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(54) Title: ALKENYL-CO-MALEIMIDE/DIENE RUBBER COMPOSITION

(57) Abstract: A process for forming a diene rubber-grafted centipede polymer includes reacting an amine with a copolymer including maleimide- and alkanyl-derived units. The amine includes at least one functional group capable of grafting to a diene rubber. The copolymer is co-cured with a diene rubber to form the grafted centipede polymer.
ALKENYL-CO-MALEIMIDE/DIENE RUBBER COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to poly(alkenyl-co-maleimide) polymers and to the use of such polymers with diene rubbers to produce high damping additives.

Imidization between a maleic anhydride and a primary amine group as well as the synthesis of monofunctional N-alkyl and N-aryl maleimides are known. The latter class of compounds has been used to improve the heat stability of (co)polymers prepared from vinyl monomers. In one method, the maleimide first is reacted with a bulk resin(s) followed by copolymerization with other monomers such as acrylonitrile, butadiene, styrene, methyl methacrylate, vinyl chloride, vinyl acetate and the like. Typical bulk resins include ABS, polyblends of poly(acrylonitrile-co-butadiene) and poly(styrene-co-acrylonitrile), PVC, SAN, PMMA, and the like. An alternative practice is to produce copolymers of maleimides with other monomers (such as styrene and optionally acrylonitrile) and to blend these with a bulk resin(s). In any event, the polymer compositions are adjusted so that the copolymers are fully compatible with the bulk resin(s) as shown by the presence of a single glass transition point \( T_g \).

Two or more polymers may be blended together to form a wide variety of random or structured morphologies to obtain products that potentially offer desirable combinations of characteristics. However, obtaining many potential combinations through simple blending may be difficult or even impossible in practice. Frequently, the two polymers are thermodynamically immiscible, which precludes generating a truly homogeneous product. This immiscibility is not always a problem since a two-phase structure can be desirable for some applications. However, the situation at the interface between these two phases can lead to problems. The typical case is one of high interfacial tension and poor adhesion between the two phases. This interfacial tension contributes, along with high viscosities, to the inherent difficulty of imparting a desired degree of dispersion to random mixtures and to their subsequent lack of stability, giving rise to gross separation or stratification during processing or use. Poor adhesion leads, in part, to weak and brittle mechanical behavior often observed in dispersed blends and may render some highly structured morphologies impossible.

Providing extended grafted copolymer having the impact strength of polypropylene, the elastomeric properties of a block copolymer, high damping properties, and thermostability remains highly desirable.
SUMMARY OF THE INVENTION

The present invention provides a process for forming a diene rubber-grafted centipede polymer. The process includes reacting an amine with a copolymer that includes a maleimide and at least one monomer unit chosen from vinyl aromatic hydrocarbons, R¹R²ethylenes, and alkyl vinyl ethers. The amine is further functionalized with at least one functional group capable of grafting to a diene rubber. The copolymer is cocured with a diene rubber to form the diene rubber-grafted centipede polymer.

In another aspect of the present invention, a second amine, which is saturated, is reacted with the above-described copolymer. The copolymer is then reacted with the first amine.

In another aspect, a co-curable rubber composition that includes a diene rubber and a copolymer is provided. The copolymer includes at least one maleimide unit formed from the reaction of maleic anhydride with an unsaturated amine, and at least one unit chosen from vinyl aromatic hydrocarbons, alkyl vinyl ethers, and R¹R²ethylenes. The alkyl group of the alkyl vinyl ether can be substituted or unsubstituted, linear or branched, having between 1 and 20 carbons; the R¹ and R² substituents of the R¹R²ethylenes independently can be hydrogen or substituted or unsubstituted C₁-C₂₀ alkyl groups.

The following definitions apply hereinafter unless a contrary intention is expressly indicated:

"vinyl aromatic" and "alkenyl benzene" are used interchangeably;
"maleic anhydride" encompasses dicarboxylic acids, including maleic anhydride, which can form a copolymer with an alkenyl benzene, an alkyl vinyl ether, or an R¹R²ethylene, the copolymer having units reacted through the dicarboxylic acid which are capable of reaction with an amine functional group;
"maleimide" encompasses the reaction product of an amine and a maleic anhydride, described above; and
"R¹R²ethylene" is a monomer of the general formula R¹R²C=CH₂ where R¹ and R² are the same or different substituents on the same or different carbon atoms of the ethylene group, and are selected from hydrogen and substituted C₁-C₂₀ alkyl groups.
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The backbone of the polymer composition can be formed by copolymerization of a maleic anhydride with a second monomer, such as butadiene, styrene, or methyl vinyl ether. A portion of the maleic anhydride units are imidized with a primary amine with others being grafted to a diene rubber via a grafting agent such as an unsaturated amine. The polymer compositions of the present invention preferably contain 100 parts by weight (pbw) of a grafted polymer of a poly(alkenyl-co-maleimide) having at least one unreacted functional group grafted thereto capable of further reacting with a rubber; about 1 to about 10,000 pbw rubber; and optionally from about 10 to 3,000 pbw, preferably about 30 to 1000 pbw, of an extender such as an oil or low molecular weight compound.

The poly(alkenyl-co-maleimide) used to form the graft copolymer can be a centipede polymer formed by imidizing a poly(alkenyl-co-maleic anhydride) with at least one primary amine, preferably at least two different primary amines. If two amines are used, the first preferably is functionalized with at least one additional functional group capable of graft reacting with a diene rubber, and the second preferably is saturated. The centipede polymer has a high molecular weight spine and many relatively short side chains. The length of the main chain usually is longer than the entanglement length (defined herein as an order of magnitude of 100 repeating units) while the length of the side chains preferably is smaller than or equal to the entanglement length.

The alkenyl units of the poly(alkenyl-co-maleimide) centipede polymer can be formed from vinyl aromatic hydrocarbons, \( R_1^1 R_2^2 \) ethylenes, alkyl vinyl ethers, and mixtures thereof. Suitable vinyl aromatic hydrocarbons include styrene, \( \alpha \)-methylstyrene, p-methylstyrene, 4-phenylstyrene, m-methylstyrene, p-tert-butylstyrene, dimethylstyrene, and the like. Suitable alkyl vinyl ethers include those where the alkyl group contains 1 to about 20 carbon atoms in the backbone and may be linear or branched and substituted or unsubstituted. (Substituted groups, such as \( C_2-C_{20} \) alkoxyalkyl groups, when used preferably do not react with the remaining components of the centipede polymers.) Examples of \( R_1^1, R_2^2, \) and alkyl groups (from alkyl vinyl ethers) independently can be substituted or unsubstituted alkyl groups containing 1 to about 20 carbons such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, isopentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, cyclopropyl, 2,2-dimethylcyclopropyl, cyclopentyl, cyclohexyl, methoxymethyl, methoxyethyl, methoxypropyl, methoxybutyl, methoxypentyl,
methoxyhexyl, methoxyheptyl, methoxyoctyl, methoxynonyl, methoxydecyl, ethoxymethyl, ethoxyethyl, ethoxypropyl, ethoxybutyl, ethoxypentyl, ethoxyhexyl, ethoxyheptyl, ethoxyoctyl, ethoxynonyl, ethoxydecyl, propoxymethyl, propoxyethyl, propoxypropyl, propoxybutyl, propoxypentyl, propoxyhexyl, propoxyheptyl, propoxyoctyl, propoxynonyl, propoxydecyl, butoxybutoxymethyl, butoxyethyl, butoxypropyl, butoxybutyl, butoxypentyl, butoxyhexyl, butoxyheptyl, butoxyoctyl, butoxynonyl, butoxydecyl, pentyloxyethyl, pentyloxybutyl, pentyloxypentyl, pentyloxyhexyl, pentyloxyoctyl, pentyloxynonyl, pentyloxydecyl, hexyloxyethyl, hexyloxybutyl, hexyloxydecyl, heptyloxyethyl, heptyloxybutyl, heptyloxydecyl, octyloxyethyl, octyloxybutyl, octyloxydecyl, deoxyethyl, decyloxybutyl, decyloxypropyl, decyloxypentyl, decyloxyhexyl, decyloxyheptyl, 1-methylethyl, 1-methylpropyl, 1-methylbutyl, 1-methylpentyl, 1-methylhexyl, 1-methylheptyl, 1-methyloctyl, 1-methylnonyl, 1-methyldecyl, 2-methylpropyl, 2-methylbutyl, 2-methypentyl, 2-methylhexyl, 2-methyloctyl, 2,3-dimethylbutyl, 2,3,3-trimethylbutyl, 3-methylpentyl, 2,3-dimethylpentyl, 2,4-dimethylpentyl, 2,3,3,4-tetramethylpentyl, 3-methylhexyl, 2,5-dimethylhexyl, and the like. Preferred alkenyl monomers for forming these copolymers are styrene and isobutylene.

A poly(alkenyl-co-maleimide) can be formed by reacting, under substantially dry conditions at from about 100°C to about 300°C and from about slightly above vacuum to about 20 atm, a poly(alkenyl-co-maleic anhydride) and at least one primary amine. Preferred polymers of this type are typically formed by reacting a poly(styrene-co-maleic anhydride), poly(isobutylene-co-maleic anhydride), or poly(methyl vinyl ether-co-maleic anhydride) with at least one primary amine. The poly(alkenyl-co-maleic anhydride) can be converted to poly(alkenyl-co-maleimide) by reaction with an amine functionalized with at least one group capable of graft reacting to a diene rubber, and, optionally, a second amine which is saturated. Suitable functional groups include alkenyl, alkynyl, hydroxyl, carboxyl, formyl, amino, cyano, and mixtures thereof.

For purposes of this invention, poly(alkenyl-co-maleimide) and poly(alkenyl-co-maleic anhydride) encompass random and stereospecific copolymers, including copolymers having alternating alkenyl-contributed units and maleimide- or maleic
anhydride-contributed units along the polymer backbone. Such alternating structures typically would be described as poly(alkenyl-alt-maleimide) and poly(alkenyl-alt-maleic anhydride), respectively; however, these polymers also are intended to be encompassed in the terms poly(alkenyl-co-maleimide) and poly(alkyl-co-maleic anhydride).

Processes for forming poly(alkenyl-co-maleic anhydride) polymers are known. Preparing copolymers from electron donors such as vinyl aromatic hydrocarbons, R1R2ethylenes, or alkyl vinyl ethers, and from electron acceptors such as maleic anhydride as a result of complexation of the electron acceptor monomers may be carried out in the absence or presence of an organic free radical initiator in bulk, or in an inert hydrocarbon or halogenated hydrocarbon solvent such as benzene, toluene, hexane, carbon tetrachloride, chloroform, etc. For the imidization step, the reactants preferably are dry mixed in the absence of solvents in a suitable mixing apparatus such as a Brabender mixer which preferably has been purged with an inert gas such as N2 or Ar. The primary amine(s) may be added in a singular charge or in sequential partial charges into a reactor containing a charge of poly(alkenyl-co-maleic anhydride). Preferably, the primary amine(s) is/are charged at a ratio of at least 1.0 mole of amine per 1.0 mole of maleic anhydride in the poly(alkenyl-co-maleic anhydride).

Poly(alkenyl-co-maleic anhydride) contains from about 5 to 99 mole percent of units derived from maleic anhydride with the remainder being units derived from alkenyl monomer(s). Poly(alkenyl-co-maleic anhydride) preferably contains from 20 to 60 mole percent units derived from maleic anhydride, most preferably 45 to 55 mole percent units derived from maleic anhydride and 55 to 45 mole percent units derived from alkenyl monomer(s). The two types of units can be randomly or alternately distributed along the chain, although an alternating distribution along the polymer backbone chain is preferred. The poly(alkenyl-co-maleic anhydride) has a weight average molecular weight (Mw) of from about 1,000 to about 500,000 or higher, more typically between about 10,000 and 500,000, and even more typically between about 150,000 and 450,000.

Using two different primary monoamines, a first amine, which is further functionalized with at least one functional group capable of grafting to a diene rubber, and a second amine, which is saturated, such as octylamine and oleylamine, in the preparation of the poly(alkenyl-co-maleimide) is preferred.

(Similarly, the same or different poly(alkenyl-co-maleimides) can be used in the preparation of the grafted poly(alkenyl-co-maleimide)/diene rubber copolymers.)
Suitable primary amines that can serve as the first amine include oleylamine, erucyl erucamide, erucamide, aleylamine, allylamine, amino styrene, vinyl benzyl amine, ethylene diamine, diethylene triamine, triethylene triamine, tetraethylene pentamine, pentaethylene hexamine, xyylene diamine, hexamethylene diamine, polyoxypropylene diamine, polyoxypropylene triamine, polyoxyethylene diamine, polyoxyethylene triamine, and mixtures thereof. A preferred primary amine which can serve as the first amine is oleylamine. Suitable primary amines that can serve as the second amine, include alkyl amines; alkyl benzyl amines; alkyl phenyl amines; alkoxybenzyl amines; alkyl aminobenzoates; alkoxy aniline; and other linear or branched primary amines containing from 1 to 50 carbon atoms, preferably 6 to 30 carbon atoms, in the alkyl and alkoxy substituents. The alkyl and alkoxy substituents on these primary amines can be linear or branched and saturated or unsaturated; however no aromatic rings may be directly bonded to the amine group. Exemplary amines include hexylamine, octylamine, dodecylamine, and the like.

The first amine can be added to the polymer composition in the range of about 1-99% of the total amine concentration, more preferably between about 60-99%. The second amine can be added to the polymer composition in the range of about 1-99% of the total amine concentration, more preferably between about 1-40%. The poly(alkenyl-co-maleic anhydride) is converted to poly(alkenyl-co-maleimide) by reacting the unsaturated amine simultaneously with, or subsequently to, the saturated amine.

Grafting of diene rubbers and poly(alkenyl-co-maleimides) is performed by utilizing the remaining functional group of the first amine. Suitable functional groups include alkenyl, alkynyl, primary amine, secondary amine, carboxyl, formyl, hydroxyl, cyano, and mixtures thereof. Preferred functional groups are alkenyl, such as those present in unsaturated amines of the general formula

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{R}^3 \quad \text{R}^4 \\
\text{C} & \quad \text{C} \\
\text{R}^5 \quad \text{R}^6
\end{align*}
\]

wherein \( \text{R}^3, \text{R}^4, \text{R}^5, \) and \( \text{R}^6 \) are the same or different, and are chosen from hydrogen and linear or branched alkyl chains wherein the total number of carbons is not greater than about 40, and mixtures thereof. The poly(alkenyl-co-maleimide) containing residual functional groups which are unsaturated is then grafted reacted
with a suitable diene rubber. The resultant copolymers have superior damping capabilities.

Suitable rubbers include diene rubbers such as isoprene rubber, natural rubbers, EPDM natural rubbers, emulsion polymerized styrene/butadiene rubber (SBR), solution-polymerized random SBR, high-trans SBR (trans content in the butadiene units 70-95%), low cis butadiene rubber (BR), high cis BR, styrene/isoprene rubber, butadiene/isoprene rubber, solution polymerized random styrene-butadiene-isoprene copolymer rubber (SIBR), emulsion polymerized SIBR, emulsion polymerized halogenated butyl rubber, ethylene-propylene-diene terpolymer rubber, epichlorohydrin rubber, and block copolymers such as high vinyl SBR-low vinyl SBR-block copolymer rubber, and polystyrene-polybutadiene-polystyrene block copolymer, and mixtures thereof. A particularly preferred combination is a mixture of styrene-butadiene-styrene rubber and butadiene rubber.

An exemplary process for preparing the polymer and high damping material of this invention includes the steps of:

a) combining a poly(alkenyl-co-maleic anhydride) and a primary amine that contains at least one additional functional group capable of grafting, under substantially dry conditions sufficient to react substantially most of the anhydride moieties to form a poly(alkenyl-co-maleimide);

b) adding a second amine, which is saturated, to the reaction mixture such that all remaining anhydride moieties are converted to maleimide moieties (this step may be performed concurrently with, or prior to, step a);

c) graft reacting the product of steps a and b with a rubber through the first amine, and

d) optionally, adding an extender to the polymer composition.

Copolymers such as those of the present invention, can be prepared by any means known in the art such as blending, milling, or internal batch mixing. A rapid and convenient method of preparation involves heating a mixture of the components to a temperature of from about 50° to about 290°C. Such polymers can be made by mixing and dynamically heat-treating the components described above. As for the mixing equipment, any conventional, generally known equipment such as an open-type mixing roll, closed-type Banbury mixer, closed type Brabender mixer, extruding machine, kneader, continuous mixer, etc., is acceptable. Mixing in an inactive gas environment, such as N₂, Ar, or CO₂, also is preferable.
The graft reaction is believed to be accomplished by contacting the unreacted functional group from the first amine with a diene rubber, whereupon interaction and crosslinking take place. The functional groups of the first amine react to form covalent chemical bonds with the unreacted double bonds in the diene rubber. The centipede polymer is thus grafted to the diene rubber through covalent chemical functional linkages. The contacting can be accomplished by combining solutions of the polymeric reactants in suitable solvents, such as benzene, toluene, and other inert organic and inorganic solvents, in a suitable reaction vessel. Heating accelerates the reaction and is generally preferred. More preferably, contacting can be accomplished without solvents by mixing pre-formed pellets of the neat functionalized polymers and adding the grafting agent and melt processing in a physical blender or mixer at temperatures of from about 20° to about 350°C, preferably about 50° to about 300°C, most preferably 65° to about 150°C.

A curing agent can accelerate the crosslinking reaction between the diene rubber and the copolymer. The agent can be any agent known in the art for accelerating the crosslinking reaction, including free-radical and anionic catalysts. A preferred agent is sulfur. Other preferred catalysts include accelerators, such as N-t-butyl-benzothiazole sulfenamine, benzothiazyl disulfide, and tetramethyl thiuram monosulfide.

Amounts of poly(alkenyl-co-maleimide) and diene rubber reacted into the grafted compositions of the immediate invention may vary somewhat depending upon the properties desired in the finished composition. In general, amounts of diene rubber included in the grafted composition may range from about 1 to about 99% (by weight) based on total weight of composition. Preferred amounts of diene rubber are from 5 to 50% (by wt.) with a particularly preferred amount being from about 10 to 40% (by wt.). The amounts of poly(alkenyl-co-maleimide) centipede polymer included in the grafted composition may range from about 1 to about 99% (by wt.) based on total weight of composition. Preferred amounts of the centipede polymer are from 1 to 40% (by wt.) with a particularly preferred amount being from about 1 to 30% (by wt.). An extender is preferably added in the amount of about 10 to about 90% (by wt.) of the total composition, more preferably about 30 to 90% (by wt.).
The grafted polymer composition can have added thereto extenders such as extender oils and low molecular weight compounds or components. Suitable extender oils include those well known in the art such as naphthenic, aromatic, and paraffinic petroleum oils and silicone oils. Examples of low molecular weight organic compounds or components useful as extenders in the compositions of the present invention are low molecular weight organic materials having a number average molecular weight ($M_n$) of less than 20,000, preferably less than 10,000, and most preferably less than 5,000. Although there is no particular limitation to the material that may be employed, the following is a list of exemplary appropriate materials:

1) Softening agents, namely aromatic naphthenic and paraffinic softening agents for rubbers or resins;

2) Plasticizers, namely plasticizers composed of esters including phthalic, mixed phthalic, aliphatic dibasic acid, glycol, fatty acid, phosphoric and stearic esters, epoxy plasticizers, other plasticizers for plastics, and phthalate, adipate, sebacate, phosphate, polyether, and polyester plasticizers for NBR;

3) Tackifiers, namely coumarone resins, coumarone-indene resins, terpene phenol resins, petroleum hydrocarbons, and rosin derivative;

4) Oligomers, namely crown ether, flourine-containing oligomers, polybutenes, xylene resins, chlorinated rubber, polyethylene wax, petroleum resins, rosin ester rubber, polyalkylene glycol diacylate, liquid rubber (polybutadiene, SBR, butadiene-acrylonitrile rubber, polychloroprene, etc.), silicone oligomers, and poly($\alpha$-olefins);

5) Lubricants, namely hydrocarbon lubricants such as paraffin and wax, fatty acid lubricants such as higher fatty acid and hydroxy-fatty acid, fatty acid amide lubricants such as fatty acid amide and alkylene-bis-fatty acid amide, ester lubricants such as fatty acid-lower alcohol ester, fatty acid-polyhydric alcohol ester and fatty acid-polyglycol ester, alcoholic lubricants such as
fatty alcohol, polyhydric alcohol, polyglycol and polyglycerol, metallic soaps, and mixed lubricants;

6) petroleum hydrocarbons, namely synthetic terpene resins, aromatic hydrocarbon resins, aliphatic hydrocarbon resins, aliphatic cyclic hydrocarbon resins, aliphatic or alicyclic petroleum resins, aliphatic or aromatic petroleum resins, polymers of unsaturated hydrocarbons, and hydrogenated hydrocarbon resins.

7) accelerators, such as N-t-butyl-benzothiazole sulfenamine, benzothiazyl disulfide, and tetra-methyl thiuram monosulfide; and

8) catalysts capable of catalyzing the curing reaction.

Other appropriate low molecular weight organic materials include latices, emulsions, liquid crystals, bituminous compositions, polymers, and phosphazenes. One or more of these materials may be used as extenders.

Polymer compositions produced according to the present invention generally have high damping properties, i.e., a tan δ of at least 0.1, preferably in the range of about 0.1 to about 0.8 over the temperature range of 20° to 50°C.

Frequently, including other additives known in the rubber art to the compositions of the present application can be desired. Stabilizers, antioxidants, conventional fillers, reinforcing agents, reinforcing resins, pigments, fragrances, and the like are examples of some such additives. Specific examples of useful antioxidants and stabilizers include 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, nickel dibutylthiuram disulfide, zinc dibutyl dithiocarbamate, tris(nonylphenyl) phosphite, 2,6-di-t-butyl-4-methylphenol and the like. Exemplary conventional fillers and pigments include silica, carbon black, titanium dioxide, iron oxide, and the like. These compounding ingredients are incorporated in suitable amounts depending upon the contemplated use of the product, preferably in the range of 1 to 350 pbw additives or compounding ingredients per 100 pbw grafted copolymer.

A reinforcing material can be defined as a material added to a resinous matrix to improve the strength of the polymer. Most reinforcing materials are inorganic or high molecular weight organic products. Examples include glass fibers, asbestos, boron fibers, carbon and graphite fibers, whiskers, quartz and silica fibers, ceramic fibers, metal fibers, natural organic fibers, and synthetic organic fibers. Other elastomers and resins are also useful to enhance specific properties like damping properties, adhesion and processability. Examples of other elastomers and resins include adhesive-like products, hydrogenated polystyrene-(medium or high 3,4)-polysoprene-polystyrene block copolymers, polynorbornenes,
and the like. The foregoing materials also can be used in the centipede polymer compositions.

Polymer compositions containing diene rubber grafted poly(alkenyl-co-maleimide) and an oil or low molecular weight component extender can be prepared by any means known in the art for combining such ingredients, such as solution blending, milling, internal batch mixing, or continuous extrusion of a solid form of the centipede polymer and polypropylene compositions and the other ingredients. A rapid and convenient method of preparation involves heating a mixture of the components to a temperature of from about 50°C to about 290°C.

Polymer compositions containing oil-extended diene rubber grafted poly(alkenyl-co-maleimide) compositions can be manufactured by mixing and dynamically heat treating the components described above. As for the mixing equipment, any conventional equipment such as an open-type mixing roll, closed-type Banbury mixer, extruding machine, kneader, continuous mixer, etc., is acceptable. Mixing in an inactive gas environment, such as N₂ or Ar, is also preferable.

The composition of the present invention can be mixed in any conventional mixer such as a Banbury mixer or roll mill or extruder normally conducted at a temperature of from about 120°C to about 300°C, preferably maintaining the composition above its melting point for a few minutes up to several hours, preferably 10 to 40 minutes. A particularly useful technique is to add any fillers in the beginning of the mixing cycle to take maximum advantage of heating time and to prevent surface bleeding and overheating when forming the molded articles.

The resultant polymer composition may be molded in appropriate press ovens and the like to form products in the form of extruded pellets, preferably as small as possible since smaller pellets provide short heating times and better flow when utilized in flow molding. Ground pellets may also be utilized.

The extended diene rubber grafted centipede polymers can be used in high temperature applications including uses in injection molding or in any other compositions typically used for elastomeric properties. Of course, molded polymers produced from compositions containing diene rubber grafted poly(alkenyl-co-maleimide) compositions retain elastomeric characteristics and are useful in high temperature applications and/or high damping applications.

A convenient measurement of damping is the parameter tan δ. A forced oscillation is applied to a material at frequency and the transmitted force and phase shift are measured. The phase shift angle delta is recorded. The value of tan δ is
proportional to the ratio of energy dissipated to energy stored. The measurement can be made by any of several commercial testing devices, and may be made by a sweep of frequencies at a fixed temperature, then repeating that sweep at several other temperatures, followed by the development of a master curve of tan δ vs. frequency by curve alignment. (An alternate method is to measure tan δ at constant frequency (such as at 5 Hz) over a temperature range.) Advantageously, this high degree of absorption of energy can be accompanied by good mechanical and thermal stability. These properties are important because parts made from the subject polymers often are repeatedly cycled and subjected to various forces of compression, tension, bending, and the like.

The composition of the present invention can be used in the manufacture of any product in which one or more of a high degree of softness, heat resistance, decent mechanical properties, elasticity, and high damping is important. The composition can be used in all industry fields, in particular, in the fabrication of automotive parts, tire tread rubbers, house-hold electrical appliances, industrial machinery, precision instruments, transport machinery, constructions, engineering, and medical instruments.

Representative examples of the use of the extended graft polymers of the present invention are damping materials and vibration restraining materials. These uses involve connecting materials such as sealing materials, packing, gaskets and grommets, supporting materials such as mounts, holders and insulators, and cushion materials such as stoppers, cushions, and bumpers. These materials are also used in equipment producing vibration or noise and household electrical appliances, such as in air-conditioners, laundry machines, refrigerators, electric fans, vacuums, dryers, printers and ventilator fans. Further, these materials are also suitable for impact absorbing materials in audio equipment and electronic or electrical equipment, sporting goods and shoes. Further, as super low hardness rubbers, these materials are applicable for use in appliances, damping rubbers, and as low hardness plastics, it is preferable for molding materials. Further, because the present compositions can be used to control the release of internal low molecular weight materials out from the compositions, it is useful as a release support to emit materials such as fragrance materials, medical materials and other functional materials. The compositions of the present invention also possess utility in applications of use in liquid crystals, adhesive materials and coating materials.
Specific examples of uses of the compositions of the present invention as damping materials include

- in audio equipment, such as in insulators for a portable CD or a CD mounted on a vehicle, mike holders for home video cassette recorder, radio cassette recorder, karaoke or handy mike, etc., an edge cone of a speaker, a tape holder of a radio cassette, a holder of a portable mini disk player, an optical disk holder of a digital video disk, etc.;

- in information relating equipment, such as in insulators for a hard disk, insulators for motors such as a spindle motor for HHD and stepping motor, insulators for floppy disk drive, insulators for CD-ROM of personal computer, and a holder for optical disk;

- in communication equipment, such as in a holder for compact high performance mike or speaker of a portable telephone, a pocket bell or PHS, a microphone holder for a wireless equipment, and a disk holder for portable note type electronic equipment;

- in home electronics equipment, such as in insulators for CD-ROM of home TV game, insulators for cassette holder or CD-ROM of cassette holder or game machine, a holder of high performance mike, and cone edge of speaker; and

- in other applications, such as in damping materials for printer head of a word processor, printer of personal computer, small or middle handy type printer, or name printers, and insulators for CD-ROM used for measure equipment.

The present invention is described in more detail with reference to the following non-limiting examples.

EXAMPLES

Example 1: Preparation of Centipede Polymer

To a 6L kneader-extruder (Jaygo, Inc.) equipped with sigma blades was added 1.36 kg Scripset 520™ poly(maleic anhydride-alt-styrene) (Hercules Inc.; Wilmington, Delaware), 771 g octylamine of 99% purity (Aldrich Chem. Co.; Milwaukee, Wisconsin), and 167.82 g oleylamine (Aldrich) at 65°C. Mixing with a blade speed of 25 rpm and a screw speed of 66 rpm was done for 10 minutes before 1000 mL water was added. Mixing continued for another 10 minutes over which the temperature was raised to 100°C. The vapor generated was vented through a 64 mm pore at the top lid. Ten minutes later, the temperature of the
mimer was adjusted to rise to 200°C at a rate of about 3°C per minute. Mixing was further continued isothermally for 2 more hours at 200°C. Then, the temperature was adjusted to 100°C.

About 10 g of the product was taken out of the mixer and was analyzed by FTIR. No trace of maleic anhydride absorption peaks, i.e., at 1779 and 1855 cm\(^{-1}\) and amino-group peaks, i.e., at 3330 cm\(^{-1}\) were seen, which is indication that the product was fully reacted.

Then, 1.36 kg of DTDP oil (C.P. Hall Co.) was added to the mixer. After 30 minutes, the final product was extruded through a 64 mm die.

Example 2-7: Diene Rubber-Grafted Copolymer

Rubber blends were prepared from the components shown below in Table 1. The SBR was Duradene™ 753 oil-extended high-styrene SBR (20.4 pbw per 100 pbw (phr) aromatic oil) which contains 33% bound styrene and has a \(T_g\) of -47°C. The cis-BR was Diene™ 600 polybutadiene.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (pbw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>96.80</td>
</tr>
<tr>
<td>cis-BR</td>
<td>20.00</td>
</tr>
<tr>
<td>carbon black</td>
<td>70.00</td>
</tr>
<tr>
<td>aromatic oil</td>
<td>18.25</td>
</tr>
<tr>
<td>stearic acid (processing aid)</td>
<td>2.00</td>
</tr>
<tr>
<td>wax (processing aid, protection against (O_2) oxidation)</td>
<td>1.50</td>
</tr>
<tr>
<td>N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylene-diamine (antioxidant)</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 1: Amounts (in pbw) of components in blends, generally

For each example, a blend of the ingredients was kneaded by a method listed in Table 3. A 310 g Brabender mixer was set to a temperature of 110°C with a stir speed of 60 rpm. SBR and the cis-BR or blend were first added to the mixer. After 30 seconds, the carbon black, aromatic oil, stearic acid, wax, and N-(1,3-
dimethylbutyl)-N'-phenyl-p-phenylene-diamine antioxidant were added and, after five minutes, this mixture was removed from the mixer. The mixer was cooled and reset to 110°C. The mixture was returned to the mixer, stirred for an additional 4 minutes at 110°C, then cooled to 75°C. The curatives shown above were added at this point along with, for Examples 3-7, the centipede polymer. The mixture was blended for an additional 80 seconds, then cooled. These conditions are summarized in Table 2, immediately below.

Six of these compositions were prepared. A comparative, Example 2, used only extender oil and rubber (i.e., did not include any of the product of Example 1) whereas Examples 3-7 used varying amounts of the centipede polymer from Example 1 to partially replace or supplement the extender and/or rubber. The amounts of these materials (in pbw) for each example are shown in Table 3.

**Table 2: Reaction Conditions for Representative Grafting Reaction**

<table>
<thead>
<tr>
<th>Master Batch Stage</th>
<th>Initial Temperature</th>
<th>110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 seconds</td>
<td>Charge polymers</td>
</tr>
<tr>
<td></td>
<td>30 seconds</td>
<td>Charge carbon black and all pigments</td>
</tr>
<tr>
<td></td>
<td>5 minutes</td>
<td>Cooling</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remill Batch Stage</th>
<th>Initial Temperature</th>
<th>110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 seconds</td>
<td>Charge master batch stock</td>
</tr>
<tr>
<td></td>
<td>4 minutes</td>
<td>Cooling</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Final Batch Stage</th>
<th>Initial Temperature</th>
<th>75°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 seconds</td>
<td>Charge remilled stock and centipede polymer</td>
</tr>
<tr>
<td></td>
<td>30 seconds</td>
<td>Charge curing agent and accelerators</td>
</tr>
<tr>
<td></td>
<td>80 seconds</td>
<td>Cooling</td>
</tr>
</tbody>
</table>
Table 3: Relative Amounts of Extender, Rubber, and Centipede Polymer

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Oil</th>
<th>BR</th>
<th>Polymer from Ex. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (comp)</td>
<td>35.05</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>30.05</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>27.05</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>20.05</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>35.05</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>35.05</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

The final stock was sheeted and molded at 165°C for ~15 minutes. Tensile strength, tear strength, and hysteresis loss were measured and the results are shown in Table 4.

Measurement of tensile strength was based on conditions of ASTM-D 412 at 22°C. Test specimen geometry was in the form of a ring having a width of 13 mm and a thickness of 19 mm. The specimen was tested at a specific gauge length of 2.54 cm. The measurement of tear strength was based on conditions of ASTM-D 624 at 170°C. Test specimen geometry was taken in the form of a nicked ring (ASTM-D 624-C). The specimen was tested at the specific gauge length of 4.445 cm. Hysteresis loss was measured with a Dynastat™ viscoelastic analyzer. Test specimen geometry was in the form of a strip of a length of 30 mm and a width of 15 mm. Testing conditions of 5 Hz frequency and 0.5% strain were used.

Table 4: Results of Physical Testing

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus at 23°C, 300% elongation (kg/cm)</td>
<td>250±11</td>
<td>287±6</td>
<td>272±2</td>
<td>325±7</td>
<td>286±3</td>
<td>224±8</td>
</tr>
<tr>
<td>Tensile strength @ 23°C (MPa)</td>
<td>18.8±0.2</td>
<td>21.2±1.2</td>
<td>20.6±0.5</td>
<td>21.7±0.7</td>
<td>19.2±0.9</td>
<td>19.3±0.2</td>
</tr>
<tr>
<td>Max. elongation @ 23°C (%)</td>
<td>537±23</td>
<td>538±35</td>
<td>552±14</td>
<td>511±8</td>
<td>506±16</td>
<td>590±24</td>
</tr>
<tr>
<td>Tear strength @ 170°C (kg/cm)</td>
<td>55±3</td>
<td>54±5</td>
<td>53±6</td>
<td>42±6</td>
<td>48±4</td>
<td>51±3</td>
</tr>
<tr>
<td>Travel at tear @ 170°C (%)</td>
<td>455±15</td>
<td>446±25</td>
<td>431±31</td>
<td>343±33</td>
<td>413±23</td>
<td>489±32</td>
</tr>
<tr>
<td>tan δ at 23°C</td>
<td>0.1915</td>
<td>0.1955</td>
<td>0.1954</td>
<td>0.1887</td>
<td>0.2028</td>
<td>0.2014</td>
</tr>
<tr>
<td>tan δ at 50°C</td>
<td>0.1650</td>
<td>0.1585</td>
<td>0.1769</td>
<td>0.1875</td>
<td>0.1996</td>
<td>0.1953</td>
</tr>
</tbody>
</table>

As can be seen in Table 4, the rubber compositions of Examples 2-7 exhibited well balanced tensile strength, tear strength, and damping properties.
The tensile strength and damping properties of the modified rubber compounds (i.e., Examples 3-7 which contained the grafted polymer from Example 1) were better than that of Example 2 (which utilized only oil and butadiene rubber) if consideration is based on the same modulus conditions.

Accordingly, the polymers developed are suitable as high damping additives in rubber compounds, and the polymers can be used as alternatives for oils or plasticizers.
We claim:

1. A method for forming a diene rubber-grafted polymer, comprising:
   a) providing an imidized copolymer by reacting
      1) a copolymer comprising
         A) maleimide units and
         B) other units derived from at least one of
            i) a vinyl aromatic hydrocarbon,
            ii) \( \text{R}^1\text{R}^2\text{ethene} \) in which \( \text{R}^1 \) and \( \text{R}^2 \) independently are
                substituted or unsubstituted \( \text{C}_1 \) to \( \text{C}_{20} \) alkyl groups,
            and
            iii) an alkyl vinyl ether in which the alkyl group is
                substituted or unsubstituted having between 1 and 40
                carbons; and
      2) an amine comprising at least one functional group capable of
         grafting to a diene rubber;
   b) reacting said imidized copolymer with a diene rubber to form said
      diene rubber-grafted polymer; and
   c) optionally, adding an extender to the diene rubber-grafted polymer.

2. The method of claim 1, wherein the reaction of step (a) further
   includes a second amine, said second amine being saturated.

3. The method of claim 2, wherein the reaction of step (a) comprises:
   a) reacting said copolymer with said second amine to provide an
      intermediate imidized product, and
   b) reacting said intermediate imidized product with said first amine to
      provide said imidized copolymer.

4. The method of any of claims 2 to 3, wherein said second amine is a
   primary amine selected from alkyl amines; alkyl benzyl amines; alkyl phenyl
   amines; alkoxybenzyl amines; alkyl aminobenzoates; and alkoxy aniline; containing
   from 1 to 50 carbon atoms in the alkyl and alkoxy substituents in the primary
   amine.

5. The method of any of claims 1 to 4, wherein said extender comprises
   one or more of softening agents, plasticizers, tackifiers, oligomers, lubricants,
   petroleum hydrocarbons, silicone oil, aromatic oil, naphthenic oil, and paraffinic oil.
6. The method of any of claims 1 to 5, wherein step (b) includes mixing about 1 to 40% (by wt.) of said imidized copolymer with 1 to 50% (by wt.) of said diene rubber, optionally followed by addition of 30 to 90% (by wt.) extender.

7. The method of any of claims 1 to 6, wherein the imidization reaction of step (a) is carried out in the absence of a solvent.

8. The method of any of claims 1 to 7, wherein said amine has the general formula:

$$\text{H}_2\text{N} \quad \text{C} \quad \text{C} \quad \text{R}^3 \quad \text{R}^4$$

wherein $\text{R}^3$, $\text{R}^4$, $\text{R}^5$, and $\text{R}^6$ independently are hydrogen and linear or branched alkyl chains wherein the total number of carbons is not greater than about 40.

9. The method of any of claims 1 to 7, wherein said amine comprises at least one of oleylamine, erucyl erucamide, erucamide, aleylamine, allylamine, amino styrene, vinyl benzyl amine, ethylene diamine, diethylene triamine, triethylene triamine, tetrathylene pentamine, pentaethylene hexamine, xylene diamine, hexamethylene diamine, polyoxypropylene diamine, polyoxypropylene triamine, polyoxyethylene diamine, and polyoxyethylene triamine.

10. The method of claim 9 wherein said amine is oleylamine.

11. The method of any of claims 1 to 10, wherein said vinyl aromatic hydrocarbon is at least one of styrene, $\alpha$-methylstyrene, p-methylstyrene, 4-phenylstyrene, m-methylstyrene, o-methylstyrene, p-tert-butylstyrene, and dimethylstyrene.

12. The method of any of claims 1 to 11, wherein the reaction of step (b) is carried out in the absence of a solvent.

13. The method of any of claims 1 to 12, wherein said diene rubber comprises at least one of polyisoprene, natural rubber, EPDM, SBR, butadiene rubber, styrene-isoprene rubber, butadiene-isoprene rubber, random styrene-butadiene-isoprene copolymer rubber, emulsion polymerized halogenated butyl rubber, and epichlorohydrin rubber.
14. A co-curable rubber composition comprising:
   a) a diene rubber; and
   b) a copolymer comprising
      1) at least one maleimide unit formed by reacting a maleic
         anhydride unit with an unsaturated amine, and
      2) at least one unit derived from a vinyl aromatic hydrocarbon, an
         alkyl vinyl ether in which the alkyl group is substituted or
         unsubstituted, having between 1 and 40 carbons, and
         \( \text{R}^1\text{R}^2 \) ethylene monomers, in which \( \text{R}^1 \) and \( \text{R}^2 \) independently are
         hydrogen or substituted or unsubstituted \( \text{C}_1 \) to \( \text{C}_{29} \) alkyl groups.

15. The co-curable composition of claim 14 further including units formed
    by reacting maleic anhydride with a saturated amine.

16. The co-curable composition of claim 15 wherein the composition,
    when cured, has a \( \tan \delta \) of at least 0.18.

17. A co-curable rubber composition comprising:
   a) a diene rubber,
   b) a copolymer comprising a maleic anhydride unit, and at least one
      other unit derived from vinyl aromatic hydrocarbons, \( \text{R}^1\text{R}^2 \) ethylenes,
      and alkyl vinyl ethers,
   c) a saturated amine, and
   d) an unsaturated amine.