

METHOD OF PREPARING A MICROCRYSTALLINE CELLULOSE REINFORCED POLYMER COMPOSITE

TECHNICAL FIELD

5 [0001] Various embodiments relate to a method of preparing microcrystalline cellulose reinforced polymer composite, and microcrystalline cellulose reinforced polymer composite prepared by the method.

BACKGROUND

10 [0002] In recent years, biomaterial-based reinforced polymeric composites have found applications in various fields ranging from biomedical industry, to automotive or construction industry. By using cellulosic fillers, it is possible to significantly improve mechanical properties of polymers, including plastic materials. High-strength cellulose materials are particularly suitable for this purpose, as they exhibit outstanding mechanical properties,
15 appear to be toxicologically benign, and may be produced sustainably from renewable raw materials.

[0003] To achieve effective reinforcement, however, homogeneous dispersion of the cellulosic materials in nanocomposite materials is the primary requirement. A key challenge concerns the hydrophobicity of polyolefins such as polypropylene (PP), as it has
20 compatibility issues when fillers with polar surfaces, such as cellulose, are used. Furthermore, other problems which may prevent successful melt-compounding of cellulosic materials with polymers relate to mechanical degradation of the cellulosic materials under high shear forces applied during thermoplastic compounding, and thermal degradation of the cellulosic materials during melt processing at elevated temperatures.

25 [0004] Various methods of producing biomaterial-based reinforced polymeric composites have been developed. Such methods, however, do not resolve the issues highlighted above or are not carried out in a cost effective manner. Notably, the methods require additional processing steps or modifications to improve dispersion stability of cellulosic materials in hydrophobic polyolefins.

30 [0005] For example, in one reported method for dispersing cellulose in a polymer resin, multiple steps that involve chemical modification of cellulosic materials were carried out.

The cellulose was oxidized to have a carboxyl group (-COOH) content of 0.1 to 3 mmol/g, and after oxidation, surfactants were introduced for chemical adsorption onto the cellulose, before mixing the oxidized cellulose with the resin, for improved stability for dispersing cellulosic materials in a polymer resin.

5 [0006] In another reported method, cellulosic fibers were incorporated into a fiber-reinforced polypropylene resin through a compounding process, whereby a pelleting step was carried out on the cellulosic fibers to form cellulosic fiber pellets to facilitate dispersion. Not only does this method require the cellulosic fibers to undergo an additional pelleting step, it also fails to address the degradation issues mentioned above.

10 [0007] In view of the above, there exists a need for improved methods to prepare polymer composite materials that overcome or at least alleviate one or more of the above-mentioned problems.

SUMMARY

15 [0008] In a first aspect, there is provided for a method of preparing a microcrystalline cellulose reinforced polymer composite, the method comprising

- a) providing discrete pieces of a microcrystalline cellulose,
- b) mixing the discrete pieces of the microcrystalline cellulose with a first polyolefin in an organic solvent under agitation, wherein the first polyolefin
20 dissolves at least substantially in the organic solvent and the discrete pieces of the microcrystalline cellulose disperse in the organic solvent, to form a dispersion, and
- c) precipitating the microcrystalline cellulose reinforced polymer composite from the dispersion using a non-solvent.

25 [0009] In another aspect, there is provided for a microcrystalline cellulose reinforced polymer composite prepared by a method according to the first aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The invention will be better understood with reference to the detailed description
30 when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0011] **FIG. 1A** is a scanning electron microscope (SEM) image of microcrystalline cellulose (MCC). Scale bar denotes 100 μm .

[0012] **FIG. 1B** is a SEM image of microcrystalline cellulose (MCC) after pre-processing (i.e. after jet-milling). Scale bar denotes 10 μm .

5 [0013] **FIG. 2A** is a SEM image of PP/MCC 5 wt% prepared by direct mixing. Scale bar denotes 100 μm . PP represents polypropylene, and MCC represents microcrystalline cellulose.

[0014] **FIG. 2B** is a SEM image of PP/MCC 5 wt% prepared by direct mixing. Scale bar denotes 10 μm .

10 [0015] **FIG. 2C** is a SEM image of 5 wt% jMCC, which was obtained from diluting master batch PP/jMCC composite. Scale bar denotes 100 μm . jMCC represents jet milled microcrystalline cellulose.

[0016] **FIG. 2D** is a SEM image of 5 wt% jMCC, which was obtained from diluting master batch PP/jMCC composite. Scale bar denotes 10 μm .

15 [0017] **FIG. 3** is a photograph of 5 wt% jMCC/PP diluted master batch composite.

[0018] **FIG. 4A** is a SEM image of microcrystalline cellulose before pre-processing. Scale bar denotes 100 μm .

[0019] **FIG. 4B** is a SEM image of microcrystalline cellulose after pre-processing (i.e. after jet-milling). Scale bar denotes 10 μm .

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DETAILED DESCRIPTION

[0020] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced.

25 [0021] Various embodiments refer in a first aspect to a method of preparing a microcrystalline cellulose reinforced polymer composite. The method comprises providing discrete pieces of a microcrystalline cellulose, mixing the discrete pieces of the microcrystalline cellulose with a first polyolefin in an organic solvent under agitation, wherein the first polyolefin dissolves at least substantially in the organic solvent and the
30 discrete pieces of the microcrystalline cellulose disperse in the organic solvent, to form a

dispersion, and precipitating the microcrystalline cellulose reinforced polymer composite from the dispersion using a non-solvent.

[0022] Homogeneous dispersion of microcrystalline cellulose in polymers is a primary requirement for fillers of microcrystalline cellulose to effectively reinforce the polymers and enhance the polymers' mechanical properties. Even though fillers of microcrystalline cellulose have polar surfaces with -OH groups capable of forming hydrogen bonds, given that hydrophobic polymers do not have -OH groups nor form hydrogen bonds, the fillers of microcrystalline cellulose may end up forming aggregates when they are being incorporated into hydrophobic polymers due to their incompatibility. As the fillers aggregate instead of dispersing homogenously in the hydrophobic polymers, the aggregates may become a material defect that does not reinforce, but instead compromises the mechanical integrity of the polymer composite. Generally, interfacial interaction (e.g. adhesion) between the fillers and hydrophobic polymers are adversely affected when aggregates form. An example of microcrystalline cellulose fillers aggregation may be seen when fillers of microcrystalline cellulose are incorporated into a hydrophobic polymer such as polypropylene (PP) to form a PP/MCCs polymer composite.

[0023] Advantageously, various embodiments according to a method disclosed herein are able to address compatibility issues relating to use of hydrophobic polymers such as polyolefins and fillers of microcrystalline cellulose (MCCs), resulting in formation of microcrystalline cellulose reinforced polymer composite with improved mechanical properties. In this regard, microcrystalline cellulose was surprisingly found by the present inventors to be more cost effective for preparing microcrystalline cellulose reinforced polymer composite, as compared to other cellulose materials such as cellulose nanocrystal (CNC), which refers generally to cellulose having a nearly perfect crystalline structure. The cost effectiveness of using microcrystalline cellulose may be due to avoidance of additional processing steps which are required to produce the other cellulose materials. For example, to form CNC, an extraction process to extract highly ordered, crystalline regions from natural bulk cellulose microfibrils, which further contains disordered amorphous regions, is required. Furthermore, since CNC is typically produced with the use of sulfuric acid, and such CNC has sulfate ester groups on its surface, CNC then requires additional treatment before mixing

with a polyolefin, and this additional treatment increases the cost of using CNC for forming a cellulose reinforced polymer composite.

[0024] Microcrystalline cellulose, on the other hand, may suffer from issues such as non-homogenous dispersion (e.g. aggregation) in hydrophobic polymers like other cellulosic materials. As mentioned above, this may be due to presence of polar hydroxyl (-OH) groups on microcrystalline cellulose, which results in difficulties in dispersing of the microcrystalline cellulose in the non-polar hydrophobic polymers. As the aggregates provide lower surface area and interfacial interaction, this may lead to weaker or defective regions of the nanocomposites. To this end, various embodiments according to the method disclosed herein are able to address these issues using an approach that improves (1) the dispersion of microcrystalline cellulose fillers in hydrophobic polymers and (2) the interfacial interaction between the hydrophobic polymers and microcrystalline cellulose fillers by creating, for example, higher surface area and surface roughness of the microcrystalline cellulose fillers to provide more interactions between the hydrophobic polymers and microcrystalline cellulose fillers. The improved interfacial interaction in turn promotes adhesion between the hydrophobic polymers and microcrystalline cellulose fillers. In so doing, this avoids the need for further processing using methods, and/or is different from methods, such as chemical modification to introduce functional groups on the hydrophobic polymers and/or microcrystalline cellulose fillers required in state of the art methods to achieve improved interfacial interaction through hydrogen and/or covalent bonding.

[0025] Advantageously, the improved interfacial interaction due to improved surface area and/or surface roughness of the microcrystalline cellulose filler is able to address or at least alleviate above-mentioned problems relating to presence of polar hydroxyl (-OH) groups on microcrystalline cellulose, which results in difficulties in dispersing the microcrystalline cellulose in the non-polar hydrophobic polymers.

[0026] To improve dispersion of microcrystalline cellulose fillers in hydrophobic polymers, for example, various embodiments disclosed herein involve use of a jet milling process to treat microcrystalline cellulose particles. This means that streams of high velocity compressed gas may be applied to mill the microcrystalline cellulose, which reduce the size, alter the shape, and/or increase the surface area and surface roughness of the microcrystalline cellulose particles. Since the grain size distribution of jet milled microcrystalline cellulose is

usually narrower than that of mechanical mills and with the improved size homogeneity, polymer composites of considerably better uniform mechanical properties may be prepared. Subsequently, the milled microcrystalline cellulose particles may be dispersed in an organic solvent and mixed with a first hydrophobic polymer such as a polyolefin or a hydrocarbon polyolefin to form the microcrystalline cellulose reinforced polymer composite.

[0027] Furthermore, mixing of the microcrystalline cellulose with the first hydrophobic polymer in the present method may circumvent problems relating to degradation of microcrystalline cellulose that may arise during extrusion or compounding processes due to high shear forces and elevated temperatures (i.e. more than 180 °C) that are applied, respectively. Through mixing of the milled microcrystalline cellulose and the first hydrophobic polymer, the first hydrophobic polymer may coat the microcrystalline cellulose, and this may help to prevent the coated microcrystalline cellulose from degrading under high shear forces and/or elevated temperatures in subsequent mechanical processing. In various embodiments, the coated microcrystalline cellulose may even be processed under harsher conditions such as at a temperature of greater than 180 °C or 190 °C, which are typical temperatures at which microcrystalline cellulose degrades, without degradation of the microcrystalline cellulose.

[0028] With the above in mind, various embodiments refer in a first aspect to a method of preparing a microcrystalline cellulose reinforced polymer composite.

[0029] As used herein, the term "cellulose" refers to a linear polysaccharide polymer composed of β -1,4 linked D- glucose molecules, and which is a major component of plant cell walls. The term "microcrystalline cellulose", on the other hand, refers to a purified, partially depolymerized cellulose, which may be prepared by treating alpha-cellulose obtained as a pulp from fibrous plant material. Accordingly, the term "microcrystalline cellulose" as used herein does not include cellulose obtained directly as a pulp from fibrous plant material. Treating of the alpha-cellulose may, for example, be carried out using a mineral acid such as hydrochloric acid. The degree of polymerization is typically less than 400.

[0030] The method may comprise providing discrete pieces of a microcrystalline cellulose. The phrase "discrete pieces" as used herein refers to each piece of a material that constitutes an individually distinct piece of its own. To form discrete pieces of the

microcrystalline cellulose, the microcrystalline cellulose may be subjected to any suitable size reduction process, which may avoid mechanical and thermal degradations of the microcrystalline cellulose and result in a narrow particle size distribution. An example of such a suitable size reduction process may be jet milling, otherwise termed as air jet milling or fluid energy milling.

[0031] According to various embodiments, providing the discrete pieces of the microcrystalline cellulose may comprise jet milling the microcrystalline cellulose. In jet milling, the microcrystalline cellulose may be exposed to streams of high velocity compressed gas in a chamber. The gas may be air or other gas that aids in milling of the microcrystalline cellulose. Using energy from such high velocity compressed gas, the microcrystalline cellulose may be milled into discrete pieces. Additionally, jet milling may also increase surface area and surface roughness, and/or alter the shape of the microcrystalline cellulose.

[0032] Advantageously, discrete pieces of microcrystalline cellulose having reduced sizes allow for more homogenous dispersion of microcrystalline cellulose in hydrophobic polymers, for example, a polyolefin such as polypropylene exemplified herein, and improved interfacial interactions between the microcrystalline cellulose and hydrophobic polymers. Moreover, due to sifting effect of jet mills, screening is unnecessary, as the oversize fraction is usually less than 1 % of the particle size distribution.

[0033] As mentioned above, the grain size distribution of the discrete pieces in a jet mill is usually narrower than that of mechanical mills. As a result of improved size homogeneity, polymer composites of considerably better uniform mechanical properties such as elongation at yield and at break, flexural modulus, and heat deflection temperature, may be prepared.

[0034] In various embodiments, jet milling may result in each discrete piece of the microcrystalline cellulose having a size of 100 μm or less, preferably in the range of 2 μm to 100 μm and more preferably in the range of 2 μm to 20 μm . Jet milling may also result in a size of less than 20 μm , less than 10 μm , or less than 5 μm . The term “size” as used herein refers to the maximum length of a particle (e.g. each discrete piece of microcrystalline cellulose) that is measured from one point to another across the center of the particle.

[0035] After reducing the size of the microcrystalline cellulose, the discrete pieces of microcrystalline cellulose may be mixed with a first hydrophobic polymer, for example, a

first polyolefin, in an organic solvent under agitation according to various embodiments. In specific embodiments, the microcrystalline cellulose may be mixed with a first polyolefin in an organic solvent under agitation.

[0036] The first polyolefin may be dissolved at least substantially in the organic solvent, while the discrete pieces of microcrystalline cellulose may be dispersed in the organic solvent, to form a dispersion. By the term “at least substantially”, it means that at least 90 wt%, such as at least 92 wt%, 95 wt%, 99 wt % or 100 wt % of the added first polyolefin dissolves in the organic solvent. In other words, the microcrystalline cellulose may not be dissolved in the organic solvent, and remains as discrete pieces within the polymeric solution formed by the dissolved first polyolefin in the organic solvent. In some embodiments, the first polyolefin is completely dissolved in the organic solvent.

[0037] The microcrystalline cellulose and the first polyolefin may be added at the same time or in a sequential manner to the organic solvent. In some embodiments, the microcrystalline cellulose and the first polyolefin may each be added separately to an organic solvent, to respectively form a dispersion containing the microcrystalline cellulose in the organic solvent and a polymeric solution containing the first polyolefin dissolved in the organic solvent, before mixing the dispersion and the polymeric solution together. The mixing may be carried out to facilitate homogenous dispersion of the microcrystalline cellulose in the polymer composite, which effectively reinforces the polymer composite's mechanical properties. Agitation during mixing may prevent aggregation of discrete pieces of the microcrystalline cellulose.

[0038] Generally, any organic solvent which is able to at least substantially dissolve the first polyolefin, while dispersing the microcrystalline cellulose therein, may be used. In various embodiments, the organic solvent may be selected from the group consisting of xylene, toluene, and a mixture thereof. In certain embodiments, the organic solvent is xylene.

[0039] In various embodiments, the discrete pieces of microcrystalline cellulose may be mixed with the organic solvent to obtain a concentration of 0.05 g/mL to 0.15 g/mL, 0.1 g/mL to 0.15 g/mL, or 0.05 g/mL to 0.1 g/mL. In other words, the concentration of the microcrystalline cellulose in the organic solvent may be 0.05 g/mL to 0.15 g/mL, 0.1 g/mL to 0.15 g/mL, or 0.05 g/mL to 0.1 g/mL, in various embodiments. Advantageously, a concentration in such ranges allows for further dilution in subsequent use, which in turn

allows for easier transport of the dispersion since the dilution, e.g. adding more organic solvent, can be carried out later. In certain embodiments, concentration of the microcrystalline cellulose in the organic solvent is 0.1 g/mL.

[0040] Regarding the concentration between the first polyolefin and microcrystalline cellulose, the concentration of the first polyolefin in the dispersion may be 1:10 w/v to 2:10 w/v, 1.5:10 w/v to 2:10 w/v, or 1:10 w/v to 1.5:10 w/v, of the microcrystalline cellulose to the first polyolefin. In specific embodiments, the concentration of the first polyolefin in the dispersion may be 1:10 w/v of the microcrystalline cellulose to the first polyolefin.

[0041] The mixing of the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may be carried out at a temperature in the range of 100 °C to 150 °C, 110 °C to 150 °C, 120 °C to 150 °C, 130 °C to 150 °C, 140 °C to 150 °C, 100 °C to 140 °C, 110 °C to 140 °C, 120 °C to 140 °C, 100 °C to 130 °C, 110 °C to 130 °C, 120 °C to 130 °C, 100 °C to 120 °C, 110 °C to 120 °C, or 100 °C to 110 °C, according to various embodiments. In some embodiments, the mixing may be carried out at a temperature of 120 °C.

[0042] In various embodiments, the mixing of the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may be carried out for a time period in the range of 1 hour to 5 hours, 2 hours to 5 hours, 3 hours to 5 hours, 4 hours to 5 hours, 1 hour to 4 hours, 2 hours to 4 hours, 3 hours to 4 hours, 1 hour to 3 hours, 2 hours to 3 hours, or 1 hour to 2 hours. In specific embodiments, the mixing of discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may be carried out for a time period of 3 hours.

[0043] Apart from the concentrations of materials, temperatures and durations described above, mixing of the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may be advantageously carried out without a dispersant for various embodiments. The present method, accordingly, circumvents the use of dispersant to achieve homogenous dispersion of microcrystalline cellulose in the first polyolefin.

[0044] As mentioned above, the microcrystalline cellulose and the first polyolefin may not be added at the same time to an organic solvent. In such embodiments, where polyolefin is used as the first hydrophobic polymer, mixing the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may comprise

dispersing the discrete pieces of the microcrystalline cellulose in the organic solvent under agitation for a time period in the range of 10 minutes to 40 minutes, 20 minutes to 40 minutes, 30 minutes to 40 minutes, 10 minutes to 30 minutes, 10 minutes to 20 minutes, or 20 minutes to 30 minutes, prior to adding the first polyolefin. In specific embodiments, mixing of the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation may comprise dispersing the discrete pieces of the microcrystalline cellulose in the organic solvent under agitation for a time period of 20 minutes, prior to adding the first polyolefin.

[0045] In various embodiments, the first polyolefin may be a hydrocarbon polyolefin. As used herein, the expression “hydrocarbon polyolefin” refer to a polyolefin containing at least predominantly, or only hydrogen and carbon with one or more unsaturated carbon-carbon bonds. Such polyolefin includes, for example, one or more polymers formed from alkenes, alkynes, cycloalkenes and/or cycloalkynes. The hydrocarbon polyolefin may be unsubstituted or substituted with additional chemical groups. In various embodiments, the first polyolefin is a polymer formed from an alkene, such as a C₂₋₂₀ alkene, a C₂₋₁₂ alkene, a C₂₋₅ alkene, or a C₂₋₃ alkene. In some embodiments, the first polyolefin may comprise polypropylene, polyethylene or a copolymer thereof. Non-limiting examples of such a copolymer may include a copolymer of polypropylene, a copolymer of polyethylene, and/or a copolymer of polypropylene and polyethylene. In some embodiments, the first polyolefin may be polypropylene.

[0046] In various embodiments, the first polyolefin may be grafted with at least one polar functional group selected from the group consisting of maleic anhydride, hydroxylate, carboxylate, acrylate, or combination thereof to improve the compatibility with the microcrystalline cellulose and so as to improve dispersion of the microcrystalline cellulose within the matrix formed by the first polyolefin. As demonstrated by the present inventors with results shown in **TABLE 2** below, microcrystalline cellulose reinforced polymer composite prepared using polypropylene grafted with maleic anhydride has shown further improved mechanical properties such as elongation at yield, elongation at break, flexural modulus and heat deflection temperature.

[0047] After mixing, the discrete pieces of microcrystalline cellulose and the first polyolefin may form a dispersion.

[0048] The dispersion may be in the form of a liquid or a slurry. Since the discrete pieces of microcrystalline cellulose are dispersed in the polymeric solution formed by at least substantially dissolving the first polyolefin in the organic solvent, the microcrystalline cellulose may be incorporated in a matrix formed from the first polyolefin. A non-solvent may be added to the dispersion comprising the microcrystalline cellulose and the first polyolefin to precipitate the microcrystalline cellulose reinforced polymer composite from the dispersion. The non-solvent may, for example, be a polar solvent such as an alcohol or an aqueous medium. In various embodiments, the non-solvent may be selected from the group consisting of ethanol, acetone, and a mixture thereof. In specific embodiments, the non-solvent is ethanol. In other specific embodiments, the non-solvent is acetone.

[0049] The method as described herein may further comprise drying the microcrystalline cellulose reinforced polymer composite which is precipitated from the dispersion. The drying may be carried out by any suitable method. For example, the microcrystalline cellulose reinforced polymer composite may be placed in a drying oven/chamber and exposed to air for evaporating any residual solvent.

[0050] The process mentioned above may be used to form a “master batch”, which may be subsequently processed by blending or melt compounding with other polymers, which may be the same as or different from the first polyolefin, so as to achieve specific weight percentages of the microcrystalline cellulose and/or polymer according to application requirements. The “master batch” may, for example, be diluted to contain 1 weight percent (wt%) to 10 wt%, such as 2 wt% to 8 wt% or 4 wt% to 6 wt%, of the microcrystalline cellulose reinforced polymer composite in its final form. In so doing, dispersion of the microcrystalline cellulose in the polymer composite may be improved and discolouration of the resultant polymer composite may be reduced.

[0051] For subsequent processing of the “master batch”, the method as described herein may further comprise physically working the microcrystalline cellulose reinforced polymer composite to form discrete pieces of the microcrystalline cellulose reinforced polymer composite, each discrete piece having a size of 100 μm or less, 90 μm or less, 80 μm or less, 70 μm or less, 60 μm or less, 50 μm or less, 40 μm or less, 30 μm or less, 20 μm or less, 10 μm or less, 5 μm or less, 1 μm or less, or 0.5 μm or less. By the term “physically working”, it means subjecting the microcrystalline cellulose reinforced polymer composite to a physical

process such as cutting, pounding, grinding, and/or milling to reduce size of the microcrystalline cellulose reinforced polymer composite to discrete pieces. For example, the microcrystalline cellulose reinforced polymer composite may be physically worked to form discrete pieces of the microcrystalline cellulose reinforced polymer composite, each discrete piece having a size of 100 μm or less, preferably in the range of 2 μm to 100 μm and more preferably in the range of 2 μm to 20 μm .

[0052] Physically working the microcrystalline cellulose reinforced polymer composite to form discrete pieces of the microcrystalline cellulose reinforced polymer composite may be carried out so that each discrete piece may have a size of 1 μm or less after physically working the microcrystalline cellulose reinforced polymer composite. In such sizes, the microcrystalline cellulose reinforced polymer composite may be present as a powder, which may advantageously allow for easier and/or more uniform blending in its use as a “master batch”, for subsequent diluting, mixing, blending or melt compounding with the same or a different polymer from the first polyolefin, so as to achieve specific weight percentages of the microcrystalline cellulose and/or polymer according to application requirements.

[0053] Examples of a suitable process for forming such discrete pieces of the microcrystalline cellulose reinforced polymer composite may particularly include, but not limited to, grinding using a pulverizer machine, or by a jet milling process such as that described above.

[0054] After physically working to form discrete pieces of microcrystalline cellulose reinforced polymer composite, the discrete pieces of microcrystalline cellulose reinforced polymer composite may be further blended with a second hydrophobic polymer. As mentioned above, this may be carried out to adjust specific weight percentages of the microcrystalline cellulose and/or polymer according to application requirements. The blending may be any suitable process, such as but not limited to, extrusion or melt-compounding. Accordingly, the method as described herein may further comprise melt-compounding the discrete pieces of the microcrystalline cellulose reinforced polymer composite with a second hydrophobic polymer. The second hydrophobic polymer may be a polyolefin, such as a hydrocarbon polyolefin, where examples have already been provided above. In various embodiments, the present method may further comprise melt-compounding the discrete pieces of the microcrystalline cellulose reinforced polymer composite with a

second polyolefin. This may, for example, be carried out via extrusion and/or via a twin extruder machine.

[0055] In embodiments wherein the microcrystalline cellulose reinforced polymer composite is blended with a second polyolefin, the amount of the microcrystalline cellulose to the combined amount of the first polyolefin and the second polyolefin may be in the range of 30:70 to 70:30 by weight, such as 40:60 to 70:30, 50:50 to 70:30, 60:40 to 70:30, 30:70 to 60:40, 30:70 to 50:50, 30:70 to 40:60, 40:60 to 60:40, or 50:50 by weight. In specific embodiments, the amount of the microcrystalline cellulose to the combined amount of the first polyolefin and the second polyolefin may be in the range of 30:70 to 70:30 by weight.

[0056] In various embodiments, the second polyolefin and the first polyolefin may be formed of the same or different polymers. In embodiments wherein the second polyolefin and the first polyolefin comprise two or more different polymers, amount of each polymer in the second polyolefin and the first polyolefin may be the same or different. In specific embodiments, the first polyolefin and the second polyolefin may be formed of the same polyolefin. In various embodiments, the second polyolefin may comprise polypropylene, polyethylene or a copolymer thereof. Non-limiting examples of such a copolymer may include a copolymer of polypropylene, a copolymer of polyethylene, and a copolymer of polypropylene and polyethylene. In some embodiments, the second polyolefin may be polypropylene.

[0057] Various embodiments refer in another aspect to a microcrystalline cellulose reinforced polymer composite prepared by a method as described according to the first aspect.

[0058] Embodiments and features of the microcrystalline cellulose reinforced polymer composite are derived from the method already described above, and advantages associated with embodiments and features of the method as described above may be applicable to embodiments and features of the microcrystalline cellulose reinforced polymer composite. Compared to microcrystalline cellulose reinforced polymer composite derived using microcrystalline cellulose that has not undergone jet milling, the present microcrystalline cellulose reinforced polymer composite has smaller sized microcrystalline cellulose with increased surface roughness, which led to better dispersion of microcrystalline cellulose in the polymer composite. This may be seen from the SEM images depicted in **FIG. 4A** and

FIG. 4B, whereby the size is smaller and the surface roughness is increased for microcrystalline cellulose that has undergone jet milling.

[0059] Advantageously, the thus obtained composites may demonstrated improved mechanical properties compared to composites formed from conventional processes.

5 [0060] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

10 [0061] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0062] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

15 [0063] The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

[0064] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

20 [0065] Advantages associated with various embodiments of the present method as described above may be applicable to the present microcrystalline cellulose reinforced polymer composite, and vice versa.

[0066] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups,
25 those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

EXPERIMENTAL SECTION

[0067] Various embodiments disclosed herein refer to a method of preparing cellulose
30 composite using pre-processing and master batch method to improve dispersion of the cellulose material in the polymer composite and to reduce discolouration of the resultant

polymer composite. The method of producing a polymer composite may include pre-processing cellulosic fillers by jet-milling, forming a cellulose master batch by directly mixing cellulose and polymer (30 weight percent (wt%) of cellulose in the master batch), and diluting the master batch to 1 wt% to 10 wt% of the cellulose reinforced polymer composite.

- 5 The preparation of the master batch involves a straightforward mixing process that is described in more detail in the examples below.

[0068] The present method of preparing a polymer composite containing microcrystalline cellulose, which is comprised in the matrix of the polymer, does not require any chemical modifications to attach specific functional groups to the cellulose and polymer.

- 10 Advantageously, the present method circumvents the need for sophisticated processes as it involves pre-processing of microcrystalline cellulose followed by a preparation step of cellulose master batch through solution mixing to prepare the microcrystalline cellulose reinforced polymer composite. In spite of minimal procedures of the present method, cellulose reinforced polymer composites with enhanced mechanical performance for various applications such as automotive, aerospace, and special functions are achieved.

[0069] According to various embodiments of the present method, microcrystalline cellulose was first pre-treated by reducing the size of cellulose which may serve to improve the cellulose dispersibility in polymer solution, followed by the preparation of a concentrated cellulose master batch by direct solution mixing of cellulose and the polymer without any chemical modifications.

- 20 [0070] Air jet milling, sometimes referred to as fluid energy milling, may be employed to effectively reduce the size of particles from a range of 20 μm to 100 μm , to less than 10 μm . In this micronization method, high velocity compressed air streams are injected into a chamber where the starting raw materials are fed by a rate-controlled feeder. Considering the need for a facile approach, direct mixing is a more preferable mixing method, and therefore the addition of pre-mixing techniques/steps prior to extrusion/melt-mixing could facilitate the preparation of composites with homogeneously dispersed cellulosic materials.

[0071] The present method is described, by way of non-limiting examples, as set forth below.

- 30 [0072] **Example 1: Preparation of jMCC master batch by jet milling process**

[0073] Microcrystalline cellulose (MCC) purchased from FMC biochemical was jet milled to reduce the size of cellulose (jMCC) and to improve the dispersion of cellulose in polypropylene solution. The dry milling of the MCC was performed using Micronizer® Jetmill by Sturtevant at a feed rate of 300 grams per hour was operated in order to obtain finer particles. To determine the milled particle size, particles size analysis was performed using Laser diffraction particle size analyzer.

[0074] The structure of starting materials and the morphology of MCC and pre-processed (e.g. jet milled) MCC were shown in **FIG. 1A** and **FIG. 1B**. As summarized in **TABLE 1**, the commercial MCC from FMC biopolymer has an average particle size of 140 μm , and then commercial MCC were milled down to an average particle size of 5 μm as characterized by particle size analyzer and as seen in SEM images. The SEM images of the MCC and jMCC particles show similar results as particle size analysis. In **TABLE 1**, Dx (50) represents the median diameter of the particle size distribution, it is the value of the particle diameter at 50% of the cumulative distribution. In this regard, Dx (10) and Dx (90) represent the value of the particle diameter based on 10% and 90% of the cumulative distribution, respectively. For example, if Dx (10) is 23 μm , it means that 10% of the particles have a diameter of 23 μm or less.

[0075] **TABLE 1: Particle size analysis**

μm	MCC (Before)	Pre-processed MCC (After)
Dx (10)	23	2
Dx (50)	58	5
Dx (90)	138	17

[0076] From a comparison of the SEM images depicted in **FIG. 4A** and **FIG. 4B**, it can be seen that the size is smaller and the surface roughness is increased for microcrystalline cellulose that has undergone jet milling. Due to the smaller size and higher surface roughness of the jet-milled microcrystalline cellulose, there is improved compatibility with polypropylene, hence better dispersion in the polypropylene solution.

[0077] **Example 2: Preparation of PP/jMCC master batch by solution mixing process**

[0078] This example shows the preparation of non-functionalized jMCC master batch via solution mixing process in which thermoplastic polymer is used as a carrier with 1:2 weight ratio of clay to polymer.

[0079] The jet milled MCCs were dispersed in organic solvent which is suitable for polyolefin polymer. After that the jMCC was sonicated and homogenized to obtain the good dispersion. Both jMCC and PP were mixed, precipitated and dried to produce jMCC/PP master batch powder.

[0080] To prepare the master batch composites, xylene was used as a solvent. jMCC was dispersed in xylene at a concentration of 0.1 g/mL by string, homogenization and sonication for 20 min, respectively and repeat twice. PP was dissolved in xylene at a concentration of 1:10 w/v ratio of fillers to polymer at 120 °C by stirring until polymer was dissolved. Aliquots of the jMCC dispersion and PP polymer solution were combined in a flask and the mixtures were stirred for 2 h with an agitator. After that the PP/jMCC master batch was precipitated with ethanol and washed with ethanol to remove the residual solvent. The master batch was dried by oven air to evaporate most of the solvent and grinded by pulverizer machine to produce jMCC master batch powder. Master batch composites powder containing 70 wt% of jMCC was thus produced.

[0081] **Example 3: Preparation of highly dispersed cellulose/polypropylene nanocomposite**

[0082] The effect of MCC and jMCC (i.e. from the master batch) on the mechanical properties of nanocomposite material, which are prepared through a melt blending process using a twin screw extruder machine, is studied. Moreover, dispersion of filler in polymer matrix was also used to understand the reinforced mechanism of composite material.

[0083] jMCC master batch composites were diluted to PP/jMCC 5 wt% composition for processing in a twin screw extruder machine. Briefly, appropriate parts of master batch composite melt-mixed with PP pellets were directly compounded using a 40 mm Leistritz co-rotating twin screw extruder. The extrusion conditions were: barrel temperature zone 1 and 2 at 170 °C and the rest were set at 190 °C, screw speed 250 rpm with output 3 kg per hour. All samples were injection molded into testing specimens for mechanical testing including tensile, flexural, and impact properties followed by ASTM standard testing.

[0084] The morphology of the composites was studied with SEM and the homogeneous dispersion of the filler in the PP matrix can be clearly seen from the images. For PP/MCC composite (**FIG. 2A** and **FIG. 2B**), some aggregates were observed, but this could also be because the MCC particles were not fully exfoliated during the melt-mixing process. The PP/jMCC composite (**FIG. 2C** and **FIG. 2D**) did not show any significant aggregates, suggesting a more homogenous dispersion of the filler, more likely due to better incorporation of jMCC into the PP matrix, which could have been facilitated by the pre-mixing process, corroborating the improvement observed in the mechanical properties for this composite.

[0085] The reinforcement in thus obtained composites showed increased mechanical properties compared to the directly mixed composites. More specifically, the composites containing PP and jMCC showed significantly higher reinforcement. The higher reinforcement obtained when ground particles are pre-mixed could be attributed to the enhanced dispersibility gain as shown in **TABLE 2**. Referring to **TABLE 2**, “non-processed” denotes results from microcrystalline cellulose reinforced polymer composite comprising microcrystalline cellulose, while “pre-processed fillers” denotes results from microcrystalline cellulose reinforced polymer composite comprising jet-milled microcrystalline cellulose. All the samples were mixed with polypropylene as first olefin and with 5 wt% microcrystalline cellulose as fillers. The term “D” represents direct mixing of the microcrystalline cellulose with polypropylene, while “MBMA” represents a microcrystalline cellulose masterbatch containing maleic anhydride grafted polypropylene, obtainable by mixing of the microcrystalline cellulose with polypropylene grafted with maleic anhydride. The term “HDT” in **TABLE 2** represents heat deflection temperature, otherwise termed as heat distortion temperature.

[0086] **TABLE 2: Summary of mechanical properties of neat PP and composites.**

Mechanical properties	PP	Non-processed		Pre-processed fillers	
		D-MCC5	MBMA-MCC5	D-jMCC5	MBMA-jMCC5
Elongation at yield (%)	6	6	6	8	8
Elongation at break (%)	69	20	18	44	104

Flexural modulus (kg/cm ²)	11500	12044	13400	13552	16410
HDT (°C)	98	94.2	104	113	116

[0087] Photographs of the melt-processed nanocomposite pellets (**FIG. 3**) containing 5% w/w of the cellulose prepared by pre-processing and master batching provide a first indication of the higher thermal stability of the cellulose, which related to compounding formulation and processing conditions.

[0088] As mentioned above, various embodiments involve development of thermoplastic composite material comprising filler dispersion technology and processing technology.

[0089] For filler dispersion technology, unmodified microcrystalline cellulose (MCC) was used to derive the reinforcing material. Firstly, MCCs were jet milled to reduce the MCC particle size in order to improve dispersion of filler in polymer solution, then the master batch process is employed to achieve high dispersion and maintain a homogeneous dispersion of jMCC, and processed to form composites with a high concentration of the jMCC by a solution method. The composites may be further processed with additional polymer to produce composites with a final MCC concentration after dilution via melt-processing techniques such as compounding with extrusion and yet maintaining a high level of dispersion of the jMCC fillers.

[0090] For processing technology, the polymer base used for this invention has been produced by innovative techniques including pre-processed fillers technology and compounding technology. Key characteristics of cellulose are formulation, processing condition of extrusion process since MCC can be degraded under temperature and shear easily (e.g. screw design, temperature profile, and mixing technique).

[0091] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

CLAIMS

1. A method of preparing a microcrystalline cellulose reinforced polymer composite, the method comprising
 - a) providing discrete pieces of a microcrystalline cellulose,
 - b) mixing the discrete pieces of the microcrystalline cellulose with a first polyolefin in an organic solvent under agitation, wherein the first polyolefin dissolves at least substantially in the organic solvent and the discrete pieces of the microcrystalline cellulose disperse in the organic solvent, to form a dispersion, and
 - c) precipitating the microcrystalline cellulose reinforced polymer composite from the dispersion using a non-solvent.
2. The method according to claim 1, wherein providing the discrete pieces of the microcrystalline cellulose comprises jet milling the microcrystalline cellulose.
3. The method according to claim 1 or 2, wherein each discrete piece of the microcrystalline cellulose has a size of 100 μm or less.
4. The method according to any one of claims 1 to 3, wherein the organic solvent is selected from the group consisting of xylene, toluene, and a mixture thereof.
5. The method according to any one of claims 1 to 4, wherein concentration of the microcrystalline cellulose in the organic solvent is 0.05 g/mL to 0.15 g/mL.
6. The method according to any one of claims 1 to 5, wherein concentration of the first polyolefin in the dispersion is 1:10 w/v to 2:10 w/v of the microcrystalline cellulose to the first polyolefin.
7. The method according to any one of claims 1 to 6, wherein mixing the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation is carried out at a temperature in the range of 100 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$.

8. The method according to any one of claims 1 to 7, wherein mixing the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation is carried out for a time period in the range of 1 hour to 5 hours.
- 5 9. The method according to any one of claims 1 to 8, wherein mixing the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation is carried out without a dispersant.
- 10 10. The method according to any one of claims 1 to 9, wherein mixing the discrete pieces of the microcrystalline cellulose with the first polyolefin in the organic solvent under agitation comprises dispersing the discrete pieces of the microcrystalline cellulose in the organic solvent under agitation for a time period in the range of 10 minutes to 40 minutes prior to adding the first polyolefin.
- 15 11. The method according to any one of claims 1 to 10, wherein the first polyolefin is a hydrocarbon polyolefin.
12. The method according to any one of claims 1 to 11, wherein the first polyolefin comprises polypropylene, polyethylene or a copolymer thereof.
- 20 13. The method according to any one of claims 1 to 12, wherein the non-solvent is selected from the group consisting of ethanol, acetone, and a mixture thereof.
14. The method according to any one of claims 1 to 13, further comprising drying the microcrystalline cellulose reinforced polymer composite which is precipitated from the dispersion.
- 25 15. The method according to any one of claims 1 to 14, further comprising physically working the microcrystalline cellulose reinforced polymer composite to form discrete pieces of the microcrystalline cellulose reinforced polymer composite, each discrete piece having a size of 100 μm or less.
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16. The method according to claim 15, further comprising melt-compounding the discrete pieces of the microcrystalline cellulose reinforced polymer composite with a second polyolefin.
- 5 17. The method according to claim 16, wherein the first polyolefin and the second polyolefin are formed of the same polyolefin.
18. The method according to claim 16 or 17, wherein the second polyolefin comprises polypropylene, polyethylene or copolymers thereof.
- 10 19. The method according to any one of claims 16 to 18, wherein amount of the microcrystalline cellulose to the combined amount of the first polyolefin and the second polyolefin is in the range of 30:70 to 70:30 by weight.
- 15 20. A microcrystalline cellulose reinforced polymer composite prepared by a method according to any one of claims 1 to 19.