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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 June 2014 (26.06.2014)

(10) International Publication Number
WO 2014/100301 A1

(51) International Patent Classification:
C09D 123/08 (2006.01) ***H01L 51/44*** (2006.01)

(21) International Application Number:
PCT/US2013/076323

(22) International Filing Date:
19 December 2013 (19.12.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/739,557 19 December 2012 (19.12.2012) US
61/739,562 19 December 2012 (19.12.2012) US
61/739,572 19 December 2012 (19.12.2012) US

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

(72) Inventors: **PESEK, Steven, C.**; 2806 Bear Trails, Orange, Texas 77632 (US). **SMITH, Charles, Anthony**; 5231 Glenbrook Drive, Vienna, West Virginia 26105 (US).

(74) Agent: **SAUERBRUNN, Linda, K.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, Chestnut Run Plaza 721/2340, 974 Centre Road, PO Box 2915 Wilmington, Delaware 19805 (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, 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, KZ, LA, LC, LK, LR, LS, LT, 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, 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))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: CROSS-LINKED POLYMERS AND THEIR USE IN PHOTOVOLTAIC MODULES

(57) Abstract: The present invention is directed to photovoltaic prelaminate assemblies and modules comprising novel cross-linked polymers. The herein-described photovoltaic prelaminate assemblies and modules, which have encapsulant layer(s) comprising certain hydroxyl-containing crosslinking compounds, as well as optionally adjuvants, show improved creep resistance and exceptional stretch when compared to conventional ethylene acrylic or methacrylic acid copolymers or ionomers thereof.

WO 2014/100301 A1

TITLE OF THE INVENTION

CROSS-LINKED POLYMERS AND THEIR USE IN PHOTOVOLTAIC MODULES

FIELD OF THE INVENTION

The present invention is directed to photovoltaic prelaminate assemblies and modules comprising novel cross-linked polymers. The herein-described photovoltaic prelaminate assemblies and modules, which have encapsulant layer(s) comprising certain hydroxyl-containing crosslinking compounds, as well as optionally adjuvants, show improved creep resistance and exceptional stretch when compared to conventional ethylene acrylic or methacrylic acid copolymers or ionomers thereof.

BACKGROUND OF THE INVENTION

Several patents, patent applications and publications are cited in this description in order to more fully describe the state of the art to which this invention pertains. The entire disclosure of each of these patents, patent applications and publications is incorporated by reference herein.

The use of photovoltaic or solar cells is expanding rapidly because they provide a sustainable energy resource. Solar cells can typically be categorized into two types based on the light absorbing material used, i.e., bulk or wafer-based solar cells and thin film solar cells.

Monocrystalline silicon (c-Si), poly- or multi-crystalline silicon (poly-Si or mc-Si) and ribbon silicon are the materials used most commonly in forming the more traditional wafer-based solar cells. Solar cell modules derived from wafer-based solar cells often comprise a series of self-supporting wafers (or cells) that are soldered together. The wafers generally have a thickness of between about 180 and about 240 µm. A panel of soldered solar cells, along with a layer of conductive paste and/or electrical wirings such as conducting wires and bus bars deposited thereon, is often referred to as a solar cell layer or assembly.

To form a weather resistant module that may be used for at least 20 years, the solar cell assembly is typically sandwiched or laminated between polymeric encapsulant layers or sheets. These front and back sheets insulate the solar cells from the environment and provide mechanical support to the module. It is also possible to have one layer of encapsulant which can flow and deform around the solar cells, thus supplying the needed mechanical support.

This structure is in turn sandwiched or laminated between outer protective layers or sheets. In general, a solar cell module derived from wafer-based solar cell(s) has a laminate structure comprising, in order of position from the front sun-facing side to the back non-sun-facing side: (1) a front outer protective layer or “front sheet,” (2) a front encapsulant layer, (3) a solar cell assembly or layer, (4) a back encapsulant layer, and (5) a back outer protective layer or “back sheet.”

In modules having this structure, it is essential that the materials positioned towards the sun-facing side of the solar cell assembly, i.e., the front sheet and the front encapsulant layer, have good transparency to allow sufficient sun light to reach the solar cells. In addition, some modules may comprise bi-facial solar cells. Bi-facial solar cells are able to generate electrical power by receiving sunlight directly on their sun-facing side and also by receiving sunlight that is reflected back to the opposite side, although it does not face the sun. Plainly, in bifacial modules it is essential that the materials surrounding both faces of the solar cells assembly be sufficiently transparent.

The front and back encapsulant sheets are typically made of polymeric materials, such as acid copolymers, ionomers, poly(ethylene vinyl acetates) (EVA), poly(vinyl acetals) (e.g., poly(vinyl butyrals) (PVB)), polyurethanes, poly(vinyl chlorides), polyethylenes (e.g., linear low density polyethylenes), polyolefin block copolymer elastomers, copolymers of α-olefins and α,β-ethylenically unsaturated carboxylic acid esters) (e.g., ethylene methyl acrylate copolymers and ethylene butyl acrylate copolymers), silicone elastomers, epoxy resins, and combinations of two or more of these polymeric materials. Among them, EVA has been the most popular choice for the solar cell encapsulant material.

Glass and flexible metal or plastic films have been used as the front and back protective layers in wafer-based solar cell modules. Glass remains the most desirable choice, however, due to its mechanical and optical properties.

Thin film solar cells are an alternative to wafer-based solar cells. The materials commonly used for such cells include 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, organic semiconductors, and the like. By way of example, thin film solar cells are described in U.S. Patent Nos. 5,507,881; 5,512,107; 5,948,176; 5,994,163; 6,040,521; 6, 123,824; 6,137,048; 6,288,325; 6,258,620; 6,613,603; and 6,784,301; and U.S. Patent Publication Nos. 20070298590; 20070281090; 20070240759; 20070232057; 20070238285; 20070227578; 20070209699; 20070079866; 20080223436; and 20080271675, for example.

EVA is commonly cross-linked with peroxides to prevent creep, but free-radical chemistry can be difficult to control. In addition, unreacted radicals can cause long-term changes or degradation, such as yellowing, cracking, and increased modulus.

While ionomers tend to exhibit less creep than EVA's, this phenomenon has been seen in photovoltaic cells which use these resin materials. There is a need in photovoltaic modules to use materials with little or no "creep", so that the modules cannot shift when the encapsulant is heated and the material therefore deforms to a point of compromising the visual quality, performance or integrity of the module. Additionally, it is known to add silanes to resins and photovoltaic module encapsulants to enhance adhesion. However, how the addition of silane to a diol-containing resin would affect creep has not been previously described.

Crosslinking occurs when chemical bonds are formed between polymeric moieties that are present. Crosslinking can allow the formation of polymeric networks that can enhance the overall strength of the material made from the composition, and allow improved elongation, mechanical integrity, and resistance to break.

Crosslinking by various methods is known. For example, ethylene vinyl acetate (EVA) is often crosslinked with peroxides to form sheets and encapsulants. However, unlike the crosslinking accomplished by the present invention, the crosslinking of EVA with peroxide can form gel and can lead to the degradation of the EVA. See, for example, U.S. Pat. No. 6,093,757, issued July 25, 2000 to Pern.

It has been found, and is shown in the examples included herein, that adding a hydroxyl-containing crosslinking agent to the ionomers in the melt can act to cross-link the ionomer, thus making the material more creep-resistant. While not wishing to be bound by theory, it is believed that the hydroxyl-containing crosslinking agent reacts with the carboxylate groups of the ionomers to form esters, which then cross-link the ionomers. As shown in the examples and figures included herein, the cross-linked ionomers exhibit good tensile strength as well. Additionally, the materials exhibit greater elongation with integrity when compared to sheets or films without the hydroxyl-containing crosslinking agent addition. The term “elongation with integrity”, as used herein, refers to the ability of a film to stretch by 10% or greater without incurring any defects that would impair performance. Non-limiting examples of such defects include breaking, stretching and necking down to a thin fiber-like construction, and material unable to support its own weight.

SUMMARY OF THE INVENTION

Provided herein is a photovoltaic prelaminate assembly having one or more encapsulant layer(s), comprising a polymer composition which comprises an ethylene copolymer, where the ethylene copolymer comprises copolymerized units of ethylene, about 5 to about 90 wt% of copolymerized units of a first α,β-unsaturated carboxylic acid having 3 to 10 carbon atoms; and optionally about 2 to about 40 wt% of copolymerized units of a derivative of a second α,β-unsaturated carboxylic acid having 3 to 10 carbon atoms. These weight percentages of the copolymerized units are based on the total weight of the ethylene copolymer. Optionally, at least a portion of the carboxylic acid groups of the copolymerized units of the α,β-unsaturated carboxylic acid units are neutralized to form carboxylate salts. The acid copolymer composition also includes a hydroxyl-containing crosslinking agent, and may optionally include an adjuvant.

Further provided herein is a photovoltaic module comprising a photovoltaic prelaminate assembly, which comprises the herein described ethylene copolymer composition as its encapsulant layer(s).

Further provided herein are photovoltaic prelaminate assemblies and modules which comprise encapsulants which are a product of cross-linking the acid copolymer composition described herein, wherein at least two of the carboxylic acid groups of the ethylene copolymer are reacted with two or more of the hydroxyl groups of the hydroxyl-containing crosslinking agent, to form cross-links between two or more ethylene copolymers

BRIEF DESCRIPTION OF THE FIGURES/DRAWINGS

FIGURE 1 is a graphical representation of the tensile elongation of a polymer composition of the invention compared to that of a control material.

FIGURE 2 is a differential scanning calorimetry (DSC) trace of a polymer composition of the invention.

FIGURE 3 is a differential scanning calorimetry (DSC) trace of a control material.

FIGURE 4 is a graphical representation of the laminate creep resistance of several polymer compositions of the invention compared to that of a control material.

FIGURE 5 is a graphical representation of the viscosity shear rate of a polymer composition of the invention compared to that of a control material.

DETAILS OF THE INVENTION

The following definitions apply to the terms as used throughout this specification, unless otherwise limited in specific instances.

Moreover, unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including the definitions herein, will control.

Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, suitable methods and materials are described herein.

As used herein, the term "about" means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such.

The term “or”, as used herein, is inclusive; more specifically, the phrase “A or B” means “A, B, or both A and B”. Exclusive “or” is designated herein by terms such as “either A or B” and “one of A or B”, for example.

In addition, the ranges set forth herein include their endpoints unless expressly stated otherwise in limited circumstances. Further, when an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed.

Moreover, where a range of numerical values is recited herein, unless otherwise stated in specific circumstances, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range. Finally, when the term “about” is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

When materials, methods, or machinery are described herein with the term “known to those of skill in the art”, or a synonymous word or phrase, the term signifies that materials, methods, and machinery that are conventional at the time of filing the present application are encompassed by this description. Also encompassed are materials, methods, and machinery that are not presently conventional, but that will have become recognized in the art as suitable for a similar purpose.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” "containing," "characterized by," “has,” “having” or any other synonym or variation thereof refer to a non-exclusive inclusion. For example, a process, method, article, or apparatus that is described as comprising a particular list of elements is not necessarily limited to those particularly listed elements but may further include other elements not expressly listed or inherent to such process, method, article, or apparatus.

The transitional phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. "A 'consisting essentially of' claim occupies a middle ground between closed claims that are written in a 'consisting of' format and fully open claims that are drafted in a 'comprising' format."

Where an invention or a portion thereof is described with an open-ended term such as “comprising,” it is to be understood that, unless otherwise stated in specific circumstances, this description also includes a description of the invention using the term “consisting essentially of” as they are defined above.

The indefinite articles “a” and “an” are employed to describe elements and components of the invention. The use of these articles means that one or at least one of these elements or components is present. Although these articles are conventionally employed to signify that the modified noun is a singular noun, as used herein the articles “a” and “an” also include the plural, unless otherwise stated in specific instances. Similarly, the definite article “the”, as used herein, also signifies that the modified noun may be singular or plural, again unless otherwise stated in specific instances.

As used herein, the term “copolymer” refers to polymers comprising copolymerized units or residues resulting from copolymerization of two or more comonomers. In this connection, a copolymer may be described herein with reference to its constituent comonomers or to the amounts of its constituent comonomers, for example “a copolymer comprising ethylene and 9 weight % of acrylic acid”, or a similar description. Such a description may be considered informal in that it does not refer to the comonomers as copolymerized units; in that it does not include a conventional nomenclature for the copolymer, for example International Union of Pure and Applied Chemistry (IUPAC) nomenclature; in that it does not use product-by-process terminology; or for another reason. As used herein, however, a description of a copolymer with reference to its constituent comonomers or to the amounts of its constituent comonomers means that the copolymer contains copolymerized units (in the specified amounts when specified) of the specified comonomers. It follows as a corollary that a copolymer is not the product of a reaction mixture containing given comonomers in given amounts, unless expressly stated in limited circumstances to be such.

The term “acid copolymer” refers to a polymer comprising copolymerized units of an α-olefin, an α,β-ethylenically unsaturated carboxylic acid, and optionally other suitable comonomer(s), such as an α,β-ethylenically unsaturated carboxylic acid ester.

The term “(meth)acrylic”, as used herein alone or in combined form, such as “(meth)acrylate”, refers to acrylic or methacrylic, for example, “acrylic acid or methacrylic acid”, or “alkyl acrylate or alkyl methacrylate”.

The terms “solar cell” or “photovoltaic module” as used herein refer to any article that can convert light into electrical energy. Suitable solar cells include, but are not limited to, wafer-based solar cells (e.g., solar cells comprising materials selected from c-Si, mc-Si, heterojunction with intrinsic thin layer (HIT), and mixtures thereof), gallium arsenide (GaAs), cast mono c-Si, organic semiconductors, tandem and multiple junction cells, and combinations thereof, and thin film solar cells (e.g., solar cells comprising materials selected from a-Si, μc-Si, CdTe, CIS, CIGS, copper zinc tin sulfide (CZTS), light absorbing dyes, organic semiconductors, and mixtures thereof). A solar cell assembly may comprise one or a plurality of solar cells. The plurality of solar cells may be electrically interconnected or arranged in a flat plane. In addition, the solar cell assembly may further comprise conductive pastes in wafer-based solar cells, conductive coatings in thin film solar cells, or electrical wirings deposited upon either type of solar cells.

The term “photovoltaic prelaminate assembly” and “solar cell prelaminate assembly”, as used herein, refer to the structure of components of a photovoltaic module arranged in suitable order before they are laminated.

The solar cell module may have a front, sun-facing or light-incident side and a back, non-sun-facing side. In such a configuration, all the laminated layers that are positioned between the light source and the front, sun-facing side of the solar cell assembly should have sufficient transparency to allow light to reach the solar cells. The other laminated layers positioned behind the back, non-sun-facing side of the solar cell assembly need not be transparent.

Alternatively, the solar cell layer may be bifacial. In solar cell modules comprising bifacial solar cell layers, all the laminated layers comprised in the module, with the exception of the solar cell assembly, should be sufficiently transparent to allow light or reflected light to reach the solar cells.

The encapsulant materials useful in this invention can also comprise polymeric materials, such as acid copolymers, ionomers, poly(ethylene vinyl acetates) (EVA), poly(vinyl acetals) (e.g., poly(vinyl butyrals) (PVB)), polyurethanes, poly(vinyl chlorides), polyethylenes (e.g., linear low density polyethylenes), polyolefin block copolymer elastomers, copolymers of α-olefins and α,β-ethylenically unsaturated carboxylic acid esters) (e.g., ethylene methyl acrylate copolymers and ethylene butyl acrylate copolymers), silicone elastomers, epoxy resins, and combinations of two or more of these polymeric materials.

When the photovoltaic prelaminate assembly or module comprises an encapsulant layer that comprises an ionomer, the term “ionomer” refers to a polymer that is produced by partially or fully neutralizing an acid copolymer as described above. More specifically, the ionomer comprises ionic groups that are metal ion carboxylates, for example, alkali metal carboxylates, alkaline earth metal carboxylates, transition metal carboxylates and mixtures of such carboxylates. Such polymers are generally produced by partially or fully neutralizing the carboxylic acid groups of precursor or parent polymers that are acid copolymers, as defined herein, for example by reaction with a base. An example of an alkali metal ionomer as used herein is a sodium ionomer (or sodium neutralized ionomer), for example a copolymer of ethylene and methacrylic acid wherein all or a portion of the carboxylic acid groups of the copolymerized methacrylic acid units are in the form of sodium carboxylates.

The term “laminate”, as used herein alone or in combined form, such as “laminated” or “lamination” for example, refers to a structure having at least two layers that are adhered or bonded firmly to each other. The layers may be adhered to each other directly or indirectly. “Directly” means that there is no additional material, such as an interlayer or an adhesive layer, between the two layers, and “indirectly” means that there is additional material between the two layers. Layers or films can be “laminated” together by heat and pressure, or can be co-extruded so that the layers adhere to each other.

The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting.

Finally, all percentages, parts, ratios, and the like set forth herein are by weight, unless otherwise stated in specific instances.

Provided herein is a photovoltaic prelaminate assembly comprising a polymer composition which comprises an ethylene copolymer, which in turn comprises copolymerized units of ethylene, about 5 to about 90 wt% of copolymerized units, preferably about 5 to about 30 wt% of copolymerized units, of a first α,β-unsaturated carboxylic acid having 3 to 10 carbon atoms; and optionally about 2 to about 40 wt% or preferably from about 5 to 30 wt%, of copolymerized units of a derivative of a second α,β-unsaturated carboxylic acid having 3 to 10, preferably 3 to 8, carbon atoms. The weight percentages of the copolymerized units are based on the total weight of the ethylene copolymer, and the sum of the weight percentages of the copolymerized units is 100 wt%. Optionally at least a portion of the carboxylic acid groups of the copolymerized units of the α,β-unsaturated carboxylic acid units are neutralized to form carboxylate salts. The polymer composition further comprises a hydroxyl-containing crosslinking agent; and, optionally, also comprises an adjuvant.

Suitable α-olefin comonomers may include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3 methyl-1-butene, 4-methyl-1-pentene, and the like and mixtures of two or more thereof. In one preferred copolymer, the α-olefin is ethylene.

Suitable first α,β-ethylenically unsaturated acid comonomers may include, but are not limited to, carboxylic acids, including acrylic acids, methacrylic acids, itaconic acids, maleic acids, maleic anhydrides, fumaric acids, monomethyl maleic acids, and mixtures of two or more thereof. In one preferred copolymer, the α,β-ethylenically unsaturated carboxylic acid is selected from acrylic acids, methacrylic acids, and mixtures of two or more thereof. In another preferred copolymer, the α,β-ethylenically unsaturated carboxylic acid is methacrylic acid.

The ethylene copolymers may further comprise copolymerized units of one or more other comonomer(s), such as a second α,β-ethylenically unsaturated carboxylic acid having 2 to 10, or preferably 3 to 8 carbons, or derivatives thereof. Suitable acid derivatives include acid anhydrides, amides, and esters. Esters are preferred. Specific examples of preferred esters of unsaturated carboxylic acids include, but are not limited to, methyl acrylates, methyl methacrylates, ethyl acrylates, ethyl methacrylates, propyl acrylates, propyl methacrylates, isopropyl acrylates, isopropyl methacrylates, butyl acrylates, butyl methacrylates, isobutyl acrylates, isobutyl methacrylates, tert-butyl acrylates, tert-butyl methacrylates, octyl acrylates, octyl methacrylates, undecyl acrylates, undecyl methacrylates, octadecyl acrylates, octadecyl methacrylates, dodecyl acrylates, dodecyl methacrylates, 2-ethylhexyl acrylates, 2-ethylhexyl methacrylates, isobornyl acrylates, isobornyl methacrylates, lauryl acrylates, lauryl methacrylates, 2-hydroxyethyl acrylates, 2-hydroxyethyl methacrylates, glycidyl acrylates, glycidyl methacrylates, poly(ethylene glycol) acrylates, poly(ethylene glycol)methacrylates, poly(ethylene glycol) methyl ether acrylates, poly(ethylene glycol) methyl ether methacrylates, poly(ethylene glycol) behenyl ether acrylates, poly(ethylene glycol) behenyl ether methacrylates, poly(ethylene glycol) 4-nonylphenyl ether acrylates, poly(ethylene glycol) 4-nonylphenyl ether methacrylates, poly(ethylene glycol) phenyl ether acrylates, poly(ethylene glycol) phenyl ether methacrylates, dimethyl maleates, diethyl maleates, dibutyl maleates, dimethyl fumarates, diethyl fumarates, dibutyl fumarates, dimethyl fumarates, vinyl acetates, vinyl propionates, and mixtures of two or more thereof. In one preferred ethylene compolymer, the first α,β-ethylenically unsaturated carboxylic acid is the same as the second α,β-ethylenically unsaturated carboxylic acid; in another preferred ethylene copolymer, however, the first and the second α,β-ethylenically unsaturated carboxylic acids are different. In one preferred copolymer, the suitable additional comonomers are selected from methyl acrylates, methyl methacrylates, butyl acrylates, butyl methacrylates, glycidyl methacrylates, vinyl acetates, and mixtures of two or more thereof. In another preferred copolymer, however, the precursor acid copolymer does not incorporate other additional comonomers.

Suitable precursor acid copolymers have a melt flow rate (MFR) of about 1 to about 4000 g/10 min, or about 1 to 1000 g/10 min, or about 20 to about 400 g/10 min, as determined in accordance with ASTM method D1238-89 at 190°C and 2.16 kg.

Finally, suitable precursor acid copolymers may be synthesized as described in U.S. Patent Nos. 3,404,134; 5,028,674; 6,500,888; 6,518,365, or 8,399,096, for example. Some of these methods are also described in detail in U. S. Pat. No. 8,334,033, issued to Hausmann, et al.

To obtain the ionomers useful in the present invention, the precursor acid copolymers are partially neutralized by reaction with one or more bases. An example of a suitable procedure for neutralizing the precursor acid copolymers is described in U.S. Patent Nos. 3,404,134 and 6,518,365. After neutralization, about 1% to about 90%, or about 10% to about 60%, or about 20% to about 55%, of the hydrogen atoms of carboxylic acid groups present in the precursor acid are replaced by other cations. Stated alternatively, about 1% to about 90%, or about 10% to about 60%, or about 20% to about 55%, of the total content of the carboxylic acid groups present in the precursor acid copolymer are neutralized. In another alternative expression, the acid groups are neutralized to a level of about 1% to about 90%, or about 10% to about 60%, or about 20% to about 55%, based on the total content of carboxylic acid groups present in the precursor acid copolymers as calculated or measured for the non-neutralized precursor acid copolymers. The neutralization level can be tailored for the specific end-use.

The ionomers comprise cations as counterions to the carboxylate anions. Suitable cations include any positively charged species that is stable under the conditions in which the ionomer composition is synthesized, processed and used. In some preferred ionomers, the cations used are metal cations, which may be monovalent, divalent, trivalent, multivalent, or mixtures thereof. Useful monovalent metal cations include but are not limited to cations of sodium, potassium, lithium, silver, mercury, copper, and the like, and mixtures thereof. Useful divalent metal cations include but are not limited to cations of beryllium, magnesium, calcium, strontium, barium, copper, cadmium, mercury, tin, lead, iron, cobalt, nickel, zinc, and the like, and mixtures thereof. Useful trivalent metal cations include but are not limited to cations of aluminum, scandium, iron, yttrium, and the like, and mixtures thereof. Useful multivalent metal cations include but are not limited to cations of titanium, zirconium, hafnium, vanadium, tantalum, tungsten, chromium, cerium, iron, and the like, and mixtures thereof. It is noted that when the metal cation is multivalent, complexing agents such as stearate, oleate, salicylate, and phenolate radicals may be included, as described in U.S. Patent No. 3,404,134. In another preferred composition, the metal cations used are monovalent or divalent metal cations. Preferred metal cations are sodium, lithium, magnesium, zinc, potassium and mixtures thereof. In yet another preferred composition, the cations of sodium, zinc and mixtures thereof are more preferred.

The resulting neutralized ionomer will have a melt index, as determined in accordance with ASTM method D1238-89 at 190°C and 2.16 kg, that is lower than that of the corresponding ethylene copolymer.

The acid copolymer composition also includes a hydroxyl-containing crosslinking agent. As used herein, the term “hydroxyl-containing crosslinking agent” refers to any molecule that is miscible with the ethylene copolymer and that has two or more hydroxyl groups. Generally, any hydroxyl-containing crosslinking agent can be contemplated for use with the present invention. Combinations of two or more hydroxyl-containing crosslinking agents may also be used. Examples of suitable hydroxyl-containing crosslinking agents include, without limitation, dihydroxyl, trihydroxyl and multihydroxyl compounds. Of note are glycols, such as propylene glycol; sorbitol; glycerol; poly(alkylene glycols), such as PEG600 and PEG2000; glycerol monstearate; and polyvinyl alcohol. Preferred are diols, such as 1,4-butanediol, 1,3-propanediol and 1,6-hexanediol. 1,4-Butanediol is particularly preferred.

The hydroxyl-containing crosslinking agent is included in the acid copolymer composition in an amount of up to about 5 wt%, preferably about 2 wt% or less or about 1.5 wt% or less, more preferably about 1 wt% or less, 0.5 wt% or less, or 0.25 wt% or less, or 0.1 wt%, based on total weight of the acid copolymer composition.

Those of skill in the art are able to determine an appropriate level of cross-linking based on the physical properties that are desired in the cross-linked composition. For example, higher levels of cross-linking are correlated with a higher flex modulus, better high temperature adhesion, lower melt indices, and better heat resistance. However, consideration should be made to adjust the level of cross-linking so that the desired end use performance is obtained. For example, a level of cross-linking may be desirable at which the creep or displacement properties are controlled or minimized at the expected stress level and temperature range for said article. A level chosen by these criteria allows for the ease of processing of the cross-linked resin, through extrusion and any other secondary or forming/shaping process.

Those of skill in the art are also aware that the time required to obtain a desired level of cross-linking depends directly on the concentration of carboxylic acid groups and hydroxyl–containing groups. Likewise, the time required to obtain a desired level of cross-linking can depend inversely on the temperature at which the cross-linking reaction is carried out, and also can depend inversely or in another negative logarithmic relationship on the melt index of the polymer blend.

Cross-linking reactions can require heat, but the reaction may also be carried out using catalysis, or by using a combination of heat and catalysis. For example, esterification reactions are known to be catalyzed by acid catalysts and by base catalysts.

While any hydroxyl-containing crosslinking agent compound can be used for the purposes described herein, 1,4-butanediol has been shown to have particularly good cross-linking capabilities. Generally, amounts of 5% by weight of 1,4-butanediol can be added, although preferably an amount of 2% or less, or more preferably an amount of 1.5% or less, or more preferably about 1 wt% or less, 0.5 wt% or less, or 0.25 wt% or less, or 0.1 wt% or less is used. All percentages are based on the total weight of the composition.

The hydroxyl-containing crosslinking agent can be added to the ionomer in any convenient manner. One particularly useful way is to add the agent to the ionomer flake in the pre-mix chamber of an extruder. Another way to introduce this agent is through an injection port. As these materials are mixed, generally by tumbling or dry-auger blending, before going into the extruder, the cross-linking agent is incorporated into the polymer composition and may react so that the cross-linking occurs in the ionomer as it is extruded. Alternatively, the cross-linking reaction can take place during melt mixing or extrusion of the melt.

The polymer composition described herein may optionally comprise one or more adjuvants. The term adjuvant as used herein refers to “additives that contribute to the effectiveness of the primary ingredient” (The Condensed Chemical Dictionary, 10th Ed., revised by Gessner G. Hawley, Van Nostrand Reinhold Co., New York, NY, 1981). Without wishing to be held to theory, it is believed that the adjuvants contribute to the effectiveness of the crosslinking agent(s), for example, by enhancing the kinetics of the acid or base catalysis. Examples of suitable adjuvants include silanes. When silanes are used, they can be added in amounts of between 0.025 and 0.1 weight percent (wt%). Non-limiting examples of preferred silanes include N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, and combinations thereof. Available from any convenient source, the silane adjuvants can be added to the base resin in weight percent amounts of 0.025, 0.25, 0.1, and 1.0, based on the total weight of the polymer composition.

The adjuvant can be added at the same time and in the same manner as the hydroxyl-containing crosslinking agent, or by any other known method. In the case of extrusion processing, the typical temperature range is generally between about 120°C and 300°C, depending on the melt point, melt viscosity and specific equipment configuration. The reaction will be dependent on the time and temperature parameters set forth and established through the entire series of process steps. The degree of reaction can be affected by the level of moisture within the resin, or any added moisture. In general, increased levels of moisture decrease the degree of reaction. Depending on the desired end result, this may be an undesirable effect. Alternatively, moisture can advantageously be used as a limiting means to reduce the extent of the cross-linking. Catalysts may also be included, such as the creation of either acid or base conditions to catalyze the cross-linking. Alternatively, a specific catalyst, such as dibutyl tin oxide or similar compound, could be employed.

The present invention also includes photovoltaic prelaminate assemblies and modules made therefrom, which comprise one or more encapsulant layers of a product of the cross-linking of the polymer composition as described above, so that at least a portion of the carboxylic acid groups of one or more ethylene copolymer molecules are reacted with at least two hydroxyl groups of the hydroxyl-containing crosslinking agent, thereby forming cross-links between or within the ethylene copolymer molecules. . In one embodiment, at least a portion of the carboxylic acid groups of two or more ethylene copolymer molecules are reacted with at least two hydroxyl groups of the hydroxyl-containing crosslinking agent, thereby forming cross-links between the ethylene copolymer molecules.

Without wishing to be held to theory, it is hypothesized that during the extrusion process, the crosslinking agent and optionally, the adjuvant compound will react with the resin to form a low-density level of crosslinks in at least an intermolecular fashion. The crosslinking agent can react with carboxylic acid groups thus forming an ester-bond, and can additionally react via trans-esterification with existing or thus-formed ester-bonds. This reactivity can be controlled via selection of the crosslinking agent and specific resin composition containing reactive functional groups. One skilled in the art can utilize conventional understanding of relative reactivity and dependencies on adjacent chemical groups/atoms, steric hindrance, and other molecular/structural effects. Again without wishing to be held to theory, it is hypothesized that the adjuvant compound enhances the crosslink density by forming or by promoting the formation of ester-bonds. Additionally, the choice of other pendant functional groups within silane adjuvants may enable other reactions to occur. For example, amino-groups could form an amide bond and epoxy groups can react with hydroxyl groups to form additional hydroxyl side-groups. Alternatively, epoxy groups may initiate various other reactions via a free-radical pathway.

The resulting cross-linked polymer composition, may have a MFR of 25 g/10 min or less, or about of 20 g/10 min or less, or about 10 g/10 min or less, or about 5 g/10 min or less, or about 0.7 to about 5 g/10 min, as determined in accordance with ASTM method D1238-89 at 190ºC and 2.16 kg.

The polymer composition described herein may further contain other additives known within the art. The additives include, but are not limited to, processing aids, flow enhancing additives, lubricants, pigments, dyes, flame retardants, impact modifiers, nucleating agents, anti-blocking agents such as silica, thermal stabilizers, UV absorbers, UV stabilizers, dispersants, surfactants, chelating agents, coupling agents, reinforcement additives, such as glass fiber, fillers and the like. General information about suitable additives, suitable levels of the additives in the ionomeric polymers, and methods of incorporating the additives into the ionomeric polymers may be found in reference texts such as, for example, the *Kirk Othmer Encyclopedia*, the *Modern Plastics Encyclopedia*, McGraw-Hill (New York, 1995) or the *Wiley Encyclopedia of Packaging Technology*, 2d edition, A.L. Brody and K.S. Marsh, Eds., Wiley-Interscience (Hoboken, 1997). Four types of additives are of note for use in the ionomeric polymers, specifically thermal stabilizers, UV absorbers, hindered amine light stabilizers (HALS), and silane coupling agents. Further information about these four types of additives, such as preferred examples and suitable levels in ionomeric polymers, may be found in the reference texts cited above and in U.S. Patent No. 7,641,965, for example.

The present invention includes the use of the aforementioned polymer compositions in encapsulant sheets for photovoltaic prelaminate assemblies and photovoltaic modules made from these assemblies. Further provided are encapsulant sheets comprising or made from a product of crosslinking the polymer composition.

The difference between a film and a sheet is the thickness; however, there is no set industry standard as to when a film becomes a sheet. As used herein, the term “film” refers to a structure having a thickness of about 1 mil (0.025 mm) or less, and the term “sheet” refers to a structure having a thickness of greater than about 1 mils (0.025 mm). Suitable encapsulant sheets have a Young’s modulus of less than or equal to about 600 MPa, or about 100 to about 550 MPa, as determined in accordance with ASTM D5026-06 at 30ºC and 1 minute of load duration. Further, the encapsulant sheet may have a total thickness of about 1 to about 120 mils (about 0.025 to about 3 mm), or about 5 to about 100 mils (about 0.127 to about 2.54 mm), or about 5 to about 45 mils (about 0.127 to about 1.14 mm), or about 10 to about 35 mils (about 0.25 to about 0.89 mm), or about 10 to about 30 mils (about 0.25 to about 0.76 mm). When a solar cell module includes more than one encapsulant sheet, the thickness of each of the sheets is independently selected.

In addition, the encapsulant sheets may have a smooth or rough surface on one or both sides prior to lamination. In one solar cell module, the encapsulant sheet may have rough surfaces on both sides to facilitate de-airing during the lamination process. Rough surfaces can be created by mechanically embossing or by melt fracture during extrusion of the sheets followed by quenching so that surface roughness is retained during handling. The surface pattern can be applied to the sheet through common art-recognized processes. For example, the as-extruded sheet may be passed over a specially prepared surface of a die roll positioned in close proximity to the exit of the die which imparts the desired surface characteristics to one side of the molten polymer. Thus, when the surface of such a die roll has minute peaks and valleys, the polymer sheet cast thereon will have a rough surface on the side that is in contact with the roll, and the rough surface generally conforms respectively to the valleys and peaks of the roll surface. Such die rolls are described in, e.g., U.S. Patent No. 4,035,549 and U.S. Patent Publication No. 20030124296. Again, the surface pattern of the encapsulant sheets would disappear after the lamination process.

For example, the sheets comprising the polymer compositions may be formed through dipcoating, solution casting, compression molding, injection molding, lamination, melt extrusion casting, blown film, extrusion coating, tandem extrusion coating, or by any other procedures that are known to those of skill in the art. Preferably, the sheets are formed by an extrusion method, such as melt extrusion casting, melt coextrusion casting, melt extrusion coating, or tandem melt extrusion coating processes.

In those solar cell modules in which an encapsulant layer is positioned at the front, sun-facing side of the solar cell assembly, the encapsulant layer should be sufficiently transparent to permit efficient operation of the module. Suitable front encapsulant layers preferably have a haze of about 1.5% or less, or about 1% or less, as determined in accordance with ASTM D1003. Alternatively, suitable encapsulant layers may have a yellowness index (YI) of about 1.5 or less, or about 1 or less.

In addition to one or more solar cells, one or more thin glass sheets and one or more encapsulant sheets, the solar cell modules may further comprise additional films, rigid sheets, or other polymeric encapsulant sheets.

Suitable sheets or films for use as one of the outer protective layers include, without limitation, conventional glass sheets, plastic sheets, metal sheets, ceramic sheets, plastic films and metal films.

Suitable conventional glass sheets may have a thickness of about 2 mm or more and include not only window glass, plate glass, silicate glass, sheet glass, low iron glass, tempered glass, tempered CeO-free glass, and float glass, but also colored glass, specialty glass (such as those containing ingredients to control solar heating), coated glass (such as those sputtered with metals (e.g., silver or indium tin oxide) for solar control purposes), low E-glass, Toroglas® glass (Saint-Gobain N.A. Inc., Trumbauersville, PA), Solexia™ glass (PPG Industries, Pittsburgh, PA), Starphire® glass (PPG Industries) and Solite™ glass (Asahi Glass Co., Ltd. (Japan)).

Thin glass sheets may also be used herein, and refer to a glass sheet or film having a thickness of less than 2.0 mm, or about 1.9 mm or less, or about 1.8 mm or less, or about 1.7 mm or less, or about 1.6 mm or less, or about 1.5 mm or less, or about 1.2 mm or less, or about 1 mm or less, or about 0.8 mm or less, or about 0.1 to about 0.8 mm, or about 0.2 to about 0.7 mm, or about 0.2 to about 0.6 mm. They may be selected from any suitable types of glass sheets, such as block or rolled thin glass sheets. Some types of such thin glass sheets have been used as substrates for liquid crystal devices and are commercially available from, e.g., Praezisions Glas & Optik GmbH (Germany), Pilkington (Toledo, OH), Matsunami Glass Ind., Ltd. (Japan), Nippon Sheet Glass Company, Ltd. (Japan), Nippon Electric Glass Co., Ltd. (Japan), and Asahi Glass Co., Ltd. (Japan).

In general, glass sheets that are useful in the present invention include float glass, rolled glass or cast glass. Each of these types of glass can be optionally strengthened by tempering, heat treatment, chemical treatment or a combination thereof. Also, low iron glasses can find particular use for the "sunny side" of the solar cell module, which in this instance, is the first outer protective layer.

Suitable plastic sheets comprise materials such as polycarbonates, acrylics, polyacrylates, cyclic polyolefins (e.g., ethylene norbornene polymers), polystyrenes (preferably metallocene-catalyzed polystyrenes), polyamides, polyesters, fluoropolymers, polypropylenes, polyethylene copolymers with α-olefins, or combinations of two or more of these materials.

In certain instances, the combined thickness of the first and second outer protective layers can be less than about 3.2 mm.

When a non-transparent sheet, such as aluminum, steel or galvanized steel, or a ceramic plate is used, it is used in a back protective layer or back sheet that is positioned towards the rear, non-sun-facing side of the solar cell assembly.

Suitable plastic film layers include, without limitation, polymers such as polyesters (e.g., poly(ethylene terephthalate) and poly(ethylene naphthalate)), polycarbonates, polyolefins (e.g., polypropylene, polyethylene, and cyclic polyolefins), norbornene polymers, polystyrenes (e.g., syndiotactic polystyrene), styrene-acrylate copolymers, acrylonitrile-styrene copolymers, polysulfones (e.g., polyethersulfone, polysulfone, etc.), nylons, poly(urethanes), acrylics, cellulose acetates (e.g., cellulose acetate, cellulose triacetate, etc.), cellophanes, poly(vinyl chlorides) (e.g., poly(vinylidene chloride)), fluoropolymers (e.g., polyvinyl fluoride, polyvinylidene fluoride, polytetrafluoroethylene, ethylene-tetrafluoroethylene copolymers and the like) and combinations of two or more thereof. The plastic film may also be a bi-axially oriented polyester film (preferably poly(ethylene terephthalate) film) or a fluoropolymer film (e.g., Tedlar®, Tefzel®, and Teflon® films, from E. I. du Pont de Nemours and Company, Wilmington, DE (DuPont)). Further the films used herein may be in the form of a multi-layer film, such as a fluoropolymer/polyester/ fluoropolymer multilayer film (e.g., Tedlar®/PET/Tedlar® or TPT laminate film available from Isovolta AG., Austria or Madico, Woburn, MA).

When the solar cell assembly comprises thin film solar cells, the solar cell module also comprises a substrate or superstrate on which the thin film solar cells are deposited. Suitable substrates and superstrates are sheets and films that are described above as the outer protective layers, including the thin glass sheets. Suitable substrates and superstrates are also stable under the conditions under which the solar cells and solar cell assemblies are fabricated and operated. When thin film solar cells are used, the general structure will comprise, in any operative order (i.e., that allows the operation of the module as a solar cell module as described herein) a first outer protective layer having a first and a second side; an encapsulant layer comprising a polymer composition; a solar cell assembly having a light incident side, said light incident side facing the first outer protective layer; a second outer protective layer having a first and a second side, wherein said first side of said second outer protective layer is facing the solar cell assembly; and a metal support having a first side and a second side, said first side of said metal support attached to said second side of said second outer protective layer of the laminated layers of the solar cell module; wherein the polymer composition has a Young's modulus of less than or equal to about 600 MPa, as determined in accordance with ASTM D5026-06 at 30°C and 1 minute of load duration; and wherein said solar cell assembly is comprised of one or more thin film cells deposited on either the second side of said first outer protective layer or on the first side of said second outer protective layer.

The solar cell modules may further comprise other functional film or sheet layers embedded within the module. Such functional layers, such as, for example, dielectric layers or barrier layers, may comprise or may be derived from any of the polymeric films described above. In addition, the functional layers may be coated with additional functional coatings. For example, poly(ethylene terephthalate) films coated with a metal oxide coating, such as those described within U.S. Patent Nos. 6,521,825 and 6,818,819 and European Patent No. EP1182710, may function as oxygen and moisture barrier layers in the solar cell modules.

If desired, a layer of nonwoven glass fiber (scrim) may also be included between the solar cell layers and the encapsulants to facilitate deaeration during the lamination process and/or to serve as reinforcement for the encapsulants. The use of such scrim layers is described within, e.g., U.S. Patent Nos.

5,583,057; 6,075,202; 6,204,443; 6,320,115; and 6,323,416 and European Patent No. EP0769818.

If desired, one or both surfaces of the protective layers (i.e., the front and/or the back sheets), the encapsulant layers, and other layers incorporated within the solar cell module may be treated prior to the lamination process to enhance the adhesion to other laminate layers. This adhesion enhancing treatment may take any form known within the art and includes flame treatments (see, e.g., U.S. Patent Nos. 2,632,921; 2,648,097; 2,683,894; and 2,704,382), plasma treatments (see e.g., U.S. Patent No. 4,732,814), electron beam treatments, oxidation treatments, corona discharge treatments, chemical treatments, chromic acid treatments, hot air treatments, ozone treatments, ultraviolet light treatments, sand blast treatments, solvent treatments, and combinations of two or more thereof. Also, the adhesion strength may be further improved by further applying an adhesive or primer coating on the surface of the laminate layer(s). For example, U.S. Patent No. 4,865,711 describes a film or sheet with improved bondability, which has a thin layer of carbon deposited on one or both surfaces. Other exemplary adhesives or primers for use within the layers of the solar cell module may include silanes, poly(allyl amine) based primers (see e.g., U.S. Patent Nos. 5,411,845; 5,770,312; 5,690,994; and 5,698,329), and acrylic based primers (see e.g., U.S. Patent No. 5,415,942). The adhesive or primer coating may take the form of a monolayer of the adhesive or primer and have a thickness of about 0.0004 to about 1 mil (about 0.00001 to about 0.03 mm), or preferably, about 0.004 to about 0.5 mil (about 0.0001 to about 0.013 mm), or more preferably, about 0.004 to about 0.1 mil (about 0.0001 to about 0.003 mm).

In addition, when a polymeric film is incorporated as an outside surface layer of the solar cell module, the outside surface may be provided with an abrasion resistant hardcoat. Any material known for use in abrasion resistant hardcoats may be used. For example, the hardcoat may comprise polysiloxanes or cross-linked (thermosetting) polyurethanes. Also suitable are oligomeric-based coatings, such as those described in U.S. Patent Application Publication

No. 2005/0077002, which are prepared by the reaction of (A) a hydroxyl-containing oligomer with isocyanate-containing oligomer or (B) an anhydride-containing oligomer with epoxide-containing compound. In certain modules, the hardcoat may comprise a polysiloxane abrasion resistant coating, such as those described in U.S. Patent Nos. 4,177,315; 4,469,743; 5,415,942; and 5,763,089.

Any suitable lamination process may be used to prepare the solar cell modules. In one suitable process, the component layers of the solar cell module in sheet form are stacked in the desired order to form a pre-lamination assembly. The assembly is then placed into a bag capable of sustaining a vacuum ("a vacuum bag"), and the air is drawn out of the bag by a vacuum line or other means. The bag is sealed while the vacuum is maintained (e.g., at least about 27-28 in Hg (689-711 mm Hg)), and the sealed bag is placed in an autoclave and the pressure is raised to about 150 to about 250 psi (about 11.3 to about 18.8 bar), a temperature of about 130°C to about 180°C, or about 120°C to about 160°C, or about 135°C to about 155°C, or about 145°C to about 155°C, for about 10 to about 50 min, or about 20 to about 45 min, or about 20 to about 40 min, or about 25 to about 35 min. A vacuum ring may be substituted for the vacuum bag. One type of suitable vacuum bag is described within U.S. Patent No. 3,311,517. Following the heat and pressure cycle, the air in the autoclave is cooled without adding additional gas to maintain pressure in the autoclave. After about 20 min of cooling, the excess air pressure is vented and the laminates are removed from the autoclave.

Alternatively, the photovoltaic prelaminate assembly may be heated in an oven at about 80°C to about 120°C, or about 90°C to about 100°C, for about 20 to about 40 min, and thereafter, the heated assembly is passed through a set of nip rolls so that the air in the void spaces between the individual layers may be squeezed out, and the edge of the assembly sealed. The assembly at this stage is referred to as a pre-press.

The pre-press may then be placed in an air autoclave where the temperature is raised to about 120°C to about 160°C, or about 135°C to about 160°C, at a pressure of about 100 to about 300 psi (about 6.9 to about 20.7 bar), or preferably about 200 psi (13.8 bar). These conditions are maintained for about 15 to about 60 min, or about 20 to about 50 min, after which the air is cooled while no further air is introduced to the autoclave. After about 20 to about 40 min of cooling, the excess air pressure is vented and the laminated products are removed from the autoclave.

The solar cell modules may also be produced through non-autoclave processes. Suitable non-autoclave processes are described, e.g., in U.S. Patent Nos. 3,234,062; 3,852,136; 4,341,576; 4,385,951; 4,398,979; 5,536,347; 5,853,516; 6,342,116; and 5,415,909, U.S. Patent Publication No. 20040182493, European Patent No. EP1235683 B1, and PCT Patent Publication Nos. WO9101880 and WO03057478. Generally, the non-autoclave processes include heating the pre-lamination assembly and the application of vacuum, pressure or both. For example, the assembly may be successively passed through heating ovens and nip rolls.

In this connection, the encapsulant sheets are generally supplied as sheets having a substantially uniform thickness. When the encapsulant sheets are laid up with the solar cell assembly in the pre-press assembly, there may be gaps or voids in which portions of the solar cell assembly are not in contact with the encapsulant sheets. During the lamination process, however, the polymeric encapsulant sheets melt or soften to some degree. Under the pressure that is applied during the process, the encapsulant also flows around the surface peaks or contours of the solar cell assembly. Thus, any voids between the solar cell assembly and the encapsulant sheets are filled during the lamination process to provide solar cell modules in which the encapsulant is in good contact with the solar cell assembly.

If desired, the edges of the laminated solar cell module may be sealed to reduce moisture and air intrusion and potential degradative effects on the efficiency and lifetime of the solar cells. Suitable edge seal materials include, but are not limited to, butyl rubber, polysulfide, silicone, polyurethane, polypropylene elastomers, polystyrene elastomers, block elastomers, styrene-ethylene-butylene-styrene (SEBS), and the like.

Encapsulant sheets comprising the polymer composition may be formed by any suitable method, including without limitation dipcoating, solution casting, compression molding, injection molding, lamination, melt extrusion casting, blown film, extrusion coating, tandem extrusion coating, or by a combination of two or more of these methods. Preferably, the sheets are formed by an extrusion method, such as melt extrusion casting, melt coextrusion casting, melt extrusion coating, or tandem melt extrusion coating processes.

The following examples are provided to describe the invention in further detail. These examples, which set forth a preferred mode presently contemplated for carrying out the invention, are intended to illustrate and not to limit the invention.

EXAMPLES

Materials and Methods

"Resin A" was an ionomer of an ethylene acid copolymer comprising copolymerized repeat units of ethylene and about 21.7 wt% of copolymerized repeat units of methacrylic acid. Resin A was neutralized to a level of about 26% with a base having sodium cations as counterions. The melt index of the Resin A base resin was about 24 g/10 min, and that of Resin A was about 1.8 g/10 min. The polymers and additives were blended and extruded using a 28-mm twin-screw compounding extruder manufactured by Werner-Pfleiderer Corp. of Tamm, Germany. The extruded was equipped with a 6-mm single hole die and the melt strand was passed through a water bath for cooling and then cut into pellets using a Conair cutter.

1,4-Butane diol was obtained from the Aldrich Chemical Company, Inc. (Cat. No. B8, 480-7 99% purity), and added to the base resin in weight percent amounts of 1.0, 1.5 and 2.0 wt%.

When the adjuvants were used, they were added in amounts of between 0.025 and 0.1 weight percent (wt%). The examples included below used N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, and combinations thereof, and were added to the base resin in weight percent amounts of 0.025, 0.25 and 0.1 wt%.

The formed strand-cut pellets containing the blended polymer, hydroxyl-containing crosslinking agent, and optionally adjuvant, were dried and compression molded into plaques. Specimens were then punched out of the plaques and used for conducting tensile measurements.

These bars were index marked, weight added (where noted), then loaded and placed into an oven. Periodically, the oven was cooled, samples were removed and the “permanent” amount of elongation was measured. The samples were then placed back into the oven for additional exposure time, and the temperature was increased as noted.

Examples

Comparative Example A and Example 1

As described above, polymers were obtained, prepared and extruded to produce test specimens in the form of tensile strips. The tensile creep was measured according to ASTM D2990-09. The strips were then hung in an oven with a weight (82 g) attached to the bottom. As shown in Table 1 and **Figure 1**, the tensile strip of Comparative Example A, achieved an elongation of less than 400% before mechanical integrity was lost. The strip of Example 1, continued to elongate to at least 1400% over a period of greater than 500 hours, without a loss of mechanical integrity.

DSC traces were obtained according to ASTM D3418-08, using a Model DSC 821 differential scanning calorimeter available from Mettler Toledo, Inc., of Columbus, OH. The results are shown in **Figures 2 and 3**.

Table 1

	Time, hr	0	16	24	92	116	140	164	188	262	284	287	290	307	315	334
	Temp, deg C	23	70	75	75	78	80	80	80	82	82	84	89	89	89	89
<u>EXAMPLE</u> **<u>RESIN 'A' with 1.0 wt% 1,4-butanediol</u>**																
Elongation in mm																
Sample 1		5.0	7.0	8.0	8.0	9.0	11.0	11.0	11.5	14.5	14.5	14.5	26.0	33.0	35.0	41.0
Sample 2		5.0	7.5	8.5	9.5	10.5	12.0	12.5	12.5	15.0	15.5	16.0	29.0	37.0	38.0	44.0
Sample 3		5.0	8.0	8.0	9.0	10.5	12.0	12.5	12.5	15.0	16.0	16.0	29.5	38.0	39.0	45.0
Sample 4		5.0	7.0	8.0	9.0	9.5	11.0	11.5	12.5	15.0	15.0	15.0	29.0	37.5	39.0	43.0
Distance		10.0	15.5	16.5	18.5	21.0	24.0	25.0	25.0	30.0	31.5	32.0	58.5	75.0	77.0	89.0
Percent Elongation		0.0	55.0	65.0	85.0	110.0	140.0	150.0	150.0	200.0	215.0	220.0	485.0	650.0	670.0	790.0
<u>COMPARATIVE EXAMPLE</u> **<u>RESIN 'A" (control)</u>**																
Elongation in mm													Broke			
Sample CA1		5.0	7.0	8.0	9.0	11.0	14.0	14.5	15.0	20.5	21.0	21.0				
Sample CA2		5.0	8.0	9.0	10.0	12.0	14.5	16.0	16.5	22.5	24.5	24.5				
Sample CA3		5.0	7.0	8.5	9.5	11.0	14.0	15.0	15.5	21.0	23.0	23.0				
Sample CA4		5.0	7.0	8.0	9.0	10.0	13.0	14.0	14.5	20.0	21.0	21.0				
Distance		10.0	15.0	17.5	19.5	23.0	28.5	31.0	32.0	43.5	47.5	47.5	0.0			
Percent Elongation		0.0	50.0	75.0	95.0	130.0	185.0	210.0	220.0	335.0	375.0	375.0	5.0			

Comparative Example B and Examples 2-7

As described above, additives were added to Resin A (Comparative Example B) in the weight percent amounts indicated below in Table 2, and dog-bone plaques were formed. These plaques were die-cut using a punch and conformed to ASTM D638-10, Type V.

The tensile creep was measured according to ASTM D2990-09. Two indelible marks 10mm apart were put onto each plaque. The plaques were then suspended in an oven at the temperatures indicated in Table 3, below, and heated for the times indicated. No weight was applied to the bottom of the plaques. Table 3 shows the amount of elongation measured for each sample. These data show that the addition of 1,4-butanediol, N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, and 3-glycidoxypropyl trimethoxysilane positively enhanced the tensile creep properties of the control Resin A (C.E. B). This is also shown in **Figure 4**.

Table 2

	Resin Additives Compounded into Resin, weight percent		
Resin Identification	**1,4-Butanediol**	**N-(2-aminoethyl-3-aminopropyl) trimethoxysilane**	**3-Glycidoxypropyl trimethoxysilane**
Resin 'A', Comp. Ex. B	0	0	0
Resin 'B'	1	0	0
Resin 'C	0	0.025	0.025
Resin 'D'	1	0.025	0.025
Resin 'E'	0.05	0	0.1
Resin 'F'	0.05	0	0.25
Resin 'G'	0.1	0	0.25
Resin 'H'	0.25	0	0

Table 3

Test Conditions		Tensile Creep Index Mark Separation (mm)						
Total Time (hrs.)	**Oven Temp (°C)**	**Resin 'A' C.E. B**	**Resin 'B' Ex.2**	**Resin 'C' Ex.3**	**Resin 'D' Ex.4**	**Resin 'E' Ex.5**	**Resin 'F' Ex.6**	**Resin 'G' Ex.7**
0	23	10	10	10	10	10	10	10
18	95	21.43	10.2	14.76	10	13.15	12.22	11.27
42	95	57	10.29	19.35	10	15.53	12.81	11.43
113	95	Failed*	10.72	36.21	10	16.67	13.2	12.28
138	95		10.34	45.06	10	17.4	14	12.26
163	100		10.56	Failed*	10	36.76	17.48	14.43
186	100		10.37		9.76	Failed*	27.63	17.91
210	100		10.38		9.9		62.29	21.9
282	100		10.67		10		192.37	28.9
305	100		10.52		9.95		Failed*	29.77
451	100		10.68		9.94			35.47
474	100		10.89		9.98			38.75
499	100		10.94		9.85			37.85
546	100		10.73		9.92			39.59
620	100		10.51		10.05			42.1

***When the resin sample "failed", it elongated to the point of loss of mechanical integrity, therefore unable to support its own weight. .**

Comparative Example C and Example 8

The rheology of both the control Resin A (Comparative Example C) and Resin H (Example 8, Resin A + 0.25 wt% 1,4-butanediol) were measured. A Bohlin Instruments RH7 Advanced Capillary Rheometer, available from Bohlin Instruments of East Brunswick, NJ, was used to measure melt viscosity at 190 °C, 210 °C, and 230 °C and at various shear rates as shown in **Figure 5**. The data show that there was only a modest change (increase) in melt viscosity at these shear rates and temperatures. Therefore, cross-linked compositions are expected to be readily and easily processible by conventional melt processing methods (e.g., extrusion, blown-film, injection molding, etc.).

Additionally, die swell was measured for both Comparative Example C and Example 8. The measurement represents how much larger in diameter a strand swells as it came out of the rheometer at a given shear stress/flow rate/temperature. Comparative Example C had a die swell of 41%, and Example 8 had a die swell of 73%, which was an indication that the molecular weight distribution has been broadened and most likely some higher molecular weight material had been created in the latter.

As shown in Table 4, melt draw and tension were measured for both Comparative Example C and Example 8 on a Bohlin Instruments RH7 Advanced Capillary Rheometer at 190°C and a crosshead speed of 2.26 mm/min. The haul-off die had a diameter of 2mm, a length of 20 mm, and a 180 degree (flat) entry angle. The following data shows the maximum haul-off speed (M/min) and haul-off force (N) at maximum haul-off speed for Comparative Example C and Example 8:

Table 4

Resin	Max Haul-off Speed (M/min)	Haul-off Force (N)
Comp. Ex. C	300	0.07
Comp. Ex. C	281	0.07
Comp. Ex. C	247	0.06
Comp. Ex. C	179	0.07
Comp. Ex. C	243	0.07
Comp. Ex. C	243	0.07
Comp. Ex. C	281	0.06
Comp. Ex. C	242	0.06
Comp. Ex. C	282	0.06
Comp. Ex. C	282	0.06
Average	**258**	**0.065**

Resin	Max Haul-off Speed (M/min)	Haul-off Force (N)
Example 8	< 25	0.16
Example 8	< 25	0.24
Example 8	< 25	0.23
Example 8	< 25	0.22
Example 8	< 25	0.17
Example 8	< 25	0.24
Example 8	< 25	0.31
Example 8	< 25	0.30
Average	**< 25**	**0.234**

As can be seen in the data above, the melt tension for Example 8 was much higher than that of the Comparative Example C, although the maximum haul-off speed was reduced. Additionally, the melt tension at 10-25 meters/min for Comparative Example C was about 0.06 Newtons, and thus was fairly independent of draw speed. Also, the melt tension of Comparative Example C was much lower than the melt tension of Example 8, which was measured at 0.234 Newtons.

In summary, these Examples demonstrate that the cross-linking system described herein modifies the rheology, including the creep properties, of the acid copolymer resins and of their ionomers. The extrusion melt pressure and extruder torque necessary to process these compositions were not substantially affected by the crosslinking, however.

While certain of the preferred embodiments of this invention have been described and specifically exemplified above, it is not intended that the invention be limited to such embodiments. Various modifications may be made without departing from the scope and spirit of the invention, as set forth in the following claims.

CLAIMS

What is claimed is:

1. A photovoltaic prelaminate assembly, comprising one or more encapsulant layers, each encapsulant layer comprising:
   a polymer composition comprising
   an ethylene copolymer, said ethylene copolymer comprising copolymerized units of ethylene, about 5 to about 90 wt% of copolymerized units of a first α,β-unsaturated carboxylic acid having 3 to 10 carbon atoms; and optionally about 2 to about 40 wt% of copolymerized units of a derivative of a second α,β-unsaturated carboxylic acid having 3 to 10 carbon atoms; wherein the weight percentages of the copolymerized units are based on the total weight of the ethylene copolymer and the sum of the weight percentages of the copolymerized units is 100 wt%; and wherein optionally at least a portion of the carboxylic acid groups of the copolymerized units of the α,β-unsaturated carboxylic acid units are neutralized to form carboxylate salts;
   a hydroxyl-containing crosslinking agent; and optionally,
   an adjuvant.
2. A photovoltaic prelaminate assembly, comprising one or more encapsulant layers, each encapsulant layer comprising a product of cross-linking the polymer composition of Claim 1, wherein at least a portion of the carboxylic acid groups or carboxylate groups of the two or more ethylene copolymers are reacted with at least two of the hydroxyl groups of the hydroxyl-containing crosslinking agent, so that the hydroxyl-containing crosslinking agent forms a cross-link between two or more ethylene copolymer molecules.
3. The photovoltaic prelaminate assembly of Claim 1, wherein about 5% to about 90% of the total content of the carboxylic acid groups present in the ethylene copolymer have been neutralized to form carboxylate groups having counterions.

4. The photovoltaic prelaminate assembly of Claim 1, Claim 2 or Claim 3, wherein the ethylene copolymer comprises about 10 wt% to about 30 wt% of copolymerized units of the α,β-ethylenically unsaturated carboxylic acid.
5. The photovoltaic prelaminate assembly of Claim 4, wherein the α,β-ethylenically unsaturated carboxylic acid is selected from the group consisting of acrylic acids, methacrylic acids, and mixtures of two or more of an acrylic acid and a methacrylic acid.
6. The photovoltaic prelaminate assembly of Claim 1, Claim 2 Claim 3, wherein the hydroxyl-containing crosslinking agent comprises a diol.
7. The photovoltaic prelaminate assembly of Claim 6, wherein the hydroxyl-containing crosslinking agent comprises 1,4-butanediol.
8. The photovoltaic prelaminate assembly of Claim 1, Claim 2 or Claim 3, wherein the adjuvant comprises a silane selected from the group consisting of N-(2-aminoethyl-3-aminopropyl) trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, and combinations thereof, in amounts of between about 0.025 and 2.0 wt%.
9. The photovoltaic prelaminate assembly of Claim 3, wherein the counter ion is sodium or zinc.
10. The photovoltaic prelaminate assembly of Claim 1, Claim 2 or Claim 3, wherein the one or more encapsulant layers exhibit an elongation of at least 10%, as determined by ASTM D2990-09.
11. A photovoltaic module comprising the photovoltaic prelaminate assembly of Claim 1, Claim 2, or Claim 3.

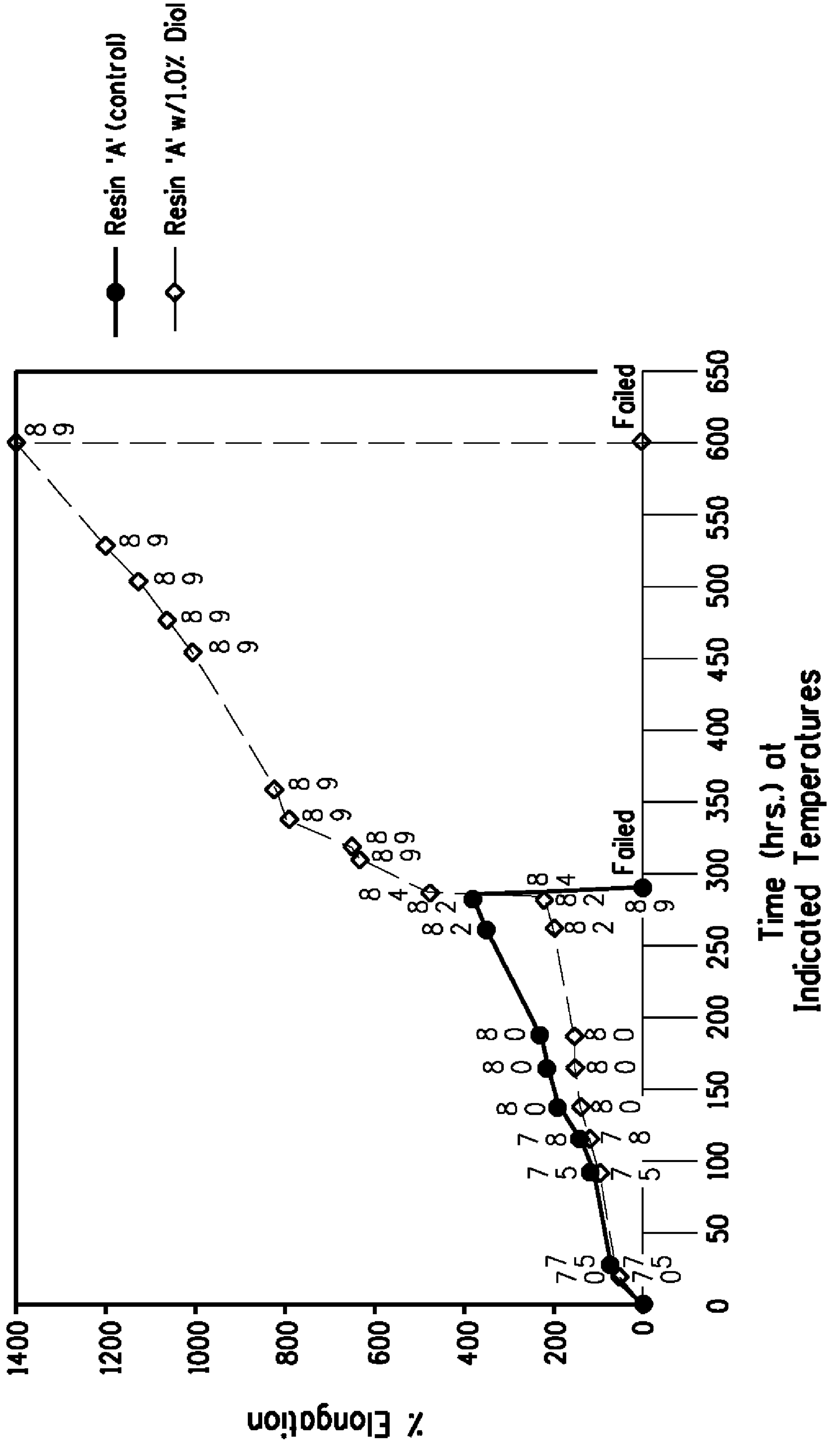
Resin 'A' (control)
Resin 'A' w/1.0% Diol
% Elongation
0
200
400
600
800
1000
1200
1400
0
50
100
150
200
250
300
350
400
450
500
550
600
650
Failed
Failed
Time (hrs.) at Indicated Temperatures

FIG. 1

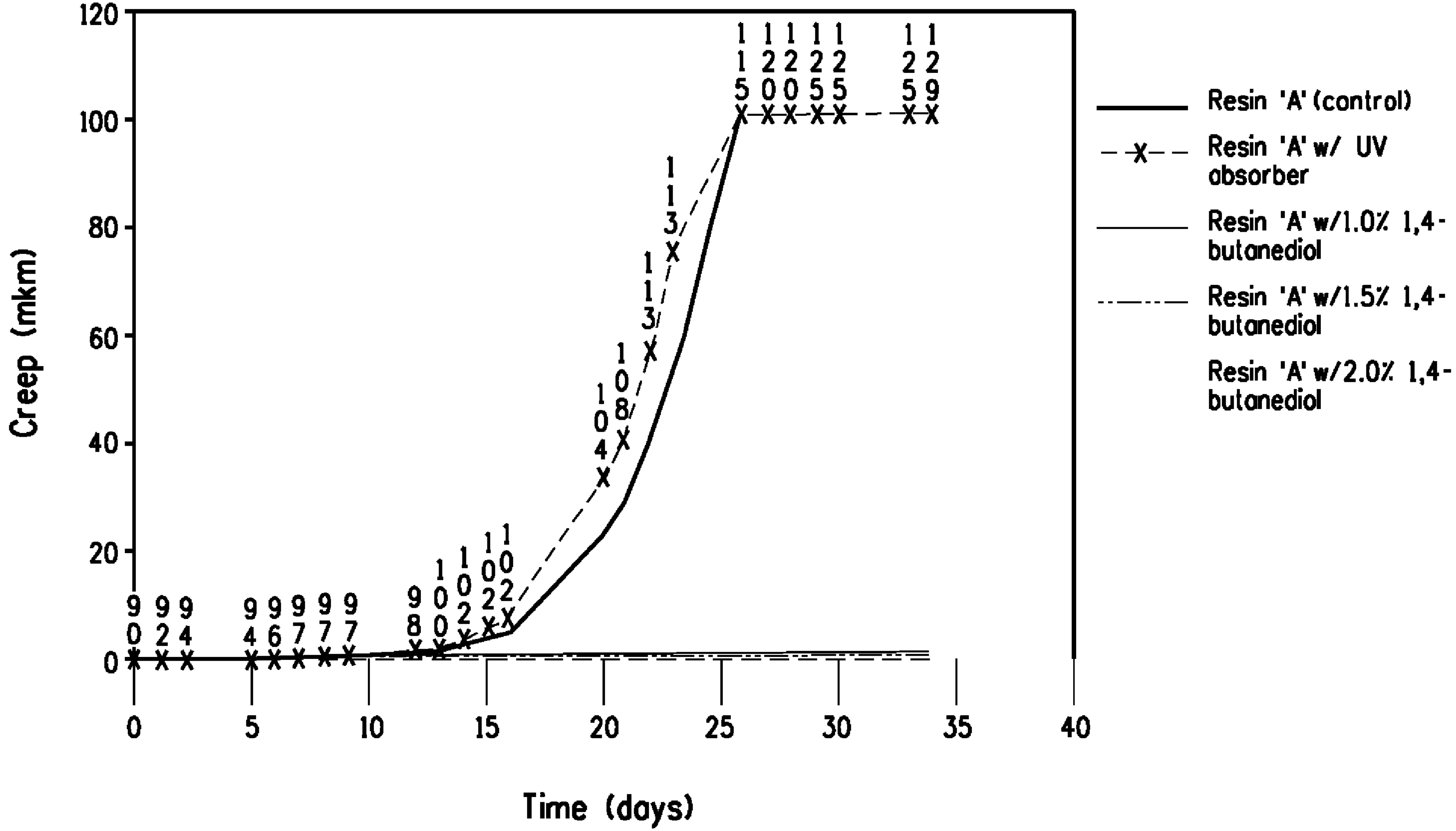
Creep (mkm)
120
100
80
60
40
20
0
Time (days)
0
5
10
15
20
25
30
35
40
90
92
94
94
96
97
97
97
98
100
102
102
102
104
108
113
113
115
120
120
125
125
125
129
Resin 'A' (control)
Resin 'A' w/ UV absorber
Resin 'A' w/1.0% 1,4-butanediol
Resin 'A' w/1.5% 1,4-butanediol
Resin 'A' w/2.0% 1,4-butanediol

FIG. 2

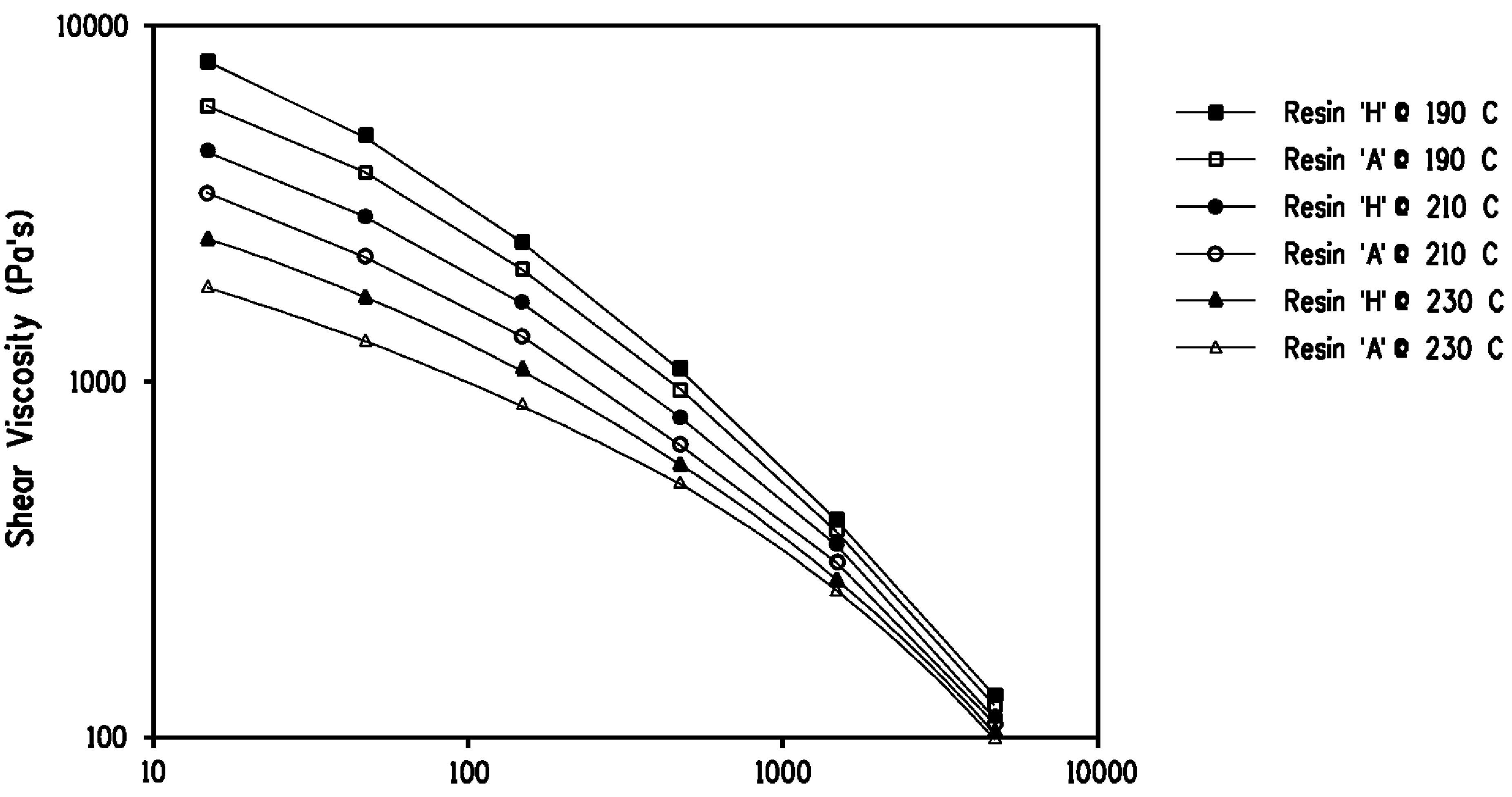
Shear Viscosity (Pa's)
10000
1000
100
10
100
1000
10000
Shear Rate (1/s)
Resin 'H' @ 190 C
Resin 'A' @ 190 C
Resin 'H' @ 210 C
Resin 'A' @ 210 C
Resin 'H' @ 230 C
Resin 'A' @ 230 C

FIG. 3

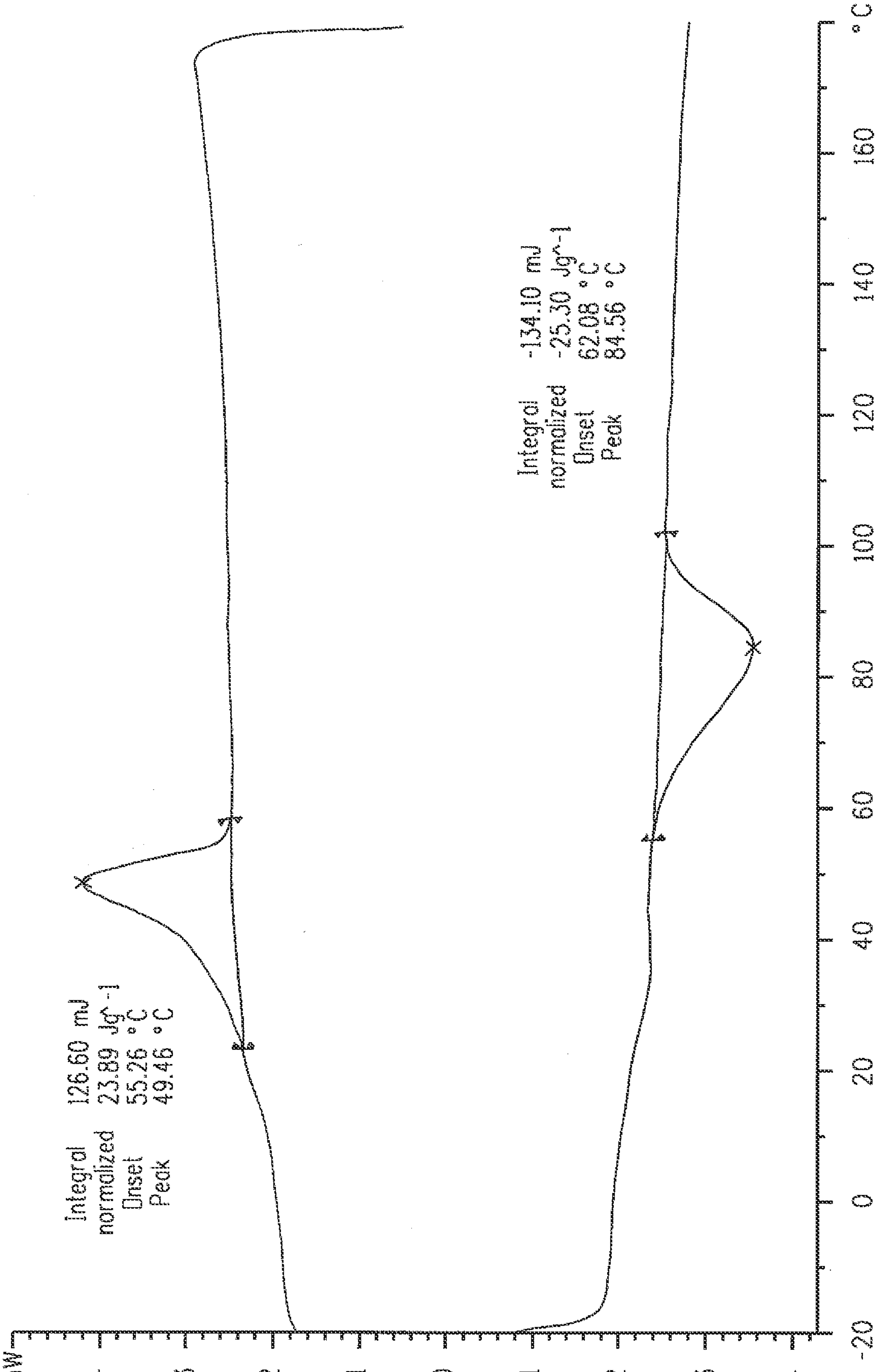
mW
4
3
2
1
0
-1
-2
-3
-4
-20
0
20
40
60
80
100
120
140
160
°C
Integral 126.60 mJ
normalized 23.89 Jg^-1
Onset 55.26 °C
Peak 49.46 °C
Integral -134.10 mJ
normalized -25.30 Jg^-1
Onset 62.08 °C
Peak 84.56 °C

FIG. 4

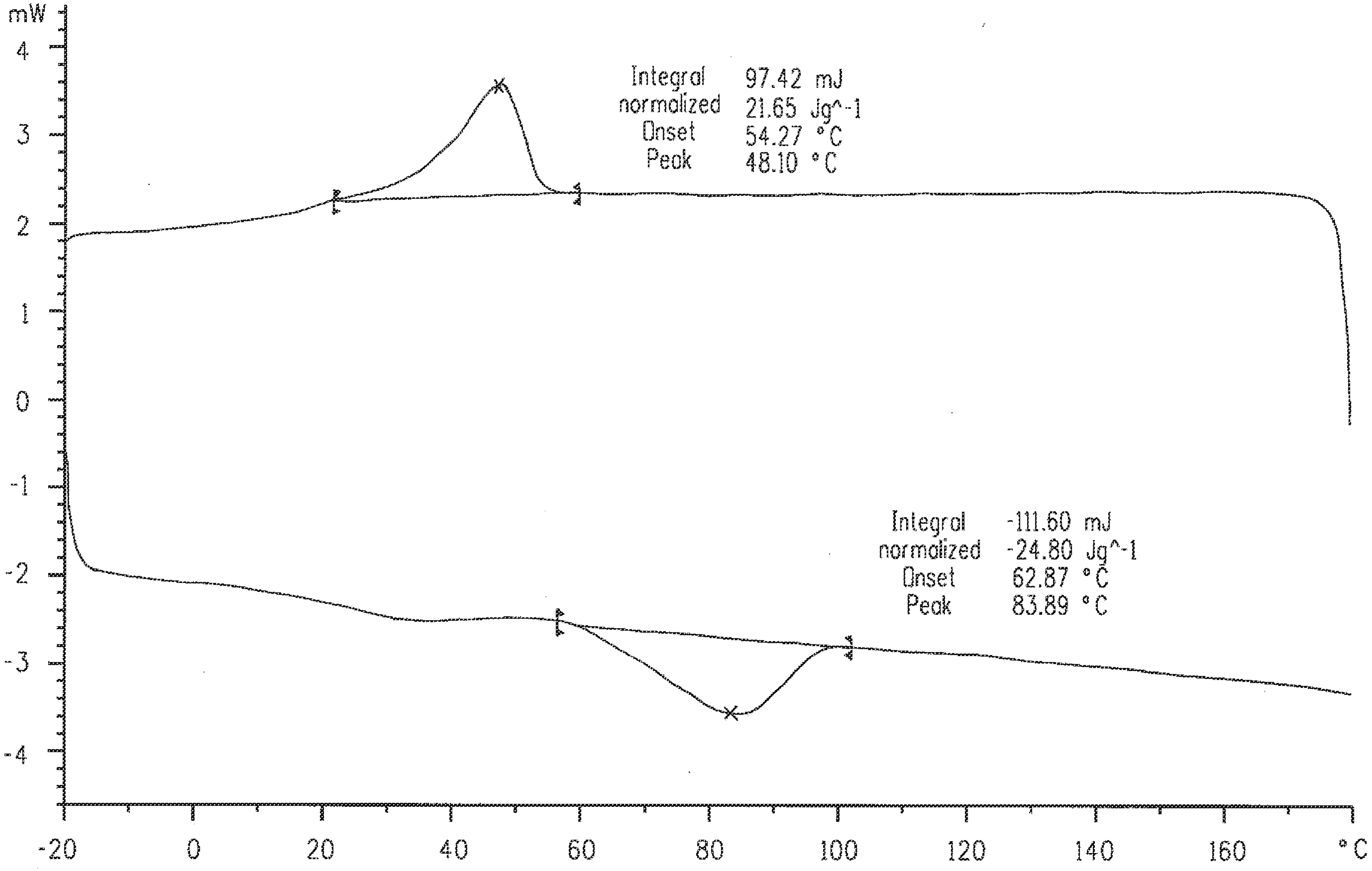
mW
4
3
2
1
0
-1
-2
-3
-4
Integral 97.42 mJ
normalized 21.65 Jg^-1
Onset 54.27 °C
Peak 48.10 °C
Integral -111.60 mJ
normalized -24.80 Jg^-1
Onset 62.87 °C
Peak 83.89 °C
-20
0
20
40
60
80
100
120
140
160
°C

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/076323

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D123/08 H01L51/44
ADD.

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)
C09D H01L C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 395 895 A (TAGOSHI HIROTAKA [JP] ET AL) 7 March 1995 (1995-03-07) examples 1,2; tables 2-5 -----	1-11
Y	US 2010/108125 A1 (HAYES RICHARD ALLEN [US] ET AL) 6 May 2010 (2010-05-06) examples 1,2; tables 2-5 -----	1-11
X	JP 2001 326374 A (DAINIPPON PRINTING CO LTD) 22 November 2001 (2001-11-22) abstract -----	1-4,6,11
A	EP 0 246 329 A1 (SHOWA DENKO KK [JP]) 25 November 1987 (1987-11-25) examples 1-4 -----	1-11
Y	GB 1 337 052 A (GULF RESEARCH DEVELOPMENT CO) 14 November 1973 (1973-11-14) page 1, lines 63-72; claim 1 -----	1-11

☐ 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 7 April 2014	Date of mailing of the international search report 14/04/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schmidt, Helmut

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/076323

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5395895 A	07-03-1995	CA 2098565 A1	06-05-1993
		JP 3329458 B2	30-09-2002
		US 5395895 A	07-03-1995
		WO 9309179 A1	13-05-1993
US 2010108125 A1	06-05-2010	CN 102047442 A	04-05-2011
		EP 2286465 A2	23-02-2011
		JP 2011522442 A	28-07-2011
		KR 20110037987 A	13-04-2011
		US 2010108125 A1	06-05-2010
		WO 2009149000 A2	10-12-2009
JP 2001326374 A	22-11-2001	JP 4480106 B2	16-06-2010
		JP 2001326374 A	22-11-2001
EP 0246329 A1	25-11-1987	EP 0246329 A1	25-11-1987
		WO 8702977 A1	21-05-1987
GB 1337052 A	14-11-1973	CA 944500 A1	26-03-1974
		DE 2148122 A1	06-04-1972
		FR 2108620 A5	19-05-1972
		GB 1337052 A	14-11-1973
		NL 7113458 A	05-04-1972