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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
28 September 2017 (28.09.2017)

WIPO | PCT

(10) **International Publication Number**
WO 2017/165746 A1

(51) **International Patent Classification**:
C08F 20/06 (2006.01) ***C08F 220/18*** (2006.01)
C08F 20/18 (2006.01) ***C08L 33/08*** (2006.01)
C08F 12/06 (2006.01) ***C08L 33/10*** (2006.01)
C08F 120/18 (2006.01) ***C08L 33/12*** (2006.01)
C08F 220/06 (2006.01)

(21) **International Application Number**:
PCT/US2017/023986

(22) **International Filing Date**:
24 March 2017 (24.03.2017)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
62/313,284 25 March 2016 (25.03.2016) US

(71) **Applicant**: **ARKEMA FRANCE** [FR/FR]; 420 Rue d'Estienne d'Orves, 92700 Colombes (FR).

(72) **Inventors; and**
(71) **Applicants** *(for US only)*: **CHERIAN, Zeena** [US/US]; 304 Landers Ct., Exton, Pennsylvania 19341 (US). **VERMOGEN, Alexandre** [FR/FR]; 9 rue des Alpes, 69510 Soucieu en Jarrest (FR). **YOCCA, Kevin R.** [US/US]; 660 N. Limerick Road, Schwenksville, Pennsylvania 19473 (US). **LYONS, Jason M.** [US/US]; 333 Winding Way, King of Prussia, Pennsylvania 19406 (US). **HAJJI, Philippe** [FR/FR]; Lieu dit Biers, 69380 Chatillon d'Azergues (FR).

(74) **Agents**: **ROLAND, Thomas** et al.; Arkema, Inc., 900 First Avenue, King of Prussia, Pennsylvania 19406 (US).

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

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

[Continued on next page]

(54) **Title**: ENHANCED MELT STRENGTH THERMOPLASTIC FORMULATION

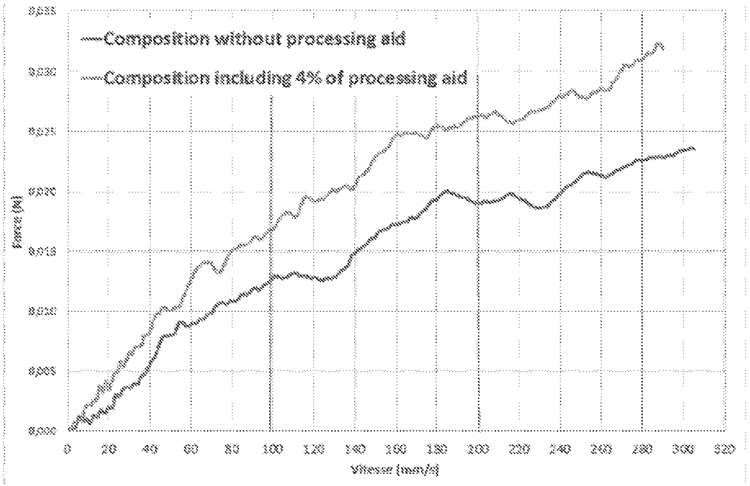

Figure 1. Melt strength curves of the pure thermoplastic matrix and the compound including 4% of an acrylic processing aid.

(57) **Abstract**: The invention relates to a thermoplastic formulation having a thermoplastic matrix and 1-40 percent by weight of a high molecular weight acrylic processing aid, with a weight average molecular weight of greater than 100,000 g/mol. The formulation has a high melt strength, yet is processable under typical melt processing conditions. The formulation is useful for melt-processed products, including extruded products such as extruded sheet, foam, co-extruded profiles, blown films, and other objects typically formed by a heat processing operation.

WO 2017/165746 A1

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

ENHANCED MELT STRENGTH THERMOPLASTIC FORMULATION

FIELD OF THE INVENTION

The invention relates to a thermoplastic formulation having a thermoplastic matrix and 1-40 percent by weight of a high molecular weight thermoplastic processing aid, with a weight average molecular weight of greater than 100,000 g/mol. The formulation has a high melt strength, yet is processable under typical melt processing conditions. The formulation is useful for melt-processed products, including extruded products such as extruded sheet, foam, co-extruded profiles, blown films, and other objects typically formed by a heat processing operation.

BACKGROUND OF THE INVENTION

Thermoplastics are highly versatile polymers which are easily melt-processed into many different shapes, such as profiles, sheets, rods; molded and blow molded into films and objects; and extruded or co-extruded over many other thermoplastic substrates.

The melt strength of a thermoplastic polymer formulation is a key factor in the success of many melt-process operations. In a foam, higher melt strength prevents uncontrolled expansion of the foam cells, to provide a small, uniform cell size. Higher melt strength also prevents a foam from collapsing prior to cooling, and locks in the foam structure. In other melt-processing operations, the high melt strength allows the pulling of a hot, extruded solid or foamed material through sizing or calibrating equipment. When co-extruding a thermoplastic, high melt strength provides the polymer melt with integrity, so a continuous material is formed without gaps.

One way to increase the melt strength of a polymer formulation is to increase the average molecular weight of the polymer. While this approach results in a high melt strength, the melt viscosity can quickly increase to the point that the melt is too thick to process in typical melt processing equipment. Higher melt strength is also known to result from the presence of the higher degree of long chain branching and network/cross-linked structures that can be found in the very high molecular weight process aids. Long chain branching can be introduced in polymers via irradiation or by modification of the polymerization process.

Melt processing aids, which are high molecular weight compatible polymers, have been used in the PVC industry (US 2009/0093560) to increase the melt strength of a PVC formulation.

In the paper "Effect of High Molecular Weight Acrylic Copolymers on the Viscoelastic Properties of Engineering Resins", *Journal of Vinyl & Additive Technology* – 2006, p 143-150, N. Mekhilef et al. measured the effects of acrylic process aids of 2.5 to 4.9 million Daltons on acrylic and polycarbonate formulations. The present invention uses acrylic process aids at much higher molecular weights, which allows for a lower usage of the process aid. The lower usage of a process aid leads to less effect on mechanical properties such as modulus and hardness of articles made with Applicant's formulation.

There is a need for a high melt strength thermoplastic formulation having a low enough melt viscosity that allows for processing under typical melt-processing conditions.

Surprisingly, it has now been found that low levels of high molecular weight thermoplastic processing aids can be added to a thermoplastic matrix to significantly increase the melt strength of the thermoplastic formulation, with little or no increase in melt viscosity – allowing the high melt strength formulation to be melt processed in typical equipment under typical conditions. The high molecular weight acrylic processing aids have a molecular weight of greater than 100,000 g/mol. The thermoplastic formulation, in which the processing aid can be used at lower levels, has a minimal effect on mechanical properties such as modulus and hardness in articles made with Applicant's formulation. Due to the low use levels and the shear thinning behavior of the high molecular weight process aid with high polydispersity, the viscosity at typical processing conditions can be minimally affected.

SUMMARY OF THE INVENTION

The invention relates to a high melt strength thermoplastic formulation comprising:

a) a thermoplastic matrix comprising a thermoplastic polymer;
b) 1 to 40 weight percent of a high molecular weight acrylic process aid,

wherein said high molecular weight acrylic process aid has a molecular weight or greater than 100,000 g/mol.

The invention further relates to a high strength thermoplastic formulation in which the matrix may optionally be impact-modified.

The invention further relates to articles that are made from the high impact strength thermoplastic formulation, and also to melt processes for forming those articles.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the melt strength curves of the pure thermoplastic matrix and the compound including 4% of an acrylic processing aid of Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a thermoplastic formulation having a high melt strength, yet where the formulation is processable under typical melt-processing conditions. The formulation contains 1-40 weight percent, preferably from 3 to 25 weight percent, and most preferably from 5 to 15 weight percent, of a high molecular weight acrylic polymer process aid, and a matrix thermoplastic polymer, that is optionally impact modified.

“Copolymer” is used to mean a polymer having two or more different monomer units. “Polymer” is used to mean both homopolymer and copolymers. Polymers may be straight chain, branched, star comb, block, or any other structure. The polymers may be homogeneous, heterogeneous, and may have a gradient distribution of co-monomer units. All references cited are incorporated herein by reference. As used herein, unless otherwise described, percent shall mean weight percent. Molecular weight is a weight average molecular weight as measured by GPC. In cases where the polymer contains some cross-linking, and GPC cannot be applied due to an insoluble polymer fraction, soluble fraction/ gel fraction or soluble faction molecular weight after extraction from gel is use.

Acrylic Process Aid

The acrylic polymer process aids of the invention are high molecular weight acrylic polymers. Other polymers miscible with polymethyl methacrylate may also be used in conjunction with the high molecular weight acrylic polymer, including but not limited to polylactic acid and polyvinylidne fluoride. By “high molecular weight” is meant that the polymers have a weight average molecular weight of greater than 100,000 g/mol, preferably greater than 500,000 g/mol, more preferably greater than 1 million g/mol, and more preferably greater than 5 million g/mol. Acrylic polymers having a weight average molecular weight of 8 million g/mol or greater are also contemplated by the invention.

The acrylic process aid preferably contains at least 50 weight percent of methyl methacrylate monomer units, and optionally comonomers, up to 50 weight percent. The methyl methacrylate monomer units, make up from greater than 50 to 100 percent of the monomer mixture, preferably from 70 to 100 weight percent, and more preferably from 80 to 100 weight percent. 0 to less than 50 weight percent of other acrylate and methacrylate monomers or other ethylenically unsaturated monomers, included but not limited to, styrene, alpha methyl styrene, acrylonitrile, and crosslinkers at low levels may also be present in the monomer mixture. Suitable acrylate and methacrylate comonomers include, but are not limited to, methyl acrylate, ethyl acrylate and ethyl methacrylate, butyl acrylate and butyl methacrylate, iso-octyl methacrylate and iso-octyl acrylate, lauryl acrylate and lauryl methacrylate, stearyl acrylate and stearyl methacrylate, isobornyl acrylate and isobornyl methacrylate, methoxy ethyl acrylate and methoxy methacrylate, 2-ethoxy ethyl acrylate and 2-ethoxy ethyl methacrylate, and dimethylamino ethyl acrylate and dimethylamino ethyl methacrylate monomers. (Meth) acrylic acids such as methacrylic acid and acrylic acid can be useful for the monomer mixture. In addition to carboxyl functionality, other functionality can be added to the high molecular weight acrylic process aid through functional comonomers, including epoxy (such as glycidyl methacrylate), hydroxyl, and anhydride functional groups. Functional monomer units (monomer units having a functional group) can be present at up to 70 weight percent of the acrylic polymer, preferably up to 50 weight percent.

Most preferably the acrylic polymer is a copolymer having 70 – 99.5 weight percent and more preferably 80 to 99 percent of methyl methacrylate units and from 0.5 to 30 weight percent of one or more C_{1-8} straight or branched alkyl acrylate units.

In one embodiment, the polydispersity index of the high molecular weight acrylic process aid is in the range of 1.5 to 50, preferably from 2 to 40, and most preferably from 3 to 30.

The high molecular weight acrylic process aid has a Tg of from -60 to 140°C, preferably from 0 to 120°C.

The acrylic polymer can be an alloy with one or more compatible polymers, including ASA, PVDF and PLA. Preferred alloys are PMMA/polyvinylidene fluoride (PVDF) alloys, and PMMA/polylactic acid (PLA) alloys. The alloy contains 20 to 99 weight percent, preferably 50 to 95 weight percent, and more preferably 60-90 weight percent of the thermoplastic matrix, and 5 to 40 weight percent, preferably 10 to 30 weight percent of the compatible polymer.

While the high molecular weight acrylic process aid can be formed by any known polymerization process, such as emulsion, suspension, solution and reverse emulsion polymerization, emulsion polymerization is the preferred process for producing the high molecular weight acrylic polymer.

Thermoplastic polymer matrix

The polymer matrix of the invention is a thermoplastic, and preferably a thermoplastic that is compatible with the high molecular weight acrylic process aid. By compatible, as used herein, means that the polymers can be homogeneously mixed in the melt, without phase separation on a macro level. Useful matrix thermoplastic polymers include, but are not limited to, styrenic-based polymers, polyesters, polycarbonate, polyvinylidene fluoride, and thermoplastic polyurethane (TPU), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), PET-co-PEN, glycol-modified polyethylene terephthalate (PETG), PET-co-PETG, polycarbonate (PC), acrylonitrile-styrene-acrylate (ASA) copolymers, high-impact polystyrene (HIPS), polyether ether ketone (PEEK), polyether ketone (PEKK), acrylonitrile-butadiene-styrene (ABS) copolymers, polyolefins, and functional polyolefins. Acrylic and polyvinyl chloride matrices are not included in the invention.

The thermoplastic polymer can be an alloy with one or more compatible polymers, including but not limited to, ASA, PVDF and PLA. The alloy contains 2 to 95 weight percent, preferably 5 to 90 weight percent, and more preferably 20-80 weight percent of the thermoplastic homopolymer or copolymer, and 5 to 98 weight percent, preferably 10 to 95 weight percent and more preferably 20 to 80 weight percent of the compatible polymer.

The thermoplastic polymer matrix may contain additives, including impact modifiers, and other additives typically present in polymer formulations, including but not limited to, stabilizers, plasticizers, fillers, coloring agents, pigments, dyes, antioxidants, antistatic agents, surfactants, toner, refractive index matching additives, matting agents, cross-linked polymer beads, additives with specific light diffraction, light absorbing, or light reflection characteristics, and dispersing aids. In one embodiment, an additive is provided to help prevent degradation of the composition upon exposure to radiation, such as high levels of UV radiation or gamma radiation. Useful radiation stabilizers include, but are not limited to poly(ethylene glycol), poly(propylene glycol), butyl lactate, and carboxylic acids such as lactic acid, oxalic acid, acetic acid, or a mixture thereof. For foaming, a chemical blowing agent, such as monosodium citrate may be incorporated directly into the thermoplastic formulation, especially in a compounding step below the activation temperature of the blowing agent, or dry blended into the formulation immediately before foam extrusion.

Useful impact modifiers include block copolymers, graft copolymers, and core/shell impact modifiers that are refractive-index matched to the matrix polymer. In a preferred embodiment, the impact modifier comprises at least 50 weight percent of acrylic monomer units. The impact modifier may be present at a level of from 0 to 80 weight percent, preferably 5 to 45, and more preferably from 10 to 30 weight percent, based on the total layer of matrix polymer and all additives. The level of impact modifier can be adjusted to meet the toughness needs for the end use of the composition. Core-shell impact modifiers are multi-stage, sequentially-produced polymer having a core/shell particle structure of at least two layers. In one embodiment, the core-shell impact modifier has a soft (elastomeric) core, and a hard shell (greater than a Tg of 20°C). Preferentially, the core-shell modifier comprises three layers made of a hard core layer, one or more intermediate elastomeric layers, and a hard shell layer. Preferably the impact modifier is a core-shell structure, in which the shell contains at least 50 weight percent of methyl methacrylate monomer units. In one embodiment, the core-shell impact modifier has a hard core (with a Tg greater than 30°C, and more preferably greater than 50°C). In one embodiment, the core-shell impact modifier is made entirely of acrylic monomer units.

Processing

The thermoplastic matrix polymer, high molecular weight acrylic processing aid, and optional impact modifiers and other additives are blended in the melt. Two or more of the components of the thermoplastic formulation may first be dry blended, then melt blended. In one embodiment, the high molecular weight acrylic polymer, thermoplastic matrix polymer and optionally impact modifier are melt blended together and formed into pellets. The pellets are then added with other components, such as dyes, fillers, and blowing agents at the melt processer operation.

In one embodiment, heat compounding can be accomplished by typical twin screw extrusion into a thermoplastic formulation. Single screw extruders, and extruders of other designs are also contemplated by the invention

In another embodiment, emulsions of one or more of the high molecular weight process aid, matrix polymer and/or impact modifier can be blended as liquid dispersions, and the blend can be dried, such as by spray drying, coagulation, or freeze drying, to form a powder blend. The powder blend can then be further compounded with other components of the thermoplastic formulation either by dry blending or melt blending. Powder-powder blending is contemplated. An intermediate step, in which the spray-dried powder(s) are extrusion melt compounded into pellets for further melt compounding is also contemplated.

Typical melt processing operations in which the high melt strength thermoplastic formulation of the invention having a manageable melt viscosity may be useful include, but are not limited to, extrusion, co-extrusion, injection molding, compression molding, film extrusion, and blow molding operations. The high molecular weight, high polydispersity formulation of the invention undergoes significant shear thinning, so its effect on high shear viscosity will be minimal. Process aids of the invention having higher levels of long chain branching can more effectively increase the melt strength.

Uses:

The thermoplastic formulations of the invention are useful in melt-processing applications that can benefit from a high melt strength with little increase in melt viscosity. These include, but are not limited to foams, profile coextrusion, thermoforming, melt blown films. One of ordinary skill in the art, based on the description and examples provided, can easily imagine other processes that can benefit from a high melt strength, low melt viscosity thermoplastic formulation.

In a foam process, a chemical or gaseous foaming agent is added to the polymer melt, and that melt expands upon exiting the extruder. A high melt strength formulation provides several advantages in a foaming operation. The high melt strength provides control over the expansion of the individual cells, allowing for a more uniform cell size, and smaller cell size. Die swell of the foam is also better controlled. The high melt strength also helps to prevent the collapse of the cells, once formed. Further, the extruded foam can be more easily sized and/or calendared without deforming the foamed article, due to the higher melt strength of the polymer formulation.

In profile co-extrusion, higher melt strength acrylic provides more continuity in the thermoplastic formulation, leading to little or no gaps or pit marks in the thermoplastic layer, and further there is an increase in die swell to better match the coextruded substrate.

Higher melt viscosity of an extruded thermoplastic decreases the amount of sag for rods, sheets, and other articles upon leaving the die, and also less sagging for thermoplastic layers in a co-extrusion.

Higher melt viscosity thermoplastic formulations allow for better control in a blown-film process, assuring a continuous thin film, without defects.

Within this specification embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that embodiments may be variously combined or separated without parting from the invention. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the invention described herein.

EXAMPLES:

Molecular Weight **:** The mass average molecular weight (Mw) of the polymers is measured by size exclusion chromatography (SEC).

Example 1:

Acrylic Processing Aid Preparation

Charged into a reactor, with stirring, were 8600 g of water, 5.23 g of Na_2CO_3 and 38.20 g of sodium lauryl sulfate, and the mixture was stirred until complete dissolution. Three vacuum-nitrogen purges were carried out in succession and the reactor left under a slight vacuum. The reactor was then heated. At the same time, a mixture comprising 4687.2 g of methyl methacrylate and 520.8 g of n-butyl acrylate was nitrogen-degassed for 30 minutes. Next, the mixture was rapidly introduced into the reactor using a pump. When the temperature of the reaction mixture reached 55 degrees centigrade, 7.81 g of potassium persulfate dissolved in 98.08 g of water were introduced. The line was rinsed with 50 g of water. The reaction mixture was left to rise in temperature to the exothermal peak. The polymerization was then left to completion for 60 minutes after the exothermal peak. The reactor was cooled down to 30 degrees centigrade and the latex removed. The latex is dried by spray drying.

The molecular weight of the acrylic processing aid described in this example was about 6 million g/mol.

Another processing aid with specific anti-sticking composition such, as the one described in the patent EP 0367 198 B1 could also be used in the process. The two processing aids would be co-spray dried using 10 wt. % of the anti-sticking processing aid and 90 wt. % of the processing aid described by the preparation earlier in this example. Co-spray drying as used in this example consists of blending the two acrylic processing aid latexes and then isolating the blend by spray drying. This results in a final powder particle or grain comprised of both processing aids.

Compound Preparation

2,000 grams (95 wt. %) of acrylonitrile-styrene-acrylate (ASA) copolymer are added to 105 grams (5 wt. %) of the processing aid combination described above with 90 wt. % of the high molecular weight component and 10 wt. % of the anti-sticking processing aid. The ASA formulation is melt compounded in a twin screw extruder in order to homogenize the thermoplastic matrix and processing aids. The ASA formulation should have both high melt strength and improved anti-sticking (better metal release).

Example 2:

Acrylic Processing Aid Preparation

Charged into a reactor, with stirring, were 8600 g of water, 5.23 g of Na_2CO_3 and 38.20 g of sodium lauryl sulfate, and the mixture was stirred until complete dissolution. Three vacuum-nitrogen purges were carried out in succession and the reactor left under a slight vacuum. The reactor was then heated. At the same time, a mixture comprising 4687.2 g of methyl methacrylate and 520.8 g of n-butyl acrylate was nitrogen-degassed for 30 minutes. Next, the mixture was rapidly introduced into the reactor using a pump. When the temperature of the reaction mixture reached 55 degrees centigrade, 7.81 g of potassium persulfate dissolved in 98.08 g of water were introduced. The line was rinsed with 50 g of water. The reaction mixture was left to rise in temperature to the exothermal peak. The polymerization was then left to completion for 60 minutes after the exothermal peak. The reactor was cooled down to 30 degrees centigrade and the latex removed. The latex is dried by spray drying.

The molecular weight of the acrylic processing aid described in this example was about 6 million g/mol.

Thermoplastic Resin Description

A standard, commercial segmented block copolymer consisting of successive hard or rigid blocks and soft or flexible segments was used. For this example, a copolymer with polyamide rigid blocks and polyether soft blocks was used.

Compound Preparation

4 weight % of the acrylic processing aid was introduced in the melt compounding step, along with the thermoplastic resin matrix copolymer.

Melt Strength

RHEOTENS GOTTFERT equipment was used to compare the melt strength of the different compositions with and without a processing aid. Roll speed at break (mm/s) and strength at break (N) were reported.

The melt strength curves of the pure thermoplastic matrix and the compounded thermoplastic formulation including 4% of an acrylic processing aid are shown in Figure 1. Melt strength and stress ratio are reported in Table 1.

Ratio compound / pure matrix	100mm/s	200mm/s	280mm/s
Force improvement (%)	30%	38%	40%

Table 1. Melt strength and Force ratio from the compound including 4% of an acrylic processing aid to the pure thermoplastic matrix.

Within the evaluation conditions, the compound including 4% of an acrylic processing aid shows an increase from 30 to 40% from the thermoplastic matrix. Moreover, the thermoplastic formulation including 4% of an acrylic processing aid also reported better melt extension at low acceleration conditions (Table 2).

Acceleration conditions	Thermoplastic reference	Compound including 4% of an acrylic processing aid
Low	Reference	Better than reference
High	Reference	Identical than reference

Table 2. Comparison of the melt extension quality of pure thermoplastic resin and with 4% of an acrylic processing aid.

Aspects of the invention include:

1. A high melt strength thermoplastic formulation comprising:

a) a thermoplastic matrix comprising at least one thermoplastic polymer;

b) 1 to 40 weight percent of a high molecular weight acrylic process aid, wherein said high molecular weight acrylic process aid has a molecular weight or greater than 100,000 g/mol.

2. The high melt strength thermoplastic formulation of aspect 1, wherein said thermoplastic matrix is selected from the group consisting of styrenic-based polymers, polyesters,

polycarbonate, polyvinylidene fluoride, and thermoplastic polyurethane (TPU), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), PET-co-PEN, glycol-modified polyethylene terephthalate (PETG), PET-co-PETG, polycarbonate (PC), acrylonitrile-styrene-acrylate (ASA) copolymers, high-impact polystyrene (HIPS), polyether ether ketone (PEEK), polyether ketone ketone (PEKK), acrylonitrile-butadiene-styrene (ABS) copolymers, polyolefins, and functional polyolefins.

3. The high melt strength thermoplastic formulation of any of aspects 1 or 2, wherein said acrylic process aid has a molecular weight of greater than 500 g/mol, preferably greater than 1 million g/mol, more preferably greater than 5 million g/mol, and more preferably greater than 8 million g/mol.

4. The high melt strength thermoplastic formulation of any of aspects 1 to 3, wherein said acrylic process aid comprises 50 to 100 weight percent of methyl methacrylate monomer units, and from 0 to 50 weight percent of one or more monomer units selected from the group consisting of (meth)acrylates, styrene, alpha methyl styrene, acrylonitrile, glycidyl methacrylate, and (meth)acrylic acid.

5. The high melt strength thermoplastic formulation of any of aspects 1 to 4, wherein said acrylic process aid comprises up to 50 weight percent of functional monomer units.

6. The high melt strength thermoplastic formulation of any of aspects 1 to 5, wherein said acrylic process aid is formed by an emulsion polymer process.

7. The high melt strength thermoplastic formulation of any of aspects 1 to 6, wherein said thermoplastic matrix further comprises from 2 to 95 weight percent of one or more compatible polymers, based on the weight of the polymers in the thermoplastic matrix.

8. The high melt strength thermoplastic formulation of any of aspects 1 to 17, wherein said thermoplastic matrix further comprises from 5 to 60 weight percent of one or more impact modifiers.

9. The high melt strength thermoplastic formulation of any of aspects 1 to 8, wherein said impact modifiers are core-shell impact modifiers having a shell comprising methyl methacrylate monomer units, and a hard core.

10. The high melt strength thermoplastic formulation of aspect 8, wherein said impact modifiers are core-shell impact modifiers having a shell comprising methyl methacrylate monomer units, and a soft core with a Tg of less than -20°C.

11. The high melt strength thermoplastic formulation of any of aspects 1 to 10, wherein said thermoplastic polymer matrix further comprises at least one additive selected from the group consisting of stabilizers, plasticizers, fillers, coloring agents, pigments, dyes, antioxidants, antistatic agents, surfactants, toner, refractive index matching additives, matting agents, cross-linked polymer beads, additives with specific light diffraction, light absorbing, or light reflection characteristics, and dispersing aids.

12. The high melt strength thermoplastic formulation of aspect 1, wherein said high molecular weight process aid has a polydispersity index of from 1.5, preferably from 2 to 40, and most preferably from 3 to 30.

13. An article formed from the high melt strength thermoplastic formulation of any of aspects 1 to 12.

14. The article of claim 13, wherein said article is a sheet, film, rod, profile, or co-extruded sheet, film, profile, or co-extruded capstock over a substrate, and may be solid or a foam.

15. A process for forming the article of aspects 13 and 14, wherein said process is selected from the group consisting of extrusion, co-extrusion, injection molding, compression molding, film extrusion, and blow molding.

What is claimed is:

1. A high melt strength thermoplastic formulation comprising:

a) a thermoplastic matrix comprising a thermoplastic polymer;

b) 1 to 40 weight percent of a high molecular weight acrylic process aid, wherein said high molecular weight acrylic process aid has a molecular weight or greater than 100,000 g/mol.

2. The high melt strength thermoplastic formulation of claim 1, wherein said thermoplastic matrix is selected from the group consisting of styrenic-based polymers, polyesters, polycarbonate, polyvinylidene fluoride, and thermoplastic polyurethane (TPU), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), PET-co-PEN, glycol-modified polyethylene terephthalate (PETG), PET-co-PETG, polycarbonate (PC), acrylonitrile-styrene-acrylate (ASA) copolymers, high-impact polystyrene (HIPS), polyether ether ketone (PEEK), polyether ketone ketone (PEKK), acrylonitrile-butadiene-styrene (ABS) copolymers, polyolefins, and functional polyolefins.

3. The high melt strength thermoplastic formulation of claim 1, wherein said acrylic process aid has a molecular weight of greater than 500,000 g/mol.

4. The high melt strength thermoplastic formulation of claim 3, wherein said acrylic process aid has a molecular weight of greater than 1 million g/mol.

5. The high melt strength thermoplastic formulation of claim 4, wherein said acrylic process aid has a molecular weight of greater than 5 million g/mol.

6. The high melt strength thermoplastic formulation of claim 1, wherein said acrylic process aid comprises 50 to 100 weight percent of methyl methacrylate monomer units, and from 0 to 50 weight percent of one or more monomer units selected from the group consisting of (meth)acrylates, styrene, alpha methyl styrene, acrylonitrile, glycidyl methacrylate, and (meth)acrylic acid.

7. The high melt strength thermoplastic formulation of claim 1, wherein said acrylic process aid comprises up to 50 weight percent of functional monomer units.

8. The high melt strength thermoplastic formulation of claim 1, wherein said acrylic process aid is formed by an emulsion polymer process.

9. The high melt strength thermoplastic formulation of claim 1, wherein said thermoplastic matrix further comprises from 2 to 95 weight percent of one or more compatible polymers, based on the weight of the polymers in the thermoplastic matrix.

10. The high melt strength thermoplastic formulation of claim 9, wherein said compatible polymer is selected from the group consisting of polylactic acid and polyvinylidene fluoride.

11. The high melt strength thermoplastic formulation of claim 1, wherein said thermoplastic matrix further comprises from 5 to 60 weight percent of one or more impact modifiers.

12. The high melt strength thermoplastic formulation of claim 11, wherein said impact modifiers are core-shell impact modifiers having a shell comprising methyl methacrylate monomer units, and a hard core.

13. The high melt strength thermoplastic formulation of claim 11, wherein said impact modifiers are core-shell impact modifiers having a shell comprising methyl methacrylate monomer units, and a soft core with a Tg of less than -20°C.

14. The high melt strength thermoplastic formulation of claim 1, wherein said thermoplastic polymer matrix further comprises at least one additive selected from the group consisting of stabilizers, plasticizers, fillers, coloring agents, pigments, dyes, antioxidants, antistatic agents, surfactants, toner, refractive index matching additives, matting agents, cross-linked polymer beads, additives with specific light diffraction, light absorbing, or light reflection characteristics, and dispersing aids.

15. The high melt strength thermoplastic formulation of aspect 1, wherein said high molecular weight process aid has a polydispersity index of from 1.5, preferably from 2 to 40, and most preferably from 3 to 30.

16. An article formed from the high melt strength thermoplastic formulation of claim 1.

17. The article of claim 16, wherein said article is a sheet, film, rod, profile, or co-extruded sheet, film, profile, or co-extruded capstock over a substrate.

18. The article of claim 16, wherein said article comprises a foam.

19. A process for forming the article of claim 18, wherein said process is selected from the group consisting of extrusion, co-extrusion, injection molding, compression molding, film extrusion, and blow molding.

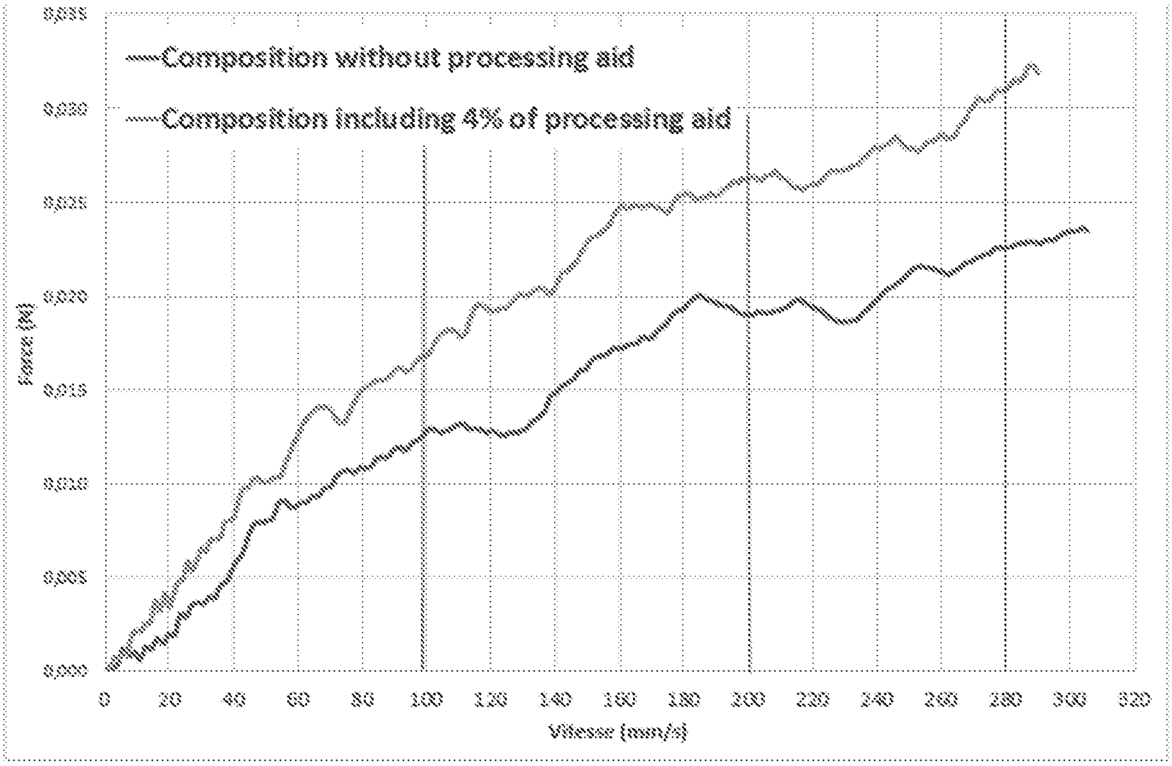

Figure 1. Melt strength curves of the pure thermoplastic matrix and the compound including 4% of an acrylic processing aid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/23986

A. CLASSIFICATION OF SUBJECT MATTER
IPC - C08F 20/06, 20/18, 120/06, 120/18, 220/06, 220/18; C08L 33/08, 33/10, 33/12 (2017.01)
CPC - C08F 20/06, 20/18, 120/06, 120/18, 220/06, 220/18; C08L 33/08, 33/10, 33/12

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2011/0305862 A1 (RACHWAL, LB) 15 December 2011; paragraphs [0022]-[0023], [0026]-[0029], [0031], [0039], [0042], [0044], [0049], [0073]; claims 13-14	1, 3-6, 8, 11, 14, 16-19 --- 2, 7, 9-10, 12-13, 15
Y	US 2010/0048797 A1 (GIROIS, S et al.) 25 February 2010; paragraphs [0023]-[0027], [0044]-[0045], [0057]	2
Y	US 2002/161126 A1 (CRUZ, CA et al.) 31 October 2002; paragraphs [0042]-[0044],	7
Y	US 2013/0172456 A1 (E I DU PONT DE NEMOURS AND COMPANY) 04 July 2013; paragraphs [0016]-[0017], [0030]-[0031]	9-10
Y	WO 2006/053984 A1 (ARKEMA) 26 May 2006; page 5, paragraph 5; page 6, paragraph 4; page 7, paragraph 1; page 9, paragraphs 3-5; page 23, paragraph 3; page 26 paragraph 3	12-13, 15
Y	US 2015/0284521 A1 (EXONMOBIL CHEMICAL PATENTS INC) 08 October 2015; entire document	1-19
Y	US 2013/0136881 A1 (FAN, XS et al.) 30 May 2013; entire document	1-19
Y	US 2011/0160383 A1 (KWON, KH et al.) 30 June 2011; entire document	1-19

☐ 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 18 May 2017 (18.05.2017)	Date of mailing of the international search report 15 JUN 2017
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774