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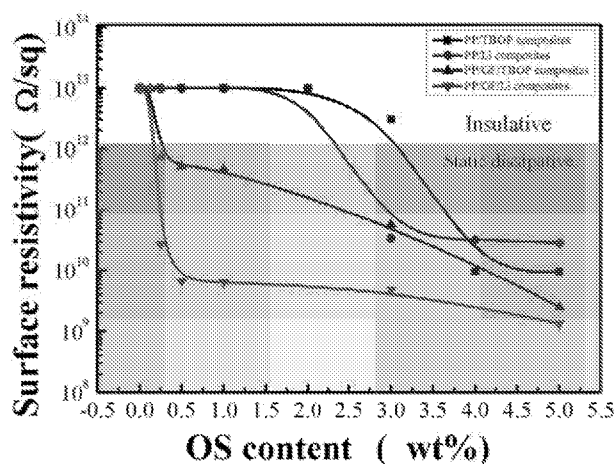


Fig. 1

(57) Abstract: A composite material comprise polypropylene or polyethylene, mineral fibers and an organic salt. The use of a sulfonimide salt for providing antistatic properties to a polyolefin based composite material reinforced with mineral fibers, and the use of mineral fibers for enhancing the electric conductivity of a polyolefin based composite comprising a sulfonimide salt.



POLYOLEFIN BASED COMPOSITE MATERIAL

TECHNICAL FIELD

The present invention relates to antistatic composite materials based on polyolefin and mineral fibers. More specifically, the invention relates to polyolefin based composite material, in particular a composite material comprising polypropylene or polyethylene, mineral fibers, in particular glass fibers, and an organic salt, in particular a sulfonimide salt.

10 BACKGROUND ART

Polypropylene (PP) has been widely used as packing materials, electric appliances, and automobile parts, etc. PP has very low moisture absorption and shows high electric insulation. Therefore, PP is easily charged by static electricity. The accumulated electrostatic charges may generate discharges and even create the danger of explosions.

15 On the other hand, glass fiber (GF) reinforced PP composites combine the comprehensive properties of reinforcing GF and the PP matrix. External forces could be transferred to glass fibers by the interface between the matrix and the reinforcing fibers, so the interface between PP and GF influences the properties of the final composites significantly. GF itself shows insulation properties. It would be highly valuable to provide GF with antistatic properties for the easy handling and for the further fabrication of antistatic polymer/GF composites. Research works have been investigated on the antistatic PP materials by the incorporating of conductive fillers and antistatic agents. However, there is still a need in enhancing the antistatic performance of PP/GF composites. It is therefore important to provide antistatic PP/GF composites because such composites can be not only used as the internal dusts-free parts but also applied as the industrial components that need dissipating static electricity.

SUMMARY OF THE INVENTION

After numerous trials, it has been surprisingly found that organic salts, in particular sulfonamide salts, and mineral fibers have significant synergistic effects in polyolefin matrix of a composite material.

A first object of the invention is a polyolefin based composite material comprising at least a polyolefin matrix, mineral fibers and at least one organic salt.

A method for manufacturing said composite material is another object of the invention. Said method comprises the mixing of the polyolefin, the mineral fibers and the organic salt, and the forming of the composite material.

Another object of the present invention is the use of a sulfonimide salt, for providing antistatic properties to a polyolefin based composite material reinforced with mineral fibers.

Still another object of the present invention is the use of mineral fibers, in particular glass fibers, for enhancing the electric conductivity of a polyolefin based composite comprising a sulfonimide salt.

Still another object of the present invention is the combined use of mineral fibers, in particular glass fibers, and of a sulfonimide salt, for providing antistatic properties to a polyolefin based material.

15

DESCRIPTION OF THE FIGURES

Fig.1 is a graph showing the Surface Resistivity of binary PP/OSs blends and ternary PP/GF/OSs composites with 30 wt.% of GF as a function of OSs loadings.

Fig.2 is a graph showing the Surface resistivity of PP/GF/OSs composites as a function of GF contents at the constant 1wt% OSs.

Fig. 3 are SEM images of cross-fracture surface of:

- PP/GF (A);
- PP/GF/Li-TFSI (in a ratio of 70-30-1) (B);
- PP/GF/Li-TFSI (70-30-3) (C);
- PP/GF/Li-TFSI (70-30-5) (D);
- PP/GF/TBOP-TFSI (70-30-1) (B');
- PP/GF/TBOP-TFSI (70-30-3) (C');
- PP/GF/TBOP-TFSI (70-30-5) (D').

Fig.4 represents two graphs showing:

(A) the storage modulus E' as a function of temperature by Dynamic Mechanical Analysis (DMA);

(B) the loss factor $\tan(\delta)$ of PP/GF/OSs composites as a function of temperature by DMA.

Fig. 5 represents two graphs showing:

- (A) the FTIR of Glass Fiber with Li-TFSI between 800 and 900 cm^{-1} ; and
- 5 - (B) the FTIR of Glass Fiber with TBOP-TFSI between 800 and 900 cm^{-1} .

Fig.6 represents two graphs showing:

- (A) Thermogravimetric Analysis (TGA) curves for samples of pure OSs and GF/OSs mixture; and
- 10 - (B) Derivative Thermogravimetric (DTG) curves for samples of pure OSs and GF/OSs mixture.

Fig.7 is a graph showing the Dynamic storage modulus G' as functions of ω for PP filled with GF of various content at 190°C.

Fig. 8 represents optic microscopy images, with a scale bar of 100 μm of

- (A) PP/GF (in a ratio 95-5);
- 15 - (B) PP/GF (in a ratio 90-10);
- (C) PP/GF (in a ratio 80-20);
- (D) PP/GF (in a ratio 70-30).

DETAILED DESCRIPTION OF THE INVENTION

20 In the following description, the expression “between...and...” should be understood as including the mentioned limits.

The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e. to at least one) of the grammatical object of the article.

25 The term “and/or” includes the meanings “and”, “or” and also all the other possible combinations of the elements connected to this term.

30 The terms “comprise” and “comprising” are used in the inclusive, open sense, meaning that additional elements may be included. Throughout this specification, unless the context requires otherwise the word “comprise”, and variations, such as “comprises” and “comprising”, will be understood to imply the inclusion of a stated element or step or group of element or steps but not the exclusion of any other element or step or group of element or steps.

A subject of the present invention is a polyolefin based composite material. This composite material comprises at least a polyolefin matrix, mineral fibers and at least one organic salt.

The polyolefin matrix may be selected from the typical polyolefin thermoplastic polymers known by the person skilled in the art. Preferably, the polyolefin matrix may be
5 polyethylene (PE) or polypropylene (PP).

The polyolefin based composite material according to the invention may comprise from 55 wt.% to 90 wt.% of polyolefin, preferably from 70 wt.% to 85 wt.%, relative to the total weight of the composite material.

Polyolefins in this invention can be either a propylene polymer or an ethylene polymer.
10 The propylene polymer can be a homopolymer, a random-copolymer, a block-copolymer, blends of the above polypropylenes or a toughened polymer or a filled polymer of any of the above polypropylenes. For economic reasons, for highest flexural modulus and for highest heat distortion temperatures homopolypropylenes are most preferred. The ethylene polymer can be any polyethylene from very low density to very high density, as long as
15 melt viscosity is within the specified range, whereby high molecular polyethylenes are preferred for improved overall toughness.

Polyolefins such as polyethylenes and polypropylenes and their manufacture are also well known to those skilled in the art. Other olefin polymers of 4-8 carbon atoms can also be used either alone or preferably as copolymers with ethylene or propylene. Such higher
20 olefin polymers and copolymers are also known in the art.

Polyolefins of the invention may also be modified polyolefins, notably either an acid modified propylene polymer or an acid modified ethylene polymer. The base polymer for the modified propylene can again be a homopolymer, a random copolymer, a block copolymer or a toughened polymer or a filled polymer of any of the above described
25 polypropylenes. Homopolymers and copolymers are preferred most. The base resin for the modified ethylene polymer can again be any polyethylene from very low density to very high density.

The acid modified polyolefin may be modified with 0.05 to 3.0 weight percent, preferably 0.5 to 1 weight percent, of a carboxylic acid or a derivative thereof. The grafting of the
30 polyolefin can be carried out in the melt state, in solution or in suspension as described in the state-of-the-art literature.

Mineral fibers are typically used in composite material as reinforcement materials, to add rigidity and greatly impede crack propagation. The mineral fibers may be short fiber-reinforced materials or continuous fiber-reinforced materials. Mineral fibers may be

chosen in the group consisting of: glass fibers, carbon fibers, boron fibers, potassium titanate fibers, quartz fibers, basalt fibers, ceramic fibers or any combinations thereof. In the present invention, the mineral fibers are very preferably glass fibers.

5 It is perfectly possible according to the invention for the composition to comprise several types of fillers. Preferably, the filler used most can be glass fibers, of the so-called chopped type, notably having a diameter between 7 and 14 μm (micrometers). These fillers can have surface oiling that ensures mechanical adhesion between the fibers and the polyolefin matrix.

10 Mineral fibers may have a non-circular cross-sectional area or a circular cross-sectional area. The cross-sectional area may be for instance longitudinally oval, elliptical or almost rectangular.

The glass fibre itself can thereby be selected from the group comprising E-glass fibres, A-glass fibres, C-glass fibres, D-glass fibres, M-glass fibres, S-glass fibres and/or R-glass fibres, E-glass fibres being preferred. The glass fibres per se can also be provided with a
15 pre-treatment, such as a silane compound, or an amino- or epoxysilane coating.

The polyolefin based composite material according to the invention may comprise from 10 wt.% to 45 wt.% of mineral fibers, preferably from 15 wt.% to 30 wt.%, relative to the weight of polyolefin.

The expression "organic salt" in the present text refers to a salt having an organic anion.

20 The composite material according to the invention may contain a single organic salt. However, it is not excluded in the context of this invention to use a mixture of several salts consisting of different anions and/or of different cations. The salt may consist of a fluorinated monoanion or polyanion and of one or more cations. Generally, the organic salt according to the invention can be described by the overall formula below:



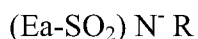
in which:

- A represents an organic anion;
- M1 and M2 represent cations;
- n, l and p, independently selected between 1 and 5, represent respectively the
30 charges of the fluorinated anion, of the cation M1 and of the cation M2;
- m, selected between 1 and 2, represents the stoichiometry of the cation M1.

The cation(s) may be selected, independently of one another, from metal cations and organic cations. The cation(s) may be monocharged cations or polycharged cations. As

metal cation, mention may preferably be made of alkali metal cations, alkaline-earth metal cations and cations of d-block elements. As organic cation, mention may be made of imidazolium cations, pyrrolidinium cations, pyridinium cations, guanidinium cations, ammonium cations and phosphonium cations. According to one preferred embodiment, the organic salt comprises at least one alkali metal cation, preferably at least one lithium cation or sodium cation, and more preferentially at least one lithium cation. Said organic salt may be an organic lithium salt or an organic sodium salt, preferably an organic lithium salt. According to another preferred embodiment, the organic salt comprises at least one phosphonium cation, preferentially at least one tetraalkylphosphonium cation. Said organic salt may be very preferably an octyltributylphosphonium salt. Alternatively, the organic salt may comprise at least one alkaline-earth metal cation, preferably at least one magnesium cation. Alternatively, the organic salt may comprise at least one cation of d-block elements, preferably at least one yttrium cation.

Among the anions that can be used in the present invention, sulfonimide anions may be advantageous, and fluorinated sulfonimide anions may be more particularly advantageous. The organic anion may in particular be selected from the anions having the following general formula:



in which:

- Ea represents a fluorine atom or a group having preferably from 1 to 10 carbon atoms, selected from fluoroalkyls, perfluoroalkyls and fluoroalkenyls,
- R represents a substituent.

Preferably, Ea may represent F or CF₃.

According to a first embodiment, R represents a hydrogen atom.

According to a second embodiment, R represents a linear or branched, cyclic or non-cyclic hydrocarbon-based group, preferably having from 1 to 10 carbon atoms, which can optionally bear one or more unsaturations, and which is optionally substituted one or more times with a halogen atom, a nitrile function, or an alkyl group optionally substituted one of several time by a halogen atom. Moreover, R may represent a nitrile group -CN.

According to a third embodiment, R represents a sulfinate group. In particular, R may represent the group -SO₂-Ea, Ea being as defined above. In this case, the fluorinated anion may be symmetrical, i.e. such that the two Ea groups of the anion are identical, or non-symmetrical, i.e. such that the two Ea groups of the anion are different. Moreover, R may represent the group -SO₂-R', R' representing a linear or branched, cyclic or non-cyclic

hydrocarbon-based group, preferably having from 1 to 10 carbon atoms, which can optionally bear one or more unsaturations, and which is optionally substituted one or more times with a halogen atom, a nitrile function, or an alkyl group optionally substituted one of several time by a halogen atom. In particular, R' may comprise a vinyl or allyl group.

5 Furthermore, R may represent the group $-\text{SO}_2-\text{N}^-\text{R}'$, R' being as defined above or else R' represents a sulfonate function $-\text{SO}_3^-$.

Cyclic hydrocarbon-based group may preferably refer to a cycloalkyl group or to an aryl group. "Cycloalkyl" refers to a monocyclic hydrocarbon chain, having 3 to 8 carbon atoms. Preferred examples of cycloalkyl groups are cyclopentyl and cyclohexyl. "Aryl" refers to a

10 monocyclic or polycyclic aromatic hydrocarbon group, having 6 to 20 carbon atoms. Preferred examples of aryl groups are phenyl and naphthyl. When the group is a polycyclic group, the rings may be condensed or attached by σ (sigma) bonds.

According to a fourth embodiment, R represents a carbonyl group. R may in particular be represented by the formula $-\text{CO}-\text{R}'$, R' being as defined above.

- 15 The organic anion that can be used in the present invention may advantageously be selected from the group consisting of:
- $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$ (i.e. bis(trifluoro-methane-sulfonyl)-imide anion, commonly denoted TFSI),
 - $\text{FSO}_2\text{N}^-\text{SO}_2\text{F}$ (i.e. bis(fluorosulfonyl)imide anion, commonly denoted FSI),
 - 20 - $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{F}$, and
 - $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$.

The organic salt that can be used in the present invention may advantageously be selected from the group consisting of octyl-tributyl-phosphonium bis(trifluoro-methane-sulfonyl)-imide (commonly denoted TBOP-TFSI) and lithium

25 bis(trifluoromethanesulfonyl)imide (commonly denoted Li-TFSI).

According to one embodiment, the organic salt may be an ionic liquid (IL), and preferably a room temperature ionic liquid (RTIL).

Organic salts of bis(trifluoro-methane-sulfonyl)-imide are particularly interesting firstly because they are thermally stable. This may be advantageous since the mixing with the

30 other components of the composite material may be carried out under high temperature. Secondly, bis(trifluoro-methane-sulfonyl)-imide salts do not have acidic protons. Thus, no carbene can be formed, and the anion is chemically more stable. Thirdly, bis(trifluoro-methane-sulfonyl)-imide salts are known to show high electrochemical stability, so they can be used as electrolytes with excellent electrochemical performance.

The polyolefin based composite material according to the invention may comprise from 0.1 wt.% to 5 wt.% of organic salts, preferably from 0.2 wt.% to 1 wt.%, relative to the weight of polyolefin.

5 In addition, the composite material according to the present invention may optionally comprise at least one additive. Examples of the additives, which may be advantageously used, comprise, but are not limited to, a colorant, a pigment, a lubricant, a light stabiliser, a heat stabiliser, a flame retardant, a plasticizer, a nucleating agent, a surfactant, an antioxidant, an antistatic agent, a dispersant, a surface active agent, a filler, and the like.

10 The composite material may be prepared by any typical method known by the person skilled in the art. Preferably, every component is kept under anhydrous conditions before processing. A method for manufacturing the composite material according to the invention may comprise the mixing of the polyolefin, the mineral fibers and the organic salt, and the forming of the composite material. The mixing step may be preferably a melt-mixing step, i.e. the mixing is performed at a temperature which allows the components to melt.
15 Preferably, the temperature may be higher than 100°C, more preferably higher than 130°C, even more preferably higher than 170°C, but preferably lower than 300°C. Said mixing step may be a polymer compounding step. After mixing, the composite material may be formed into the desired shape: sheets, films, extrudates... The forming step may for instance comprise an extrusion step, a molding step, a casting step, or a pressing step.

20 The obtained composite material show very interesting properties, such as:

- Good antistatic properties: the composite material according to the invention has a resistivity of preferably less than 10^{12} Ω/square, more preferably between 10^6 Ω/square and 10^{12} Ω/square, and even more preferably between 10^7 Ω/square and 10^{11} Ω/square.

25 The electrical conductivity may be measured as disclosed in the examples by an ultrahigh resistivity meter at 100 V. The composite material was sampled as a 500-μm-thick film.

- Good mechanical properties: the composite material according to the invention has a stiffness at least as high as, and preferably higher than, the polymer matrix reinforced by the mineral fibers without any organic salt. The composite material according to the invention may preferably have a dynamic storage modulus, at room temperature, higher
30 than 2 GPa, more preferably between 3 GPa and 4 GPa. Additionally, the tensile strength and/or the static modulus of the composition material according to the invention can preferably be at least as high as, and preferably higher than, the polymer matrix reinforced by the mineral fibers without any organic salt.

Mechanical and rheology behavior may be measured as disclosed in the examples using a rotated rheometer and a modal of parallel-plate. Dynamic mechanical analysis may be used to determine dynamic storage modulus and dynamic loss tangent at 5 Hz as a function of the temperature.

- 5 Without wishing to be bound by any theory, the inventors believe that the interesting properties obtained with the composite material according to the invention are due to a synergistic effect between the organic salts and the mineral fibers inside the polyolefin matrix: mineral fibers advantageously enhances the electrical conductivity of polyolefin/organic salts blends, whereas the organic salt improves the compatibility
10 between the polyolefin matrix and the mineral fibers, which seems to strengthen the interfacial adhesion between mineral fibers and the polyolefin.

Another object of the present invention is the use of a sulfonimide salt, for providing antistatic properties to a polyolefin based composite material reinforced with mineral fibers.

- 15 Still another object of the present invention is the use of mineral fibers, in particular glass fibers, for enhancing the electric conductivity of a polyolefin based composite comprising a sulfonimide salt.

- Still another object of the present invention is the combined use of mineral fibers, in particular glass fibers, and of a sulfonimide salt, for providing antistatic properties to a
20 polyolefin based material.

Should the disclosure of any patents, patent applications and publications, which are incorporated herein by reference, conflicts with the description of the present invention to the extent that it may render a term unclear, the present description shall take precedence.

- 25 The invention will now be further described in examples, which are given by way of illustration and which are no intended to limit the specification or the claims in any manner.

EXAMPLES

- 30 1. Materials

Polypropylene (PP) used is commercially available from Sumitomo Co. Ltd (Japan) with the trade name of AH561. Both organic salts (tribuyl-octylphosphonium bis(trifluoro-

methanesulfonyl)imide (TBOP-TFSI) and Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI)) are commercially available from Solvay (Belgium). The short glass fibers (GF) are commercial grade 568H available from by Jushi Co.Ltd (China).

2. Preparation of composite materials

5 All components were kept dried under vacuum at 80°C for 12h before processing. The binary and ternary composites were prepared by direct mixing of PP, GF, and organic salts (OSs) in a batch mixer (Haake PolyLab QC), at 50rpm and 190°C for 5min. After melt-mixing, samples were hot-pressed at 200°C and 10MPa into 500-μm-thick films, followed by the cold-pressing at room temperature. The obtained sheets were used for the following
10 characterization.

Except mentioned otherwise, the GF contents and the OSs loadings in this text were calculated based on only the amount of matrix PP by weight.

3. Characterization methods

Electrical conductivity was measured by an ultrahigh resistivity meter, with a piece of URS
15 probe electrode (Model MCP-HT450) at 100V. The sample thickness was about 500μm.

The microstructure of cross-fractured surface of samples was obtained using field emission scanning electron microscopy (FESEM, SEM-JSM 6700). An acceleration voltage of 3kV was used for the samples and the fractured surface was coated with a thin layer of gold before the SEM observation.

20 Rheology behavior was carried out by rotated rheometer (Anton Paar Co. Ltd. Austria) with a type of MCR 302 and a modal of parallel-plate. The dynamic storage modulus (G') and dynamic loss tangent ($\tan\delta=G''/G'$) were evaluated as a function of frequency at 190°C with a strain amplitude of 15%. Dynamic mechanical analysis (DMA, TA-Q800) was carried out in multi-frequency strain mode. The dynamic loss ($\tan\delta$) was determined at
25 5Hz and a heating rate of 3°C/min, at 0~150 °C.

The Fourier transform infrared spectroscopy (FTIR) measurements were carried out in transmittance mode on grinding samples by FTIR spectroscopy (FTIR, Bruker Tensor). The FTIR spectra were recorded at a resolution of 2cm⁻¹, and 64 scans from 4000 to 400cm⁻¹ were averaged.

30 Thermogravimetric analysis (TGA, TA-Q500) was carried out at a heating rate of 20°C/min from room temperature to 550°C, in a high purity N₂ atmosphere.

A polarized optical microscope (POM, Olympus BX51-P) with a hot stage unit was used to study the morphologies of PP/GF blends. All the samples were heated to 200°C.

4. Antistatic performance of PP/GF/OS composites

Figure 1 shows the electrical conductivity of binary PP/OSs blends and ternary PP/GF/OSs composites with 30 wt.% of GF as a function of OS loadings. Generally speaking, the antistatic materials usually have the resistivity of less than 10^{12} Ω/sq. Neat PP is insulative with the electrical resistivity of higher than 10^{13} Ω/sq.

For the binary PP/OSs blends without GF, the decreasing of the resistivity was observed at the OS loadings of more than 2 wt.%. Antistatic properties are achieved at the OS loadings of more than 3 wt.%. It should also be noted that an excess bleeding was observed for the TBOP-TFSI incorporated PP sample during the melt mixing, indicating the immiscibility between the TBOP-TFSI with PP matrix. Without GF, TBOP-TFSI forms big aggregate in the PP matrix with even 1 wt.% loading. Li-TFSI is also incompatible with the PP matrix. It is therefore concluded that the single incorporation of the OSs (without mineral fibers) is not applicable for fabrication the antistatic PP materials.

In contrast, it is clear from Figure 1 that the ternary PP/GF/OSs composites show totally different conductivity behaviors from the binary PP/OSs blends. At the constant 30 wt.% of GF, the addition of OSs induces significant enhancement in the electrical conductivity for both TBOP-TFSI and Li-TFSI systems as compared with the samples without OSs. The electrical conductivity of PP/GF/TBOP-TFSI and PP/GF/Li-TFSI composites with 0.25 wt.% OSs are 10^{11} Ω/sq and 10^{10} Ω/sq, respectively. The values are much lower than the PP blends at the same OSs loading. For the ternary composites with Li-TFSI, the electrical conductivity levels off at the loading of about 0.5 wt.% and the surface resistivity is in the range of 10^9 Ω/sq, indicating the excellent antistatic performance by the incorporation of Li-TFSI. It should be emphasized that no excess organic salts were observed during the melt compounding and the storage of the composites, indicating that the GF can stabilize the OSs in the ternary composites.

Figure 2 shows the surface resistance of PP/GF/Li-TFSI and PP/GF/TBOP-TFSI composites at the constant 1 wt.% of OSs (loading based only on the PP content). The inventors found that the conductivity increases with increasing GF contents in the composites with less than 30 wt.% GF. For the both systems, the highest electrical conductivity occurs at the GF contents ranging from 20 wt.% to 30 wt.%.

5. Mechanical performance of PP/GF/OS composites

Figure 4 shows the storage modulus and the loss factor $\tan(\delta)$ curves of the neat PP, PP/GF binary (comparative examples), and the PP/GF/OSs ternary composites (according to the invention). Addition of GF enhances the storage modulus of PP significantly due to the strengthening effects of GF for PP over the whole temperature range. The ternary composites with Li-TFSI have almost similar storage modulus with the binary PP/GF composites, which means that PP/GF/OSs ternary composites with Li-TFSI has mechanical properties equivalent to PP/GF binary composite. The TBOP-TFSI exhibits significantly strengthening effects on the binary PP/GF composites. The only 5 wt.% addition of TBOP-TFSI induces the much higher storage modulus in the whole temperature range than the binary PP/GF composites. The storage modulus for the PP/GF composites is 2.7 GPa at room temperature, while that for the PP/GF/TBOP composites is 3.2 GPa. Without wishing to be bound by any theory, the inventors believe that the strengthening function of TBOP-TFSI is originated from the compatibility effects of TBOP-TFSI for the GF and the PP matrix.

6. Study of the synergistic effect between the organic salts and the mineral fibers inside the polyolefin matrix

The inventors surprisingly found that the GF and the OSs show synergistic effects for the antistatic PP composites. GF enhances the electrical conductivity of PP/OSs blends and OSs improves the compatibility between PP and GF. In particular, the maximum electrical conductivity was achieved upon the GF content of 20-30 wt.% at the constant OSs loadings. On the other hand, the OSs, especially TBOP-TFSI, strengthen the interfacial adhesion between PP and GF. Hereunder, the inventors tried to elucidate the mechanism for such synergistic effects.

Figure 3 shows the SEM images of cryo-fractured surface of PP/GF/TBOP-TFSI and PP/GF/Li-TFSI composites with the indicated OS content. For the binary PP/GF composite without OS, clear gap was observed between the GF and the matrix, indicating the incompatibility between the GF and the matrix. However, with the addition of OSs in the composites, the gap between the GF and matrix gradually disappears. Such phenomenon was very clear at the 5 wt.% loadings of both TBOP-TFSI and Li-TFSI. This result indicates that both TBOP-TFSI and Li-TFSI improve the interfacial adhesion between PP and GF.

The inventors also show with Figure 3 that TBOP-TFSI is more effective to improve the compatibility between the fibers and the matrix than Li-TFSI. For the sample with 5 wt.% TBOP-TFSI, the GF was embedded in the PP matrix and the surface of fiber is not smooth. The inventors assume that the long alkyl chains of TBOP-TFSI have stronger interactions

with the PP matrix and that the TBOP-TFSI is more compatible with the PP matrix than Li-TFSI.

The synergistic effect of GF and OSs may also be observed on the storage modulus and the loss factor $\tan(\delta)$ curves of Figure 4. The relaxation peak of neat PP at about 8°C is attributed to the T_g of PP. The simple addition of GF does not change the relaxation peak, indicating the immiscibility between PP and GF. The improved miscibility can be observed for the ternary PP/GF/OSs composites, as evidenced by the almost invisible T_g relaxation for both PP/GF/Li-TFSI and PP/GF/TBOP-TFSI composites.

The interfacial adhesion can be measured by the loss factor $\tan(\delta)$ of T_g peak for the short fiber reinforced polymer composites. The relationship of interfacial adhesion and the maximum values of $\tan(\delta)$ for composites $(\tan\delta_{\max})_c$ and polymer matrix $(\tan\delta_{\max})_m$ could be described by:

$$(\tan\delta_{\max})_c = (\tan\delta_{\max})_m - \alpha V_f$$

where the subscript c, m, and f denote composite, matrix, and fiber, respectively. V_f is the volume fraction of filler. From the value of α , the degree of the interaction between fibers and matrix can be estimated. In the present cases, it was calculated that $\alpha_{\text{TBOP-TFSI}}$ is 0.062 and $\alpha_{\text{Li-TFSI}}$ is 0.046. The fact that $\alpha_{\text{TBOP-TFSI}}$ is larger than $\alpha_{\text{Li-TFSI}}$ indicates the stronger interfacial adhesion for the TBOP-TFSI incorporated composites. The results are consistent with both the SEM results and the storage modulus data.

The special interactions between GF and the OSs used have been considered. It has been found that both GF and OSs have very high polarity. The inventors have simply grinded the GF with 5 wt.% OSs and the prepared GF/OSs mixture was used for further characterization.

Figure 5 shows the FTIR spectra of the GF/OSs mixture. The absorption peak at 869 cm^{-1} is assigned to be the -Si-OH stretching vibrations of glass fibers for neat GF. The peak shifts to the lower wavenumber for the both two GF/OSs mixture samples. The absorption peaks for GF/Li-TFSI sample and GF/TBOP-TFSI sample are at 863 and 866 cm^{-1} respectively. Such shifts after the grinding could be attributed to the strong Lewis acid-base interaction between cation and electron-donating oxygen atoms of OH in GF. The fact that GF/TBOP-TFSI sample has smaller shifting than the GF/Li-TFSI sample indicates that Li-TFSI exhibits stronger interactions with GF than TBOP-TFSI.

The specific interactions between GF and OSs can be further confirmed by the TGA analysis of the neat OSs and the GF/OSs mixture, as shown in Figure 6. It has been found that the maximum degradation temperature ($T_{\max}$) of TBOP-TFSI shifts from 393°C for the

neat sample to 431°C for the grinded GF/TBOP-TFSI mixture sample. The significant higher degradation temperature shifting proves again the specific interactions between the GF and TBOP-TFSI. The same situation was observed for the GF/Li-TFSI system. The $T_{\max}$ of neat Li-TFSI is 416°C and it shifts to 435°C after grinding with GF.

5 Once we conclude the surface absorption of the OSs on the surface of GF in the PP matrix, it is easy to explain the significant enhancement in the electrical conductivity with the addition of GF at the constant OS loadings. The incompatibility between OS and PP leads to the aggregation of OS and also the bleeding of the excess OS in the PP matrix. Such aggregation leads to the lack of ionic path network and the materials show low electrical
10 conductivity even with high loading. However, the inventors surprisingly found that the addition of GF leads to the surface absorption of both anions and cations of the OSs. GF has the large aspect ratio and it easily form network in the PP matrix. In other words, the GF presents a perfect orbit for the movements of the ions in the composites. Therefore, the GF not only diminishes the bleeding phenomenon of OSs and the aggregation of OSs in
15 the PP matrix at the high OSs loadings, but also enhances the electrical conductivity. Especially, it has been found that with increasing the GF content in the composites, the fibers form the contact network in the PP matrix. Once the formation of the GF network, the ions of OSs on the surface of glass fibers form perfect ionic network. Therefore, one can achieve the best electrical conductivity of the ternary composites. Both the rheology
20 analysis and optical microscopy have been used to detect the formation of GF network in the PP matrix, as shown in Figure 7 and Figure 8, respectively. The clear plateau of the storage modulus at about 30 wt.% of GF indicates the formation of the GF networks in the melt state. On the other hand, the OM images of Figure 8 provide the direct observation of the GF fibers in the PP matrix. The glass fibers contact each other and the network forms at
25 the GF content of about 20-30 wt.%. Therefore, we observed good antistatic performance with 20-30 wt.% GF at the constant OSs contents.

7. Scalability of the composite manufacturing

The composite material was prepared as disclosed above, except that after melt-mixing, samples were prepared by injection molding by Haake minijet to ISO 527-2-5A standard
30 specimens. The obtained specimens were used for the following characterization: Surface resistivity (same method as disclosed above), and mechanical strength (crosshead speed of 5 mm/min in tensile test).

Sample (wt.%)	Surface resistivity ($\Omega/\square$)
NEAT-PP	$>10^{13}$
PP-GF (70-30)	$>10^{13}$

PP-GF-LiTFSI (70-30-0.175)	2.68×10^{10}
PP-GF-LiTFSI (70-30-0.35)	6.57×10^9

Table 1: Surface resistivity

Sample	Tensile modulus (%)	Strength at break (MPa)
NEAT-PP	524 ± 59	26 ± 1
PP-GF (70-30)	1865 ± 35	31 ± 1
PP-GF-LiTFSI (70-30-0.175)	2115 ± 68	34 ± 1
PP-GF-LiTFSI (70-30-0.35)	1960 ± 86	35 ± 0.5

Table 2: Mechanical properties

These results demonstrate that composite materials obtained according to the invention show excellent mechanical properties even at low LiTFSI concentration: with 0.175% w/w

5 LiTFSI (versus total PP + GF weight), the composite material shows reinforced mechanical properties while good antistatic properties.

CLAIMS

1. A polyolefin based composite material comprising at least a polyolefin matrix, mineral fibers and at least one organic salt.
2. The polyolefin based composite material according to claim 1, wherein the
5 polyolefin is selected from the group consisting of polypropylene and polyethylene.
3. The polyolefin based composite material according to claim 1 or claim 2, wherein it comprises from 55 wt.% to 90 wt.% of polyolefin, preferably from 70 wt.% to 85 wt.%, relative to the total weight of the composite material.
4. The polyolefin based composite material according to anyone of claims 1 to 3,
10 wherein the mineral fibers are glass fibers.
5. The polyolefin based composite material according to anyone of claims 1 to 4, wherein it comprises from 10 wt.% to 45 wt.% of mineral fibers, preferably from 15 wt.% to 30 wt.%, relative to the weight of polyolefin.
6. The polyolefin based composite material according to anyone of claims 1 to 5,
15 wherein the organic salt comprises a metal cation selected from alkali metal cations, alkaline-earth metal cations and cations of d-block elements.
7. The polyolefin based composite material according to claim 6, wherein the metal cation is a lithium cation or a sodium cation, and more preferentially at least one lithium cation.
8. The polyolefin based composite material according to anyone of claims 1 to 5,
20 wherein the organic salt comprises an organic cation selected from imidazolium cations, pyrrolidinium cations, pyridinium cations, guanidinium cations, ammonium cations and phosphonium cations.
9. The polyolefin based composite material according to claim 8, wherein the
25 organic cation is a tetraalkylphosphonium cation, preferably an octyltributylphosphonium cation.
10. The polyolefin based composite material according to anyone of claims 1 to 9, wherein the organic salt comprises a sulfonimide anion.
11. The polyolefin based composite material according to claim 10, wherein the
30 organic salt comprises a fluorinated sulfonimide anion.

12. The polyolefin based composite material according to claim 11, wherein the fluorinated sulfonimide anion is selected from the group consisting of $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$, $\text{FSO}_2\text{N}^-\text{SO}_2\text{F}$, $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{F}$, and $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$.

13. The polyolefin based composite material according to anyone of claims 1 to 12,
5 wherein the organic salt is selected from the group consisting of octyl-tributyl-phosphonium bis(trifluoromethanesulfonyl)imide and lithium bis(trifluoromethanesulfonyl)imide.

14. The polyolefin based composite material according to anyone of claims 1 to 13,
10 wherein it comprises from 0.1 wt.% to 5 wt.% of organic salts, preferably from 0.2 wt.% to 1 wt.%, relative to the weight of polyolefin.

15. The polyolefin based composite material according to anyone of claims 1 to 14,
wherein it comprises:
- from 55 wt% to 90 wt% of polyolefin, preferably from 70 wt% to 85 wt%;
- from 10 wt% to 45 wt% of mineral fibers, preferably from 15 wt% to 30 wt% and
15 - from 0.1wt% to 5 wt% of an organic salt, preferably between 0.2 wt% and 1 wt%.

16. The polyolefin based composite material according to anyone of claims 1 to 15,
wherein it has a resistivity of less than $10^{12} \Omega/\text{square}$, preferably between $10^6 \Omega/\text{square}$ and $10^{12} \Omega/\text{square}$, and more preferably between $10^7 \Omega/\text{square}$ and $10^{11} \Omega/\text{square}$.

17. Method for manufacturing the composite material according to anyone of claims
20 1 to 16, wherein said method comprises the mixing of polyolefin, mineral fibers and organic salt, and the forming of the composite material.

18. Use of a sulfonimide salt, for providing antistatic properties to a polyolefin based composite material reinforced with mineral fibers.

19. Use of mineral fibers, in particular glass fibers, for enhancing the electric
25 conductivity of a polyolefin based composite comprising a sulfonimide salt.

20. Combined use of mineral fibers, in particular glass fibers, and of a sulfonimide salt, for providing antistatic properties to a polyolefin based material.

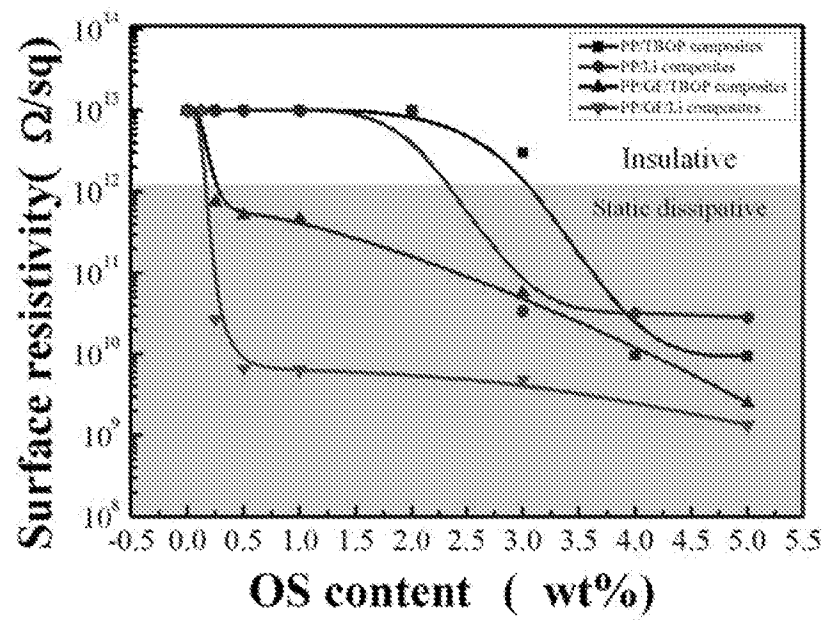


Fig. 1

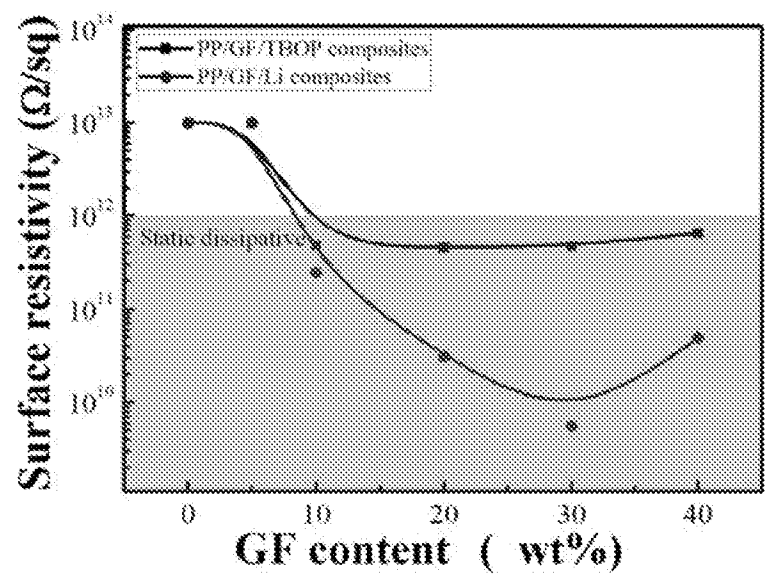


Fig. 2

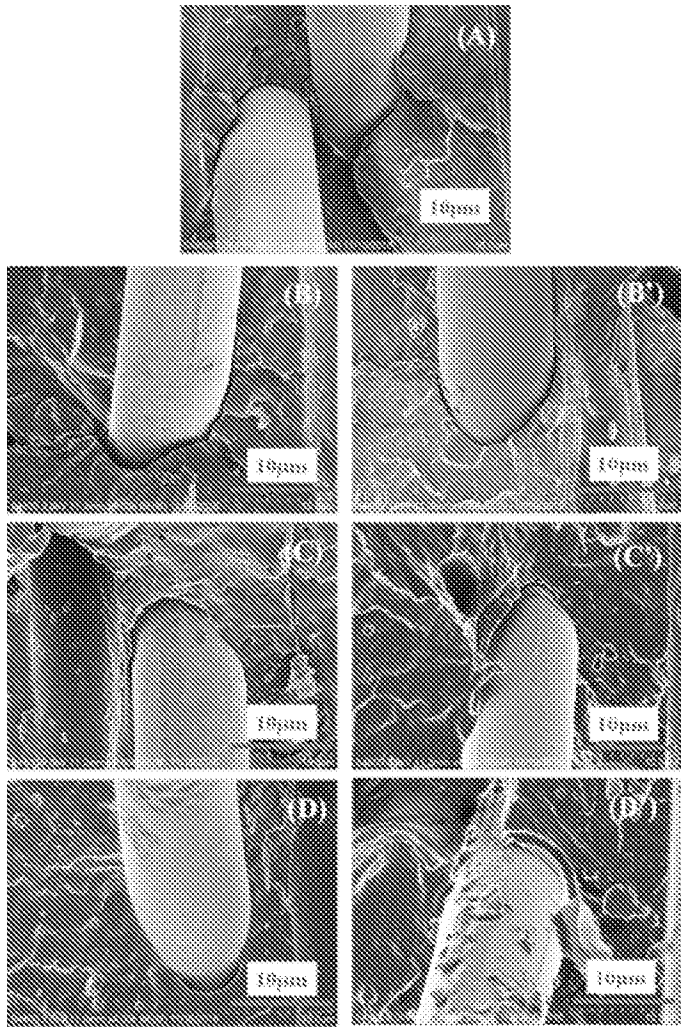


Fig. 3

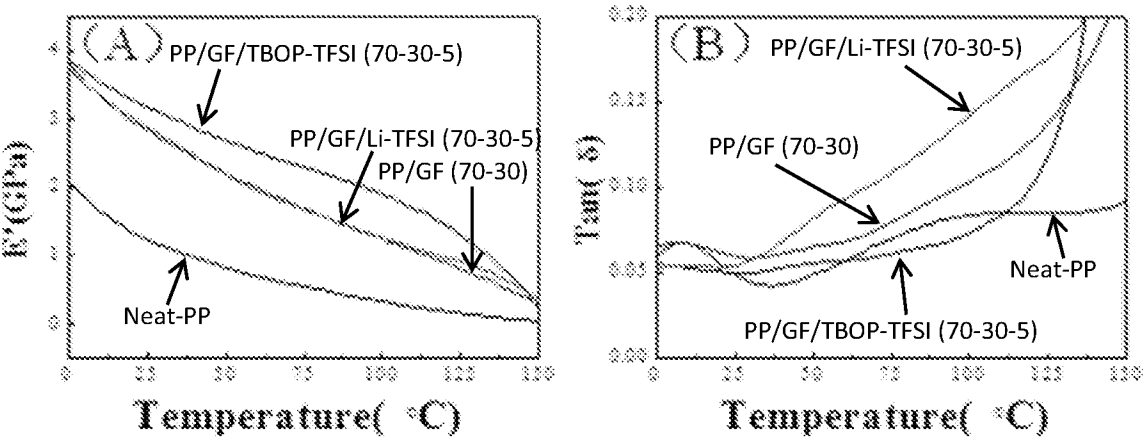


Fig. 4

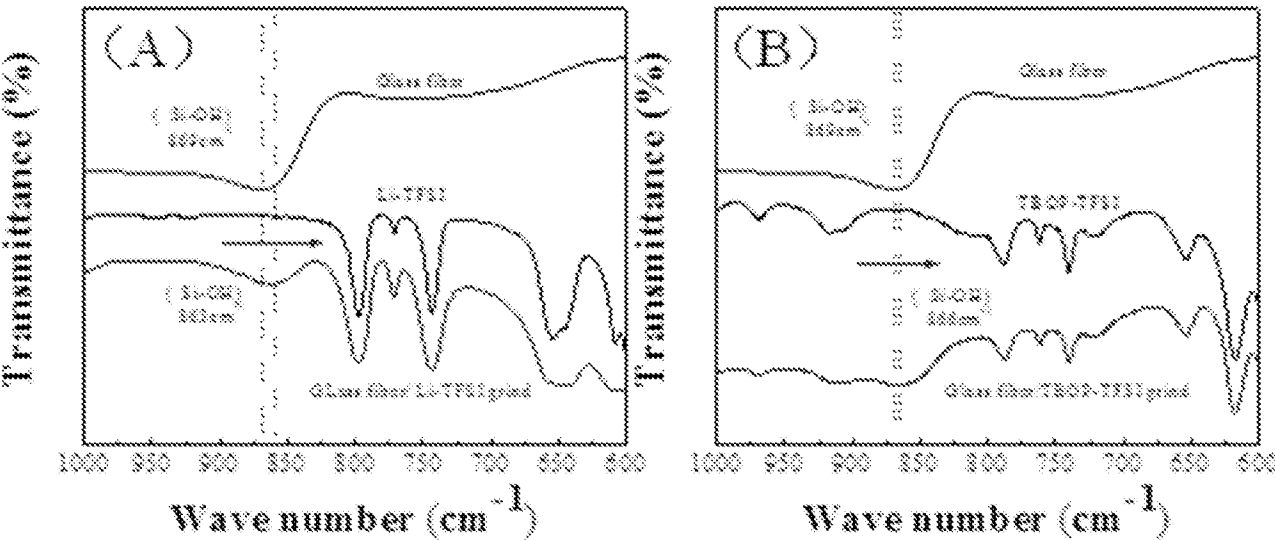


Fig. 5

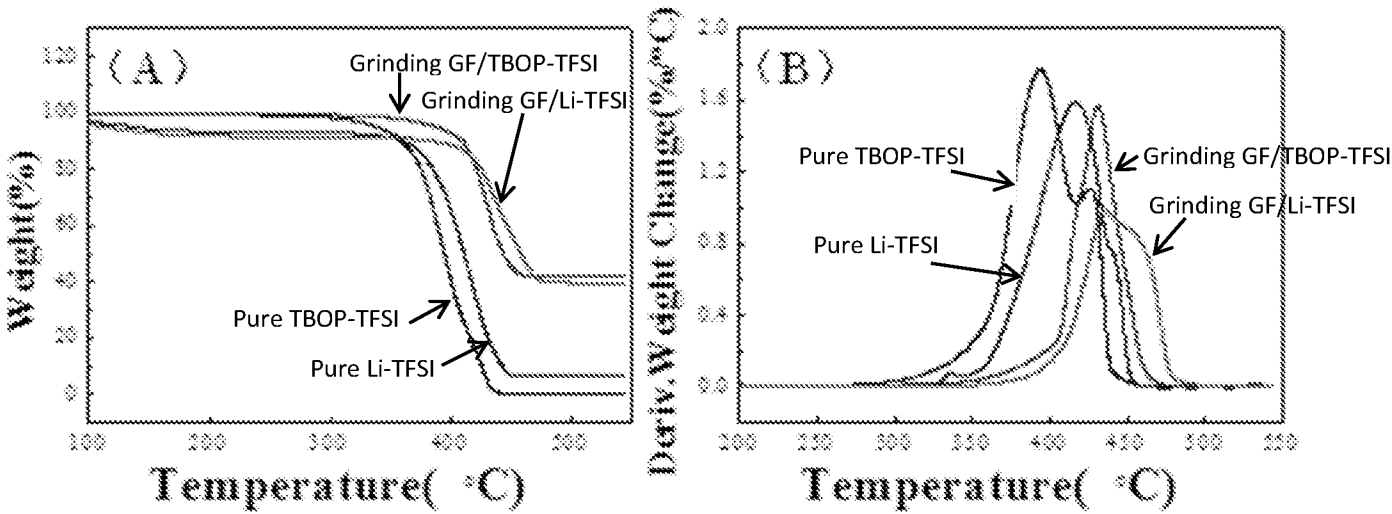


Fig. 6

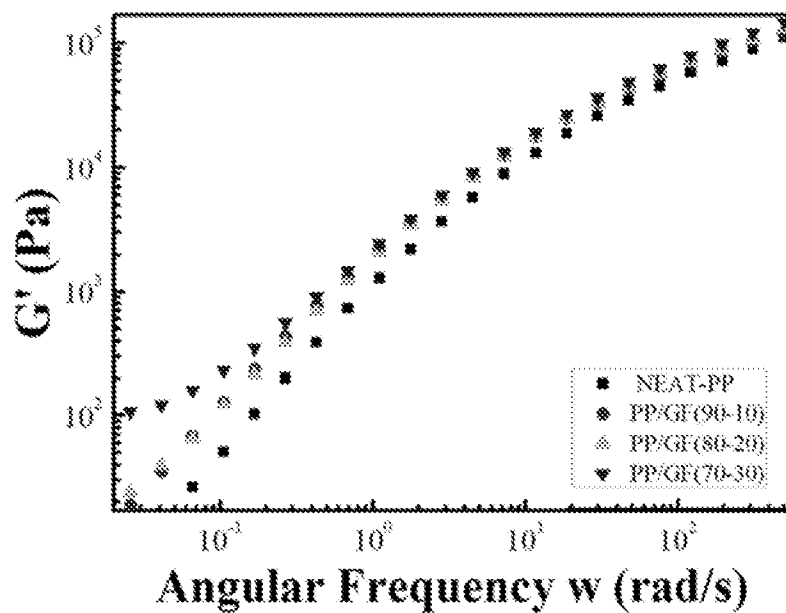


Fig. 7

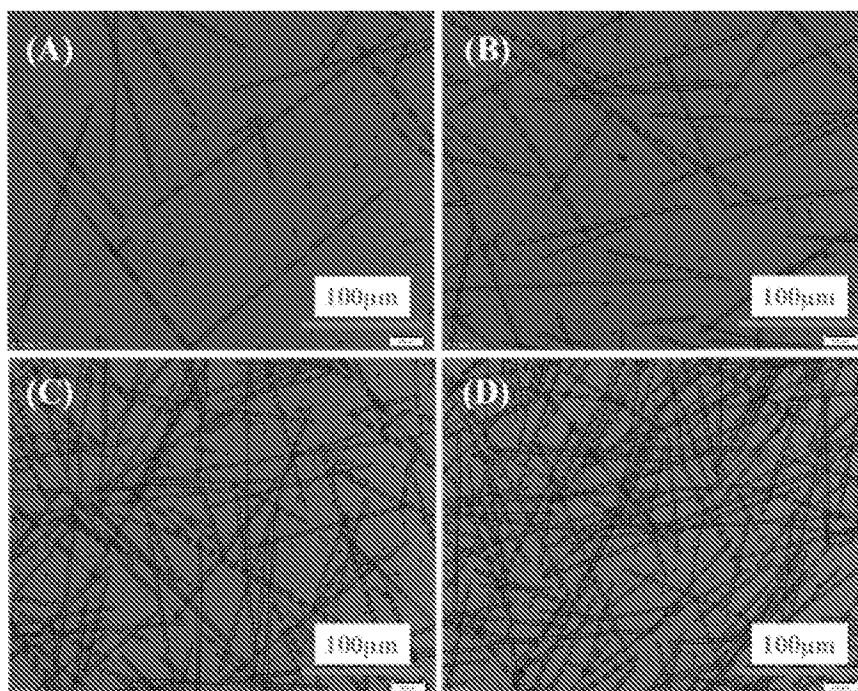


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2017/077621

A. CLASSIFICATION OF SUBJECT MATTER

C08L 23/04(2006.01)i; C08L 23/10(2006.01)i; C08K 7/14(2006.01)i; C08K 5/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L23/-; C08K7/-; C08K5/-

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)

WPI,EPODOC,CNPAT:polyolefin, polypropylene, polyethylene, antistatic, glass fibers,metal cation, imidazolium, pyrrolidinium, pyridinium, guanidinium, ammonium,phosphonium, sulfonimide,trifluoro methane sulfonyl imide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101792551 A (NEW CENTURY ELECTRICAL MFG ZHONGSHAN CO. LTD.) 04 August 2010 (2010-08-04) example 6, claims 1 and 3	1-9, 14-17
Y	CN 101792551 A (NEW CENTURY ELECTRICAL MFG ZHONGSHAN CO. LTD.) 04 August 2010 (2010-08-04) example 6, claims 1 and 3	10-13, 18-20
Y	CN 106010322 A (FUJIMORI KOGYO CO.) 12 October 2016 (2016-10-12) paragraphs [[0056], [0057] and [0063]	10-13, 18-20
Y	CN 105081327 A (NANTONG GAOXIN ANTIWEAR TECHNOLOGY CO. LTD.) 25 November 2015 (2015-11-25) claim 1	10-13, 18-20
Y	CN 102485786 A (LIAONING GENIUS ADVANCED MATERIAL CO. LTD.) 06 June 2012 (2012-06-06) claim 1	10-13, 18-20
Y	CN 102485784 A (CHI, JIANPING) 06 June 2012 (2012-06-06) claims 1-3	10-13, 18-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

11 October 2017

Date of mailing of the international search report

13 December 2017

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2017/077621

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	101792551	A	04 August 2010	CN	101792551	B	22 August 2012
CN	106010322	A	12 October 2016	JP	2016179664	A	13 October 2016
				TW	201637860	A	01 November 2016
				KR	20160115691	A	06 October 2016
CN	105081327	A	25 November 2015	WO	2017035918	A1	09 March 2017
CN	102485786	A	06 June 2012	CN	102485786	B	17 December 2014
CN	102485784	A	06 June 2012	None			