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(54) Title: PROCESS FOR PREPARING POLYMER-GRAPHENE COMPOSITES

(57) Abstract: The present disclosure relates to a process for preparing polymer-graphene composites. The process involves homogenizing graphite, a polymer, and a fluid medium at a pre-determined shear rate to obtain a homogenized mixture comprising polymer particles and exfoliated graphene. The homogenized mixture is then concentrated at a pre-determined temperature in a controlled manner to remove fluid medium to obtain powder containing polymer particles- exfoliated graphene. The powder is further blended with an additional polymer with or without additives to obtain a polymer-graphene-composite. The process of the present disclosure is a fast/rapid, simple, and cost effective way to achieve a polymer composite with good mechanical properties in polymers at a low cost. The polymer-graphene composites can be used in a wide range of commercial applications.



PROCESS FOR PREPARING POLYMER-GRAPHENE COMPOSITES

FIELD

The present disclosure relates to a process for preparing polymer-graphene composites.

DEFINITIONS

As used in the present disclosure, the following terms are generally intended to have the meaning as set forth below, except to the extent that the context in which they are used indicates otherwise.

Polymer-graphene concentrate/masterbatch: The term “polymer-graphene concentrate/masterbatch” refers to a polymer graphene mixture wherein more than 20 % concentration of graphene is integrated with the polymer in powder form intended for making polymer composite.

Polymer-graphene Composite: The term “polymer-graphene composites” refers to composites wherein polymer graphene in concentrate/masterbatch form is integrated by kinetic and/or melt mixing with polymers.

Graphene nanoplatelets: The term “graphene nanoplatelets” refers to a class of carbon nanoparticles having “platelet” morphology, i.e., with the Particle size ranging from 0.2 - 100 micron and (more specifically 1-25 micron) and the thickness ranges from 0.33 nm to 10 nm.

Exfoliation of graphite The term “exfoliation of graphite” refers to the process of breaking down of large graphite particles (e.g. particles of thickness greater than 100 nm, containing hundreds of atomic layers) to nano graphite and graphene platelets of thickness less than 10 nm containing less than 30 atomic layers, ideally to graphene platelets of thickness less than 3 nm containing less than 10 atomic layers.

Graphene: The term “graphene” refers to the allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex. It is the basic structural element of graphite

Graphite: The term “graphite” refers to a naturally-occurring as well as a synthetically obtained form of crystalline carbon.

Shear rate: The term “shear rate” refers to the ratio of velocity and distance and is measured in sec^{-1} .

BACKGROUND

Recently, graphene has been used as alternative carbon-based filler in the preparation of polymer composites to provide thermal, electrical, and mechanical properties to the polymer. Typical methods for preparing polymer-graphene composites employ conventional melt compounding of dry powdered graphene into the polymers, or employ liquid phase techniques using solvents that dissolve the polymer and mix the liquid phase with the polymer dissolved therein with a solvent dispersion of graphene nanoplatelets. However, these methods have certain drawbacks, such as limitations in terms of the solvents that can be used, low concentrations of polymer that can be dissolved, and poor physical properties of the mixture, namely stickiness, and slow drying rates. Further, it is difficult to convert the mixture to dry granule or powder form.

Further, conventionally, in the liquid phase technique for the preparation of polymer-graphene composites the polymer is dissolved in the solvent followed by addition of graphite results in soft mass. The soft mass is then sheared to get the graphene polymer master batch. The so obtained soft mass is required to be dried to remove the solvent, however, after removal of solvent, the soft mass becomes hard mass. Still further, the removal of solvent from the soft mass is very difficult as the solvent gets trapped in the polymer mass. Moreover, to process the hard mass, it has to be dried and then crushed. Crushing the dried hard mass is also a very tedious and energy intensive process.

Therefore, there is felt a need to provide a process that mitigates the drawbacks mentioned hereinabove.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows:

An object of the present disclosure is to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

Another object of the present disclosure is to provide a process for the preparation of polymer particle-exfoliated graphene concentrate.

Still another object of the present disclosure is to provide a process for the preparation of polymer-graphene composites.

- 5 Yet another object of the present disclosure is to provide a simple, cost effective, and rapid process for the preparation of polymer-graphene composites.

Other objects and advantages of the present disclosure will be more apparent from the following description, which is not intended to limit the scope of the present disclosure.

SUMMARY

- 10 The present disclosure relates to a process for the preparation of polymer-graphene composites. The process involves forming an initial mixture containing graphite, a polymer, and a fluid medium. The so obtained mixture is homogenized by shear mixing at a shear rate of at least 10^5 sec^{-1} to form a homogenized mixture. The fluid medium is selected such that the polymer is not soluble in the fluid or is sparsely soluble, i.e., less than 1 % of the polymer
- 15 is soluble in the fluid medium. The homogenized mixture is concentrated at a pre-determined temperature in a controlled manner to remove the fluid medium to obtain a powder containing polymer particles-exfoliated graphene wherein the powder is in the form of free flowing powder. The polymer-graphene composite is then obtained by blending the so obtained powder containing polymer particles-exfoliated graphene with an additional
- 20 polymer by kinetic or melt blending process. The polymer-graphene composite can be in the form of free flowing powder or beads.

The average particle size of the polymer is less than 500 microns. The process step of mixing graphite with the polymer is carried out at a temperature below the softening point of the polymer.

25 DETAILED DESCRIPTION

Recently, the unique thermal, mechanical, and electrical properties of graphene have garnered a lot of attention in various applications, especially in the preparation of polymer-graphene composites. The polymer-graphene composites, due to their excellent thermal, mechanical, and electrical properties, find applications in various fields, such as electronic devices,

sensors, energy storage, electrostatic discharge (ESD), and electromagnetic (EMI) shielding, and biomedical applications.

Conventional processes for preparing the polymer-graphene composites have certain drawbacks, such as limitations in terms of the solvents that can be used and low concentrations of polymer that can be dissolved. Further, the polymer-graphene mixture is obtained in the form of solid and sticky mass resulting in an extremely slow drying rate. Also, it is difficult to convert the solid and sticky mass to dry granule or powder form.

The present disclosure envisages a process for preparing the polymer-graphene composites that mitigates the drawbacks mentioned hereinabove. The process of the present disclosure employs discrete fine polymer particles, which do not swell, soften, or get sticky during the preparation process. Further, due to the low solubility of the polymer in the fluid medium, the separation process is rapid, and simple.

In an aspect of the present disclosure, there is provided a process for preparing the polymer-graphene composites.

In an embodiment of the present disclosure, the polymer-graphene composites are prepared using polymer particles-exfoliated graphene concentrate/ masterbatch. The preparation of the polymer particles-exfoliated graphene concentrate/ masterbatch is given in detail as below:

Initially, graphite, polymer, and fluid medium are mixed to form an initial mixture. The mixture of graphite, polymer, and fluid medium is homogenized by shear mixing at a shear rate of at least 10^5 sec^{-1} to form a homogenized mixture.

The ratio of graphite to the polymer is in the range of 0.1: 99.9 to 99.9:0.1. In an embodiment, the ratio of the graphite to the polymer can be varied from 1:10 to 10:1; most preferably the ratio is kept from 1:3 to 3:1.

The fluid medium is selected such that the polymer is not soluble or is sparsely soluble in the fluid medium. In an embodiment of the present disclosure, the solubility of the polymer in the fluid medium is less than 1 %. The fluid medium may comprise a liquid or more than one liquid or a combination of liquid and gas, or a combination of liquid and solid. Use of such fluid medium retains the structural integrity of the polymer particles, allowing them to effectively shear the graphite particles under high shear mixing conditions. Further, the low solubility of the polymer in the fluid medium ensures that the resultant polymer-graphene

composites are in the form of free flowing powder which can be readily dispersed in the powder polymer matrix.

The solid (polymer and graphite) to the solvent ratio can be varied from 1:10 to 1: 1.5.

5 In the present disclosure, the shear rate is important for exfoliation of the graphite to graphene. If the shear rate is lower than 10^5 sec^{-1} , the extent of graphite exfoliation becomes low. If the amount of graphite exfoliation is low, then the improvement in the mechanical properties of the final polymer composite is reduced.

10 In accordance with the present disclosure, graphite is used as the starting material, which is inexpensive, and thus making the process cost effective. Graphite during the high shear mixing process is exfoliated to obtain the mixture comprising polymer particles and exfoliated graphene.

In accordance with the embodiments of the present disclosure, the average particle size of the polymer is less than 500 microns.

15 Typically, the polymer can be any thermoplastic polymer, including, but not limited to, polyvinyl chloride, polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, Nylon, polyamide, thermoplastic polyurethane, polycarbonate, polystyrene, and combinations thereof. It is observed that if the thermosetting polymer (instead of thermoplastic polymers) used in the process of the present disclosure, the free flowing dry powder of polymer-graphene concentrate or polymer graphene composite cannot be
20 formed/obtained.

In an embodiment, the high shear mixing is carried out using a stator rotor mixer. In an embodiment, the rotor speed is in the range between 5000 and 10000 RPM.

In an embodiment of the present disclosure, the high shear mixing is carried out at a temperature below the softening point of the polymer.

25 The softening point of the polymer can be in the range of 25 °C to 150 °C. Typically the softening temperature of the polymer is 50 °C to 120 °C

The softening temperature of the polymer is determined by ASTM D1525 / ISO 306 method. It is known in the art that thermoplastic polymers do not exhibit an exact melting point that indicates the precise transition from the solid to the liquid state. However, there is a gradual

softening of the thermoplastic polymers as the temperature increases. The softening temperature of the polymer is determined by ASTM D1525 / ISO 306 method in which the Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen (polymer) to a depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. A test specimen is placed in the testing apparatus so that the penetrating needle rests on its surface at least 1 mm from the edge. A load of 50N is applied to the specimen. The specimen is then lowered into an oil bath at 23 °C. The bath is raised at a rate of 50° or 120° C per hour until the needle penetrates 1 mm.

- 10 The homogenized mixture which is obtained by shear mixing the polymer powder and graphite in the fluid medium at the predetermined shear rate wherein the polymer is not soluble or having the solubility less than 1%, can be in the form of a slurry. The homogenized mixture remains as slurry and never swells or forms a mass/lump, even after mixing at a predetermined shear rate. This shearing of the graphite in the presence of the polymer, creates particle to particle shear and helps in exfoliation.

Once the shearing process is over the homogenized mixture/slurry can be concentrated at a pre-determined temperature in a controlled manner to remove the fluid medium to obtain the polymer particles-exfoliated graphene master batch/ concentrate in the form of free flowing powder.

- 20 In an embodiment the homogenized mixture comprising the polymer particles and exfoliated graphene is dried at a pre-determined temperature, to obtain the polymer-graphene concentrate/masterbatch. The pre-determined temperature can be in the range of 50 °C to 100 °C, typically the pre-determined temperature is in the range of 70 °C to 80 °C.

- 25 The drying can be carried out by using known techniques, such as rotary evaporation, to recover most of the fluid followed by vacuum oven or convection oven drying to remove any residual fluid. Thorough drying of the mixture comprising the polymer particles and exfoliated graphene provides a free flowing powder of the polymer particles-exfoliated graphene concentrate/masterbatch.

- 30 In an embodiment the graphite, polymer and fluid in which the polymer is not soluble, is added in a container used for high shear to obtain dry slurry. The ratio of Polymer: Graphite can be varied from 1:10 to 10:1. Most preferably, the ratio is in the range of 1:3 to 3:1. The

ratio of solid to fluid medium in the container can be varied from 1:10 to 1: 1.5. The slurry is sheared in the high shear mixer. The rotor speed is kept between 5000-10000 RPM. This high shearing is carried out for 10 minutes to 300 minutes, more preferably 60-150 minutes. Once the shearing is completed, the slurry is dried in a controlled manner by removing the fluid
5 medium under vacuum. This dried powder is called as polymer particles-exfoliated graphene master batch/ concentrate.

In the next step, the polymer particles-exfoliated graphene concentrate/masterbatch is blended with an additional polymer using kinetic or melt blending process to obtain polymer-graphene composites in the form of a free flowing powder or beads.

10 The process of the present disclosure further comprises the addition of at least one additive at the time of blending the polymer-graphene concentrate with an additional polymer using kinetic or melt blending process to obtain the polymer-graphene composite.

In accordance with the present disclosure, the additive is selected from the group comprising impact modifier, octyl tin, wax, TiO₂, graphene, glycerol monostearate, and ester of montanic
15 acids and the like. Typically, the impact modifier is high molecular-weight copolymer with pigment affinic groups.

In accordance with the embodiment of the present disclosure, the average particle size of the additional polymer is less than 500 microns. The additional polymer can be any thermoplastic polymer and is at least one selected from the group consisting of polyvinyl chloride,
20 polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, Nylon, polyamide, thermoplastic polyurethane, polycarbonate, and polystyrene.

In an embodiment of the present disclosure, the polymer and the additional polymer are same.

In another embodiment of the present disclosure, the polymer and the additional polymer are different.

25 The use of same or different polymer in the preparation of polymer-graphene composites and /or polymer-graphene concentrate will affect the mechanical properties and can be chosen as per the requirement.

In accordance with the present disclosure, the particle size of the polymer and the additional polymer employed in the preparation of desired polymer graphene composite requires to be

below 500 microns because the polymers having such particle size (below 500 microns) do not swell, or soften, and do not get sticky during the preparation process.

Typically, the average particle size of the polymer and additional polymer is less than 150
5 micron.

The polymers having particle size more than 500 microns are not desirable as the higher particle size polymers will not pass through the shear zone and will not be useful to give particle to particle shear in the process.

The conventional process relied on liquid phase techniques using solvents, wherein there is
10 generally a strict limitation regarding the type of the solvent that can be used, as the polymer need to get dissolved in the solvent. As the polymer gets dissolved in the solvent, removing that solvent becomes very difficult. More specifically removing the residual solvent requires very long time as the solvent get trapped in the polymer mass and required lot of time. Further, as the solvent remained in the polymer mass, the polymer mass remains soft and
15 hence grinding becomes difficult. Sometimes cryogenic drying is required to convert that solid mass into hard mass for grinding. However, the low solubility of the polymer in the fluid medium in accordance with the present disclosure places much less limitation on the type of fluid that could be used in the process. The low solubility of the first polymer in the fluid medium also results in the elimination of certain conventional process steps, such as
20 concentration/ isolation of the composites, grinding of mass, as the masterbatch obtained in accordance with the present disclosure is a free flowing powder, making the process of the present disclosure simple, rapid, and cost effective.

In the conventional process graphene is prepared initially and then it is kinetically mixed with the polymer and then extruded to get the polymer composite beads. Whereas, in the process
25 of the present disclosure graphene is prepared in the presence of the polymer by employing high shear mixing. This shearing of the graphite in the presence of polymer creates particle to particle shear and helps in exfoliation. The presence of the polymer at the time of high shear not only improves the graphene quantity, but also coats the polymer with graphene. Therefore, the polymer coated graphene helps in the dispersion of the graphene into the
30 polymer matrix and create uniform composite which in turn helps in improving the mechanical properties. If the dispersion of the graphene in the polymer matrix is not uniform, it will create defects in the composite creating weak spots in the polymer composite. Once the

shearing process is over the slurry is very easy to dry to obtain the polymer graphene concentrate /master batch in the form of free flowing powder.

The exfoliation of graphite to graphene during high shear mixing with polymer provides polymer particles-exfoliated graphene concentrate/ master batch/composite having enhanced
5 physical and chemical properties that can be used in a wide range of commercial applications.

In an exemplary embodiment of the present disclosure, there is provided a process for preparing polyvinyl chloride - graphene composites. The process comprising mixing graphite and polyvinyl chloride particles in a ratio in the range of 1:3 to 3:1 and a fluid medium to obtain a mixture. The so obtained mixture is homogenized by shear mixing at a shear rate of
10 at least 10^5 sec^{-1} to obtain homogenized mixture containing polyvinyl chloride particles and exfoliated graphene. In an embodiment, the graphite and polyvinyl chloride particles are mixed, in a fluid medium wherein polyvinyl chloride is partially soluble in the fluid medium. The so obtained homogenized mixture is concentrated at a temperature in the range of 70 °C to 80 °C, at a rotation speed in the range of 5000-10000 RPM to remove the fluid medium to
15 obtain polyvinyl chloride-exfoliated graphene concentrate powder. The so obtained polyvinyl chloride-exfoliated graphene concentrate powder is blended with an additional polyvinyl chloride to form a polyvinyl chloride -graphene composite. The ratio of the concentrate powder to the additional polyvinyl chloride is in the range of 1:5 to 1:20.

The present disclosure is further described in light of the following experiments which are set
20 forth for illustration purpose only and not to be construed for limiting the scope of the disclosure. The following experiments can be scaled up to industrial/commercial scale and the results obtained can be extrapolated to industrial scale.

EXPERIMENTAL DETAILS:

Experiment 1:

25 Process for the preparation of polymer graphene master batch/ concentrate in accordance with the present disclosure:

In a container 100 gm of graphite and 200 gm of polyvinyl chloride (PVC) polymer were charged followed by 600 gm of methanol to obtain a resultant mixture. The so obtained

resultant mixture was stirred in a high shear Silverson Mixer having the rotation speed at 8000 RPM for 120 minutes to obtain slurry.

After 120 minutes, methanol was removed from the slurry by vacuum evaporation to obtain a free flowing powder of 300 gm of the polymer graphene master batch/ concentrate.

Experiment 2:

Process for preparation of the polymer graphene composite in accordance with the present disclosure:

3000 gm of polyvinyl chloride was taken in a kinetic mixer along with 57 gm of Tin stabilizer and the other additives as given in table that are required for making a stable extrudable polymer compound in the kinetic mixer.

300 gm of polymer graphene master batch/concrete obtained in experiment 1 was added to the kinetic mixer along with the PVC polymer and other powder additives. The kinetic mixture was rotated at 600 RPM to obtain a powder graphene polymer composite as given in Table 1.

Table 1: Polymer-Graphene composite

	Batch	X5T (polymer graphene composite with 1 % Graphene)	XG2M2 (polymer graphene composite with 3% Graphene)	F4M4 (graphene generated in absence of polymer)
Sl.no	Material	gms	gms	gms
1	PVC - K57 (K57 is the grade of the PVC polymer)	3000	3000	3000
2	Impact Modifier -	90	90	90

	B564			
4	BYK 9077 (High molecular-weight copolymer with pigment affinic groups)	20	0	0
5	Octyl Tin	39	57	57 10
6	AC316 (Wax)	15	15	15
7	TiO ₂	15	15	15
8	Graphene	30	100	100
9	GMS (glycerol monostearate)	24	24	24
10	Licowax E (Ester of montanic acids)	19.5	19.5	19.5 20

The ratio of polymer graphene master batch/ concentrate polyvinyl chloride (the second polymer) is 1:1 to 1:50, more specifically 1: 5 to 1:20.

25

The mixture of PVC and polymer graphene master batch/ concentrate was mixed for 20-40 minutes. The temperature of the mixture increases while mixing the PVC and polymer graphene master batch/ concentrate. The mixture was stirred till the temperature of the mixture reached between 80-110 °C, more precisely between 90-100 °C.

30

After the required temperature was obtained the kinetic mixing was stopped. The material from the kinetic mixer was removed and cooled to obtain a free flowing powder polymer graphene composite. The so obtained powder was extruded in a single screw extruder by keeping the extrusion temperature in the range of 130 to 200 °C. The extruder has three

heating elements which are kept at 155-185-195 °C for getting melt extrusion of PVC-graphene composite and the extrudate was cut with a cutter to get polymer composite beads. The so obtained polymer graphene composite beads were then tested for its mechanical properties.

5

The final PVC-graphene composite was tested for its mechanical properties such as tensile modulus, stress@yield, flexural modulus, flexural strength and Izod impact strength. **Table 2** shows the effect of graphene on the mechanical properties of the PVC polymer composite compared with the control sample without graphene.

10

Table 2:

Property	UOM	PVC Control	X5T (polymer graphene composite with 1 % Graphene)	XG2M2 (polymer graphene composite with 3% Graphene)	F4M4 (graphene generated in absence of polymer)
Tensile Modulus	Mpa	2780	2870	3690	3330
Stress @Yield	Mpa	52	56.8	64.3	56.1
Flexural Modulus	Mpa	2380	3000	3030	2950
Flexural Strength	Mpa	80.9	88.4	98.4	88.4
Izod Impact strength	J/m	74	56.1	38.41	-----

It is evident from table 2 that tensile modulus, stress yield, and flexural strength increase with increase in the percentage of the graphene.

15 From table 2, it is evident that incorporation of more amount of graphene increase the mechanical properties of the PVC.

X5T is the polymer graphene composite in accordance with the present disclosure wherein the graphene content is 1 % and polymer graphene composite was obtained by shear method.

XG2M2 is the polymer graphene composite in accordance with the present disclosure wherein the graphene content is 3 % and polymer graphene composite was obtained by particle-particle shear method.

F4M4 is made by just shearing graphite in the absence of (PVC) polymer.

- 5 It is observed from the results obtained in Table 2 that the particle to particle shearing method gives 15-23 % improvement in tensile strength of the PVC. Whereas, normal shear of graphite only improves 8% of the tensile strength of PVC.

The tensile modulus is increased by 33 % in accordance with the process of the present disclosure however; there is an increase of tensile modulus of only 20 % without particle to
10 particle shearing method. Therefore, it is evident that the process of the present disclosure gives better exfoliation which in turn gives better mechanical values.

TECHNICAL ADVANCEMENTS

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of:

- 15 - polymer-graphene composites having enhanced physical and chemical properties;
- a simple, rapid, and cost-effective process for the preparation of polymer-graphene concentrate /master batch;
- a simple, rapid, and cost-effective process for the preparation of polymer-graphene composites; and
- 20 - low solubility of the polymer in the fluid medium that aids the exfoliation of graphite to graphene in the presence of the polymer particles by providing particle to particle shear and provides the product in the form of a free flowing powder.

Throughout this specification the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated element, integer or step,
25 or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression “at least” or “at least one” or “a” suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to

achieve one or more of the desired objects or results. While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Variations or modifications to the formulation of this invention, within the scope of the invention, may occur to those
5 skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this invention.

The numerical values given for various physical parameters, dimensions, and quantities are only approximate values and it is envisaged that values higher or lower than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of
10 the invention unless there is a statement in the specification to the contrary.

While considerable emphasis has been placed herein on the specific features of the preferred embodiment, it will be appreciated that many additional features can be added and that many changes can be made in the preferred embodiment without departing from the principles of the disclosure. These and other changes in the preferred embodiment of the disclosure will be
15 apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

CLAIMS:

1. A process for preparing polymer-graphene composites, said process comprising the following steps:
 - a. forming an initial mixture containing graphite, a polymer and a fluid medium,
5 wherein the ratio of the graphite to the polymer is in the range of 1:10 to 10:1, preferably the ratio is in the range of 1:3 to 3:1, and wherein said polymer is partially soluble in said fluid medium;
 - b. homogenizing said mixture obtained in step a) by shear mixing at a shear rate
10 of at least 10^5 sec^{-1} to form homogenized mixture comprising polymer particles and exfoliated graphene;
 - c. concentrating said homogenized mixture at a pre-determined temperature in a controlled manner to remove said fluid medium and obtain powder containing polymer particles-exfoliated graphene masterbatch/concentrate; and
 - d. blending said powder with an additional polymer to form polymer-graphene
15 composites.
2. The process as claimed in claim 1, wherein the average particle size of said polymer is less than 500 microns.
3. The process as claimed in claim 1, wherein said polymer has a solubility of less than 1% in said fluid medium.
- 20 4. The process as claimed in claim 1, wherein mixing of said graphite with said polymer in step a) is carried out at a temperature below the softening point of said polymer.
5. The process as claimed in claims 1 and 4, wherein mixing of said graphite with said polymer in step a) is carried out at a temperature in the range of 25°C to 150°C .
6. The process as claimed in claim 1, wherein said fluid medium is at least one selected
25 from the group consisting of water, alcohol, and hydrocarbon.
7. The process as claimed in claimed 1, wherein said fluid medium is selected from the group consisting of methanol, ethanol, propanol, butanol, toluene, and hexane.

8. The process as claimed in claim 1, wherein said pre-determined temperature is in the range of 50 °C to 100 °C, preferably in the range of 70 °C to 80 °C.
9. The process as claimed in claim 1, wherein said mixture is concentrated in a controlled manner by distilling said fluid medium at a speed of rotation in the range of 5000-10000 RPM.
10. The process as claimed in claim 1, wherein said polymer and said additional polymer is a thermoplastic polymer.
11. The process as claimed in claim 1, wherein said polymer and said additional polymer is same or different.
12. The process as claimed in claim 1, wherein said polymer and said additional polymer is independently selected from the group consisting of polyvinyl chloride, polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, nylon, polyamide, thermoplastic polyurethane, polycarbonate, and polystyrene.
13. The process as claimed in claim 1, wherein the ratio of said powder to said additional polymer in step d) is in the range of 1:1 to 1:50, preferably the ratio is in the range of 1:5 to 1:20.
14. The process as claimed in claim 1, wherein said blending in step d) is carried out by kinetic or melt blending process .
15. The process as claimed in claim 1, wherein at least one additive is added while blending the polymer particles-exfoliated graphene concentrate with said additional polymer using kinetic or melt blending process to form said polymer-graphene composite.
16. The process as claimed in claim 15, wherein said additive is selected from the group consisting of impact modifier, octyl tin, wax, TiO₂, graphene, glycerol monostearate, and Ester of montanic acids.
17. The process as claimed in claim 16, wherein said impact modifier is a high molecular-weight copolymer with pigment affinic groups.
18. The process as claimed in claim 1, wherein said polymer particles-exfoliated graphene concentrate is in the form of free flowing powder.

19. The process as claimed in claim 1, wherein said polymer-graphene composite is in the at least one form selected from free flowing powder and beads.
20. A process for preparing polyvinyl chloride -graphene composites as claimed in claim 1, said process comprising the following steps:
- 5 a. forming an initial mixture containing graphite, polyvinyl chloride and fluid medium, wherein the ratio of graphite to polyvinyl chloride is in the range of 1:3 to 3:1, and wherein the polyvinyl chloride is partially soluble in the fluid medium;
 - b. homogenizing the mixture obtained in step a) by shear mixing at a shear rate of at least 10^5 sec^{-1} to obtain a homogenized mixture,;
 - 10 c. concentrating the homogenized mixture at a temperature in the range of 70°C to 80°C at a rotation speed in the range of 5000-10000 RPM to remove the fluid medium to obtain powder containing polyvinyl chloride-exfoliated graphene masterbatch/concentrate; and
 - d. blending the powder with an additional polyvinyl chloride to form a polyvinyl
15 chloride-graphene composite, wherein the ratio of the powder to the additional polyvinyl chloride is in the range of 1:5 to 1:20.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2018/052494

A. CLASSIFICATION OF SUBJECT MATTER

C08F114/06, C08F2/02, C08K9/04 Version=2018.01

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)

C08F; C08K

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

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

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP2016519191A RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY. 30 JUNE 2016 (2016-06-30) paragraphs [0042]-[0043], [0047], [0057], [0072], [0109], [0111], claims 1-6, 18 and 23, page 6 line 16-27	1-20
Y	WO2011144321A1 STICHTING DUTCH POLYMER INSTITUTE. 24 NOVEMBER 2011 (2011-11-24) abstract, page 1, claims 2, 4, 15, page 2 line 23-32	1-20
Y	CN102786615B SICHUAN PROVINCE JINLU RESIN CO. LTD. 07 MAY 2014 (2014-05-07) abstract, page 1, [0005], [0013], [0015], [0028]-[30], Examples 1-5, claims 1, 3-5	1-20

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

* Special categories of cited documents:

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"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

23-07-2018

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2018/052494

Citation	Pub.Date	Family	Pub.Date
JP 2016519191 A	30-06-2016	EP 2994308 A1	16-03-2016
		US 2016083552 A1	24-03-2016
		WO 2014172619 A1	23-10-2014
WO 2011144321 A1	24-11-2011	EP 2395043 A1	14-12-2011