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(54) Title: COMPOSITE FILM COMPRISING ULTRA-DRAWN UHMWPE AND ONE OR MORE (CO-) ADDITIVES

(57) **Abstract:** The present invention relates to composite films comprising ultra-drawn UHMWPE and one or more (co-) additives, wherein one or more additives are chosen from the group of inorganic fillers and one or more (co-) additives are chosen from the group of UV-stabilizers. An object of the present invention is to fabricate ultra-drawn polymer composite films with a high thermal conductivity without defects. Another object of the present invention is to fabricate ultra-drawn polymer composite films with both high transparency and high thermal conductivity.

Title: Composite film comprising ultra-drawn UHMWPE and one or more (co-) additives

FIELD OF THE INVENTION

The present invention relates to composite films comprising ultra-drawn UHMWPE and one or more (co-) additives, generally to generate transparent films with a high thermal conductivity. More specifically, it relates to materials suitable for applications in windows, heat sinks, solar cells, micro-chips and light emitting diodes.

BACKGROUND OF THE INVENTION

CN109265786 relates to a UHMWPE composite material with high thermal conductivity, and a preparation method thereof, wherein the UHMWPE composite material with high thermal conductivity is prepared from 98-99% of UHMWPE with copper plated on the surface, and 1-2% of an antioxidant. The preparation method comprises: modifying the surface of UHMWPE as a matrix by using a biomass dopamine, carrying out chemical copper plating, and carrying out molding pressing on the modified UHMWPE and a small amount of an antioxidant to prepare the sample.

US2016368182 relates to a process for preparing a high thermal conductivity and high heat capacity oriented ultrahigh molecular weight polyethylene (UHMWPE) product; said process comprising the following steps: feeding UHMWPE at the nip of at least one set of first rollers having a first pre-determined roller speed and a first pre-determined temperature to obtain a pre-laminate; and hot stretching said pre-laminate using at least one set of second rollers at a second pre-determined roller speed and a second pre-determined temperature to obtain the oriented UHMWPE product having a thermal conductivity in the range of 70 to 200 W/mK and a heat capacity in the range of 6 to 25 MJ/m^{3}K, wherein the molecular weight distribution of UHMWPE is at least 12.3.

Methods for manufacturing high-strength high-modulus UHMWPE films are known in the art. US 5,756,660 describes polymerization of UHMWPE over a specific catalyst, followed by compression moulding, rolling and stretching to form a polymer film. US 5,106,555 describes a method for compression molding / stretching of UHMWPE. US 5,503,791 describes a polyethylene film manufactured by extruding a solution of a polyolefin in a first solvent, followed by cooling, the removal of the solvent and stretching of the film. Current methods of production of high modulus UHMWPE include the gel-spinning technique, a well-known method capable of producing multi-filament fibers or bundles of very small monofilaments as described in U.S. Pat. No. 4,551,296. These fibers are produced by various manufacturers including DSM High Performance Fibers in the Netherlands under the trade name Dyneema.

An article written by Sheng Shen et al, "Polyethylene nanofibres with very high thermal conductivities", NATURE NANOTECHNOLOGY, GB, (20100401), vol. 5, no. 4, doi:10.1038/nnano.2010.27, ISSN 1748-3387, pages 251 – 255 reports the fabrication of high-quality ultra-drawn polyethylene nanofibres with diameters of 50–500 nm and lengths up to tens of millimeters. The thermal conductivity of the nanofibres was found to be as high as 104 W m−1 K−1.

Thermal management is vital to lifetime and performance of a wide variety of electronic devices including solar cells, light-emitting diodes (LEDs) and chips. With the widespread application of electronics, effective thermal management with thermally conductive materials has become a major technological challenge. Therefore, new and high thermally conductive materials with a high visible light transmission are needed, especially for the thermal management of windows where the combination of high transparency and a high thermal conductivity is desired.

In general, thermal conductive materials include metals, ceramics, carbon materials and polymer composites. Compared with other thermal conductive materials, polymer composites have been explored extensively in the past decades due to their low density, ease of processing, electrical resistivity and corrosion resistance. Normally, the thermal conductivity of polymers is enhanced with highly thermal conductive additives and the increase in thermal conductivity is limited to within one order of magnitude (< 10 W m-1 K-1), resulting from the high thermal interface resistance between the additive and the polymer matrix. Also, polymer composites with a high concentration of fillers are non-transparent due to visible light scattering and/or absorbance of fillers.

Ultra-drawn, highly oriented and chain-extended polymers were studied extensively due to their high thermal conductivity and mechanical properties even without additives. Solution- spun, ultra-drawn UHMWPE fibers have a thermal conductivity between

10 and 20 W m-1 K-1 which is at least one order of magnitude higher than isotropic polymers. The maximum thermal conductivity of ultra-drawn, nascent UHMWPE films with a draw ratio of more than 200 is ~ 50 W m-1 K-1 and ultra-drawn nanofibers with a thermal conductivity of ~ 104 W m-1 K-1 were also reported with a draw ratio of ~410. Unfortunately, the latter result was obtained with rather unpractical fiber spinning operations and/or ultra-drawing procedures which limits the usefulness of these fibers.

In addition, it is tempting to expect that composites consisting of highly oriented systems with inorganic fillers might have an even higher thermal conductivity. However, inorganic fillers like graphene in ultra-drawn polymers usually cause defects and cracks at the interface between the filler and the highly anisotropic matrix. These defects or cracks cause light scattering and premature fractures upon ultra-drawing.

Cooling is an increasing problem in the build environment, automotive, trains, planes, electronics, solar cells and LEDs. So called low e-glass is used in windows to reduce the cost of air conditioning. Cooling is hardly done in solar cells and LEDs.

In the recent past, fluorescent windows, transparent solar cells, IR reflecting windows, and patterned (fluorescent) windows have been proposed. In all cases, heating-up of the systems is a disadvantage and none of these systems are neutral grey. The term neutral grey refers to materials, films or coatings where the absorption in the visible light region is more or less constant. In other words, it does not change the spectrum of, for instance, sunlight.

There are no systems in the scientific literature that are transparent (non-light scattering), neutral gray, with a high metal-like thermal conductivity.

An object of the present invention is to fabricate ultra-drawn polymer composite films with a high thermal conductivity without defects.

Another object of the present invention is to fabricate ultra-drawn polymer composite films with both high transparency and high thermal conductivity.

BRIEF SUMMARY OF THE INVENTION

The present invention thus relates to a composite film comprising ultra-drawn UHMWPE and one or more (co-) additives, wherein one or more additives are chosen from the group of inorganic fillers and one or more (co-) additives are chosen from the group of UV-stabilizers.

The present inventors found that one or more of the above identified objects can be achieved by using special components to increase the thermal conductivity of ultra- drawn Ultra-high molecular weight polyethylene (UHMWPE) to metal-like values. In one aspect, the invention provides a neutral gray window composed of such a composite film.

UV-stabilizers or UV absorbers refer to compounds that absorb ultraviolet light generally in the wavelength range from 330 to 400 nanometers (nm). Thus absorbed, UV light cannot then lead to formation of free radicals which will result in polymer degradation. Additives to impart UV stabilizing properties or antioxidant properties to polymers have been disclosed in US 5.438,142, which is hereby incorporated by reference, especially hindered amines, diazoarenes, aroyls including benzophenones, benzotriazoles. Benzotriazoles (BZT's) and their derivatives, in particular 2- (2'-hydroxyphenyl)-benzotriazoles, are especially useful as UV light absorbers and stabilizers. BZT's are able to eliminate excitation energy through proton transfer, thus preventing damage to the polymer backbone.

The present invention thus relates to using benzotriazoles and their derivatives as a co-additives in combination with single and multiwall nanotubes and graphene in a composite film comprising ultra-drawn UHMWPE. The present inventors found that a high transmission was generated which was interpreted in terms of a reduced void content inside the composite films and an improved dispersion of the graphene, both of which decrease light scattering. The present inventors found that using a surprising and synergistic mixture of BZT and graphene results in ultra-drawn UHMWPE/graphene composite films which have both a high transparency and a high thermal conductivity. Alternatives for graphene such as single wall and multiwall carbon nanotubes are also conceived.

In an embodiment of the present invention the group of inorganic fillers comprises a carbon-based material, such as graphene, single wall carbon nanotubes and multiwall carbon nanotubes. Graphene is a two-dimensional carbon isotope having superior properties such as high charge mobility, high thermal conductivity and high flexibility. Multilayer graphene is able to maintain the superior properties of monolayer graphene and simultaneously has various energy band structures (electronic structures) depending on the stacking order of graphene and the number of layers thereof. Carbon nanotubes are tube-shaped materials having a hexagonal honeycomb pattern in which one carbon atom is bonded to three other carbon atoms.

In a typical composite film according to the present invention there is less than 1 % wt/wt graphene and less than 5 % wt/wt of (co-) additives. In general the ratio of (co-) additives to graphene is quite high. Preferentially, the (co-) additives /graphene ratio is at least 2 and more preferentially it is at least 5. Typically, the (co-) additives /graphene ratio is less than 50.

Preferably, typical composite films have less than 5 % wt/wt (co-) additives and more preferably less than 2-3 % wt/wt (co-) additives. Preferably, materials have more than 0.2 % wt/wt BZT and more preferably more than 0.5 % wt/wt (co-) additives.

In combination with a heat sink (water, phase change materials, Seebeck device) this results in a cold windows which generate thermal or electrical energy and save cooling and/or air conditioning cost.

In an embodiment of the present invention the ratio (co-) additives / inorganic fillers is in a range of 50-2.

In an embodiment of the present invention the ratio (co-) additives / inorganic fillers is in a range of 40-5.

In an embodiment of the present invention the amount of inorganic fillers is less than 1 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

In an embodiment of the present invention the amount of (co-) additives is in a range of 0.2 wt% - 5 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

In an embodiment of the present invention the amount of (co-) additives is in a range of 0.5 wt% - 3 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

In an embodiment of the present invention the Young's modulus of the composite film is in a range of 50 - 200 GPa.

In an embodiment of the composite film graphene is used as inorganic filler, especially graphene having a platelet planar size of about 0.3 – about 5μm and a platelet thickness of <50nm.

In an embodiment of the present invention the composite film has a thermal conductivity of at least 30 W m-1 K-1, preferably at least 50 W m-1 K-1.

In an embodiment of the present invention the composite film has a transmission at 550 nm of at least 80%, the transmission being measured according to the method disclosed in the description.

The present invention also relates to the use of a composite film as discussed above in one or more applications chosen from the group of windows, heat sinks, electronics, solar cells, micro-chips and light emitting diodes.

The present invention relates to a method for manufacturing a composite film comprising the steps of:

- providing UHMWPE powder,
- dispersing UHMWPE powder, inorganic fillers and (co-) additives in a solvent,
- gel casting the dispersion thus obtained, and removal of solvent, e.g. by drying the film,
- solid-state drawing of the films obtained from gel casting.

The present invention also relates to an extrusion process for the production of UHMWPE composite films as discussed above. The process according to the present invention comprises the following steps:

a) dispersing an inorganic filler and (co-) additives in a suitable solvent,
b) adding UHMW-PE to the dispersion thus obtained and preparing a slurry,
c) feeding the slurry thus obtained to an extruder,
d) converting the slurry in the extruder into a solution of UHMWPE in the solvent;
e) passing the solution of step d) through a slit die to form a film,
e) cooling the film thus obtained to form a gel film,
f) removing at least partly the solvent from the gel film thus obtained,
g) drawing films in at least one drawing step before, during or after removing the solvent.

Hereinafter, the present invention will be described with reference to the accompanying examples and comparative examples. However, it should be understood that the invention can be embodied in various forms and thus is not limited to the embodiments described herein.

Hereinafter, Examples of the present invention will be described in detail.

EXAMPLES AND COMPARATIVE EXAMPLES

Ultra-high molecular weight polyethylene (UHMWPE) with a molecular weight (Mw) ~ 4×10^3 kg/mol and dispersity index (Đ) ~ 7 was received from DSM (Geleen, The Netherlands) and graphene nanoplatelets (particle size < 2 µm, specific surface area ~750 m^2/g) were purchased from Sigma-Aldrich. 2-(2H-benzotriazol-2-yl)-4, 6-ditertpentylphenol (BZT) was purchased from BASF (Germany). Paraffin oil was purchased from Thermo Fisher Scientific Incorporated (The Netherlands). Xylene was purchased from Biosolve BV (The Netherlands). All materials were used directly as received without further purification.

Comparative example 1

Ultra-drawn UHMW-PE films were prepared by gel casting and solid-state drawing. UHMWPE powder (1 % wt/wt) was added to xylene and the dispersion was degassed by ultra-sonication at room temperature for 30 minutes. Subsequently, the mixture was stirred continuously in an oil bath at about 125 ℃ until the Weissenberg effect was observed. Subsequently, the mixture was heated for 120 minutes at 120 ℃ to completely dissolve the UHMW-PE in the xylene. The solutions were cast in aluminum trays and quenched to room temperature. A dry film was obtained after xylene evaporation at room temperature. To prepare ultra-drawn films, the as-prepared films were first cut into small strips with dimensions of 12 mm × 15 mm which were ultra-drawn at 120 ℃. The draw ratio was measured by measuring the displacement of ink marks.

The thermal conductivity of the ultra-drawn films was determined with the so-called Angstrom method. The average thermal conductivities are listed below in Table 1:

Table 1: Draw ratio vs thermal conductivity

Draw Ratio	Thermal conductivity [W/mK]
30	15
60	35
90	38

The transmittance spectra of films with different drawn ratios were measured in the range of 300-800 nm on a Shimadzu (Japan) UV-3102 PC spectrophotometer at a 1-nm interval, equipped with a MPC-3100 multi-purpose large sample compartment. The samples were sandwiched between two glass slides and were coated by a few drops of paraffin oil to avoid surface light scattering. The transmission of the ultra-drawn films at 550 nm is listed below in Table 2:

Table 2: Draw ratio vs transmission

Draw Ratio	Transmission [%]
30	88
60	89
90	89

Comparative example 2

Ultra-drawn UHMW-PE films containing graphene were prepared by gel casting and solid-state drawing. Graphene (0.1 wt% relative UHMWPE) was dispersed in 200 mL xylene under ultra-sonication for 30 minutes. UHMWPE powder and antioxidant were then added to the dispersion before degassing with a second ultra-sonication at room temperature for 30 minutes. Subsequently, the mixture was stirred continuously in an oil bath at 125 ℃ until the Weissenberg effect was observed. Subsequently, the mixture was heated for 120 minutes at 125 ℃ to completely dissolve the UHMW-PE in the xylene. The solutions were cast in aluminum trays and quenched to room temperature. A dry film was obtained after xylene evaporation at room temperature. To prepare ultra-drawn films, the as-prepared films were first cut into small strips with dimensions of 12 mm × 15 mm which were ultra-drawn at 120 ℃. The draw ratio was measured by measuring the displacement of ink marks. The thermal conductivity of the ultra-drawn films was determined with the so-called Angstrom method. The average thermal conductivities are listed below in Table 3:

Table 3: Draw ratio vs thermal conductivity

Draw Ratio	Thermal conductivity
30	10
70	5
90	-

The samples could not be drawn to higher draw ratios due to premature failure of the films.

The transmittance spectra of films with different drawn ratios were measured in the range of 300-800 nm on a Shimadzu (Japan) UV-3102 PC spectrophotometer at a 1-nm interval, equipped with a MPC-3100 multi-purpose large sample compartment. The samples were sandwiched between two glass slides and were coated by a few drops of paraffin oil to avoid surface light scattering. The transmission of the ultra-drawn films at 550 nm and a sample-to-detector distance of 15 cm is listed below in Table 4:

Table 4: Draw ratio vs transmission

Draw Ratio	Transmission [%]
30	75
70	70
90	-

The samples have excessive light scattering.

Example 1 (according to the invention)

Ultra-drawn UHMW-PE films were prepared by gel casting and solid-state drawing. Graphene (0.1 wt% to UHMWPE) and BZT (2 or 3 wt% to UHMWPE) were dispersed in 200 mL xylene under ultra-sonication for 30 minutes.

UHMWPE powder and antioxidant were then added to the dispersion before degassing with a second ultra-sonication at room temperature for 30 minutes. Subsequently, the mixture was stirred continuously in an oil bath at about 125 ℃ until the Weissenberg effect was observed. Subsequently, the mixture was heated for 120 minutes at 125 ℃ to completely dissolve the UHMW-PE in the xylene. The solutions were cast in aluminum trays and quenched to room temperature. A dry film was obtained after xylene evaporation at room temperature. To prepare ultra- drawn films, the as-prepared films were first cut into small strips with dimensions of 12 mm × 15 mm which were ultra-drawn at 120 ℃. The draw ratio was measured by measuring the displacement of ink marks.

The thermal conductivity of the ultra-drawn films was determined with the so-called Angstrom method. The average thermal conductivities are listed below in Table 5:

Table 5: Draw ratio vs thermal conductivity

Draw Ratio	Thermal conductivity
30	35
70	60
90	75

The transmittance spectra of films with different drawn ratios were measured in the range of 300-800 nm on a Shimadzu (Japan) UV-3102 PC spectrophotometer at a 1-nm interval, equipped with a MPC-3100 multi-purpose large sample compartment. The samples were sandwiched between two glass slides and were coated by a few drops of paraffin oil to avoid surface light scattering. The transmission of the ultra-drawn films at 550 nm is listed below in Table 6:

Table 6: Draw ratio vs transmission

Draw Ratio	Transmission [%]
30	85
70	85
90	85

The samples according to Example 1 hardly showed light scattering and had some absorption related to the presence of the graphene in the transparent, high thermal conductivity ultra-drawn polyethylene/graphene nanocomposite films

On basis of the above experiments the present inventors have shown that transparent, ultra-drawn, ultra-high molecular weight polyethylene (UHMWPE)/ graphene nanocomposite films with a high thermal conductivity were successfully fabricated by solution-casting and solid-state drawing. It was found that the low optical transmittance (<75%) of ultra-drawn UHMWPE/graphene composite films was drastically improved (>90%) by adding 2-(2H-benzotriazol-2-yl)-4, 6-ditertpentylphenol (BZT) as a second additive. The high transmission was interpreted in terms of a reduced void content inside the composite films and an improved dispersion of the graphene both of which decrease light scattering. A high specific thermal conductivity (~75 W m^{-1} K^{-1} ρ^{-1} of ultra-drawn UHMWPE/graphene/BZT composite films was obtained which is higher than most metals and polymer nanocomposites. Such transparent films are candidates for thermal management applications due to a combination of low density, ease of processing and high thermal conductivity.

Compared with the pure ultra-drawn UHMWPE film (Comparative example 1), ultra-drawn films with BZT alone or graphene alone (Comparative example 2) show little improvement thermal conductivity or even a reduced thermal conductivity, while the thermal conductivity of ultra-drawn UHMWPE/graphene/BZT nanocomposite (Example 1) is enhanced with more than a factor 2, which illustrates that the inorganic filler is indeed effective in improving thermal conductivity. The present inventors assume that the mechanism of generating highly transparent, ultra-drawn polymer nanocomposite films is based on the assumption that BZT improves the dispersion of the graphene and decreases micro-voids in the ultra-drawn UHMWPE composite films.

As discussed above UHMWPE films with draw ratios of 30 and 70 were fabricated by simple solution-casting and solid-state drawing and the transparency of the films was studied using UV-vis spectroscopy. Both light scattering and absorption of light are influenced by film thickness and in order to eliminate this effect the absorption was divided by the film thickness. Pure UHMWPE films (PE-30 and PE-70, respectively) exhibit a slight deviation from a flat curve (Figure 1a and b) which is usually attributed to light scattering in the drawn films originating from micro-voids parallel to the drawing direction. The addition of graphene (GN) to the ultra-drawn UHMWPE films (PE-GN-30 and PE-GN-70, respectively) increases the absorption and the scattering of light enormously. The present inventors found that the addition of 2 wt% of BZT reduces this light scattering and transparent glass-like films are obtained in the visible wavelength range. Therefore BZT was added to the UHMWPE/GN films. The addition of both BZT (2 wt %) and graphene (0.1 wt %) to the ultra- drawn UHMWPE films resulted in films with very little visible light scattering which appeared transparent upon visual inspection although BZT shows a high absorbance of UV light (Figure 1c and d). From these data, it is clear that there is a low visible light transmission in ultra-drawn PE- GN films due to light scattering while PE-BZT-GN films show a high visible light transmission.

Results obtained by the present inventors indicate that the increased light scattering in ultra-drawn UHMWPE films upon addition of graphene can be circumvented by adding BZT. The present inventors assume that BZT not only decreases the voids in ultra-drawn UHMWPE but also improves the dispersion of the graphene, both of which reduce light scattering enormously. Wide angle X-ray scattering (WAXS) results indicate that the unit cell parameters and the Herman's orientation function of the ultra-drawn UHMW-PE did not change upon addition of the graphene/BZT mixtures. The present inventors assume that adding BZT and graphene hardly influences the melting temperature and crystallinity of ultra-drawn composite films.

The present inventors now propose a certain explanation but are not bound to it at all. Adding pure inorganic fillers like graphene causes a large number of additional defects at the interfaces of graphene and polyethylene in ultra-drawn films, which results in a large increase in light scattering and a decrease in visible light transmission. In PE-BZT-GN ultra-drawn films, BZT restricts the void formation to some extent and it fills the interfaces between graphene and polyethylene, which improves the visible transmission of ultra-drawn PE-BZT-GN film. BZT reduces light scattering mainly due to the similar refractive index of BZT ($n = 1.575$) and PE ($n = 1.57$ parallel to the drawing direction and $n = 1.52$ perpendicular to the drawing direction).

The present inventors also studied the thermal conductivity of the ultra-drawn films with different draw ratio. The thermal conductivity of the solution-cast ultra-drawn polyethylene films increases with an increasing draw ratio due to an increase in degree of chain orientation and chain extension. The addition of graphene and BZT increases the thermal conductivity of ultra-drawn films with more than a factor 2, while the addition of BZT alone or graphene alone has a minor effect or even a negative effect because the voids or defects in films increase phonon scattering which decreases the thermal conductivity. Rather surprisingly, the thermal conductivity of PE-BZT-GN ultra-drawn film increases quite a lot compared to the reference samples and a maximum thermal conductivity of 75 W m^{-1} K^{-1} is found at a draw ratio of 100 due to the extremely high thermal conductivity of graphene, the high conductivity of chain-extended polyethylene chains and the reduction of defects in the films.

Commercial solution-spun and ultra-drawn UHMWPE fibers have a typical thermal conductivity of ~15 W m^{-1} K^{-1} and ultra-drawn UHMWPE films based on so-called nascent or virgin UHMWPE exhibit a thermal conductivity of ~50 W m^{-1} K^{-1}.The maximum value for the thermal conductivity of PE-BZT-GN ultra-drawn film is about 3-fold higher than that of stainless steel (~18 W m^{-1} K^{-1}) but low in comparison to metallic thermally conductive materials, such as copper (~380 W m^{-1} K^{-1}), aluminum (~240 W m^{-1} K^{-1}) and silver (~420 W m^{-1} K^{-1}). However, these metals, as normal thermal conductive materials, are reflective and/or non-transparent. More importantly, in many applications the specific conductivity (e.g. per unit weight) is more important that the absolute conductivity. Solution-cast ultra-drawn UHMWPE films outperform steel and copper and that maximum values close to aluminum can be obtained, which is higher than that of most of metals and polymer nanocomposite.

Thermal conductivities of ultra-drawn composite films were characterized based on the Angstrom method for measuring in-plane thermal conductivity. (A. J. Angstrom Ann. Der Phys. Und Chemie. 1861, 114, 33). The thermal conductivity was determined by measuring the amplitude difference and the phase difference in temperature at two points.

CLAIMS

1. Composite film comprising ultra-drawn UHMWPE and one or more (co-) additives, wherein one or more additives are chosen from the group of inorganic fillers and one or more (co-) additives are chosen from the group of UV-stabilizers.

2. Composite film according to claim 1, wherein the group of inorganic fillers comprises a carbon-based material, such as graphene, single wall carbon nanotubes and multiwall carbon nanotubes.

3. Composite film according to one or more of the preceding claims, wherein the group of UV-stabilizers comprises hindered amines, diazoarenes, aroyls including benzophenones and benzotriazoles and their derivates, especially 2-(2H-benzotriazol-2-yl)-4, 6-ditertpentylphenol (BZT).

4. Composite film according to one or more of the preceding claims, wherein the ratio (co-) additives / inorganic fillers is in a range of 50-2.

5. Composite film according to claim 4, wherein the ratio (co-) additives / inorganic fillers is in a range of 40-5.

6. Composite film according to one or more of the preceding claims, wherein the amount of inorganic fillers is less than 1 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

7. Composite film according to one or more of the preceding claims, wherein the amount of (co-) additives is in a range of 0.2 wt% - 5 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

8. Composite film according to claim 7, wherein the amount of (co-) additives is in a range of 0.5 wt% - 3 wt%, based on the total weight of the ultra-drawn UHMWPE composite film.

9. Composite film according to one or more of the preceding claims, wherein the Young's modulus of the composite film is in a range of 50 - 200 GPa.

10. Composite film according to one or more of the preceding claims, wherein graphene is used as inorganic filler, especially graphene having a platelet planar size of about 0.3 – about 5μm and a platelet thickness of <50nm.

11. Composite film according to one or more of the preceding claims having a thermal conductivity of at least 30 W m^{-1} K^{-1}, preferably at least 50 W m^{-1} K^{-1}.

12. Composite film according to one or more of the preceding claims having a transmission at 550 nm of at least 80%, the transmission being measured according to the method disclosed in the description.

13. The use of an composite film according to one or more of the preceding claims in one or more applications chosen from the group of windows, heat sinks, electronics, solar cells, micro-chips and light emitting diodes.

14. A method for manufacturing a composite film according to one or more of the claims 1-12 comprising the steps of:

a) dispersing an inorganic filler and (co-) additives in a suitable solvent,
b) adding UHMW-PE to the dispersion thus obtained and preparing a slurry,
c) feeding the slurry thus obtained to an extruder,
d) converting the slurry in the extruder into a solution of UHMWPE in the solvent;
e) passing the solution of step d) through a slit die to form a film,
e) cooling the film thus obtained to form a gel film,
f) removing at least partly the solvent from the gel film thus obtained,
g) drawing films in at least one drawing step before, during or after removing the solvent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/059548

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/18 C08K3/04 C08K5/00 C08K5/3475 C08L23/06
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J C08K C08L

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	LIHUA SHEN ET AL: "Improving the Transparency of Ultra-Drawn Melt-Crystallized Polyethylenes: Toward High-Modulus/High-Strength Window Application", ACS APPLIED MATERIALS & INTERFACES, vol. 8, no. 27, 13 July 2016 (2016-07-13), pages 17549-17554, XP055708207, US ISSN: 1944-8244, DOI: 10.1021/acsami.6b04704 abstract "Experimental Section"; page 17550, column 1 ----- -/--	1-13 14

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

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Meiser, Wibke

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International application No
PCT/EP2020/059548

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	REN PENG-GANG ET AL: "Synergistic effect of BN and MWCNT hybrid fillers on thermal conductivity and thermal stability of ultra-high-molecular-weight polyethylene composites with a segregated structure", JOURNAL OF POLYMER RESEARCH, SPRINGER NETHERLANDS, NL, vol. 23, no. 2, 8 January 2016 (2016-01-08), pages 1-11, XP035842075, ISSN: 1022-9760, DOI: 10.1007/S10965-015-0908-Y [retrieved on 2016-01-08]	1-13
A	abstract "Experimental"; page 21, column 2	14

Y	US 2016/368182 A1 (MATHUR AJIT BEHARI [IN] ET AL) 22 December 2016 (2016-12-22)	1-13
A	paragraph [0001] paragraph [0032] claims 1-14	14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/059548

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		EP 3110856 A2	04-01-2017
		JP 6557672 B2	07-08-2019
		JP 2017506696 A	09-03-2017
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