The invention relates to a method for marking a polymer composition by melt mixing a composition composed of a polymer having at least one isocyanate reactive group and a thermoplastic polyurethane, wherein the thermoplastic polyurethane is less than 5% by weight of the composition, wherein the polymer is not a polyamide. Preferably the polymer is a polyester, a liquid crystalline polymer or a polycarbonate. The invention further relates to a polymer composition produced by the present invention. The invention further relates to an article composed of the polymer composition produced by the present invention.
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THERMOPLASTIC POLYURETHANE ADDITIVES FOR CHAIN EXTENSION AND REACTIVE EXTRUSION

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority upon United States provisional application serial no. 60/057,923, filed September 4, 1997, the contents of which are herein incorporated in their entirety by this reference.

FIELD OF THE INVENTION

The present invention relates to a method for increasing the molecular weight of a polymer composition by melt mixing a composition composed of a polymer having at least one isocyanate reactive group and a thermoplastic polyurethane.

BACKGROUND OF THE INVENTION

There is a growing need for producing high molecular weight polymers. In particular, high molecular weight polyesters and copolyesters can be used in a number of different applications. For example, high molecular weight polyesters can be used as reinforcing agents in rubber articles. Additionally, high molecular weight polyesters can be extruded and molded into a wide variety of useful articles. A problem associated with the production of high molecular weight polyesters is the amount of time it takes to produce a polymer with the desired molecular weight. Upon extended heating, the polymer can undergo thermal degradation, which ultimately reduces the molecular weight of the polymer.

One approach for increasing the molecular weight of a polymer involves the addition of a compound that is capable of reacting with the polymer. This is referred to in the art as "chain extension." U.S. Patent No. 4,071,503 to Thomas et al. discloses
the reaction between a polycarbodiimide and a polyester in order to increase the molecular weight and melt strength. U.S. Patent No. 4,568,720 to Aharoni et al. and Jacques et al. (Polymer, Vol. 37, No. 7, pp 1189-1200, 1996) disclose the use of phosphite compounds as chain extenders. Cardi et al. (J. Applied Polymer Science, Vol. 50, pp 1501-1509, 1993) discloses the chain extension of poly(ethylene terephthalate) with 2,2'-bis(2-oxazoline). U.S. Patent No. 4,857,603 to Akkapeddi et al. discloses the chain extension of poly(ethylene terephthalate) with poly lactams. Bikiaris et al. (Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 34, 1337-1342, 1996) investigated the combination of diimidodiepoxides with poly(ethylene terephthalate) and poly(butylene terephthalate) in order to increase the molecular weight of the polyester. None of these references, however, disclose the use of a thermoplastic polyurethane as a chain extender.

The prior art discloses the combination of polyurethanes and polymers in order to increase the mechanical properties of the resultant blend. U.S. Patent No. 5,519,094 to Tseng et al. and U.S. Patent No. 5,258,445 to Sperk et al. disclose the combination of a thermoplastic polyurethane, a polyester, and a glass fiber to produce a molding composition. International Patent No. WO 95/26432 to Wagner et al. disclose the preparation of an abrasion resistant polyester blend composed of a thermoplastic polyester, a thermoplastic polyurethane, and optionally, nonpolymeric additives that exhibits improved processing safety. Canadian Patent No. 1,111,984 (hereafter CA '111) discloses a poly(butylene terephthalate)/polyurethane molding composition. Tseng et al., Sperk et al., Wagner et al., and CA '111 teach one of ordinary skill in the art to use a higher amounts of polyurethane in order to increase or enhance the mechanical properties of the blend. These references are not concerned with increasing the molecular weight of a polymer.

In light of the above it would be very desirable to have a method for increasing the molecular weight polymer that does not require the use of toxic or hazardous materials that can react with the polymer.
SUMMARY OF THE INVENTION

In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a method for making a polymer composition, comprising melt mixing a composition comprising a polymer having at least one isocyanate reactive group and a thermoplastic polyurethane, wherein the thermoplastic polyurethane is less than 5% by weight of the composition, wherein the polymer is not a polyamide.

The invention further relates to a polymer composition produced by the present invention.

The invention further relates to an article comprising the polymer composition produced by the present invention.

Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention may be understood more readily by reference to the following detailed description of preferred embodiments of the invention and the Examples included therein.
Before the present methods are disclosed and described, it is to be understood that this invention is not limited to specific synthetic methods or to particular formulations, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

The singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise.

"Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

The term "isocyanate reactive group" is any group that can react with an isocyanate moiety as shown in Equation I. Examples of isocyanate reactive groups include, but are not limited to a hydroxyl group, an amino group, a carbonate group, or a carboxyl group.

![Equation I](image)

A "carbonyl compound" is any carboxylic acid, ester, acid halide, or anhydride.

The term "dicarbonyl compound" is any dicarboxylic acid, diester, diacid halide, or dianhydride.
The term "glycol" is any compound that possesses at least two hydroxyl groups. Additionally, a glycol can be any precursor compound that is readily converted to a compound possessing two hydroxyl groups. An example of such a compound is hydroquinone (I), which can be converted to biphenol (II) using techniques known in the art.

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In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a method for making a polymer composition, comprising melt mixing a composition comprising a polymer having at least one isocyanate reactive group and a thermoplastic polyurethane, wherein the thermoplastic polyurethane is less than 5% by weight of the composition, wherein the polymer is not a polyamide.

The polymer used in the present invention has at least one isocyanate reactive group. The role of the isocyanate reactive group with respect to producing a polymer composition will be discussed below. In one embodiment, the polymer comprises a polyester, a liquid crystalline polymer, a polycarbonate, or a combination thereof.

In one embodiment, the polymer comprises a polyester. Polyesters useful in the present invention comprise the reaction product between (1) at least one first glycol
component comprising an aliphatic glycol, a cycloaliphatic glycol, an aromatic glycol,
or a combination thereof, and (2) at least one first dicarbonyl component comprising an
aliphatic dicarbonyl compound, a cycloaliphatic dicarbonyl compound, an aromatic
dicarbonyl compound, or a combination thereof.

In one embodiment, the first glycol component comprises a first glycol
compound comprising ethylene glycol; propylene glycol; 1,3-propanediol; 1,4-
butanediol; 1,6-hexanediol; 1,8-octanediol; 1,10-decanediol; 2,2-dimethyl-1,3-
propanediol; 1,4-cyclohexanediethanol; diethylene glycol; polyethylene glycol;
polypropylene glycol; polytetramethylene glycol, or a combination thereof. In one
embodiment, the first glycol compound comprises ethylene glycol; 1,3-propanediol;
1,4-butanediol, or 1,4-cyclohexanediethanol. In another embodiment, the first glycol
compound has from 2 to 10 carbon atoms. In another embodiment, the first glycol
component further comprises a second glycol compound, wherein the second glycol
compound comprises glycerol, trimethylolpropane, pentaerythritol, or a combination
thereof. In this embodiment, the second glycol component behaves as a branching
agent, which forms branches off the polymer backbone.

Examples of first dicarbonyl compounds that can react with the glycol
component to produce the polyester include, but are not limited to, terephthalic acid,
isophthalic acid, naphthalenedicarboxylic acid, cyclohexanedicarboxylic acid, or a
combination thereof. In one embodiment, the first dicarbonyl component comprises
terephthalic acid, cyclohexanedicarboxylic acid, or naphthalenedicarboxylic acid. Any
of the isomers of naphthalenedicarboxylic acid and cyclohexanedicarboxylic acid are
useful in the present invention. For example, the cis-, trans-, or cis/trans isomers of
cyclohexanedicarboxylic acid can be used. In one embodiment, the 2,6-isomer of
naphthalenedicarboxylic acid can be used.

In another embodiment, the polyester further comprises the reaction product of a
second dicarbonyl compound comprising a C_4 to C_{40} dicarbonyl compound. The
second dicarbonyl is a modifying dibasic acid. In one embodiment, the second dicarbonyl compound comprises succinic acid, glutaric acid, adipic acid, sebacic acid, dimer acid, or a combination thereof. Dimer acid comprises the dimerization product of unsaturated fatty acids, wherein the fatty acid has from 14 to 24 carbon atoms. In one embodiment, the first dicarbonyl component comprises at most 65 mole % of the second dicarbonyl compound, wherein the sum of the dicarbonyl compounds of the first dicarbonyl component equals 100 mole %.

In another embodiment, the first dicarbonyl component further comprises a third dicarbonyl compound, wherein the third dicarbonyl compound comprises trimellitic acid, trimellitic anhydride, pyromellitic anhydride, or a combination thereof. The third dicarbonyl compound can also behave as a branching agent as described above.

In one embodiment, the polyester has an inherent viscosity of from 0.2 to 1.5 dL/g, preferably from 0.3 to 1.2 dL/g as determined in 60/40 phenol/tetrachloroethane. Examples of polyesters useful in the present invention include, but are not limited to, poly(butylene terephthalate), poly(propylene terephthalate), poly(ethylene terephthalate), poly(ethylene naphthalate), poly(cyclohexanediethylene terephthalate), or a combination thereof. In one embodiment, the polyester is poly(ethylene-2,6-naphthalate) or poly(1,4-cyclohexanediethylene terephthalate). In a preferred embodiment, the polyester comprises poly(ethylene terephthalate) or poly(butylene terephthalate).

In another embodiment, the polymer can be a copolyester. Any combination of the glycols and dicarbonyl compounds described above can be used to prepare copolyesters useful in the present invention. In one embodiment, the copolyester is the condensation product between poly(ethylene terephthalate) and polyethylene glycol.

In another embodiment, the polymer comprises a liquid crystalline polymer. Any of the liquid crystalline polymers disclosed in U.S. Patent Nos. 4,169,933 and
4,161,470 are useful in the present invention, which are hereby incorporated by reference in their entirety.

In one embodiment, the liquid crystalline polymer comprises the reaction product between a second glycol component and a first carbonyl component. In one embodiment, the second glycol component comprises hydroquinone, biphenol, cyclohexanediethanol, or a combination thereof. In one embodiment, the first carbonyl component comprises $p$-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, $p$-acyloxybenzoic acid, 2,6-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid, or a combination thereof, preferably $p$-hydroxybenzoic acid, 2,6-naphthalenedicarboxylic acid, or terephthalic acid. In one embodiment, the liquid crystalline polyester has a molecular weight of from 5,000 to 25,000.

A variety of polycarbonates can be used in the present invention. In one embodiment, the polycarbonate comprises bisphenol A polycarbonate.

Any thermoplastic polyurethane known in the art is useful in the present invention. Examples of thermoplastic polyurethanes than can be used in the present invention are disclosed in U.S. Patent Nos. 4,822,827; 4,376,834, and 4,567,236, which are incorporated by reference in their entirety. The thermoplastic polyurethanes of the present invention can be both rigid and elastomeric.

In one embodiment, the thermoplastic polyurethane comprises the reaction product between a polyisocyanate and a diol component. Examples of polyisocyanates include, but are not limited to, a methylenebis(phenyl isocyanate), a cycloaliphatic diisocyanate, a cyclohexylene diisocyanate, or a combination thereof. In one embodiment, any of the 4,4'-isomer, the 2,4'-isomer, or combinations thereof of methylenebis(phenyl isocyanate) can be used. Examples of other methylenebis(phenyl isocyanates) include, but are not limited to, $m$- and $p$-phenylene diisocyanates; chlorophenylene diisocyanates; $\alpha$, $\alpha'$-xyylene diisocyanate: 2,4- and 2,6-toluene
diisocyanate and mixtures of these latter two isomers; toluidine diisocyanate, hexamethylene diisocyanate; 1,5-naphthalene diisocyanate, or isophorone diisocyanate.

In one embodiment, the methylenebis(cyclohexyl isocyanate) is the 4,4'-isomer, the 2,4'-isomer and mixtures thereof. Any of the geometric isomers including trans/trans, cis/trans, cis/cis and mixtures thereof can be used. Examples of cycloaliphatic diisocyanates include, but are not limited to, cyclohexylene diisocyanates (1,2-; 1,3-; or 1,4-), 1-methyl-2,5-cyclohexylene diisocyanate, 1-methyl-2,4-cyclohexylene diisocyanate, 1-methyl-2,6-cyclohexylene diisocyanate, 4,4'-isopropylidenebis(cyclohexyl isocyanate), or 4,4'-diisocyanatodicyclohexyl.

In another embodiment, the isocyanate is a modified form of methylenebis(phenyl isocyanate). These isocyanates have been reacted with an aliphatic glycol or a mixture of aliphatic glycols, such as described in U.S. Pat. Nos. 3,394,164; 3,644,457; 3,883,571; 4,031,026; 4,115,429; 4,118,411; and 4,299,347, which are hereby incorporated by reference in their entirety.

In one embodiment, the diol component comprises at least one cycloaliphatic diol and at least one diol extender. In one embodiment, the cycloaliphatic diol comprises 1,3-cyclobutanediol; 1,3-cyclopentanediol; 1,2-cyclohexanediol; 1,3-cyclohexanediol; 1,4-cyclohexanediol, 2-cyclohexene-1,4-diol; 2-methyl-1,4-cyclohexanediol; 2-ethyl-1,4-cyclohexanediol; 1,3-cycloheptanediol; 1,4-cycloheptanediol; 2-methyl-1,4-cycloheptanediol; 4-methyl-1,3-cycloheptanediol; 1,3-cyclooctanediol; 1,4-cyclooctanediol; 1,5-cyclooctanediol, 5-methyl-1,4-cyclooctanediol; 5-ethyl-1,4-cyclooctanediol; 5-propyl-1,4-cyclooctanediol; 5-butyl-1,4-cyclooctanediol; 5-hexyl-1,4-cyclooctanediol; 5-heptyl-1,4-cyclooctanediol; 5-octyl-1,4-cyclooctanediol; 4,4'-methylenebis(cyclohexanol); 4,4'-methylenebis(2-methylcyclohexanol); 4,4'-methylenebis(3-methylcyclohexanol); 3,3'-methylenebis(cyclohexanol); 4,4'-ethylenebis(cyclohexanol);
4,4'-propylenebis(cyclohexanol); 4,4'-butylenebis(cyclohexanol);
4,4'-isopropylidenebis(cyclohexanol); 4,4'-isobutylenebis(cyclohexanol);
4,4'-dihydroxydicyclohexyl; 4,4'-carbonylbis(cyclohexanol);
3,3'-carbonylbis(cyclohexanol); 4,4'-sulfonylbis(cyclohexanol),
5 4,4'-oxybis(cyclohexanol), or a combination thereof.

In one embodiment, the diol extender comprises ethylene glycol;
1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 1,2-propanediol;
1,3-butane-diol; 2,3-butanediol; 1,3-pentanediol; 1,2-hexanediol;
10 3-methylpentane-1,5-diol; 1,9-nonanediol; 2-methyloctane-1,8-diol;
1,4-cyclohexanedimethanol; hydroquinone bis(hydroxyethyl)ether; diethylene glycol;
di(propylene glycol; tri(propylene glycol; ethanolamine; N-methyl-diethanolamine;
N-ethylidioethanolamine, or a combination thereof.

In one embodiment, the diol component can be an ester diol formed by
15 esterifying an aliphatic dicarboxylic acid with an aliphatic diol listed above. Examples
of aliphatic dicarboxylic acids include, but are not limited to, adipic acid, azelaic, acid,
or glutaric acid. In one embodiment, from about 0.01 to about 0.8 mole of dicarboxylic
acid per mole of diol are reacted to produce the ester diol.

In one embodiment, the diol component is the reaction product between an
20 aliphatic diol or triol and a lactone. In one embodiment, 0.01 to 2 moles of lactone per
mole of diol or triol are reacted with one another to produce the diol component.
Examples of aliphatic diols in this embodiment include, but are not limited to,
1,4-cyclohexanedimethanol, neopentyl glycol, hexane-1,6-diol, ethylene glycol,
25 butane-1,4-diol, or trimethyleneolpropane. Examples of aliphatic triols include, but are not
limited to, glycerol or trimethyleneolpropane. In one embodiment, the lactone is epsilon-
caprolactone.

In one embodiment, the cycloaliphatic diol is from 10 to 90% by weight of the
dil component and the dil extender is from 10 to 90% by weight of the dil
component, wherein the sum of the weight percentages of the cycloaliphatic dil and
dil extender is equal to 100%.

5 In another embodiment, a polyol is used to prepare the thermoplastic
polyurethane. Examples of polyols include, but are not limited to, a polyether polyol,
a polyester polyol, a hydroxy-terminated polycarbonate, a hydroxy-terminated
polybutadiene, a hydroxy-terminated polybutadiene-acrylonitrile copolymer, a
hydroxy-terminated copolymer of a dialkyl siloxane and alkylene oxide, or a
combination thereof. In one embodiment, the molecular weight of the polyol is from
about 1,250 to about 10,000, preferably, from about 2,000 to about 8,000.

Examples of polyether polyols include, but are not limited to, polyoxyethylene
glycol or polyoxypropylene glycol. In one embodiment, polyoxyethylene glycol or
polyoxypropylene glycol can be capped with 1) ethylene oxide residues; 2) random and
block copolymers of ethylene oxide and propylene oxide; 3) propoxylated tri- and
tetrahydric alcohols such as glycerine, trimethylolpropane, or pentaerythritol; 4)
polytetramethylene glycol, or 5) random and block copolymers of tetrahydrofuran and
ethylene oxide and/or propylene oxide. In one embodiment, the polyether polyol is a
random and block copolymer of ethylene and propylene oxide or polytetramethylene
glycol. Other examples of polyether polyols useful in the present invention include, but
are not limited to vinyl reinforced polyether polyols, such as the polymerization product
between styrene and/or acrylonitrile and the polyether polyol.

25 In one embodiment, a polyether ester can be prepared by reacting a polyether
polyol described above with a di- or trifunctional aliphatic or aromatic carboxylic acid.
Examples of useful carboxylic acids include, but are not limited to, adipic acid, azelaic
acid, glutaric acid, isophthalic acid, terephthalic acid, or trimellitic acid. In one
embodiment, the polyester polyol is the polymerization product between

epsilon-caprolactone and ethylene glycol or ethanolamine. In one embodiment, the
polyester polyol is prepared by the esterification of a polycarboxylic acid such as phththalic acid, terephthalic acid, succinic acid, glutaric acid, adipic acid, or azelaic acid and with a polyhydric alcohol such as ethylene glycol, butanediol, glycerol, trimethylolpropane, 1,2,6-hexanetriol, or cyclohexanemethanol and the like. In one embodiment, the polyester polyol is prepared by esterifying a dimeric or trimeric fatty acid, optionally mixed with a monomeric fatty acid such as oleic acid, with a long chain aliphatic diol such as hexane-1,6-diol.

In one embodiment, a polyether diamine useful in the present invention is JEFFAMINE®, which is manufactured by Jefferson Chemical Company.

In one embodiment, polycarbonates used to make the thermoplastic polyurethanes of the present invention containing hydroxyl groups useful in the present invention are prepared by reacting a diol, such as propane-1,3-diol, butane-1,4-diol, hexan-1,6-diol, diethylene glycol, triethylene glycol, or dipropylene glycol, with a diarylcarbonate (e.g. diphenylcarbonate) or with phosgene.

In one embodiment, silicon-containing polyethers useful in the present invention are copolymers of alkylene oxides with dialkylsiloxanes such as dimethylsiloxane. The silicon-containing polyethers disclosed in U.S. Pat. No. 4,057,595, which is hereby incorporated by reference in its entirety, can be used in the present invention.

In one embodiment, hydroxy-terminated poly-butadiene copolymers sold under the tradename POLY BD® Liquid Resins manufactured by Arco Chemical Company are useful in the present invention. In one embodiment, hydroxy- and amine-terminated butadiene/acrylonitrile copolymers sold under the tradename HYCAR® hydroxyl-terminated (HT) Liquid Polymers and amine-terminated (AT) Liquid Polymers, respectively, can be used in the present invention.
In one embodiment, the thermoplastic polyurethane is ISOPLAST®, which is manufactured by the Dow Chemical Company. There are a number of different thermoplastic polyurethanes sold under the tradename ISOPLAST®; however, these thermoplastic polyurethanes are typically the reaction product between methylenedioxy(phenyl isocyanate) and a number of different glycols. In one embodiment, the thermoplastic polyurethane is ISOPLAST® 301, which is the reaction product between methylenedioxy(phenyl isocyanate), 1,6-hexanediol, cyclohexanedimethanol, and polytetramethylene glycol.

In one embodiment, the thermoplastic polyurethane is from 1 to 4%, preferably from 1 to 3%, more preferably from 1 to 2%, or even more preferably from 1 to 1.5% by weight of the mixture, wherein the sum of the weight percentages of the thermoplastic polyurethane and the polymer is equal to 100%.

One advantage of the present invention is that only a small amount of thermoplastic polyurethane is required to increase the molecular weight of the polymer. Moreover, by using higher amounts of thermoplastic polyurethane, which is disclosed in the prior art, the viscosity of the resultant composite also increases. The higher the viscosity, the more difficult it is to extrude the composite. The present invention avoids these processing problems by using only a small amount of thermoplastic polyurethane.

In one embodiment, the polymer is poly(butylene terephthalate) and the thermoplastic polyurethane is ISOPLAST® 301.

Other additives known in the art can be added to the polymer composition. Examples of additives include, but are not limited to, a colorant, a filler, a processing aid, a plasticizer, a nucleating compound, a stabilizer, an antioxidant, a mold release agent, a flame retardant, a reinforcing agent, an epoxy compound, or a combination thereof. In one embodiment, the reinforcing agent comprises glass fiber, carbon fiber, calcium carbonate, talc, iron oxide, mica, montmorillonite, clay, kaolin, wollastonite, or
a combination thereof. In one embodiment, the additive can be melt mixed with the polymer and the thermoplastic polyurethane.

The polymer of the present invention and the thermoplastic polyurethane can be melt mixed using a number of techniques known in the art. In one embodiment, melt mixing can be performed by a Brabender Plastograph, Haake plastograph melt mixer (Rheocord 90), a single screw extruder, or a twin screw extruder (such as Werner Pfleiderer equipment). The temperature and time required to melt mix the polymer and thermoplastic polyurethane depend upon the polymer and thermoplastic polyurethane selected; however, one of ordinary skill in the art can deduce these parameters. In one embodiment, melt mixing can be reactive extrusion. A number of prior art techniques extrude two or more components merely to blend the components. This is not the case with reactive extrusion, which involves chemically reacting the components in order to produce a new compound. This is one reason why low amounts of thermoplastic polyurethane are required in the present invention when compared to prior art methods. The present invention is not concerned with the formation of a simple blend.

The invention further relates to the polymer compositions produced by the present invention.

Not wishing to be bound by theory, it is believed that during melt mixing, the thermoplastic polyurethane depolymerizes to produce an isocyanate intermediate in situ. The polymer, which has at least one isocyanate reactive group, reacts with the isocyanate intermediate. This ultimately results in the chain extension of the polymer, which increases the molecular weight of the polymer. Additionally, the process of the present invention does not use toxic and hazardous isocyanates, which are disclosed in the art as chain extenders, to increase the molecular weight of the polymer.

In one embodiment, if two or more polymers are melt mixed with the
thermoplastic polyurethane, then a copolymer is formed. In this embodiment, the copolymer composition can be a block and/or graft copolymer. The formation of the block and/or graft copolymers depends upon the location of the isocyanate reactive group on the polymer.

Any of the polymer composites of the present invention can be melt processed and extruded as pellets or chips. The polymer composites can also be molded or shaped to produce a desired article by using extrusion, pultrusion, injection molding, or compression molding techniques.

EXAMPLES

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the methods and compositions of matter claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at room temperature and pressure is at or near atmospheric.

All of the following examples were prepared using poly(butylene terephthalate) (PBT) having an initial molecular weight of 15,000 as determined by gel permeation chromatography against poly(ethylene terephthalate) standards. The thermoplastic polyurethane utilized in these examples was ISOPLAST® 301, which is manufactured by Dow Chemical. Melt processing was done by mixing on a twin screw extruder with a set point of 240 °C. A feed rate of 50 lbs/hr was utilized providing a residence time of 90 seconds. The examples were extruded into a cold water bath and pelletized. All compositions are reported on a weight % basis. All formulations contain 2.25 wt % “additives” which consist of antioxidants, stabilizers and processing aids. Molecular
weight was obtained by gel permeation chromatography (GPC).

**Examples 1-3**

Example 1 is a comparative example that does not contain a thermoplastic polyurethane additive of this invention. In Example 1, the molecular weight of poly(butylene terephthalate) decreased in the absence of thermoplastic polyurethane (from 15,000 to 14,500). Examples 2 and 3 are representative examples of this invention containing 1.5 and 3 wt% of the thermoplastic polyurethane respectively.

Examples 2 and 3 are of higher molecular weight than the control, which indicates that chain extension occurred during the melt processing of the thermoplastic polyurethane and PBT. The data in Table 1 demonstrate that the addition of a small amount of thermoplastic polyurethane increases the molecular weight of the polymer.
Table 1: Molecular Weight of Thermoplastic Polyurethane Chain Extended Polyesters

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Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.
What is claimed is:

1. A method for making a polymer composition, comprising melt mixing a composition comprising a polymer having at least one isocyanate reactive group and a thermoplastic polyurethane, wherein the thermoplastic polyurethane is less than 5% by weight of the composition, wherein the polymer is not a polyamide.

2. The method of Claim 1, wherein the polymer comprises a polyester, a liquid crystalline polymer, a polycarbonate, or a combination thereof.

3. The method of Claim 1, wherein the polymer comprises a polyester.

4. The method of Claim 3, wherein the polyester comprises the reaction product between (1) a first glycol component comprising an aliphatic glycol, a cycloaliphatic glycol, an aromatic glycol, or a combination thereof, and (2) a first dicarbonyl component comprising an aliphatic dicarbonyl compound, a cycloaliphatic dicarbonyl compound, an aromatic dicarbonyl compound, or a combination thereof.

5. The method of Claim 4, wherein the first glycol component comprises a first glycol compound comprising ethylene glycol; propylene glycol; 1,3-propanediol; 1,4-butanediol; 1,6-hexanediol; 1,8-octanediol; 1,10-decanediol; 2,2-dimethyl-1,3-propanediol; 1,4-cyclohexanedimethanol; diethylene glycol; polyethylene glycol; polypropylene glycol; polytetramethylene glycol, or a combination thereof.

6. The composite of Claim 4, wherein the first glycol compound comprises ethylene glycol; 1,3-propanediol; 1,4-butanediol, or 1,4-cyclohexanedimethanol.
7. The method of Claim 4, wherein the first glycol component further comprises a second glycol compound, wherein the second glycol compound comprises glycerol, trimethylpropane, pentaerythritol, or a combination thereof.

8. The method of Claim 4, wherein the first glycol component comprises at least 50 mole % ethylene glycol; 1,3-propanediol; 1,4-butanediol; 1,4-cyclohexanediol; or a combination thereof, wherein the sum of the glycol compounds of the first glycol component equals 100 mole %.

9. The method of Claim 4, wherein the first dicarbonyl component comprises a first dicarbonyl compound comprising terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, cyclohexanedicarboxylic acid, or a combination thereof.

10. The method of Claim 4, wherein the first dicarbonyl component comprises at least 35 mole % of the first dicarbonyl compound, wherein the sum of the dicarbonyl compounds of the first dicarbonyl component equals 100 mole %.

11. The composite of Claim 4, wherein the polyester further comprises the reaction product of a second dicarbonyl compound comprising a C₄ to C₄₀ dicarbonyl compound.

12. The method of Claim 12, wherein the second dicarbonyl compound comprises succinic acid, glutaric acid, adipic acid, sebacic acid, dimer acid, or a combination thereof.

13. The method of Claim 11, wherein the first dicarbonyl component comprises at most 65 mole % of the second dicarbonyl compound, wherein the sum of the dicarbonyl compounds of the first dicarbonyl component equals 100 mole %.
14. The method of Claim 4, wherein the first dicarbonyl component further comprises a third dicarbonyl compound, wherein the third dicarbonyl compound comprises trimellitic acid, trimellitic anhydride, pyromellitic dianhydride, or a combination thereof.

15. The method of Claim 2, wherein the polyester has an inherent viscosity of from 0.2 to 1.5 dL/g as determined in 60/40 phenol/tetrachloroethane.

16. The method of Claim 2, wherein the polyester comprises poly(butylene terephthalate), poly(propylene terephthalate), poly(ethylene terephthalate), poly(ethylene naphthalate), poly(cyclohexanediethylene terephthalate), or a combination thereof.

17. The method of Claim 1, wherein the polymer comprises a liquid crystalline polymer.

18. The method of Claim 17, wherein the liquid crystalline polyester comprises the reaction product between a second glycol component and a carbonyl component.

19. The method of Claim 18, wherein the second glycol component comprises hydroquinone, biphenol, cyclohexanediethanol, or a combination thereof.

20. The method of Claim 18, wherein the carbonyl component comprises p-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, p-acyloxybenzoic acid, 2,6-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid, or a combination thereof.

21. The method of Claim 17, wherein the liquid crystalline polyester has a molecular weight of from 5,000 to 25,000.
22. The method of Claim 1, wherein the thermoplastic polyurethane comprises the reaction product between a polyisocyanate and a diol component.

23. The method of Claim 22, wherein the polyisocyanate comprises a methylenebis(phenyl diisocyanate), a cycloaliphatic diisocyanate, a cyclohexylene diisocyanate, or a combination thereof.

24. The method of Claim 22, wherein the diol component comprises at least one cycloaliphatic diol and at least one diol extender.

25. The method of Claim 24, wherein the cycloaliphatic diol comprises
   1,3-cyclobutanediol; 1,3-cyclopentanediol; 1,2-cyclohexanediol;
   1,3-cyclohexanediol; 1,4-cyclohexanediol, 2-cyclohexene-1,4-diol;
   2-methyl-1,4-cyclohexanediol; 2-ethyl-1,4-cyclohexanediol;
   1,3-cycloheptanediol; 1,4-cycloheptanediol; 2-methyl-1,4-cycloheptanediol;
   4-methyl-1,3-cycloheptanediol; 1,3-cyclooctanediol; 1,4-cyclooctanediol;
   1,5-cyclooctanediol, 5-methyl-1,4-cyclooctanediol; 5-ethyl-1,4-cyclooctanediol;
   5-propyl-1,4-cyclooctanediol; 5-butyl-1,4-cyclooctanediol;
   5-hexyl-1,4-cyclooctanediol; 5-heptyl-1,4-cyclooctanediol;
   5-octyl-1,4-cyclooctanediol; 4,4'-methylenebis(cyclohexanol);
   4,4'-methylenebis(2-methylcyclohexanol);
   4,4'-methylenebis(3-methylcyclohexanol); 3,3'-methylenebis(cyclohexanol);
   4,4'-ethylenebis(cyclohexanol); 4,4'-propylenebis(cyclohexanol);
   4,4'-butylenebis(cyclohexanol); 4,4'-isopropylidenebis(cyclohexanol);
   4,4'-isobutylenebis(cyclohexanol); 4,4'-dihydroxydicyclohexyl;
   4,4'-carbonylbis(cyclohexanol); 3,3'-carbonylbis(cyclohexanol);
   4,4'-sulfonylbis(cyclohexanol), 4,4'-oxybis(cyclohexanol), or a combination thereof.
26. The method of Claim 24, wherein the diol extender comprises ethylene glycol; 1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 1,2-propanediol; 1,3-butanediol; 2,3-butanediol; 1,3-pentanediol; 1,2-hexanediol; 3-methylpentane-1,5-diol; 1,9-nonanediol; 2-methyloctane-1,8-diol; 1,4-cyclohexanedimethanol; hydroquinone bis(hydroxyethyl)ether; diethylene glycol; dipropylene glycol; tripropylene glycol; ethanolamine; N-methyl-diethanolamine; N-ethyl-diethanolamine, or a combination thereof.

27. The method of Claim 24, wherein the cycloaliphatic diol is from 10 to 90 % by weight of the diol component and the diol extender is from 10 to 90 % by weight of the diol component, wherein the sum of the cycloaliphatic diol and diol extender is equal to 100 %.

28. The method of Claim 22, further comprising a polyol.

29. The method of Claim 28, wherein the polyol comprises a polyether polyol, a polyester polyol, a hydroxy-terminated polycarbonate, a hydroxy-terminated polybutadiene, a hydroxy-terminated polybutadiene-acrylonitrile copolymer, a hydroxy-terminated copolymer of a dialkyl siloxane and alkylene oxide, or a combination thereof.

30. The composite of Claim 1, wherein the thermoplastic polyurethane comprises the reaction product between a methylenebis(phenyl isocyanate) and a diol component.

31. The composite of Claim 1, wherein the thermoplastic polyurethane comprises the reaction product between methylenebis(phenyl isocyanate), 1,6-hexanediol, cyclohexanedimethanol, and polytetramethylene glycol.
32. The method of Claim 1, wherein the thermoplastic polyurethane is from 1 to 4% by weight of the composition.

33. The method of Claim 1, wherein the thermoplastic polyurethane is from 1 to 3% by weight of the composition.

34. The method of Claim 1, wherein the thermoplastic polyurethane is from 1 to 2% by weight of the composition.

35. The method of Claim 1, wherein the thermoplastic polyurethane is from 1 to 1.5% by weight of the composition.

36. The method of Claim 1, further comprising an additive comprising a colorant, a filler, a processing aid, a plasticizer, a nucleating compound, a stabilizer, an antioxidant, a mold release agent, a flame retardant, a reinforcing agent, an epoxy compound, or a combination thereof.

37. The method of Claim 36, wherein the reinforcing agent comprises glass fiber, carbon fiber, calcium carbonate, talc, iron oxide, mica, montmorillonite, clay, kaolin, wollastonite, or a combination thereof.

38. The method of Claim 1, wherein the melt mixing step is performed by a Brabender Plastograph, Haake plastograph melt mixer, a single screw extruder, or a twin screw extruder.


40. An article comprising the polymer composition of Claim 39.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 CO8L67/02 CO8L69/00 CO8L101/00 CO8G81/00 CO8G85/00 CO8G18/10

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)

IPC 6 CO8L CO8G

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**X** Further documents are listed in the continuation of box C. **X** Patent family members are listed in annex.

* Special categories of cited documents:

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**E** earlier document but published on or after the international filing date

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**O** document referring to an oral disclosure, use, exhibition or other means

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**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.

**S** document member of the same patent family

**Date of the actual completion of the international search**

22 December 1998

**Date of mailing of the international search report**

04/01/1999

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-5040, Tx. 31 651 epc nl, Fax: (+31-70) 340-3016

Authorized officer

Krische, D
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