50 weight percent based upon either the combined weight of the thermoplastic polypropylene and rubber components (without fillers, oils etc.) or the weight of the thermoplastic vulcanizate.

The major portion of polymers in the thermoplastic vulcanizate are the semi-crystalline polypropylene: the thermoplastic random copolymer of ethylene. and a crosslinkable rubber. Examples of semi-crystalline polypropylene are polypropylene. its copolymers and mixtures thereof.

The rubber may be a polyolefin such as EPDM rubber which. because of the random nature of its repeat structure or side groups. tends not to crystallize. Examples of the rubber include EPDM rubber. butyl rubber. halobutyl rubber. halogenated (e.g. brominated) copolymer of p-alkylstyrene and an isomonoolefin of from 4 to 7 carbon atoms (e.g. isobutylene). natural rubber. homo or copolymers of at least one diene monomer. or combinations thereof. Minor amounts of other polymers may be added to modify flow properties. such as fillers or diluents. or as additives. such as polymeric antioxidants. Non-polymeric materials such as oils. fillers. diluents and additives (discussed in a later paragraph) may be present in large amounts. Amounts of most of the components to the blend will be specified either 1) per 100 parts by weight of the blend of the semi-crystalline polypropylene and the rubber or 2) per 100 parts by weight of rubber.

The semi-crystalline polypropylene is desirably from about 6 to about 85 weight percent. more desirably from about 7 to about 75. and preferably from about 8 to about 60 weight percent of the thermoplastic vulcanizate. Desirably the rubber is from about 5 to about 70. more desirably about 10 to about 50 and preferably from about 15 to 45 weight percent of the thermoplastic vulcanizate. Desirably the other conventional components to TPV. e.g. fillers. oils. curatives. processing aids. etc.. are from about 0. 1. 2. or 10 to about 87. 88 or 89 weight percent of the TPV. more desirably from about 0. 1. 2. or 15 to about 81. 82 or 83 and preferably from about 0. 1. 2. or 25 to about 75. 76 or 79 weight percent.

The semi-crystalline polypropylene is desirably from about 15 to about 80 parts by weight. more desirably from about 25 to about 75 parts by weight. and preferably from about 25 to about 50 parts by weight per 100 parts of the blend of semi-crystalline polypropylene and the unsaturated rubber. The rubber is desirably from about 20 to about 85 parts by weight, more desirably from about 25 to about 75 parts by weight and preferably from about 50 to about 75 parts by weight per 100 parts by weight of said blend. If the amount of semi-crystalline polypropylene is based on the amount of rubber, it is desirably from about 17.5 to about 320 parts by weight, more desirably from about 33 to about 300 parts and preferably from about 33 to about 200 parts by weight per 100 parts by weight of the rubber.

The terms "blend" and "thermoplastic vulcanizate" used herein mean a mixture ranging from small particles of crosslinked rubber well dispersed in a semi-crystalline polypropylene matrix to co-continuous phases of the semi-crystalline polypropylene and a partially to fully crosslinked rubber or combinations thereof. The term "thermoplastic vulcanizate" indicates the rubber phase is at least partially vulcanized (crosslinked).

The term "thermoplastic vulcanizate" refers to compositions that may possess the properties of a thermoset elastomer and are reprocessable in an internal mixer. Upon reaching temperatures above the softening point or melting point of the semi-crystalline polypropylene phase, they can form continuous sheets and/or molded articles with what visually appears to accomplish complete knitting or fusion of the thermoplastic vulcanizate under conventional molding or shaping conditions for thermoplastics.

Subsequent to dynamic vulcanization (curing) of the rubber phase of the thermoplastic vulcanizate, desirably less than 5 weight percent of the rubber is extractable from the specimen of the thermoplastic vulcanizate in boiling xylene. Techniques for determining extractable rubber as set forth in U.S. Patent 4,311,628, are herein incorporated by reference.

The semi-crystalline polypropylene comprises semi-crystalline thermoplastic polymers from the polymerization of monoolefin monomers (e.g. 2 to 10 carbon atoms) by a high pressure, low pressure, or intermediate pressure process; or by Ziegler-Natta catalysts, or by metallocene catalysts. It may have any tacticity (e.g. isotactic and syndiotactic) or be a copolymer such as impact modified polypropylene or a random polypropylene copolymer. Desirably the monoolefin monomers converted to repeat units are at least 80, 85 or 93 percent monoolefins of the formula $CH_2 = C(CH_3)-H$. The polypropylene can be a homopolymer as well as a reactor copolymer polypropylene. Desirably it has a melting temperature peak of at least 120°C.

The rubber can be any rubber that can react and be crosslinked under crosslinking conditions. These rubbers can include natural rubber, EPDM rubber, butyl rubber, halobutyl rubber, halogenated (e.g. brominated) copolymers of p-alkylstyrene and an isomonoolefin, homo or copolymers from at least one conjugated diene, or combinations thereof. EPDM, butyl and halobutyl rubbers are referred to as rubbers low in residual unsaturation and are preferred when the vulcanizate needs good thermal stability or oxidative stability. The rubbers low in residual unsaturation desirably have less than 10 weight percent repeat units having unsaturation. Desirably excluded from rubbers are acrylate rubber and epichlorohydrin rubber. For the purpose of this invention, copolymers will be used to define polymers from two or more monomers, and polymers can have repeat units from one or more different monomers.

The rubber is desirably an olefin rubber such as EPDM-type rubber. EPDM-type rubbers are generally terpolymers derived from the polymerization of at least two different monoolefin monomers having from 2 to 10 carbon atoms, preferably 2 to 4 carbon atoms, and at least one polyunsaturated olefin having from 5 to 20 carbon atoms. Said monoolefins desirably have the formula $CH_2=CH-R$ where R is H or an alkyl of 1-12 carbon atoms and are preferably ethylene and propylene. Desirably the repeat units from at least two monoolefins (and preferably from ethylene and propylene) are present in the polymer in weight ratios of 25:75 to 75:25 (ethylene:propylene) and constitute from about 90 to about 99.6 weight percent of the polymer. The polyunsaturated olefin can be a straight chained, branched, cyclic, bridged ring, bicyclic, fused ring bicyclic compound, etc., and preferably is a nonconjugated diene. Desirably repeat units from the nonconjugated polyunsaturated olefin is from about 0.4 to about 10 weight percent of the rubber.

The rubber can be a butyl rubber. halobutyl rubber. or a halogenated (e.g. brominated) copolymer of p-alkylstyrene and an isomonoolefin of 4 to 7 carbon atoms. "Butyl rubber" is defined a polymer predominantly comprised of repeat units from isobutylene but including a few repeat units of a monomer which provides sites for crosslinking. The monomers which provide sites for crosslinking can be a polyunsaturated monomer such as a conjugated diene or divinyl benzene. Desirably from about 90 to about 99.5 weight percent of the butyl rubber are repeat units derived from the polymerization of isobutylene. and from about 0.5 to about 10 weight percent of the repeat units are from at least one polyunsaturated monomer having from 4 to 12 carbon atoms. Preferably the polyunsaturated monomer is isoprene or divinylbenzene. The polymer may be halogenated to further enhance reactivity in crosslinking. Preferably the halogen is present in amounts from about 0.1 to about 10 weight percent. more preferably about 0.5 to about 3.0 weight percent based upon the weight of the halogenated polymer; preferably the halogen is chlorine or bromine. The brominated copolymer of p-alkylstyrene. having from about 9 to 12 carbon atoms. and an isomonoolefin. having from 4 to 7 carbon atoms. desirably has from about 88 to about 99 weight percent isomonoolefin. more desirably from about 92 to about 98 weight percent. and from about 1 to about 12 weight percent p-alkylstyrene. more desirably from about 2 to about 8 weight percent based upon the weight of the copolymer before halogenation. Desirably the alkylstyrene is p-methylstyrene and the isomonoolefin is isobutylene. Desirably the percent bromine is from about 2 to about 8. more desirably from about 3 to about 8. and preferably from about 5 to about 7.5 weight percent based on the weight of the halogenated copolymer. The halogenated copolymer is a complementary amount. i.e.. from about 92 to about 98. more desirably from about 92 to about 97. and preferably from about 92.5 to about 95 weight percent. These polymers are commercially available from Exxon Chemical Co.

Other rubber such as natural rubber or homo or copolymers from at least one conjugated diene can be used in the dynamic vulcanizate. These rubbers are higher in unsaturation than EPDM rubber and butyl rubber. The natural rubber and said homo or copolymers of a diene can optionally be partially hydrogenated to increase thermal and oxidative stability. The synthetic rubber can be nonpolar or polar depending on the comonomers. Desirably the homo or copolymers of a diene have at least 50 weight percent repeat units from at least one conjugated diene monomer having from 4 to 8 carbon atoms. Comonomers may be used and include vinyl aromatic monomer(s) having from 8 to 12 carbon atoms and acrylonitrile or alkyl-substituted acrylonitrile monomer(s) having from 3 to 8 carbon atoms. Other comonomers desirably used include repeat units from monomers having unsaturated carboxylic acids. unsaturated dicarboxylic acids. unsaturated anhydrides of dicarboxylic acids. and include divinylbenzene. alkylacrylates and other monomers having from 3 to 20 carbon atoms. Examples of synthetic rubbers include synthetic polyisoprene. polybutadiene rubber. styrene-butadiene rubber. butadiene-acrylonitrile rubber. etc. Amine-functionalized. carboxy-functionalized or epoxy-functionalized synthetic rubbers may be used. and examples of these include maleated EPDM. and epoxy-functionalized natural rubbers. These materials are commercially available.

The thermoplastic vulcanizates of this disclosure are generally prepared by melt-mixing the semi-crystalline polyolefin(s) (e.g. polypropylene). the rubber. and other ingredients (filler, plasticizer. lubricant. stabilizer. etc.) in a mixer heated to above the melting temperature of the semi-crystalline polypropylene. The optional fillers. plasticizers. additives etc.. can be added at this stage or later. After sufficient molten-state mixing to form a well mixed blend. vulcanizing agents (also known as curatives or crosslinkers) are generally added. In some embodiments it is preferred to add the vulcanizing agent in solution with a liquid. for example rubber processing oil. or in a masterbatch which is compatible with the other components. It is convenient to follow the progress of vulcanization by monitoring mixing torque or mixing energy requirements during mixing. The mixing torque or mixing energy curve generally goes through a maximum after which mixing can be continued somewhat longer to improve the fabricability of the blend. If desired, one can add some of the ingredients after the dynamic vulcanization is complete. The random thermoplastic copolymer(s) of ethylene can be added before during, or after vulcanization. After discharge from the mixer, the blend containing vulcanized rubber and the thermoplastic can be milled, chopped, extruded, pelletized, injection-molded, or processed by any other desirable technique. It is usually desirable to allow the fillers and a portion of any plasticizer to distribute themselves in the rubber or semi-crystalline polypropylene phase before the rubber phase or phases are crosslinked. Crosslinking (vulcanization) of the rubber can occur in a few minutes or less depending on the mix temperature, shear rate, and activators present for the curative. Suitable curing temperatures include from about 120°C or 150°C for a semi-crystalline polypropylene phase to about 250°C, more preferred temperatures are from about 150°C or 170°C to about 225°C or 250°C. The mixing equipment can include Banbury™ mixers, Brabender™ mixers, and certain mixing extruders.

The thermoplastic vulcanizate can include a variety of additives. The additives include particulate fillers such as carbon black, silica, titanium dioxide, colored pigments, clay, zinc oxide, stearic acid, stabilizers, antidegradants, flame retardants, processing aids, adhesives, tackifiers, plasticizers, wax, discontinuous fibers (such as wood cellulose fibers) and extender oils. When extender oil is used it can be present in amounts from about 5 to about 300 parts by weight per 100 parts by weight of the blend of semi-crystalline polypropylene and rubber. The amount of extender oil (e.g., hydrocarbon oils and ester plasticizers) may also be expressed as from about 30 to 250 parts, and more desirably from about 70 to 200 parts by weight per 100 parts by weight of said rubber. When non-black fillers are used, it is desirable to include a coupling agent to compatibilize the interface between the non-black fillers and polymers. Desirable amounts of carbon black, when present, are from about 5 to about 250 parts by weight per 100 parts by weight of rubber.

Thermoplastic vulcanizate compositions of the invention are useful for making a variety of articles such as tires, hoses, belts, gaskets, moldings and molded parts. They are particularly useful for making articles by extrusion, injection molding, blow molding, and compression molding techniques. They also are useful for modifying thermoplastic resins and in particular polyolefin resins. The compositions can be blended with thermoplastic resins using conventional mixing equipment making a rubber modified thermoplastic resin. The properties of the modified thermoplastic resin depend upon the amount of thermoplastic vulcanizate composition blended.

The stress-strain properties of the compositions are determined in accordance with the test procedures set forth in ASTM D412. These properties include tension set (TS), ultimate tensile strength (UTS), 50% modulus (M50), 100% modulus (M100), and ultimate elongation at break (UE). The tear strength is measured according to ASTM D623. The hardness is measured according to ASTM D2240, with a 5 second delay using either the Shore A or Shore D scale. Compression set (CS) is determined in accordance with ASTM D-395, Method B, by compressing the sample for 22 hours at 100°C. Oil swell (OS) (percent change in weight) is determined in accordance with the ASTM D-471 by submerging the specimen in IRM 903 oil and unless otherwise specified is for 24 hours at 125±2°C. Especially preferred compositions of the invention are rubbery compositions having tension set values of about 50% or less which compositions meet the definition for rubber as defined by ASTM Standards, V. 28, page 756 (D1566). More preferred compositions are rubbery compositions having a Shore D hardness of 60 or below, or a 100% modulus of 18 MPa or less, or a Young's modulus below 250 MPa.

EXAMPLES

Tables I through XI provide additional experimental data on polyethylenes and thermoplastic random ethylene copolymers blended with either thermoplastic vulcanizates or the precursors to thermoplastic vulcanizates. The ethylene homopolymers and some of the ethylene copolymers which are not truly random when blended with the thermoplastic vulcanizates or their precursors are control examples. The examples of thermoplastic random copolymers of ethylene blended with thermoplastic vulcanizates or their precursors are examples of the invention.

Tables I and II show the composition of several ethylene copolymers and the composition of several thermoplastic vulcanizates used in later tables. Table X also shows several ethylene polymers or copolymers.

The trade name Exact™ is being used by Exxon for some of their metallocene polymerized ethylene copolymers. The trade name Engage™ is being used by DuPont Dow Elastomers. In Table I several experimental polymers (e.g. those with SLP prefixes) from Exxon were used in the experimentation. but similar commercially available ethylene copolymers are currently available under the Exact trade name.

Table III shows the variation in physical properties achieved with varying amounts of four different thermoplastic random ethylene copolymers of ethylene and 1-butene. The Shore A hardness may increase or decrease from the addition of the thermoplastic random ethylene copolymers depending upon the particular thermoplastic random ethylene copolymer used. Tensile strength usually increases along with ultimate elongation and relative toughness. The oil swell and the compression set at 100°C typically increase with the addition of thermoplastic random ethylene copolymer. Control samples (with a C suffix) are generally a thermoplastic vulcanizate without a thermoplastic random ethylene copolymer.

Table IV illustrates blends of a thermoplastic vulcanizate and thermoplastic random ethylene copolymers and their physical properties. These copolymers vary from those in Table III in that they are copolymers of ethylene with 1-octene.

Tables V and VI illustrate further blends of ethylene or ethylene copolymers with thermoplastic vulcanizates. In these examples. ultimate elongation increases.

Table VII lists several conventional ethylene copolymers used in later tables.

Table VIII illustrates blends of conventional ethylene copolymers and thermoplastic vulcanizates. The elongation to break of the blends and the toughness are generally less than the control without ethylene copolymers. There are increases in elongation and toughness with Vistalon^{TM} 808 and 4709, but they adversely affect other properties such as increasing oil swell.

Table IX shows blends of the precursors of a thermoplastic vulcanizate or a thermoplastic vulcanizate with a thermoplastic random ethylene copolymer. The purpose of this table is to demonstrate that the thermoplastic random ethylene copolymer can be added before or after curing and some changes in the physical properties can be anticipated. Generally if added after cure, it is believed the thermoplastic random ethylene copolymer causes lower final Brabender torque, slightly higher elongation to break and, as a result of the higher elongation, a slightly higher toughness. The oil swell is expected to decrease from adding the thermoplastic random ethylene copolymer after vulcanization.

Table X shows several additional ethylene polymers or copolymers both within and outside of the definition of the thermoplastic random ethylene copolymer.

Table XI shows the physical properties of blends of a thermoplastic vulcanizate and the ethylene copolymers and thermoplastic random ethylene copolymers. The ultimate elongation increases more dramatically for the thermoplastic random ethylene copolymers than for the other copolymers and homopolymers.

To better illustrate the difference between the thermoplastic random ethylene copolymers and other copolymers of similar total comonomer concentration, Table XII was prepared. The physical properties shown are the ultimate elongation and 100 percent modulus for blends of thermoplastics and the ethylene homopolymers or copolymers. The first and third examples are thermoplastic random ethylene copolymers according to this disclosure. The second and fourth examples are not within the description of a thermoplastic random ethylene copolymer of this disclosure. As can be seen from the data, the ultimate elongation is dramatically better for the first and third examples than for the other examples outside the scope of this disclosure. As can be seen by the 100 percent modulus data. the first and third compositions have lower modulus. i.e.. are softer than the second and fourth compositions which are outside the scope of this disclosure.

Table XIII was prepared to illustrate that a TPV using butyl rubber. nitrile rubber or natural rubber instead of EPDM rubber would have improved ultimate elongation and tensile strength when blended with a random ethylene copolymer (plastomer).

Table I
Characterization of Metallocene Polymerized Ethylene Copolymers (Plastomers)

Material	ethylene (wt%)	1-butene (wt%)	1-octene (wt%)	Melt Index***	Density	Tm Peak °C
SLP-0609	86	14	-	1.1	0.905	~100
SLP-0432	84.4	15.6	-	1.4	0.895	~85
SLP-0566	78.3	21.7	-	0.85	0.881	~68
SPL-0121	77.5	22.5	-	2.3	0.881	~68
Exact 4033*	≈78	≈22	-	0.8	0.880	~68
Engage™ 8100**	~75	-	~25	1	0.870	60
Engage™ 8150**	~73	-	~27	0.5	0.868	55
Engage™ 8401**	~80	-	~20	30	0.885	76
Engage™ 8480**	~85	-	~15	1	0.902	100

* Available from Exxon
** Available from DuPont Dow Elastomers
*** Melt index is ASTM D-1238 (E)

Table II
Thermoplastic Vulcanizates:Polypropylene Concentration and Rubber Type

Thermoplastic Vulcanizate	Rubber Type	PP Concentration. Wt.%	Rubber Concentration. Wt. %
TPV-1	EPDM	13.4%	28.5
TPV-2	EPDM	58.3%	14.5
TPV-3	EPDM	9.4%	26.7
TPV-4	Natural	10.0%	32
TPV-5	Nitrile	15.0%	48
TPV-6	Butyl	16.0%	42

The residual of the thermoplastic vulcanizates being conventional TPV components including oils. fillers, processing aids. curatives. etc.

Table III
Physical Properties of a TPV and a Plastomer (random copolymer of ethylene and 1-butene)

	1C	2	3	4	5	6	7	8	9
TPV-1	100.0g	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
SLP-0609		3.4	6.7	10.0	13.4				
SLP-0432						3.4	6.7	10.0	13.4
Polypropylene:Plastomer Ratio	100:0	100:25	100:50	100:75	100:100	100:25	100:50	100:75	100:100
Plastomer concentration, wt. %	0.0%	3.2%	6.3%	9.1%	11.8%	3.2%	6.3%	9.1%	11.8%
Physical Properties, Unaged									
Hardness, Shore A	59	61	63	64	65	62	62	63	65
50% Modulus, MPa	1.75	1.85	1.88	2.01	2.05	1.81	1.81	1.93	1.97
100% Modulus, MPa	2.42	2.51	2.54	2.66	2.69	2.47	2.46	2.57	2.61
Tensile Strength, MPa	6.07	6.38	8.08	8.82	9.50	6.51	7.93	8.89	9.44
Ultimate Elongation %	456	474	567	591	621	488	565	610	637
Toughness, MJ/m^3	16.72	18.21	25.24	28.30	30.83	18.88	24.72	28.84	31.74
% Tension Set 100%E, 10 min 21°C	8.0	9.0	10.5	11.5	12.5	8.5	10.0	12.0	12.5
% Compression set 22 hrs. @100C	26.4	28.6	29.5	30.3	31.4	28.5	28.0	28.6	28.6
% Compression set 22 hrs. @21°C	16.5	15.9	16.1	15.8	14.9	15.8	15.8	16.1	14.4
% Oil Swell, 24 hours, 125°C	92.4	113.7	118.5	120.2	118.5	106.	120.5	116.3	108.4

Table III
Physical Properties of TPV and a Plastomer (random copolymer of ethylene and 1-butene)

	10C	11	12	13	14
TPV-1	100.0g	100.0	100.0	100.0	100.0
SLP-0556		3.4	6.7	10.0	13.4
Polypropylene:Plastomer Ratio	100:0	100:25	100:50	100:75	100:100
Plastomer concentration, wt. %	0.0%	3.2%	6.3%	9.1%	11.8%
Physical Properties, Unaged					
Hardness, Shore A	61	61	60	59	59
50% Modulus, MPa	1.72	1.69	1.73	1.66	1.70
100% Modulus, MPa	2.37	2.36	2.39	2.32	2.33
Tensile Strength, MPa	5.61	7.10	8.27	8.90	9.86
Ultimate Elongation %	433	527	589	620	668
Toughness, MJ/m^3	14.95	21.18	26.18	28.79	32.34
% Tension Set 100 E, 10 min 21°C	7.5	8.0	7.5	7.5	7.5
% Compression set 22 hrs @100C	25.0	27.2	28.7	28.5	29.0
% Compression set 22 hrs @21°C	14.6	14.8	14.4	13.6	14.0
% Oil Swell, 24 hours, 125°C	96.7	119.7	121.2	118.6	116.4

Table III
Physical Properties of a TPV and a Plastomer (random copolymer of ethylene and 1-butene)

	15C	16	17	18	19
TPV-1	100.0g	100.0	100.0	100.0	100.0
SPL-0121		3.4	6.7	10.0	13.4
Polypropylene:Plastomer Ratio	100:0	100:25	100:50	100:75	100:00
Plastomer concentration, wt. %	0.0%	3.2%	6.3%	9.1%	11.8%
Physical Properties, Unaged					
Hardness, Shore A	60	61	60	59	58
50% Modulus, MPa	1.68	1.71	1.65	1.66	1.63
100% Modulus, MPa	2.37	2.37	2.30	2.29	2.26
Tensile Strength, MPa	5.90	6.61	7.10	7.06	8.50
Ultimate Elongation %	435	511	554	565	672
Toughness, MJ/m^3	15.51	19.77	22.56	22.90	30.72
% Tension Set 100 E, 10 min 21°C	7.5	7.5	7.5	8.5	7.5
% Compression set 22 hrs @100C	25.0	26.7	29.7	28.5	31.7
% Compression set 22 hrs @21°C	14.1	14.6	14.8	13.5	12.9
% Oil Swell, 24 hours, 125°C	95.6	115.1	118.3	115.3	109.9

Table IV
Physical Properties of a TPV and a Plastomer (random copolymer of ethylene and 1-octene)

	20	21	22	23	24C
TPV-1	100.0	100.0	100.0	100.0	100.0
Engage 8100	3.4	6.7	10.0	13.4	
Engage 8150					
Engage 8401					
Engage 8480					
Polypropylene:Plastomer Ratio	100:25	100:50	100:75	100:100	100:0
Physical Properties, Unaged					
Hardness, Shore A	59	57	56	55	62
50% Modulus, MPa	1.66	1.50	1.47	1.45	1.69
100% Modulus, MPa	2.29	2.12	2.06	2.04	2.37
Tensile Strength, MPa	5.32	5.34	5.83	6.14	5.45
Ultimate Elongation %	436	478	579	622	421
Toughness, MJ/m^3	14.57	15.91	20.73	23.10	14.23
% Tension set, 100 % E, 10 min., 21°C	7.5	6.5	6.5	7.5	7.0
% Compression set 22 hrs. @100C	29.6	32.3	34.4	37.6	28.2
% Oil Swell 24 hrs @ 125C	111.1	117.1	113.0	117.4	94.3

Table IV
Physical Properties of a TPV and a Plastomer (random copolymer of ethylene and 1-octene)

	25	26	27	28	29	30	31C
TPV-1	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Engage 8100							
Engage 8150	3.4	13.4					
Engage 8401			3.4	13.4			
Engage 8480					3.4	13.4	
Polypropylene:Plastomer Ratio	100:25	100:100	100:25	100:100	100:25	100:100	100:0
Physical Properties, Unaged							
Hardness, Shore A	61	57	62	61	64	67	63
50% Modulus, MPa	1.61	1.37	1.68	1.6	1.78	2.06	1.77
100% Modulus, MPa	2.26	1.97	2.33	2.18	2.46	2.69	2.46
Tensile Strength, MPa	5.94	6.73	4.95	4.37	6.38	8.17	5.85
Ultimate Elongation %	492	636	404	450	500	627	453
Toughness, MJ/m^3	17.58	24.30	12.84	13.53	19.13	29.2	16.34
% Tension set, 100 % E, 10 min., 21°C	7.5	6.5	7.5	9.0	9.0	12.0	7.5
% Compression set 22 hrs. @100C	31.5	41.1	28.5	35.0	29.8	39.8	27.8
Weight Gain							
% Oil Swell 24 hrs @ 125C	116.8	123.0	103.4	97.1	108.4	108.5	94.5

Table V
Physical Properties of Blends of a TPV with a Plastomer

	32C	33	34	35
TPV-2	100.0 g	100.0	100.0	100.0
Exact SLP-0566		11.2	24.9	43.9
Polypropylene:Plastomer Ratio	100:0	100:19	100:43	100:74
Physical Properties, Unaged				
Hardness, Shore D	55.5	52	52	49
50% Modulus, MPa	15.07	13.31	11.81	10.86
100% Modulus, MPa	14.51	12.93	11.60	10.84
Tensile Strength, MPa	16.86	20.66	20.77	22.32
Ultimate Elongation %	438	548	589	625
Toughness, MJ/m^3	64.9	79.8	79.2	84.6
% Tension set, 100 % E, 10 min, 21°C	60.5	57.0	47.0	44.5

Table VI
Physical Properties of Blends of a TPV and a Plastomer (random copolymer of ethylene and 1-butene)

	36	37	38
TPV-3	100.0	100.0	100.0
Exact SLP-0566		6.4	13.6
Polypropylene:Plastomer Ratio	100:0	100:68	100:144
Physical Properties, Unaged			
Hardness, Shore A	51	53	55
50% Modulus, MPa	1.21	1.21	1.28
100% Modulus, MPa	1.83	1.83	1.86
Tensile Strength, MPa	5.68	8.03	10.07
Ultimate Elongation %	471	609	690
Toughness, MJ/m^3	15.15	24.83	31.10
% Tension set, 100% E, 10 min. 21°C	6.5	6.5	6.5
% Compression set 22 hrs. @ 100°C	25.4	28.8	32.5
% Compression set 22 hrs @ 21°C.	13.9	12.7	13.8
% Oil Swell wt. gain, 24 hours, 125°C	79.8	112.2	135.0
Tear Strength N/m^2	19.78	25.54	29.00

Table VII
Conventional Ethylene Copolymers

EPDM/EPR Samples	C2 (wt.%)	ML (1+4) @ 125°C	Mol. Wt. Dist.
Vistalon™ 2504	52	26	Broad
Vistalon™ 8510	51	49	Narrow
Vistalon™ 606	48	65	Broad
Vistalon™ 7500	50	91	Narrow/Tailored Ends
Vistalon™ 808	77	46	Medium
Vistalon™ 4709	75	81	

Vistalon™ is available from Exxon.

Table VIII
Physical Properties of Blends of TPV with Conventional Ethylene Copolymers

	39C (Avg)	40C	41C	42C	43C	44C	45C
TPV-1	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Vistalon™ 7500		3.4	13.4				
Vistalon™ 606				3.4	13.4		
Vistalon™ 808						3.4	13.4
Polypropylene:EPR Ratio	100:0	100:25	100:100	100:25	100:100	100:25	100:100
Physical Properties, Unaged							
Hardness, Shore A	62	57	48	57	45	62	60
50% Modulus, MPa	1.72	1.47	1.01	1.46	0.93	1.64	1.55
100% Modulus, MPa	2.40	2.07	1.41	2.06	1.23	2.31	2.14
Tensile Strength, MPa	5.56	3.93	2.19	4.30	1.91	6.26	7.03
Ultimate Elongation %	421	327	283	378	318	495	629
Toughness, MJ/m^3	14.54	8.41	4.44	10.54	4.55	18.35	25.37
% Tension Set, 100% E, 10 min, 21°C	8	7.5	8.0	7.5	10.0	8.5	9.0
% Compression set, 22 hrs @ 100C	25.9	28.5	39.2	27.6	42.4	25.5	31.6
% Oil Swell, 24 hrs @125	97.38	119.2	153.1	124.9	154.4	115.4	134.6

Table VIII
Physical Properties of Blends of TPV with Conventional Ethylene Copolymers

	46C	47C	48C	49C	50C	51C
TPV-1	100.0	100.0	100.0	100.0	100.0	100.0
Vistalon™ 2504	3.4	13.4				
Vistalon™ 8510			3.4	13.4		
Vistalon™ 4709					3.4	13.4
Polypropylene:EPR Ratio	100:25	100:100	100:25	100:100	100:25	100:100
Physical Properties, Unaged						
Hardness, Shore A	58	46	59	47	61	58
50% Modulus, MPa	1.46	.92	1.48	.98	1.59	1.45
100% Modulus, MPa	2.06	1.26	2.09	1.34	2.27	2.06
Tensile Strength, MPa	4.00	1.87	4.34	1.95	6.92	9.50
Ultimate Elongation %	338	258	374	257	526	655
Toughness, MJ/m^3	8.84	3.46	10.50	3.63	20.52	29.35
% Tension Set, 100% E, 10 min, 25°C	8.5	8.5	8.5	10.0	7.5	7.0
% Compression set, 22 hrs @100C	30.2	38.0	26.8	43.3	29.9	40.0
% Oil Swell, 24 hrs @ 125C	117.1	136.3	120.3	143.6	122.0	140.5

Table IX
Physical Properties of Blends of a TPV and a Plastomer

	52C	53	54	55C
TPV-1	100.0	100.0	100.0	100.0
Exact SLP-0566		13.3 before cure	13.3 after cure	
Polypropylene:Plastomer Ratio	100:0	100:100	100:100	100:0
Physical Properties, Unaged				
Hardness, Shore A		61	63	59
50% Modulus, MPa	1.6	1.6	1.5	1.5
100% Modulus, MPa	2.5	2.3	2.2	2.2
Tensile Strength, MPa	4.7	7.0	6.6	4.5
Toughness, MJ/m^3	7.6	20.8	22.5	8.8
Ultimate Elongation, %	265	504	567	311
% Oil Swell, 24 hrs at 125C	87.8	164.5	142.3	117.0
% Compression Set, 22 hours @100°C	24.2	34.2	43.0	32.2
% Compression Set, 22 hours @21°C	13.7	15.7	17.1	16.8
Tear Strength N/m^2	18.65	30.99	30.36	21.61
% Tension Set, 1100 % E, 10 min, 21°C	5.5	7.0	6.5	6.5

Table X
Ethylene Copolymers

Ethylene Copolymers	MI	Melting Temp. C	Density	Polymer Catalyst
Exceed™ 350D60	1	119	0.917	Metallocene/single site catalyst
Escorene™ LL1001	1	122	0.918	Ziegler Natta/multiple site catalyst
Exceed™ 377D60	1	120	0.922	Metallocene/single site catalyst
Escorene™ HD6706 Control	7	130	0.952	Ziegler Natta/multiple site catalyst

Table XI
Physical Properties of Blends of TPV and Ethylene Copolymers

	56	57	58	59	60C	61	62	63	64
TPV-1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Exceed™ 350D60	3.4	6.7	10.0	13.4					
Escorene™ LL1001						3.4	6.7	10.0	13.4
Polypropylene:Ethylene Copolymer Ratio	100:25	100:50	100:75	100:100	100:0	100:25	100:50	100:75	100:100
Physical Properties, Unaged									
Hardness, Shore A	66	69	71	74	63	65	67	70	73
50% Modulus, MPa	1.90	2.13	2.34	2.57	1.68	1.86	2.02	2.24	2.40
100% Modulus, MPa	2.58	2.80	3.00	3.19	2.37	2.53	2.69	2.89	3.03
Tensile Strength, MPa	7.10	8.10	9.02	9.33	6.20	6.34	6.86	7.43	7.43
Ultimate Elongation %	529	581	613	623	481	492	517	567	568
Toughness, MJ/m^3	21.9	26.7	30.7	32.4	17.8	19.0	21.5	25.4	26.18
Tear Strength (N/m^2)	25.76	28.88	32.95	36.53	21.84	25.32	27.21	30.74	32.77
% Tension Set, 100% E, 10 min., 21°C	9.0	12.0	13.0	14.5	6.5	9.0	10.0	13.0	11.5
% Compression set, 22 hrs @100°C	31.8	31.7	33.3	35.7	27.3	28.8	28.7	28.3	29.3
% Compression set, 22 hrs, 21°C	16.2	17.6	17.6	17.9	14.5	15.9	18.4	18.8	18.6
% Oil Swell, 24 hrs @ 125C	116.4	123.9	119.0	113.7	96.3	114.0	126.2	174.0	117.5
% Oil Swell, 24 hrs, 60°C	58.5	49.3	46.5	41.7	66.1	60.7	55.3	53.2	49.4

Table XI
Physical Properties of Blends of TPV and Ethylene Copolymers

	65C	66C	67	68	69	70
TPV-1	100.0	100.0	100.0	100.0	100.0	100.0
Exceed™ 377D60			3.4	6.7	10.0	13.4
Polypropylene:Ethylene Copolymer Ratio	100:0	100:0	100:25	100:50	100:75	100:100
Physical Properties, Unaged						
Hardness, Shore A	64	63	66	69	73	74
50% Modulus, MPa	1.72	1.69	1.90	2.15	2.45	2.68
100% Modulus, MPa	2.40	2.37	2.57	2.82	3.10	3.31
Tens. Strength, MPa	5.70	6.02	6.88	8.03	8.87	9.70
Ult. Elongation %	447	467	530	578	609	642
Toughness, MJ/m^3	15.7	17.0	21.6	26.6	30.5	34.6
Tear Strength (N/m^2)	22.70	22.18	26.28	30.85	34.23	36.65
% Tension Set, 100% E, 10 min., 21°C	7.5	7.5	9.5	12.5	13.0	15.5
% Compression set, 22 hrs @100C	27.8	27.7	28.9	32.4	31.3	32.0
% Compression set, 22 hrs, 21°C	15.2	14.0	17.0	18.1	18.1	21.1
% Oil Swell, 24 hrs @ 125C	97.5	94.1	115.6	123.2	121.3	114.4
% Oil Swell, 24 hrs, 60°C	65.3	63.1	61.3	53.2	48.4	43.3

Table XII
Comparison of Effects of Different Ethylene Copolymers on Physical Properties of a TPV Data from Table XI Samples Plus Extra Data

	Ultimate Elongation %				100% Modulus, MPa			
Polypropylene:Ethylene Copolymer Ratio	100:25	100:50	100:75	100:100	100:25	100:50	100:75	100:100
PE Copolymer, parts per 100 parts TPV-1	3.4	6.7	10.0	13.4	3.4	6.7	10.0	13.4
Exceed™ 350D60	529	581	613	623	2.58	2.8	3	3.2
Escorene™ LL1001	492	517	567	568	2.53	2.69	2.89	3.04
Escorene™ HD6706 (Control)	489	508	518	535	2.7	3.04	3.28	3.63
Exceed™ 377D60	530	578	609	642	2.57	2.82	3.1	3.31

Table XIII
Physical Properties of Blends of TPV and Plastomers where the TPV rubber is natural, nitrile rubber and butyl rubber

	71C	72	73	74	75	76C	77
TPV-4	100.0	100.0	100.0	100.0	100.0		
TPV-5						100.0	100.0
TPV-6							
Exact SLP-0121		8.1	17.7				
Exact SLP-0566				8.1	17.7		
Exact 4033							3.1
Polypropylene:Plastomer Ratio	100:0	100:84	100:18	100:84	100:18	100:0	100:21
Physical Properties, Unaged							
Hardness, Shore A	35	46	51	46	50	71	73
50% Modulus, MPa	0.63	0.78	0.88	0.73	0.95	2.61	2.68
100% Modulus, MPa	0.97	1.09	1.17	1.04	1.26	3.64	3.62
Ultimate Tensile Strength, MPa	2.58	3.83	4.25	4.55	5.65	6.14	6.34
Ultimate Elongation, %	278	420	507	491	559	224	245
% Tension Set, 100% E, 10 min, 21°C	8.5	10	11	10	10	8.5	10

Table XIII
Physical Properties of Blends of TPV and Plastomers where the TPV rubber is natural, nitrile rubber and butyl rubber

	78	79	80	81C	82	83	84	85
TPV-4								
TPV-5	100.0	100.0	100.0					
TPV-6				100.0	100.0	100.0	100.0	100.0
Exact SLP-0121								
Exact SLP-0566								
Exact 4033	6.4	9.9	13.6		3.1	6.4	9.9	13.6
Polypropylene:Plastomer Ratio	100:43	100:66	100:91	100:0	100:20	100:40	100:62	100:85
Physical Properties, Unaged								
Hardness, Shore A	76	76	76	59	60	60	60	60
50% Modulus, MPa	2.99	2.93	3.16	1.38	1.48	1.47	1.48	1.5
100% Modulus, MPa	3.87	3.74	3.94	2.07	2.17	2.13	2.12	2.14
Ultimate Tensile Strength, MPa	7.02	7.01	7.54	5.91	6.53	6.55	7.09	7.7
Ultimate Elongation, %	273	285	307	343	366	376	410	444
% Tension Set, 100% E 10 min, 21°C	12.5	14	15	7	8	8.5	9	10

While in accordance with the patent statutes the best mode and preferred embodiment has been set forth. the scope of the invention is not limited thereto. but rather by the scope of the attached claims.

WHAT IS CLAIMED IS:

1. A thermoplastic vulcanizate composition. comprising:

from about 20 to about 85 parts by weight rubber and from about 15 to about 80 parts by weight of semi-crystalline polypropylene wherein said parts by weight are based upon 100 parts by weight of said rubber and said polypropylene, and

a thermoplastic random ethylene copolymer

wherein the weight ratio of said polypropylene to said random ethylene copolymer is from about 100:5 to 100:150 and wherein said random ethylene copolymer comprises from about 70 to about 95 weight percent repeat units from ethylene and from about 5 to about 30 weight percent of repeat units from one or more other ethylenically unsaturated monomers based upon the weight of said random ethylene copolymer,

wherein said rubber comprises an ethylene-propylene-diene rubber. natural rubber. butyl rubber. halobutyl rubber. halogenated rubber copolymer of p-alkylstyrene and at least one isomonoolefin having 4 to 7 carbon atoms. a rubber homopolymer of a conjugated diene having from 4 to 8 carbon atoms. or a rubber copolymer having at least 50 weight percent repeat units from at least one conjugated diene having from 4 to 8 carbon atoms or combinations thereof.

2. A composition according to claim 1. wherein said rubber was dynamically vulcanized in the presence of at least said semi-crystalline polypropylene thereby forming said thermoplastic vulcanizate.

3. A composition according to claim 2. wherein said random ethylene copolymer has a peak melting temperature between about 50°C and about 120°C.

4. A composition according to claim 3, wherein said random ethylene copolymer comprises from about 70 to about 90 weight percent repeat units from ethylene and from about 10 to about 30 weight percent repeat units from at least one monoolefin having from 3 to 8 carbon atoms.

5. A thermoplastic vulcanizate composition according to claim 3, wherein said peak melting temperature is from about 55 to about 110°C.

6. A composition according to claim 3, wherein said peak melting temperature is from about 55 to about 100°C.

7. A composition according to claim 3, wherein said peak melting temperature is from about 55 to about 90°C.

8. A composition according to claim 5, wherein said random ethylene copolymer comprises from about 70 to about 90 weight percent repeat units from ethylene and from about 10 to about 30 weight percent repeat units from at least one monoolefin having from 3 to 8 carbon atoms.

9. A composition according to claim 7, wherein said random ethylene copolymer comprises from about 65 to about 85 weight percent repeat units from ethylene and from about 15 to about 35 weight percent repeat units from at least one monoolefin having from 3 to 8 carbon atoms.

10. A composition according to claim 1, wherein said rubber comprises ethylene-propylene-diene rubber.

11. A composition according to claim 1, wherein said rubber comprises butyl rubber, halobutyl rubber, or a halogenated rubber copolymer of p-alkylstyrene and isobutylene.

12. A composition according to claim 1, wherein said rubber comprises natural rubber.

13. A composition according to claim 1, wherein said rubber comprises a rubber homopolymer of a conjugated diene having from 4 to 8 carbon atoms or a rubber copolymer having at least 50 weight percent repeat units from at least one conjugated diene having from 4 to 8 carbon atoms or combinations thereof.

14. A process for making a thermoplastic vulcanizate composition, comprising;

blending

from about 20 to about 85 parts by weight rubber and from about 15 to about 80 parts by weight of a semi-crystalline polypropylene wherein said parts by weight are based upon 100 parts by weight of said rubber and said semi-crystalline polypropylene, and a thermoplastic random ethylene copolymer,

wherein the weight ratio of said polypropylene to said random ethylene copolymer is from about 100:5 to 100:150 and wherein said random ethylene copolymer comprises from about 70 to about 95 weight percent repeat units from ethylene and from about 5 to about 30 weight percent of repeat units from one or more other ethylenically unsaturated monomers based upon the weight of said random ethylene copolymer, and

dynamically vulcanizing said rubber after blending with said semi-crystalline polypropylene, or said random ethylene copolymer, or combinations thereof.

15. A process according to claim 14, wherein said random ethylene copolymer has a peak melting temperature from about 50 to about 120°C.

16. A process according to claim 14, wherein said random ethylene copolymer has a peak melting temperature from about 55 to about 100°C.

17. A process according to claim 14, wherein said random ethylene copolymer has a peak melting temperature from about 55 to about 90°C.

18. A process according to claim 14, wherein said thermoplastic ethylene copolymer is added and blended after said rubber is vulcanized.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/19504

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08J 5/18; C08L 23/02, 23/16
US CL :525/193, 194, 196, 197, 198, 211, 232, 237
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)

U.S. : 525/193, 194, 196, 197, 198, 211, 232, 237

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,073,597 A (PUYDAK et al) 17 December 1991 (17-12-91), see abstract.	1-18
X	US 4,311,628 A (ABDOU-SABET et al) 19 January 1982 (19-01-82), see examples.	1-18
X	US 4,088,714 A (HUFF) 09 May 1978 (09-05-78), see examples.	1-18
X	EP 0,143,131 A (BIDGESTONE TIRE COMPANY LIMITED) 05 June 1985 (05-06-85), see entire document.	1-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

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