

POLYURETHANES CONTAINING REINFORCING POLYMERS

This invention relates to polyurethane polymers.

5 Polyurethane and polyurea polymers are widely used in a large number of applications. Elastomeric polyurethanes are widely used in a variety of applications such as dynamic elastomers (for example, wheels, belts, gaskets), automobile fascia, and many others. Flexible polyurethane foams are used in many seating and cushioning applications such as home and office furniture,
10 bedding and vehicle seats. These polyurethanes are almost always made in the reaction of an organic polyisocyanate with a high equivalent weight polyol or polyamine and a chain extender or crosslinker. The high equivalent weight component is most commonly a polyether having an equivalent weight per isocyanate-reactive group in the range of about 800 to about 3000 daltons.

15 In addition, rigid polyurethane foams are used in a variety of insulation applications, notably appliance insulation, where they are foamed in-place to create an insulating layer of foam within the walls of the appliance cabinet. Laminated rigid foams are also commercially significant.

20 Good quality polyurethanes can be made using relatively inexpensive raw materials that are widely available. However, there are instances where improved physical properties are desirable. One example of this is load bearing in flexible polyurethane foams. Load-bearing, which is usually expressed in terms of indentation force deflection (IFD) or compression force deflection (CFD), can be
25 described as the ability of a foam to support an applied load, such as that of a person sitting on a foam cushion in a chair or automobile seat. Providing improved load-bearing offers several potential advantages. For example, better load-bearing can permit one to obtain equivalent product performance at lower
30 foam densities, thus reducing raw material costs and making the foam less expensive. Similarly, a higher load-bearing foam can be used in thinner sections, again resulting in reduced foam costs.

There are several known technologies for improving foam load-bearing. For example, an inorganic filler can be added into the formulation. However, this causes the foam's elongation and tear strength to decrease substantially while increasing density. The equivalent weight of the polyol component can be
5 reduced, but this causes a loss of elongation and raises the T_g (glass transition temperature) of the polyurethane. Another approach is to add crosslinkers or to use polymer polyol products of various types, but these approaches result in a loss of elongation and in making foams having poor compression sets.

10 Thus, any method of improving load-bearing ideally provides the desired load-bearing improvement while maintaining other important properties, such as tensile strength, tear strength, elongation, density, compression set and air flow within acceptable limits. Moreover, it would be highly preferable that a technology for improving load-bearing can be implemented using ordinary,
15 commonly available foaming equipment and under other processing conditions similar to those currently used in making flexible polyurethane foams.

Rigid polyurethane foams having improved properties are also desirable.

In one aspect, this invention is a polyurethane and/or polyurea foam made
20 in the reaction of:

- (a) at least one organic polyisocyanate; and
- (b) an isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per
25 molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one high-melting polymer that has a melting point of from about 45 to about 200°C, a T_g/T_m , calculated from °K, of less than 0.75 and a calculated interaction parameter with other polyurethane components χ at 300°K of more than 1.6
30 and at 400°K of less than 2.0.

In a second aspect, this invention is a process comprising
(I) forming a reaction mixture by mixing

- (a) a polyisocyanate and
- (b) a isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one high-melting polymer that has a melting point of from about 45 to about 200°C, a T_g/T_m of less than 0.75 and a calculated χ at 300°K of more than 1.6 and at 400°K of less than 2.0.
- (II) bringing the reaction mixture to a temperature above the melting temperature of component (b) (ii) for a time sufficient to melt component (b)(ii), and optionally (b)(ii) reacting with the polyisocyanate,
- (III) curing the reaction mixture to produce a polyurethane and/or polyurea, and
- (IV) cooling the polyurethane and/or polyurea to below the melting temperature T_m of component (b)(ii).

In a third aspect, this invention is a dispersion of a continuous phase of at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and a disperse phase comprising particles of at least one high-melting polymer that has a melting point of from about 45 to about 200°C, a T_g/T_m of less than 0.75 and a calculated χ at 300°K of more than 1.6 and at 400°K of less than 2.0.

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In a fourth aspect, this invention is a polyurethane and/or polyurea polymer made in the reaction of:

- (a) at least one organic polyisocyanate; and
- (b) an isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and

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- (ii) at least amorphous polymer having a T_g of greater than about 45°C and a T_g/T_m of greater than 0.65.

In a fifth aspect, this invention is a process comprising

- 5 (I) forming a reaction mixture by mixing
 - (a) a polyisocyanate and
 - (b) a isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one amorphous polymer having a T_g of greater than about 45°C and up to about 200°C and a T_g/T_m of greater than 0.65,
- 15 (II) bringing the reaction mixture to a temperature above the T_g of component (b)(ii) for a time sufficient for component (b)(ii) to undergo a phase transition to a rubbery state and become anisotropically dispersed in the reaction mixture,
- (III) curing the reaction mixture to produce a polyurethane and/or polyurea, and
- 20 (IV) cooling the polyurethane and/or polyurea to below the T_g of component (b)(ii).

In a sixth aspect, this invention is a polyurethane and/or polyurea polymer having a having a phase comprising the reaction product of an isocyanate-reactive material that is liquid at 25°C, has an isocyanate functionality of at least 2 and an equivalent weight of 500 to 8,000, and a polyisocyanate and a co-continuous, anisotropic phase of at least one amorphous polymer having a T_g of greater than about 45°C up to about 200°C and a T_g/T_m of greater than 0.65, or reaction product thereof which an organic polyisocyanate.

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In an seventh aspect, this invention is a dispersion of a continuous phase of at least one isocyanate-reactive material that is liquid at 25°C, has an average of

at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and a disperse phase comprising particles of at least one amorphous polymer having a T_g of greater than about 45°C up to about 200°C and a T_g/T_m of greater than 0.65.

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In an eight aspect, the invention the calculated value of χ at 300°K and at 400°K for the high-melting polymer/organic polyisocyanate pair for the above aspects of the invention is between 1.6 and 4.0 and between 0.74 and 2.0 respectively.

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In this invention, polyurethane and/or polyurea polymers are made from a formulation containing a certain polymeric additives. These additives can be either a high-melting crystalline polymer (referred to herein by the shorthand "high-melting polymer"), or a high T_g amorphous polymer having certain characteristics as discussed more fully below. Collectively, these polymers are referred to herein as "reinforcing" polymers.

As used in herein, a "crystalline" or "high melting" polymer is one which (a) exhibits a crystalline fraction of at least 0.3 (parts by weight per part by weight polymer) as a bulk polymer at room temperature or (b) exhibits a ratio of T_g/T_m of less than about 0.75, when the T_g and T_m are expressed in an absolute temperature scale, or both (a) and (b), and (c) does not assume an amorphous form in the polyurethane and/or polyurea polymer due to processing conditions that quench the polymer before crystallization can occur. It is recognized that substantially all "crystalline" polymers are at best partially crystalline, and contain crystalline as well as non-crystalline phases.

The term "amorphous" polymer, is used to denote a polymer which (a) exhibits a crystalline fraction of less than 0.3 as a bulk polymer at room temperature, (b) exhibits a ratio of T_g/T_m of greater than about 0.65, when the T_g and T_m are expressed in an absolute temperature scale, or (c) is a normally crystalline material that assumes an amorphous form in the polyurethane and/or polyurea polymer due to processing conditions that quench the polymer before

crystallization can occur. Preferably the T_g/T_m of the amorphous polymer is greater than 0.70, and more preferably above 0.75.

High-melting polymers suitable for use herein have a crystalline melting
5 temperature of from about 45° C, preferably from about 70°C, more preferably
from about 80°C, up to the maximum processing of the polyurethane and/or
polyurea-forming formulation. The melting temperature is typically no greater
than about 200°C, preferably no greater than about 180°C, even more preferably
no greater than about 160°C and most preferably no greater than about 150°C.

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In addition, the high-melting polymer is relatively miscible with a reacting
mixture of the isocyanate-reactive material and an organic polyisocyanate, at
temperatures above the melting temperature of the high-melting polymer and
within the range of processing temperatures used in curing the polyurethane
15 and/or polyurea-forming formulation. "Relative miscibility" involves the
calculation of interaction parameters (χ values) for the high-melting polymer and
the main other components used in the polyurethane and/or polyurea-forming
formulation. χ values are unitless values which are conveniently calculated using
Cerius², version 3 or higher software products of Molecular Simulations, Inc.
20 Details on the calculation procedures are described in K. Choi and W.H. Jo,
Macromolecules 30:1509-1514 (1997), the disclosure of which is incorporated
herein by reference. Decreasing χ values predict improving relative miscibility.
Good relative miscibility is predicted when the calculated χ value is 1.0 or below.
Preferably, χ values for the high-melting polymer and organic polyisocyanate
25 and/or the isocyanate-reactive component used in the highest concentration are
developed. More preferably, χ values are developed for both the high-melting
polymer and organic polyisocyanate and the isocyanate-reactive component used
in the highest concentration. In addition, it is preferred to develop χ values over
the temperature range that will be encountered during the processing of the
30 formulation, that is, from about 300K to about 473K, more preferably from about
350K to about 453K. The calculated χ value at 300°K is preferably higher than
1.6 to get phase separation upon cooling and at 400°K is preferably below 2.0 for

at least one of the high-melting polymer/main isocyanate-reactive component pair or the high-melting polymer/polyisocyanate pair in order to facilitate the reaction between all components throughout the temperature range. More preferably, the calculated χ value at 400°K is less than 2.0 and greater than 0.74 for at least one
5 of the high-melting polymer/main isocyanate-reactive component pair or the high-melting polymer/polyisocyanate pair. Even more preferred is a calculated χ value at 400°K of less than 1.75 for at least one of the high-melting polymer/main isocyanate-reactive component pair or the high-melting polymer/polyisocyanate pair. In a preferred embodiment, the calculated χ value at 400°K is between 0.75
10 and 1.5 for the high-melting polymer/polyisocyanate pair. An example of the polyisocyanate component is MDI, TDI or a blend thereof.

The χ values given above are calculated to normalize to a 3,000 molecular weight of the high-melting or amorphous polymer. The same miscibility
15 thresholds can also be used to identify other preferred embodiments of this invention at different molecular weights by using the value of $(\chi \text{ MW})/3000$ rather in place of the value χ itself as the basis of comparison if the molecular weights differs from 3,000. The values also use the assumption that the high-melting of amorphous polymer constitutes a volume fraction of about 0.1 of the total
20 formulation and the polyurethane or polyurethane/urea hard segment weight fraction is about 0.3.

High-melting polymers of particular interest are characterized by having a low ratio of T_g/T_m when both values are expressed in an absolute temperature
25 scale such as °K. The T_g/T_m ratio is generally less than about 0.75, and preferably less than about 0.70, more preferably less than about 0.65 and most preferably less than about 0.60. The T_g/T_m ratio may be as low as 0.35 or less, although it is believed that little additional benefit is seen when the T_g/T_m ratio drops below this value. Preferably, the T_g/T_m ratio is 0.35 or greater, more preferably about 0.40 or
30 greater, even more preferably about 0.45 or greater. The ratio of T_g/T_m for a polymer has been related to the expected maximum crystalline fraction of a polymer when crystallized under isothermal quiescent conditions. See Bicerano,

J., "Crystallization of Polypropylene and Poly(Ethylene Terephthalate)", J. Macromol. Sci.-Reviews, C38, pp. 391-479 (1998). Further, it is believed that polymers which form higher maximum crystalline fractions under isothermal quiescent conditions tend to exhibit a greater ability to form a crystalline phase in the polyurethane and/or polyurea polymer. Polymers having a T_g/T_m ratio within the aforementioned ranges tend to have maximum crystalline fractions, when crystallized under isothermal quiescent conditions, in the range of about 0.5-1.0, preferably about 0.6 to about 0.8 part by weight per part by weight of the polymer.

The crystalline phase formed by the high-melting polymer may be isotropic (that is, low aspect ratio) or preferably anisotropic (that is, aspect ratio of 2 or more, preferably at least 3, more preferably at least 5). "Aspect ratio" is used herein to mean the longest dimension of a crystallite divided by the largest cross-sectional dimension taken perpendicularly to the longest dimension.

T_g values are conveniently measured by differential scanning calorimetry. Further, it has been found that the benefits of the high-melting polymer are best seen when it has a number average molecular weight of at least about 1000, preferably about 1000-20,000, more preferably about 1,500 to about 15,000, especially about 2,000 to about 12,000, and most preferably about 2,000 to about 6,000.

Among the suitable high-melting polymers are:

(A) Aliphatic polyanhydrides of the general form $[-C(O)-(CHR)_x-C(O)-O-]_j$, wherein R is hydrogen or unsubstituted or inertly substituted hydrocarbyl, especially methyl or ethyl and most preferably hydrogen, x is a number of about 8 or more, preferably from about 10 to about 14, and j is a number that provides a molecular weight as described above. Based on interaction parameter calculations, these polymers are best used in a weight fraction of up to about 0.1 part per part by weight of the isocyanate-reactive component, and at a weight fraction of about 0.8 and above, in a formulation using MDI or TDI as the polyisocyanate, and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(B) Aliphatic polyacetals including those of the general form $[-(\text{CHR})_y\text{-O-CHR-O-}]_j$, wherein y is a number of about 8 or more, preferably from about 12-20, and R and j are as before. Based on interaction parameter calculations, these polymers are best used in a weight fraction of up to about 0.2 part per part by weight of the isocyanate-reactive component in a formulation using MDI or TDI as the polyisocyanate, and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(C) Aliphatic polyesters including those of the general form $[-(\text{CHR})_x\text{-C(O)O-}]_j$, wherein x , R and j are as before. Based on interaction parameter calculations, these polymers are best used in a weight fraction of up to about 0.2 part per part by weight of the isocyanate-reactive component in a formulation using MDI or TDI as the polyisocyanate and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(D) Aliphatic polyethers including those of the general form $[-(\text{CHR})_x\text{-O-}]_j$, wherein x , R and J are as before. Based on interaction parameter calculations, these polymers are best used in a weight fraction of about 0.5 part or above per part by weight of the isocyanate-reactive component in a formulation using MDI or TDI as the polyisocyanate and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(E) Polyhydroxyalkanoates, including those of the general form $[-(\text{CHR}^2)_o\text{-C(O)O-}]_j$, wherein R^2 is hydrogen or $\text{C}_1\text{-C}_4$ alkyl, o is a number from zero to 3, and j is as before. Among the suitable polyhydroxyalkanoates are polylactic acid (L and/or D isomers), poly(3-hydroxyl butyrate) and poly(3-hydroxyvalerate). Based on interaction parameter calculations, these polymers are best used in a weight fraction of up to about 0.25 part per part by weight of the isocyanate-reactive component in a formulation using MDI or TDI as the polyisocyanate and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(F) Aliphatic polyamides of the general form $[-(\text{CHR})_x\text{-C(O)-NH-}]_j$, wherein x , R and j are as before. Based on interaction parameter calculations, these polymers are best used in a weight fraction of about 0.8 part or more per part by weight of the isocyanate-reactive component in a formulation using MDI or TDI as the polyisocyanate and a poly(propylene oxide) polymer as the main isocyanate-reactive material.

(G) Aromatic/aliphatic polyesters including those of the general form $[-O-\{(CHR)_m-O\}_n-(CHR)_m-OC(O)-Ph-C(O)-]_j$, where each m is independently a number of at least 2 to about 30, preferably about 6 to about 24, n is a number from zero to about 5, preferably 1, 2 or 3, Ph is an unsubstituted or substituted arylene group, and R and J are as before; and

(H) Other polymers of the general form $[-(CHR)_l-X]_j$, wherein l is a number of eight or more, preferably about 10 to about 20, X is a polar linking group and R and j are as before, are also suitable.

Preferably the high-melting polymer is selected from (B), (C), (D), or a combination of (B), (C) and (D). Although not critical to the invention, it is preferred that the high-melting polymer contains isocyanate-reactive groups, so that it is capable of reacting with polyisocyanate groups to become incorporated into the polymer network through covalent bonds (that is, urethane and/or urea linkages). Any isocyanate-reactive groups are most advantageously at the termini of the chain ends. Preferred isocyanate-reactive groups are primary hydroxyl, secondary hydroxyl, primary amino and secondary amino groups. When the high-melting polymer contains isocyanate-reactive groups, its functionality (that is, average number of reactive groups per molecule), is preferably at least 2.0, more preferably from about 2.0 to about 8.0, even more preferably from about 2.0 to about 4.0, and most preferably from about 2.0 to about 3.0. This functionality may be readily produced through the appropriate selection of polymerization initiators. For example, diols to produce a functionality of 2; triols to produce a functionality of 3; or pentaerithrytol that would produce a functionality of 4, etc.

Certain amorphous polymers can be used in conjunction with or in place of the high-melting polymer. Suitable amorphous polymers are those having a glass transition temperature of at least about 45°C and up to about 200°C, preferably about 50 to about 120°C. Preferably, the suitable amorphous polymers are also relatively miscible in a reaction mixture that includes the organic polyisocyanate and the liquid isocyanate-reactive material, in the sense discussed above. When the polyurethane and/or polyurea polymer is to be used in applications where it is exposed to higher than ambient temperatures, in general the T_g of the high-

melting polymer should be higher than the expected use temperature.

The amorphous polymer forms anisotropic domains in the matrix of the polyurethane and/or polyurea polymer. These domains are preferably continuous with the polyurethane and/or urea matrix. To facilitate the formation of these domains, the amorphous polymer is preferably one that is a low viscosity fluid at the processing temperatures. A suitable means of evaluating viscosity is to perform a melt flow index test as described in ASTM D1238, under an applied load of 2.16 kg, at the desired processing temperature. Amorphous polymers having melt flow indices of 10 dg/min or more, especially 20 dg/min or more, under those conditions are preferred.

As before, it is preferred that the amorphous polymer contain isocyanate-reactive groups.

The reinforcing polymer is incorporated into a polyurethane and/or polyurea forming formulation. This can be accomplished in several ways. As the reinforcing polymer is solid at ambient temperatures, it is preferably mixed with a liquid component so that it can be fed into polyurethane foam processing equipment as a fluid stream. A particularly convenient way is to disperse the reinforcing polymer into the polyether polyol component before combining them with the polyisocyanate and curing the mixture. However, the reinforcing polymer may also be added together with other components such as chain extenders, water and/or surfactant streams. If the reinforcing polymer is not isocyanate-reactive at room temperature, it can even be blended into the polyisocyanate component and added that way.

Alternatively, the reinforcing polymer can be used in making an isocyanate-terminated prepolymer, either alone or in admixture with a polyether.

The isocyanate-reactive material has an average of at least two isocyanate-reactive groups per molecule. The isocyanate-reactive groups are any heteroatom groups that will react with an isocyanate to form a covalent bond therewith. Preferred isocyanate-reactive groups are hydroxyl, primary amine or secondary amine groups, with primary and secondary hydroxyl groups being preferred. As is well known in the art of making polyurethane and/or polyurea polymers, isocyanate-reactive materials come in many types, with the selection of a

particular type being made according to the properties that are desired in the product. Isocyanate-reactive compounds are well known in the art and include those described herein and any other commercially available polyol and/or SAN, PIPA or PHD copolymer polyols. (PIPA is the reaction of olamine with polyisocyanate to produce polyaddition products, see U.S. Patent 4,374,209. PHD stands for polyharnstoffdispersion.) Such polyols are described in Polyurethane Handbook, by G. Oertel, 2nd edition, Hanser publishers. Mixtures of one or more polyols and/or one or more copolymer polyols may also be used to produce polyurethane foams according to the present invention. A large number of suitable isocyanate-reactive materials are described in columns 3-5 of U.S. Pat. No. 4,394,491 incorporated herein by reference. However, preferred polyols for preparing flexible foams are polyether and polyester polyols having an equivalent weight per isocyanate-reactive group of from about 500 to about 8,000, preferably about 800 to about 3000, more preferably about 1000 to about 2500. These preferred polyether and polyester polyols also advantageously have a nominal functionality (number of isocyanate-reactive groups/molecule) from about 2 to about 6, preferably about 2 to about 4, more preferably about 2 to about 3. Particularly preferred are the polyether polyols that are polymers of a C₂₋₄ alkylene oxide or tetrahydrofuran. Polymers of propylene oxide which is random copolymerized or block polymerized with up to about 20 weight percent, based on the weight of the total, of ethylene oxide are more preferred for making molded or high resiliency slabstock foam, especially those having about 8-20 weight percent ethylene oxide end-capping and a primary hydroxyl content of 50% or more. Most preferred for conventional slabstock foam are nominally trifunctional polymers of propylene oxide and random copolymers of propylene oxide with up to about 15 weight percent ethylene oxide, having less than 30%, especially less than 15%, primary hydroxyl groups.

Alternative polyols that may be used include polyalkylene carbonate-based polyols and polyphosphate-based polyols. Preferred are polyols prepared by adding an alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide or a combination thereof, to an initiator having from 2 to 8, preferably 2 to 6 active hydrogen atoms. Catalysis for this polymerization can be either anionic or

cationic, with catalysts such as KOH, CsOH, Ba(OH)₂, boron trifluoride, or a double cyanide complex (DMC) catalyst such as zinc hexacyanocobaltate.

5 As the reinforcing polymer is preferably relatively miscible in the reaction polyurethane and/or polyurea formulation as discussed before, the reinforcing polymer and the isocyanate-reactive component are preferably selected together so that they have an interaction parameter (χ value) within the ranges described before.

10 The polyurethane and/or polyurea polymer is made by combining the reinforcing polymer, isocyanate-reactive material and polyisocyanate under conditions that the isocyanate-reactive material and polyisocyanate react to form a high molecular weight polymer. As the components react, the temperature of the reaction mixture exceeds the melting or glass transition temperature of the
15 reinforcing polymer, and remains at such a temperature for enough time to melt the high-melting polymer or effect a phase transition of the amorphous polymer. The necessary heat may be provided from the heat of reaction of the mixture, may be provided by externally applied heat, or some combination of both.

20 As it is necessary for the high-melting polymer to melt during the reaction, it is preferred that this polymer be used in the form of a finely divided particulate, so that rapid melting of the particles is achieved once the temperature of the reaction mixture exceeds their melting point. Similarly, an amorphous polymer is preferably provided as a finely divided particulate, to facilitate a rapid phase
25 change to a preferably low viscosity fluid.

The reaction mixture is cured to form a polyurethane and/or polyurea polymer. The curing process typically begins before the high-melting polymer is melted or the amorphous polymer undergoes a phase change, and continues
30 through the melting/phase change process and may extend until after the melting/phase change is completed. Curing can be done in any convenient way, including those methods conventionally used in making polyurethane and/or polyurea polymers. For example, when molded polymers are made, the polymer

can be fully cured in the mold, or else cured to adequate green strength so that it can be demolded without permanent deformation, and then post-cured at ambient or elevated temperature. Molds can be preheated if desired or if necessary to melt the high-melting polymer or effect the phase transition of the amorphous polymer.

5 Moreover, filled molds can be heated as necessary to effect the necessary phase transition and complete the cure. Both the so-called cold molding and hot-molding techniques for making molded flexible polyurethane foams can be used with this invention. Slabstock foaming techniques can be used for making flexible foam. Conventional pouring techniques for making rigid foams are entirely suitable. It

10 is noted that because the process must provide the heat of fusion for the high-melting polymer, or for the phase change in an amorphous polymer, curing times and/or temperatures may need to be increased somewhat, relative to conventional formulations that do not use the reinforcing polymer.

15 The cured polyurethane and/or polyurea is cooled to a temperature below the melting temperature, in the case of a high-melting polymer, or below the T_g in the case of an amorphous polymer. It is believed the reinforcing polymer in most cases will form a highly dispersed but separate domain within the polyurethane and/or polyurea matrix. In the preferred case where the polymer is crystalline, it

20 is believed to form a crystalline structure that is highly dispersed within the polyurethane and/or polyurea matrix. Thus, rather than forming discrete, low aspect ratio particles, the high-melting polymer is believed to form high surface area crystallites that are dispersed broadly through the polyurethane and/or polyurea matrix. Similarly, the amorphous polymer forms anisotropic domains

25 that are preferably co-continuous with the polyurethane and/or polyurea matrix.

Most polyurethane and/or polyurea polymers contain both "hard" and "soft" domains, which are phase segregated to a greater or lesser degree depending on the particular reactants and to some extent processing conditions. In

30 conventional polyurethane and/or urea polymers, the "hard" domains are typically considered to include mainly the reaction product of any water, chain extender and/or crosslinker (as defined below) with the polyisocyanate, whereas the "soft" domain is considered to be primarily the residue of the high equivalent weight

isocyanate-reactive component. Properties such as load-bearing (in flexible foams) are generally attributed to the formation of a well-defined hard segment. Thus, in this invention, it is preferred that the domain formed by the reinforcing polymer does not significantly disrupt the ordinary formation of hard segments in the polyurethane and or/polyurea. Thus, it is preferred that the domains attributable to the reinforcing polymer reside mainly in the soft segment of the polyurethane and/or polyurea polymer.

The organic polyisocyanates which may be used in the present invention include aliphatic, cycloaliphatic, arylaliphatic aromatic isocyanates and mixtures thereof. Aromatic isocyanates, especially aromatic polyisocyanates are preferred.

Examples of suitable aromatic isocyanates include the 4,4', 2,4' and 2,2'-isomers of diphenylmethane diisocyanate (MDI), blends thereof and polymeric and monomeric MDI blends toluene-2,4- and 2,6-diisocyanates (TDI), m- and p-phenylenediisocyanate, chlorophenylene-2,4-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimethyldiphenyl, 3-methyldiphenyl-methane-4,4'-diisocyanate and diphenyletherdiisocyanate and 2,4,6-triisocyanatotoluene and 2,4,4'-triisocyanatodiphenylether.

Mixtures of isocyanates may be used, such as the commercially available mixtures of 2,4- and 2,6-isomers of toluene diisocyanates. A crude polyisocyanate may also be used in the practice of this invention, such as crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamine or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude methylene diphenylamine. TDI/MDI blends may also be used. MDI or TDI based prepolymers can also be used, made either with polyol (b1), or any other polyol as described heretofore. Isocyanate-terminated prepolymers are prepared by reacting an excess of polyisocyanate with polyols, including aminated polyols or imines/enamines thereof, or polyamines.

Examples of aliphatic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane 1,4-

diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, saturated analogues of the above mentioned aromatic isocyanates and mixtures thereof.

For the production of flexible foams, the preferred polyisocyanates are the
5 toluene-2,4- and 2,6-diisocyanates or MDI or combinations of TDI/MDI or prepolymers made therefrom.

For flexible foam, the organic polyisocyanates and the isocyanate reactive
compounds are reacted in such amounts that the isocyanate index, defined as the
10 number or equivalents of NCO groups divided by the total number of isocyanate reactive hydrogen atom equivalents multiplied by 100, ranges from 50 to 120 and preferably between 75 and 110.

In addition to the isocyanate-reactive material, polyisocyanate and high-
15 melting polymer, various other additives and reactants may be used, according to the type of polyurethane and/or polyurea polymer being made.

For example, most polyurethane and/or polyurea polymers are made using a mixture of isocyanate-reactive components. This mixture will typically include
20 one or more high (>500) equivalent weight polyether or polyester, together with one or more chain extenders and/or crosslinkers. A chain extender is a material having an equivalent weight of less than about 250, preferably less than about 125, that has two isocyanate-reactive groups per molecule. A crosslinker has a similar equivalent weight, and has at least three isocyanate-reactive
25 groups/molecule. For flexible foam applications, water is commonly used to perform the dual function of blowing agent and chain extender. In addition, crosslinkers such as monoethanolamine, phenylene diamine, bis(3-chloro-4-aminophenyl)methane, 2,4-diamino-3,5-diethyl toluene, isopropanolamine, diisopropanolamine, N-(2-hydroxypropyl)ethylenediamine and N,N'-di(2-
30 hydroxypropyl) ethylenediamine. are commonly used.

Cellular polymers are made using a blowing agent. The blowing agent may be water (which reacts with isocyanate groups to form carbon dioxide), a low

boiling hydrocarbon such as any of the isomers of pentane, hexane, heptane, pentene, heptene, cyclopentane, cyclohexane, a gas such as carbon dioxide, an azo compound such as azohexahydrobenzodinitrile or a halogenated hydrocarbon such as dichlorodifluoroethane, vinylidene chloride and methylene chloride.

5 In the production of flexible polyurethane foams, water is preferred as a blowing agent. The amount of water is preferably in the range of from 0.5 to 10 parts by weight, more preferably from 2 to 7 parts by weight based on 100 parts by weight of the polyol ((b1) + (b2)). Carboxylic acids or salts are also used as blowing agents. It is clear that the water level in the foam formulation by
10 reacting with isocyanate influences the overall exotherm of the foaming mass and that the highest the water level in the foam formulation, the higher and the faster the exotherm. Hence higher water containing formulation will melt more readily the high-melting polymer or amorphous polymer (b2). When a hydrocarbon, hydrochlorofluorocarbon, or the hydrofluorocarbon is used as a blowing agent, the
15 amount is generally not more than 40 parts by weight of component (b) and preferably not more than 30 parts by weight of component (b). Water and a combination of hydrocarbon, hydrochlorofluorocarbon, or the hydrofluorocarbon may also be used a blowing agent.

20 A catalyst will generally be used. Representative catalysts include: (a) tertiary amines such as trimethylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-dimethylethanolamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N-dimethylpiperazine, 1,4-diazobicyclo-2,2,2-octane, bis(dimethylaminoethyl)ether and triethylenediamine; (b)
25 tertiary phosphines such as trialkylphosphines and dialkylbenzylphosphines; (c) chelates of various metals such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate and the like with metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co and Ni; (d) acidic metal salts of strong acids such as ferric chloride, stannic
30 chloride, stannous chloride, antimony trichloride, bismuth nitrate and bismuth chloride; (e) strong bases such as alkali and alkaline earth metal hydroxides, alkoxides and phenoxides; (f) alcoholates and phenolates of various metals such as

Ti(OR)₄, Sn(OR)₄ and Al(OR)₃, wherein R is alkyl or aryl, and the reaction products of the alcoholates with carboxylic acids, β-diketones and 2-(N,N-dialkylamino)alcohols; (g) salts of organic acids with a variety of metal such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni and Cu including, for example, sodium acetate, stannous octoate, stannous oleate, lead octoate and metallic driers such as manganese and cobalt naphthenate; (h) organometallic derivatives of tetravalent tin, trivalent and pentavalent As, Sb and Bi and metal carbonyls of iron and cobalt and (i) mixtures thereof.

Catalysts are typically used in small amounts, for example, each catalyst being employed from about 0.0015 to about 5% by weight of the polyurethane reaction mixture (that is, all of the components used to make the foam). Amine catalysts tend to be used in amount toward the higher end of the aforementioned range, whereas metallic catalysts tend to be used in quantities of 1% or lower.

In addition, other useful additives such as surfactants, chain extending agents, fillers such as calcium carbonate, pigments such as titanium dioxide, iron oxide, chromium oxide, azo/diazo dyes, phthalocyanines, dioxazines and carbon black and additional polyols can be used if desired.

Suitable processes for making molded and slabstock flexible polyurethane foams are described, for example, in *Dow Polyurethanes—Flexible Foams*, 2d edition, Herrington, R. et al., ed., 1997, as well as the references described therein.

Flexible polyurethane foams made in accordance with the invention tend to have excellent load-bearing properties at an equivalent density, which are obtained without significant loss of most other desirable physical properties, notably tensile strength, tear strength, elongation and humid aged compression set. In particular, this invention provides a method for making a high resiliency foam having the following combination of properties:

Core density of 30-50 kg/m³, as measured according to ASTM 3574-95;

Ratio of 50% compression force deflection, measured according to Peugeot D-41 1003-86 and expressed in KPa, to core density expressed in kg/m³ of greater than 0.15;

Ratio of 40% indentation force deflection, measured according to ISO 2439-97 and expressed in Newtons to core density in kg/m³ of at least about 7.1;

Tensile strength of at least 150 kPa and elongation of at least 90%, measured according to ASTM 3574-95;

Tear strength of at least 1.8 N/m, as measured according to ASTM D 3574-95; and

75% humid age compression set of less than 30 %; and

Air flow of at least 1.0 cubic foot/minute, measured according to ASTM D 3574-95.

Flexible polyurethane and/or polyurea foams according to the invention are useful as, for example, transportation vehicle seating, such as in automobiles, two-wheeled vehicles (motorized or not), watercraft, snowmobiles, all-terrain vehicles, aircraft and the like, as well as for furniture cushions and mattresses or other bedding applications.

The process of the invention is suitable for reaction injection molding applications in which the main isocyanate-reactive material is an ethylene oxide-capped poly(propylene oxide) polyol or an amine-terminated polyether, the chain extender is an aromatic diamine such as diethyltoluene diamine and the polyisocyanate is MDI or a polymeric MDI.

Similarly, the invention is applicable to making polyurethane films, coating and adhesives.

The following examples are given to illustrate the invention and should not be interpreted as limiting in anyway. Unless stated otherwise, all parts and percentages are given by weight.

A description of the raw materials used in the examples is as follows.

- 5 SPECFLEX™ NC 632 is a glycerine/sorbitol initiated propylene oxide polymer capped with ethylene oxide available under the Tradename SPECFLEX from The Dow Chemical Company. The average hydroxyl number is 32, average equivalent weight is about 1726 and the functionality is between 4 and 5.
- 10 SPECFLEX™ NC 700 is a 40% SAN based copolymer polyol with an average hydroxyl number of 20 available from The Dow Chemical Company.
- 15 NIAX A-300 is a proprietary delayed action amine catalyst available from CK-Witco-OSI Specialties.
- 15 NIAX A-400 is a proprietary delayed action amine catalyst available from CK-Witco-OSI Specialties.
- 20 DABCO™ 33 LV is a triethylene diamine catalyst available as a 33 percent solution in dipropylene glycol available from Air Products and Chemicals Inc. under the trademark DABCO.
- 25 DEOA is diethanolamine.
- 25 TEGOSTAB B8708 is a silicone based surfactant obtained from T. Goldschmidt Ag.
- 30 VORANATE™ T-80 is an 80/20 blend of 2,4/2,6 isomers of Toluene diisocyanate available from The Dow Chemical Company under the Tradename VORANATE.
- PPDL2 is a polypentadecalactone polyester based polymer prepared from pentadecalactone and a diol initiator,

the preparation of which is described herein. PDDL2 has a T_m of about 92°C, a T_g/T_m (K) of 0.573 and a calculated χ at 400°K of a PDDL2/polyol/MDI blend of 1.46 and at 300°K of 3.27.

5

DYNACOLL 7380 is a polyester polyol available from Degussa Huels and has an OH number of 29, a melting point of about 67°C, a T_g/T_m of 0.62 and a calculated χ composite at 400°K of a DYNACOLL/polyol TDI blend of 1.13 and at 300°K of 2.79.

10

FOMREZ 66-56 is polyester polyol of same chemical composition as Dynacoll 7380 but with a shorter chain (OH number 56). The material has a melting point of about 64°C, a T_g/T_m of 0.61 and a calculated χ composite at 400°K of a FOMREZ/polyol/ TDI blend of 0.60 and at 300 deg K of 1.47. FOMREZ 66-56 is available from Crompton-Witco.

15

General experimental conditions were as follows.

20 Preparation of PPDL2. Pentadecalactone, PDL (100 g) and 1,6-hexane diol (6.0 g) in a 10:1 molar ratio are added to a vessel and heated to 150°C under a nitrogen atmosphere with mixing. Tin(II)-2-ethyl hexanoate (0.5 g), a catalyst, is added and the temperature of the reaction is raised to 190°C. The progress of the polymerization is monitored by observing the disappearance of the PDL. When
25 the polymerization is complete, the resulting hot polymer melt is poured into 700 mL of anhydrous toluene. The resulting solution is cooled to allow the polymer to precipitate. The resulting precipitate is isolated by filtration, washed with hexane and dried in a vacuum oven at room temperature to constant weight. The resulting polyester diol is isolated as a white crystalline solid having a T_g of -50°C
30 and T_m 89°C. A number average molecular weight of 2,770 was obtained as measured by MALDI-TOF mass spectroscopy.

General Foam Formulation HR Molded and Free Rise Foams

In addition to the components listed in the working examples, the basic foam formulation used for HR foams contained the following components, in percent by weight of the polyol and/or polyol blend.

Formulation A

	Water	3.7
	DEOA	1.0
10	NIAX A-300	0.25 (contains 50% water)
	NIAX A-400	0.1 (contains 30% water)
	DABCO 33 LV	0.3
	TEGOSTAB B 8708	0.80
	DABCO DC 5164	0.20

15

Bench and Machine Molded and Free Rise Foams

For examples 1-4 and 5 containing the high melting polymer, the product was added to the NC 632 polyol, water, catalyst, silicone premix as a fine powder, then dispersed under stirring at 3,000 RPM for 30 s, before adding the isocyanate, stirring for another 5 s and pouring the reactants in a cardboard box in case of free rise foam, or in a 30 x 30 x 10 mm aluminum mold heated at 60°C which was subsequently closed, in case of molding.

25 Test Procedures

	Density	is measured according to ISO 845-95 and is expressed in kg/m ³ .
30	Airflow	is measured by test method ASTM D3574-95 and reported in cubic feet/min (cfm).
	IFD	is indentation force deflection as measured by ISO 2439-97 and

		is reported in Newton at 40 % foam deflection.
5	CFD	is compression force deflection as measured by Peugeot D-41-1003-86 test method and is reported as kilo pascals under 25 %; 50 % and 65 % deflections.
	CS	is dry compression set as measured by Peugeot D-45.1046-83 test method (70 % CD) and is reported as percent.
10	75 % CS	is dry compression set as measured according to ISO 1856-80.
	Elongation	is measured by Peugeot D-41.1050.85 test method and is reported in percent.
15	Tensile strength	is measured by Peugeot D-41.1050.85 test method and is reported in kilo pascals.
	Tear strength	is measured by Peugeot D-41.1048-81 test method and is reported in Newton/meter.
20	Resiliency	is measured by ASTM 3574-95 test method and is reported in percent.
25	HACS	is a humid aging compression set test as measured by ASTM D3574-95 (75 % CD) and is reported as percent.

Examples 1 to 4

30 Bench scale tests were done to determine the effect of replacing part of a high functional polyol in a flexible foam formulation with PPDL2. The foam formulation A was used and the properties of the resulting molded and free rise foam are given in Tables 1, 2 and 3 respectively.

TABLE 1
INITIAL BENCH SCALE STUDY ON MOLDED AND FREE RISE FOAM

Foam Number	Ref A	1	2	3	4
NC 632	80	75	70	65	60
NC 700	20	20	20	20	20
PPDL2 powder	0	5	10	15	20
T-80	44.8	44.8	44.8	44.8	44.8
Index	100	100	100	100	99
Demold time (min)	4	4	4	5	5
Mold fill time (s)	43	44	44	47	49
(Part weight)	333	332	340	338	336
Molded density	37	37	37.8	37.6	37.3
Temperature at mold fill (C)	70	68	69	67	73
Time to reach 90 deg C (s)	80	87	87	87	88
Demold Temperature (C)	133	130	129	123	122
FREE RISE FOAM					
Cream Time (s)	10-11	9	10	10	10
Gel time (s)	65	65	63	68	80
Rise time (s)	85	105	104	100	91

5 Mold fill time is the time when the foam starts extruding through the mold vent holes. The temperature at mold fill is the temperature recorded in the core of the foam with a very thin thermocouple at the time when the mold is filled. Time to reach 90°C is the time at which the thermocouple indicates that the foam core temperature has reached the temperature of 90°C which is the melting point of

10 PPDL-2. Hence one can see that PPDL-2 has melted before the end of foam rise and after the mold has been filled. Demold temperature, recorded just before the mold lid is opened, shows that core temperature is much higher than the melting point of PPDL-2.

15 Free rise foam reactivity data show that substituting solid PPDL-2 for liquid NC-632 does not change dramatically the reaction profile. Only curing tends to slow down, not surprisingly, as shown by the longer demold times at high

PPDL-2 concentrations.

TABLE 2

5 PROPERTIES OF MOLDED FOAMS PRODUCED ACCORDING TO THE FORMULATIONS OF TABLE 1

Foam Number	Ref A	1	2	3	4
40 % IFD	244	247	303	330	380
Core Density	34.7	33.7	35.0	35.4	36.9
25 % CFD	3.5	3.4	4.3	4.9	5.4
50 % CFD	5.2	5.2	6.5	7.5	9.0
65 % CFD	8.4	8.7	11	12.5	15.9
Airflow	3.4	3.2	3.1	3.7	3.5

10 The results in Table 2 show that the addition of the PPDL2 polymer increases the hardness of the foam as measured by CFD and IFD. It was unexpected to observe this increase in hardness as diol (PPDL2) is replacing the high functional polyol (NC 632). The substitution of part of the high functional polyol with the PPDL2 also need not decrease the airflow through the foam.

TABLE 3

15

PROPERTIES OF FREE RISE FOAM PREPARED ACCORDING TO THE FORMULATIONS OF TABLE 1

Foam Number	Ref A	1	2	3	4
Core Density	28.3	28.7	29.3	29.4	31.8
50 % CFD	3.4	4.0	4.5	4.8	6.3
Airflow	4.4	4.3	4.3	4.5	4.4

20

As observed for the molded foam, an unexpected increase in the hardness of the foam was obtained upon substitution of PPDL2 for part of the high functional polyol.

25 Example 5

Bench scale tests were done to determine the effect of replacing part of a high functional polyol in a flexible foam formulation with Dynacoll 7380. The foam formulations and the properties of the resulting foam are given in Table 4.

TABLE 4

INITIAL BENCH SCALE STUDY ON MOLDED FOAM

Foam Number	Ref B*	Ref C*	5
NC 632	80	72	72
NC 700	20	20	20
Dynacoll 7380	0	0	8
Fomrez 66-56	0	8	0
Index	100	100	100
Demold time (min)	4	4	4
(Part weight)	331	328	335
40 % IFD (N)	236	235	279
Core density (kg/m ³)	34.7	34.0	36.4
50% CFD	5.0	5.3	6.2
Airflow (CFM)	4.6	4.5	4.6
75% HACS	16.8	19.7	19.9

5

*Ref's B&C are not part of the present invention.

The results in Table 4 show that Fomrez 66-56, which has a chi factor at 300°K below 1.6, does not give any hardness increase while Dynacoll 7380, which has a chi factor of 2.79 at 300°K, shows higher foam load-bearing.

10

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

15

WHAT IS CLAIMED IS:

1. A polyurethane and/or polyurea foam made in the reaction of:
 - (a) at least one organic polyisocyanate; and
 - 5 (b) an isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one high-melting polymer that has a melting point of
10 from about 45 to about 200°C, a T_g/T_m of less than 0.75 and a calculated interaction parameter with other polyurethane components χ at 300°K of more than 1.6 and at 400°K of less than 2.0.
- 15 2. A process comprising
 - (I) forming a reaction mixture by mixing
 - (a) a polyisocyanate and
 - (b) a isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at
20 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one high-melting polymer that has a melting point of from about 40 to about 200°C, a T_g/T_m of less
25 than 0.75 and a calculated χ at 300°K of more than 1.6 and a calculated χ at 400°K of less than 2.0.
 - (II) bringing the reaction mixture to a temperature above the melting temperature of component (b) (ii) for a time sufficient to melt component (b)(ii),
 - 30 (III) curing the reaction mixture to produce a polyurethane and/or polyurea, and
 - (IV) cooling the polyurethane and/or polyurea to below the melting temperature of component (b)(ii).

3. A dispersion of a continuous phase of at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and a disperse phase comprising particles of at least one high-melting polymer that has a melting point of from about 70 to about 200°C, a T_g/T_m of less than 0.75 and a calculated χ at 300°K of more than 1.6 and a calculated χ at 400°K of less than 2.0.
4. A polyurethane and/or polyurea polymer made in the reaction of:
- (a) at least one organic polyisocyanate; and
 - (b) an isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least amorphous polymer having a T_g of greater than about 45°C and a T_g/T_m of less than 0.75.
5. A process comprising
- (I) forming a reaction mixture by mixing
 - (a) a polyisocyanate and
 - (b) a isocyanate-reactive component that includes
 - (i) at least one isocyanate-reactive material that is liquid at 25°C, an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and
 - (ii) at least one amorphous polymer having a T_g of greater than about 45°C and up to about 200°C and a T_g/T_m of greater than 0.65,
 - (II) bringing the reaction mixture to a temperature above the T_g of component (b) (ii) for a time sufficient for component (b)(ii) to undergo a phase transition to a rubbery state and become anisotropically dispersed in the reaction mixture,
 - (III) curing the reaction mixture to produce a polyurethane and/or polyurea, and
 - (IV) cooling the polyurethane and/or polyurea to below the T_g of component (b)(ii).

6. A polyurethane and/or polyurea polymer having a having a phase comprising the reaction product of an isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an
5 equivalent weight of 500 to 8,000, and a polyisocyanate and a co-continuous, anisotropic phase of at least one amorphous polymer having a T_g of greater than about 45°C up to about 200°C and a T_g/T_m of greater than 0.65, or reaction product thereof which an organic polyisocyanate.
- 10 7. A dispersion of a continuous phase of at least one isocyanate-reactive material that is liquid at 25°C, has an average of at least 2 isocyanate-reactive groups per molecule and an equivalent weight of 500 to 8,000, and a disperse phase comprising particles of at least one amorphous polymer having a T_g of greater than about 45°C up to about 200°C and a T_g/T_m of greater than 0.65.

15