(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 May 2017 (04.05.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/075499 A1

(51) International Patent Classification:
B32B 27/08 (2006.01) *B32B 15/085* (2006.01)
B32B 27/32 (2006.01) *B32B 15/20* (2006.01)
B32B 7/12 (2006.01) *B32B 27/06* (2006.01)
B32B 7/02 (2006.01)

(21) International Application Number:
PCT/US2016/059533

(22) International Filing Date:
28 October 2016 (28.10.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/247,564 28 October 2015 (28.10.2015) US
62/314,716 29 March 2016 (29.03.2016) US

(71) Applicants: **MADICO, INC.** [US/US]; 64 Industrial Parkway, Woburn, Massachusetts 01801 (US). **SC INNOVATION, LLC** [US/US]; 1301 McKinney, Suite 1100, Houston, Texas 77010 (US).

(72) Inventors: **TEMCHENKO, Marina**; 15 Sherwood Road, Swampscott, Massachusetts 01907 (US). **AUGUSTYNIAK, Martin**; 900 Chairfactory Road, Elma, New York 14059 (US). **LIM, Sam**; 90 Garfield Avenue, Lynn, Massachusetts 01905 (US). **COMEAU, Charles Robert, Jr.**; 37 Drumlin Hill Road, Groton, Massachusetts 01450 (US).

(74) Agent: **SMITH, Paul A.**; Finch & Maloney PLLC, 50 Commercial Street - Suite 300, Manchester, New Hampshire 03101 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: MULTILAYER COMPOSITE FILMS FOR ARCHITECTURAL APPLICATIONS

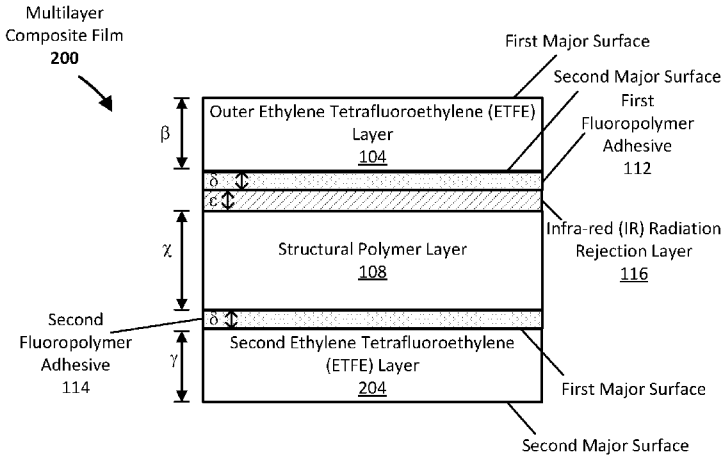

FIG. 2

(57) Abstract: A multilayer composite film that includes an outer ETFE layer adhered to a polyethylene terephthalate (PET) layer. These layers are adhered together by a fluoropolymer adhesive. The multilayer composite film also include an infra-red (IR) radiation rejection layer that reflects or absorbs more than 50% of incident IR radiation. A second ETFE layer can be adhered to an inner surface of the structural polymer layer. The composite films are useful in structural applications and can withstand environmental exposure.

WO 2017/075499 A1

MULTILAYER COMPOSITE FILMS FOR ARCHITECTURAL APPLICATIONS

TECHNICAL FIELD

[0001] The present disclosure relates generally to multilayer polymer films. Specifically, the present disclosure relates to multilayer composite films for architectural applications.

BACKGROUND

[0002] Ethylene tetrafluoroethylene (ETFE) can be used in some architectural applications in place of conventional architectural glasses or plastics (e.g., tempered silicate glass, glass ceramics, polycarbonate). This is due, in part, to the light weight, visible light transparency and translucency, thermal stability, and flexibility exhibited by ETFE sheets. When used as a roofing material in architectural applications, ETFE is often either configured in a single layer that is supported by a network of cables or as a series of pneumatic cushions formed by joining of between two and five layers of ETFE together and inflating a space defined by the joined ETFE layers (and also sometimes supported by a network of cables).

[0003] Fabricating and maintaining a pneumatic cushion is currently an industry standard method of using ETFE for architectural elements. ETFE is extruded as a single sheet or a multi-layer sheet. ETFE sheets are joined together to form an envelope, which is then assembled into an architectural panel by attaching the envelope to a frame made from a structural material (e.g., aluminum, steel). The frame and the attached envelopes are in turn joined to supports of an architectural structure. The ETFE envelopes are inflated to form the pneumatic cushion. Pressure is maintained within the ETFE pneumatic cushions using a pressurization unit (such as a compressor) that maintains an internal pressure of the ETFE pneumatic cushions at approximately 220 Pa, thus providing structural stability to the pneumatic pillow.

SUMMARY

[0004] An example of the present disclosure includes a multilayer composite film including: an outer ethylene tetrafluoroethylene (ETFE) layer having a first major surface and a second major surface, the first major surface configured as an exterior surface of the multilayer

composite film and the second major surface opposite the first major surface; a structural polymer layer proximate to the second major surface of the outer ETFE layer; a first fluoropolymer adhesive layer disposed between the second major surface of the outer ETFE layer and the structural polymer layer, the first fluoropolymer adhesive layer adhering the outer ETFE layer and the structural polymer layer together; a second ETFE layer having a first major surface and a second major surface, the first major surface of the second ETFE layer proximate to the structural polymer layer and the second major surface of the second ETFE layer configured as an interior surface opposite the first major surface of the outer ETFE layer; and a second fluoropolymer adhesive disposed between the first major surface of the second ETFE layer and the structural polymer layer, the second fluoropolymer adhesive layer adhering the second ETFE layer and the structural polymer layer together.

[0005] In an embodiment, the multilayer composite film further includes a fire retardant rating of V0 when tested according to a UL94 standard. In an embodiment, the multilayer composite film further includes an infra-red (IR) radiation rejection layer disposed in or on at least one of the structural polymer layer, the first fluoropolymer adhesive layer, the second fluoropolymer adhesive layer, and the outer ETFE layer, the IR radiation rejection layer configured to reflect at least 40% of incident IR radiation. In an embodiment of the multilayer composite film, wherein the IR radiation rejection layer includes a metal layer disposed on one of the structural polymer layer and the ETFE layer, the metal layer having a reflectance of greater than 40% for wavelengths of radiation between 700 nm and 1000 nm and having a transmittance of visible light having wavelengths between 400 nm and 700 nm greater than 50%. In an embodiment of the multilayer composite film, wherein the metal layer is one of a copper film, a silver film, a gold film, a nickel film, a metal oxide film, an aluminum film, and combinations thereof. In an embodiment of the multilayer composite film, wherein the metal layer has a thickness between 1 nm and 500 nm. In an embodiment of the multilayer composite film, wherein the IR radiation rejection layer includes at least one of titanium dioxide nanoparticles, silver particles, gold particles, and aluminum nanoparticles disposed in at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer. In an embodiment of the multilayer composite film, wherein the multilayer composite film has a young's modulus of at least 1000 MPa and an ultimate tensile strength of at least 146 MPa. In an embodiment of the multilayer composite film, wherein the multilayer composite film exhibits a yield point under tensile strain of at least 40 MPa. In an embodiment of the multilayer composite film, wherein

the outer ETFE layer has a thickness of between 25 microns and 125 microns. In an embodiment of the multilayer composite film, wherein the second ETFE layer has a thickness from 25 microns to 125 microns. In an embodiment of the multilayer composite film, wherein the multilayer composite film where structural polymer layer is a polyethylene terephthalate (PET) layer. In an embodiment of the multilayer composite film, wherein multilayer composite film where the structural polymer layer has a thickness from 50 microns to 250 microns. In an embodiment of the multilayer composite film, wherein the multilayer composite film where at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer includes a fluoropolymer resin, an ultra-violet light absorbent component, and a crosslinking component. In an embodiment of the multilayer composite film, wherein the multilayer composite film where the fluoropolymer resin is at least 40 weight % of at least one of the first fluoropolymer layer and the second fluoropolymer layer. In an embodiment of the multilayer composite film, wherein the multilayer composite film where the fluoropolymer resin consists essentially of fluoropolymer-based polymers. In an embodiment of the multilayer composite film, wherein the multilayer composite film where at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer has a thickness from 5 microns to 30 microns. In an embodiment of the multilayer composite film, wherein the multilayer composite film further includes a perimeter edge configured to form a cord edge, where the second major surface of the second ETFE layer is adhered to itself using at least one of an adhesive and an adhesive tape. In an embodiment of the multilayer composite film, the multilayer composite film further including a rigid structure disposed within a volume defined by the cord edge. In an embodiment of the multilayer composite film, wherein the multilayer composite film has a haze value of less than 16%. In an embodiment of the multilayer composite film, wherein the multilayer composite film has a haze value of from 2% to 14%.

[0006] An example of the present disclosure includes a multilayer composite film including: an outer fluorinated polymer layer having a first major surface and a second major surface, the first major surface configured as an exterior surface of the multilayer composite film and the second major surface opposite the first major surface; a non-fluorinated polymer layer proximate to the second major surface of the outer fluorinated polymer layer; a first fluoropolymer adhesive layer disposed between the second major surface of the outer fluorinated polymer layer and the non-fluorinated polymer layer, the first fluoropolymer adhesive layer adhering the outer fluorinated polymer layer and the non-fluorinated polymer layer together; and a portion of the

multilayer composite film defining an integral tube, the integral tube including a perimeter edge of the multilayer composite film curled back onto the multilayer composite film and permanently adhered to the multilayer composite film.

[0007] In an embodiment of the multilayer composite film, wherein the integral tube forms a cord edge. In an embodiment of the multilayer composite film, wherein the multilayer composite film further includes a first sheet of the multilayer composite film joined to a second sheet of the multilayer composite film. In an embodiment of the multilayer composite film, wherein the first sheet is joined to the second sheet using at least one of a lapp joint, a lapp joint and a strip, and a butt joint. In an embodiment of the multilayer composite film, wherein the first sheet is joined to the second sheet by at least one of an adhesive tape, an adhesive, and a heat seal. In an embodiment of the multilayer composite film, wherein the non-fluorinated polymer layer comprises PET. In an embodiment of the multilayer composite film, further including an IR reflecting layer or IR absorbing agent. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is an ETFE layer. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is a polyvinyl fluoride layer. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is an ethylene chlorotrifluoroethylene layer. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is a polyvinylidene fluoride layer. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is a polychlorotrifluoroethylene layer. In an embodiment of the multilayer composite film, wherein the outer fluorinated polymer layer is a polyfluoroethylenepropropylene layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1A is a cross-sectional view of an ETFE-containing multilayer composite film comprising a single ETFE layer, in an embodiment.

[0009] FIG. 1A' is a cross-sectional view of an ETFE-containing multilayer composite film comprising a single ETFE layer, in an embodiment.

[0010] FIG. 1B is a cross-sectional view of an ETFE-containing multilayer composite film that includes particles that can reflect and/or absorb IR radiation, in an embodiment.

[0011] FIG. 2. is a cross-sectional view of an ETFE-containing multilayer composite film comprising two layers of ETFE, in an embodiment.

[0012] FIG. 3 is a graph of stress-strain data for both of an ETFE-containing multilayer composite film and a film comprising an ETFE bilayer.

[0013] FIG. 4 is a graph of reflectance data for an ETFE-containing multilayer composite film, in an embodiment.

[0014] FIGS. 5A-5C illustrate various joint configurations for joining multilayer composite films together, in embodiments.

[0015] FIG. 6 is a cross-sectional view of an ETFE-containing multilayer composite film configured for use as a structural panel, in another embodiment.

[0016] FIG. 7A is a cross-sectional view of an ETFE-containing multilayer composite film configured for use as a structural panel, in an embodiment.

[0017] FIG. 7B is a cross-sectional view of an ETFE-containing multilayer composite film configured for attachment to a support cable, in an embodiment.

[0018] The figures depict various embodiments of the present disclosure for purposes of illustration only. Numerous variations, configurations, and other embodiments will be apparent from the following detailed discussion.

DETAILED DESCRIPTION

OVERVIEW

[0019] ETFE films have drawbacks that limit their applicability to architectural applications. For example, ETFE films have mechanical properties that do not generally lend themselves to use for structural elements of architectural applications. For example ETFE films generally have a low Young's modulus (about 800 MPa to about 1500 MPa) and have a relatively low yield point, after which the ETFE films deform elastically.

[0020] To overcome these properties, ETFE films are usually applied to architectural applications by configuring the ETFE film as a pneumatic cushion, as described above. An alternative embodiment uses single-ply ETFE panels that are supported by a network or grid of support cables that are separated by about one meter (m). Fabricating pneumatic cushions and maintaining pressure within the pneumatic cushions adds expense to the maintenance of the individual structural elements and the architectural application as a whole. Similarly, fabricating and maintaining a network of support cables adds expense to the use of ETFE as an architectural element and also detracts from the aesthetic appeal of the otherwise transparent ETFE architectural elements.

[0021] To improve the convenience with which ETFE films can be applied to architectural elements (e.g., roofs and walls), embodiments of the present disclosure include a multilayer composite film that includes an outer ETFE layer adhered to a structural polymer film, such as

polyethylene terephthalate (PET), among others, by an adhesive. In some embodiments, the multilayer composite film may also include an infra-red (IR) radiation rejection layer that reflects at least 40% of incident IR radiation (light having a wavelength from 700 nm to 1000 nm), thus reducing the amount of IR radiation transmitted into an area defined, at least in part, by the optically transparent multilayer composite film. Variations and additional embodiments will be apparent upon reading the present disclosure.

[0022] Another advantage of using embodiments described herein as an architectural element is that the improved rigidity (from the flexural modulus of the structural polymer being higher than that of ETFE) and strength can increase the spacing (e.g., from the current 1 m spacing to at least 15 m) between support cables of a corresponding network, thus improving the visual appeal of ETFE architectural elements.

[0023] Yet another advantage of embodiments described herein is reduction in the haze in architectural elements using a multilayer composite film of the present disclosure compared to architectural components that currently use only ETFE. Current ETFE architectural components are about 250 μm thick. This thickness of ETFE has a visibly hazy appearance (measured according to ASTM D1003-13). Embodiments disclosed herein have a haze value of less than 20%, less than 16%, less than 12%, less than 10%, less than 8% and in some cases between 2% and 14% and in other cases about 6% (as measured according to ASTM D1003-13 using a BYK Gardner Haze Guard Plus haze meter). Embodiments described herein can include one or more layers of ETFE, each of which is as thin as 25 μm. A structural polymer layer used as a component of the multilayer composite film can be selected to have greater clarity (i.e., lower haze) than ETFE, thus further improving the visual clarity and aesthetic appearance of the architectural components using an embodiment of the multilayer composite film compared to single ply ETFE architectural components currently used.

EXAMPLE MULTILAYER COMPOSITE FILM

[0024] FIG. 1A is a cross-sectional view of an example multilayer composite film 100, in an embodiment. The multilayer composite film 100 includes an ETFE layer 104, a structural polymer layer 108, an adhesive 112, and an optional IR radiation rejection layer 116. The multilayer composite film 100 has a thickness, indicated by α in FIG. 1A, that can be within any of the following ranges: 50 to 1000 μm, 100 to 1000 μm, 200 to 1000 μm, 200 to 800 μm, 200 to 600 μm, greater than 100 μm, greater than 200 μm, greater than 500 μm, less than 3 mm, less

than 2 mm, less than 1 mm, less than 800 μm, less than 500 μm, less than 400 μm or less than 300 μm.

[0025] The outer ETFE layer 104 of the multilayer composite film 100 is shown in this example as including a single sheet of ETFE material. In other examples, not shown, the ETFE layer 104 can include multiple ETFE sheets to form the outer ETFE layer 104. Other embodiments can include one, two, three or more ETFE sheets that may be separated by other layers of a composite film or may be adjacent each other (such as the example shown in FIG. 2 and described below). The outer ETFE layer 104 has a thickness, indicated by β in FIG. 1A, that can be, for example, within any of the following ranges: 25 microns (μm) to 250 μm; 25 μm to 100 μm; 25 μm to 75 μm; 25 μm to 50 μm; 50 μm to 150 μm; 50 μm to 100 μm; 75 μm to 200 μm; 75 μm to 100 μm; 100 μm to 200 μm. The outer ETFE layer 104 is also shown as including a first major surface and a second major surface. These will be used for convenience to describe the structure and fabrication of the multilayer composite film 100 in more detail below.

[0026] The outer ETFE layer 104 is configured to be disposed as an exterior-facing surface of the multilayer composite film 100. More specifically, for convenience of explanation, the first major surface of the outer ETFE layer 104 can be used to form an exterior surface (i.e., exposed to the earth's atmosphere) of an architectural application. Placing the outer ETFE layer 104 at an exterior surface employs many of the beneficial properties of ETFE material that may otherwise be lacking in more conventional architectural materials. For example, the low surface energy of ETFE helps shed water and resist accumulation of atmospherically born contaminants (e.g., soot, dirt, dust, pollen). ETFE, and more generally fluorinated polymers, can also exhibit resistance to solvation or other chemical degradation caused by atmospherically borne contaminants and chemicals intentionally applied (e.g., cleaners, detergents) and unintentionally applied (e.g., a spill) to an exterior surface of an architectural application. This low surface energy improves the longevity of the multilayer composite film 100 because the film can resist chemically induced degradation. Furthermore, ETFE transmits as much as 90% or 95% of the intensity of incident visible light (e.g., radiation between wavelengths of 400 nanometers (nm) and 700 nm). This high transmissivity of ETFE is appealing in many architectural applications in which natural light is desired.

[0027] It will be appreciated that other fluorinated polymers may be substituted for the outer ETFE layer 104, as well as other ETFE layers identified in other embodiments described below. Alternative fluorinated polymers include, but are not limited to, ethylene chlorotrifluoroethylene

(ECTFE), polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), and polyfluoroethylenepropropylene (FEP), perfluoroalkyl-tetrafluoroethylene (PFA), Lumiflon® (a copolymer of chlorotrifluoroethylene and modified hydroxyl-functionalized vinyl ethers and available from Asahi Glass Company, Ltd. of Tokyo, Japan), Zeffle ® (a copolymer of tetrafluoroethylene and modified hydroxyl-functionalized vinyl esters and available from ® (available from Daikin Industries, Ltd. of Osaka, Japan), fluorinated polymethacrylates, fluorinated epoxy films, CTFE/VDF (chlorotrifluoroethylene-vinylidene fluoride copolymer), TFE/HFP (tetrafluoroethylene-hexafluoropropylene copolymer), HFP/VDF (hexafluoropropylene-vinylidene fluoride), TFE-PFMe (tetrafluoroethylene-perfluoromethylether copolymer), among others.

[0028] While the outer ETFE layer 104 has many features advantageous for an exterior-facing surface of an architectural element, the mechanical properties (e.g., Young's modulus) of ETFE complicate the use of ETFE films alone in architectural applications. For at least this reason, the multilayer composite film 100 includes at least one structural polymer layer 108, as shown in FIG. 1A.

[0029] The structural polymer layer 108 of the multilayer composite film 100 adds structural integrity (e.g., higher Young's modulus, flexural modulus, ultimate tensile strength) to the multilayer composite film 100 without compromising the benefits of the outer ETFE layer 104 described above. One example of a polymer used for the structural polymer layer 108 is polyethylene terephthalate (PET).

[0030] For example, ETFE can have a Young's modulus of approximately 800 MPa (mega pascals) to 1500 MPa, a flexural modulus of approximately 1.2 GPa (giga pascals), and an ultimate tensile strength of approximately 46 MPa (within normal measurement variation and natural variation between samples). In contrast, PET can exhibit a Young's modulus of approximately 2000 MPa to approximately 4000 MPa, a flexural modulus of approximately 8.3 GPa to approximately 14 GPa, and an ultimate tensile strength of approximately 60 MPa to approximately 140 MPa (within normal measurement variation and natural variation between samples).

[0031] Furthermore, in many embodiments the polymer selected for use as the structural polymer layer 108 does not substantially decrease the transparency, translucence or clarity of the outer ETFE layer 104 while at the same time improving the structural properties of the multilayer composite film, as explained above. The structural polymer layer 108 can exhibit

visible light transmission of greater than 40%, greater than 75%, greater than 85%, greater than 90% or greater than 95% at thicknesses of 25μm, 50 μm, 100 μm, 150 μm, 200 μm, 300 μm, and 400 μm. When used in conjunction with the ETFE layer 104 (or with a second ETFE layer 204 described below in the context of a multilayer composite film 200), the haze of the multilayer composite films of the present disclosure can be as low as from 2% to 16% (in some cases about 6%) and have visible light transmittances of as high (or higher) as 40%, 75%, 85%, 90%, or 95%. These improvements are present even for multilayer composite films having a comparable thickness to ETFE architectural films currently used (often as thick as 250 mm) because the structural polymer layer 108 can be selected to have an equivalent or higher visible light transmittance than ETFE (or other fluoropolymers used in place of ETFE). Furthermore, because the structural polymer layer 108 has improved mechanical properties over ETFE (and other fluoropolymers), the overall thickness of some embodiments of multilayer composite films can be reduced compared to ETFE architectural films currently used, thus further increasing the relative clarity and light transmittance of multilayer composite films described herein.

[0032] The structural polymer layer 108 can have a thickness, indicated by χ in FIG. 1A, that can be, for example, within any of the following ranges: 25 microns (μm) to 250 μm; 25 μm to 100 μm; 25 μm to 75 μm; 25 μm to 50 μm; 50 μm to 150 μm; 50 μm to 100 μm; 75 μm to 200 μm; 75 μm to 100 μm; 100 μm to 200 μm; greater than 50 μm, greater than 100 μm, greater than 150 μm, less than 2 mm, less than 1 mm, less than 800 μm, less than 500 μm, less than 300 μm or less than 200 μm. In part, the thickness of the structural polymer layer 108 is selected based on the various material properties (e.g., Young's modulus, flexural modulus, ultimate tensile strength, among others).

[0033] Polymers other than PET can be used for the structural polymer 108. Alternatives to PET include polymer films that have beneficial mechanical properties and high transmissivities to visible light. For example, the structural polymer layer 108 can exhibit a Young's modulus of greater than 500 MPa, greater than 1000 MPa or greater than 4000 MPa and visible light transmission of greater than 40%, greater than 90%, greater than 95% or greater than 99% for a film having a thickness of 100 μm. The polymers can be extruded films or free-standing films that may include, but are not limited to: polypropylene, polyethylene, polyethylene vinyl acetate, polycarbonates, cellulose and cellulose derivatives, polyamide-imide, polyurethanes, polyacrylates, polymethacrylates, polythiophenes, poly(3,4-ethylenedioxythio-phene)/polystyrene sulfonate, polystyrene, biopolymers, fluoropolymers, chlorofluoropolymers,

vinylfluoropolymers, poly (vinyl chloride), polyethers, polyimides, polyetherimides, polyphenylsulfone, and combinations thereof.

[0034] The adhesive 112 of the multilayer composite film 100 is used to join the structural polymer layer 108 to the second major surface of the outer ETFE layer 104, as shown in FIG. 1A. The adhesive can be a fluoropolymer adhesive 112 that has high thermal stability, hydrolysis resistance, and UV stability. These properties facilitate long term adhesion between the structural polymer layer 108 and the outer ETFE layer 104 even when subjected to months and years of solar-induced heating and solar irradiation, respectively. Furthermore, the strength of adhesion between the structural polymer layer 108 and the outer ETFE layer 104 provided by the fluoropolymer adhesive 112 can, in some embodiments, be within any of the following ranges: from 1 Newton(N)/centimeter (cm) to 10 N/cm; from 1 N/cm to 5 N/cm; from 1 N/cm to 3 N/cm; from 2 N/cm to 10 N/cm; from 2 N/cm to 7 N/cm; from 3 N/cm to 7 N/cm; from 5 N/cm to 10 N/cm; from 5 N/cm to 10 N/cm; greater than 3 N/cm, greater than 5 N/cm or greater than 7 N/cm. The fluoropolymer adhesive 112 has a thickness, indicated by δ in FIG. 1A, that can be within any of the following ranges: 2 μm to 50 μm; 2 μm to 30 μm; 5 μm to 30 μm; 10 μm to 30 μm; 15 μm to 30 μm. Examples of fluoropolymer resins used as a component of the fluoropolymer adhesive 112 include fluoro-copolymer resins and fluoropolymer resins that are terpolymers. Other example fluoropolymer resins used as a component of the fluoropolymer adhesive 112 include, but are not limited to, perfluoroalkyl vinyl ethers such as Lumiflon® (available from Asahi Glass Company, Ltd. of Tokyo, Japan) and tetrafluoroethylene based copolymers, such as Zeffle® (available from Daikin Industries, Ltd. of Osaka, Japan). In some embodiments, the fluoropolymer adhesive 112 may be free of adhesives other than fluoropolymers (e.g., free of acrylic, polyol and other adhesives).

[0035] In other embodiments, the fluoropolymer adhesive 112 includes one or more non-fluorinated components in addition to the fluorinated resin component. In one example, the fluoropolymer adhesive 112 includes an amine or hydroxyl polyol fluorinated resin. In another example, the fluoropolymer adhesive 112 may include a polyester polyol adhesive component, such as Adcote 76R40 (available from Rohm and Haas of Philadelphia, Pennsylvania, United States).

[0036] Other elements that can be included in the fluoropolymer adhesive 112 composition include a UV absorber that improves the stability of the fluoropolymer adhesive 112 and underlying layers upon exposure to light include nitroxy radical based compounds, among

others. UV absorbers that can be added to the fluoropolymer adhesive 112 include Uvinul 3050, Tinuvin® 400, Tinuvin® 477, Tinuvin® 479, Tinuvin® 384-2, Tinuvin® 1600 , Tinuvin® P, Tinuvin® CarboProtect, Tinuvin® 5000 series (all of which are available from BASF of Ludwigshafen, Germany), Evesorb 74 (from Everlight Chemical of Taipei, Taiwan), and inorganic UV absorbers such as zinc oxide, cerium oxide, titanium dioxide, and transparent iron oxides. The fluoropolymer adhesive 112 composition may also include a hindered amine light stabilizer (HALS) to further improve resistance to UV light degradation and improve the performance of an included UV light absorber. Examples of HALS include but are not limited to Tinuvin® 123, Tinuvin® 171 (which are available from BASF), and combinations thereof. Flame retardants, which may also be included as a component in the fluoropolymer adhesive 112 composition include non-halogenated flame retardants such as Exolit® OP550, Exolit® OP560 (both of which are available from Clariant Manufacturing Company of Muttenz, Switzerland), Levagard®4090N (available from Rhein Chemie of Mannheim, Germany), or mixtures thereof.

[0037] Organic solvents that may be used for the synthesis of the fluoropolymer adhesive 112 include but are not limited to organic solvents such as methyl ethyl ketone (MEK), acetone, methyl isobutyl ketone (MIBK), toluene, xylene, methanol, heptane, ethyl acetate, isopropyl acetate, n-butyl acetate, or mixtures thereof. The adhesive compositions of various embodiments can be applied to polymeric film by any of a variety of methods known to those skilled in the art of film coating manufacture. Suitable application methods include application by Meyer rod coating, comma coating, spraying, slot die coating, curtain coating, dipping and/or brushing.

[0038] In some examples, the fluoropolymer adhesive 112 can be prepared by mixing a fluoropolymer resin and a crosslinking agent in an organic solvent. Other components, such as ultra-violet (UV) radiation absorbing compounds, IR reflective and/or absorbing compounds, among others, can also be added to the organic solvent. In one example, the following mixture can be assembled: 50 parts to 200 parts by weight of fluoropolymer resin; 2 parts to 20 parts by weight of UV absorber; 5 parts to 40 parts by weight of organic solvent; 5 parts to 40 parts by weight of crosslinking agent. These are then thoroughly mixed. After removal of the solvent (e.g., by evaporation, vacuum assisted evaporation, heating assisted evaporation), the now crosslinked adhesive composition may comprise at least 20%, at least 30% at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% fluoropolymer by weight. An example formulation of fluoropolymer adhesive 112 follows in Table 1.

Component Name (Supplier)	Function	Weight (grams (g))

Zeffle® GK 570 (Daikin)	Fluoropolymer component	100
Tinuvin® 384-2 (BASF)	UV absorber	4.4
Desmodur® N 3800 (Bayer)	Crosslinking agent	20
Methyl ethyl ketone (N/A)	Organic solvent	80

Table 1

[0039] Optional IR radiation rejection layer 116 of the multilayer composite film 100 may actually include one or both of IR reflecting materials and IR absorbing materials. The IR radiation rejection layer 116 reduces the amount of IR radiation passing through the multilayer composite film 100, thus reducing the IR-induced heating of the interior spaces within an architectural structure. Similarly, IR absorbing materials absorb infrared radiation in the film composite and prevent much of the incident IR radiation from reaching the interior of the structure. This in turn reduces the cooling needed for these interior spaces, improving the economic and ecological performance of the architectural structure using the multilayer composite film 100. The IR radiation rejection layer 116 has a thickness, indicated by ε in FIG. 1A that can be within any of the following ranges: from 1 nm to 100 nm; from 10 nm to 50 nm; from 50 nm to 100 nm; from 25 nm to 75 nm; from 25 nm to 50 nm; and from 50 nm to 75 nm.

[0040] The example of the IR radiation rejection layer 116 shown in FIG. 1A is that of a metal film (alternatively referred to as a metal layer) deposited onto a surface of the structural polymer layer 108. The metal layer of the IR radiation rejection layer 116 may also include multiple layers of metal. The IR radiation rejection layer 116 on the structural polymer layer 108 can be adhered to the second major surface of the outer ETFE layer 104 via the fluoropolymer adhesive 112. Metal films can be continuous or be fabricated to include a pattern of metal portions and non-metal portions (often referred to as a "frit pattern"). Examples of metals used to form a metal film for the IR radiation rejection layer 116 (deposited via, e.g., sputtering, physical vapor deposition, evaporation, among others) include, but are not limited to, aluminum, silver, copper, gold, metal oxides, combinations thereof, or other suitable metals or intermetallic compounds having an electronic structure that reflects at least 40% of incident IR radiation present in solar radiation. Sputtered metallic films can exhibit surface energies that facilitate adhesion to an opposed layer.

[0041] In other embodiments, such as the one shown in FIG. 1A', the IR radiation rejection layer 116 can be adhered to the outer ETFE layer 104 directly. In some embodiments, fluoropolymer adhesive layer 112 and IR radiation rejection layer 116 may be transposed from

the figure so that the IR rejection layer is adjacent layer 104 and the adhesive layer is adjacent layer 108. In another alternative embodiment multilayer composite film 120 shown in FIG. 1B, the separate fluoropolymer adhesive layer 112 and IR radiation rejection layer 116 are substituted for a single fluoropolymer adhesive layer 124 that also includes particles 128 that absorb and/or block IR radiation. This layer has a thickness ε' that can be in any of the ranges already introduced above as thickness δ, thickness ε, or combinations thereof. Examples of IR blocking materials (or "IR opaque pigments") include Sicopal® Black K 0095 from BASF and nanoparticles (e.g., titanium dioxide nanoparticles, silver nanoparticles, aluminum nanoparticles, and mixtures thereof).

[0042] In other examples, the particles 128 include those that alternate between reflecting IR radiation at high atmospheric temperatures (e.g., above 60°F) and transmitting IR radiation at low atmospheric temperatures (e.g., below 50°F).

[0043] Other embodiments of the IR radiation rejection layer 116 and the fluoropolymer adhesive/IR layer 124 may include IR reflective dyes, IR absorbent dyes, UV absorbent dyes, light stabilizers, antioxidants, flame retardants, and mixtures thereof, in examples. Flame retardants may be added to any of the embodiments described herein to provide a flame resistance rating of V0 as measured according to the Underwriters Laboratories (UL) standard UL94, edition number 6, dated March 28, 2013. Embodiments described herein may also meet other fire related standards such as National Fire Protection Association (NFPA) standard 701, 2015 edition, and ASTM standard E84-16 for "Surface Burning Characteristics of Building Materials." Furthermore, absent additional flame retardants, embodiments such as the multilayer composite film 100 (described above), multilayer composite film (200), as well as various combinations that include multiple layers of any one or more of the individual layers 104, 108, 112, 116, 124, and 204 may be configured to comply with one or more of UL standard UL94, edition number 6, dated March 28, 2013, National Fire Protection Association (NFPA) standard 701, 2015 edition, and ASTM standard E84-16 for "Surface Burning Characteristics of Building Materials."

[0044] Regardless of the selection or composition of the IR radiation rejection layer 116 and the fluoropolymer adhesive/IR layer 124, the multilayer composite film 100 can still retain most of or all of the optical light transmissivity described above and is not only translucent but also transparent.

ALTERNATIVE EMBODIMENTS

[0045] FIG. 2 illustrates an ETFE multilayer composite film 200 that includes the multilayer composite film 100 and a second ETFE layer 204 attached to a surface of the structural polymer layer 108 opposite that of the outer ETFE layer 104. The second ETFE layer 204, configured to be disposed on as a surface on an interior of an architectural structure opposite the exterior surface, has a thickness, indicated in FIG. 2 by γ, within any of the following ranges: 25 microns (μm) to 250 μm; 25 μm to 100 μm; 25 μm to 75 μm; 25 μm to 50 μm; 50 μm to 150 μm; 50 μm to 100 μm; 75 μm to 200 μm; 75 μm to 100 μm; 100 μm to 200 μm. A second fluoropolymer adhesive layer 114 that can have the same dimensions and composition as the fluoropolymer adhesive layer 112 and/or a fluoropolymer adhesive/IR layer 124 (shown only in FIG. 1B) may be disposed between the second ETFE layer 204 and the structural polymer layer 108. IR reflectors or absorbents and other particles or dyes can be disposed in or adjacent to any of the adhesive layers 112, 114 that are used to join opposed polymer films. These layers have been described above and need no further description.

EXPERIMENTAL EXAMPLE

[0046] Example composite films were prepared according to the following procedure. A solution of fluoropolymer-based adhesive was prepared according to the formulation described above in Table 1. The prepared fluoropolymer-based adhesive solution was applied to a 125 □m thick PET (V0 fire rating per UL94) film, which functioned as the structural polymer layer described above, at a coating weight of 15 g/m^2. A first 25 μm thick ETFE film was laminated onto the fluoropolymer-based adhesive bearing PET film. The fluoropolymer-based adhesive was then applied on the opposite side of the PET film at a coating weight of 15 g/m^2 and then laminated with a second 25 μm thick ETFE film.

[0047] The prepared experimental examples were subjected to uniaxial testing using an INSTRON 3360 dual column testing system. The experimental examples were strained at a uniform strain rate of 50 millimeters/minute. The stress-strain curve of the experimental example appears in FIG. 3 along with a comparison to a 250 μm thick sheet of ETFE control sample that was strained separately but used the same uniaxial testing machine and strain rate identified above.

[0048] As apparent upon inspection of the data presented in the graph of FIG. 3, the experimental example exhibits significantly higher Young's modulus than the ETFE alone. The

experimental example also exhibits a single yield point at about 5% strain (at a stress of about 70 MPa) and had an ultimate yield stress of approximately 146 MPa (within normal measurement tolerances and natural variation within a population of samples).

[0049] The experimental example was also subjected to 96 hours of highly accelerated stress testing (HAST) to test the adhesion between the layers. The HAST testing was performed at 121˚C, 100% Relative Humidity (RH) and 1 atm. The experimental example was also tested using the Damp Heat Test (International Electrochemical Commission standard number IEC60721) at 85C, 85% (RH), for 1000 hours. Despite the known difficulties of adhering ETFE to dissimilar polymers, no delamination, blistering, or cracking was observed at the end of 96 hours of HAST testing or at the end of 1000 hours for the Damp Heat Test. This confirms that the fluoropolymer-based adhesive strongly adheres the PET film to the ETFE film. The experimental example was also subjected to the Vertical Burning test and exhibited self-extinguishing behavior.

[0050] FIG. 4 illustrates a graph of reflectance data exhibited by an experimental example of a multilayer composite film of the present disclosure fabricated from two layers of ETFE film between which was adhered a layer of Vikuiti™ film. The experimental sample was exposed to incident light having a plurality of wavelengths approximating a solar light wavelength distribution. IR reflectance data was collected using a PERKIN ELMER 950 spectrophotomer. These results are shown in FIG. 4. As is shown, IR reflectance is approximately 100% for IR wavelengths from approximately 780 nm to approximately 1000 nm. At the same time, reflectance in the visible range was less than 20%.

EXAMPLE CONFIGURATIONS FOR ARCHITECTURAL APPLICATION

[0051] FIGS. 5A-5C illustrate various joints that can be used for joining multilayer composite films together, in embodiments. The joints enable individual sheets of multilayer composite films of the present disclosure to be joined together into a larger architectural panel. For example, individual sheets can be joined together to produce an architectural panel that is, for example, anywhere from 1x1 m to 25x25 m square before requiring external support (such as from a network of support cables). FIG. 5A illustrates a lap joint in which individual sheets of the multilayer composite film 200 are overlapped by a distance designated in FIG. 5A as a seal width. The individual sheets can be joined using, for example, a heat seal that welds the sheets together, or an adhesive tape (e.g., a polyester base or a polyamide base thermoplastic heat

activated adhesive tape) or an adhesive (e.g., a heat activated adhesive) disposed between the overlapping portions of the individual sheets of the multilayer composite film 200.

[0052] FIG. 5B illustrates a butt joint in which proximate perimeter edges of two sheets of multilayer composite films 200 are butted together end-to-end and joined at the seal indicated using, for example, any of the techniques described above in the context of FIG. 5A. FIG. 5C illustrates a variation of the butt joint shown in FIG. 5B. In FIG. 5C, a strip 504 of single layer film or multilayer composite film 200 (or ETFE or other compatible polymer used as an outer layer 104) is joined to one or optionally both of the major surfaces of the sheets of multilayer composite films 200 joined via a butt joint so as to cover and extend beyond the butt joint. It will be appreciated that the multilayer composite films 100, 118, and 120 may be substituted for any of the films and/or strips shown in FIGS. 5A, 5B, and 5C. An adhesive, for example a fluoropolymer adhesive such as a perfluoroalkyl vinyl ether, may be used in one or more of the seals between the polymer composite films or between the polymer composite film and one or more of strip 504. The tensile strength of these joints may be equal to, or better than, the tensile strength of the composite film itself.

[0053] In any of the above figures, a seal width can be in any of the following ranges: from 0.5 cm to 10 cm; from 0.5 cm to 5 cm; from 0.5 cm to 2.5 cm; from 1 cm to 10 cm; from 1 cm to 5 cm; from 2 cm to 7 cm, greater than 1.0 cm, or less than 10 cm.

[0054] FIG. 6 illustrates another embodiment of a multilayer composite film 200 configured to form a "cord edge" 500 that defines a volume and is formed by curling the multilayer composite film 200 around a rigid cord (such as EPDM rubber) that is then slid into a channel of a retaining structure. In various embodiments the structure may be erected before or after the cord edge is inserted into the channel. The retaining structure can be attached or anchored (directly or indirectly) to the structure of the building or architectural application in which the multilayer composite film 200 is used as an element. In the embodiment illustrated, the second major surface is adhered to itself to form the cord edge 500. The cord edge 500 may be inserted into the structural channel prior to sealing the composite. For instance, the cord and cord edge may be inserted into the channel and the seal region then clamped and sealed. In other cases, the cord edge is sealed around the cord and is then slid into the channel to secure the composite film to the structure. In one example, a first major surface may be fabricated from a different material than the second major surface because the first and second major surfaces need not be adhered together. For instance, the second major surface can be a fluoropolymer such as perfluoroalkyl

vinyl ether and first major surface can be a non-fluorinated polymer including polyethyleneterephthalate-based materials such as PET. In these embodiments, the second major surface may be the side of the composite that is exposed to the environment. As in the example of FIG. 6, the composite film can be adhered to itself using an adhesive, an adhesive tape or by welding, such as polymer welding, heat welding or ultrasonic welding. Adhesives can include, for example, fluorinated polymers such as perfluoroalkyl vinyl ether.

[0055] FIG. 7A illustrates an example of the multilayer composite film 200 configured for use as an architectural element. In this example, one perimeter edge of the multilayer composite film 200 has been curled so that the second major surface of the second ETFE layer 204 contacts the first major surface of the outer ETFE layer 104. The two ETFE layers 204 may then be joined (e.g., using an adhesive, adhesive tape, or by heat sealing) around a cord to form the cord edge 500 as described above. In another embodiment, the composite film can be rolled onto itself to form a cord edge in which the space typically occupied by a cord is filled by spiraled composite film material.

[0056] FIG. 7B illustrates an alternative configuration for attaching a sheet or panel of the multilayer composite film 200 to a support cable. In this example a strip 704 of either ETFE or of the multilayer composite film 200 is sealed to the sheet and/or panel of multiple sheets of the multilayer composite film 200 around a support cable 708. The seal widths indicated in FIG. 7B can be on the order of those described above. The same or similar sealing and adhesion techniques can be used.

[0057] It will be appreciated that the multilayer composite films 100, 118, and 120 may be substituted for any of the films and/or strips shown in FIGS. 6, 7A, and 7B.

FURTHER CONSIDERATIONS

[0058] The foregoing description of the embodiments of the disclosure has been presented for the purpose of illustration; it is not intended to be exhaustive or to limit the claims to the precise forms disclosed. Persons skilled in the relevant art can appreciate that many modifications and variations are possible in light of the above disclosure.

[0059] The language used in the specification has been principally selected for readability and instructional purposes, and it may not have been selected to delineate or circumscribe the inventive subject matter. It is therefore intended that the scope of the disclosure be limited not by this detailed description, but rather by any claims that issue on an application based hereon.

Accordingly, the disclosure of the embodiments is intended to be illustrative, but not limiting, of the scope of the invention, which is set forth in the following claims.

What is claimed is:

1. A multilayer composite film comprising:

an outer ethylene tetrafluoroethylene (ETFE) layer having a first major surface and a second major surface, the first major surface configured as an exterior surface of the multilayer composite film and the second major surface opposite the first major surface;

a structural polymer layer proximate to the second major surface of the outer ETFE layer;

a first fluoropolymer adhesive layer disposed between the second major surface of the outer ETFE layer and the structural polymer layer, the first fluoropolymer adhesive layer adhering the outer ETFE layer and the structural polymer layer together;

a second ETFE layer having a first major surface and a second major surface, the first major surface of the second ETFE layer proximate to the structural polymer layer and the second major surface of the second ETFE layer configured as an interior surface opposite the first major surface of the outer ETFE layer; and

a second fluoropolymer adhesive layer disposed between the first major surface of the second ETFE layer and the structural polymer layer, the second fluoropolymer adhesive layer adhering the second ETFE layer and the structural polymer layer together.

2. The multilayer composite film of claim 1, further comprising a fire retardant rating of V0 when tested according to a UL94 standard.

3. The multilayer composite film of claim 1, further comprising an infra-red (IR) radiation rejection layer disposed in or on at least one of the structural polymer layer, the first fluoropolymer adhesive layer, the second fluoropolymer adhesive layer, and the outer ETFE layer, the IR radiation rejection layer configured to reflect at least 40% of incident IR radiation.

4. The multilayer composite film of claim 3 wherein the IR radiation rejection layer comprises a metal layer disposed on one of the structural polymer layer and the outer ETFE layer, the metal layer having a reflectance of greater than 40% for wavelengths of radiation

between 700 nm and 1000 nm and having a transmittance of visible light having wavelengths between 400 nm and 700 nm greater than 50%.

5. The multilayer composite film of claim 4, wherein the metal layer is one of a copper film, a silver film, a gold film, a nickel film, a metal oxide film, an aluminum film, and combinations thereof.

6. The multilayer composite film of claim 4, wherein the metal layer has a thickness between 1 nm and 500 nm.

7. The multilayer composite film of claim 3, wherein the IR radiation rejection layer comprises at least one of titanium dioxide nanoparticles, silver particles, gold particles, and aluminum nanoparticles disposed in at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer.

8. The multilayer composite film of any one of claims 1-3, wherein the multilayer composite film has a Young's modulus of at least 1000 MPa and an ultimate tensile strength of at least 146 MPa.

9. The multilayer composite film of claim 8, wherein the multilayer composite film exhibits a yield point under tensile strain of at least 40 MPa.

10. The multilayer composite film of any one of claims 1-3, wherein the outer ETFE layer has a thickness of between 25 microns and 125 microns.

11. The multilayer composite film of any one of claims 1-3, wherein the second ETFE layer has a thickness from 25 microns to 125 microns.

12. The multilayer composite film of any one of claims 1-3, wherein structural polymer layer is a polyethylene terephthalate (PET) layer.

13. The multilayer composite film of any one of claims 1-3, wherein the structural polymer layer has a thickness from 50 microns to 250 microns.

14. The multilayer composite film of any one of claims 1-3, wherein at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer includes a fluoropolymer resin, an ultra-violet light absorbent component, and a crosslinking component.

15. The multilayer composite film of claim 14, wherein the fluoropolymer resin is at least 40 weight % of at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer.

16. The multilayer composite film of claim 15, wherein the fluoropolymer resin consists essentially of fluoropolymer-based polymers.

17. The multilayer composite film of any one of claims 1-3, wherein at least one of the first fluoropolymer adhesive layer and the second fluoropolymer adhesive layer has a thickness from 5 microns to 30 microns.

18. The multilayer composite film of any one of claims 1-3, further comprising a perimeter edge configured to form a cord edge, wherein the second major surface of the second ETFE layer is adhered to itself using at least one of an adhesive and an adhesive tape.

19. The multilayer composite film of claim 18, further comprising a rigid structure disposed within a volume defined by the cord edge.

20. The multilayer composite film of any one of claims 1-3, further comprising a haze value of less than 16%.

21. The multilayer composite film of any one of claims 1-3, further exhibiting a haze value of from 2% to 14%.

22. A multilayer composite film comprising:

an outer fluorinated polymer layer having a first major surface and a second major surface, the first major surface configured as an exterior surface of the multilayer composite film and the second major surface opposite the first major surface;

a non-fluorinated polymer layer proximate to the second major surface of the outer fluorinated polymer layer;

a first fluoropolymer adhesive layer disposed between the second major surface of the outer fluorinated polymer layer and the non-fluorinated polymer layer, the

first fluoropolymer adhesive layer adhering the outer fluorinated polymer layer and the non-fluorinated polymer layer together; and

a portion of the multilayer composite film defining an integral tube, the integral tube comprising a perimeter edge of the multilayer composite film curled back onto the multilayer composite film and permanently adhered to the multilayer composite film.

23. The multilayer composite film of claim 22, wherein the integral tube forms a cord edge.

24. The multilayer composite film of claim 22, further comprising a first sheet of the multilayer composite film joined to a second sheet of the multilayer composite film.

25. The multilayer composite film of claim 24, wherein the first sheet is joined to the second sheet using at least one of a lap joint, a lap joint and a strip, and a butt joint.

26. The multilayer composite film of claim 24 or 25, wherein the first sheet is joined to the second sheet by at least one of an adhesive tape, an adhesive, and a heat seal.

27. The multilayer composite film of any one of claims 22-24, wherein the non-fluorinated polymer layer comprises PET.

28. The multilayer composite film of claim 27, further comprising an IR reflecting layer or IR absorbing agent.

29. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is an ETFE layer.

30. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is a polyvinyl fluoride layer.

31. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is an ethylene chlorotrifluoroethylene layer.

32. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is a polyvinylidene fluoride layer.

33. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is a polychlorotrifluoroethylene layer.

34. The multilayer composite film of any one of claims 22-24, wherein the outer fluorinated polymer layer is a polyfluoroethylenepropropylene layer.

35. An architectural structure comprising the composite film of any one of the preceding claims.

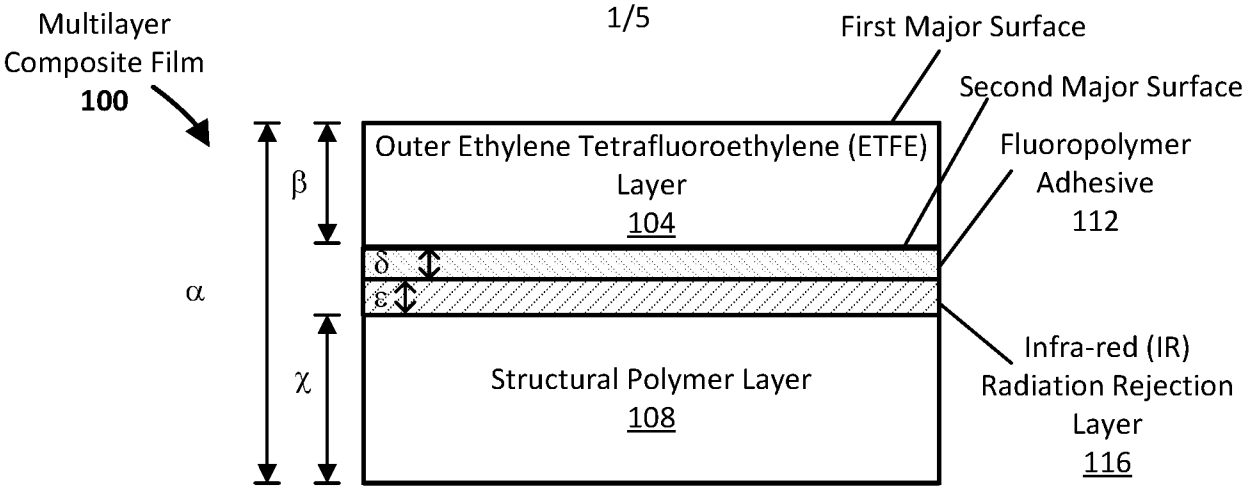

FIG. 1A

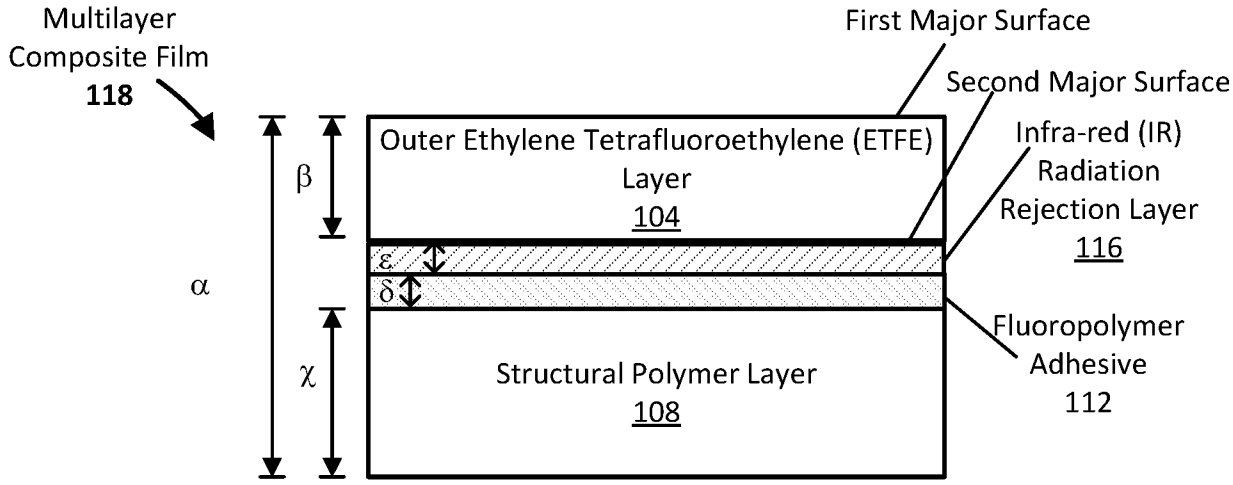

FIG. 1A'

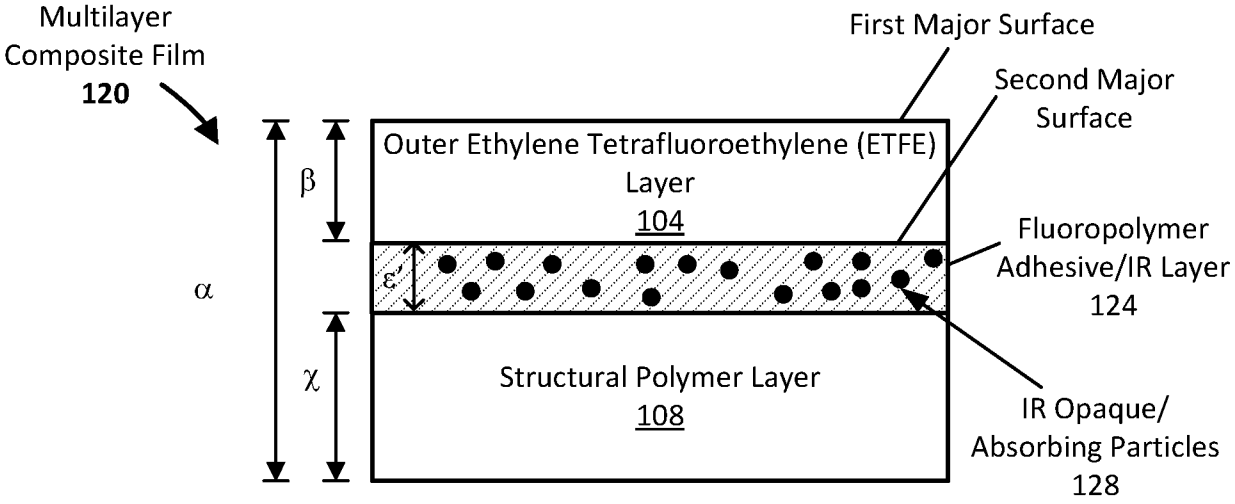

FIG. 1B

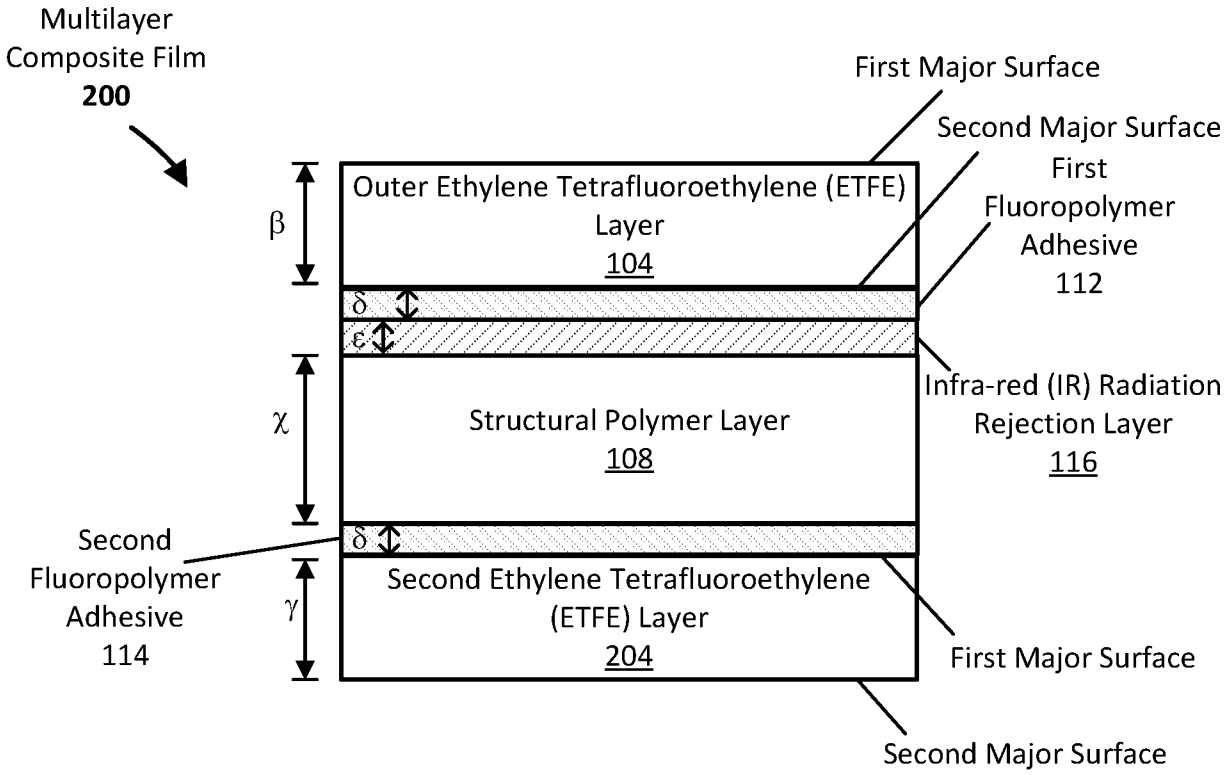
Multilayer
Composite Film
200
First Major Surface
Second Major Surface
First
Fluoropolymer
Adhesive
112
Outer Ethylene Tetrafluoroethylene (ETFE)
Layer
104
β
δ
ε
χ
Structural Polymer Layer
108
Infra-red (IR) Radiation
Rejection Layer
116
Second
Fluoropolymer
Adhesive
114
δ
γ
Second Ethylene Tetrafluoroethylene
(ETFE) Layer
204
First Major Surface
Second Major Surface

FIG. 2

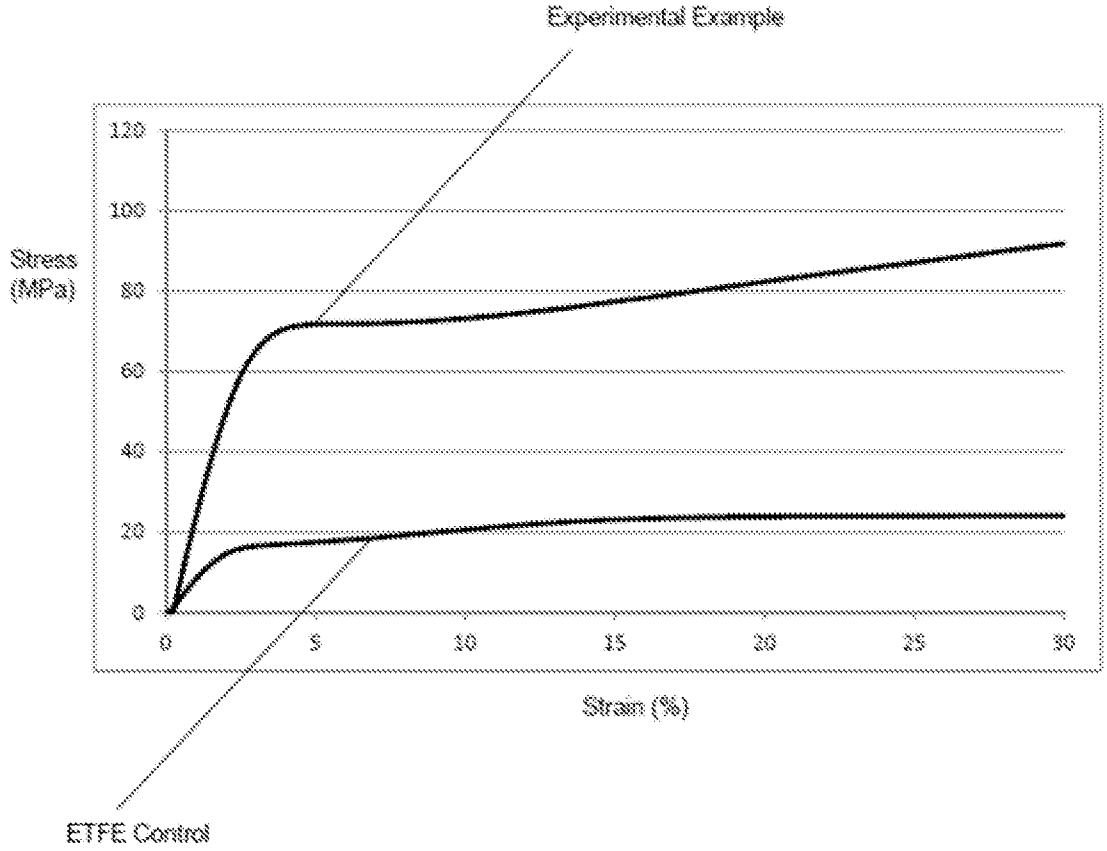
Experimental Example
Stress (MPa)
120
100
80
60
40
20
0
0
5
10
15
20
25
30
Strain (%)
ETFE Control

FIG. 3

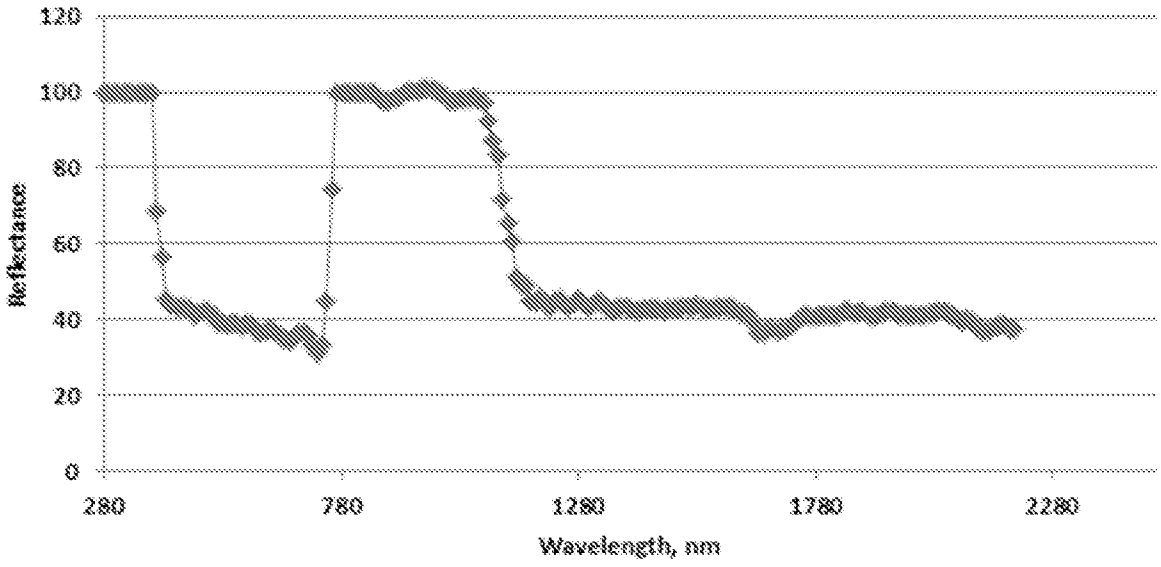
Reflectance
120
100
80
60
40
20
0
280
780
1280
1780
2280
Wavelength, nm

FIG. 4

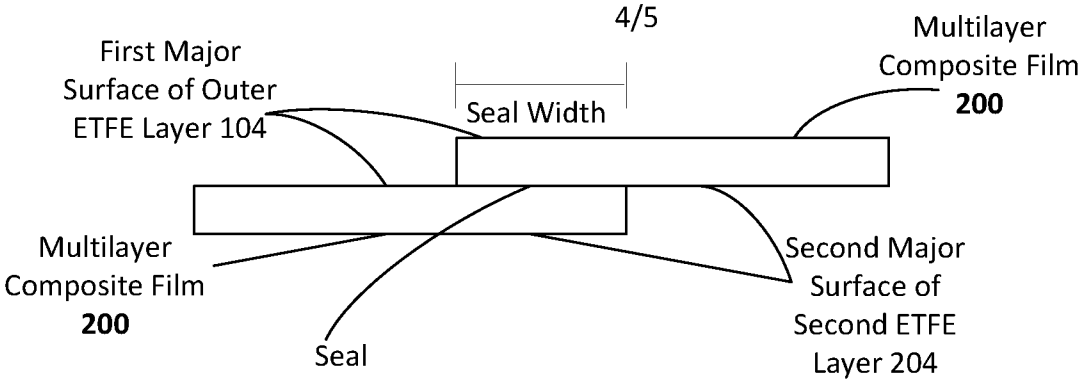

FIG. 5A

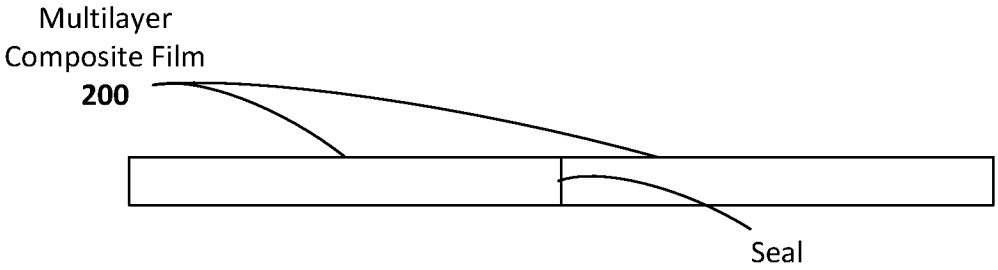

FIG. 5B

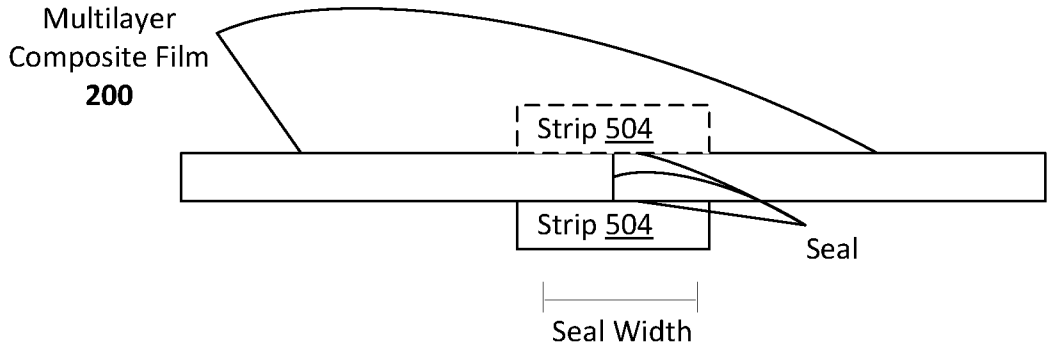

FIG. 5C

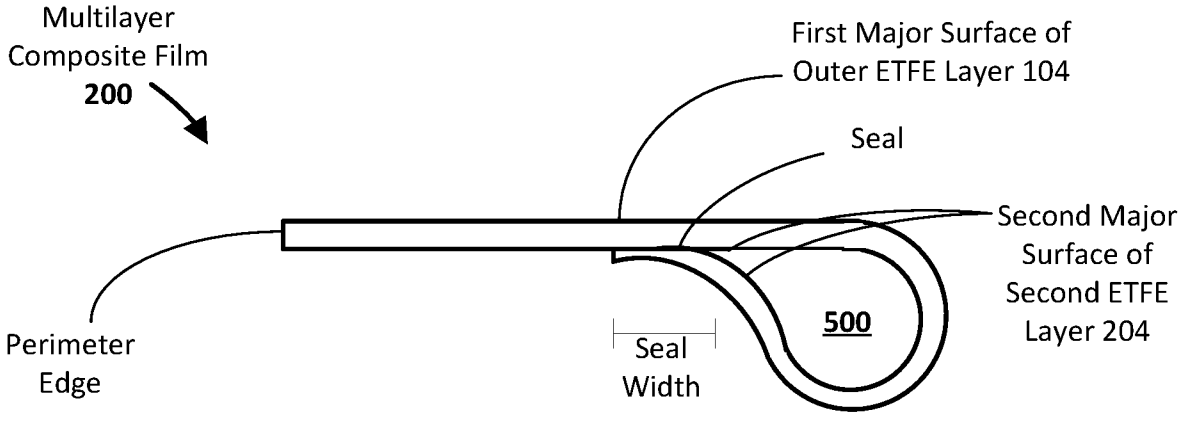

FIG. 6

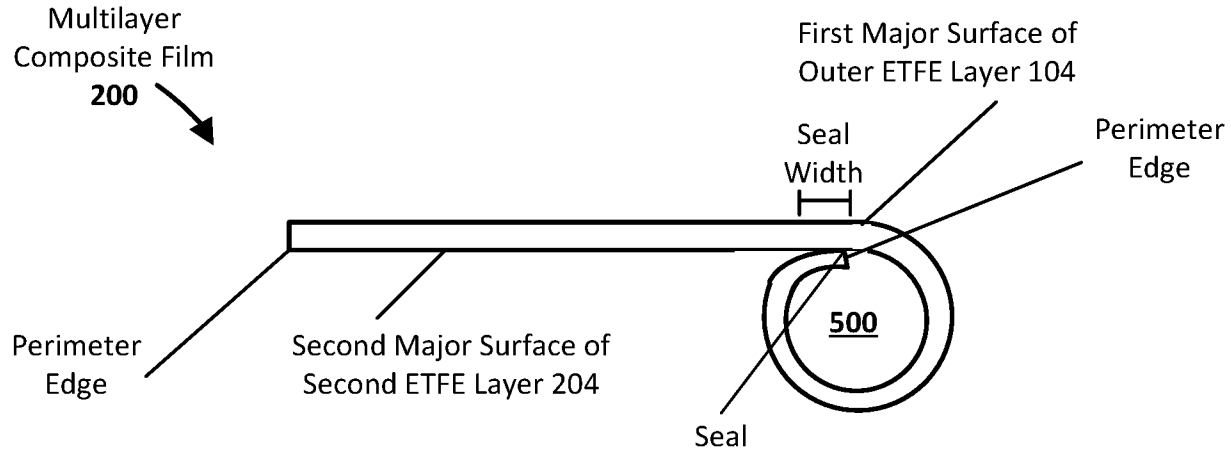
Multilayer
Composite Film
200
First Major Surface of
Outer ETFE Layer 104
Seal
Width
Perimeter
Edge
500
Perimeter
Edge
Second Major Surface of
Second ETFE Layer 204
Seal

FIG. 7A

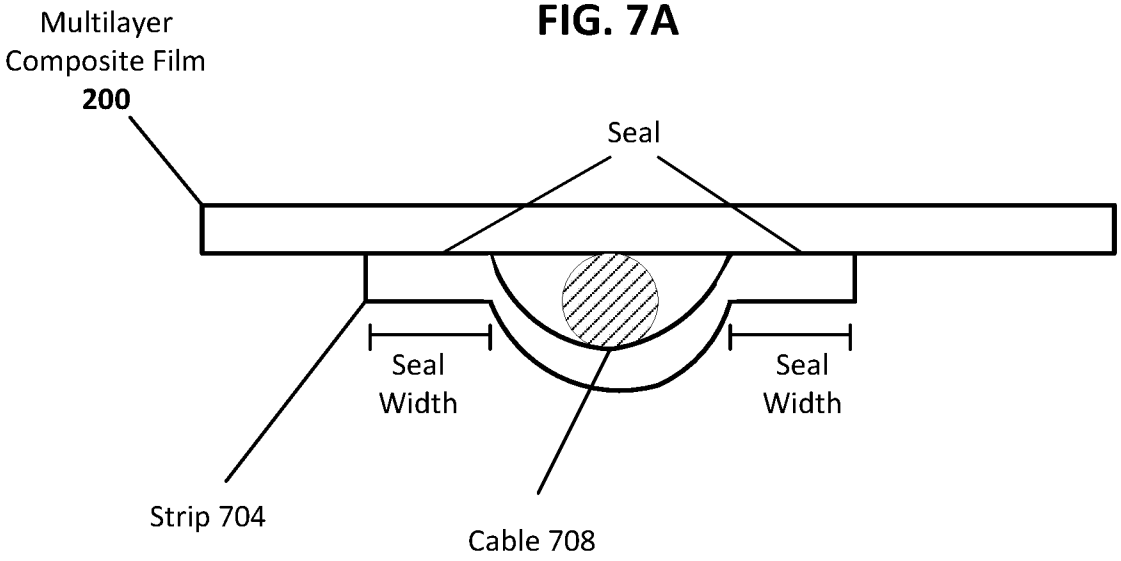
Multilayer
Composite Film
200
Seal
Seal
Width
Seal
Width
Strip 704
Cable 708

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/059533

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/08(2006.01)i, B32B 27/32(2006.01)i, B32B 7/12(2006.01)i, B32B 7/02(2006.01)i, B32B 15/085(2006.01)i, B32B 15/20(2006.01)i, B32B 27/06(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)
B32B 27/08; A61L 2/10; B32B 5/24; H01L 31/0216; B32B 5/00; B32B 3/10; B05D 5/10; B32B 38/00; B32B 27/00; B32B 7/12; B32B 27/32; B32B 7/02; B32B 15/085; B32B 15/20; B32B 27/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: multilayer, film, ETFE, ethylene tetrafluoroethylene copolymer, fluoropolymer, adhesive, infrared reflection, tube

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0247686 A1 (HONEKER, C. C. et al.) 13 October 2011 See paragraphs [0022], [0033], [0035]; claims 1, 2, 14; and figure 1.	1,2,8-21
Y		3-7
A		22-34
Y	US 2007-0059499 A1 (YUASA, A. et al.) 15 March 2007 See claim 1; figure 1; and paragraph [0073].	3-7
A	US 2012-0063952 A1 (HONG, K. C. et al.) 15 March 2012 See claims 1, 2; and figure 1.	1-34
A	US 2010-0119760 A1 (KIRK, II, P. A. et al.) 13 May 2010 See paragraphs [0014], [0027]; claim 1; and figure 1.	1-34
A	EP 2749407 A1 (SAINT-GOBAIN PERFORMANCE PLASTICS CORPORATION) 02 July 2014 See claims 1-5; and figure 1.	1-34

☐ 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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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	Date of mailing of the international search report
15 February 2017 (15.02.2017)	**15 February 2017 (15.02.2017)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
LEE, Ki Cheul
Telephone No. +82-42-481-3353

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/059533

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0247686 A1	13/10/2011	AU 2011-226610 A1	04/10/2012
		AU 2011-226610 B2	12/12/2013
		CN 102811857 A	05/12/2012
		EP 2544896 A2	16/01/2013
		EP 2544896 A4	02/12/2015
		JP 2013-522075 A	13/06/2013
		MX 2012010452 A	03/10/2012
		WO 2011-113008 A2	15/09/2011
		WO 2011-113008 A3	12/01/2012
US 2007-0059499 A1	15/03/2007	CA 2535668 A1	28/07/2005
		CA 2535668 C	12/10/2010
		CN 100484846 C	06/05/2009
		CN 1644467 A	27/07/2005
		CN 2764731 Y	15/03/2006
		EP 1640148 A1	29/03/2006
		EP 1640148 A4	20/10/2010
		EP 1640148 B1	29/02/2012
		JP 4353185 B2	28/10/2009
		KR 10-2006-0034302 A	21/04/2006
		TW 200524733 A	01/08/2005
		US 7862876 B2	04/01/2011
		WO 2005-068180 A1	28/07/2005
US 2012-0063952 A1	15/03/2012	CN 103282200 A	04/09/2013
		EP 2613938 A2	17/07/2013
		EP 2613938 A4	30/04/2014
		JP 2013-542096 A	21/11/2013
		KR 10-2013-0080843 A	15/07/2013
		WO 2012-033626 A2	15/03/2012
		WO 2012-033626 A3	03/05/2012
US 2010-0119760 A1	13/05/2010	CA 2743476 A1	20/05/2010
		CA 2743476 C	16/12/2014
		CN 102264542 A	30/11/2011
		CN 105172293 A	23/12/2015
		EP 2356768 A2	17/08/2011
		EP 2358530 A1	24/08/2011
		EP 2358530 A4	25/12/2013
		JP 2012-508497 A	05/04/2012
		JP 2012-508657 A	12/04/2012
		JP 2014-132079 A	17/07/2014
		JP 5498501 B2	21/05/2014
		JP 5638531 B2	10/12/2014
		JP 5987011 B2	06/09/2016
		KR 10-2011-0082612 A	19/07/2011
		RU 2011123471 A	20/12/2012
		RU 2483930 C2	10/06/2013
		US 2010-0266852 A1	21/10/2010

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/059533

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2011-0310932 A1	22/12/2011
		US 8824578 B2	02/09/2014
		US 8859100 B2	14/10/2014
		US 8859102 B2	14/10/2014
		WO 2010-055387 A2	20/05/2010
		WO 2010-055387 A3	28/10/2010
		WO 2010-056377 A1	20/05/2010
EP 2749407 A1	02/07/2014	CN 103909710 A	09/07/2014
		CN 103909710 B	17/08/2016
		US 2014-194023 A1	10/07/2014

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/059533

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 35
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.