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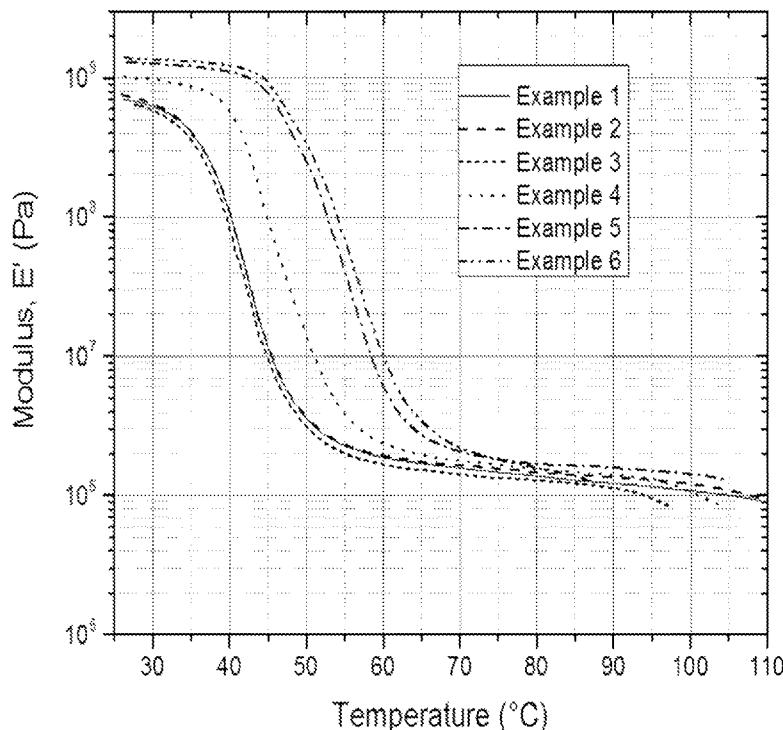
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[Continued on next page]

(54) Title: MULTILAYER INTERLAYERS HAVING HIGH TG AND HIGH MODULUS



(57) Abstract: A multilayer interlayer structure having a low M_w /high T_g layer and a high M_w layer, the interlayer having a high E' modulus and a higher T_g . The high T_g layer has a T_g of at least 50 $^{\circ}\text{C}$ and a weight average molecular weight of not more than 160,000. The high M_w layer has a molecular weight greater than 160,000. The interlayer structure has increased stiffness without having to increase its thickness, and has an increased T_g to enable the structure to be used in applications that require good modulus at outdoor temperatures.

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MULTILAYER INTERLAYERS HAVING HIGH Tg AND HIGH MODULUS

1. FIELD OF THE INVENTION

[0001] The present invention relates to multilayer poly(vinyl acetal) interlayers, and more particularly to multilayer poly(vinyl acetal) interlayers having a high glass transition temperature and that are more rigid at higher temperatures. The multilayer poly(vinyl acetal) interlayers having a higher glass transition temperature and higher rigidity can be used as an interlayer for laminated glass in more demanding structural applications that experience higher ambient temperature conditions.

2. BACKGROUND OF THE INVENTION

[0002] Generally, laminated multiple layer glass panels refer to a laminate comprised of a polymer sheet or interlayer sandwiched between two panes of glass. The laminated multiple layer glass panels are commonly utilized in architectural window applications, in the windows of motor vehicles, airplanes, trains and other modes of transporting people and goods, and in photovoltaic solar panels. The first two applications are commonly referred to as laminated safety glass. The main function of the interlayer in the laminated safety glass is to absorb energy resulting from impact or force applied to the glass, keep the layers of glass bonded even when the force is applied and the glass is broken, and prevent the glass from breaking up into sharp pieces. Additionally, the interlayer generally gives the glass a much higher sound insulation rating, reduces UV and/or IR light transmission, and enhances the aesthetic appeal of the associated window. In regards to the photovoltaic applications, the main function of the interlayer is to encapsulate the photovoltaic solar panels which are used to generate and supply electricity in commercial and residential applications.

[0003] The interlayer is generally produced by mixing a polymer resin such as poly(vinyl acetal) with one or more plasticizers and melt blending or melt

processing the mix into a sheet by any applicable process or method known to one of skill in the art, including, but not limited to, extrusion. Other additional additives may optionally be added for various other purposes. After the interlayer sheet is formed, it is typically collected and rolled for 5 transportation and storage and for later use in the multiple layer glass panels, as described below. Interlayer sheets of the appropriate size and thickness are sometimes cut, stacked and shipped in such stacks for later use in the multiple layer glass panels.

[0004] The following offers a simplified description of the manner in which 10 multiple layer glass panels are generally produced in combination with the interlayers. First, at least one interlayer sheet, either monolithic or comprising several coextruded or prelaminated layers (“multilayer interlayers”), is placed between two substrates, such as glass panels, and any excess interlayer is trimmed from the edges, creating an assembly. It is not uncommon for 15 multiple monolithic interlayer sheets to be placed within the two substrates creating a multiple layer glass panel with multiple monolithic interlayers. It is also not uncommon for multilayer interlayer sheets that comprise several coextruded or prelaminated layers, or multilayer interlayer sheets in combination with monolithic interlayer sheets to be placed within the two substrates creating a multiple layer glass panel with multilayer interlayers. 20 Then, air is removed from the assembly by an applicable process or method known to one of skill in the art; e.g., through nip rollers, vacuum bag, vacuum ring, vacuum laminator, or another de-airing mechanism. Additionally, the interlayer is partially press-bonded to the substrates by any method known to 25 one of ordinary skill in the art. In a last step, in order to form a final unitary structure, this preliminary bonding is rendered more permanent by a high temperature and pressure lamination process known to one of ordinary skill in the art such as, but not limited to, autoclaving.

[0005] A structural poly(vinyl acetal) interlayer, Saflex™ DG41 (a poly(vinyl 30 butyral) polymer (“DG41”) having a weight average molecular weight (M_w) of

about 170,000), is commercially available for applications in the architectural space. While the glass transition temperature ("Tg") of DG41 is suitable for many architectural applications (~46°C), it would be desirable to raise the Tg of the interlayer to take advantage of a full range of applications it could have 5 in the architectural space. Higher Tg products are desirable as they may be suitable for more demanding architectural applications that are exposed to consistently higher temperatures, especially those that require high modulus at higher ambient temperatures.

[0006] One methodology to increase the Tg of the poly(vinyl acetal) 10 interlayer is to reduce the amount of plasticizer in the poly(vinyl acetal) resin. Reducing the amount of plasticizer, however, decreases the flowability of the polymer composition making processing quite difficult. DG41 is already difficult to process in extrusion compared to other more highly plasticized polymers owing to its lower level of plasticizer level of about 20 parts of 15 plasticizer per hundred parts resin. The low plasticizer level in DG41 decreases its flowability, resulting in reduction in melt flowability and manifests itself as a large pressure drop between the head of the extruder or the melt pump to the back face of the die plate with a corresponding drop in extruder output or capacity. Although the processing of DG41 is difficult, it 20 remains at an acceptable level. However, attempting to increase the Tg of the poly(vinyl acetal) interlayer by further dropping the amount of plasticizer may so decrease the flowability of the polymer composition so as to make its processing unacceptable.

[0007] Increasing the plasticizer level assists in improving the polymer 25 flowability, thereby facilitating processing in the extruder manifesting itself as a lower pressure between the extruder head or melt pump to the back face of the die. However, increasing the plasticizer level also decreases the Tg of the interlayer.

[0008] It would be desirable to provide a poly(vinyl acetal) thermoplastic 30 resin that has both an enhanced Tg and high E' modulus (which is a measure

of the layer's stiffness or rigidity), and that has good flowability. The increase in Tg cannot be accomplished by a mere drop in the amount of plasticizer since, as already mentioned, the processing conditions suffer through large pressure drops resulting in a loss in output capacity. It would also be desirable 5 to provide the flexibility of not having to increase the thickness of the layers in order to achieve a higher interlayer rigidity.

3. SUMMARY OF THE INVENTION

[0009] The inventors have discovered a multilayer interlayer that has 10 elevated Tg and higher E' modulus, with the flexibility if desired of maintaining the same thickness of the multilayer interlayer. The composition has a high melt flow index, thereby providing a composition that is more flowable.

[0010] There is now provided a multilayer interlayer structure comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a 15 weight average molecular weight (M_w) greater than 160,000; and
(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a glass transition temperature (Tg) of at least 46°C. The high glass transition temperature (Tg) layer desirably has a melt flow index of at least 0.65 20 grams/10 minutes when measured at 190°C and under a load of 2.16 kilograms

[0011] Also provided is a multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a 25 weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C; and

(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal)

resin, wherein the high Tg layer has a glass transition temperature (Tg) of at least 46°C.

[0012] Also provided is a multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C;

(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin, wherein the high Tg layer has a glass transition temperature (Tg) of at least 46°C; and

(C) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C,

wherein the high Tg layer is disposed between the high M_w layers.

4. BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is an illustration of a glass panel containing a multilayer interlayer.

[0014] FIG. 2 is an illustration of an extrusion device for extruding compositions useful to make interlayer sheets.

[0015] FIG. 3 is a graph showing the rigidity of the interlayers as determined by modulus for a variety of poly(vinyl acetal) resins having different glass transition temperature (Tg) values, some of which are high glass transition temperature (Tg) core layers.

5. DETAILED DESCRIPTION OF THE INVENTION

[0016] The term “multilayer interlayer” is at least two layers of poly(vinyl acetal) resin. The multiple layers may be separately extruded layers, co-extruded layers, or any combination of separately and co-extruded layers. Thus the multilayered interlayer could comprise, for example: two or more 5 single-layer interlayers combined together (“plural-layer interlayer”); two or more layers co-extruded together (“co-extruded interlayer”); two or more co-extruded interlayers combined together; a combination of at least one single-layer interlayer and at least one co-extruded interlayer; and a combination of at least one plural-layer interlayer and at least one co-extruded interlayer.

10 **[0017]** A multilayered interlayer comprises at least two polymer layers (e.g., a single layer or multiple layers co-extruded) disposed in direct or indirect contact with each other, desirably in direct contact with each other, wherein each layer comprises a polymer resin, as detailed more fully below. When three or more layers are employed, at least three of the layers can be 15 referred to as skin layers and one or more one or more core layers. As used herein, “skin layer” generally refers to outer layers of the interlayer and “one or more core layers” generally refers to one or more of the inner layer(s) disposed between the skin layers. At least one side of a one or more core layers can be in direct contact with at least one side of a skin layers or may be 20 indirect contact with a skin layers, such as through a polymer layer. Thus, one exemplary multilayer embodiment would be: high M_w /high Tg/high M_w (e.g. a skin layer/core layer/skin layer), or a high M_w /high Tg (e.g. skin/core), high M_w /high Tg/high M_w /polymer film (e.g. skin/core/skin/polymer), or high M_w /high Tg/high Tg/high M_w (e.g. skin/core/core/skin), or high M_w /high Tg/high 25 Tg/high M_w /polymer (e.g. skin/core/core/skin/polymer), or a high M_w /high Tg/high M_w /high Tg/high M_w . The multilayer interlayer can also have more than three layers (e.g., 4, 5, 6, or up to 10 or more individual layers, so long as at least one of the layers is a high M_w layer and one is a high Tg layer). The multilayer interlayer can contain two, three, four, or more of the high M_w 30 layers, and two or more of them can be in direct contact with each other or

with a high Tg layer or with other types of layers. The multilayer interlayer can contain two, three, four, or more high Tg layers, and two or more of them can be in direct contact with each other or with the high M_w layer or with other types of layers. Desirably, in the multilayer interlayer structure having at least 5 three layers, at least one of the high Tg layers is disposed between two high M_w layers, or put another way, forms one or more core layers. By disposed is meant its location and the layer does not necessarily have to be in direct contact with the reference layers. Desirably, in a multilayer interlayer structure having at least 3 layers, the multilayer has at least 2 outer layers 10 having a high M_w resin, or put another way, forms one or more skin layers.

[0018] There is now provided a multilayer interlayer structure comprising:

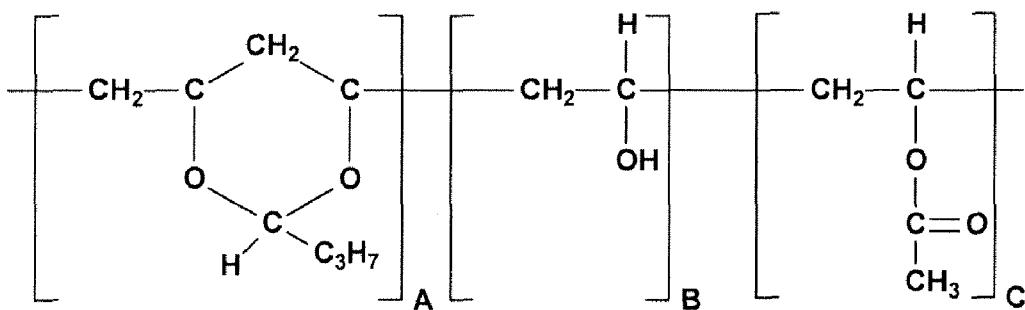
(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000; and 15 (B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a glass transition temperature (Tg) of at least 46°C.

[0019] The poly(vinyl acetal) resin in both the high M_w and high Tg layers is a thermoplastic resin, but the poly(vinyl acetal) resin in the high M_w layer and high Tg layer may be different types of poly(vinyl acetal) resin or have 20 different properties, as further described below. Their method of manufacture is not limited. The poly(vinyl acetal) resin can be produced by known aqueous or solvent acetalization processes, such as by reacting PVOH with an aldehyde such as butyraldehyde in the presence of an acid catalyst, separation, stabilization, and drying of the resin. Such acetalization processes are disclosed, for example, in U.S. Pat. Nos. 2,282,057 and 2,282,026 and Vinyl Acetal Polymers, in Encyclopedia of Polymer Science & Technology, 3rd edition, Volume 8, pages 381-399 (2003), the entire disclosures of which are incorporated herein by reference.

[0020] Poly(vinyl acetal) resins typically have a residual hydroxyl content, 30 an ester content, and an acetal content. As used herein, residual hydroxyl

content (calculated as PVOH) refers to the weight percent of moieties having a hydroxyl group remaining on the polymer chains. For example, poly(vinyl acetal) can be manufactured by hydrolyzing poly(vinyl acetate) to PVOH, and then reacting the PVOH with an aldehyde, such as butyraldehyde, 5 propionaldehyde, and the like, and desirably butyraldehyde, to make a polymer having repeating vinyl butyral units. In the process of hydrolyzing the poly(vinyl acetate), typically not all of the acetate side groups are converted to hydroxyl groups. Further, reaction with butyraldehyde typically will not result in the conversion of all hydroxyl groups on the PVOH to acetal groups. 10 Consequently, in any finished poly(vinyl butyral), there typically will be residual ester groups such as acetate groups (as vinyl acetate groups) and residual hydroxyl groups (as vinyl hydroxyl groups) as side groups on the polymer chain and acetal (e.g. butyral) groups (as vinyl acetal groups). As used herein, residual hydroxyl content is measured on a weight percent basis 15 per ASTM 1396.

[0021] An example of a polyvinyl butyral structure is used to further illustrate how the weight percentages are based from the moiety unit to which is bonded the relevant pendant group:



20 **[0022]** Taking the above structure of a polyvinyl butyral, the butyral or acetal content is based on the weight percentage of the unit A in the polymer, and OH content is based on the weight percentage of the unit B in the polymer (a polyvinyl OH moiety or PVOH), and the acetate or ester content is based on the weight percentage of unit C in the polymer.

[0023] Notably, for a given type of plasticizer, the compatibility of the plasticizer in the polymer is largely determined by the hydroxyl content of the polymer. Polymers with greater residual hydroxyl content are typically correlated with reduced plasticizer compatibility or capacity, typically due to 5 the hydrophobicity of the plasticizer being more compatible with fewer hydrophilic groups present on the polymer chain. Conversely, polymers with a lower residual hydroxyl content typically will result in increased plasticizer compatibility or capacity. Generally, this correlation between the residual hydroxyl content of a polymer and plasticizer compatibility/capacity can be 10 manipulated and exploited to allow for addition of the proper amount of plasticizer to the polymer resin and to stably maintain differences in plasticizer content between multiple interlayers.

[0024] The hydroxyl group content of the poly(vinyl acetal) resin used to make the composition or a layer is not particularly limited, but suitable 15 amounts are from at least about 6, or at least about 8, or at least about 10, or at least about 11, or at least about 12, or at least about 13, or at least about 14, or at least about 15, or at least about 16, or at least about 17, and in each case up to about 35 wt.% PVOH. For example, suitable weight percent (wt.%) hydroxyl groups ranges calculated as PVOH include about 6 to 35, or 6 20 to 30, or 6 to 25, or 6 to 23, or 6 to 20, or 6 to 18, or 6 to 17, or 6 to 16, or 6 to 15, or 7 to 35, or 7 to 30, or 7 to 25, or 7 to 23, or 7 to 20, or 7 to 18, or 7 to 17, or 7 to 16, or 7 to 15, or 8 to 35, or 8 to 30, or 8 to 25, or 8 to 23, or 8 to 20, or 8 to 18, or 8 to 17, or 8 to 16, or 8 to 15, or 9 to 35, or 9 to 30, or 9 to 25, or 9 to 23, or 9 to 20, or 9 to 18, or 9 to 17, or 9 to 16, or 9 to 15, or 10 to 25, or 10 to 30, or 10 to 25, or 10 to 23, or 10 to 20, or 10 to 18, or 10 to 17, or 10 to 16, or 10 to 15, or 11 to 35, or 11 to 30, or 11 to 25, or 11 to 23, or 11 to 20, or 11 to 18, or 11 to 17, or 11 to 16, or 11 to 15, or 12 to 35, or 12 to 30, or 12 to 25, or 12 to 23, or 12 to 20, or 12 to 18, or 12 to 17, or 12 to 16, or 12 to 15, or 13 to 35, or 13 to 30, or 13 to 25, or 13 to 23, or 13 to 20, or 13 to 18, or 13 to 17, or 13 to 16, or 13 to 15, or 14 to 35, or 14 to 30, or 14 to 25, or 14 to 30

23, or 14 to 20, or 14 to 18, or 14 to 17, or 14 to 16, or 14 to 15, or 15 to 35, or 15 to 30, or 15 to 25, or 15 to 23, or 15 to 20, or 15 to 18, or 15 to 17, or 15 to 16, or 16 to 35, or 16 to 30, or 16 to 25, or 16 to 23, or 16 to 20, or 16 to 18, or 16 to 17, or 17 to 35, or 17 to 30, or 17 to 25, or 17 to 23, or 17 to 20, or 17 to 5 18. If desired, the hydroxyl number chosen can be on the lower end of the ranges. In general, a poly(vinyl acetal) polymer having a lower hydroxyl number has the capability of absorbing more plasticizer and absorbing it more efficiently.

[0025] The poly(vinyl acetal) resin used to make the composition or sheet 10 can also comprise 20 wt.% or less, or 17 wt.% or less, or 15 wt.% or less of residual ester groups, including 13 wt.% or less, or 11 wt.% or less, or 9 wt.% or less, or 7 wt.% or less, or 5 wt.% or less, or 4 wt.% or less residual ester groups calculated as polyvinyl ester, *e.g.*, acetate, with the balance being an 15 acetal, preferably butyraldehyde acetal, but optionally including other acetal groups in a minor amount, for example, a 2-ethyl hexanal group (see, for example, U.S. Patent No. 5,137,954, the entire disclosure of which is incorporated herein by reference). Suitable ranges of residual ester groups by wt.% include 0 to 20, or 0 to 17, or 0 to 15, or 0 to 13, or 0 to 11, or 0 to 9, or 0 to 7, or 0 to 5, or 0 to 4, or 0 to 20, or 0 to 17, or 0 to 15, or 0 to 13, or 0 20 to 11, or 0 to 9, or 0 to 7, or 0 to 5, or 0 to 4, or 1 to 20, or 1 to 17, or 1 to 15, or 1 to 13, or 1 to 11, or 1 to 9, or 1 to 7, or 1 to 5, or 1 to 4, or 1 to 20, or 1 to 17, or 1 to 15, or 1 to 13, or 1 to 11, or 1 to 9, or 1 to 7, or 1 to 5, or 1 to 4, or 2 to 20, or 2 to 17, or 2 to 15, or 2 to 13, or 2 to 11, or 2 to 9, or 2 to 7, or 2 to 5, or 2 to 4, or 3 to 20, or 3 to 17, or 3 to 15, or 3 to 13, or 3 to 11, or 3 to 9, or 25 3 to 7, or 3 to 5, or 3 to 4, or 3 to 20, or 3 to 17, or 3 to 15, or 3 to 13, or 3 to 11, or 3 to 9, or 3 to 7, or 3 to 5, or 3 to 4, or 4 to 20, or 4 to 17, or 4 to 15, or 4 to 13, or 4 to 11, or 4 to 9, or 4 to 7, or 4 to 5, or 6 to 20, or 6 to 17, or 6 to 15, or 6 to 13, or 6 to 11, or 6 to 9. As with the residual hydroxyl group measurement, the weight percent of residual ester groups (*e.g.* acetate) is

based on the moiety in the polymer backbone onto which is linked the acetate group, including the pendant acetate group.

[0026] The poly(vinyl acetal) resin used in the invention can also have an acetal content of at least 50 wt.%, or at least 55 wt.%, or at least 60 wt.%, or at least 65 wt.%, or at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, and in each case up to 94 wt.%. Suitable ranges include 50 to 94, or 50 to 93, or 50 to 92, or 50 to 91, or 50 to 90, or 50 to 89, or 50 to 88, or 50 to 86, or 50 to 85, or 55 to 94, or 55 to 93, or 55 to 92, or 55 to 91, or 55 to 90, or 55 to 89, or 55 to 88, or 55 to 86, or 55 to 85, or 60 to 94, or 60 to 93, or 60 to 92, or 60 to 91, or 60 to 90, or 60 to 89, or 60 to 88, or 60 to 86, or 60 to 85, or 65 to 94, or 65 to 93, or 65 to 92, or 65 to 91, or 65 to 90, or 65 to 89, or 65 to 88, or 65 to 86, or 65 to 85, or 70 to 94, or 70 to 93, or 70 to 92, or 70 to 91, or 70 to 90, or 70 to 89, or 70 to 88, or 70 to 86, or 70 to 85, or 75 to 94, or 75 to 93, or 75 to 92, or 75 to 91, or 75 to 90, or 75 to 89, or 75 to 88, or 75 to 86, or 75 to 85, 80 to 94, or 80 to 93, or 80 to 92, or 80 to 91, or 80 to 90, or 89 to 89, or 80 to 88, or 80 to 86, or 80 to 85, 85 to 94, or 85 to 93, or 85 to 92, or 85 to 91, or 85 to 90, or 85 to 89, or 85 to 88, or 85 to 86, or 90 to 94, or 90 to 93, or 90 to 92.

[0027] The combination of OH, ester, and acetal ranges is not particularly limited. Some of the range combinations can be those corresponding to the checked boxes in Table 1 below.

TABLE 1

OH wt.%	Ester wt%														
	0- 20	20	1-	2-	2-	2-	2-8	2-6	3-	3-	3-	3-9	4-	4-	4-
6-25	X	X		X	X	X	X	X	X	X	X	X	X	X	X
7-25	X	X		X		X	X				X	X	X	X	X
8-25	X	X		X							X			X	X
9-25	X	X		X											
10-25	X	X		X											

6-23		X	X	X	X	X	X	X	X	X	X	X	X	X	X
8-23		X		X							x		X	X	
9-23		X		X											
6-20		X	X	X	X	X	X	X	X	X	X	X	X	X	X
8-20		X		X							x		X	X	
9-20		X		X											
10-20		X		X											
6-18		X	X	X	X	X	X	X	X	X	X	X	X	X	X
9-18		X		X											
10-18		X		X											
6-15		X	X	X	X	X	X	X	X	X	X	X	X	X	X
8-15		X		X							X		X	X	
10-15		X		X											
Acetal	50-	65-	70-	70-	90-	70-	75-	65-	70-	75-	65-	75-	70-	75-	
Wt.%	94	89	92	88	92	91	91	91	91	91	89	89	88	88	

[0028] The acetal groups can be vinyl propynal groups, vinyl butyral groups, and the like, and are desirably vinyl butyral groups.

[0029] The high Mw layer, or at least one of the skin layers, has a weight 5 average molecular weight (M_w) of greater than 160,000, preferably at least 165,000, or at least 170,000, or at least 175,000, or at least 180,000, or at least 185,000, and in each case can be up to about 250,000 Daltons, as measured by size exclusion chromatography using the low angle laser light scattering (SEC/LALLS) method of Cotts and Ouano in tetra-hydrofuran. The 10 term “molecular weight” means the weight average molecular weight (M_w). The method for determining the molecular weight as set forth in this description includes using hexafluorisopropanol as the mobile phase (0.8 mL/minute). Each sample is prepared by weighing approximately 20 milligrams of resin into a 25 mL flask and adding 10 mL of the mobile phase. 15 The flask is then placed in an automated shaking device until the polymer is fully dissolved. The analysis is performed using a three-detector system that includes a Viscotek GPCmax (with an autosampler, pump, and degasser), a

Viscotek triple detector TDA302 (RALL/LALLS, Viscometer, and DRI combination) with a column oven (commercially available from Malvern Instruments, Malvern, UK). The separation is performed by three Viscotek mixed bed columns, including a type I-MB (one low and two high range 5 molecular weight) maintained at 45°C. The complete detector set up is calibrated using a narrow poly(methyl methacrylate) standard (commercially available from Viscotek) with a reported molecular weight of 93,458, an intrinsic viscosity of 0.615, and a differential index of refraction (dn/dc) value of 0.1875. The refractive index of the mobile phase is 1.2649 and a dn/dc 10 value of 0.189 is used for PVB. Viscotek Omnisec 4.7.0 software (commercially available from Malvern Instruments) is used for data calculations.

[0030] The high Tg layer, or the one or more core layers, has an Mw of 160,000 or less, or 155,000 or less, or 150,000 or less, or 145,000 or less, or 15 140,000 or less, or 135,000 or less, or 130,000 or less, or 125,000 or less, or 120,000 or less, or 115,000 or less, or 110,000 or less, or 105,000 or less, or 100,000 or less, or 95,000 or less, or 90,000 or less, or 85,000 or less, or 80,000 or less, and in each case, at least 45,000, or at least 50,000.

[0031] The lower molecular weight poly(vinyl acetal) resins that can be 20 used in the high Tg layer allow one to decrease the amount of plasticizer (which will increase the Tg of the poly(vinyl acetal) resin) while maintaining equivalent or lower extrusion pressures. By lowering the amount of plasticizer used, the E' (storage) modulus can also be increased. Merely lowering the amount of plasticizer to increase the Tg of a conventional molecular weight 25 poly(vinyl acetal) resin renders the resin too difficult to process. Even though there may not necessarily be a correlation between the molecular weight and the Tg of the poly(vinyl acetal) resin at equivalent plasticizer loadings, it has been discovered that lowering the molecular weight of the poly(vinyl acetal) resin and lowering the amount of plasticizer allows one to adequately process 30 thermoplastic resins having high Tg values while also providing for an

increased E' modulus. Thus, it has been found that it is desirable to employ a lower molecular weight (M_w) poly(vinyl acetal) resin for high Tg applications.

[0032] Examples of suitable M_w ranges for the high Tg layers or one or more core layers include 45,000 to 160,000, or 45,000 to 155,000, or 45,000 to 150,000, or 45,000 to 145,000, or 45,000 to 140,000, or 45,000 to 135,000, or 45,000 to 130,000, or 45,000 to 125,000, or 45,000 to 120,000, or 45,000 to 115,000, or 45,000 to 110,000, or 45,000 to 105,000, or 45,000 to 100,000, or 45,000 to 95,000, or 45,000 to 90,000, 50,000 to 160,000, or 50,000 to 155,000, or 50,000 to 150,000, or 50,000 to 145,000, or 50,000 to 140,000, or 50,000 to 135,000, or 50,000 to 130,000, or 50,000 to 125,000, or 50,000 to 120,000, or 50,000 to 115,000, or 50,000 to 110,000, or 50,000 to 105,000, or 50,000 to 100,000, or 50,000 to 95,000, or 50,000 to 90,000, or 60,000 to 160,000, or 60,000 to 155,000, or 60,000 to 150,000, or 60,000 to 145,000, or 60,000 to 140,000, or 60,000 to 135,000, or 60,000 to 130,000, or 60,000 to 125,000, or 60,000 to 120,000, or 60,000 to 115,000, or 60,000 to 110,000, or 60,000 to 105,000, or 60,000 to 100,000, or 60,000 to 95,000, or 60,000 to 90,000, 70,000 to 160,000, or 70,000 to 155,000, or 70,000 to 150,000, or 70,000 to 145,000, or 70,000 to 140,000, or 70,000 to 135,000, or 70,000 to 130,000, or 70,000 to 125,000, or 70,000 to 120,000, or 70,000 to 115,000, or 70,000 to 110,000, or 70,000 to 105,000, or 70,000 to 100,000, or 70,000 to 95,000, or 70,000 to 90,000, 80,000 to 160,000, or 80,000 to 155,000, or 80,000 to 150,000, or 80,000 to 145,000, or 80,000 to 140,000, or 80,000 to 135,000, or 80,000 to 130,000, or 80,000 to 125,000, or 80,000 to 120,000, or 80,000 to 115,000, or 80,000 to 110,000, or 80,000 to 105,000, or 80,000 to 100,000, or 80,000 to 95,000, or 80,000 to 90,000, 90,000 to 160,000, or 90,000 to 155,000, or 90,000 to 150,000, or 90,000 to 145,000, or 90,000 to 140,000, or 90,000 to 135,000, or 90,000 to 130,000, or 90,000 to 125,000, or 90,000 to 120,000, or 90,000 to 115,000, or 90,000 to 110,000, or 90,000 to 105,000, or 90,000 to 100,000, or 100,000 to 160,000, or 100,000 to 155,000, or 100,000 to 150,000, or 100,000 to 145,000, or 100,000 to 140,000, or

100,000 to 135,000, or 105,000 to 160,000, or 105,000 to 155,000, or 105,000 to 150,000, or 105,000 to 105,000, or 105,000 to 140,000, or 105,000 to 135,000, or 105,000 to 130,000, 110,000 to 160,000, or 110,000 to 155,000, or 110,000 to 150,000, or 110,000 to 145,000, or 110,000 to 5 140,000, or 110,000 to 135,000, or 110,000 to 130,000.

[0033] The compositions of the high M_w layers and high Tg layers are predominately poly(vinyl acetal) types of resin. In this regard, the compositions of the high M_w layers and high Tg layers, and optionally any one or more additional layers, contain poly(vinyl acetal) in an amount of at least 60 10 wt.%, or at least 65 wt.%, or at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.% or at least 95 wt.%, and in each case up to 98 wt.%. In each case, the poly(vinyl acetal) resin is desirably a polyvinyl butyral ("PVB") resin.

[0034] The compositions of the high M_w layers and high Tg layers, and 15 optionally one or more additional layers, also contain at least one plasticizer. Plasticizers work by embedding themselves between chains of polymers, spacing them apart (increasing the "free volume") and thus significantly lowering the glass transition temperature (Tg) of the polymer resin (typically by 0.5 to 4°C/phr), making the material softer and more flowable. In this 20 regard, the amount of plasticizer in the interlayer can be adjusted to affect the glass transition temperature values. The glass transition temperature is the temperature that marks the transition from the glassy state of the interlayer to the elastic state. In general, higher amounts of plasticizer loading will result in lower Tg. Conventional, previously utilized multilayer interlayers generally 25 have a Tg in the range of about 0°C for acoustic (noise reducing) interlayer up to 46°C for hurricane, structural and aircraft interlayer applications, which at the upper end of the Tg range are difficult to process. An interlayer's glass transition temperature is also correlated with the stiffness of the interlayer: the higher the glass transition temperature, the stiffer the interlayer. Generally, an 30 interlayer with a glass transition temperature of 30°C or higher increases

laminated glass strength and torsional rigidity. A softer interlayer (generally characterized by an interlayer with a glass transition temperature of lower than 30°C), on the other hand, contributes to the sound dampening effect (*i.e.*, the acoustic characteristics).

5 **[0035]** The high Tg layer, or one or more core layers, advantageously have a Tg of at least 46°C, or at least 46.5°C, or at least 47°C, or at least 50.0°C, or at least 51°C, or at least 52°C, or at least 53°C, or at least 54°C, or at least 55°C, or at least 56°C, or at least 57°C, or at least 58°C, or at least 59°C, or at least 60°C. The upper limit is not particularly limited. It can be up to 80°C,
10 or up to 75°C, or up to 70°C, or up to 65°C. Suitable ranges include 46°C-80°C, or 46°C-78°C, or 46°C-75°C, or 46°C-73°C, or 46°C-70°C, or 46°C-68°C, or 46°C-65°C, or 46°C-63°C, or 46.5°C-80°C, or 46.5°C-78°C, or 46.5°C-75°C, or 46.5°C-73°C, or 46.5°C-70°C, or 46.5°C-68°C, or 46.5°C-65°C, or 46.5°C-63°C, or 47°C-80°C, or 47°C-78°C, or 47°C-75°C, or 47°C-
15 73°C, or 47°C-70°C, or 47°C-68°C, or 47°C-65°C, or 47°C-63°C, or 50°C-80°C, or 50°C-78°C, or 50°C-75°C, or 50°C-73°C, or 50°C-70°C, or 50°C-68°C, or 50°C-65°C, or 50°C-63°C, 51°C-80°C, or 51°C-78°C, or 51°C-75°C, or 51°C-73°C, or 51°C-70°C, or 51°C-68°C, or 51°C-65°C, or 51°C-63°C, 53°C-80°C, or 53°C-78°C, or 53°C-75°C, or 53°C-73°C, or 53°C-70°C, or
20 53°C-68°C, or 53°C-65°C, or 53°C-63°C, 55°C-80°C, or 55°C-78°C, or 55°C-75°C, or 55°C-73°C, or 55°C-70°C, or 55°C-68°C, or 55°C-65°C, or 55°C-63°C, 57°C-80°C, or 57°C-78°C, or 57°C-75°C, or 57°C-73°C, or 57°C-70°C, or 57°C-68°C, or 57°C-65°C, or 57°C-63°C.

25 **[0036]** The glass transition temperature is determined by rheometric dynamic analysis using the following procedure. The poly(vinyl acetal) sheet is molded into a sample disc of 25 millimeters (mm) in diameter. The poly(vinyl acetal) sample disc is placed between two 25 mm diameter parallel plate test fixtures of a Rheometrics Dynamic Spectrometer II. The poly(vinyl acetal) sample disc is tested in shear mode at an oscillation frequency of 1
30 Hertz as the temperature of the poly(vinyl acetal) sample is increased from

–20 to 70°C at a rate of 2°C/minute. The position of the maximum value of tan delta (damping) plotted as dependent on temperature is used to determine Tg. Experience indicates that the method is reproducible to within +/–1°C.

[0037] As used herein, the amount of plasticizer, or any other component 5 in the interlayer, can be measured as parts per hundred parts resin (phr), on a weight per weight basis. For example, if 30 grams of plasticizer is added to 100 grams of polymer resin, then the plasticizer content of the resulting plasticized polymer would be 30 phr. As used herein, when the plasticizer content of the interlayer is given, the plasticizer content is determined with 10 reference to the phr of the plasticizer in the melt that was used to produce the interlayer.

[0038] The high M_w layer or any one or more of the skin layers can contain at least 15, or at least 17, or at least 20, or at least 23, or at least 25, or at 15 least 27, or at least 30, or at least 32, or at least 35 phr plasticizer, and up to 80, or up to 70, or up to 60, or up to 50, or up to 45, or up to 40, or up to 35, or up to 30 phr plasticizer. Suitable ranges of plasticizer in phr within a high M_w layer or any one or more of the skin layers include 15 to 80, or 15 to 70, or 15 to 60, or 15 to 50, or 15 to 45, or 15 to 40, or 15 to 35, or 15 to 30, 20 to 80, or 20 to 70, or 20 to 60, or 20 to 50, or 20 to 45, or 20 to 40, or 20 to 35, or 20 to 20 30, 25 to 80, or 25 to 70, or 25 to 60, or 25 to 50, or 25 to 45, or 25 to 40, or 25 to 35, or 25 to 30, 30 to 80, or 30 to 70, or 30 to 60, or 30 to 50, or 30 to 45, or 30 to 40, or 30 to 35, or 35 to 30, 35 to 80, or 35 to 70, or 35 to 60, or 35 to 50, or 35 to 45, or 35 to 40 phr plasticizer.

[0039] The Tg of the high M_w layer is not particularly limited. It can be, if 25 desired, lower than the Tg of at least one of the high Tg layers, optionally less than 50°C, or less than 46°C. The optionally lower Tg of the high M_w layer or skin layer can contribute to a higher glass/interlayer adhesion, or a better ability to absorb impact energy. Optionally, the Tg of one or more or all of the high M_w layers or one or more or all of the skin layers is not greater than 30 55°C, or not greater than 52°C, or not greater than 49°C, or not greater than

48°C, or not greater than 47°C, or not greater than 46°C, or less than 46°C, or not greater than 45°C, or not greater than 44°C, or not greater than 43°C, or not greater than 42°C, or not greater than 41°C, or not greater than 40°C, or not greater than 39°C, or not greater than 38°C, or not greater than 37°C, or 5 not greater than 36°C, or not greater than 37°C, or not greater than 36°C, or not greater than 35°C, or not greater than 34°C, or not greater than 33°C, or not greater than 32°C, or not greater than 31°C, or not greater than 30°C, and in each case at least 25°C.

10 **[0040]** The Tg of the high M_w layer or one or more skin layers can, if desired, be at least 1°C, or at least 2°C, or at least 3°C, or at least 4°C, or at least 5°C, or at least 6°C, or at least 7°C, or at least 8°C, or at least 9°C, or at least 10°C, or at least 11°C, or at least 12°C, or at least 13°C, or at least 14°C, or at least 15°C, or at least 16°C, or at least 17°C, or at least 18°C less than the Tg of the high Tg layer or one or more one or more core layers.

15 **[0041]** The high Tg layer or any of the one or more core layers can contain at least 5, or at least 8, or at least 10, or at least 13, or at least 15, or at least 17, or at least 20, and up to 28, or up to 25, or up to 23, or up to 20, or up to 18, or up to 17, or up to 15, or up to 13, or up to 10, or up to 9, or up to 8, or up to 7 parts plasticizer per hundred parts of poly(vinyl acetal) resin. Suitable ranges of plasticizer in phr within a layer include 5 to 28, or 5 to 25, or 5 to 23, or 5 to 20, or 5 to less than 20, or 5 to 19, or 5 to 18, or 5 to 17, or 5 to 15, or 5 to 13, or 5 to 10, or 5 to 9, or 5 to 8, or 5 to 7, 8 to 28, or 8 to 25, or 8 to 23, or 8 to 20, or 8 to less than 20, or 8 to 19, or 8 to 18, or 8 to 17, or 8 to 15, or 8 to 13, or 8 to 10, or 10 to 28, or 10 to 25, or 10 to 23, or 10 to 20, or 10 to 25, or 10 to 19, or 10 to 18, or 10 to 17, or 10 to 15, or 10 to 13, or 13 to 28, or 13 to 25, or 13 to 23, or 13 to 20, or 13 to less than 20, or 13 to 19, or 13 to 18, or 13 to 17, or 13 to 15, or 15 to 28, or 15 to 25, or 15 to 23, or 15 to 20, or 15 to less than 20, or 15 to 19, or 15 to 18, or 15 to 17, or 17 to 28, or 17 to 25, or 17 to 23, or 17 to 20, or 17 to less than 20, or 17 to 19, or 30 17 to 18, 20 to 28, or 20 to 25, or 20 to 23, or 23 to 28, or 23 to 25.

[0042] Desirably, the high Tg layer (or one or more one or more core layers) has less plasticizer than the high M_w layer (or one or more of the skin layers). Since a reduction in the amount of plasticizer present in high Tg layer or one or more core layers contributes toward an increase in Tg, and a higher amount of plasticizer in the high M_w layers or skin layer (relative to the high Tg layers or one or more core layers) assists with increasing adhesion to glass, it is desirable to use less plasticizer in the high Tg layers or one or more core layers than the amount of plasticizer present in one or more of the high M_w layers or skin layers. Desirably, the high Tg layers or one or more core layers has at least 2, or at least 4, or at least 5, or at least 7, or at least 9, or at least 10, or at least 11, or at least 12, or at least 15, or at least 17, or at least 19, or at least 20 phr less plasticizer than is present in the high M_w layers or one or more skin layers.

[0043] The adjustments in the amount of plasticizer in the high Tg layers or one or more core layers are made possible by the use of poly(vinyl acetal) polymers having a lower molecular weight (M_w), and the reduced amount of plasticizer allows one to make a higher Tg layer or one or more core layers, while the lower molecular weight poly(vinyl acetal) resin also allows one to make the high Tg layers or core layers at acceptable rates. The increase in Tg also improves the E' modulus of the high Tg layers or one or more core layers, and therefore also improves the E' modulus of the whole multilayer interlayer. The adjustment between the selection of molecular weight and the amount of plasticizer in the high Tg layers or a one or more core layers allows one to take advantage of a variety of properties and opens up large processing and application windows. For example, if a particular application does not require a high end Tg, the invention allows one to increase the amount of plasticizer to further improve the flowability of the polymer and increase the output (capacity) of the extruder while maintaining a compositional Tg of at least 46°C. Alternatively, with an increase in flowability, the capacity or output of the extruder can be maintained constant

while decreasing the extrusion temperature, thereby saving on energy costs. The extrusion temperature is the temperature of the polymer at the entrance to the die head. If none of these objectives are paramount and maximizing the Tg of the interlayer is desired, as noted above, the amount of plasticizer 5 can be reduced to a lower end of the range, made possible with the use of lower molecular weight polymers, while maintaining reasonable polymer flowability at extrusion temperatures not exceeding 240°C, or even not exceeding 235°C, or even not exceeding 230°C. By maintaining extrusion temperatures not exceeding 240°C, the formation of undesirable degradation 10 by-products is minimized.

[0044] The type of plasticizer used in any of the layers is not particularly limited. The plasticizer can be a compound having a hydrocarbon segment of 30 or less, or 25 or less, or 20 or less, or 15 or less, or 12 or less, or 10 or less carbon atoms, and in each case at least 6 carbon atoms. Suitable 15 conventional plasticizers for use in these interlayers include esters of a polybasic acid or a polyhydric alcohol, among others. Suitable plasticizers include, for example, triethylene glycol di-(2-ethylhexanoate) ("3GEH"), triethylene glycol di-(2-ethylbutyrate), triethylene glycol diheptanoate, tetraethylene glycol diheptanoate, dihexyl adipate, dioctyl adipate, hexyl 20 cyclohexyladipate, diisononyl adipate, heptylnonyl adipate, dibutyl sebacate, butyl ricinoleate, castor oil, dibutoxy ethyl phthalate, diethyl phthalate, dibutyl phthalate, trioctyl phosphate, triethyl glycol ester of coconut oil fatty acids, phenyl ethers of polyethylene oxide rosin derivatives, oil modified sebacic 25 alkyd resins, tricresyl phosphate, and mixtures thereof. A desirable plasticizer is 3GEH.

[0045] High refractive index plasticizers may be used in the composition of the invention, either alone or in combination with another plasticizer. Examples of the high refractive index plasticizers include, but are not limited to, esters of a polybasic acid or a polyhydric alcohol, polyadipates, epoxides, 30 phthalates, terephthalates, benzoates, toluates, mellitates and other specialty

plasticizers, among others. Examples of high refractive index plasticizers include, but are not limited to, dipropylene glycol dibenzoate, tripropylene glycol dibenzoate, polypropylene glycol dibenzoate, isodecyl benzoate, 2-ethylhexyl benzoate, diethylene glycol benzoate, propylene glycol dibenzoate, 5 2,2,4-trimethyl-1,3-pentanediol dibenzoate, 2,2,4-trimethyl-1,3-pentanediol benzoate isobutyrate, 1,3-butanediol dibenzoate, diethylene glycol di-o-toluate, triethylene glycol di-o-toluate, dipropylene glycol di-o-toluate, 1,2-octyl dibenzoate, tri-2-ethylhexyl trimellitate, di-2-ethylhexyl terephthalate, bis-phenol A bis(2-ethylhexanoate), ethoxylated nonylphenol, and mixtures 10 thereof. Examples of more preferred high refractive index plasticizers are dipropylene glycol dibenzoates and tripropylene glycol dibenzoates.

[0046] In addition to the use of a plasticizer, various adhesion control agents (“ACAs”) can be used with the poly(vinyl acetal) resins and in the high M_w layers and high T_g layers, and optionally any one or more additional 15 layers. ACAs in the multilayer interlayer formulation control adhesion of the interlayer to glass to provide energy absorption on impact of the glass laminate. In various embodiments of interlayers of the present disclosure, the interlayer can comprise about 0.003 to about 0.15 parts ACAs per 100 parts resin; about 0.01 to about 0.10 parts ACAs per 100 parts resin; and about 20 0.01 to about 0.04 parts ACAs per 100 parts resin. Such ACAs, include, but are not limited to, the ACAs disclosed in U.S. Patent No. 5,728,472 (the entire disclosure of which is incorporated herein by reference), residual sodium acetate, potassium acetate, magnesium bis(2-ethyl butyrate), and/or magnesium bis(2-ethylhexanoate).

25 **[0047]** Anti-blocking agents may also be added to the composition of the present invention to reduce the level of blocking of the interlayer. Anti-blocking agents are known in the art, and any anti-blocking agent that does not adversely affect the properties of the interlayer may be used. A particularly preferred anti-blocking agent that can be successfully used as in 30 the multilayer interlayer while not affecting optical properties of the interlayer

or the adhesive properties of the interlayer to glass is a fatty acid amide (see, for example, U.S. Patent No. 6,825,255, the entire disclosure of which is incorporated herein).

[0048] Other additives may be incorporated into the composition to 5 enhance its performance in a final product and impart certain additional properties to the interlayer. Such additives include, but are not limited to, dyes, pigments, stabilizers (e.g., ultraviolet stabilizers), antioxidants, flame retardants, IR absorbers or blockers (e.g., indium tin oxide, antimony tin oxide, lanthanum hexaboride (LaB₆) and cesium tungsten oxide), processing 10 aides, flow enhancing additives, lubricants, impact modifiers, nucleating agents, thermal stabilizers, UV absorbers, UV stabilizers, dispersants, surfactants, chelating agents, coupling agents, adhesives, primers, reinforcement additives, and fillers, among other additives known to those of ordinary skill in the art.

15 **[0049]** The high Tg layer, or core layer, or an interlayer sheet that will be used at a high Tg interlayer in the multilayer interlayer structure, has a melt flow index ("MFI") of at least 0.65 grams/10 minutes when measured at 190 °C and under a load of 2.16 kilograms. The molecular weight of the poly(vinyl acetal) resin and the amount of plasticizer can be adjusted to provide an MFI 20 of at least 0.65 grams/10 minutes when measured at 190 °C and under a load of 2.16 kilograms. At these MFI levels, the high Tg interlayer composition/molten thermoplastic is reasonably flowable and within a commercially acceptable output during extrusion. The high MFI of the 25 composition with lowered molecular weight resin provides a wider processing window while providing a sheet that has improved stiffness and Tg. The MFI is desirably at least 0.65, or can be at least 0.70, or at least 0.80, or at least 0.90, or at least 1, or at least 1.1, or at least 1.2, or at least 1.4, or at least 1.5, or at least 1.8, or at least 2, or at least 3, or at least 5, or at least 7, or at least 10, each expressed as grams/10 min. While there is no particular upper limit, 30 for practical considerations, such as retaining mechanical strength, the MFI

should not exceed 40, or should not exceed 30, or should not exceed 25 grams/10 min. If the MFI is too low, processability becomes too difficult at commercially useful rates. If the MFI is excessively high, the mechanical properties of the sheet can deteriorate. Suitable ranges include 0.65-40, or 5 0.65-30, or 0.65-25, or 0.7-40, or 0.7-30, or 0.7-25, or 0.8-40, or 0.8-30, or 0.8-25, or 0.9-40, or 0.9-30, or 0.9-25, or 1-40, or 1-30, or 1-25, or 1.1-40, or 1.1-30, or 1.1-25, or 1.2-40, or 1.2-30, or 1.2-25, or 1.4-40, or 1.4-30, or 1.4-25, or 1.5-40, or 1.5-30, or 1.5-25, or 1.8-40, or 1.8-30, or 1.8-25, or 2-40, or 2-30, or 2-25, or 3-40, or 3-30, or 3-25, or 5-40, or 5-30, or 5-25, or 7-40, or 7-10 30, or 7-25, or 10-40, or 10-30, or 10-25. The MFI is determined according to ASTM D1238-13, Procedure A.

[0050] The thermoplastic composition of the high Tg layers or a one or more core layers can have a solution viscosity of 120 centipoise ("cps") or less. The molecular weight of the poly(vinyl acetal) resin and the amount of 15 plasticizer can be adjusted to provide a solution viscosity of the high Tg thermoplastic composition (that includes resin and plasticizer) of 125 cps or less. The solution viscosity as used herein is determined by placing the sheet samples in a crucible overnight to dry; determining the sheet sample weight by formula: Wt. sheet = 3.195(100+phr)/100; placing the sheet in 4 oz. bottle 20 with 39.57 grams Methanol to dissolve; placing the bottle in a constant temperature water bath at 20 +/- 0.1 °C for 1 hour but not to exceed 1.5 hours, placing a viscometer (e.g. Cannon No. 400) in water bath for 5min. to equilibrate, transferring 10 mls of solution to viscometer by pipette; and timing the solution flow between viscometer marks; then multiplying the time (sec.) 25 with the Viscometer factor to determine viscosity in cps (1.038 for the Cannon No. 400). Suitable solution viscosities of the high Tg composition or one or more core layers and thermoplastic composition include, in cps, are 125 or less, 120 or less, or 110 or less, or 100 or less, or 90 or less, or 85 or less, or 80 or less, or 70 or less, or 65 or less, or 60 or less, or 55 or less, or 50 or 30 less, or 45 or less, or 40 or less, or 35 or less, or 30 or less. Additionally or in

the alternative, the solution viscosity is at least 5 cps, or at least 10 cps. Suitable ranges of solution viscosity include, in cps, 5-125, or 10-125, or 5-120, or 10-120, or 5-110, or 10-110, or 5-100, or 10-10, or 5-95, or 10-95, or 5-90, or 10-90, or 5-85, or 10-85, or 5-80, or 10-80, or 5-70, or 10-70, or 5-65, 5 or 10-65, or 5-60, or 10-60, or 5-55, or 10-55, or 5-50, or 10-50, or 5-45, or 10-45, or 5-40, or 10-40, or 5-35, or 10-35, or 5-30, or 10-30.

[0051] Co-additives such as anti-blocking agents, colorants and UV inhibitors (in liquid, powder, or pellet form) are often used and can be mixed into the thermoplastic resin or plasticizer prior to arriving in the extruder 10 device or combined with the thermoplastic resin inside the extruder device. These additives are incorporated into the thermoplastic composition, and by extension the resultant multilayer interlayer, to enhance certain properties of the interlayer and its performance in a multiple layer glass panel product (or photovoltaic module).

15 [0052] The multilayer interlayer can be made by any suitable process known to one of ordinary skill in the art of producing interlayers. For example, it is contemplated that the multilayer interlayers may be formed through dipcoating, solution casting, compression molding, injection molding, melt extrusion, melt blowing or any other procedures for the production and 20 manufacturing of an interlayer known to those of ordinary skill in the art.

[0053] In some embodiments of the extrusion process, a co-extrusion process may be utilized. Co-extrusion is a process by which multiple layers of polymer material are extruded simultaneously. Generally, this type of extrusion utilizes two or more extruders to melt and deliver a steady volume 25 throughput of different thermoplastic melts of different viscosities or other properties through a co-extrusion die into the desired final form. The thickness of the multiple polymer layers leaving the extrusion die in the co-extrusion process can generally be controlled by adjustment of the relative speeds of the melt through the extrusion die and by the sizes of the individual 30 extruders processing each molten thermoplastic resin material.

[0054] The high M_w layers and high T_g layers can be in direct contact with each other or can be indirectly disposed adjacent to each other through another layer. Desirably, at least one of the high M_w layers and at least one of the high T_g layers are in direct contact with each other. The high M_w layers and high T_g layers desirably are also directly bonded to each other. The bond is desirably a heat bond as would occur when the layers are laid up against each other and the multilayer interlayer heated to above the T_g of all layers. This can occur by laying up the cool layers against each other, or by co-extruding the layers.

5 **[0055]** As noted above, the thickness of the multilayer interlayer of the invention does not have to be increased to obtain a higher E' modulus. Accordingly the thickness, or gauge, of each interlayer sheet in the multilayer interlayer can be from about at least 5 mils, or at least 10 mils, or at least 15 mils, and can be as thick as desired. The sheet can be as thick as 90 mils, or 10 120 mils, or more depending on the desired application. Examples of ranges include from about 5 mils to 120 mils (0.12 mm to 3.03 mm), or 15 mils to 90 mils (about 0.38 mm to about 2.286 mm), or about 30 mils to about 60 mils (about 0.762 to 1.52 mm), or about 15 mils to about 35 mils (about 0.375 to about 0.89 mm). The thickness, or gauge, of the multilayer interlayer 15 structure depends on how many sheets are laminated or co-extruded, and is not particularly limited, but generally will be greater than 30 mils, or greater than 60 mils (1.52 mm) as desired for the particular application.

20 **[0056]** The multilayer interlayer of the invention also can now be used in applications which require maintaining good modulus at higher temperatures, such as outdoor applications that undergo regular intermittent stresses, 25 caused by such factors as walking or running, or that are load bearing under temperature conditions that may exceed 35°C. Examples of applications in which the multilayer interlayer of the invention is suited include outdoor stairs, outdoor platforms, pavement or sidewalk skylights, ballustrades, curtain walls, 30 flooring, and other demanding structural applications.

[0057] The multilayer interlayer can be incorporated into a multiple layer panel. As used herein, a multiple layer panel can comprise a single substrate, such as glass, acrylic, or polycarbonate with a multilayer interlayer sheet disposed thereon, and most commonly, with a thin polymer film further disposed over the multilayer interlayer. The combination of multilayer interlayer sheet and polymer film is commonly referred to in the art as a bilayer. A typical multiple layer panel with a bilayer construct is: (glass) // (multilayer interlayer) // (polymer film) where the multilayer interlayer can comprise at least 2 interlayers as noted above. The polymer film supplies a smooth, thin, rigid substrate that affords better optical character than that usually obtained with a multilayer interlayer alone and functions as a performance enhancing layer. Polymer films differ from multilayer interlayers, as used herein, in that polymer films do not themselves provide the necessary penetration resistance and glass retention properties, but rather provide performance improvements, such as infrared absorption characteristics. Poly(ethylene terephthalate) ("PET") is the most commonly used polymer film. Generally, as used herein, a polymer film is thinner than a multilayer interlayer, such as from about 0.001 to 0.2 mm thick.

[0058] Further, the multiple layer panel can be what is commonly known in the art as a solar panel, with the panel further comprising a photovoltaic cell, as that term is understood by one of ordinary skill in the art, encapsulated by the multilayer interlayer(s). In such instances, the interlayer is often laminated over the photovoltaic cell, with a construct such as: (glass) // (multilayer interlayer) // (photovoltaic cell) // (multilayer interlayer) // (glass or polymer film).

[0059] The interlayers of the present disclosure will most commonly be utilized in multiple layer panels comprising two substrates, preferably a pair of glass interlayers, with the interlayers disposed between the two substrates. An example of such a construct would be: (glass) // (multilayer interlayer) // (glass), where the multilayer interlayer can comprise multilayered interlayers

as noted above. Further, the multiple layer panel can contain a polymer film, such as (glass)//(multilayer interlayer)//polymer film//(glass). These examples of multiple layer panels are in no way meant to be limiting, as one of ordinary skill in the art would readily recognize that numerous constructs other than 5 those described above could be made with the interlayers of the present disclosure.

[0060] Such a glass pane structure is further illustrated in Figure 1. A glass panel 1 comprises a pair of glass substrates 2, and a multilayer interlayer 3 containing a first high M_w layer 4, a high Tg layer 5, and a second 10 high M_w layer 6. The glass panel also contains a bilayer structure 7 made up of the multilayer interlayer 3 and a polymer film 8. The multilayer interlayer 3 in this case contains a high Tg layer disposed between two high M_w layers. A first side of the high Tg layer 5 is in direct contact with a side of a first high M_w layer 4, and a second side of the high Tg layer 5 is also in direct contact with 15 a side of the second high M_w layer 6.

[0061] The typical glass lamination process comprises the following steps: (1) assembly of the two substrates (e.g., glass) and interlayer; (2) heating the assembly via an IR radiant or convective means for a short period; (3) passing the assembly into a pressure nip roll for the first deairing; (4) heating the 20 assembly a second time to about 50°C to about 120°C to give the assembly enough temporary adhesion to seal the edge of the interlayer; (5) passing the assembly into a second pressure nip roll to further seal the edge of the interlayer and allow further handling; and (6) autoclaving the assembly at temperatures between 135°C and 150°C and pressures between 150 psig 25 and 200 psig for about 30 to 90 minutes.

[0062] Other means for use in de-airing of the interlayer-glass interfaces (steps 2 to 5) known in the art and that are commercially practiced include vacuum bag and vacuum ring processes in which a vacuum is utilized to remove the air.

[0063] An alternate lamination process involves the use of a vacuum laminator that first de-airs the assembly and subsequently finishes the laminate at a sufficiently high temperature and vacuum.

[0064] The high Tg interlayer sheet can be made by any suitable process known to one of ordinary skill in the art of producing interlayer sheets. For example, it is contemplated that the high Tg interlayer sheets may be formed through dipcoating, solution casting, compression molding, injection molding, melt extrusion, melt blowing or any other procedures for the production and manufacturing of an interlayer sheet known to those of ordinary skill in the art.

5 **[0065]** In one method, the high Tg interlayer sheets can be made by any conventional sheet extrusion device. The extruder can be a single or twin screw extruder. There is now also provided a process in which the high Tg interlayer poly(vinyl acetal) sheet can be made by:

10 (i) providing an extrusion system comprising a die and an extruder having a barrel;

15 (ii) feeding a poly(vinyl acetal) resin and a plasticizer into the barrel and passing a molten thermoplastic composition comprising the poly(vinyl acetal) resin and plasticizer through the extruder and the die to produce an extruded sheet, wherein the melt flow index (MFI) of the molten thermoplastic resin is at least 0.65 g/10 min when measured at 190°C at a loading of 2.16 kilograms; and

20 (iii) cooling the sheet to produce an interlayer sheet having a glass transition temperature (Tg) of at least 46.0°C.

[0066] Reference to FIG. 2 is made to further illustrate the process of the invention along with additional features.

[0067] As illustrated, there is provided an extrusion system made up of an extruder 1, a filter 2, a die 4, and a melt pump 3 disposed between the filter 2 and the die 4.

[0068] In the extruder device 1, the particles of the thermoplastic composition 10 comprising poly(vinyl acetal) resin and plasticizers, and other

additives described above, are fed through a feed system 11 (e.g. hopper) into the barrel 12 of the extruder 1 and heated by heating elements 13 to form a molten thermoplastic composition in the barrel 12 that is generally uniform in temperature and composition. Generally, in the extrusion process, 5 thermoplastic resin and plasticizers, including any of those resins and plasticizers described above, are pre-mixed and fed into an extruder device. For example, the process of the invention can include feeding a pre-mix into an extruder 1, wherein the pre-mix is obtained by combining a thermoplastic poly(vinyl acetal) resin and a plasticizer, and optionally other additives first to 10 make a pre-mix, and feeding the pre-mix to the barrel 12. This method is particularly useful when using a single screw extruder. Alternatively, there can be provided at least two streams fed to the barrel 12 of an extruder (not shown), one stream comprising a poly(vinyl acetal) thermoplastic resin and a second stream comprising a plasticizer, combining the two streams inside the 15 barrel of an extruder. This technique is particularly useful when using a twin-screw extruder. The at least two streams can be combined inside the extruder by melting the poly(vinyl acetal) resin inside the extruder in the presence of the plasticizer.

[0069] The thermoplastic particles are propelled down the barrel 12 through the action of the rotating screw 14 powered by a motor 15, and with a combination of shear forces and heat, melts the thermoplastic solids within the barrel 12 into a molten thermoplastic composition that is propelled through a filter 2 to filter out particles. Passage through a filter 2 is a cause for pressure drop, and to compensate, a melt pump 3, such as a gear pump, can 20 be located between the filter 2 and die 4. The extruder die 4 is the component of the thermoplastic extrusion process which gives the final high Tg interlayer sheet product its profile. A plurality of shapes can be imparted to the end of the high Tg interlayer sheet by the die so long as a continuous profile is 25 present.

[0070] The thermoplastic composition of the invention is desirably brought to a temperature of 240 °C or less within the barrel 12. When the composition experiences temperatures higher than 240 °C, there is generally a risk of significant build-up of yellow color because poly(vinyl acetal) resins tend to 5 form decomposition by-products at higher temperatures. The molten thermoplastic polymer composition is desirably brought to a temperature within the barrel 12 of 240 °C or less, or 238 °C or less, or 235 °C or less, or 233 °C or less, or 232 °C or less, or 230 °C or less, or 228 °C or less, or 226 °C or less, or 225 °C or less, or 220 °C or less, and in each case at a temperature 10 of at least 150 °C.

[0071] The molten thermoplastic composition is fed from the outlet 16 of the melt pump 3 and fed through a line 17 to a die 4. In this illustration, the thermoplastic composition experiences a pressure drop between the outlet 16 of the melt pump and the exit to the die 4, and the magnitude of the pressure 15 drop affects the throughput and capacity of the extrusion process. As the flowability of the thermoplastic composition increases so does the throughput of the extrusion device. The flowability of the thermoplastic composition will manifest itself by the pressure drop between the melt pump and the exit of the die. Since the thermoplastic compositions of the invention are flowable even 20 with low amounts of plasticizer made possible by the use of poly(vinyl acetal) resins having a low M_w , it is now possible to process the thermoplastic resin in a commercially acceptable manner while obtaining an interlayer sheet having high Tg. In the process of the invention, a reasonable pressure drop across 25 the melt pump outlet and the die exit is obtainable while simultaneously obtaining an interlayer sheet having a Tg of 46 °C or more or 50.0 °C or more made at acceptable extrusion rates.

[0072] The flowability of the thermoplastic composition in the extruder can be expressed as a composition having a high melt flow index (MFI) at the conditions in the extruder. The MFI of the thermoplastic composition in the

process of the invention can be at least 0.65 grams/10 min when measured at 190 °C at a loading of 2.16 kilograms.

[0073] The interlayer at the state after the extrusion die forms the melt into a continuous profile will be referred to as an “extruded sheet.” At this stage in 5 the process, the extrusion die has imparted a particular profile shape to the thermoplastic composition, thus creating the extruded sheet. The extruded sheet is highly viscous throughout. At least a portion or the whole of the extruded sheet as it exits the die is molten. In the extruded sheet, the thermoplastic composition as it exits the die has not yet been cooled to a 10 temperature at which the sheet generally completely “sets.” Thus, after the extruded sheet leaves the extrusion die, generally the next step is to cool the polymer melt sheet with a cooling device 5 to make a high Tg interlayer sheet having a Tg of at least 46.0 °C. Cooling devices include, but are not limited to, spray jets, fans, cooling baths, and cooling rollers. The cooling step functions 15 to set the extruded sheet into a high Tg interlayer sheet of a generally uniform non-molten cooled temperature. In contrast to the extruded sheet, this interlayer sheet is not in a molten state. Rather, it is the set final form cooled interlayer sheet product. Once the interlayer sheet has been cooled and set, it is cut with knives 6 and pulled through with a roller/winding system 7.

20 **[0074]** The high Tg layers or one or more core layers of a multilayer interlayer of the invention desirably has a storage modulus E' at 40 °C of at least 300,000,000 pascals, or at least 400,000,000 pascals, or at least 500,000,000 pascals, or at least 600,000,000 pascals, or at least 700,000,000 pascals, or at least 800,000,000 pascals. There is no particular upper limit, 25 although practically the monolithic interlayer can obtain an E' modulus as high as 3,000,000,000 pascals, or as high as 2,000,000,000 pascals, or as high as 1,500,000,000 pascals at 40 °C.

[0075] High Tg layers or one or more core layers of a multilayer interlayer of the invention desirably also, or in the alternative, has a storage modulus E' 30 at 50 °C of at least 6,000,000 pascals, or at least 7,000,000 pascals, or at

least 8,000,000 pascals, or at least 9,000,000 pascals, or at least 10,000,000 pascals, or at least 20,000,000 pascals, or at least 30,000,000 pascals, or at least 40,000,000 pascals, or at least 50,000,000 pascals, or at least 60,000,000 pascals, or at least 70,000,000 pascals, or at least 80,000,000 pascals, or at least 90,000,000 pascals, or at least 100,000,000 pascals. There is no particular upper limit, although practically the multilayer interlayer (or layers of the multilayer interlayer) can obtain an E' modulus as high as 1,000,000,000 pascals, or as high as 900,000,000 pascals, or as high as 800,000,000 pascals at 50 °C.

10 [0076] The storage E' modulus of an interlayer or multilayer interlayer is measured according to ASTM D5026-06 (Reapproved 2014). The E' modulus is obtained by the Dynamic Mechanical Analysis using the RSA-II instrument. A 9 mm wide and 0.765 mm thick sample is clamped at the top and bottom and placed in tension. The length of the sample between the clamps is 22 mm. A sinusoidal tensile strain of magnitude 0.01% is applied at a frequency of 1 Hz to the specimen over a range of temperatures and the resulting stress response is measured. Modulus which is a measure of resistance of the material to deformation is obtained from the ratio of stress to strain. For an oscillatory tensile deformation, E' is the real part of the complex modulus and is referred to as the storage modulus. Temperature control is provided by an oven chamber and the heating rate is 3 °C/minute.

15 [0077] Glass panels made with the multilayer interlayers of the invention have the capability of maintaining acceptable levels of creep resistance, which is 1 mm or less, even at the low poly(vinyl acetal) resins molecular weights.

20 [0078] Glass panels containing the multilayer interlayers of the invention can exhibit a creep of not more than 1 mm at 100 °C and at 1000 hours, or not more than 0.9 mm, or not more than 0.8 mm, or not more than 0.7 mm, or not more than 0.6 mm, or not more than 0.5 mm, or not more than 0.4 mm.

25 [0079] The method for determining creep is to laminate the multilayer interlayer between two sheet of glass, one sheet measuring 6"x6" and the

other 6"x7". The glass panel test specimen is hung by the exposed 1" section of glass in an oven set at 100°C. The test specimen is then removed at the predetermined intervals and measured to determine how much of the 6"x6" piece of glass has slipped down from its original position relative to the 6"x7" 5 glass. The predetermined intervals are at 100, 250, 500, and 1000 hours.

Examples

10 [0079] A laboratory extrusion trial was conducted using a 1.25" extruder outfitted with an extrusion die. The extrusion system is outfitted with a filter at the head of the extruder, followed by a gear pump, followed by the die, and the speed of the gear pump was held constant at 44 rpm for all examples. The extrusion rate was measured over the course of the test and was approximately 47-48 g/min for all examples.

15 [0080] Triethylene glycol di-(2-ethylhexanoate) plasticizer (3GEH) was used in all cases, at varying levels as described in the table below. The same amount of adhesion control agents was added in all cases in the premix.

20 [0081] Pressure transducers were mounted at the outlet of the gear pump. The pressure at the gear pump relative to the control illustrates the effect of lowering the molecular weight of the PVB resin.

[0082] A control Saflex™ DG41 sheet was used to measure Tg and compare with the experimental cases. Saflex™ DG41 PVB is a commercial product for structural applications, and was used because it is available in the marketplace.

25 [0083] Table 2 below lists the effect of resin type and plasticizer loading on the pressure at the outlet of the gear pump, as well as the Tg of the interlayer for each case. The gear pump pressure is an indicator of an improvement in flowability of the thermoplastic resin in an extrusion environment.

Table 2

Example	PVB Resin Weight Average MW	Plasticizer (phr)	Gear Pump Outlet Pressure (psi)	Glass Transition Temperature Tg (°C)	MFI (190/2.16)	Solution Viscosity
1 (control) Saflex™ DG41	170	20	4466	46.1	0.57	155
2 (control)	170	20	4240	46.2	Not analyzed	Not analyzed
3	130	20	3000	45.8	1.40	84.3
4	130	15	3700	51.5	1.03	97.6
5	130	10	4390	58.8	0.70	82.4
6	50	10	920	60.1	20	14.9

[0084] It can be seen that Example 2 demonstrates essentially the same glass transition temperature as the control sheet of Example 1 (46.2°C v. 46.1°C). Example 3 demonstrates almost the same glass transition temperature (45.8°C) as Examples 1 and 2, showing that Tg is not a function of the molecular weight (M_w) of the poly(vinyl acetal) resin. Similarly, a comparison of Example 5 and Example 6 also demonstrates that the Tg is not a function of the resin molecular weight (M_w) since both are plasticized at the same level (10 phr) and have similar Tg (58.8°C v. 60.1°C).

[0085] However, the examples do demonstrate that with a lower molecular weight resin, the amount of plasticizer can be reduced, which in turn elevates the Tg of the composition, and that this can be achieved at acceptable rates (as indicated by the lower pressure drop). Examples 4, 5 and 6, which employ a resin having a lower M_w and lower amounts of plasticizer, produce a sheet having a high Tg (exceeding 50°C). In addition, the increase in Tg is not at the expense of acceptable rates as indicated by pressure drops at about the same amount as the control or lower.

[0086] Example 3, with a lower MW resin and equivalent plasticizer as Examples 1 and 2, demonstrates that the molecular weight of the resin allows for a lower pressure at the gear pump due to improved flowability as indicated by its higher MFI value of 1.4 (compared to Example 1 at 0.57). Example 6

also demonstrates the same point where the pressure reduction at the gear pump is about 79% relative to Example 1 due to its dramatically higher MFI of 20 and about 78% relative to Example 2.

[0087] Examples 4, 5 and 6 demonstrate that higher Tg monolithic 5 poly(vinyl acetal) interlayers can be extruded at lower or almost equivalent pressure drops as Example 2. As the pressure at the gear pump starts to increase due to further drops in the plasticizer level (as can be seen in Example 5), the flowability of the thermoplastic resin can be improved by continuing to lower the molecular weight of the resin to compensate for the 10 low plasticizer levels (as seen in Example 6). This effect can be seen in Example 6 that has the same low plasticizer level as Example 5, yet has a significantly improved flowability as indicated by its low pressure requirement and higher MFI, compared to all other examples, at the gear pump due to the reduction in molecular weight.

15 **[0088]** The Examples 3-6 indicate the effect of improved flowability by higher MFI values compared to the control Example 1 employing a resin of higher M_w . While the MFI starts to decrease as the amount of plasticizer is lowered (Examples 3-5), the MFI remains higher than the control and can be dropped further by employing a resin having a lower M_w at the low plasticizer 20 levels.

[0089] Finally, the very low pressure of Example 6 suggests that the resin of Example 6 can be used in blends with higher molecular weight (M_w) resins to control process conditions while achieving a higher Tg product.

[0090] The rheological properties of the interlayer sheets made in 25 Examples 1-6 were also studied. FIG. 3 shows that the sheets of Examples 3, 4, 5 and 6 possess significantly higher storage modulus E' at all temperatures of 30 °C or more, such as at 40 °C and 50 °C and within the range of 30-65 °C, or 30-60 °C, or 30-55 °C, and the differences were quite large at 40-55 °C, or 40-50 °C. The modulus is also higher at temperatures of 50-55 °C, 30 suggesting that these formulations perform better than control Examples 1

and 2 in structural applications that may be exposed to higher than room temperature conditions.

5 [0091] It is intended that the invention not be limited to the particular embodiments disclosed as the best mode contemplated for carrying out this invention, and that the invention will include all embodiments falling within the scope of the appended claims.

10 [0092] It will further be understood that any of the ranges, values, or characteristics given for any single component of the present invention can be used interchangeably with any ranges, values, or characteristics given for any of the other components of the invention, where compatible, to form an embodiment having defined values for each of the components, as given herein throughout.

CLAIMS

1. A multilayer interlayer comprising:
 - (A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000; and
 - (B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a glass transition temperature (Tg) of at least 46°C.
- 10 2. The multilayer interlayer of claim 1, wherein the high Tg layer has a melt flow index (MFI) of at least 0.65 grams/10 minutes when measured at 190°C and under a load of 2.16 kilograms.
- 15 3. The multilayer interlayer of claim 1, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.
4. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 100,000.
- 20 5. The multilayer interlayer of claim 1, wherein the high Tg layer further comprises a plasticizer in an amount of at least 5 parts per hundred parts of the poly(vinyl acetal) resin.
- 25 6. The multilayer interlayer of claim 1, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) that does not exceed 140,000 in the high Tg layer and plasticizer in an amount ranging from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin.

7. The multilayer interlayer of claim 1, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about 5 to 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50 °C, and the high M_w layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not exceeding 46 °C.

10 8. The multilayer interlayer of claim 1, wherein glass transition temperature (Tg) of the high M_w layer is at least 4 °C less than the glass transition temperature (Tg) of the high Tg layer.

15 9. The multilayer interlayer of claim 1, wherein the high M_w layer and the high Tg layer each have a plasticizer, and the at least one high Tg layer has at least 7 phr less plasticizer than the high M_w layer.

20 10. The multilayer interlayer of claim 1, wherein the high M_w layer has a weight average molecular weight (M_w) of at least 180,000, plasticizer in an amount of at least 20 phr, and a glass transition temperature (Tg) of less than 46 °C, and the high Tg layer has a weight average molecular weight (M_w) of not greater than 150,000, plasticizer in an amount of less than 20 phr, a glass transition temperature (Tg) of at least 46 °C, and an E' modulus at 50 °C of at least 10,000,000 pascals.

25 11. The multilayer interlayer of claim 1, comprising at least two high M_w layers, with the high Tg interlayer disposed between the at least two high M_w layers.

12. A multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 5 46°C; and

(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin, wherein the high Tg layer has a glass transition temperature (Tg) of at 10 least 46°C.

13. The multilayer interlayer of claim 12, wherein the high Tg layer has a solution viscosity not exceeding 120 cps, and wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does 15 not exceed 100,000.

14. The multilayer interlayer of claim 12, wherein the high Tg layer comprises poly(vinyl acetal) resin has a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about 5 to 20 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50°C,

and the high M_w layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not 25 exceeding 46°C.

15. The multilayer interlayer of claim 12, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.

16. The multilayer interlayer of claim 12, the wherein Tg of the high M_w layer is at least 4 °C less than the glass transition temperature (Tg) of the high Tg layer.

5 17. A multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46 °C;

10 (B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin, wherein the high Tg layer has a glass transition temperature (Tg) of at least 46 °C; and

15 (C) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46 °C,

wherein the high Tg layer is disposed between the high M_w layers.

20

18. The multilayer interlayer of claim 17, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.

25 19. The multilayer interlayer of claim 17, the wherein glass transition temperature (Tg) of at least one of the high M_w layers is at least 4 °C less than the glass transition temperature (Tg) of the high Tg layer.

30 20. The multilayer interlayer of claim 17, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about

5 to 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50 °C,

and wherein at least one of the high M_w layers comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 5 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not exceeding 46 °C.

21. The multilayer interlayer of claim 1, wherein the high Tg layer has a glass transition temperature (Tg) of at least 50 °C.

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22. The multilayer interlayer of claim 1, wherein said high Tg layer has a glass transition temperature (Tg) of at least 52 °C.

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23. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.7.

24. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.7.

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25. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.9.

26. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 1.

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27. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 1.2.

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28. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 2.

29. The multilayer interlayer of claim 1, wherein the high Tg layer has a solution viscosity not exceeding 100 cps.
- 5 30. The multilayer interlayer of claim 1, wherein the high Tg layer and the high M_w layer contain at least 80 wt.% poly(vinyl acetal) resin.
- 10 31. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 150,000.
32. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 140,000.
- 15 33. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 120,000.
- 20 34. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 100,000.
- 25 35. The multilayer interlayer of claim 1, wherein the amount of plasticizer in the high Tg layer is at least 8 parts per hundred parts of the poly(vinyl acetal) resin.
- 30 36. The multilayer interlayer of claim 1, the wherein glass transition temperature (Tg) of the high M_w layer is at least 8 °C less than the glass transition temperature (Tg) of the high Tg layer.

37. The multilayer interlayer of claim 1, wherein the poly(vinyl acetal) resin in the high Tg and high M_w layers comprises polyvinyl butyral.

5 38. The multilayer interlayer of claim 1, wherein the poly(vinyl acetal) resin has a hydroxyl group content of 14 wt.% to 23 wt.%.

39. The multilayer interlayer of claim 38, wherein the vinyl butyral group content of the poly(vinyl acetal) resin is at least 60 wt%.

10 40. The multilayer interlayer of claim 1, wherein the entire multilayer interlayer has a thickness ranging from 15 mils to 60 mils.

15 41. The multilayer interlayer of claim 1, wherein the entire multilayer interlayer has a thickness ranging from 15 mils to 60 mils and the E' modulus of the high Tg interlayer at 40°C is at least 300,000,000 pascals and the E' modulus of the high Tg interlayer at 50°C is at least 10,000,000 pascals.

20 42. The multilayer interlayer of claim 41, wherein the E' modulus at 40°C is at least 600,000,000 pascals and an E' modulus at 50°C of at least 50,000,000 pascals.

25 43. The multilayer interlayer of claim 1, wherein the E' modulus of the high Tg interlayer at 40°C is at least 600,000,000 pascals and the E' modulus of the high Tg interlayer at 50°C is at least 50,000,000 pascals.

30 44. The multilayer interlayer of claim 1, comprising at least two high M_w layers, with the high Tg interlayer disposed between the at least two high M_w layers.

45. The multilayer interlayer of claim 1, wherein the multilayer interlayer is laminated to a glass substrate.

5 46. The multilayer interlayer of claim 1, wherein the multilayer interlayer is disposed between two layers of glass.

10 47. The multilayer interlayer of claim 1, further comprising a glass substrate and a polymer film, the polymer film being a different polymer than poly(vinyl acetal).

AMENDED CLAIMS
received by the International Bureau on 20 May 2016 (20.05.16)

1. A multilayer interlayer comprising:
 - (A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000; and
 - (B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a glass transition temperature (Tg) of at least 46°C.
2. The multilayer interlayer of claim 1, wherein the high Tg layer has a melt flow index (MFI) of at least 0.65 grams/10 minutes when measured at 190°C and under a load of 2.16 kilograms.
3. The multilayer interlayer of claim 1, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.
4. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 100,000.
5. The multilayer interlayer of claim 1, wherein the high Tg layer further comprises a plasticizer in an amount of at least 5 parts per hundred parts of the poly(vinyl acetal) resin.
6. The multilayer interlayer of claim 1, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) that does not exceed 140,000 in the high Tg layer and plasticizer in an amount ranging from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin.

7. The multilayer interlayer of claim 1, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about 5 to 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50°C, and the high M_w layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not exceeding 46°C.

8. The multilayer interlayer of claim 1, wherein the glass transition temperature (Tg) of the high M_w layer is at least 4°C less than the glass transition temperature (Tg) of the high Tg layer.

9. The multilayer interlayer of claim 1, wherein the high M_w layer and the high Tg layer each have a plasticizer, and the at least one high Tg layer has at least 7 phr less plasticizer than the high M_w layer.

10. The multilayer interlayer of claim 1, wherein the high M_w layer has a weight average molecular weight (M_w) of at least 180,000, plasticizer in an amount of at least 20 phr, and a glass transition temperature (Tg) of less than 46°C, and the high Tg layer has a weight average molecular weight (M_w) of not greater than 150,000, plasticizer in an amount of less than 20 phr, a glass transition temperature (Tg) of at least 46°C, and an E' modulus at 50°C of at least 10,000,000 pascals.

11. The multilayer interlayer of claim 1, comprising at least two high M_w layers, with the high Tg interlayer disposed between the at least two high M_w layers.

12. A multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C; and

(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin, wherein the high Tg layer has a glass transition temperature (Tg) of at least 46°C.

13. The multilayer interlayer of claim 12, wherein the high Tg layer has a solution viscosity not exceeding 120 cps, and wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 100,000.

14. The multilayer interlayer of claim 12, wherein the high Tg layer comprises poly(vinyl acetal) resin has a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about 5 to 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50°C,

and the high M_w layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not exceeding 46°C.

15. The multilayer interlayer of claim 12, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.

16. The multilayer interlayer of claim 12, wherein the Tg of the high M_w layer is at least 4°C less than the glass transition temperature (Tg) of the high Tg layer.

17. A multilayer interlayer comprising:

(A) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C;

(B) a high Tg layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) of 160,000 or less and a plasticizer in an amount of from 2 to 20 parts per hundred parts of the poly(vinyl acetal) resin, wherein the high Tg layer has a glass transition temperature (Tg) of at least 46°C; and

(C) a high M_w layer comprising a poly(vinyl acetal) resin having a weight average molecular weight (M_w) greater than 160,000 and a plasticizer, wherein the high M_w layer has a glass transition temperature (Tg) of less than 46°C,

wherein the high Tg layer is disposed between the high M_w layers.

18. The multilayer interlayer of claim 17, wherein the high Tg layer has a solution viscosity not exceeding 120 cps.

19. The multilayer interlayer of claim 17, wherein the glass transition temperature (Tg) of at least one of the high M_w layers is at least 4°C less than the glass transition temperature (Tg) of the high Tg layer.

20. The multilayer interlayer of claim 17, wherein the high Tg layer comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) not exceeding 150,000 and plasticizer in an amount ranging from about

5 to 20 parts per hundred parts of the poly(vinyl acetal) resin and has a glass transition temperature (Tg) of at least 50°C,

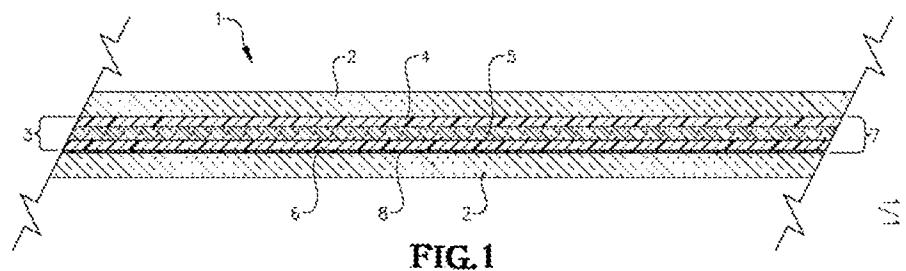
and wherein at least one of the high M_w layers comprises poly(vinyl acetal) resin having a weight average molecular weight (M_w) of at least 180,000 and plasticizer in an amount of at least 23 phr and has a glass transition temperature (Tg) not exceeding 46°C.

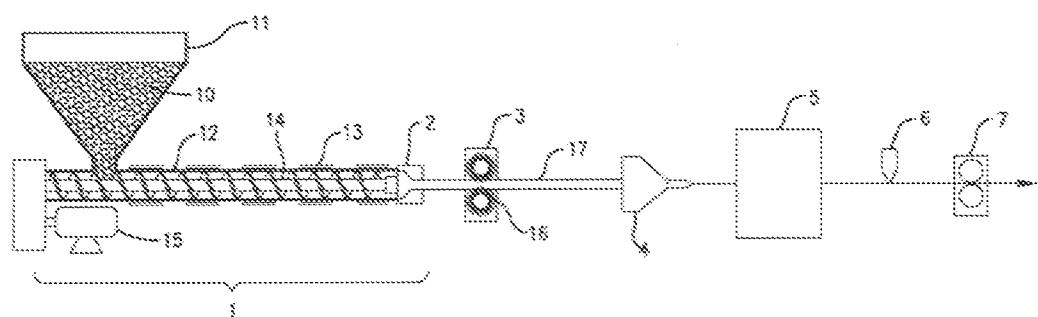
21. The multilayer interlayer of claim 1, wherein the high Tg layer has a glass transition temperature (Tg) of at least 50°C.
22. The multilayer interlayer of claim 1, wherein said high Tg layer has a glass transition temperature (Tg) of at least 52°C.
23. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.7.
24. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.8.
25. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 0.9.
26. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 1.
27. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 1.2.
28. The multilayer interlayer of claim 2, wherein the high Tg layer has a melt flow index (MFI) of at least 2.

29. The multilayer interlayer of claim 1, wherein the high Tg layer has a solution viscosity not exceeding 100 cps.
30. The multilayer interlayer of claim 1, wherein the high Tg layer and the high M_w layer contain at least 80 wt.% poly(vinyl acetal) resin.
31. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 150,000.
32. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 140,000.
33. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 120,000.
34. The multilayer interlayer of claim 1, wherein the weight average molecular weight (M_w) of the poly(vinyl acetal) resin in the high Tg layer does not exceed 100,000.
35. The multilayer interlayer of claim 1, wherein the amount of plasticizer in the high Tg layer is at least 8 parts per hundred parts of the poly(vinyl acetal) resin.
36. The multilayer interlayer of claim 1, wherein the glass transition temperature (Tg) of the high M_w layer is at least 8°C less than the glass transition temperature (Tg) of the high Tg layer.

37. The multilayer interlayer of claim 1, wherein the poly(vinyl acetal) resin in the high Tg and high M_w layers comprises polyvinyl butyral.
38. The multilayer interlayer of claim 1, wherein the poly(vinyl acetal) resin has a hydroxyl group content of 14 wt.% to 23 wt.%.
39. The multilayer interlayer of claim 38, wherein poly(vinyl acetal) resin has a vinyl butyral group content of at least 60 wt%.
40. The multilayer interlayer of claim 1, wherein the entire multilayer interlayer has a thickness ranging from 15 mils to 60 mils.
41. The multilayer interlayer of claim 1, wherein the entire multilayer interlayer has a thickness ranging from 15 mils to 60 mils and the E' modulus of the high Tg interlayer at 40°C is at least 300,000,000 pascals and the E' modulus of the high Tg interlayer at 50°C is at least 10,000,000 pascals.
42. The multilayer interlayer of claim 41, wherein the E' modulus at 40°C is at least 600,000,000 pascals and an E' modulus at 50°C of at least 50,000,000 pascals.
43. The multilayer interlayer of claim 1, wherein the E' modulus of the high Tg interlayer at 40°C is at least 600,000,000 pascals and the E' modulus of the high Tg interlayer at 50°C is at least 50,000,000 pascals.
44. The multilayer interlayer of claim 1, wherein the multilayer interlayer is laminated to a glass substrate.
45. The multilayer interlayer of claim 1, wherein the multilayer interlayer is disposed between two layers of glass.

46. The multilayer interlayer of claim 1, further comprising a glass substrate and a polymer film, the polymer film being a different polymer than poly(vinyl acetal).



**FIG. 2**

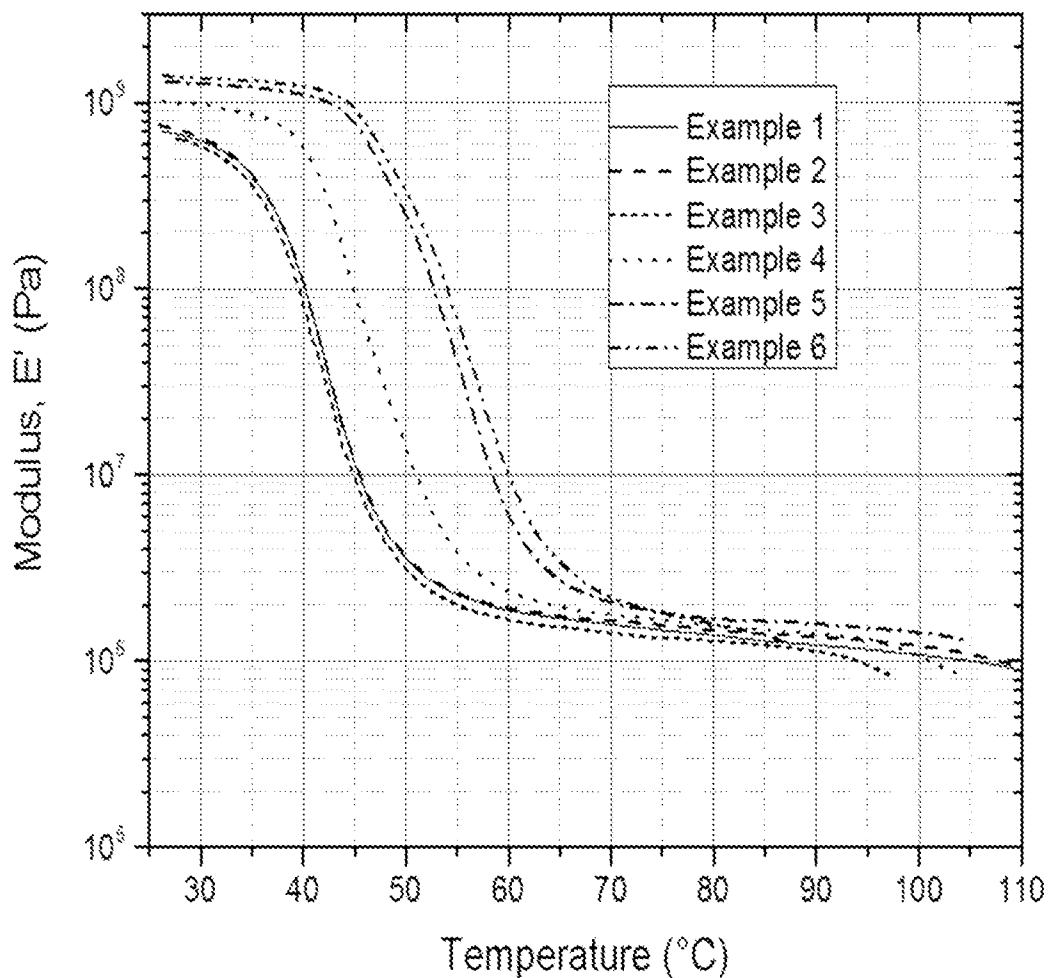


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/063896

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/30(2006.01)i, B32B 17/10(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B 27/30; B32B 17/10; B32B 27/42; B32B 3/26; B32B 27/08; C08F 18/08; H01L 31/0203; B32B 27/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: interlayer, multilayer, polyvinyl acetal, Mw, molecular weight, Tg, Glass Transition Temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012-0263958 A1 (IWAMOTO T. et al.) 18 October 2012 See paragraphs [0036], [0038], [0040], claims 1, 3 and figure 1.	1-47
A	US 2012-0244329 A1 (IWAMOTO T. et al.) 27 September 2012 See table 1 and claims 1, 7.	1-47
A	US 2013-0236711 A1 (SOLUTIA INC.) 12 September 2013 See claim 8.	1-47
A	US 2013-0074931 A1 (CHEN W et al.) 28 March 2013 See claims 18, 21, 22.	1-47
A	US 2011-0076459 A1 (LU J. et al.) 31 March 2011 See claim 1.	1-47

 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
06 April 2016 (06.04.2016)Date of mailing of the international search report
08 April 2016 (08.04.2016)Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/063896**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/063896

Box No. I Nucleotide and/or amino acid sequence(s) (Continuation of item 1.c of the first sheet)

1. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of a sequence listing:
 - a. forming part of the international application as filed:
 - in the form of an Annex C/ST.25 text file.
 - on paper or in the form of an image file.
 - b. furnished together with the international application under PCT Rule 13ter.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.
 - c. furnished subsequent to the international filing date for the purposes of international search only:
 - in the form of an Annex C/ST.25 text file (Rule 13ter.1(a)).
 - on paper or in the form of an image file (Rule 13ter.1(b) and Administrative Instructions, Section 713).
2. In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
3. Additional comments:

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2015/063896**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

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

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

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

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

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

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

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

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

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/063896

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0263958 A1	18/10/2012	CN 102666421 A CN 102666421 B CN 104558997 A EP 2518031 A1 JP 2011-207762 A JP 2015-038019 A JP 4789024 B2 JP 5829846 B2 KR 10-2012-0105011 A WO 2011-078313 A1	12/09/2012 31/12/2014 29/04/2015 31/10/2012 20/10/2011 26/02/2015 05/10/2011 09/12/2015 24/09/2012 30/06/2011
US 2012-0244329 A1	27/09/2012	CN 102686530 A CN 102686530 B CN 102686531 A CN 102686531 B CN 104649592 A EP 2520551 A1 EP 2520551 A4 JP 2012-076985 A JP 2012-076986 A JP 2015-166308 A JP 4751965 B1 JP 4751966 B1 KR 10-2012-0099737 A KR 10-2012-0120183 A US 2012-0244364 A1 US 2014-0093739 A1 US 2014-0227536 A1 US 8632887 B2 US 8734937 B2 WO 2011-081190 A1 WO 2011-081191 A1	19/09/2012 22/07/2015 19/09/2012 04/02/2015 27/05/2015 07/11/2012 03/09/2014 19/04/2012 19/04/2012 24/09/2015 17/08/2011 17/08/2011 11/09/2012 01/11/2012 27/09/2012 03/04/2014 14/08/2014 21/01/2014 27/05/2014 07/07/2011 07/07/2011
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/063896

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0076459 A1	31/03/2011	EP 2758237 A4 JP 2014-528990 A KR 10-2014-0070613 A TW 201313470 A WO 2013-043189 A1	24/06/2015 30/10/2014 10/06/2014 01/04/2013 28/03/2013