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(71) Applicant *(for all designated States except US)*: **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **FU, Bo** [CN/CN]; Room 401, Building #49, 839 Chenhua Road, Songjiang District, Shanghai 201600 (CN). **WU, Qiuju** [CN/CN]; Room 401, Building #26, 199 Baiyang Road, Pudong New District, Shanghai 201204 (CN).

(74) Agent: **NTD PATENT AND TRADEMARK AGENCY LIMITED**; 10th Floor, Block A, Investment Plaza, 27 Jinrongdajie, Xicheng District, Beijing 100033 (CN).

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(54) Title: SOLAR CELL BACKSHEET WITH IMPROVED ADHESION TO ENCAPSULANT

(57) Abstract: Disclosed herein is a heat pressed multi-layer fluoropolymer film or sheet that has improved bonding strength to a polyolefin film or sheet and methods for preparing the same, wherein the methods comprisesthe steps of: (a) providing a multi-layer pre-lamination assembly comprising an oriented fluoropolymer film or sheet layer positioned next to an oriented polyester film or sheet layer, wherein the fluoropolymer film or sheet layer is positioned to provide one of the two opposite outer surface layers of the assembly, and wherein the oriented fluoropolymer film or sheet layer consists essentially of a fluoropolymer and the oriented polyester film or sheet layer consists essentially of a polyester; and (b) heat pressing the multi-layer pre-lamination assembly by a heat press means to obtain the heat pressed multi- layer fluoropolymer film or sheet, wherein the heat press means is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of about 0.01-50 Kgf/cm^2 and a heat of about 150°C-260°C. Further disclosed herein are solar cell modules comprising backsheets formed of the heat pressed multi-layer fluoropolymer films or sheets.

SOLAR CELL BACKSHEET WITH IMPROVED ADHESION TO ENCAPSULANT

Field of Disclosure

The disclosure herein is a multi-layer fluoropolymerfilm or sheet with improved adhesion to other polymeric material and solar cell modules comprising the same.

Background

In solar cell modules, electrically interconnected solar cells are often encapsulated by front and back encapsulant materials and the encapsulated solar cells are then sandwiched by a transparentfrontsheet and a backsheet. The backsheets of the solar cell modules are used as supports and barriers from the environment. Among the prior art backsheets, those comprising fluoropolymers (such as those having a multi-layer structure of polyvinyl fluoride/polyethylene terephthalate /polyvinyl fluoride (PVF/PET/PVF)) havebeen used widely due to theirsuperior weatherability,mechanical, electrical and barrier properties. However, one drawback of such fluoropolymer containing backsheets is that the bonding between the fluoropolymer film and the encapsulant material (e.g., ethylene/vinyl acetate copolymer (EVA)) may deteriorate over time and therefore cause de-lamination of the solar cell modules. Thus, there is still a need to develop fluoropolymer containingbacksheetshaving good adhesion to the encapsulant material.

Summary

The purpose of the present disclosure is to provide a method for obtaining a heat pressed multi-layer fluoropolymer film or sheet that has improved bonding strength to a polyolefin film, the method comprising, (i) providing a multi-layer pre-lamination assembly comprising a first oriented fluoropolymer film or sheet layer positioned next to an oriented polyester film or sheet layer, wherein the first fluoropolymer film or sheet layer is positioned to provide one of the two opposite

outer surface layers of the assembly, and wherein the first oriented fluoropolymer film or sheet layer consists essentially of fluoropolymer and the oriented polyester film or sheet layer consists essentially of polyester; and (ii) heat pressing the multi-layer pre-lamination assembly by a heat press means to obtain the heat pressed multi-layer fluoropolymer film or sheet, wherein the heat press means is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of 0.01-50 Kgf/cm^2 and a heat of 150°C-260°C.

In one embodiment of the method, the heat press means used in step (ii) is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of 0.1-50 Kgf/cm^2, or preferably 0.5-50 Kgf/cm^2, or more preferably 0.5-30 Kgf/cm^2 and a heat of 150°C-245°C, or preferably 160°C-220°C, or more preferably 160°C-200°C.

In a further embodiment of the method, the heat press means used in step (ii) is a pair of hot flat plates and in step (ii), the multi-layer pre-lamination assembly is heat pressed between the pair of hot flat plates for 0.1-30 sec, or preferably 0.5-30 sec, or more preferably 0.5-20 sec.

In a yet further embodiment of the method, the heat press means used in step (ii) comprises one or more pairs of heated nip rolls and the multi-layer pre-lamination assembly is passed through the one or more pairs of heated nip rolls at a line speed of 0.01-100 m/min, or preferably 0.1-50 m/min, or more preferably 0.5-30 m/min.

In a yet further embodiment of the method, wherein, prior to step (ii), the multi-layer pre-lamination assembly is pre-heated to a temperature of 150°C-260°C, or preferably 150°C-245°C, or more preferably 160°C-220°C, or yet more preferably 160°C-200°C. In such embodiments, the multi-layer pre-lamination assembly may bepre-heated by infra-red heat, air heat, flame heat, electron beam, or laser; or preferably the multi-layer pre-lamination assembly is heated by an infra-red oven.

In a yet further embodiment of the method, the fluoropolymer is derived from fluoromonomersselected from the group consisting of vinyl fluorides, vinylidene fluorides, tetrafluoroethylenes, hexafluoropropylenes, fluorinated ethylene propylenes, perfluoroalkoxys,chlorotrifluoroethlyenes, and combinations of two or more thereof. Or, the fluoropolymer may be selected from the group consisting of

polyvinyl fluorides, polyvinylidene fluorides, and combinations thereof; or more preferably from polyvinyl fluorides.

In a yet further embodiment of the method, the polyester is selected from the group consisting of polyethylene terephthalates, polybutylene terephthalates, polytrimethylene terephthalates, polyethylene naphthalates, and combinations of two or more thereof; or preferably from polyethylene terephthalates.

In a yet further embodiment of the method, the multi-layer pre-lamination assembly is in the form of a bi-layer assembly that consists essentially of the first oriented fluoropolymer film or sheet layer and the oriented polyester film or sheet layer.

In a yet further embodiment of the method, the multi-layer pre-lamination is in the form of a tri-layer assembly that consists essentially of the first oriented fluoropolymer film or sheet layer, the oriented polyester film or sheet layer, and a second oriented fluoropolymer film or sheet layer consisting essentially of fluoropolymer that is the same or different than the fluoropolymer forming the first oriented fluoropolymer film or sheet layer, wherein the oriented polyester film or sheet layer is positioned between the first and the second oriented fluoropolymer film or sheet layers and the first and second oriented fluoropolymer film or sheet layers provide two opposite outer surface layers of the multi-layer pre-lamination assembly.

Further provided herein is a heat pressed multi-layer fluoropolymer film or sheet prepared by any of the methods described above.

In one embodiment of the heat pressed multi-layer fluoropolymer film or sheet, the heat pressed multi-layer fluoropolymer film or sheet is laminated to a polyolefin film or sheet in such a way that the first oriented fluoropolymer film or sheet layer is positioned next to the polyolefin film or sheet, and the bonding strength between the heat pressed multi-layer fluoropolymer film or sheet and the polyolefin film or sheet, measured according to ASTM D903-38, is at least 17 N/cm, or preferably at least 20 N/cm, or more preferably at least 40 N/cm. In such embodiments, the polyolefin film or sheet may comprise a polyolefinic composition, wherein the polyolefinic composition comprises a material selected from the group consisting of

ethylene/vinyl acetate copolymers, ionomers, polyethylenes, ethylene/acrylate ester copolymers, acid copolymers, and combinations of two or more thereof; or preferably from ethylene/vinyl acetate copolymers.

Yet further provided herein is a solar cell module comprising one or a plurality of solar cells, a back encapsulant sheet laminated to a back side of the solar cells, and a backsheet laminated to a back side of the back encapsulant sheet, wherein the back encapsulant sheet comprises a polyolefin, and wherein the backsheet is formed of any of the heat pressed multi-layer fluoropolymer films or sheets described above.

In one embodiment of the solar cell module, the polyolefin comprised in the back encapsulant sheet is selected from the group consisting of ethylene/vinyl acetate copolymers, ionomers, polyethylenes, ethylene/acrylate ester copolymers, acid copolymers, and combinations of two or more thereof; or preferably from ethylene/vinyl acetate copolymers.

In accordance with the present disclosure, when a range is given with two particular end points, it is understood that the range includes any value that is within the two particular end points and any value that is equal to or about equal to any of the two end points.

Detailed Description

Disclosed herein is aheat pressed multi-layer film or sheetcomprising at least one oriented fluoropolymerfilm or sheet layer (hereinafter “heat pressed multi-layer fluoropolymer film or sheet”). The terms “film” and “sheet” are used interchangeably herein to refer to a continuous thin flat structure with a uniform thickness. In general, a sheet may have a thickness greater than about 100 μm while a film may have a thickness of about 100 μm or less. In accordance with the present disclosure, the heat pressed multi-layer fluoropolymer film or sheet is obtained by:(a) providing a multi-layer pre-lamination assembly comprising an oriented fluoropolymer film or sheet layer positioned next to an oriented polyester film or sheet layer, wherein the fluoropolymer film or sheet layer is positioned to provide one of the two opposite outer surface layers of the assembly, and wherein the oriented fluoropolymer film or

sheet layer comprises or consists essentially of a fluoropolymer and the oriented polyester film or sheet layer comprises or consists essentially of a polyester; and (b) heat pressing the multi-layer pre-lamination assembly by a heat press means to obtain the heat pressed multi-layer fluoropolymer film or sheet, wherein the heat press means is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of about 0.01-50 kilograms-force per square centimeter (Kgf/cm^2) and a heat of about 150°C-260°C.

When it is said that a film or sheet "comprises or consists essentially of (a particular polymer)", it is meant that the film or sheet is made from (i) a material comprising the particular polymer and other components or (ii) a material consisting of the particular polymer and optionally certain other components, provided that the inclusion of the certain other components do not negatively affect the mechanical, physical, and adhesion properties of the film or sheet.

The term "oriented"as used hereinrefers to an orientation process, under which a polymeric film or sheet is uni-axially or bi-axially stretched in transverse and/or machine directions to achieve a combination of mechanical and physical properties. Stretching apparatus and processes to obtain uni-axially or bi-axially oriented filmsor sheets are known in the art and may be adapted by those skilled in the art to produce the filmsor sheets disclosed herein. Examples of such apparatus and processes include, for example, those disclosed in U.S. PatentNos. 3,278,663; 3,337,665; 3,456,044; 4,590,106; 4,760,116; 4,769,421; 4,797,235; and 4,886,634.

The oriented fluoropolymer films or sheets used herein may comprise or consist essentially of a fluoropolymer derived from fluoromonomersselected from homopolymers and copolymers of vinyl fluorides (VF), vinylidene fluorides (VDF), tetrafluoroethylenes (TFE), hexafluoropropylenes (HFP),fluorinated ethylene propylenes (FEP and EFEP), perfluoroalkoxys (PFA), chlorotrifluoroethlyenes (CTFE), and combinations of two or more thereof. More specific exemplary fluoropolymers used herein include, without limitation, polyvinyl fluorides (PVF), polyvinylidene fluorides (PVDF),ethylene chlorotrifluoroethlyene copolymers (ECTFE),polychlorotrifluoroethylene (PCTFE),ethylene tetrafluoroethylene copolymers (ETFE), and combinations of two or more thereof (such as THV, a

combination of TFE, HFP and VDF). In some embodiments, fluoropolymers or fluoromonomers may be copolymerized or blended with non-fluoropolymers to form oriented fluoropolymer films or sheets (such as HTE, a combination of HFP, TFE and ethylene).

In one embodiment, oriented fluoropolymer films or sheets used herein are oriented PVF films or sheets comprising or consisting essentially of PVF, which is a thermoplastic fluoropolymer with repeating units of $-(CH_2CHF)_n-$. PVF may be prepared by any suitable process, such as those disclosed in U.S. Patent No. 2,419,010. In general, PVF has insufficient thermal stability for injection molding and is thus usually made into films or sheets via a solvent extrusion or casting process.In accordance withthe present disclosure, the oriented PVFfilm or sheet may be prepared byany suitable process, such as casting or solvent assistedextrusion. For example, U.S. Patent No. 2,953,818 discloses an extrusion process for the preparation of orientablefilms from PVF and U.S. Patent No. 3,139,470 discloses a process for preparing oriented PVF films.

Also in accordance withthe present disclosure, the oriented fluoropolymer films or sheets used herein may also include those that have undergone various surface treatments to improve their bonding properties to other films or sheets. Exemplary surface treatments include, without limitation, chemical treatment (see e.g., U.S. Patent No. 3,122,445), flame treatment (see e.g., U.S. Patent No. 3,145,242), and electrical discharge treatment (see e.g., U.S. Patent No. 3,274,088).

The oriented PVFfilms or sheets used herein may also be obtained commercially. For example, suitable oriented PVF films or sheets may be purchased from E.I. du Pont de Nemours and Company (U.S.A.) (hereafter “DuPont”) under the trade name Tedlar®.

In another embodiment, the oriented fluoropolymer films or sheets used herein are oriented PVDF films or sheets comprising or consisting essentially of PVDF, which is a thermoplastic fluoropolymer with repeating units of $-(CH_2CF_2)_n-$ .Commercially available oriented PVDF films or sheets, include, without limitation,Kynar™ PVDF films from Arkema Inc. (U.S.A.) and Denka DX films from Denka Group (Japan).

The oriented polyester filmsor sheetsused herein may comprise or consist essentially ofa polyester selected from polyethylene terephthalates (PET), polybutylene terephthalates (PBT), polytrimethylene terephthalates (PTT), polyethylene naphthalates(PEN), and combinations of two or more thereof. In a preferred embodiment, the oriented polyester film or sheet consists essentially of PET. Useful polyesters may be branched or linear, vary in density and molecular weight, and combinations thereof.

In addition to the oriented fluoropolymer film or sheet layer and the oriented polyester film or sheet layer, the multi-layer pre-lamination assembly may optionally further comprises other additional layers. For example, in one embodiment, the multi-layer pre-lamination assemblyis in the form of a bi-layer assemblythat consists essentially ofa first outer surface layer formed of an oriented fluoropolymerfilm or sheet (e.g., an oriented PVF film or sheet) and a second (opposite) outer surfacelayer formed of an oriented polyester film or sheet (e.g., an oriented PET film or sheet). Such a bi-layer assembly may be denoted herein, e.g., as a “PVF/PET” bi-layer assembly, while the multi-layer fluoropolymer film or sheet derived therefrom may be denoted herein, e.g., as a “PVF/PET” bi-layer fluoropolymer film or sheet. In a further embodiment, the multi-layer pre-lamination assemblyis in the form of a tri-layer assemblythat consistsessentially oftwo opposite outer surface layers each formed of an oriented fluoropolymer film or sheet (e.g., oriented PVF films or sheets) and an inner layer formed of an oriented polyester film or sheet (e.g., an oriented PET film or sheet). Such a tri-layer assembly may be denoted herein, e.g., as a “PVF/PET/PVF” tri-layer assembly, while the multi-layer fluoropolymer film or sheet derived therefrom may be denoted herein, e.g., as a “PVF/PET/PVF” tri-layer film or sheet. As used herein, when a multi-layer assembly, film or sheet is said to “consist essentially of”, it is meant that, in addition to the listed component layers, adhesives may or may not be also included in the subject multi-layer assembly, film or sheet to improve the bonding between the component layers. Thus, in accordance withthe present disclosure, adhesives may be applied between any pair of adjacent layers of the multi-layer pre-lamination assembly. Suitable adhesives may include, but are

not limited to, polyurethanes, acrylics, epoxies, polyolefins and combinations of two or more thereof.

The heat pressing process disclosed herein includessetting the heat press means at such conditions that the multi-layer pre-lamination assemblyreceives a pressure of about 0.01-50 Kgf/cm^2, or about 0.1-50 Kgf/cm^2, or about 0.5-50 Kgf/cm^2, or about 0.5-30 Kgf/cm^2, and a heatof about 150°C-260°C, or about 150°C-245°C, or about 160°C-220°C, or about 160°C-200°C. As used herein, "receives a pressure of" means that the film or sheet is subjected to an average pressure of a certain force per unit area over the heat pressed portion of the film or sheet. As used herein, "receives a heat of" means that as the film or sheet is contacted with a pressing surface that is heated to a certain temperature, the pressing surface applies the heat to the heat pressed portion of the film or sheet.

Any suitable heat press means may be used herein, which may include, without limitation, nip rolls, calendar rolls, flat bed laminators andhot flat plate press machines. In one embodiment, two or more rolls may be used in a horizontal or vertical configuration to heat press a multi-layer fluoropolymer film.In a more specific embodiment, a three-roll extrusion coating line (model number KXE1222, Davis-Standard, U.S.A.) with a horizontal roll configuration may be used. A multi-layer fluoropolymer film or sheet may beunwound and passed between an upstream roll (steel) and acentralroll (rubber) under heat and pressure, and then cooled by a downstream roll (PTFE sleeved) before being wound up. The roll temperatures, the line speed, and the nip pressure (i.e., the pressure imposed on the films by the upstream and central rolls) can all be adjusted. A film or sheet may receive a heat that is the surface temperature of the heated rolls (e.g., the upstream steel roll and central rubber roll). The surface temperatures of the heated rolls may be the same or different. In one embodiment, the upstream steel roll may be at a higher temperature than the central rubber roll. When the film or sheet is pressed between two rolls having different surface temperatures, the film or sheet receives a heat that is the combined average temperature of the two rolls. In another embodiment, multiple nip rolls may be used to further control the heat pressing of the multi-layer fluoropolymer film.

In those embodiments wherein hot flat plates are used, it is preferred that the multi-layer pre-lamination assembly is kept under pressure for about 0.1-30 sec, or about 0.5-30 sec, or about 0.5-20 sec. In those embodiments wherein heated nip rolls or calendar rolls are used, it is preferred that the line speed of the rolls are kept at about 0.01-100 m/min, or about 0.1-50 m/min, or about 0.5-30 m/min. Further, in certain embodiments, the heat pressing process may further comprise a pre-heating step wherein the multi-layerpre-lamination assemblyispre-heated to a temperature of about 150°C-260°C by a heating source prior to the heat pressing step. The heating source used herein may include, without limitation, infra-red (IR) heat (e.g., an IR oven), air heat, flameheat, electron beam and laser, and the like. In one embodiment, the multi-layerpre-lamination assemblyis first pre-heated (e.g., by an IR oven) to a temperature of about 150°C-260°C and then placed and pressedbetweena pair of hot flat plates for about 0.1-30 sec, wherein the pair of hot flat plates is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of about 0.05-50 Kgf/cm^2 and a heat of about 150°C-260°C.

In one embodiment, the multi-layer pre-lamination assembly is first pre-heated (e.g., by an IR oven) to a temperature of about 150°C-260°C and then passed between at least one pair of heated nip rolls, wherein the at least one pair of heated nip rollsis set at a line speed of about 0.01-100 m/min and other conditions are set such that the multi-layer pre-lamination assembly receives a pressure of about 0.05-50 Kgf/cm^2 and a heat of about 150°C-260°C. Those skilled in the art will understand that a variety of configurations may be used for controlling the heating, pressing and cooling of the multi-layer fluoropolymer film.

In one embodiment, the heat pressed multi-layer fluoropolymer film or sheet disclosed herein may have a total thickness of about 10-500 μm, or about 50-400 μm, or about 75-350 μm, while each of the oriented fluoropolymer film or sheet layers may have a thickness of about 5-100μm, or about 10-50μm, or about 20-40 μm, while each of the oriented polyester film or sheet layers may have a thickness of about 5-500 μm, or about 50-350 μm, or about 100-300 μm.

As demonstrated by the examples provided herebelow, when the heat pressed multi-layer fluoropolymerfilm or sheet disclosed herein was laminated to an

ethylene/vinyl acetate copolymer (EVA) sheet in such a way that the surface layer of the oriented fluoropolymer film or sheet was in direct contact with the EVA sheet, the bonding strength between the multi-layer fluoropolymer film or sheet and the EVA sheet was very much improved compared to the bonding strength between the multi-layer fluoropolymer film or sheetthat was not heat pressed and an EVA sheet. For example, when a prior art un-pressedmulti-layer fluoropolymer film orsheet was laminated to an EVA sheet, its bonding strength to the EVA sheet wasonly 10.1N/cm. However, when a heat pressed multi-layer fluoropolymer film orsheet (as described above) was laminated to an EVA sheet in the same manner, itsbonding strength tothe EVA sheet could be increased to up to 84.1N/cm.

Therefore, in accordance with the present disclosure, when the heat pressed multi-layer fluoropolymerfilm or sheet is laminated to a polyolefinfilm or sheet (e.g., an EVA film or sheet), the bonding strength between the heat pressed multi-layer fluoropolymerfilm or sheet and the polyolefinfilm or sheet may reach a level of at least about 17N/cm, or at least about 20 N/cm, or at least about 40 N/cm.

Further disclosed herein is a solar cell module comprising one or a plurality of solar cells, a back encapsulant sheet laminated to a backside of the solar cells, and a backsheet laminated to a backside of the back encapsulant sheet, wherein the back encapsulant sheetcomprises a polyolefin, and wherein the backsheet is formed of the heat pressed multi-layer fluoropolymer film or sheet disclosed above.

The solar cells used herein may be any photoelectric conversion device that can convert solar radiation to electrical energy. In one embodiment, solar cells may be formed of photoelectric conversion bodies with electrodes formed on both main surfaces thereof. The photoelectric conversion bodies may be made of any suitable photoelectric conversion materials, such as, crystalline silicon (c-Si), amorphous silicon (a-Si), microcrystalline silicon (μc-Si), cadmium telluride (CdTe), copper indium selenide ($CuInSe_2$ or CIS), copper indium/gallium diselenide ($CuIn_xGa_{(1-x)}Se_2$ or CIGS), light absorbing dyes, and organic semiconductors. The front electrodes may be formed of conductive paste, such as silver paste, applied over the front surface of the photoelectric conversion body by any suitable printing process, such as screen printing or ink-jet printing. The front conductive paste may comprise a

plurality of parallel conductive fingers and one or more conductive bus bars perpendicular to and connecting the conductive fingers, while the back electrodes may be formed by printing metal paste over the entire back surface of the photoelectric conversion body. Suitable metals forming the back electrodes include, but are not limited to, aluminum, copper, silver, gold, nickel, molybdenum, cadmium, and alloys thereof. In another embodiment, both electrodes of the photoelectric conversion body can be on the same surface thereof. In a particular embodiment, both the anode and cathode are located on the back surface of the photoelectric conversion body, forming a back contact solar cell.

When in use, the solar cells typically have a front (or top) surface facing towards the solar radiation and a back (or bottom) surface facing away from the solar radiation. Therefore, each component layer within a solar cell module has a front surface (or side) and a back surface (or side).

In accordance withthe present disclosure, the back encapsulant sheet that is laminated to the back side of the solar cells may comprise a polyolefin, including without limitation, ethylene/vinyl acetate copolymers (EVA), ionomers, polyethylenes, ethylene/acrylate ester copolymers (such as poly(ethylene-co-methyl acrylate) and poly(ethylene-co-butyl acrylate)), acid copolymers, and combinations of two or more thereof. In one embodiment, the back encapsulant sheet comprises EVA. EVA-based encapsulant sheets useful herein can be commercially obtained from Bridgestone (Japan) under the tradename EVASKY™;Sanvic Inc. (Japan) under the tradename Ultrapearl™; Bixby International Corp. (U.S.A.) under the tradename BixCure™; orRuiYang Photovoltaic Material Co. Ltd. (China) under the trade name Revax™.Exemplary ionomer-based encapsulant sheets include, without limitation, DuPont™ PV5300 series encapsulant sheets and DuPont™ PV5400 series encapsulant sheets from DuPont.

In one embodiment, the backsheet of the solar cell module is formed of the heat pressed tri-layer fluoropolymer film or sheet disclosed above (for example with a structure of fluoropolymer/polyester/fluoropolymer, or more particularly PVF/PET/PVF). In a further embodiment, the backsheet is formed of the heat

pressed bi-layer fluoropolymer film or sheet disclosed above (for example with a structure of fluoropolymer/polyester, or more particularly PVF/PET).

The solar cell modules disclosed herein may further comprise a transparent front encapsulant sheetlaminated to a front surface of the solar cell(s), and a transparent frontsheet further laminated to a front surface of the front encapsulant sheet.

Suitable materials for the transparent front encapsulant sheet includewithout limitation, compositions comprisingEVA, ionomers, poly(vinyl butyral) (PVB), polyurethane (PU), polyvinylchloride (PVC), polyethylenes, polyolefin block elastomers, ethylene/acrylate ester copolymers (such as poly(ethylene-co-methyl acrylate) and poly(ethylene-co-butyl acrylate)), acid copolymers, silicone elastomers, epoxy resins, and the like.

Any suitable glass or plastic sheets can be used as the transparent front sheet. Suitable materials for the plastic frontsheet may include, without limitation, glass, polycarbonate, acrylics, polyacrylate, cyclic polyolefins, ethylene norbornene polymers, metallocene-catalyzed polystyrene, polyamides, polyesters, fluoropolymers and the like and combinations thereof.

Any suitable lamination process may be used to produce the solar cell modules disclosed herein. In one embodiment, the process includes: (a) providing a plurality of electrically interconnected solar cells; (b) forming a pre-lamination assemblywherein the solar cells are laid over a back encapsulant sheet, which is further laid over a backsheet, wherein the backsheet is formed of the heat pressed multi-layer fluoropolymer film or sheet disclosed above; and (c) laminating the pre-lamination assemblyunder heat and pressure.

In a further embodiment, the process includes: (a) providing a plurality of electrically interconnected solar cells; (b) forming a pre-lamination assemblywherein the solar cells are sandwiched between a transparent front encapsulant sheet and a back encapsulant sheet, which is further sandwiched between a transparent frontsheet and a backsheet, wherein the backsheet is formed of the heat pressed multi-layer fluoropolymer film or sheet disclosed above; and (c) laminating the pre-lamination assemblyunder heat and pressure.

In one embodiment, the module lamination process is performed using a ICOLAM 10/08 laminator purchased from Meier Solar Solutions GmbH (Germany) at about 135°C-150°C and about 1 atmfor about 10 to about 25 minutes.

Examples

Materials Used:

- PVF film: Tedlar® PV2001, an oriented polyvinyl fluoride film (38 μm thick) obtained from DuPont;
- EVA sheet: Revax™ 767 (瑞福 767) ethylene/vinyl acetate sheet (500 μm thick) obtained from RuiYangPhotovoltaic Material Co. Ltd. (China);
- PET film: corona treated (both sides) Melinex™ S oriented polyethylene terephthalate film (250 μm thick) obtained from DuPont Teijin Films (U.S.A.);
- PVF/PET/PVF film: a laminated tri-layer film having a structure of "PVF film/PET film/PVF film", which was prepared by laminating one layer of PET film between two layers of PVF films using Liofol LA 2692 polyurethane adhesives and hardener UR7395 (bother purchased from Henkel AG&Co. Germany) at a ratio of 11:1.

Comparative Examples CE1-CE3 and Examples E1-E9:

In CE1, a number of laminatedsheets having a structure of "glass/EVA sheet/PVF/PET/PVFfilm" were prepared by first positioning one layer of EVA sheet (7X10 cm) between one layer of a 3.2 mm thick glass sheet (7x10 cm) and one layer ofPVF/PET/PVF film (7x12 cm), that was not heat pressed, to form a multi-layer pre-lamination structure, which was then subjectedto vacuum lamination at 145ºC and 1 atm for 15 minutes, using a ICOLAM 10/08 laminator, to form the final laminated sheets.In additional, about half way along the length of the pre-lamination structure, a piece of fluorinated ethylene propylene(FEP) release film was positioned between the EVA sheet and the PVF/PET/PVF film prior to vacuum lamination process. This way, after removing the FEP release film, the PVF/PET/PVF film would have a loose end that is not bonded to the EVA sheet. Thereafter, along the length of each of the laminated sheets, two test strips (2.54 cm wide and 12 cm long) were cut out and

the bonding strength between the PVF/PET/PVF film and the EVA sheet were measured in accordance with ASTM D903-98 using an Instron5566 tester (purchased from Instron (U.S.A.)). The bonding strengthof a total of6strips prepared as so was measured and their average was calculated and tabulated in Table 1.

In CE2-CE3 and E1-E9, a number of heat pressedPVF/PET/PVF films were obtained by placing PVF/PET/PVF films in an infrared (IR) oven (model number 10831010, purchased from Shanghai Yuejin Medical Instruments Factory, China)for a certain period of time, followed by pressing the heated PVF/PET/PVFfilms between a pair of hot flat plates for a certain period of time. The temperature of the IR oven, the residence time of the films in the IR oven, the temperature of the hot flat plates, the pressure that was imposed on the films by the hot flat plates, and the residence time of the films being pressed by the hot flat plates are listed in Table 1.

By the same lamination process described above in CE1, laminated sheets of "glass/EVA sheet/heat pressedPVF/PET/PVF film" were prepared and the bonding strengthbetween the heat pressedPVF/PET/PVF films and the EVA sheets in each of the examples (CE2-CE3 and E1-E9) were determined by thesame method used in CE1and tabulated in Table 1.

TABLE 1

Sample	Temperature of IR Oven (°C)	Time in IR Oven (seconds)	Temperature of Hot Plates (°C)	Time between Hot Plates (seconds)	Pressure of Hot Plates (Kgf/cm^2)	[3]Bonding Strength (N/cm)
CE1	[2]NA	[2]NA	[2]NA	[2]NA	[2]NA	10.1
E1	210	10	210	1	10.55	81.1
[1]E2	[2]NA	[2]NA	210	1	10.55	65.3
E3	210	10	190	2	10.55	18.5
E4	220	10	220	1	10.55	84.1
[1]E5	[2]NA	[2]NA	220	1	10.55	60.5
E6	210	10	190	3	10.55	19.8
CE2	150	10	150	3	10.55	10.3
E7	160	10	160	10	10.55	17.8
CE3	150	10	150	10	10.55	10.3
E8	210	10	190	10	10.55	25.3

[1]E9	[2]NA	[2]NA	190	10	10.55	19.6

Note:

- [1] In examples E2, E5, and E9, the PVF/PET/PVF film underwent hot plate pressing without the heat treatment by IR ovens;
- [2] NA stands for "not applicable";
- [3] The bonding strength measured was between the PVF/PET/PVFfilm (heat pressed PVF/PET/PVF films in CE2-CE3 and E1-E9) and the EVA sheet.

As demonstrated above, the heat pressed PVF/PET/PVF films disclosed herein had improved bonding strength with the EVA sheets (ranging from 17.8-84.1 N/cm in E1-E9) compared to that of the PVF/PET/PVF films that were not heat pressed (10.1 N/cm in CE1).

Examples E10-E12:

In E10-12, a number of heat pressedPVF/PET/PVF films were obtained using a three-roll extrusion coating line (model number KXE1222, purchased from Davis-Standard, U.S.A.). Specifically, the PVF/PET/PVF films were first pressed and then passed between the upstream rolls (heated steel rolls) and the centralrolls (heated rubber rolls), and then cooled by the downstream rolls (PTFE sleeved rolls) before being wound up. The roll temperatures, the line speed, and the nip pressure (i.e., the pressure imposed on the films by the upstream and centralrolls)are listed in Table 2. Roll temperatures for the upstream, central and downstream rolls are the average surface temperatures of each roll measured along the length of the roll (i.e., at multiple locations) for a given set temperature of the oil bath used to heat the roll.

By the same process described above in CE1, laminated sheets of "glass/EVA sheet /heat pressedPVF/PET/PVF film" were prepared and the bonding strength between the heat pressed PVF/PET/PVF films and the EVA sheets in each of the examples (E10-12) were determined by the same method used in CE1 and tabulated in Table 2.

TABLE 2

Sample	Upstream Roll Temp (°C)	CentralRoll Temp (°C)	Combined Avg. Temp Upstream & Central Rolls (°C)	DownstreamRollTemp (°C)	Line Speed (m/min)	Nip Pressure (Kgf/cm^2)	[2]BondingStrength (N/cm)
CE1	[1]NA	[1]NA	[1]NA	[1]NA	[1]NA	[1]NA	10.1
E10	205	176	190.5	75	10	3	70.0
E11	212	181	196.5	75	20	3	54.7
E12	172	148	160	75	10	3	24.9

[1] NA stands for "not applicable";

[2] The bonding strength measured was between the PVF/PET/PVF film (heat pressed PVF/PET/PVF films in CE4 and E10-E12) and the EVA sheet.

As demonstrated herein, the heat pressed PVF/PET/PVFfilms disclosed herein, had improved bonding strength with the EVA sheets (ranging from 24.9-70.0 N/cm in E10-E12) compared to that of the PVF/PET/PVF films that were not heat-pressed (10.1 N/cm in CE1).

What is Claimed is:

1. A method for obtaining a heat pressed multi-layer fluoropolymer film or sheet that has improved bonding strength to a polyolefin film, the method comprising, (i) providing a multi-layer pre-lamination assembly comprising a first oriented fluoropolymer film or sheet layer positioned next to an oriented polyester film or sheet layer, wherein the first fluoropolymer film or sheet layer is positioned to provide one of the two opposite outer surface layers of the assembly, and wherein the first oriented fluoropolymer film or sheet layer consists essentially of fluoropolymer and the oriented polyester film or sheet layer consists essentially of polyester; and (ii) heat pressing the multi-layer pre-lamination assembly by a heat press means to obtain the heat pressed multi-layer fluoropolymer film or sheet, wherein the heat press means is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of 0.01-50 Kgf/cm^2 and a heat of 150℃-260℃.

2. The method of Claim 1, wherein in step (ii), the heat press means is set at such conditions that the multi-layer pre-lamination assembly receives a pressure of 0.1-50 Kgf/cm^2, or preferably 0.5-50 Kgf/cm^2, or more preferably 0.5-30 Kgf/cm^2 and a heat of 150℃-245℃, or preferably 160℃-220℃, or more preferably 160℃-200℃.

3. The method of Claim 1 or 2, wherein the heat press means is a pair of hot flat plates and in step (ii), the multi-layer pre-lamination assemblyis heat pressed between the pair of hot flat plates for 0.1-30 sec, or preferably 0.5-30 sec, or more preferably 0.5-20 sec.

4. The method of any of Claims 1-3, wherein the heat press means comprises one or more pairs of heated nip rolls and in step (ii), the multi-layer pre-lamination assemblyis passed through the one or more pairs of heated nip

rolls at a line speed of 0.01-100 m/min, or preferably 0.1-50 m/min, or more preferably 0.5-30 m/min.

5. The method of any of Claims 1-4, wherein, prior to step (ii), the multi-layer pre-lamination assembly is heated to a temperature of 150℃-260℃, or preferably 150℃-245℃, or more preferably 160℃-220℃, or yet more preferably 160℃-200℃.

6. The method of Claim 5, wherein, prior to step (ii), the multi-layer pre-lamination assembly is heated by infra-red heat, air heat, flame heat, electron beam, or laser; or preferably the multi-layer pre-lamination assembly is heated by an infra-red oven.

7. The method of any of Claims 1-6, wherein the fluoropolymer is derived from fluoromonomersselected from the group consisting of vinyl fluorides, vinylidene fluorides, tetrafluoroethylenes, hexafluoropropylenes, fluorinated ethylene propylenes, perfluoroalkoxys,chlorotrifluoroethlyenes, tetrafluoroethylenes, and combinations of two or more thereof.

8. The method of Claim 7, wherein the fluoropolymer is selected from the group consisting of polyvinyl fluorides, polyvinylidene fluorides, and combinations thereof, or more preferably the fluoropolymer is selected from polyvinyl fluorides.

9. The method of any of Claims 1-8, wherein the polyester is selected from the group consisting of polyethylene terephthalates, polybutylene terephthalates, polytrimethylene terephthalates, polyethylene naphthalates, and combinations of two or more thereof; or preferably the polyester is selected from polyethylene terephthalates.

10. The method of any of Claims 1-9, wherein the multi-layer pre-lamination assembly is in the form of a bi-layer assembly that consists essentially of the first oriented fluoropolymer film or sheet layer and the oriented polyester film or sheet layer.

11. The method of any of Claims 1-9, wherein the multi-layer pre-lamination is in the form of a tri-layer assembly that consists essentially of the first oriented fluoropolymer film or sheet layer, the oriented polyester film or sheet layer, and a second oriented fluoropolymer film or sheet layer consisting essentially of fluoropolymer that is the same or different than the fluoropolymerforming the first oriented fluoropolymer film or sheet layer, wherein the oriented polyester film or sheet layer is positioned between the first and the second oriented fluoropolymer film or sheet layers and the first and second oriented fluoropolymer film or sheet layers provide two opposite outer surface layers of the multi-layer pre-lamination assembly.

12. A heat pressed multi-layer fluoropolymer film or sheet prepared by the method of any of Claims 1-11.

13. The heat pressed multi-layer fluoropolymer film or sheet of Claim 12, wherein the heat pressed multi-layer fluoropolymer film or sheet is laminated to a polyolefin film or sheet in such a way that the first oriented fluoropolymer film or sheet layer is positioned next to the polyolefin film or sheet, and the bonding strength between the heat pressed multi-layer fluoropolymer film or sheet and the polyolefin film or sheet, measured according to ASTM D903-38, is at least 17 N/cm, or preferably at least 20 N/cm, or more preferably at least 40 N/cm.

14. The heat pressed multi-layer fluoropolymer film or sheet of Claim 13, wherein the polyolefin film or sheet comprises a polyolefinic composition, and wherein the polyolefinic composition comprises a material selected from the group

consisting of ethylene/vinyl acetate copolymers, ionomers, polyethylenes, ethylene/acrylate ester copolymers, acid copolymers, and combinations of two or more thereof; or preferably the polyolefinic composition comprises a material selected from the group consisting of ethylene/vinyl acetate copolymers.

15. A solar cell module comprising one or a plurality of solar cells, a back encapsulant sheet laminated to a back side of the solar cells, and a backsheet laminated to a back side of the back encapsulant sheet, wherein the back encapsulant sheet comprises a polyolefin, and wherein the backsheet is formed of the heat pressed multi-layer fluoropolymer film or sheet recited in any of Claims 12-14.

16. The solar cell module of Claim 15, wherein the polyolefin comprised in the back encapsulant sheet is selected from the group consisting of ethylene/vinyl acetate copolymers, ionomers, polyethylenes, ethylene/acrylate ester copolymers, acid copolymers, and combinations of two or more thereof; or preferably the polyolefin comprised in the back encapsulant sheet is selected from ethylene/vinyl acetate copolymers.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/076226

A. CLASSIFICATION OF SUBJECT MATTER

See extra shee

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)

IPC:B32B37, B29C43, H01L31

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

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

WPI, EPODOC,CNPAT,CNKI: cell, backsheet, polyfluoro+, polyester, heat, press+, orient+, stretch+, adhesion, PTFE, PVF, PET

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO2011044417A2 (DU PONT DE NEMOURS&CO E I), 14 Apr. 2011(14.04.2011), claims 1-20, page 6, lines 18-33,page 7, lines16-17, page 8, lines21-29, page 16, line 5-14, page 17, lines 9-10, figures 1,2	1-16
A	CN101431107A (DU PONT DE NEMOURS&CO E I),13 May 2009(13.05.2009),claims 1-13	1-16
A	CN100495735C (ZHOU JUNHUA),3 Jun. 2009(03.06.2009),the whole document	1-16

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

* Special categories of cited documents:

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"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
08 Aug.2012 (08.08.2012)	**13 Sep. 2012 (13.09.2012)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer CHEN，Xiujuan Telephone No. (86-10)62085042

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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PCT/CN2012/076226

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
WO2011044417A2	14.04.2011	CN102039664A	04.05.2011
		WO2011044417A3	06.10.2011
		US2011247681A	13.10.2011
		CN102576763A	11.07.2012
CN101431107A	13.05.2009	none	
CN100495735C	03.06.2009	CN101097967A	02.01.2008

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

B32B 37/06 (2006.01) i

B29C43/00 (2006.01) i

H01L31/042 (2006.01) i