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- (54) **Title:** HIGHLY FILLED POLYURETHANE COMPOSITES

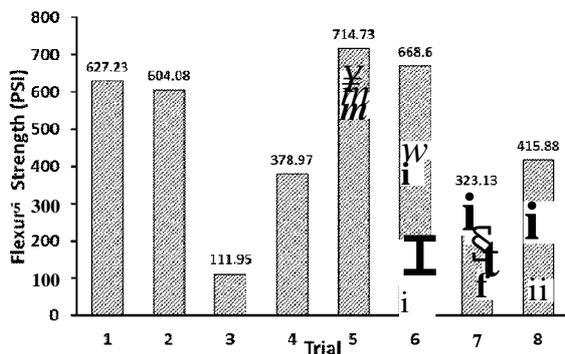


Figure 1

(57) **Abstract:** Composite materials and methods for their preparation are described herein. The composite materials can comprise (a) a polyurethane and (b) from 35% to 90% by weight, based on the total weight of the composite, of a particulate filler dispersed in the polyurethane. The polyurethane can be formed by the reaction of (i) one or more isocyanates selected from the group consisting of diisocyanates, polyisocyanates, and mixtures thereof, and (ii) one or more polyols. The one or more polyols that form the polyurethane comprise a high hydroxyl number polyol having a hydroxyl number of at least 250 mg KOH/g. In some cases, the one or more polyols that form the polyurethane can have a weight average equivalent weight of from 200 to 1100 amu. In some cases, the one or more polyols that form the polyurethane can include less than 5% by weight, based on the total weight of the one or more polyols that form the polyurethane, of one or more flexible polyols having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3.



HIGHLY FILLED POLYURETHANE COMPOSITES

TECHNICAL FIELD

This application generally relates to highly filled polyurethane composites, as well as
5 methods of making and using thereof.

BACKGROUND

Polymeric composite materials that include organic and/or inorganic fillers have become
desirable for a variety of uses because of their excellent mechanical properties and weathering
stability. Foamed versions of these materials can have a relatively low density yet the filler
10 materials can provide a composite material that is extremely strong. The polymer provided in
the composite material can help provide good toughness (i.e., resistance to brittle fracture) and
resistance to degradation from weathering to the composite when it is exposed to the
environment. Thus, polymeric composite materials including organic and/or inorganic fillers
can be used in a variety of applications, including in building materials.

15 While these types of polymeric composites have been successfully used in a variety of
applications, a need still exists for polymeric composites with improved mechanical properties
(e.g., improved flexural strength).

SUMMARY

Polyurethane composites include a polyurethane formed by the reaction of one or more
20 isocyanates and one or more polyols, and a filler dispersed throughout the polyurethane.
Generally, the selection of the one or more polyols used to form the polyurethane can influence
the physical and mechanical properties of the resulting polymeric composite.

For example, polyols are often classified as either rigid polyols or flexible polyols based
on various properties of the individual polyol and the overall flexibility of a polyurethane
25 polymer produced from the respective polyols. Generally speaking, the rigidity or flexibility of a
polyurethane formed from any single polyol is governed by one or more of the hydroxyl number,
functionality, and molecular weight of the polyol. Rigid polyols typically have a high hydroxyl
number (e.g., a hydroxyl number of greater than 175 mg KOH/g), a high functionality (e.g., a
functionality greater than 3.5), and/or a low molecular weight (e.g., a molecular weight of 1,000
30 Daltons or less). Flexible polyols typically have a lower hydroxyl number (e.g., a hydroxyl
number of less than 150 mg KOH/g), a lower functionality (e.g., a functionality of 3 or less),
and/or a higher molecular weight (e.g., a molecular weight of at greater than 1,000 Daltons).

When preparing polyurethane composites, the relative amount of rigid polyol(s) in the polyol blend used to form the polyurethane is generally carefully controlled in order to ensure that the resulting composite is not too brittle. Typically, from about 5% by weight to about 20% by weight (more particularly around 15% by weight) of one or more flexible polyols, based on
5 the total weight of the polyol blend used to form the polyurethane, is combined with from about 80% by weight to about 95% by weight (more particularly around 85% by weight) of one or more rigid polyols, based on the total weight of the polyol blend used to form the polyurethane, to afford a composite having physical and mechanical properties (e.g., flexural strength) suitable for many structural applications.

10 Surprisingly, it has been discovered that when preparing highly filled polyurethane composites (e.g., composites that include from 35% to 90% by weight particulate filler, based on the total weight of the composition), composite materials having a high flexural strength can be prepared without incorporating one or more flexible polyols in the polyol blend used to form the polyurethane. Specifically, composite materials having a high flexural strength can be prepared
15 from polyol blends that include less than 5% by weight of one or more flexible polyols, based on the total weight of the polyol blend used to form the polyurethane.

Accordingly, provided herein are composite materials. The composite materials can comprise (a) a polyurethane formed by the reaction of (i) one or more isocyanates selected from the group consisting of diisocyanates, polyisocyanates, and mixtures thereof, and (ii) one or
20 more polyols; and (b) a particulate filler. The composites can exhibit a high flexural strength. For example, the composites can exhibit a normalized flexural strength of at least 20 (e.g., a normalized flexural strength of from 20 to 50, or a normalized flexural strength of from 25 to 35).

The one or more polyols that form the polyurethane can comprise one or more high
25 hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g. In some embodiments, the one or more polyols that form the polyurethane comprise at least 95% by weight (e.g., at least 99% by weight), based on the total weight of the polyols that form the polyurethane, one or more high hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g. In certain embodiments, the
30 one or more polyols that form the polyurethane consist of one or more high hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g.

In some embodiments, the one or more polyols that form the polyurethane include less than 5% by weight (e.g., less than 1% by weight), based on the total weight of the one or more

less than 150 and a functionality of less than 3.

In some embodiments, the one or more polyois that form the polyurethane can have a weight average equivalent weight of from 200 to 1100amu (e.g., a weight average equivalent weight of from 200 to 600 amu, from 200 to 300 amu, or from 200 to 250 amu).

In some cases, the one or more polyois that form the polyurethane satisfy Eq. 1 below

$$(2.1)(F) + (0.3)(EW) - (0.0036)(F)(EW) \geq 12 \quad \text{Eq. 1}$$

wherein F is the weight average functionality of the one or more polyois that form the polyurethane; and EW is the weight average equivalent weight of the one or more polyois that form the polyurethane. In certain cases, the one or more polyois that form the polyurethane satisfy Eq. 2 below

$$(2.1)(F) + (0.3)(W) - (0.0036)(F)(W) \geq 15 \quad \text{Eq. 2}$$

wherein F is the weight average functionality of the one or more polyois that form the polyurethane; and EW is the weight average equivalent weight of the one or more polyois that form the polyurethane.

The particulate filler can be an inorganic filler, such as fly ash. In some embodiments, the total amount of particulate filler in the composite material can range from 35% to 90% by weight (from 45% to 70% by weight), based on the total weight of the composition.

Also provided are methods of preparing the composite materials described herein. The methods can include mixing (1) a particulate filler; (2) at least one isocyanate selected from the group consisting of diisocyanates, polyisocyanates, and combinations thereof; (3) one or more polyois; and (4) a catalyst. The at least one isocyanate and the one or more polyois are then allowed to react in the presence of the particulate filler and catalyst to form the composite material.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a plot illustrating the flexural strength of composites 1-8.

Figure 2 is a plot illustrating the density of composites 1-8

Figure 3 is a plot illustrating the normalized flexural strength of composites 1-8.

DETAILED DESCRIPTION

Composite materials and methods for their preparation are described herein.

The composite materials can comprise (a) a polyurethane formed by the reaction of (i) one or more isocyanates selected from the group consisting of diisocyanates, polyisocyanates, and mixtures thereof, and (ii) one or more polyols; and (b) a particulate filler.

The composites can exhibit a high normalized flexural strength. For example, in some
5 embodiments, the composites can exhibit a normalized flexural strength of at least 20 (e.g., at least 21, at least 22, at least 23, at least 24, at least 25, at least 26, at least 27, at least 28, at least 29, at least 30, at least 31, at least 32, at least 33, at least 34, at least 35, at least 36, at least 37, at least 38, at least 39, at least 40, at least 41, at least 42, at least 43, at least 44, at least 45, at least 46, at least 47, at least 48, or at least 49). In some embodiments, the composites can exhibit a
10 normalized flexural strength of 50 or less (e.g., 49 or less, 48 or less, 47 or less, 46 or less, 45 or less, 44 or less, 43 or less, 42 or less, 41 or less, 40 or less, 39 or less, 38 or less, 37 or less, 36 or less, 35 or less, 34 or less, 33 or less, 32 or less, 31 or less, 30 or less, 29 or less, 28 or less, 27 or less, 26 or less, 25 or less, 24 or less, 23 or less, 22 or less, or 21 or less).

The composites can exhibit a normalized flexural strength ranging from any of the
15 minimum values described above to any of the maximum values described above. For example, the composites can exhibit a normalized flexural strength of from 20 to 50 (e.g., a normalized flexural strength of from 20 to 40, a normalized flexural strength of from 21 to 37, a normalized flexural strength of from 23 to 37, a normalized flexural strength of from 23 to 35, a normalized flexural strength of from 23 to 33, a normalized flexural strength of from 25 to 35, or a
20 normalized flexural strength of from 25 to 33).

Isocyanates

The polyurethane systems used to form the composite materials described herein include one or more isocyanate monomers. Suitable isocyanates that can be used to form the composite
25 materials include one or more monomeric or oligomeric poly- or di-isocyanates. The monomeric or oligomeric poly- or di-isocyanate include aromatic diisocyanates and polyisocyanates. The isocyanates can also be blocked isocyanates, or pre-polymer isocyanates (e.g., castor oil pre-polymer isocyanates and soy polyol pre-polymer isocyanates). An example of a useful diisocyanate is methylene diphenyl diisocyanate (MDI). Useful MDI's include MDI
30 monomers, MDI oligomers, and mixtures thereof.

Further examples of useful isocyanates include those having NCO (*i.e.*, the reactive group of an isocyanate) contents ranging from about 25% to about 50% by weight (*e.g.*, from about 25% to about 35% by weight). Examples of useful isocyanates are found, for example, in *Polyurethane Handbook: Chemistry, Raw Materials, Processing Application, Properties*, 2nd

Edition, Ed: Gunter Oertel; Hanser/Gardner Publications, Inc., Cincinnati, OH, which is herein incorporated by reference. Suitable examples of aromatic polyisocyanates include 2,4- or 2,6-toluene diisocyanate, including mixtures thereof; p-phenylene diisocyanate; tetramethylene and hexamethylene diisocyanates; 4,4-dicyclohexylmethane diisocyanate; isophorone diisocyanate; 5 4,4-phenylmethane diisocyanate (methylene diphenyl diisocyanate; MDI); polymethylene polyphenylisocyanate; and mixtures thereof. In addition, triisocyanates may be used, for example, 4,4,4-triphenylmethane triisocyanate; 1,2,4-benzene triisocyanate; polymethylene polyphenyl polyisocyanate; methylene polyphenyl polyisocyanate; and mixtures thereof.

Suitable blocked isocyanates are formed by the treatment of the isocyanates described herein with a blocking agent (*e.g.*, diethyl malonate, 3,5-dimethylpyrazole, methylethylketoxime, and caprolactam). Isocyanates are commercially available, for example, from Bayer Corporation (Pittsburgh, PA) under the trademarks MONDUR and DESMODUR. Other examples of suitable isocyanates include MONDUR MR Light (Bayer Corporation; Pittsburgh, PA), PAPI 27 (Dow Chemical Company; Midland, MI), Lupranate M20 (BASF Corporation; Florham Park, 15 NJ), Lupranate M70L (BASF Corporation; Florham Park, NJ), Rubinate M (Huntsman Polyurethanes; Geismar, LA), Econate 31 (Ecopur Industries), and derivatives thereof.

The average functionality of isocyanates useful with the composites described herein is between about 1.5 to about 5. Further, examples of useful isocyanates include isocyanates with an average functionality of about 2 to about 4.5, about 2.2 to about 4, about 2.4 to about 3.7, 20 about 2.6 to about 3.4, and about 2.8 to about 3.2.

As indicated above, in the composite materials described herein, an isocyanate is reacted with a polyol to produce the polyurethane formulation. In general, the ratio of isocyanate groups to the total isocyanate reactive groups, such as hydroxyl groups, water and amine groups, is in the range of about 0.5:1 to about 1.5:1, which when multiplied by 100 produces an isocyanate 25 index between 50 and 150. Additionally, the isocyanate index can be from about 80 to about 120, from about 90 to about 120, from about 100 to about 115, or from about 105 to about 110. As used herein, an isocyanate may be selected to provide a reduced isocyanate index, which can be reduced without compromising the chemical or mechanical properties of the composite material.

Polyols

The polyurethane systems used to form the composite materials described herein include one or more polyols.

Any suitable polyols may be used. Suitable additional polyols for the formation of polymeric composites are known in the art, and can be selected in view of the desired properties of the polymeric composite. Polyols can be classified as either rigid polyols or flexible polyols based on various properties of the individual polyol and the overall flexibility of a polyurethane polymer produced from the respective polyols. Generally speaking, the rigidity or flexibility of a polyurethane formed from any single polyol is governed by one or more of the hydroxyl number, functionality, and molecular weight of the polyol. Rigid polyols typically have a high hydroxyl number (e.g., a hydroxyl number of greater than 175 mg KOH/g, such as a hydroxyl number of from 250 mg KOH/g to 800 mg KOH/g), a high functionality (e.g., a functionality greater than 3.5), and/or a low molecular weight (e.g., a molecular weight of 1,000 Da or less). Flexible polyols typically have a lower hydroxyl number (e.g., a hydroxyl number of less than 150 mg KOH/g, such as a hydroxyl number of from 20 mg KOH/g to 75 mg KOH/g), a lower functionality (e.g., a functionality of 3 or less), and/or a higher molecular weight (e.g., a molecular weight of at greater than 1,000 Da).

The one or more polyols that form the polyurethane can comprise one or more high hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g. For example, in some embodiments, the one or more polyols that form the polyurethane comprise at least 95% by weight (e.g., at least 96% by weight, at least 97% by weight, at least 98% by weight, at least 99% by weight, at least at least 99.5% by weight, or at least at least 99.9% by weight), based on the total weight of the polyols that form the polyurethane, one or more high hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g. In certain embodiments, the one or more polyols that form the polyurethane consist of one or more high hydroxyl number polyols (e.g., one or more rigid polyols) having a hydroxyl number of at least 250 mg KOH/g.

In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a hydroxyl number greater than 250 mg KOH/g (e.g., greater than 260 mg KOH/g, greater than 270 mg KOH/g, greater than 275 mg KOH/g, greater than 280 mg KOH/g, greater than 290 mg KOH/g, greater than 300 mg KOH/g, greater than 325 mg KOH/g, greater than 350 mg KOH/g, greater than 375 mg KOH/g, greater than 400 mg KOH/g, greater than 425 mg KOH/g, greater than 450 mg KOH/g, greater than 475 mg KOH/g, greater than 500 mg KOH/g, greater than 525 mg KOH/g, greater than 550 mg KOH/g, greater than 575 mg KOH/g, greater than 600 mg KOH/g, greater than 625 mg KOH/g, greater than 650 mg KOH/g, greater than 675 mg KOH/g, greater than 700 mg KOH/g, greater than 725 mg KOH/g, greater

than 750 mg KOH/g, or greater than 775 mg KOH/g). In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a hydroxyl number of 800 mg KOH/g or less (e.g., mg 775 KOH/g or less, 750 mg KOH/g or less, 725 mg KOH/g or less, 700 mg KOH/g or less, 675 mg KOH/g or less, 650 mg KOH/g or less, 625 mg KOH/g or less, 600 mg KOH/g or less, 575 mg KOH/g or less, 550 mg KOH/g or less, 525 mg KOH/g or less, 500 mg KOH/g or less, 475 mg KOH/g or less, 450 mg KOH/g or less, 425 mg KOH/g or less, 400 mg KOH/g or less, 375 mg KOH/g or less, 350 mg KOH/g or less, 325 mg KOH/g or less, 300 mg KOH/g or less, 290 mg KOH/g or less, 280 mg KOH/g or less, 275 mg KOH/g or less, 270 mg KOH/g or less, or 260 mg KOH/g or less).

10 The one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a hydroxyl number ranging from any of the minimum values described above to any of the maximum values described above. For example, in some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a hydroxyl number of from 250 mg KOH/g to 800 mg KOH/g (e.g., from 250 mg KOH/g to 600 mg KOH/g, from 250 mg KOH/g to 550 mg KOH/g, from 250 mg KOH/g to 450 mg KOH/g, from 250 mg KOH/g to 350 mg KOH/g, from 300 mg KOH/g to 550 mg KOH/g, from 300 mg KOH/g to 450 mg KOH/g, or from 300 mg KOH/g to 400 mg KOH/g).

In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight of 1,000 Da or less (e.g., 950 Da or less, 900 Da or less, 850 Da or less, 800 Da or less, 750 Da or less, 700 Da or less, 650 Da or less, 600 Da or less, 550 Da or less, 500 Da or less, 450 Da or less, 400 Da or less, 350 Da or less, 300 Da or less, or 250 Da or less). In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight of at least 200 Da (e.g., at least 250 Da, at least 300 Da, at least 350 Da, at least 400 Da, at least 450 Da, at least 500 Da, at least 550 Da, at least 600 Da, at least 650 Da, at least 700 Da, at least 750 Da, at least 800 Da, at least 850 Da, at least 900 Da, or at least 950 Da).

The one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight ranging from any of the minimum values described above to any of the maximum values described above. For example, in some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight of from 200 Da to 1,000 Da (e.g., from 300 Da to 600 Da, or from 400 Da to 500 Da).

In some embodiments, the one or more high hydroxyl number polyols (e.g., the one or more rigid polyols) can have a functionality of from 2 to 6 (e.g., from 1.5 to 5.5, from 1.75 to

5.25, or from 2.0 to 5.0). In certain cases, the one or more high hydroxyl number polyols (e.g., the one or more rigid polyols) can comprise polyester polyols, polyether polyols, or combinations thereof.

Examples of suitable high hydroxyl number polyols (e.g., rigid polyols) are known in the art and include, but are not limited to, CARPOL® PGP-400 (a propylene glycol-based polyether polyol commercially available from Carpenter Co., Richmond, VA), CARPOL® GP-700 (a glycerine-based polyether polyol available from Carpenter Co., Richmond, VA), CARPOL® SPA-357 and SPA-530 (sucrose/amine-based polyether polyols commercially available from Carpenter Co., Richmond, VA), CARPOL® GSP-280, GSP-355, and GSP-370 (sucrose-based polyether polyols commercially available from Carpenter Co., Richmond, VA), TEAP-265 and TEAP-335 (triethanolamine-based polyether polyols available from Carpenter Co., Richmond, VA), JEFFOL® R-425X and R-425X (Mannich-based polyether polyols available from Huntsman Corporation, Salt Lake City, UT) and TEROL® 250, 198, 352, 563, 925 and 1254 (aromatic polyester polyols commercially available from Huntsman Corporation, Salt Lake City, UT).

Optionally, the one or more polyols that form the polyurethane can include one or more additional polyols, such as a low hydroxyl number polyol (e.g., a flexible polyol). In some embodiments, the one or more polyols that form the polyurethane include less than 5% by weight (e.g., less than 4% by weight, less than 3% by weight, less than 2% by weight, less than 1% by weight, less than 0.5% by weight, or less than 0.1% by weight), based on the total weight of the one or more polyols that form the polyurethane, of one or more low hydroxyl number polyols (e.g., one or more flexible polyols) having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3. In certain embodiments, the one or more polyols that form the polyurethane are substantially free from low hydroxyl number polyols (e.g., one or more flexible polyols) having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3.

In some embodiments, the one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a hydroxyl number of less than 150 mg KOH/g (e.g., less than 140 mg KOH/g, less than 130 mg KOH/g, less than 120 mg KOH/g, less than 110 mg KOH/g, less than 100 mg KOH/g, less than 90 mg KOH/g, less than 80 mg KOH/g, less than 70 mg KOH/g, less than 60 mg KOH/g, less than 50 mg KOH/g, less than 40 mg KOH/g, or less than 30 mg KOH/g). In some embodiments, the one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a hydroxyl number of at least 20 mg KOH/g (e.g., at least 30 mg

KOH/g, at least 40 mg KOH/g, at least 50 mg KOH/g, at least 60 mg KOH/g, at least 70 mg KOH/g, at least 80 mg KOH/g, at least 90 mg KOH/g, at least 100 mg KOH/g, at least 110 mg KOH/g, at least 120 mg KOH/g, at least 130 mg KOH/g, or at least 140 mg KOH/g).

The one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a hydroxyl number ranging from any of the minimum values described above to any of the maximum values described above. For example, in some embodiments, the one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a hydroxyl number of from 20 mg KOH/g to 150 mg KOH/g (e.g., from 25 mg KOH/g to 70 mg KOH/g, from 20 mg KOH/g to 50 mg KOH/g, from 40 mg KOH/g to 50 mg KOH/g, or from 20 mg KOH/g to 100 mg KOH/g).

In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight of greater than 1,000 Da (e.g., at least 1,500 Da, at least 2,000 Da, at least 2,500 Da, at least 3,000 Da, at least 3,500 Da, at least 4,000 Da, at least 4,500 Da, at least 5,000 Da, or at least 5,500 Da). In some embodiments, the one or more high hydroxyl number polyols (e.g., one or more rigid polyols) can have a molecular weight of 6,000 Da or less (e.g., 5,500 Da or less, 5,000 Da or less, 4,500 Da or less, 4,000 Da or less, 3,500 Da or less, 3,000 Da or less, 2,500 Da or less, 2,000 Da or less, or 1,500 Da or less).

The one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a molecular weight ranging from any of the minimum values described above to any of the maximum values described above. For example, in some embodiments, the one or more low hydroxyl number polyols (e.g., one or more flexible polyols) can have a molecular weight of from 1,000 Da to 6,000 Da (e.g., from 2,500 Da to 5,000 Da, from 3,500 Da to 5,000 Da, or from 3,000 Da to 4,500 Da).

Examples of suitable low hydroxyl number polyols (e.g., flexible polyols) are known in the art and include, but are not limited to, CARPOL® PGP-1000 (propylene glycol-based polyether polyol commercially available from Carpenter Co., Richmond, VA), VORANOL® 222-056N, (a propylene glycol-based polyether polyol commercially available from The Dow Chemical Company, Midland, MI), CARPOL® PGP-4025 (an ethylene oxide-capped propylene glycol-based polyether polyol commercially available from Carpenter Co., Richmond, VA), CARPOL® GP-1000, GP-4000, and GP-5000 (glycerine-based polyether polyols commercially available from Carpenter Co., Richmond, VA), and CARPOL® GP-4520, and GP-5015 (ethylene oxide-capped glycerine-based polyether polyols commercially available from Carpenter Co., Richmond, VA).

essentially of one or more high hydroxy! number polyols (e.g., one or more rigid polyols) having a hydroxy! number of at least 250 mg KOH/g. In these embodiments, the one or more polyols that form the polyurethane can include one or more rigid polyols and optionally one or more
 5 additional polyols that are neither rigid polyols nor flexible polyols as described above, but be substantially free from low hydroxy! number polyols (e.g., flexible polyols) having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3.

In some embodiments, the one or more polyols that form the polyurethane can have a weight average equivalent weight of at least 200 amu (e.g., at least 225 amu, at least 250 amu, at
 10 least 275 amu, at least 300 amu, at least 325 amu, at least 350 amu, at least 375 amu, at least 400 amu, at least 425 amu, at least 450 amu, at least 475 amu, at least 500 amu, at least 550 amu, at least 600 amu, at least 650 amu, at least 700 amu, at least 750 amu, at least 800 amu, at least 850 amu, at least 900 amu, at least 950 amu, at least 1000 amu, or at least 1050 amu). In some
 15 embodiments, the one or more polyols that form the polyurethane can have a weight average equivalent weight of 1100 amu or less (e.g., 1050 amu or less, 1000 amu or less, 950 amu or less, 900 amu or less, 850 amu or less, 800 amu or less, 750 amu or less, 700 amu or less, 650 amu or less, 600 amu or less, 550 amu or less, 500 amu or less, 475 amu or less, 450 amu or less, 425 amu or less, 400 amu or less, 375 amu or less, 350 amu or less, 325 amu or less, 300 amu or less, 275 amu or less, 250 amu or less, or 225 amu or less).

The one or more polyols that form the polyurethane can have a weight average
 20 equivalent weight ranging from any of the minimum values described above to any of the maximum values described above. For example, the one or more polyols that form the polyurethane can have a weight average equivalent weight ranging from 200 to 1100 amu (e.g., a weight average equivalent weight of from 200 to 600 amu, from 200 to 300 amu, or from 200 to
 25 250 amu).

In some cases, the one or more polyols that form the polyurethane satisfy Eq. 1 below

$$(2.1)\{F\} + (0.3)\{EW\} - (0.0036)\{F\}\{EW\} \geq 12 \quad \text{Eq. 1}$$

wherein F is the weight average functionality of the one or more polyols that form the polyurethane; and EW is the weight average equivalent weight of the one or more polyols that
 30 form the polyurethane. In certain cases, the one or more polyols that form the polyurethane satisfy Eq. 2 below

$$(2.1)\{F\} - (0.3)\{F^{3/4}\} - (0.0036)\{F\}\{EW\} \geq 15 \quad \text{Eq. 2}$$

wherein F is the weight average functionality of the one or more polyols that form the polyurethane; and EW is the weight average equivalent weight of the one or more polyols that form the polyurethane.

5 **Fillers**

The composite materials described herein include a particulate filler. Any suitable particulate filler can be used.

The amount of organic carbon present in a filler can be estimated by measuring the material's loss-on-ignition (LOI). The LOI of a filler refers to the percent weight loss of a
10 sample of the filler upon ignition at 750°C for 2 hours, and then further heated at 750°C to a constant mass to consume any organic carbon present in the filler, as described, for example in ASTM C618-12a.

In some embodiments, the particulate filler has an LOI of at least 0.20% (*e.g.*, at least 0.25%, at least 0.30%, at least 0.35%, at least 0.40%, at least 0.45%, at least 0.50%, at least
15 0.55%, at least 0.60%, at least 0.65%, at least 0.70%, at least 0.75%, at least 0.80%, at least 0.85%, at least 0.90%, at least 0.95%, at least 1.0%, at least 1.1%, at least 1.2%, at least 1.3%, at least 1.4%, at least 1.5%, at least 1.6%, at least 1.7%, at least 1.8%, at least 1.9%, at least 2.0%, at least 2.25%, at least 2.5%, at least 2.75%, at least 3.0%, at least 3.25%, at least 3.5%, at least 3.75%, at least 4.0%, at least 4.25%, at least 4.5%, at least 4.75%, at least 5.0%, at least 5.25%,
20 at least 5.5%, at least 5.75%, at least 6.0%, at least 6.25%, at least 6.5%, at least 6.75%, at least 7.0%, at least 7.25%, at least 7.5%, at least 7.75%, at least 8.0%, at least 8.25%, at least 8.5%, at least 8.75%, at least 9.0%, at least 9.25%, at least 9.5%, at least 9.75%, at least 10.0%, at least 11%, at least 12%, at least 13%, at least 15%, at least 16%, at least 17%, at least 18%, at least 19%, at least 20%, or more).

In some embodiments, the particulate filler has an LOI of less than 25% (*e.g.*, less than 20%, less than 19%, less than 18%, less than 17%, less than 16%, less than 15%, less than 14%, less than 13%, less than 12%, less than 11%, less than 10%, less than 9.75, less than 9.5%, less than 9.25%, less than 9.0%, less than 8.75, less than 8.5%, less than 8.25%, less than 8.0%, less than 7.75, less than 7.5%, less than 7.25%, less than 7.0%, less than 6.75%, less than 6.5%, less
30 than 6.25%, less than 6.0%, less than 5.75%, less than 5.5%, less than 5.25%, less than 5.0%, less than 4.75%, less than 4.5%, less than 4.25%, less than 4.0%, less than 3.75%, less than 3.5%, less than 3.25%, less than 3.0%, less than 2.75%, less than 2.5%, less than 2.25%, less than 2.0%, less than 1.9%, less than 1.8%, less than 1.7%, less than 1.6%, less than 1.5%, less

than 1.4%, less than 1.3%, less than 1.2%, less than 1.1%, less than 1.0%, less than 0.95%, less than 0.90%, less than 0.85%, less than 0.80%, less than 0.75%, less than 0.70%, less than 0.65%, less than 0.60%, less than 0.55%, less than 0.50%, less than 0.45%, less than 0.40%, less than 0.35%, less than 0.30%, or less than 0.25%).

5 The particulate filler can have an LOI ranging from any of the minimum values described above to any of the maximum values described above. For example, the particulate filler can have an LOI ranging from 0.10% to 25% (*e.g.*, from 0.15% to 15%, from 0.20% to 10%, from 0.20% to 6.0%, from 0.20% to 5.0%, or from 0.20% to 1.0%).

10 In some embodiments, the particulate filler has a BET surface area, as measured using ASTM C1069 - 09, of at least 0.75 m²/g (*e.g.*, at least 1.0 m²/g, at least 1.1 m²/g, at least 1.2 m²/g, at least 1.3 m²/g, at least 1.4 m²/g, at least 1.5 m²/g, at least 1.6 m²/g, at least 1.7 m²/g, at least 1.8 m²/g, at least 1.9 m²/g, at least 2.0 m²/g, at least 2.5 m²/g, at least 3.0 m²/g, at least 3.5 m²/g, at least 4.0 m²/g, at least 4.5 m²/g, at least 5.0 m²/g, at least 6.0 m²/g, at least 7.0 m²/g, at least 8.0 m²/g, at least 9.0 m²/g, at least 10 m²/g, at least 15 m²/g, at least 20 m²/g, at least 25 m²/g, at least 50 m²/g, at least 75 m²/g, at least 100 m²/g, at least 150 m²/g, at least 250 m²/g, at least 500 m²/g, at least 750 m²/g, or at least 1000 m²/g). In some embodiments, the particulate filler has a BET surface area, as measured using ASTM C1069 - 09, of less than 100 m²/g (*e.g.*, less than 1000 m²/g, less than 750 m²/g, less than 500 m²/g, less than 250 m²/g, less than 150 m²/g, less than 100 m²/g, less than 75 m²/g, less than 50 m²/g, less than 25 m²/g, less than 20 m²/g, less than 15 m²/g, less than 10 m²/g, less than 9.0 m²/g, less than 8.0 m²/g, less than 7.0 m²/g, less than 6.0 m²/g, less than 5.0 m²/g, less than 4.5 m²/g, less than 4.0 m²/g, less than 3.5 m²/g, less than 3.0 m²/g, less than 2.5 m²/g, less than 2.0 m²/g, less than 1.9 m²/g, less than 1.8 m²/g, less than 1.7 m²/g, less than 1.6 m²/g, less than 1.5 m²/g, less than 1.4 m²/g, less than 1.3 m²/g, less than 1.2 m²/g, less than 1.1 m²/g, less than 1.0 m²/g, or less).

25 The particulate filler can have a BET surface area ranging from any of the minimum values described above to any of the maximum values described above. For example, the particulate filler can have a BET surface area ranging from 0.75 m²/g to 1000 m²/g (*e.g.*, 0.75 m²/g to 500 m²/g, 0.75 m²/g to 150 m²/g, from 0.75 m²/g to 50 m²/g, from 0.75 m²/g to 15 m²/g, from 0.75 m²/g to 5.0 m²/g, or from 1.0 m²/g to 4.0 m²/g).

30 In some embodiments, the particulate filler can have a ratio of BET surface area to LOI ratio (*i.e.*, BET/LOI) of at least 1.0 (*e.g.*, at least 1.5, at least 2.0, at least 2.5, at least 3.0, at least 3.5, at least 4.0, at least 4.5, at least 5.0, or at least 5.5) measuring BET in m²/g and the LOI in %. In some embodiments, the particulate filler can have a ratio of BET surface area to LOI of

less than 6.0 (*e.g.*, less than 5.5, less than 5.0, less than 4.5, less than 4.0, less than 3.5, less than 3.0, less than 2.5, less than 2.0, or less than 1.5).

The particulate filler can have a ratio of BET surface area to LOI from any of the minimum values described above to any of the maximum values described above. For example,
5 the particulate filler can have a ratio of BET surface area to LOI from 1.0 to 6.0 (*e.g.*, from 1.5 to 5.5, or from 2.0 to 5.0).

In some embodiments, the particulate filler can comprise an inorganic filler. In certain
embodiments, the particulate filler can include fly ash. The term "fly ash" is used herein
generally to refer to ash by-products of the combustion of pulverized coal (*e.g.*, in electrical
10 power generation plants). The term fly ash, as used herein, can thus include flue-ash (*i.e.*, fine
ash particles generated during the combustion of coal that rise with flue gases, and are captured
with particle filtration equipment before the exiting the chimney of a coal-fired power plant),
bottom ash (*e.g.*, ash produced during the combustion of coal which does not rise with flue
gases), as well as a combination thereof (*i.e.*, coal ash).

15 Fly ash is formed of mineral matter that is typically of very fine particle size, ranging
from less than 1 micron to over 100 microns in some cases. The fly ash particles possess a
substantially spherical shape as a consequence of the high temperature melting and coalescence
in the furnace of the mineral matter accompanying the coal. The fine particle size and spherical
shape are advantageous properties of the fly ash and are in marked contrast to the properties of
20 many conventional fillers such as ground limestone or calcium carbonate, which are typically
relatively coarse with an irregular, blocky particle shape.

Mineralogically, fly ash is predominantly amorphous, or non-crystalline, in nature as a
result of the rapid quenching of clay/shale minerals as they rapidly pass through the boiler flame
and dust collection system of the power plant. For some fly ashes, the amorphous material can
25 be described as an aluminosilicate glass similar in composition to the mineral mullite
(Al₆Si₂O₁₃); for other fly ashes, it can be described as a calcium aluminosilicate glass similar in
composition to the mineral anorthite (CaAl₂Si₂O₈). Fly ashes can also contain smaller amounts
of a variety of other mineral components derived from thermal modification of accessory
minerals present in the coal. These can include mullite, quartz (SiO₂), ferrite spinel (Fe₃O₄),
30 hematite (Fe₂O₃), dicalcium silicate (Ca₂SiO₄), tricalcium aluminate (Ca₃Al₂O₆), and lime
(CaO). These mineral components can occur as inclusions in the glass particles and/or as discrete
particles.

It is commonly known that the chemical composition of fly ash changes as a result of the type of coal being burned in the boiler. These differences are largely in the relative proportions of the element calcium present in the ash. For example, high rank bituminous coals generally have a low calcium content and produce an ash with relatively low calcium, typically less than 5% CaO; whereas low rank thermal coals generally have much higher content of calcium, typically in the range 8-20% CaO for lignite coals and 20-30% CaO, or higher, for subbituminous coals. These differences are recognized by ASTM specifications, such as ASTM C-618, and by Canadian specifications that classify the ashes based on their CaO content.

Current ASTM C-618 (Coal Fly Ash or Calcined Natural Pozzolan for Use in Concrete) specifications include only two designations or classes of fly ash: "Class F" and "Class C" fly ashes. The "Class F" designation generally incorporates fly ashes originating from the combustion of bituminous and lignite coals and the "Class C" designation generally incorporates ashes from the combustion of subbituminous coals. These designations are based on the chemical composition of the fly ash in such a way that when the sum of the element oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) derived from chemical analysis of the ash is equal to or greater than 70% by weight, then the fly ash is designated a "Class F" fly ash. When the sum of the element oxides is equal to or greater than 50% by weight, the fly ash is designated as a "Class C" fly ash. In Canada, as mentioned above, fly ashes have certain designations based on their CaO content. In particular, a fly ash is considered a "Class F" when it includes less than 8% CaO, a "Class CI" when it includes 8-20% CaO, and a "Class CH" when it includes greater than 20% CaO.

The fly ash can be a lignite fly ash, a subbituminous fly ash, a bituminous fly ash, or a blend of two or more fly ashes (*e.g.*, a subbituminous/bituminous fly ash blend). The fly ash can be a Class C fly ash, a Class F fly ash, or a blend thereof. In certain embodiments, the particulate filler includes fly ash having an LOI ranging from 0.20% to 10% (*e.g.*, from 0.20% to 5.0%, or from 0.20% to 1.0%), a BET surface area ranging from 0.75 m²/g to 15 m²/g (*e.g.*, from 0.75 m²/g to 5.0 m²/g, or from 1.0 m²/g to 4.0 m²/g), and/or a BET surface area to LOI ratio ranging from 1.0 to 6.0 (*e.g.*, from 1.5 to 5.5, or from 2.0 to 5.0).

Other suitable fillers include, by way of example, graphite, activated carbon, amorphous carbon (*e.g.*, carbon black), absorptive clays (*e.g.*, absorptive silicate minerals such as kaolin), other combustion ashes (*e.g.*, ashes produced by firing one or more fuels including industrial gases, petroleum coke, petroleum products, municipal solid waste, paper sludge, wood, sawdust, refuse derived fuels, switchgrass, or other biomass material), glass particles, sand, granite dust,

slate dust, and combinations thereof. These fillers can be used alone, or in combination with fly ash. In some embodiments, the particulate filler consists of or consists essentially of fly ash.

The composites described herein can include at least 35% by weight particulate filler, based on the total weight of the composite (*e.g.*, at least 40% by weight, at least 45% by weight, 5 at least 50% by weight, at least 55% by weight, at least 60% by weight, at least 65% by weight, at least 70% by weight, at least 75% by weight, at least 80% by weight, or at least 85% by weight). In some embodiments, the composites can include 90% or less by weight particulate filler, based on the total weight of the composite (*e.g.*, less than 85% by weight, less than 80% by weight, less than 75% by weight, less than 70% by weight, less than 65% by weight, less than 10 60% by weight, less than 55% by weight, less than 50% by weight, less than 45% by weight, or less than 40% by weight).

The particulate filler can be present in the composition in an amount from any of the minimum values described above to any of the maximum values described above. For example the total amount of particulate filler in the composite material can range 35% to 90% by weight, 15 based on the total weight of the composition (*e.g.*, from 40% to 90% by weight, from 50% to 85% by weight, or from 60% to 80% by weight).

Additional Components

One or more catalysts are added to facilitate curing and can be used to control the curing 20 time of the polyurethane matrix. Examples of suitable catalysts include amine-containing catalysts (such as 1,4-diazabicyclo[2.2.2]octane (DABCO or triethylenediamine and tetramethylbutanediamine), tin catalysts (*e.g.*, an organotin catalyst such as dimethyltin oleate), as well mercury- and bismuth-containing catalysts. In some embodiments, 0.01 wt% to 2 wt% catalyst or catalyst system (*e.g.*, 0.025 wt% to 1 wt%, 0.05 wt% to 0.5 wt %, or 0.1 wt% to about 25 0.25 wt%), based on the total weight of the polyurethane, can be used.

Additional components useful with the composite materials described herein include additional fillers, foaming agents, blowing agents, surfactants, chain-extenders, crosslinkers, coupling agents, UV stabilizers, fire retardants, antimicrobials, anti-oxidants, and pigments. Though the use of such components is well known to those of skill in the art, some of these 30 additional additives are further described herein.

One or more additional fillers can be used in the composite materials described herein. Examples of additional fillers useful with the composite materials include other types of ash such as those produced by firing fuels including industrial gases, petroleum coke, petroleum products, municipal solid waste, paper sludge, wood, sawdust, refuse derived fuels, switchgrass

or other biomass material. The one of more additional fillers can also include ground/recycled glass (*e.g.*, window or bottle glass); milled glass; glass spheres; glass flakes; calcium carbonate; aluminum trihydrate (ATH); silica; sand; ground sand; silica fume; slate dust; crusher fines; red mud; mica; talc; wollastonite; alumina; feldspar; bentonite; quartz; garnet; saponite; beidellite; 5 granite; calcium oxide; calcium hydroxide; antimony trioxide; barium sulfate; magnesium oxide; titanium dioxide; zinc carbonate; zinc oxide; nepheline syenite; perlite; diatomite; pyrophyllite; flue gas desulfurization (FGD) material; soda ash; trona; inorganic fibers; soy meal; pulverized foam; and mixtures thereof.

In some embodiments, inorganic fibers or organic fibers can be included in the polymer 10 composite, *e.g.*, to provide increased strength, stiffness or toughness. Fibers suitable for use with the composite materials described herein can be provided in the form of individual fibers, fabrics, rovings, or tows. These can be added prior to polymerization and can be chopped before or during the mixing process to provide desired fiber lengths. Alternately, the fibers can be added after polymerization, for example, after the composite material exits the mixing apparatus. 15 The fibers can be up to about 2 in. in length. The fibers can be provided in a random orientation or can be axially oriented. The fibers can be coated with a sizing to modify performance to make the fibers reactive. Exemplary fibers include glass, polyvinyl alcohol (PVA), carbon, basalt, wollastonite, and natural (*e.g.*, bamboo or coconut) fibers.

The inclusion of additional fillers in the composite materials as described herein can 20 modify and/or improve the chemical and mechanical properties of the composite materials. For example, the optimization of various properties of the composite materials allows their use in building materials and other structural applications. High filler loading levels can be used in composite materials without a substantial reduction of (and potentially an improvement in) the intrinsic structural, physical, and mechanical properties of a composite. The use of filled 25 composites as building materials has advantages over composite materials made using lower filler levels or no filler. For example, the use of higher filler loading levels in building materials may allow the building materials to be produced at a substantially decreased cost.

Foaming agents and blowing agents may be added to the composite materials described herein to produce a foamed version of the composite materials. Examples of blowing agents 30 include organic blowing agents, such as halogenated hydrocarbons, acetone, pentanes, carbon dioxide, and other materials that have a boiling point below the reaction temperature. Chemical foaming agents include azodicarbonamides (*e.g.*, Celogen manufactured by Lion Copolymer Geismar); and other materials that react at the reaction temperature to form gases such as carbon

dioxide. Water is an exemplary foaming agent that reacts with isocyanate to yield carbon dioxide. The presence of water as an added component or in the filler also can result in the formation of polyurea bonds through the reaction of the water and isocyanate.

The addition of excess foaming or blowing agents above what is needed to complete the
5 foaming reaction can add strength and stiffness to the composite material, improve the water resistance of the composite material, and increase the thickness and durability of the outer skin of the composite material. Such excessive blowing agent may produce a vigorously foaming reaction product. To contain the reaction product, a forming device that contains the pressure or restrains the materials from expanding beyond the design limits may be used, such as a
10 stationary or continuous mold.

Surfactants can be used as wetting agents and to assist in mixing and dispersing the inorganic particulate material in a composite. Surfactants can also stabilize and control the size of bubbles formed during the foaming event and the resultant cell structure. Surfactants can be used, for example, in amounts below about 0.5 wt % based on the total weight of the mixture.
15 Examples of surfactants useful with the polyurethanes described herein include anionic, non-ionic and cationic surfactants. For example, silicone surfactants such as DC-197 and DC-193 (Air Products; Allentown, PA) can be used.

Low molecular weight reactants such as chain-extenders and/or crosslinkers can be included in the composite materials described herein. These reactants help the polyurethane
20 system to distribute and contain the inorganic filler and/or fibers within the composite material. Chain-extenders are difunctional molecules, such as diols or diamines, that can polymerize to lengthen the urethane polymer chains. Examples of chain-extenders include ethylene glycol; 1,4-butanediol; ethylene diamine, 4,4'-methylenebis(2-chloroaniline) (MBOCA); diethyltoluene diamine (DETDA); and aromatic diamines such as Unilink 4200 (commercially available from
25 UOP). Crosslinkers are tri- or greater functional molecules that can integrate into a polymer chain through two functionalities and provide one or more further functionalities (*i.e.*, linkage sites) to crosslink to additional polymer chains. Examples of crosslinkers include glycerin, trimethylolpropane, sorbitol, diethanolamine, and triethanolamine. In some composites, a crosslinker or chain-extender may be used to replace at least a portion of the at least one polyol
30 in the composite material. For example, the polyurethane can be formed by the reaction of an isocyanate, a polyol, and a crosslinker.

Coupling agents and other surface treatments such as viscosity reducers, flow control agents, or dispersing agents can be added directly to the filler or fiber, or incorporated prior to,

during, and/or after the mixing and reaction of the composite material. Coupling agents can allow higher filler loadings of an inorganic filler such as fly ash and may be used in small quantities. For example, the composite material may comprise about 0.01 wt % to about 0.5 wt % of a coupling agent. Examples of coupling agents useful with the composite materials
5 described herein include Ken-React LICA 38 and KEN-React KR 55 (Kenrich Petrochemicals; Bayonne, NJ). Examples of dispersing agents useful with the composite materials described herein include JEFFSPERSE X3202, JEFFSPERSE X3202RF, and JEFFSPERSE X3204 (Huntsman Polyurethanes; Geismar, LA).

Ultraviolet light stabilizers, such as UV absorbers, can be added to the composite
10 materials described herein. Examples of UV light stabilizers include hindered amine type stabilizers and opaque pigments. Fire retardants can be included to increase the flame or fire resistance of the composite material. Antimicrobials can be used to limit the growth of mildew and other organisms on the surface of the composite. Antioxidants, such as phenolic antioxidants, can also be added. Antioxidants provide increased UV protection, as well as
15 thermal oxidation protection.

Pigments or dyes can optionally be added to the composite materials described herein. An example of a pigment is iron oxide, which can be added in amounts ranging from about 2 wt % to about 7 wt %, based on the total weight of the composite material.

A method of preparing a composite material is also described herein. The method can
20 include mixing (1) a particulate filler; (2) at least one isocyanate selected from the group consisting of diisocyanates, polyisocyanates, and combinations thereof; (3) one or more polyols; and (4) a catalyst. The at least one isocyanate and the one or more polyols are allowed to react in the presence of the particulate filler and catalyst to form the composite material. In some cases, the one or more polyols can comprise a high hydroxyl number polyol having a hydroxyl
25 number of at least 250, and the one or more polyols can have a weight average equivalent weight of from 200 to 1100 amu. In some cases, the one or more polyols that form the polyurethane can comprise one or more rigid polyols having a hydroxyl number of at least 250, and the one or more polyols that form the polyurethane can include less than 5% by weight, based on the total weight of the one or more polyols that form the polyurethane, of one or more flexible polyols
30 having a hydroxyl number of less than 150 and a functionality of less than 3.

The composite material can be produced using a batch, semi-batch, or continuous process. At least a portion of the mixing step, reacting step, or both, can be conducted in a

mixing apparatus such as a high speed mixer or an extruder. The method can further include the step of extruding the resulting composite material through a die or nozzle.

In some embodiments, a mixing step of the method used to prepare the composite materials described herein includes: (1) mixing the particulate filler and the one or more polyols; (2) mixing the isocyanate with the particulate filler and the one or more polyols; and (3) mixing the catalyst with the isocyanate, the particulate filler, and the one or more polyols. In some embodiments, a mixing step of the method used to prepare the composite materials described herein includes mixing the liquid ingredients (*i.e.*, the one or more polyols, isocyanate, catalyst, surfactants, and water) and then combining the mixed liquid ingredients with the particulate filler and optional fiber. As the composite material exits the die or nozzle, the composite material may be placed in a mold for post-extrusion curing and shaping. For example, the composite material can be allowed to cure in individual molds or it can be allowed to cure in a continuous forming system such as a belt molding system.

An ultrasonic device can be used for enhanced mixing and/or wetting of the various components of the composite materials described herein. Such enhanced mixing and/or wetting can allow a high concentration of filler to be mixed with the polyurethane matrix. The ultrasonic device produces an ultrasound of a certain frequency that can be varied during the mixing and/or extrusion process. The ultrasonic device useful in the preparation of composite materials described herein can be attached to or adjacent to an extruder and/or mixer. For example, the ultrasonic device can be attached to a die or nozzle or to the port of an extruder or mixer. An ultrasonic device may provide de-aeration of undesired gas bubbles and better mixing for the other components, such as blowing agents, surfactants, and catalysts.

The composite materials described herein can be foamed. The one or more polyols and the isocyanate can be allowed to produce a foamed composite material after mixing the components according to the methods described herein. The composite materials described herein can be formed while they are actively foaming or after they have foamed. For example, the material can be placed under the pressure of a mold cavity prior to or during the foaming of the composite material. When a foaming composite material is molded by a belt molding system into a product shape, the pressure that the foamed part exerts on the belts impacts the resulting mechanical properties. For example, as the pressure of the foaming increases and if the belt system can hold this pressure without the belts separating, then the product may have higher flexural strength than if the belts allowed leaking or pressure drop.

The composite materials described herein can be formed into shaped articles and used in various applications including building materials. Examples of such building materials include siding material, roof coatings, roof tiles, roofing material, carpet backing, flexible or rigid foams such as automotive foams (*e.g.*, for dashboard, seats or roofing), component coating, and other
5 shaped articles. Examples of shaped articles made using composite materials described herein include roofing material such as roof tile shingles; siding material; trim boards; carpet backing; synthetic lumber; building panels; scaffolding; cast molded products; decking materials; fencing materials; marine lumber; doors; door parts; moldings; sills; stone; masonry; brick products; posts; signs; guard rails; retaining walls; park benches; tables; slats; and railroad ties. The
10 composite materials described herein further can be used as reinforcement of composite structural members including building materials such as doors; windows; furniture; and cabinets and for well and concrete repair. The composite materials described herein also can be used to fill gaps, particularly to increase the strength of solid surface articles and/or structural components. The composite materials can be flexible, semi-rigid or rigid foams. In some
15 embodiments, the flexible foam is reversibly deformable (*i.e.*, resilient) and can include open cells. A 8" x 1" x 1" piece of a flexible foam can generally wrap around a 1" diameter mandrel at room temperature without rupture or fracture. Flexible foams also generally have a density of less than 5 lb/ft³ (*e.g.*, 1 to 5 lb/ft³). In some embodiments, the rigid foam is irreversibly deformable and can be highly crosslinked and/or can include closed cells. Rigid foams generally
20 have a density of 1 lb/ft³ or greater (*e.g.*, 1 to 60 lb/ft³, 5 to 60 lb/ft³, 20 to 55 lb/ft³, or 30 to 50 lb/ft³).

The examples below are intended to further illustrate certain aspects of the compositions and methods described herein, and are not intended to limit the scope of the claims. All parts and percentages are provided on a per weight basis, unless indicated otherwise.

25

EXAMPLES

General Test Methods

Composite materials were characterized using the following test methods unless otherwise noted.

30

The flexural strength of a composite material was determined according to the method described in ASTM CI 185-08 (Reapproved 2012) entitled "Standard Test Methods for Sampling and Testing Non-Asbestos Fiber-Cement Flat Sheet, Roofing and Siding Shingles, and Clapboards," which is incorporated herein by reference in its entirety. *See* Section 5. Briefly, a

to measurement, the sample boards were conditioned for at least 48 hours at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. The average thickness of the sample boards was also measured as described in ASTM C1185-08, section 5.2.4. 1. For a given composite material, 4 - 6 samples
5 were made and tested and the results were averaged.

The bottom surface of each sample board was placed on supports spaced $10 \pm 1/16$ " apart. A load was applied to the top surface the sample board at the mid-span of the board. The deflection of the sample board upon a maximum applied load was then measured as described in ASTM C1185-08. The flexural strength of each sample board was then calculated using the
10 equation below

$$R = \frac{3PL}{2bd^2}$$

where R is the flexural strength (in psi), P is the maximum load (in lbs), L is the length of the span (in inches), b is the width of the sample board (in inches), and d is the average thickness of the sample board (in inches). The flexural strength of the composite material was the arithmetic
15 mean of the flexural strength measured for the sample boards formed from a composite material.

The density of a composite material was determined according to the method described in ASTM C1185-08 (Reapproved 2012) entitled "Standard Test Methods for Sampling and Testing Non-Asbestos Fiber-Cement Flat Sheet, Roofing and Siding Shingles, and Clapboards," which is incorporated herein by reference in its entirety. *See* Section 6.

20 The normalized flexural strength of a composite material was determined by dividing the flexural strength of the composite material, as determined using the method described above, by the density of the composite material, as determined using the method described above.

Preparation and Characterization of Composite Materials

Composites 1-8 were prepared using eight different polyol blends, each with varying
25 functionality and weight average equivalent weight of polyol components. *See* Table 1. For each trial, a polyol blend was prepared by mixing the polyol components with 1% water, 2% TEGOSTAB® B-8870 surfactant (commercially available from Evonik Industries AG, Essen, Germany), and 0.1% POLYCAT® 8 catalyst (commercially available from Air Products and Chemicals, Allentown, PA) at a quantity to make at least 6 samples. Each sample was prepared
30 using 175 g of fly ash and 175 g of a given polyol blend and RUBINATE® M isocyanate (31.5% NCO, commercially available from Huntsman Corporation, Salt Lake City, UT) at the calculated ratio to give 104 index. The fly ash was wetted with the polyol blend in a 1-liter cup.

The RUBINATE® M was added, and the components were mixed for 12 seconds with a drill press. The mixture was quickly poured into a ¾" x 3 ½" x 15" mold and the lid was then closed and clamped. After 6 minutes, the sample was removed and conditioned as described above before testing.

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Table 1. Polyol Components of Composites 1-8.

Trial	Functionality	Weight Average Equivalent Weight of Polyol Components (amu)	Polyol Components [†]
1	2	210	¹ CARPOL® PGP-400 (96.67%) ² CARPOL® PGP-1000 (3.33%)
2	5	217.4	³ CARPOL® SPA-530 (80%) ⁴ CARPOL® GP-2012 (20%)
3	2	1100	⁵ VORANOL® 222-056N (90%) ⁶ CARPOL® PGP-4025 (10%)
4	5	1100	⁷ CARPOL® GSP-280 (50%) ⁸ CARPOL® GP-6015 (50%)
5	2	212.2	¹ CARPOL® PGP-400 (50%) ⁹ TEROL® 250 (50%)
6	5	209.6	⁹ TEROL® 250 (40%) ⁷ CARPOL® GSP-280 (60%)
7	2	1100.59	⁶ CARPOL® PGP-4025 (47%) ¹⁰ TEROL® 198 (53%)
8	3.5	655	⁷ CARPOL® GSP-280 (25%) ⁸ CARPOL® GP-6015 (25%) ¹ CARPOL® PGP-400 (25%) ⁹ TEROL® 250 (25%)

[†] Percentage in parentheses following each polyol component is the weight percent of the polyol component in the polyol blend used to form the polyurethane, based on the total weight of all of the polyols that form the polyurethane.

¹ Propylene glycol-based polyether polyol; available from Carpenter Co., Richmond, VA

² Propylene glycol-based polyether polyol; available from Carpenter Co., Richmond, VA

³ Sucrose/amine-based polyether polyol; available from Carpenter Co., Richmond, VA

⁴ Alkylene oxide-capped glycerine; available from Carpenter Co., Richmond, VA

⁵ Propylene glycol-based polyether polyol; available from The Dow Chemical Company, Midland, MI

⁶ Alkylene oxide-capped propylene glycol-based polyether polyol; available from Carpenter Co., Richmond, VA

⁷ Sucrose-based polyether polyol; available from Carpenter Co., Richmond, VA

⁸ Glycerine-based polyether polyol; available from Carpenter Co., Richmond, VA

⁹ Aromatic polyester polyol; available from Huntsman Corporation, Salt Lake City, UT

¹⁰ Aromatic polyester polyol; available from Huntsman Corporation, Salt Lake City, UT

The flexural strength and density of Composites 1-8 were measured using the standard methods described above. As shown in Table 2 and Figure 1, composites prepared from at least 95% by weight, based on the total weight of the polyols that form the polyurethane, of one or more rigid polyols having a hydroxyl number of at least 250 (Trials 1, 2, 5, and 6) exhibit high flexural strengths ranging from 604.08 to 714.73 psi. In contrast, composites prepared from polyol blends that include a flexible polyol exhibit significantly lower flexural strengths (e.g., flexural strengths ranging from 111.95 to 415.88 psi). As shown in Table 2 and Figure 2, Composites 1-8 exhibit densities ranging from 19.62 to 23.93 lbs/cu ft.

10 **Table 2. Flexural strength, density, and normalized flexural strength of Composites 1-8.**

Trial	Flexural Strength (psi)	Density (lbs/cu ft)	Normalized Flexural Strength
1	627.23	20.45	30.67
2	604.08	23.93	25.24
3	111.95	21.83	5.13
4	378.97	22.64	16.74
5	714.73	22.88	31.24
6	668.60	23.43	28.54
7	323.13	19.62	16.47
8	415.88	21.07	19.74

The normalized flexural strength of Composites 1-8 was calculated as described above. As shown in Table 2 and Figure 3, composites prepared from at least 95% by weight, based on the total weight of the polyols that form the polyurethane, of one or more rigid polyols having a hydroxyl number of at least 250 (Trials 1, 2, 5, and 6) exhibit high normalized flexural strengths ranging from 25.24 to 31.24. In contrast, composites prepared from polyol blends that include a flexible polyol exhibit significantly lower normalized flexural strengths (e.g., normalized flexural strengths ranging from 5.13 to 19.74).

20 These results suggest that when preparing highly filled polyurethane composites (e.g., composites that include from 35% to 90% by weight particulate filler, based on the total weight of the composition), flexible polyols are not needed to prepare composite materials having a high flexural strength. On the contrary, composite materials having improved flexural strength can be prepared from polyol blends that include less than 5% by weight of one or more flexible polyols, based on the total weight of the polyol blend used to form the polyurethane.

The composites, materials and methods of the appended claims are not limited in scope by the specific composites and methods described herein, which are intended as illustrations of a few aspects of the claims and any composites, materials, and methods that are functionally equivalent are intended to fall within the scope of the claims. Various modifications of the composites, materials and methods in addition to those shown and described herein are intended to fall within the scope of the appended claims. Further, while only certain representative composites, materials, and method steps disclosed herein are specifically described, other combinations of the composite materials and method steps also are intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein; however, other combinations of steps, elements, components, and constituents are included, even though not explicitly stated. The term "comprising" and variations thereof as used herein is used synonymously with the term "including" and variations thereof and are open, non-limiting terms. Although the terms "comprising" and "including" have been used herein to describe various embodiments, the terms "consisting essentially of" and "consisting of" can be used in place of "comprising" and "including" to provide for more specific embodiments of the invention and are also disclosed.

THAT WHICH IS CLAIMED:

1. A composite comprising:
 - (a) a polyurethane formed by the reaction of (i) one or more isocyanates selected from the group consisting of diisocyanates, polyisocyanates, and mixtures thereof, and (ii) one or more polyols,
 - wherein the one or more polyols that form the polyurethane comprise a high hydroxyl number polyol having a hydroxyl number of at least 250 mg KOH/g, and
 - wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 1100 amu; and
 - (b) from 35% to 90% by weight, based on the total weight of the composite, of a particulate filler.
2. The composite of claim 1, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 600 amu.
3. The composite of any of claims 1-2, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 300 amu.
4. The composite of any of claims 1-3, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 250 amu.
5. The composite of any of claims 1-4, wherein the one or more polyols that form the polyurethane comprise at least 95% by weight, based on the total weight of the polyols that form the polyurethane, one or more high hydroxyl number polyols having a hydroxyl number of at least 250 mg KOH/g.
6. The composite of any of claims 1-5, wherein the one or more polyols that form the polyurethane consist of one or more high hydroxyl number polyols having a hydroxyl number of at least 250 mg KOH/g.
7. The composite of any of claims 1-6, wherein the high hydroxyl number polyols have a functionality of from 2 to 6.

8. The composite of any of claims 1-7, wherein **the** one or more polyols that form **the polyurethane** satisfy Eq. 1 below

$$(2.1)(F) + (0.3)(EW) - (0.036)(F)(EW) \geq 12 \quad \text{Eq. 1}$$

wherein

F is the weight average functionality of the one or more polyols that form the polyurethane; and

EW is the weight average equivalent weight of the one or more polyols **that** form the polyurethane.

9. The composite **of** any of claims 1-8, wherein the one or more polyols that form the polyurethane satisfy Eq. 2 below

$$(2.1)(F) + (0.3)(EW) - (0.036)(F)(EW) \geq 15 \quad \text{Eq. 2}$$

wherein

F is the weight average functionality of the one or more polyols that form the polyurethane; and

EW is the weight average equivalent weight of the one or more polyols that form the polyurethane.

10. The composite of any of claims 1-9, wherein the particulate filler comprises an inorganic filler.

11. The composite of claim 10, wherein the inorganic filler comprises **fly ash**.

12. The composite of any **of claims 1-11, wherein** the composite comprises from 45% to 70% by weight, based on the total weight of the composite, of the particulate filler.

13. The composite of any of claims 1-12, wherein the composite **further** comprises fibers.

14. The composite **of any of claims 1-13, wherein** the composite exhibits a normalized flexural strength of at least 20.

15. The composite of any of claims 1-14, wherein the composite exhibits a normalized **flexural** strength of from 20 to 50.

16. The composite of any of claims 1-15, wherein the composite exhibits a normalized flexural strength of from 25 to 35.
17. A composite comprising:
- (a) a polyurethane formed by the reaction of (i) one or more isocyanates selected from the group consisting of diisocyanates, polyisocyanates, and mixtures thereof, and (ii) one or more polyols,
 - wherein the one or more polyols that form the polyurethane comprise one or more rigid polyols having a hydroxyl number of at least 250 mg KOH/g, and
 - wherein the one or more polyols that form the polyurethane include less than 5% by weight, based on the total weight of the one or more polyols that form the polyurethane, of one or more flexible polyols having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3; and
 - (b) from 35% to 90% by weight, based on the total weight of the composite, of a particulate filler.
18. The composite of claim 17, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 1100 amu.
19. The composite of any of claims 17-18, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 600 amu.
20. The composite of any of claims 17-19, wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 300 amu.
21. The composite of any of claims 17-20, wherein the one or more polyols that form the polyurethane include at least 95% by weight, based on the total weight of the one or more polyols that form the polyurethane, of one or more rigid polyols having a hydroxyl number of at least 250 mg KOH/g.
22. The composite of any of claims 17-21, wherein the one or more polyols that form the polyurethane include less than 1% by weight, based on the total weight of the one or more

polyois that form the polyurethane, of one or more flexible polyois having a hydroxyi number of less than 150 mg KOH/g and a functionality of less than 3.

23. The composite of any of claims 17-22, wherein the one or more polyois that form the polyurethane do not include one or more flexible polyois having a hydroxyi number of less than 150 mg KOH/g and a functionality of less than 3.

24. The composite of any of claims 17-23, wherein the one or more rigid polyois have a functionality of from 2 to 6.

25. The composite of any of claims 17-24, wherein the one or more polyois that form the polyurethane satisfy Eq. 1 below

$$(2.1)(F) + (0.3)(EW) - (0.0036)(f)(EW) \geq 12 \quad \text{Eq. 1}$$

wherein

F is the weight average functionality of the one or more polyois that form the polyurethane; and

EW is the weight average equivalent weight of the one or more polyois that form the polyurethane.

26. The composite of any of claims 17-25, wherein the one or more polyois that form the polyurethane satisfy Eq. 2 below

$$(2.1)(F) + (0.3)(EW) - (0.0036)(F)(EW) \geq 15 \quad \text{Eq. 2}$$

wherein

F is the weight average functionality of the one or more polyois that form the polyurethane; and

EW is the weight average equivalent weight of the one or more polyois that form the polyurethane.

27. The composite of any of claims 17-26, wherein the particulate filler comprises an inorganic filler.

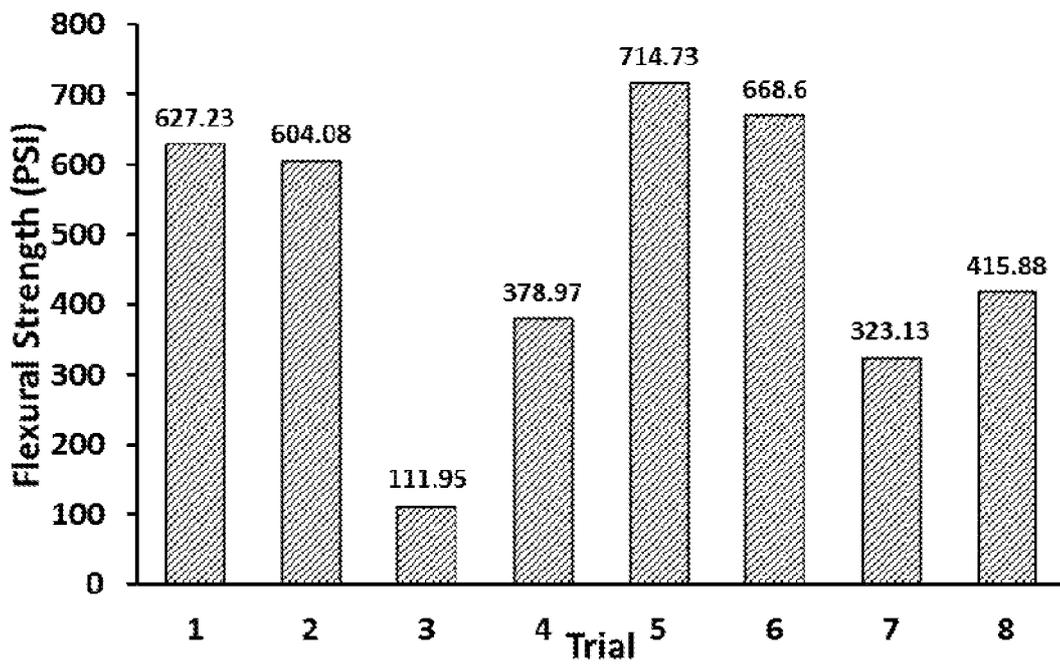
28. The composite of claim 27, wherein the inorganic filler comprises fly ash.

29. The composite of any of claims 17-28, wherein the composite comprises from 45% to 70% by weight, based on the total weight of the composite, of the particulate filler.
30. The composite of any of claims 17-29, wherein the composite further comprises fibers.
31. The composite of any of claims 17-30, wherein the composite exhibits a normalized flexural strength of at least 20.
32. The composite of any of claims 17-31, wherein the composite exhibits a normalized flexural strength of from 20 to 50.
33. The composite of any of claims 17-32, wherein the composite exhibits a normalized flexural strength of from 25 to 35.
34. A method of preparing a composite material, comprising:
mixing (1) a particulate filler; (2) at least one isocyanate selected from the group consisting of diisocyanates, polyisocyanates, and combinations thereof; (3) one or more polyols, wherein the one or more polyols that form the polyurethane comprise a high hydroxyl number polyol having a hydroxyl number of at least 250 mg KOH/g, and wherein the one or more polyols that form the polyurethane have a weight average equivalent weight of from 200 to 1100 amu; and (4) a catalyst; and
allowing the at least one isocyanate and the one or more polyols to react in the presence of the particulate filler and the catalyst to form the composite material.
35. A method of preparing a composite material, comprising:
mixing (1) a particulate filler; (2) at least one isocyanate selected from the group consisting of diisocyanates, polyisocyanates, and combinations thereof; (3) one or more polyols, wherein the one or more polyols that form the polyurethane comprise one or more rigid polyols having a hydroxyl number of at least 250 mg KOH/g, and wherein the one or more polyols that form the polyurethane include less than 5% by weight, based on the total weight of the one or more polyols that form the polyurethane, of one or more flexible polyols having a hydroxyl number of less than 150 mg KOH/g and a functionality of less than 3; and (4) a catalyst; and

allowing the at least one isocyanate and the one or more polyols to react in the presence of the particulate filler and the catalyst to form the composite material.

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Figure 1

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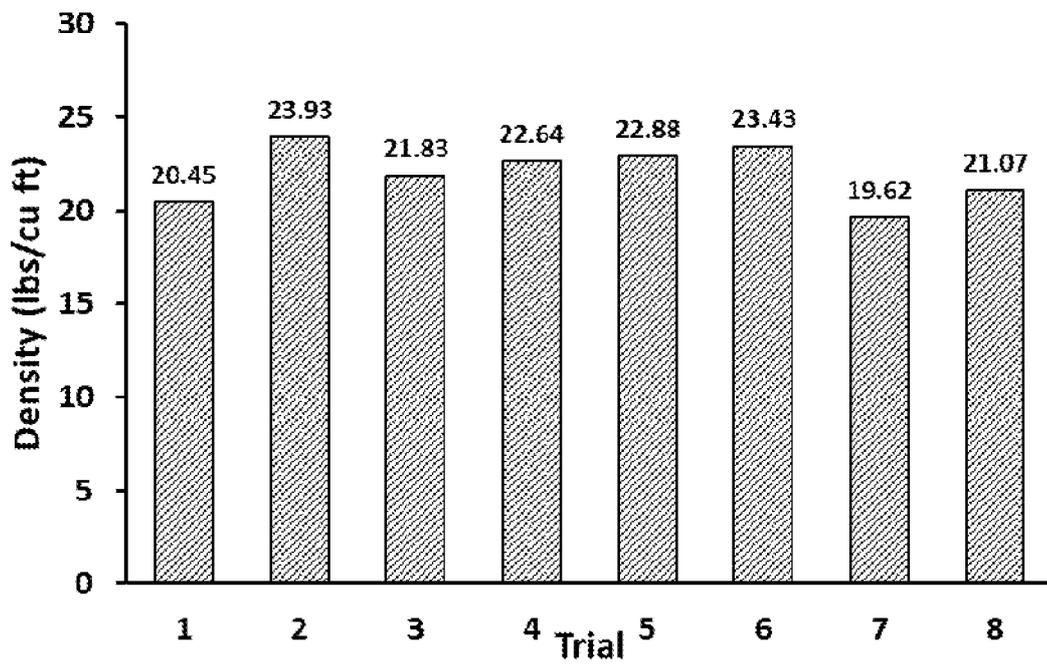


Figure 2

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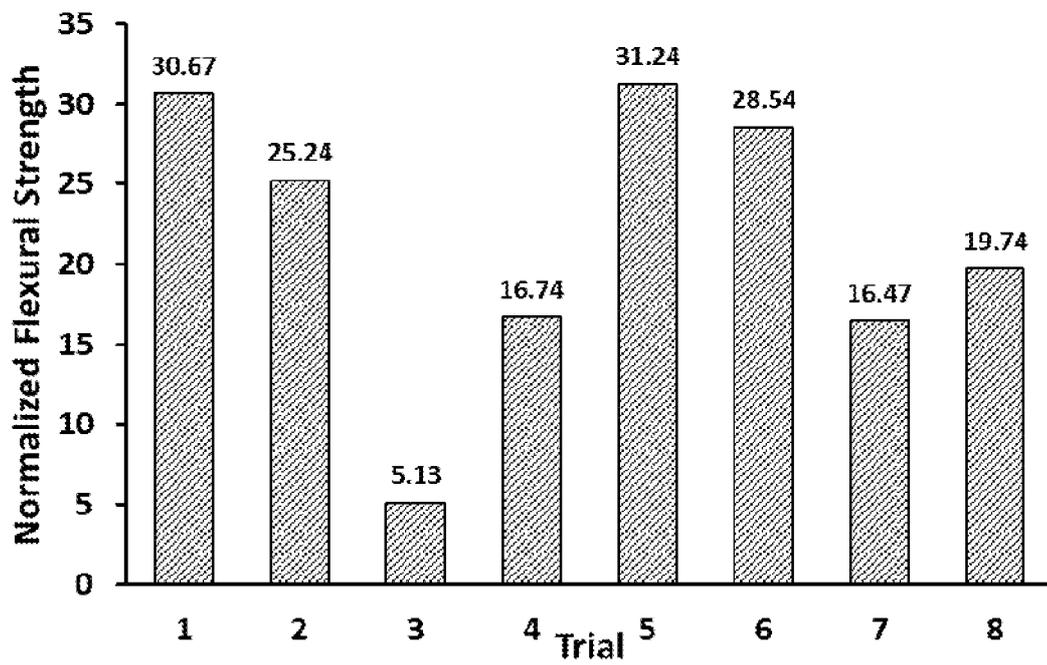


Figure 3

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/012453**A. CLASSIFICATION OF SUBJECT MATTER****C08L 75/04(2006.01)i, C08K 3/00(2006.01)i, C08G 18/28(2006.01)i**

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)

C08L 75/04; C08G 18/14; B05D 3/00; C08K 11/00; B32B 27/06; C08G 18/66; C08G 18/48; C08K 3/00; C08G 18/28

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polyurethane, isocyanate, polyol, hydroxyl number, average equivalent weight, particulate filler, catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ¹⁾	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010-0292397 A1 (BROWN, WADE) 18 November 2010 See abstract; paragraphs [0013H0026], [0029], [0033]-[0036], [0046] and [0053]-[0056]; and claims 1 and 11.	1-3,17-19,34-35
A	US 4005035 A (DEAVER, DANN T.) 25 January 1977 See abstract; column 7, line 35 - column 8, line 10; and claim 1.	1-3,17-19,34-35
A	WO 01-18087 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 15 March 2001 See claims 1-11; example V, and Table 1.	1-3,17-19,34-35
A	US 2011-0059319 A1 (RADAY, ROBERT MICHAEL) 10 March 2011 See abstract; paragraphs [0026] and [0073]-[0075]; and claims 1 and 11.	1-3,17-19,34-35
A	US 2011-0086934 A1 (HERRINGTON, RONALD M. et al.) 14 April 2011 See abstract; paragraphs [0003], [0017] and [0036]; claim V, and Table 1.	1-3,17-19,34-35

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

10 September 2015 (10.09.2015)

Date of mailing of the international search report

10 September 2015 (10.09.2015)

Name and mailing address of the ISA/KR



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/012453

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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