

Polymer nanocomposite masterbatch, polymer nanocomposite and methods for preparation thereof

The present invention relates to a method for preparation of a polymer nanocomposite masterbatch, to a polymer nanocomposite masterbatch, and to a polymer nanocomposite.

Polymer nanocomposite materials have been widely developed in many industrial applications to enhance the mechanical properties and special properties of materials, such as flame retardancy, thermal stability, and barrier properties. To achieve the target properties of nanocomposite materials, dispersions of nano filler materials in a polymer matrix is the key factor. Theoretically, a nano filler material must be separated to individual particles or platelets to provide high performance of material because agglomerated particles result in a defect of the system. Compatibility between the filler material and the polymer is an important parameter to improve the dispersion of the filler in the polymer matrix. Normally, there are two main approaches for dispersion improvement of the filler in the polymer matrix, namely (1) physical modification by using mechanical forces to break the agglomerated particles, such as sonication and homogenization and (2) chemical modification by using a chemical reaction between functional groups on the surface of the filler and a modifying agent, such as organo silane agents or acid derivative agents. However, a full dispersion of a nano filler material in a polymer matrix cannot be obtained by only using one technique. Rather, suitable methods must be designed to synergize the modifying techniques effectively.

There have been numerous attempts to prepare a polymer nanocomposite. US 2006/0267255A1 discloses a process for producing a nanoclay masterbatch by using twin screw extruder. US7514491B2 relates to a method of making polymer/clay nanocomposites by contacting aqueous slurry of inorganic clay with a polymer solution to form emulsions or micro-emulsions. US6462122B1 discloses a nanocomposite concentrate composition by melt compounding method. US8124678B2 discloses a method of making a polymer nanocomposite masterbatch by solution mixing technique.

It is an object of the present invention to provide a method for preparation of a polymer nanocomposite masterbatch and/or a polymer nanocomposite overcoming drawbacks of the prior art, in particular having high aspect ratio and/or high dispersion of filler, high strength and high impact properties.

This object is achieved by a method for preparing a polymer nanocomposite masterbatch, comprising the steps: a) dispersing a nano filler material in an organic solvent; b) contacting the nano filler material in the organic solvent with a surface functionalizing agent to form a surface functionalized nano filler material suspension; c) mixing the surface functionalized nano filler material suspension with a polymer solution to form a dissolved polymer nanocomposite masterbatch suspension; d) precipitating the dissolved polymer nanocomposite masterbatch suspension to produce a precipitation of polymer nanocomposite masterbatch; e) optionally, filtering and drying the precipitation of polymer nanocomposite masterbatch to form a polymer nanocomposite masterbatch.

A nano filler material according to the present disclosure is a filler material having the geometric size of primary particle (i.e. in case of more than one particle forming an agglomerate the size of a single particle) less than 100 nm preferably 0.01 nm to 100 nm, even more preferred 0.1 nm to 100 nm, further preferred 1 nm to 100 nm, even more preferred 10 nm to 100 nm, with respect to at least in one dimension thereof.

The inventive method is employed to produce a highly dispersed nano filler material in a polymer matrix (= polymer nanocomposite masterbatch) by using a solution mixing process. The masterbatch can be produced in various high concentration forms such as solid form, liquid form, and slurry form that may be further processed with additional polymer materials to produce polymer nanocomposite with desired final nano filler loading. The inventive polymer nanocomposite masterbatch, respectively the polymer nanocomposite, have high aspect ratio and/or high dispersion of filler, high strength and high impact properties.

Polymer nanocomposite masterbatch is polymer having dispersed therein a high amount of nano filler material.

Polymer nanocomposite is polymer having dispersed therein an amount of nano filler material.

In one embodiment, the nano filler material is selected from the group consisting of minerals, inorganic fillers, organic fillers, metal oxides, natural fibers, synthetic fibers or a mixture thereof.

In a preferred embodiment, the nano filler material is selected from montmorillonite, smectite, kaolin, bouldangerite, imogolite, layered silicate compound, organo clay modified

with quaternary ammonium salt, silica, carbon black, cellulose fiber, nano cellulose fiber, talc, calcium carbonate, alumina or a mixture thereof.

In one embodiment, the organic solvent is selected from xylene, toluene, hexane or dichlorobenzene.

In one embodiment, the dispersing step provides well dispersed nano filler material in the organic solvent.

In a preferred embodiment, the dispersing step comprising stirring the nano filler material in the organic solvent for 3 hours – 24 hours and/or sonicating for 20 – 60 minutes and/or homogenizing for 15 – 30 minutes and/or stirring for 12 - 24 hours. Preferably, the dispersing step is operated at ambient temperature or 20 – 30 °C.

In a further embodiment, the contacting step comprises homogenizing the nano filler material suspension for 15 – 30 minutes and/or adding the surface functionalizing agent and/or stirring for 2 - 6 hours at 80 – 100 °C and/or homogenizing, preferably at ambient temperature or 20 – 30 °C, for 15 – 30 minutes, and/or stirring, preferably at ambient temperature or 20 – 30 °C, for 12 – 24 hours.

The nano filler material is well dispersed in solvent before contacting for surface functionalization for achieving a well surface functionalized nano filler material which enhance the compatibility between nano filler material and polymer when respectively mixing with a polymer solution to get a polymer nanocomposite masterbatch having high aspect ratio and/or high dispersion of filler.

In one embodiment, the surface functionalizing agent is selected from the group consisting of quaternary ammonium salts, silanes, titanates, organic acid, grafted oligomer or grafted polymer.

In preferred embodiment, the surface functionalizing agent is in an amount in the range from 0.1 to 20 % by weight with respect to weight of the nano filler material, preferably 1 to 10 % by weight with respect to weight of the nano filler material.

The surface functionalizing agent can be a modifying agent or a coupling agent. The mechanism of the surface functionalization may occur by (1) physical bonding between organic cation and layer of nano filler material via exchanging the metal cation located

between the layers of layered silicate material or (2) chemical bonding, such as in case of silanes or organo silanes.

In one embodiment, the polymer solution is the solution of polymer selected from polyolefins, preferably polyethylene, polypropylene, C4-C8 alpha-polyolefins base, copolymer thereof; polyolefin rubber; polyolefin oligomer; polyolefin wax; polyaramide; polyarylamide; polycarbonate; styrene acrylonitrile; acrylonitrile butadiene styrene; polyacetal; polysulfone; polyester, preferably polybutylene terephthalate, polyethylene terephthalate; thermoplastic polyurethane elastomer; polyphenylene sulfide; polyether sulfone; polyphenylene oxide; vinyl polymers, preferably polystyrene; polyvinyl chloride; polyacrylate; polyurethanes; polyetherimide; polyetheretherketone; polyetherketone; polymethylpentene; perfluoroalkoxy; ethylene tetrafluoroethylene; polyvinylidene fluoride; fluorinated ethylene propylene; liquid crystal polymers; polyphthalamide; polyether, polysiloxane, thermoplastic polyimide; and polyamide.

In preferred embodiment, the polymer is a thermoplastic polymer selected from homopolymer polyethylene e.g., linear low density polyethylene (LLDPE), low density polyethylene (LDPE), homopolymer polypropylene, copolymer of polyethylene/polypropylene, copolymer of polyethylene or polypropylene and C4-C8 alpha-polyolefins base.

The polymer is used as a carrier of the inventive masterbatch.

In another embodiment, the mixing step comprises mixing the surface functionalized nano filler material suspension into the polymer solution and stirring for 2 – 6 hours. Preferably, the surface functionalized nano filler material suspension is a hot surface functionalized nano filler material suspension (80 – 120°C) which is added into a hot polymer solution (80 – 120°C) and then stirred at 80 – 120 °C for 2 – 6 hours.

In one embodiment, the polymer solution is prepared by (obtainable by) dissolving a polymer in a suitable organic solvent at suitable temperature, e.g. dissolving polypropylene in xylene at a weight to volume ratio of polypropylene to xylene = 1 : 10 at 120°C until the clear polypropylene solution obtained.

In one embodiment, the polymer nanocomposite masterbatch can be prepared by solution mixing process. Firstly, the nano filler material is dispersed in organic solvent (e.g. xylene) via use of sonication and homogenization to break the agglomerated particles. Importantly,

surface functionalization of nano filler material is operated to improve the compatibility between nano filler material and polymer system. After that, the suspension of surface functionalized nano filler material was added into the polymer solution (polymer dissolved in organic solvent). Finally, the polymer nanocomposite masterbatch can be produced in solid, liquid, and slurry form.

In a further embodiment, the precipitating step comprises adding a precipitant to the polymer nanocomposite masterbatch solution to form a polymer nanocomposite masterbatch precipitate then washing the precipitate by the solvent or precipitant, e.g. adding ethanol to clay/PP masterbatch solution to form clay/PP masterbatch precipitate and washing the precipitate with ethanol until no or less xylene (which is the solvent of the masterbatch solution) detected.

In a further embodiment, the wet polymer nanocomposite masterbatch is dried and grinded to form a polymer nanocomposite masterbatch powder.

In further embodiment, the method further comprises the step of compounding the polymer nanocomposite masterbatch with a (neat) polymer to form a polymer nanocomposite.

In one embodiment, the polymer nanocomposite is produced by dilution of the polymer nanocomposite masterbatch with a polymer via melt blending process of extruder machine to obtain the nanocomposite material having desired final nano filler loading.

The object is further achieved by a method for preparing a polymer nanocomposite comprising a step of compounding the inventive polymer nanocomposite masterbatch with a polymer.

Finally, the object is achieved by a polymer nanocomposite obtainable by the inventive method.

In one embodiment, the polymer is selected from polymer selected from polyolefins, preferably polyethylene, polypropylene, C4-C8 alpha-polyolefins base, copolymer thereof; polyolefin rubber; polyolefin oligomer; polyolefin wax; polyaramide; polyarylamide; polycarbonate; styrene acrylonitrile; acrylonitrile butadiene styrene; polyacetal; polysulfone; polyester, preferably polybutylene terephthalate, polyethylene terephthalate; thermoplastic polyurethane elastomer; polyphenylene sulfide; polyether sulfone; polyphenylene oxide; vinyl polymers, preferably polystyrene; polyvinyl chloride; polyacrylate; polyurethanes;

polyetherimide; polyetheretherketone; polyetherketone; polymethylpentene; perfluoroalkoxy; ethylene tetrafluoroethylene; polyvinylidene fluoride; fluorinated ethylene propylene; liquid crystal polymers; polyphthalamide; polyether, polysiloxane, thermoplastic polyimide; and polyamide.

In preferred embodiment, the polymer is a thermoplastic polymer selected from homopolymer polyethylene e.g., linear low density polyethylene (LLDPE), low density polyethylene (LDPE), homopolymer polypropylene, copolymer of polyethylene/polypropylene, copolymer of polyethylene or polypropylene and C4-C8 alpha-polyolefins base.

In a preferred embodiment, the polymer nanocomposite masterbatch comprises nano filler material in an amount in a range from 10% to 80% by weight, more preferably 20% to 60% by weight and most preferably 30% to 40% by weight, with respect to the total weight of the polymer nanocomposite masterbatch. It was surprisingly found that the inventive method for preparation of a polymer nanocomposite masterbatch provides a polymer nanocomposite masterbatch and/or a polymer nanocomposite having high aspect ratio and/or high dispersion of filler, high strength and high impact properties. The effects are even more pronounced when using the different embodiments explicitly mentioned above. The best results were achieved when combining two or more of the explicitly mentioned embodiments.

Abbreviation

Normal-clay/PP composite :Polypropylene composite comprises normal-clay

Clay-MB/PP nanocomposite :Polypropylene nanocomposite comprises nanoclay masterbatch

TEM : Transmission electron microscopy technique

SEM : Scanning electron microscopy technique

MFI : Melt flow index

HDT : Heat distortion temperature

Methods and definitions

1. Determination of mechanical properties

a) Tensile strength, %Elongation are measured by ASTM D638-14. The specimen in dumbbell shape is extended at the cross head speed of 200 mm/min by using an Instron 5565 Universal Testing machine (Instron, Canton, MA, USA). Tensile strength, Elongation are calculated by the following formula.

$$\text{Tensile strength } \left(\frac{\text{kgf}}{\text{mm}^2} \right) = \frac{\text{Load value (kgf)}}{\text{Width (mm)} \times \text{Thickness (mm)}}$$

$$\% \text{ Elongation} = \frac{\text{Extension}}{\text{Primary length}} \times 100$$

b) Flexural modulus and Flexural strength are measured by ASTM D790-15. The specimen in bar shape is measure in three-points bending by using an Instron 5565 Universal Testing machine. The specimen size is 127 mm X 12.7 mm X 3.2 mm. The test speed is 12.8 mm/min, and the support is 48 mm. Flexural modulus and Flexural strength are calculated by the following formula.

$$\text{Flexural modulus} = \frac{L^3 m}{4bd^3}$$

$$\text{Flexural strength} = \frac{3PL}{2bd^2}$$

where:

L = Support span, mm (in.),

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm (lbf/in.) of deflection,

b = Width of beam tested, mm (in.),

d = Depth of beam tested, mm (in.), and

P = Load at a given point on the load-deflection curve, N (lbf).

c) Impact strength of notched specimens is measured by ASTM D 256-10 using Universal impact tester No.258-L (Yasuda Seiki Seisakusho Ltd). The sample has 45° V-shaped cut with a depth of 2.54 mm, and is sized as 63.5 mm X 12.7 mm X 3.2 mm. There were a total of 5 samples for each sample.

2. Determination of melt flow index

The melt flow index (MFI) of sample is measured by following ASTM D 1238-13 via Dynisco Melt Flow Indexer Model No. D4004HV.

3. Determination of Heat distortion temperature

Heat distortion temperature (HDT) of sample is measured using Tinius olsen, 303/HDTM model at 120 °C/h with load cell of 0.45 MPa by following ASTM D 648-16.

The specimen size is 12.7 mm X 127 mm X 3 mm.

In the following, the invention will be described in greater detail with reference to specific examples without, however, intending to limit the scope of the application respectively. Reference will be made in this regard to the enclosed figures, wherein

Figure 1 is a TEM image of octyl silane modified clay in xylene.

Figure 2 are TEM images of octyl silane modified clay in polypropylene solution.

Figure 3 is a TEM image of normal-clay/ PP composite.

Figure 4 is a TEM image of clay-MB/PP nanocomposite.

Figure 5 are SEM images of clay-MB/PP nanocomposite prepared from different drying techniques.

Figure 6 are TEM images of clay-MB/PP nanocomposite prepared from different drying techniques.

Example

Example 1 Preparation of triethoxy (octyl) silane modified nanoclay masterbatch (Clay-MB) by solution mixing process

Clay (Closite 20 from Southern clay products) (2 g) was stirred in xylene (40 ml) by magnetic stirrer for 3 hours to intercalate the layers of clay. After that the intercalated clay/xylene suspension was sonicated for 30 minutes, highly dispersed by homogenizing process using 8,000 rpm of impeller speed for 15 minutes, and then stirred overnight at room temperature, respectively. Triethoxy (octyl) silane was selected to modify the surface of clay by homogenizing the clay/xylene suspension for 15 minutes, adding 0.2 ml triethoxy (octyl) silane into the clay/xylene suspension, heating at 80 °C for 4 hours, homogenizing 15 minutes and then stirred it overnight at room temperature. Dispersion of triethoxy (octyl) silane modified clay in xylene was observed by TEM technique showing single platelet alignment of clay layers and stacking of clay in some area as displayed in **Figure 1**.

Nanoclay masterbatch was prepared by adding hot triethoxy (octyl) silane modified clay (80°C) in hot polypropylene solution then stirring for 2 hours at 120°C. The hot polypropylene solution was prepared by dissolving polypropylene 4.0 g in xylene 40 ml at 120°C until the polypropylene completely dissolves in xylene. Dispersion of triethoxy (octyl) silane modified nanoclay in polymer solution was observed by TEM technique showing single platelet alignment of clay layers and stacking of clay in some area as displayed in **Figure 2**.

After that the suspension of Clay-MB was precipitated with ethanol and washed with ethanol for three times to remove the residual xylene. The Clay-MB precipitate was dried by oven air and grinded by pulverizer machine to produce Clay-MB powder.

Example 2 demonstrates the preparation and properties of Clay-MB/PP nanocomposite and Normal-clay/PP composite

The composition shown in **Table 1** was compounded on a 40 mm Leistritz co-rotating twin screw extruder. The extrusion conditions were: barrel temperature at 190 °C, screw speed 250 rpm with output 5 kg per hour. The properties were evaluated as presented in **Table 2**.

Table 1

Formulation	Clay-MB/PP nanocomposite (inventive) (%)	Normal-clay/PP composite (comparative) (%)
PP base	80.10	90.10
Compatibilizer ¹	4.75	4.75
Clay-MB powder	15	0
Clay	0	5
Hindered phenolic antioxidant	0.05	0.05
Diphosphonite antioxidant	0.1	0.1

¹ Compatibilizer is an oligomer or polymer functionalized with polar groups such as amines or carboxylic acids and derivatives.

Table 2 Properties of Clay-MB/PP nanocomposite and Normal-clay/PP composite

Mechanical properties	PP	Normal-clay/PP composite	Clay-MB/PP nanocomposite
Tensile at yield (kg/cm ²)	292	295	310
Tensile at break (kg/cm ²)	200	204	119
Elongation at yield (%)	6	6	5
Elongation at break (%)	69	32	80
IZOD Impact at 23 °C (kg*cm/cm)	11	6	7
IZOD Impact at 0 °C (kg*cm/cm)	-	4	4
Flexural modulus (kg/cm ²)	12562	14098	15587
Flexural strength (kg/cm ²)	394	440	467
MFI (230 °C, 2.16 kg)	10	9	9
HDT (°C)	-	114	110

As **Table 2**, Clay-MB/PP nanocomposite has higher tensile at yield, elongation at break, flexural modulus, flexural strength than normal-clay/PP composite.

In order to explain the mechanical properties of composite material, dispersion of clay in both systems was investigated by TEM technique. **Figure 3** and **Figure 4** showed dispersion of clay in polymer matrix using normal clay and clay masterbatch, respectively. The results showed that high agglomerated particle having more number of clay layers was observed in direct dose system (normal-clay/PP composite) while less amount of stacking of clay layers was observed in the inventive masterbatch system (Clay-MB/PP nanocomposite).

Example 3 demonstrates the effect of drying method of Clay-MB on dispersion of clay in polymer matrix.

The Clay-MB/PP masterbatch suspension was drying by two different drying methods; solvent evaporation and precipitation. The solvent evaporation method was prepared by evaporating the Clay-MB/PP masterbatch suspension at the room temperature, then drying

and grinding to obtain the Clay-MB/PP nanocomposite (Evaporation). The precipitation method was described in Example 1 to obtain the Clay-MB/PP nanocomposite (Precipitate). The results showed that drying method showed different dispersion behavior of nanoclay in polymer matrix as observed by SEM and TEM technique. As **Figure 5**, SEM images showed that good combination of clay and polymer matrix was observed in both techniques but the morphology of clay masterbatch is different between techniques. In case of evaporation method, the morphology of clay masterbatch showed rough surface of masterbatch particle while adhesion between small particles was observed in precipitation system.

In addition, the TEM images showed that precipitation method give higher aspect ratio of clay in polymer matrix than solvent evaporation method as compared in **Figure 6**. According to this behavior, mechanical properties of Clay-MB/PP nanocomposite prepared by precipitation method can be improved flexural modulus in 37.42 % and 6.01% as compared to PP base and evaporated ones, respectively, in **Table 3**. By this invention, high aspect ratio of clay polymer composite can be prepared providing highly mechanical properties of composite.

Table 3 Properties of Clay-MB/PP nanocomposite prepared by evaporation and precipitation technique.

Properties	PP	Clay-MB/PP nanocomposite (Evaporation)	Clay-MB/PP nanocomposite (Precipitate)
Tensile at yield (kg/cm ²)	292	292	295
Tensile at break (kg/cm ²)	200	159	170
Elongation at yield (%)	6	6	6
Elongation at break (%)	69	60	74
IZOD Impact at 23 °C (kg*cm/cm)	11	6.9	9
IZOD Impact at 0 °C (kg*cm/cm)	-	3.6	4.4
Flexural modulus (kg/cm ²)	12562	16285	17263
Flexural strength (kg/cm ²)	394	446	469
MFI (230 °C, 2.16 kg)	10	12	-

The features disclosed in the foregoing description, in the claims and in the accompanying drawings may, both separately and in any combination be material for realizing the invention in diverse forms thereof.

CLAIMS

1. A method for preparing a polymer nanocomposite masterbatch, comprising the steps:
 - a) dispersing a nano filler material in an organic solvent;
 - b) contacting the nano filler material in the organic solvent with a surface functionalizing agent to form a surface functionalized nano filler material suspension;
 - c) mixing the surface functionalized nano filler material suspension with a polymer solution to form a dissolved polymer nanocomposite masterbatch suspension;
 - d) precipitating the dissolved polymer nanocomposite masterbatch suspension to produce a precipitation of polymer nanocomposite masterbatch;
 - e) optionally, filtering and drying the precipitation of polymer nanocomposite masterbatch to form a polymer nanocomposite masterbatch.
2. The method according to claim 1, wherein the nano filler material is selected from the group consisting of minerals, inorganic fillers, organic fillers, metal oxides, natural fibers, synthetic fibers or a mixture thereof.
3. The method according to claim 1 or 2, wherein the nano filler material is selected from montmorillonite, smectite, kaolin, bouldangerite, imogolite, layered silicate compound, organo clay modified with quaternary ammonium salt, silica, carbon black, cellulose fiber, nano cellulose fiber, talc, calcium carbonate, alumina or a mixture thereof.
4. The method according to any of the preceding claims, wherein the organic solvent is selected from xylene, toluene, hexane or dichlorobenzene.
5. The method according to any of the preceding claims, wherein the dispersing step comprising stirring the nano filler material in the organic solvent for 3 hours – 24 hours and/or sonicating for 20 – 60 minutes and/or homogenizing for 15 – 30 minutes and/or stirring for 12 - 24 hours.
6. The method according to any of the preceding claims, wherein the contacting step comprises homogenizing the nano filler material suspension for 15 – 30 minutes and/or adding the surface functionalizing agent and/or stirring for 2 - 6 hours at 80 – 100 °C

and/or homogenizing the resultant mixture for 15 – 30 minutes and/or stirring for 12 – 24 hours.

7. The method according to any of the preceding claims, wherein the surface functionalizing agent is selected from the group consisting of quaternary ammonium salts, silanes, titanates, organic acid, grafted oligomer or grafted polymer.
8. The method according to any of the preceding claims, wherein the surface functionalizing agent is in an amount in the range from 0.1 to 20 % by weight with respect to weight of the nano filler material.
9. The method according to any of the preceding claims, wherein the polymer solution is a solution of a polymer selected from polyolefins, preferably polyethylene, polypropylene, C4-C8 alpha-polyolefins base, copolymer thereof; polyolefin rubber; polyolefin oligomer; polyolefin wax; polyaramide; polyarylamide; polycarbonate; styrene acrylonitrile; acrylonitrile butadiene styrene; polyacetal; polysulfone; polyester, preferably polybutylene terephthalate, polyethylene terephthalate; thermoplastic polyurethane elastomer; polyphenylene sulfide; polyether sulfone; polyphenylene oxide; vinyl polymers, preferably polystyrene; polyvinyl chloride; polyacrylate; polyurethanes; polyetherimide; polyetheretherketone; polyetherketone; polymethylpentene; perfluoroalkoxy; ethylene tetrafluoroethylene; polyvinylidene fluoride; fluorinated ethylene propylene; liquid crystal polymers; polyphthalamide; polyether, polysiloxane, thermoplastic polyimide; and polyamide.
10. The method according to any of the preceding claims, wherein the mixing step comprises mixing the surface functionalized nano filler material suspension into the polymer solution and stirring for 2 – 6 hours.
11. The method according to any of the preceding claims, further comprising the step of compounding the polymer nanocomposite masterbatch with a polymer to form a polymer nanocomposite.
12. A polymer nanocomposite masterbatch obtainable by the method according to any of the preceding claims.

13. The polymer nanocomposite masterbatch according to claim 12 comprising nano filler material in an amount in the range from 10 to 80 % by weight with respect to the total weight of the polymer nanocomposite masterbatch.
14. A method for preparing a polymer nanocomposite comprising a step of compounding the polymer nanocomposite masterbatch according to claim 12 or 13 or obtainable by the method according to any of the claims 1 to 11 with a polymer.
15. A polymer nanocomposite obtainable by the method according to claim 13.