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(54) Title: METHOD FOR MANUFACTURING AN ARTICLE FROM A COMPOSITION COMPRISING A BLEND OF ONE OR MORE VDF POLYMERS AND ONE OR MORE ACRYLIC OR METHACRYLIC ESTER POLYMERS.

(57) Abstract: The present invention relates to a method manufacturing an article having a high aspect ratio said method comprising : i) providing a uniform melted polymeric composition at a temperature comprised from 120 °C to 250 °C, said composition comprising 50% to 90% by weight of one or more thermoplastic vinylidene fluoride (VDF) polymers and 10 to 50% by weight of one or more thermoplastic acrylic or methacrylic ester polymers, ii) forming said composition into an article having a high aspect ratio at an apparent wall shear stress from $1 \cdot 10^2$ Pa to $3 \cdot 10^5$ Pa.

Description

Method for manufacturing an article from a composition comprising a blend of one or more VDF polymers and one or more acrylic or methacrylic ester polymers.

Technical Field

[0001] This application claims priority to EP Appl. No. 19155159.7 filed on 01 February 2019 the whole content of this application being incorporated herein by reference for all purposes. The present invention relates to a method for manufacturing an article having a high aspect ratio from a thermoplastic composition comprising one or more selected thermoplastic vinylidene fluoride (VDF) polymers and one or more thermoplastic acrylic or methacrylic ester polymers. The resulting articles have low haze and high total light transmittance at relatively high concentration of VDF polymer and can be manufactured easily and at a fast speed.

Background Art

[0002] Acrylic and methacrylic ester polymers are known for their transparency, polymethyl methacrylate in particular (PMMA) is widely used as glass replacement, however it is also known that such polymers are delicate and sensitive to the environment, for example humidity can cause layers or sheets of PMMA to warp and harsh chemicals and environmental factors can damage PMMA surface. Polymer blends with polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA) have been described as being capable to form compositions which combine the resistance to chemical and environmental agents of VDF polymers with the clear transparency of acrylic or methacrylic ester polymers. These blends are typically thermoplastic and can be handled with conventional melt processing techniques and can form articles such as films, sheets or layers which are transparent and can find application wherever a transparent layer is required such as, for example, in coatings, as glass panel replacement, in architectural covers, in screens for TV and other electronic devices, smart devices, and the like. However many factors

influence the light transmission properties of such articles. In articles comprising one or more vinylidene fluoride (VDF) polymers and one or more acrylic or methacrylic ester polymers it is often desirable to incorporate high levels of VDF polymers, such as 50% or more by weight or 65% or more by weight, or even 70% or more by weight in order to increase the durability of the article and to improve its resistance to environmental factors, such as humidity, UV light, or harsh chemicals which can be detrimental to the PMMA component.

[0003] However, at such high weight percentage of VDF polymers, it is often difficult to obtain transparent articles. It is in fact well known that for PVDF/PMMA blends there is a sharp increase in haze when PVDF represents more than 50% by weight of the composition, in particular in the range from 50 to 80% by weight of PVDF polymer. The same holds true, in general for most blends of VDF polymers and acrylic or methacrylic ester polymers.

[0004] Also the processing conditions appear to play a role in the transparency of articles obtained from a composition comprising one or more VDF polymers and one or more acrylic or methacrylic ester polymers, in particular we found that elevated shear stress during forming of an article may increase the haze of the article thus formed.

[0005] Without being bound by theory we believe that the transparency of an article obtained by forming a polymeric composition comprising one or more VDF polymers and one or more acrylic or methacrylic ester polymers depends by multiple factors among which homogeneity of the blend, degree of crystallinity, size of the crystals, and surface finishing play the biggest roles.

[0006] There is therefore a need to develop a process for effectively manufacturing transparent articles such as for example films, sheets or layers from polymeric compositions comprising one or more VDF polymers and one or more acrylic or methacrylic ester polymers, wherein such compositions have a high level of VDF polymers. Such process should avoid using solvents and it should be possible to run such process at the

highest possible speed for efficient industrial manufacturing of such articles.

[0007] The method of the present invention addresses such a need by selecting appropriate polymers within the blend and appropriate processing equipment and settings.

Summary of invention

[0008] The present invention relates to a method for manufacturing an article having a high aspect ratio said method comprising :
i) providing a uniform melted polymeric composition at a temperature comprised from 120 °C to 250 °C, said composition comprising 50% to 90% by weight of one or more thermoplastic vinylidene fluoride (VDF) polymers and 10 to 50% by weight of one or more thermoplastic acrylic or methacrylic ester polymers,
ii) forming said composition into an article having a high aspect ratio at an apparent wall shear stress from $1*10^2$ Pa to $3*10^5$ Pa.

[0009] The one or more VDF polymers comprises from 4 to 20 moles of molecular defects per 100 moles of VDF units wherein said molecular defects are selected from: head to head inversions, chain end groups and comonomers

[0010] The one or more acrylic or methacrylic ester polymers are selected from polymers made of recurring units wherein at least 70% by moles of said recurring units are selected from methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, acrylate, methacrylate and acrylonitrile,

[0011] The polymeric composition has, a viscosity from 100 to 6000 Pa *s, preferably from 500 to 3000 Pa s, when measured at a shear rate of 10 s^{-1} and 230°C, and a haze lower than 8% and a total light transmittance over

90% when measured across 1 mm thickness with the transparency test described herein.

Description of embodiments

[0012] The present invention relates to a method for manufacturing articles from a thermoplastic polymeric composition wherein the articles have a high aspect ratio. Articles are intended to be solid articles. The term “high aspect ratio” in the present invention refers to articles having a ratio between their largest dimension to their smallest dimension which is higher than 5. One example of “high aspect ratio” articles for which the method if the invention is particularly suitable are planar articles. “Planar articles” as used herein refers to articles such as films, sheets or layers. Planar articles according to the definition extend mainly along a flat, two dimensional surface and their thickness is at least 5 times smaller than the smallest other dimensions of the article. The term “planar articles” includes flexible articles which define a surface which can be bent and shaped in response to external stimuli such as a flexible film, and it also includes rigid shaped articles which can be obtained by shaping a sheet without changing its thickness such as for example a visor for a motorcycle helmet or a layer in a curved TV screen.

[0013] For the purpose of the present invention, the term “thermoplastic” is intended to denote polymers and/or compositions which are solid at room or usage temperature, which become soft when heated and become rigid again when they are cooled, without there being an appreciable chemical and physical properties change. Such a definition may be found, for example, in the encyclopaedia called Polymer Science Dictionary. Edited by MARK S.M. ALGER. LONDON: ELSEVIER APPLIED SCIENCE, 1989. p.476.

[0014] The expressions “vinylidene fluoride polymer” or “VDF polymer” are equivalent and used within the frame of the present invention for

designating polymers essentially made of recurring units, more than 50 % by moles of said recurring units being derived from vinylidene fluoride (VDF).

[0015] A VDF polymer useful in the present invention is preferably a polymer comprising :

(a) at least 60 % by moles, preferably at least 75 % by moles, more preferably 85 % by moles of recurring units derived from vinylidene fluoride (VDF);

(b) optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of recurring units derived from a fluorinated monomer different from VDF; and

(c) optionally from 0.1 to 5 %, by moles, preferably 0.1 to 3 % by moles, more preferably 0.1 to 1% by moles of recurring units derived from one or more hydrogenated comonomer(s), wherein for “hydrogenated comonomer” it is intended a non-halogenated comonomer,

all the aforementioned % by moles being referred to the total moles of recurring units of the VDF polymer.

[0016] The said fluorinated monomer different from VDF is advantageously selected in the group consisting of vinyl fluoride (VF_1); trifluoroethylene (VF_3); chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl)vinyl ethers, such as perfluoro(methyl)vinyl ether (PMVE), perfluoro(ethyl) vinyl ether (PEVE) and perfluoro(propyl)vinyl ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD). Preferably, the possible additional fluorinated monomer is chosen from chlorotrifluoroethylene (CTFE), hexafluoroproylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE).

[0017] The choice of the said hydrogenated comonomer(s) is not particularly limited; alpha-olefins, (meth)acrylic monomers, vinyl ether monomers, styrenic monomers may be used.

[0018] Accordingly, a VDF polymer for use in the present invention is more preferably a polymer consisting essentially of :

(a) at least 60 % by moles, preferably at least 75 % by moles, more

preferably 85 % by moles of recurring units derived from vinylidene fluoride (VDF);

(b) optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of a fluorinated monomer different from VDF; said fluorinated monomer being preferably selected in the group consisting of vinylfluoride (VF_1), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), tetrafluoroethylene (TFE), perfluoromethylvinylether (MVE), trifluoroethylene (TrFE) and mixtures therefrom,

all the aforementioned % by moles being referred to the total moles of recurring units of the VDF polymer.

[0019] As non-limitative examples of VDF polymers useful in the present invention, mention can be notably made of homopolymers of VDF, VDF/TFE copolymers, VDF/TFE/HFP copolymers, VDF/TFE/CTFE copolymers, VDF/TFE/TrFE copolymers, VDF/CTFE copolymers, VDF/HFP copolymers, VDF/TFE/HFP/CTFE copolymers and the like.

[0020] In the present invention the one or more VDF polymers must be selected among VDF polymers having 4 to 20, more preferably 4.5 to 15, even more preferably 5 to 10 moles of molecular defects per 100 moles of VDF polymer. The expression “molecular defects” in the context of the present invention indicates all the structural anomalies with respect to the regular monomer sequence of a linear VDF homopolymer. In particular in the context of the present invention are considered “molecular defects” head to head inversions, chain end groups and comonomers, these defects will be now described more in detail.

[0021] When the polymerization of VDF units is “ideal” this results in a linear chain of recurring units $–(CF_2\text{-}CH_2)-$ with two end groups at the extremities. One “head to head inversion” occurs when a unit $–CF_2\text{-}CH_2\text{-}CH_2\text{-}CF_2-$ or $–CH_2\text{-}CF_2\text{-}CF_2\text{-}CH_2-$ is formed. Commonly “head to head inversions” occur in pairs forming a sequence

$$–CF_2\text{-}CH_2\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}CF_2\text{-}CH_2-$$

in this case, since the second inversion appears to correct the first, are called “repaired inversions”. Each VDF polymer has a certain amount of

head to head inversions, their number mainly depends on the temperature of polymerization, increasing with increased temperature of polymerization. The amount of head to head inversions can be measured by NMR spectroscopy as described in the "Test Methods" section below.

[0022] Another class of molecular defects are the chain end groups. As mentioned above, an ideal PVDF chain has 2 end groups. However a certain amount of chain branching points are often formed during polymerization of VDF monomers. In general the amount of chain branching is influenced by the temperature of polymerization (higher temperature of polymerization leads to a higher amount of chain branching) and by the pressure of polymerization (higher pressure of polymerization leads to lower chain branching). Typically each chain branching point generates a new end group, therefore the amount of end groups is correlated to the amount of chain branching. The amount of chain end groups can be measured by NMR spectroscopy as described in the "Test Methods" section below.

[0023] For the purpose of the present invention also co-monomers are considered as molecular defects because co-monomers, beyond VDF, disrupt the "ideal" chain sequence of PVDF in a similar way than head to head inversions and chain branching points do.
It has been surprisingly found that the effect on the transparency of the articles obtained by the method of the invention is substantially the same irrespective from the nature of the defect, in particular the molar amount of co-monomers has an effect similar to the molar amount of head to head inversion and/or chain branching points.

[0024] VDF polymers for use in the present invention preferably have a number average molecular weight of from 10000 to 1000000 dalton, preferably from 30000 to 200000 dalton.

[0025] The expression "acrylic or methacrylic ester polymers" refers to polymers made of recurring units wherein at least 70% by moles of said recurring units are selected from methyl methacrylate, methyl acrylate, ethyl

methacrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, acrylate, methacrylate and acrylonitrile.

[0026] The expression “methyl methacrylate polymer” or “MMA polymer” are equivalent and used within the frame of the present invention for designating polymers made of recurring units, wherein more than 70 % by moles of said recurring units being derived from methyl methacrylate (MMA).

[0027] Preferred acrylic or methacrylic ester polymers for the present invention are MMA polymers. Among MMA polymers, preferred polymers are MMA polymers comprising at least 70% in moles of MMA recurring units and from 0% to 30% of other recurring units being derived from methyl acrylate, ethyl methacrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, acrylate, methacrylate and acrylonitrile. The most preferred acrylic or methacrylic ester polymer is PMMA.

[0028] The present invention relates to a method of manufacturing an article having a high aspect ratio, wherein the method comprises:
i) providing a uniform melted composition at a temperature from 120°C to 250°C comprising from 50% to 90%, preferably from 60% to 85%, more preferably from 70% to 80% by weight of one or more thermoplastic vinylidene fluoride (VDF) polymers as defined above and from 10% to 50%, preferably from 15% to 40%, more preferably from 20% to 30% by weight of one or more thermoplastic acrylic or methacrylic ester polymers as defined above, and
ii) forming said composition into an article having a high aspect ratio at an apparent wall shear stress of from $1*10^2$ Pa to $3*10^5$ Pa.

[0029] The expression “uniform melted polymeric composition” refers to a mixture of two or more melted polymers in a single phase. Such composition can be obtained with conventional techniques available to the skilled person, by selecting appropriate polymers, melting them at a temperature above the highest melting point of all the polymers in the composition (or above the highest T_g in case for some polymer T_g is higher than its melting point)

and thoroughly mixing the melted polymers so to form a single phase blend. The starting materials for obtaining the uniform melted polymeric composition can be selected from individual polymers or pre-prepared polymeric compositions in solid form, preferably in divided form such as pellets, granules or powders. In one embodiment the method of the invention comprises a step wherein the individual polymers making up the polymeric composition in divided form are loaded into a twin screw extruder, melted at a temperature above the highest melting temperature (or above the highest T_g in case for some polymer T_g is higher than its melting point), thoroughly mixed so to form a uniform melted polymeric composition, extruded, preferably trough one or more capillary dies, cooled and preferably turned into a divided form such as pellets, granules of powders of the polymeric compositions. In order to perform the method of the invention such solid polymeric composition in divided form can be then introduced into an appropriate forming equipment such as for example a single screw extruder, the temperature within such equipment can be raised to an appropriate temperature from 120°C to 250°C, high enough so to completely melt the composition, thereby providing the uniform melted polymeric composition of the invention which can then be formed into an article having a high aspect ratio in step ii) of the method.

[0030] It is in general preferred to form an article having a high aspect ratio using a single screw extruder because this type of equipment is known to provide a better control on the extruded articles. On the other hand, a twin screw extruder is more efficient in mixing up a melted polymer mixture so to ensure uniformity of the resulting composition, it is therefore preferred to pre-make such composition starting from the individual polymers into a twin screw extruder, and subsequently transfer said composition, preferably in solid pelletized form, into a single screw extruder so to form the final article having a high aspect ratio.

[0031] According to the present invention the polymers for the polymeric composition must be selected so that the resulting polymeric composition has a viscosity from 100 to 10000 Pa·s, preferably from 100 to 6000 Pa·s,

more preferably from 500 to 3000 Pa*s when measured at 230°C and at a shear rate of 10 s^{-1}. As known to the skilled person, the viscosity for a given polymer is essentially proportional to its molecular weight, however the viscosity of a blend is influenced by the viscosity of all the components, so that the addition of a low viscosity/low molecular weight component will lower the viscosity of the whole composition and vice versa. Based on this a skilled person will be able to easily select the appropriate molecular weights for the polymers to be used in the present composition thereby obtaining a viscosity in the required range.

[0032] A polymeric composition for use in the present invention must also have a haze lower than 8% and a total light transmittance over 90% when measured across 1 mm thickness with the transparency test described below in the test methods section. In general it is known that a given composition can be made more clear/less hazy by reducing the ratio between VDF polymers and acrylic or methacrylic ester polymers. Therefore also in this case a skilled person is able to provide such composition with the required degree of haze and transmittance by varying the ratio between its components.

[0033] In step ii) of the method of the present invention the uniform melted polymeric composition is formed into an article having a high aspect ratio using conventional techniques such as preferably extrusion, more preferably using a single screw extruder and a slit die, wherein the apparent wall shear stress is of from $1*10^2$ Pa to $3*10^5$ Pa, preferably from $2*10^3$ Pa to $3*10^5$ Pa, more preferably from $1*10^4$ Pa to $1*10^5$ Pa. The apparent wall shear stress can be easily calculated by measuring the composition viscosity at the forming conditions, the volumetric flow, and the geometry of the die using the formulas reported in (J.A. Brydson, Flow Properties of Polymer Melts, 2° edn., Chapter 2 and Appendix, published by George Godwin Ltd, London, 1981). In this step the uniform melted polymeric composition is typically pushed through a die, preferably a slit die. Process parameters such as pressure, viscosity of the uniform melted

polymeric composition at the temperature of forming, speed of the screw if using a screw extruder, can be controlled so that the apparent wall shear stress is within the required range.

[0034] A die which may be used to form an article having a high aspect ratio has preferably the shape of a slit, wherein its thickness is least 5 times smaller than its length.

[0035] It has been surprisingly found that using the claimed combination of composition, viscosity and shear stress it is possible to obtain articles with reduced haze and improved total light transmittance, for example articles having less than 8% haze and over 90% of total light transmittance when measured along the direction having the highest total light transmittance.

[0036] One additional parameter which can further impact crystal formation, crystal growth and, ultimately, haze and light transmittance is the cooling speed of the extruded article. In general it has been observed that using conventional extrusion techniques wherein the extruded material is cooled in a cold water bath or it is laid down on one or more cold calender rolls a satisfactory transparency is obtained. Preferably the water bath and the calender roll(s) are cooled at a Temperature below 15°C: this ensures quick solidification of articles having a relatively high thickness and can further improve the haze and light transmittance properties of the article.

[0037] As conventionally made during the extrusion of sheets and films, the calender roll can move at a speed faster than the speed at which the sheet or film is extruded thereby stretching the film or sheet which results in a thinner film or sheet and typically in imparting directional optical and mechanical properties to the resulting article.

[0038] The extrusion method described above is a preferred execution of the present invention, which however should not be intended to be limited to methods of extrusion. In fact according to the present invention the uniform melted polymeric composition can be transformed into the finished article having a high aspect ratio using, alone or in combination, any of the conventional technologies used in the plastic industry to form films, sheets

or layers, such as slit extrusion, tube extrusion, film casting, calendering, film blowing, blow molding, injection molding, compression molding, thermoforming and the like.

[0039] Articles manufactured with the method of the present invention have typically their smaller dimension from 1 micro metre to 5 mm, preferably from 100 micro meters to 3 mm.

[0040] Articles made using the method of the present invention can be used wherever a transparent layer is required such as, for example, in coatings, as glass panel replacement, in architectural covers, in screens for TV and other electronic devices, smart devices, and the like.

[0041] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0042] The invention will be now described in more detail in connection with the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

[0043] **Examples**

[0044] **Raw materials**

[0045] Thermoplastic VDF polymers: two different PVDF homopolymers have been used in the examples. PVDF 1 is a VDF homopolymer prepared by emulsion polymerization having an amount of molecular defects of 5.8 moles per 100 moles of VDF (head-to-head inversions 5 moles per 100 moles of VDF, chain end groups 0.8 moles per 100 moles of VDF) and a Melt Flow Index (measured at 5 kg and 230°C) of 18 g/10'.

[0046] PVDF 2 is VDF homopolymer prepared by suspension polymerization having an amount of molecular defects of 3.7 moles per 100 moles of VDF (head-to-head inversions 3.6 moles per 100 moles of VDF, chain end groups 0.1 moles per 100 moles of VDF) and a Melt Flow Index (measured at 5 kg 230°C) of 20 g/10'.

[0047] In all examples polymethyl methacrylate (PMMA) Acryrex CM 211 G from Chimei was used as thermoplastic methacrylic ester polymer.

[0048] **Inventive Example. 1**

A mixture containing 70% PVDF1 and 30 % of PMMA has been melted and extruded in pellets in a twin screw extruder. This composition has a viscosity of 1170 Pa*s measured at 10 s^{-1} shear and 230°C temperature. This composition has a haze of 4% and a total light transmittance of 92% when measured across 1 mm thickness with the transparency test described herein. The composition was introduced into a single screw extruder, melted at 200°C and extruded at 2.5 kg/h using a slit die 4 cm wide and 1 mm thick, which correspond to an apparent wall shear stress of 35,000 Pa . The extruded article was cooled in a water bath and collected on moving tape. This article has a haze of 1%, and a total light transmittance of 94%.

[0049] **Comparative Example 2**

The same uniform melted polymeric composition of Example 1 in the same single screw extruder was melted at 200°C and extruded at 30 kg/h, which correspond to an apparent wall shear stress of 420,000 Pa using the same slit die of Example 1. The article was cooled and collected as in Example 1. The resulting article has a haze of 60% and a total light transmittance of 85%.

[0050] **Comparative Example 3**

A mixture was prepared and extruded as in Example 1 replacing the VDF polymer PVDF1 with PVDF 2. This composition has a viscosity of 950 Pa*s measured at 10 s^{-1} shear and 230°C temperature. This composition has a haze of 52% and a total light transmittance of 89 % when measured across 1 mm thickness with the transparency test described herein. The article obtained has a haze of 50% and a light transmittance of 88% .

[0051] **Test methods**

Molecular defects: As mentioned above, the amount of molecular defects in a VDF polymer can be measured with NMR spectroscopy with techniques which are known in the art.

[0052] The amount of "head to head inversions" and of "end groups" of the polymers was measured by NMR analysis, by recording the NMR spectra at 60°C on a Varian VNMS 500 NMR spectrometer operating at 499.86 MHz for ^{1}H and 470.28 MHz for ^{19}F using a Triple HFCP-PFG probe with 5 mm 502-8 (Norell, Inc.) NMR sample tubes. The NMR experiments were carried out using 40 mg of sample solution in 0.75 ml of deuterated acetone (99.9% D, obtained from Sigma-Aldrich) with tetramethylsilane (TMS) used as an internal standard. ^{1}H NMR was performed using 45 degree pulse length of 5.05 us, 5 s relaxation delay, 2.3 s acquisition time, 16 K complex points, 7 kHz spectral width and 1500 repetitions.
^{19}F NMR was performed using 45 degree pulse length of 4.44 us, 5 s relaxation delay, 0.695 s acquisition time, 16 K complex points, 23.5 kHz spectral width and 2000 repetitions.

[0053] The determination of the amount of "head to head inversions" (HH), expressed in moles of "head to head inversions" for 100 moles of VDF monomers was obtained by the following expression:

$$HH = 100 \times I_{HH} / I_{TOT}$$

where I_{HH} are normalized integrated intensities of the corresponding "head to head inversions" signals, I_{TOT} is the sum of all the normalized integrated intensities of HH and non inverted VDF units. The method is in accordance with the established procedure described in "Russo S.; Behari K.; Shan C. J.; Polymer 1993, 34, 4777-4781".

[0054] The determination of the amount of the end groups (EG), expressed in moles of end groups for 100 moles of VDF monomers was obtained by the following expression:

$$EG = 100 \times I_{EG} / I_{TOT}$$

where I_{EG} are normalized integrated intensities of the corresponding endgroup signals, I_{TOT} is the sum of all the normalized integrated intensities of EG and VDF units.

The method is in accordance with the established procedure described in "Pianca M, Barchiesi E, Esposto G, Radice S. J Fluorine Chem. 1999;95:71–84".

[0055] Viscosity was measured according to ASTM D3835-02 using a Gottfert capillary rheometer equipped with 1 mm Hastelloy C die with a length-to-diameter ratio of 20, at 230 °C and 10 s^{-1}shear rate.

[0056] Haze and Total Light transmittance (ARTICLE) of the article having a high aspect ratio was measured according to ASTM 1003-13 (procedure A) on the article resulting from the process of the invention as is, after forming and conditioning 24 hours at room T (25°C) along the direction having the highest total light transmittance.

[0057] Haze and Total Light transmittance (COMPOSITION) for the transparency test of the polymeric composition (measured before forming the article resulting from the process of the invention) were measured with the following method:
an assembly was prepared composed by, from bottom to top, a molding metal plate (20x20x0.3 cm), a 12x12x0.02 cm film of aluminium, a 12x12x 0.02 cm film of Kapton, a 10 x 10 x 0.1 cm molding cavity.
20 grams of pellets from the polymeric composition were uniformly spread, in the molding cavity, then a second equal film of Kapton, a second equal film of Aluminum and a second equal metal plate were superimposed in this order. The assembly was put in the mold without applied force for 5 minutes, heating the mold up to 230°C and for 2 minutes under 16 tons compression. Then the assembly has been quickly transferred into a water-cooled press at a 150 bar pressure and cooled for 10 minutes. A 1mm sheet was thereby obtained which was conditioned 24 hours at room

T (25°C). The conditioned sheet was then measured for Haze and Total light transmittance according to ASTM 1003-13 (procedure A).

Claims

Claim 1

A method for manufacturing an article having a high aspect ratio said method comprising :

i) providing a uniform melted polymeric composition at a temperature comprised from 120 °C to 250 °C, said composition comprising 50% to 90% by weight of one or more thermoplastic vinylidene fluoride (VDF) polymers and 10 to 50% by weight of one or more thermoplastic acrylic or methacrylic ester polymers,

ii) forming said composition into an article having a high aspect ratio at an apparent wall shear stress from $1*10^2$ Pa to $3*10^5$ Pa.

wherein

- said one or more VDF polymers comprises from 4 to 20 moles of molecular defects per 100 moles of VDF units wherein said molecular defects are selected from: head to head inversions, chain end groups and comonomers

- said one or more acrylic or methacrylic ester polymers are selected from polymers made of recurring units wherein at least 70% by moles of said recurring units are selected from methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, acrylate, methacrylate and acrylonitrile,

- said polymeric composition having, a viscosity from 100 to 6000 Pa *s, preferably from 500 to 3000 Pa s, when measured at a shear rate of 10 s^{-1} and 230°C,

- said polymeric composition having a haze lower than 8% and a total light transmittance over 90% when measured across 1 mm thickness with the transparency test described herein.

Claim 2

A method according to claim 1 wherein said one or more vinylidene fluoride polymers comprise at least 60 % by moles, preferably at least 75 % by moles, more preferably 85 % by moles of recurring units derived from vinylidene fluoride.

Claim 3

A method according to claim 1 or 2 wherein said one or more VDF polymers are selected from homopolymers of VDF, VDF/TFE copolymers, VDF/TFE/HFP copolymers, VDF/TFE/CTFE copolymers, VDF/TFE/TrFE copolymers, VDF/CTFE copolymers, VDF/HFP copolymers, VDF/TFE/HFP/CTFE.

Claim 4

A method according to any preceding claim wherein said one or more acrylic or methacrylic ester polymers are selected from methyl methacrylate polymers ("MMA polymers") comprising at least 70% in moles of MMA recurring units and from 0% to 30% of other recurring units being derived from methyl acrylate, ethyl methacrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, acrylate, methacrylate and acrylonitrile.

Claim 5

A method according to any preceding claim wherein said uniform melted composition comprises from 60% to 85%, preferably from 70% to 80% by weight of said one or more thermoplastic vinylidene fluoride (VDF) polymers.

Claim 6

A method according to any preceding claim wherein said uniform melted composition comprises from 15% to 40%, preferably from 20% to 30% by weight of said one or more thermoplastic acrylic or methacrylic ester polymers.

Claim 7

A method according to any preceding claim wherein said uniform melted composition has a viscosity from 100 to 6000 Pa*s, preferably from 500 to 3000 Pa*s when measured at 230°C and at a shear rate of 10 s^{-1}.

Claim 8

A method according to any preceding claim wherein said composition is formed into an article having a high aspect ratio at an apparent wall shear stress of from $2*10^3$ Pa to $3*10^5$ Pa, preferably from $1*10^4$ Pa to $1*10^5$ Pa.

Claim 9

A method according to any preceding claim wherein said composition is formed into an article having a high aspect ratio using an extruder, preferably a single screw extruder.

Claim 10

A method according to any preceding claim wherein said composition is formed into an article having a high aspect ratio using a slit die having its thickness at least 5 times smaller than its length.

Claim 11

A method according to any preceding claim wherein said article having a high aspect ratio is a planar article.

Claim 12

A method according to any preceding claim wherein said article having a high aspect ratio is a film, sheet or layer.

Claim 13

A method according to any preceding claim wherein said article having a high aspect ratio has its smallest dimension of from dimension from 1 micro metre to 5 mm, preferably from 100 micro meters to 3 mm.

Claim 14

A method according to any preceding claim wherein said article having a high aspect ratio has less than 8% haze and over 90% of total light transmittance measured along the direction having the highest total light transmittance.

Claim 15

The use of an article having a high aspect ratio manufactured with the method of any preceding claim in a screen for an electronic device.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/052357

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/18 C08L27/16 B29C48/00 B29C48/08
ADD. C08L33/06 C08L33/12

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)
C08J C08L B29C B29K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/199830 A1 (SUMITOMO CHEMICAL CO [JP]) 15 December 2016 (2016-12-15)	15
Y	claims 1,18,19,20 examples 4,5,6 tables 2,4,5	1-14

Y	WO 96/40480 A1 (AVERY DENNISON CORP [US]; ENLOW HOWARD H [US] ET AL.) 19 December 1996 (1996-12-19) page 48, line 14 - page 52, line 35 example 13	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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