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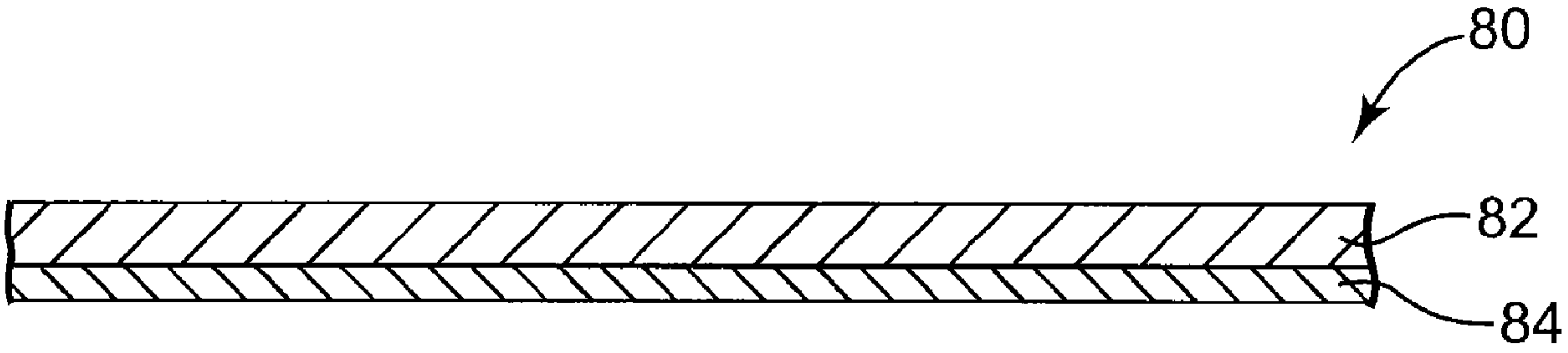
(54) Title: MULTILAYER THERMOPLASTIC FILM



(57) Abrégé/Abstract:

A thermoplastic polymer advanceable by solid state polymerization is blended with at least one dissimilar thermoplastic polymer, or an organic or inorganic particulate filler. The blend is solid state polymerized to provide a modified polymer alloy or filled polymer blend having at least one physical or chemical property different from that of the blend before solid state polymerization. The modified polymer alloy or filled polymer blend may be coextruded with a layer of thermoplastic extrusion polymer having a melt viscosity similar to that of the modified polymer alloy or filled polymer blend.

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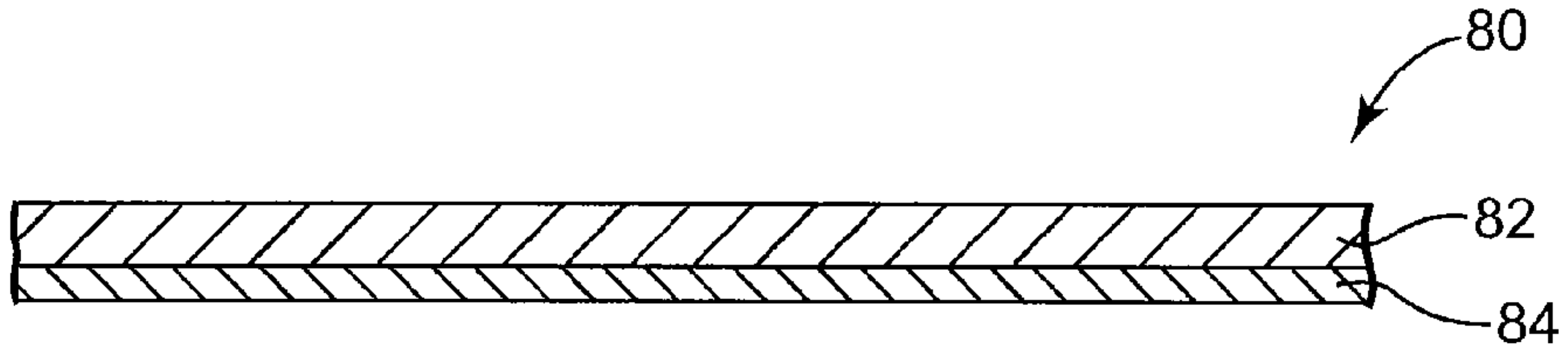

(57) Abstract: A thermoplastic polymer advanceable by solid state polymerization is blended with at least one dissimilar thermoplastic polymer, or an organic or inorganic particulate filler. The blend is solid state polymerized to provide a modified polymer alloy or filled polymer blend having at least one physical or chemical property different from that of the blend before solid state polymerization. The modified polymer alloy or filled polymer blend may be coextruded with a layer of thermoplastic extrusion polymer having a melt viscosity similar to that of the modified polymer alloy or filled polymer blend.

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MULTILAYER THERMOPLASTIC FILM

Cross Reference to Related Application

[0001] This application claims the benefit of U.S. Provisional Application No. 60/829,644 filed on October 16, 2006 by Niederst, and entitled "Multilayer Thermoplastic Film," which is incorporated herein by reference in its entirety.

Technical Field

[0002] This invention relates to multilayer thermoplastic films.

Background

[0003] It sometimes is difficult to prepare multilayer thermoplastic films. Thermoplastic films may require one or more potentially conflicting features such as adequate adhesion to a nearby surface, oil-repellence, water-repellence, lubricity or other surface-related properties; storage stability; strength, impact resistance or elasticity; chemical, abrasion or weathering resistance; low cost; or other desired properties. Multilayer films require in addition that the individual layers be capable of being formed adjacent one another, e.g., via coextrusion.

Summary of the Invention

[0004] We have found that dissimilar polymers, or a polymer and a filler, may be melt-blended and the blend thereafter subjected to solid state polymerization to provide a modified polymer alloy or filled polymer blend having one or more properties that may be superior to those of the source polymer(s), a simple blend of the source polymers, or a blend of the source polymer and filler. Without intending to be bound by theory, the solid state polymerization process may rearrange blocks or segments of the source polymer(s) to provide a new polymer alloy or filled polymer blend having unique properties. The resulting modified polymer blend may be used to form one or more layers of a multilayer thermoplastic film that might otherwise be difficult to form by coextrusion. Successful thermoplastic multilayer film coextrusion at commercially desirable extrusion rates can be difficult unless the individual film layers have similar melt viscosities, e.g., melt viscosities within about ±15% of one another at a chosen extrusion temperature and extrusion rate. The disclosed modified polymer alloy or filled polymer blends may be coextruded with a thermoplastic polymer whose melt viscosity has a given value at a chosen extrusion temperature and extrusion rate, by melt-blending dissimilar polymers or a polymer and a filler to form a blend having a lower melt viscosity than the given value, subjecting the blend to solid state polymerization to provide a modified polymer alloy or filled polymer blend whose melt viscosity is sufficiently close to the given value so that the modified polymer alloy or filled polymer blend and the thermoplastic polymer may be coextruded, and coextruding layers of the modified polymer alloy or filled polymer blend and thermoplastic polymer to form a multilayer film.

[0005] The present invention thus provides, in one aspect, a process for forming a multilayer film comprising:

a) providing a first thermoplastic polymer whose melt viscosity has a given value at a chosen temperature and extrusion rate;
b) providing a second thermoplastic polymer advanceable by solid state polymerization and having a melt viscosity at the chosen temperature and extrusion rate sufficiently unlike the given value so that the first and second thermoplastic polymers can not be coextruded to form a freestanding, self-supporting multilayer film;
c) blending the second thermoplastic polymer with:
    i) at least one dissimilar thermoplastic polymer, or
    ii) an organic or inorganic particulate filler;
d) solid state polymerizing the second thermoplastic polymer to provide a modified polymer alloy or filled polymer blend whose melt viscosity at the chosen temperature and extrusion rate is sufficiently close to the given value so that the modified polymer alloy or filled polymer blend and the first thermoplastic polymer may be coextruded to form a freestanding, self-supporting multilayer film;
e) coextruding a layer of the modified polymer alloy or filled polymer blend and a layer of the first thermoplastic polymer; and

f) cooling the coextruded layers to form a freestanding, self-supporting multilayer film.

[0006] The present invention provides, in another aspect, a freestanding, self-supporting multilayer film comprising two or more polymeric layers, wherein at least one layer comprises a modified polymer alloy or filled polymer blend comprising a thermoplastic polymer and (i) at least one dissimilar polymer or (ii) an organic or inorganic particulate filler, wherein the thermoplastic polymer has been advanced by solid state polymerization and the blend has a melt viscosity greater than that of the blend before solid state polymerization.

Brief Description of the Drawings

[0007] **Fig. 1** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for a conventional thermoplastic polymer and a thermoplastic polymer blend, as employed in Comparative Example 1.

[0008] **Fig. 2** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for a conventional thermoplastic polymer and a solid state polymerized thermoplastic polymer blend, as employed in Example 1.

[0009] **Fig. 3** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for two conventional thermoplastic polymers, as employed in Comparative Example 2.

[0010] **Fig. 4** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for two pre-compounded blends of the thermoplastic polymers shown in **Fig. 3**.

[0011] **Fig. 5** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for the blends shown in **Fig. 4** and for one of the polymers in the blends after the blends have been solid state polymerized, as employed in Example 2.

[0012] **Fig. 6** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for a filled thermoplastic polymer and for two solid state polymerized thermoplastic polymer blends, as employed in Comparative Example 3.

[0013] **Fig. 7** is a graph of apparent shear viscosity vs. apparent shear rate at 260° C for the thermoplastic materials shown in **Fig. 6** after the filled thermoplastic polymer has been solid state polymerized.

[0014] **Fig. 8** and **Fig. 9** are schematic cross-sectional views of two freestanding, self-supporting multilayer films.

Detailed Description

[0015] The term "polymer" includes homopolymers, copolymers and ter- and higher polymers, having random, block, graft or other backbone arrangements. The phrase "dissimilar polymers" refers to polymers whose backbones contain an arrangement of different materials (e.g., polymers of different monomers) and to polymers whose backbones contain different arrangements of the same materials (e.g., random and block copolymers of the same monomers). The phrase "similar polymers" refers to polymers whose backbones contain the same arrangement of the same materials. For example, the backbones in polyethylene terephthalate ("PET") and polyethylene ("PE") are arrangements of different monomers, and PET and PE are dissimilar polymers. Virgin PET and recycled PET are polymers whose backbones contain the same arrangement of the same materials, but which typically differ in chain lengths and acid numbers. Virgin PET and recycled PET are similar polymers.

[0016] The term "advanceable" when used with respect to a polymer refers to a polymer whose weight average molecular weight can be increased by solid state polymerization.

[0017] The terms "blend" and "blending" refer to any process that combines two or more polymers, or a polymer and an organic or inorganic filler, into a mixture that is at least macroscopically homogenous, and to such a mixture. The term "melt-blending" refers to any blending process carried out at or above the melting temperature (Tm) of at least one of the polymers in a blend of polymers.

[0018] The phrase "freestanding, self-supporting" when used with respect to a film means that at room temperature the film can be unwound by itself from a supply reel and wound up on a take-up reel using conventional film-handling equipment.

[0019] The phrases "solid state polymerization" and "solid state polymerizing" refer to a process which through the application of heat furthers the polymerization (e.g., increases the intrinsic viscosity) of a polymer while in solid form.

[0020] The disclosed process includes an advanceable thermoplastic polymer. A variety of advanceable polymers may be employed. Representative advanceable polymers include condensation polymers and addition polymers, with condensation polymers being preferred. Alkyd polyesters made by reacting together one or more acid anhydrides, polyols and unsaturated fatty acids, or made by transesterifying a mixture of one or more polyols and oils, may also be employed. Representative fatty acids include dehydrated castor fatty acids, linolenic fatty acids, ricinoleic fatty acids, soya fatty acids, and the like; and byproducts and combinations thereof. Representative oils include vegetable oils such as canola oil, castor oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, ground nut oil, linseed oil, peanut oil, ricinene oil, safflower oil, soybean oil, sunflower oil, tall oil, tung oil, walnut oil, wood oil, and the like; animal fats such as fish oil, lard, poultry fat, tallow, and the like; and byproducts and combinations thereof. Other advanceable polymers include polyesters and copolyesters such as PET, polybutylene terephthalate ("PBT"), polyethylene naphthalate ("PEN"), polybutylene naphthalate ("PBT") and other esters of acids and diols that will be familiar to persons having ordinary skill in the art; polylactones such as polycaprolactone; polymethyl methacrylate ("PMMA"); styrene/maleic anhydride ("SMA"); polyoxymethylene ("POM"); ketones such as polyetheretherketone ("PEEK") and polyaryletherketone ("PAEK"); thermoplastic fluoropolymers; polycarbonate ("PC"); polyurethanes; polyarylate ("PAR"); polyphenylene oxide ("PPO"); polyamides such as nylon 6, nylon 6,6, nylon 11, nylon 6,12 and nylon 12; imides such as polyimide ("PI"), polyetherimide ("PEI") and polyamideimide ("PAI"); polyphthalamide; sulfones such as polysulfone ("PSul"; polyarylsulfone ("PAS") and poly ether sulfone ("PES"); polyaminoacids; polydimethylsiloxanes; mixtures thereof; and derivatives thereof which do not interfere with solid state polymerization (e.g., appropriately substituted polymers such as halogen-substituted polymers). The disclosed blends may also include (but do not have to include) a non-advanceable polymer. Representative non-advanceable polymers that may be blended with the advanceable polymer include polyolefins such as polyethylene ("PE"), polypropylene ("PP") and polybutylene ("PB"); styrenes such as polystyrene ("PS"), poly α-methyl styrene and styrene/acrylonitrile ("SAN"); vinyls such as polyvinyl chloride ("PVC") and polyvinylnaphthalene ("PVN"); and mixtures thereof. Representative mixtures of advanceable polymers and non-advanceable polymers include mixtures of esters and olefins (for example, PET and polyethylene). Preferably all of the polymers in a blend of dissimilar polymers are thermoplastic, and more preferably all of the polymers in a blend of dissimilar polymers are advanceable thermoplastics. However, blends containing thermoplastic and non-thermoplastic (e.g., thermoset) polymers may be employed if desired.

[0021] Blends containing the disclosed polymers may be combined in a variety of ratios and in any desired order. For example, a blend of first and second dissimilar polymers may contain from about 99 to about 1 weight percent of a first polymer and from about 1 to about 99 weight percent of a second polymer, from about 95 to about 5 weight percent of a first polymer and from about 5 to about 95 weight percent of a second polymer, from about 90 to about 10 weight percent of a first polymer and from about 10 to about 90 weight percent of a second polymer, or from about 80 to about 20 weight percent of a first polymer and from about 20 to about 80 weight percent of a second polymer. More than two (for example, three or more, four or more or five or more) dissimilar polymers may be combined to make the disclosed blends. The dissimilar polymers typically will differ with respect to at least one or more physical or chemical properties. Representative such properties may include molecular weight, density, glass transition temperature (Tg), melting temperature (Tm), intrinsic viscosity (IV), melt viscosity (MV), melt index (MI), crystallinity, arrangement of blocks or segments, availability of reactive sites, reactivity with respect to various gases or liquids, acid number, surface energy, hydrophobicity, oliophobicity, moisture or oxygen permeability, transparency, heat resistance, resistance to sunlight or ultraviolet energy, adhesion to substrates including metals or plastics, and recyclability. Melt viscosity is an especially useful property that can be varied by subjecting a blend of dissimilar polymers to solid state polymerization, thereby enabling preparation of desirable polymer alloys from dissimilar polymers whose melting points differ by, for example, more than about ±50%, more than about ±10%, or more than about ±5% at temperatures of about 200-300°C and shear rates of about 50-500 Pa-sec. For properties measured on an absolute scale, the dissimilar polymer properties may for example differ by about ±5%, by about ±10%, by about ±15%, by about ±25%, by about ±50%, or by about ±100% or more. The dissimilar polymers may be in any convenient form including flakes, pellets, powder or a melt. The dissimilar polymers may optionally be dried prior to being blended. Drying may also in some instances be advantageously avoided, thus enabling an appreciable saving in processing time and equipment cost.

[0022] The disclosed advanceable thermoplastic polymer may instead or also be blended with an organic or inorganic particulate filler. A variety of organic fillers may be employed, including polymeric particles (e.g., polymeric nanoparticles), micronized organic polymers such as micronized polytetrafluoroethylene, hydrogels, core-shell polymer systems, sheathed polymer systems and other organic fillers that will be familiar to persons having ordinary skill in the art. A variety of inorganic fillers may be employed, including metal oxides such as titanium dioxide, silicon dioxide, iron oxide, zinc oxide, antimony oxide and zirconium oxide (including metal oxide nanoparticles); metal sulfides and metal sulfates such as cadmium sulfide, zinc sulfide, barium sulfate, and lithopone; metal nitrides such as boron nitride; metal oxychlorides such as bismuth oxychloride; earth compounds including clays such as sienna or umber (including clay nanoparticles); calcium carbonate; talc; wollastonite; and other inorganic fillers that will be familiar to persons having ordinary skill in the art. The disclosed advanceable thermoplastic polymer and filler may be combined in a variety of ratios. For example, a blend of polymer and filler may contain from about 15 to about 99.9 weight percent polymer and from about 85 to about 0.1 weight percent filler, from about 30 to about 99.9 weight percent polymer and from about 70 to about 0.1 weight percent filler, or from about 50 to about 99.9 weight percent polymer and from about 50 to about 0.1 weight percent filler. As one example, pigmented films are sometimes employed, e.g., for food packaging where a bright, white coloration implies a sanitary, clean environment conducive to the marketing of food-related products. A suitably white multilayer film may be obtained, for example, by adding a whitening agent such as titanium dioxide within one or all of the film layers. High pigment levels may be needed (e.g., 40 weight percent or more) in order to achieve the necessary optical properties and performance.

[0023] The disclosed blends of dissimilar polymers or of a polymer and filler may contain one or more adjuvants. Representative adjuvants include solvents, antimicrobial agents, UV absorbers, light stabilizers, antioxidants and adhesion promoters. These and other useful adjuvants will be apparent to persons having ordinary skill in the art.

[0024] The disclosed blends may be combined using equipment and techniques that will be familiar to persons having ordinary skill in the art. Melt-blending is preferred but not required. The blend desirably is homogeneous but homogeneity is not required. One convenient method for blending dissimilar polymers or a polymer and filler is to combine the ingredients in an extruder, e.g., a single screw or multiple screw extruder. The extruder may be heated at one or more locations along its length, e.g., to a temperature above that of the Tm of at least one and preferably all of the dissimilar polymers in the blend.

[0025] The blend may be finely divided (e.g., pelletized, granulated or made into flakes, using equipment and techniques that will be familiar to persons having ordinary skill in the art) before the blend is solid state polymerized. The finely divided blend may if desired be stored until such time as it can be solid state polymerized, and may if desired be subjected to an optional intermediate step such as heating or cooling to promote crystallization.

[0026] Solid state polymerization may be performed using equipment and techniques that will be familiar to persons having ordinary skill in the art. One convenient method is to place the pelletized blend in a suitable sealed vessel heated to a temperature below the melting point of the blend or below the melting point of the major component thereof (e.g., to a temperature of about 150 to about 250 °C, about 170 to about 220 °C or about 180 to about 210 °C), in an inert or nonreactive atmosphere (e.g., argon or nitrogen) for a time sufficient to provide a modified polymer alloy or filled polymer blend having at least one physical or chemical property different from that of the unmodified blend. Such time may for example be about 2 to about 24 hours, about 5 to about 20 hours or about 8 to about 16 hours.

[0027] The modified polymer alloy or filled polymer blend may be used to make multilayer films using a variety of equipment that will be familiar to persons having ordinary skill in the art, including flat film extrusion lines and blown (tubular) film lines. The extruded film may if desired be formed against a chill roll. The films may be subjected to heat treatment (including heat setting or annealing), stretching (e.g., longitudinal stretching, widthwise stretching (tentering) or biaxial stretching), surface treatments (e.g., corona treatment), metallization, and other processing or conversion steps that will be familiar to persons having ordinary skill in the art.

[0028] The resulting multilayer films may be used for a variety of applications that will be familiar to persons having ordinary skill in the art, including packaging films (e.g., for frozen, fresh or hot foods), building materials (e.g., housewrap) and decorative or graphic films. An external surface of the completed film may if desired be adhered to another film or to a substrate using an appropriate adhesive, or using a heat lamination process (e.g., a heated film or heated substrate) for films having an appropriate external layer.

[0029] **Fig. 8** shows a schematic cross-sectional view of a multilayer film **80**, in which a thicker layer **82** of unmodified polymer is adjacent a thinner layer **84** of modified polymer alloy or filled polymer. The resulting coated article might also be like article **90** in **Fig. 9**, in which a thinner layer **92** of modified polymer alloy or filled polymer blend lies atop thicker layer **94** of unmodified polymer which in turn lies atop a thinner layer **96** of modified polymer alloy or filled polymer. Persons having ordinary skill in the art will appreciate that other numbers and arrangements of the disclosed layers are possible. The disclosed multilayer films may for example contain two layers, three layers, four layers, five layers or more layers (e.g., ten or eleven layers). The layers may have a variety of thicknesses, e.g., a thickness of about 1 micrometer to about 10 millimeters, about 1 micrometer to about 1 millimeter, or about 1 micrometer to about 100 micrometers. A variety of dissimilar thermoplastic extrusion polymers may be employed, including the various thermoplastic polymers mentioned above. The dissimilar thermoplastic extrusion polymer may be different from or the same as any polymer in the modified polymer alloy or filled polymer blend. For example, the dissimilar thermoplastic extrusion polymer may be the same as the higher-melting of two dissimilar polymers in a binary polymer alloy.

[0030] The melt viscosities of the individual layers desirably are within about ±15%, ±10% or ±5% of one another at the chosen extrusion temperature and extrusion rate. If the melt viscosity and hence the flow rate of one or more of the coextruded layers is substantially different from that of another coextruded layer, the multilayer film may be deficient in one or more respects. When typical commercially available polymers are coextruded to make multilayer films, the selection of materials which match a given viscosity requirement may be quite limited. Thus existing coextrusion systems may employ layers of materials having not only very closely matched melt viscosities but also very similar other physical and chemical properties as well. Such systems may not provide broad performance characteristics and may tend to perform more like a thick monolayer film of a single material than like a true multilayer film system.

[0031] Formulators have also sought to broaden the performance properties of coextruded multilayer films by blending multiple materials in a given layer or layers.

Such blending is intended to provide a mixture of chemical or physical properties that cannot be achieved in one layer. The layer formulation may for example contain two or more materials that are typically pre-blended (pre-compounded) and then added to the film forming equipment to provide a single distinct layer. However, pre-compounding can deleteriously affect the viscosity of the blended materials, due perhaps to the effects of mechanical shear, heat, moisture or other factors encountered during the pre-compounding process. For example, when two materials with very similar melt viscosities are pre-compounded, the resulting blend may have a much lower melt viscosity than that of either starting material. Such reduced melt viscosity can dramatically limit the extent to which coextruded multilayer films can be formed using pre-compounded blends of materials in a layer. A similar reduction in melt viscosity may be observed when a polymer and a particulate filler are pre-compounded.

[0032] The disclosed processes enable the fabrication of proprietary polymer alloys and filled polymer blends possessing properties not available from commercially supplied products. One or more properties of the polymer alloy may for example be unavailable in or superior to a corresponding property of the neat starting materials or a simple blend thereof. The disclosed processes thus permit several starting materials to be combined via a melt compounding process to form an alloy or blend that may have some properties desired by an end user in a final product, but which may lack other properties (for example, a suitable melt flow rate) also needed in such final product. The pellet's properties can be modified using solid state polymerization to provide a modified polymer alloy or filled polymer blend having more satisfactory overall properties and better compatibility with other layers in a multilayer coextruded film line.

[0033] The invention is further illustrated in the following non-limiting examples, in which all parts and percentages are by weight unless otherwise indicated.

Comparative Example 1

Blended First and Second Polymers

[0034] Pre-dried samples (moisture < 100 ppm, by Karl-Fischer analysis) of KOSA™ 1101E fast-crystallizing PET ("CPET", from Invista) and DYNAPOL™ P1500HV partially crystalline copolyester (from Degussa) were combined in a 50:50 ratio, compounded in a ZSK twin-screw extruder (from Werner & Pfleiderer) and pelletized into small, cylindrical pellets. KOSA 1101E CPET is a bottle grade, 0.8 intrinsic viscosity (IV) thermoplastic polymer and is fairly hard and durable. DYNAPOL P1500HV copolyester resin is a soft, adhesive resin having a much lower melt viscosity than KOSA 1101E CPET.

[0035] The pelletized blend was dried (moisture <100 ppm, by Karl-Fischer analysis) using a CONAIR™ dryer from Conair Corp and analyzed for melt viscosity at 260° C using a DYNISCO™ LCR7000 capillary rheometer. A reference sample of dried KOSA 1101E CPET was also analyzed. **Fig. 1** shows viscosity versus shear curves for the reference sample (curve **1**) and for the blend (curve **2**). Set out below in Table 1 is a comparison of melt flow rates and shear viscosities for the reference sample and for the blend.

Table 1

Melt Viscosity Data (260° C)

	Reference (100% KOSA 1101E CPET; Curve 1)	**Blend (50% KOSA 1101E CPET/50% DYNAPOL P 1500HV; Curve 2)**	**% Difference**
Melt Flow Rate (g/10 min)	6.245	15.951	+155%
Viscosity (100 s-1)	974 Pa-s	460 Pa-s	-53%
Viscosity (200 s-1)	819 Pa-s	414 Pa-s	-49%
Viscosity (500 s-1)	611 Pa-s	339 Pa-s	-45%

[0036] The data in Table 1 shows that inclusion in the blend of DYNAPOL P1500HV polymer provided a blend whose melt viscosity was significantly lower than that of 100% KOSA PET, and well beyond the ±15% guideline for acceptable coextrusion. The blend would not be useable as a layer adjacent to a layer of KOSA PET in a coextruded multilayer film.

Example 1

Blended First and Second Polymers Subjected to Solid State Polymerization

[0037] The Comparative Example 1 pelletized blend was subjected to solid state polymerization for 16 hours at 200° C under a vacuum of about 760 mm Hg. The resulting polymer alloy pellets were dried and analyzed for melt viscosity using the method of Comparative Example 1. A reference sample of dried KOSA 1101E CPET was also analyzed. **Fig. 2** shows viscosity versus shear curves for the reference sample (curve **1**) and for the solid state polymerized blend (curve **2**). Set out below in Table 2 is a comparison of melt flow rates and shear viscosities for the reference sample and for the solid state polymerized blend.

Table 2

Melt Viscosity Data (260° C)

	Reference (100% KOSA 1101E CPET; Curve 1)	**Polymer Alloy (50% KOSA 1101E CPET/50% DYNAPOL P 1500HV; Curve 2)**	**% Difference**
Melt Flow Rate (g/10 min)	6.245	6.241	-0.10%
Viscosity (100 s-1)	974 Pa-s	954 Pa-s	-2.1%
Viscosity (200 s-1)	819 Pa-s	789 Pa-s	-3.7%
Viscosity (500 s-1)	611 Pa-s	573 Pa-s	-6.2%

[0038] The data in Table 2 shows that solid state polymerization of the blend increased the observed melt viscosity sufficiently to meet melt viscosity guidelines for acceptable coextrusion.

Comparative Example 2

Three Layer Coextrusion System

[0039] Samples of KOSA 1101E CPET (the 0.8 dl/g IV polyester used in Example 1) and EASTAR™ 6763 glycol-modified PET ("PETG", a 0.78 dl/g IV polyester from Eastman Chemical Co.), were dried to a moisture value of about 50 ppm by Karl-Fischer analysis and tested for melt viscosity at 260° C. The results are set out in **Fig. 3**, which shows viscosity versus shear curves for KOSA 1101E CPET (curve **1**) and for EASTAR™ 6763 PETG (curve **2**). Based on the melt viscosity measurements, one might assume that layers of either material, or layers containing a blend of both materials, would exhibit sufficiently similar melt viscosity at a given temperature and shear rate so that they could be coextruded. The formulations shown below in Table 3 were prepared to test this assumption.

Table 3

Layer	Formulation
Top	75% KOSA 1101E CPET + 25% EASTAR 6763 PETG
Middle	100% KOSA 1101E CPET
Bottom	25% KOSA 1101E CPET + 75% EASTAR 6763 PETG

[0040] The top and bottom layer formulations were pre-compounded by feeding pellets of the dried KOSA 1101E CPET and EASTAR 6763 PETG polymers to a commercial 75 mm twin screw extruder at a temperature of 265-280° C. The resulting extruded polymer blends were formed into pellets, allowed to crystallize, dried to a moisture value less than 50 ppm (by Karl-Fischer analysis) and tested for melt viscosity at 260° C. The results are set out in **Fig. 4**, which shows viscosity versus shear curves for the 100% KOSA 1101E CPET middle layer (curve **1**), for the 75% KOSA 1101E CPET + 25% EASTAR 6763 PETG top layer (curve **2**), and for the 25% KOSA 1101E CPET + 75% EASTAR 6763 PETG bottom layer (curve **3**). The data shows that a very substantial reduction in the top and bottom layer melt viscosities occurred during the pre-compounding process and that the melt viscosity of the pre-compounded top and bottom layers would be well below that of the KOSA 1101E CPET middle layer. It would be difficult to carry out successful coextrusion of these three layers without encountering film forming deficiencies.

Example 2

Three Layer Coextrusion System with Solid State Polymerized Middle Layer

[0041] Using the method of Example 1, the Comparative Example 2 pelletized pre-compounded blends were subjected to solid state polymerization for 12 hours at 200° C under a vacuum of about 760 mm Hg. The resulting solid state polymerized polymer alloys were tested for melt viscosity at 260° C. The results are set out in **Fig. 5**, which shows viscosity versus shear curves for the 100% KOSA 1101E CPET middle layer (curve **1**), for the solid state polymerized 75% KOSA 1101E CPET + 25% EASTAR 6763 PETG top layer (curve **3**), and for the solid state polymerized 25% KOSA 1101E CPET +

75% EASTAR 6763 PETG bottom layer (curve **2**). The data shows that the melt viscosities of the solid state polymerized top and bottom layer blends closely match the melt viscosity of the KOSA 1101E CPET middle layer, and that simultaneous coextrusion of all three layers together should be successful. A sample of the film should be bondable to a steel substrate by heating the steel to about 50-300° C and then pressing the film against the heated substrate.

Comparison Example 3

Pigmented Film

[0042] Using an extruder, 40 wt. % TiONA™ 188 Titanium Dioxide (from Millennium Chemicals) was pre-compounded into 60 wt. % KOSA 1101E CPET to provide a white version of the middle layer employed in Example 2. The pre-compounding step caused a substantial decrease in melt viscosity for the resulting filled polymer blend. The filled polymer blend was formed into pellets, allowed to crystallize, dried to a moisture value less than 50 ppm (by Karl-Fischer analysis) and tested for melt viscosity at 260° C. The results are set out in **Fig. 6**, which shows viscosity versus shear curves for the 60% KOSA 1101E CPET + 40 titanium dioxide middle layer (curve **3**), for the 75% KOSA 1101E CPET + 25% EASTAR 6763 PETG top layer (curve **1**), and for the 25% KOSA 1101E CPET + 75% EASTAR 6763 PETG bottom layer (curve **2**). The data shows that a very substantial reduction in the middle layer melt viscosity occurred during the pre-compounding process and that the melt viscosity of the pre-compounded top and bottom layers would be well above that of the filled KOSA 1101E CPET middle layer. It would be difficult to carry out successful coextrusion of these three layers without encountering film forming deficiencies.

Example 3

Three Layer Coextrusion System with Solid State Polymerized Pigmented Middle Layer

[0043] Using the method of Example 1, the Comparative Example 3 pelletized pre-compounded middle layer composition was subjected to solid state polymerization for 16 hours at 190° C under a vacuum of about 760 mm Hg. The resulting solid state polymerized filled polymer blend was tested for melt viscosity at 260° C. The results are set out in **Fig. 7**, which shows viscosity versus shear curves for the solid state polymerized 60% KOSA 1101E CPET + 40% titanium dioxide middle layer (curve **1**), for the solid state polymerized 75% KOSA 1101E CPET + 25% EASTAR 6763 PETG top layer (curve **3**), and for the solid state polymerized 25% KOSA 1101E CPET + 75% EASTAR 6763 PETG bottom layer (curve **2**). The data shows that the melt viscosities of the solid state polymerized top and bottom layer blends closely match the melt viscosity of the pigmented middle layer, and that simultaneous coextrusion of all three layers together should be successful.

[0044] Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from this invention. It should therefor be understood that this invention is not limited to the illustrative embodiments set forth above.

We claim:

1. A process for forming a multilayer film comprising:
   a) providing a first thermoplastic polymer whose melt viscosity has a given value at a chosen temperature and extrusion rate
   b) providing a second thermoplastic polymer advanceable by solid state polymerization and having a melt viscosity at the chosen temperature and extrusion rate sufficiently unlike the given value so that the first and second thermoplastic polymers can not be coextruded to form a freestanding, self-supporting multilayer film;
   c) blending the second thermoplastic polymer with:
      i) at least one dissimilar thermoplastic polymer, or
      ii) an organic or inorganic particulate filler;
   d) solid state polymerizing the second thermoplastic polymer to provide a modified polymer alloy or filled polymer blend whose melt viscosity at the chosen temperature and extrusion rate is sufficiently close to the given value so that the modified polymer alloy or filled polymer blend and the first thermoplastic polymer may be coextruded to form a freestanding, self-supporting multilayer film;
   e) coextruding a layer of the modified polymer alloy or filled polymer blend and a layer of the first thermoplastic polymer; and
   f) cooling the coextruded layers to form a freestanding, self-supporting multilayer film.

2. A process according to claim 1 wherein the second thermoplastic polymer comprises a condensation polymer.

3. A process according to claim 1 wherein the second thermoplastic polymer comprises an alkyd.

4. A process according to claim 1 wherein the dissimilar thermoplastic polymer is advanceable.

5. A process according to claim 1 wherein the dissimilar thermoplastic polymer is not advanceable.

6. A process according to claim 1 comprising blending the second thermoplastic polymer with the at least one dissimilar thermoplastic polymer.

7. A process according to claim 6 wherein the second thermoplastic polymer comprises a polyester and the dissimilar thermoplastic polymer comprises a copolyester.

8. A process according to claim 6 wherein the second thermoplastic polymer comprises polyethylene terephthalate, the dissimilar thermoplastic polymer comprises a copolyester and the modified polymer alloy has greater melt viscosity than that of the blend before solid state polymerization.

9. A process according to claim 1 wherein the modified polymer alloy has a melt viscosity within about ±15% of the first thermoplastic polymer at temperatures of about 200-300°C and shear rates of about 50-500 Pa-sec.

10. A process according to claim 1 wherein the modified polymer alloy has a melt viscosity within about ±5% of the first thermoplastic polymer at temperatures of about 200-300°C and shear rates of about 50-500 Pa-sec.

11. A process according to claim 1 comprising blending the second thermoplastic polymer with the organic particulate filler.

12. A process according to claim 1 comprising blending the second thermoplastic polymer with the inorganic particulate filler.

13. A process according to claim 12 wherein the inorganic particulate filler comprises a metal oxide.

14. A process according to claim 1 wherein the blending step comprises melt-blending.

15. A freestanding, self-supporting multilayer film comprising two or more polymeric layers, wherein at least one layer comprises a modified polymer alloy or filled polymer blend comprising a thermoplastic polymer and (i) at least one dissimilar polymer or (ii) an

organic or inorganic particulate filler, wherein the thermoplastic polymer has been advanced by solid state polymerization and the blend has a melt viscosity greater than that of the blend before solid state polymerization.

16. A multilayer film according to claim 15 wherein the thermoplastic polymer comprises a condensation polymer.

17. A multilayer film according to claim 15 wherein the thermoplastic polymer comprises an alkyd.

18. A multilayer film according to claim 15 wherein the blend comprises a thermoplastic polymer and at least one dissimilar polymer.

19. A multilayer film according to claim 15 wherein the thermoplastic polymer comprises a polyester and the dissimilar polymer comprises a copolyester.

20. A multilayer film according to claim 15 wherein the modified polymer alloy has a melt viscosity within about ±15% of the dissimilar polymer at temperatures of about 200-300°C and shear rates of about 50-500 Pa-sec.

21. A multilayer film according to claim 15 wherein the blend comprises the thermoplastic polymer and the organic particulate filler.

22. A multilayer film according to claim 15 wherein the blend comprises the thermoplastic polymer and the inorganic particulate filler.

23. A multilayer film according to claim 22 wherein the inorganic particulate filler comprises a metal oxide.

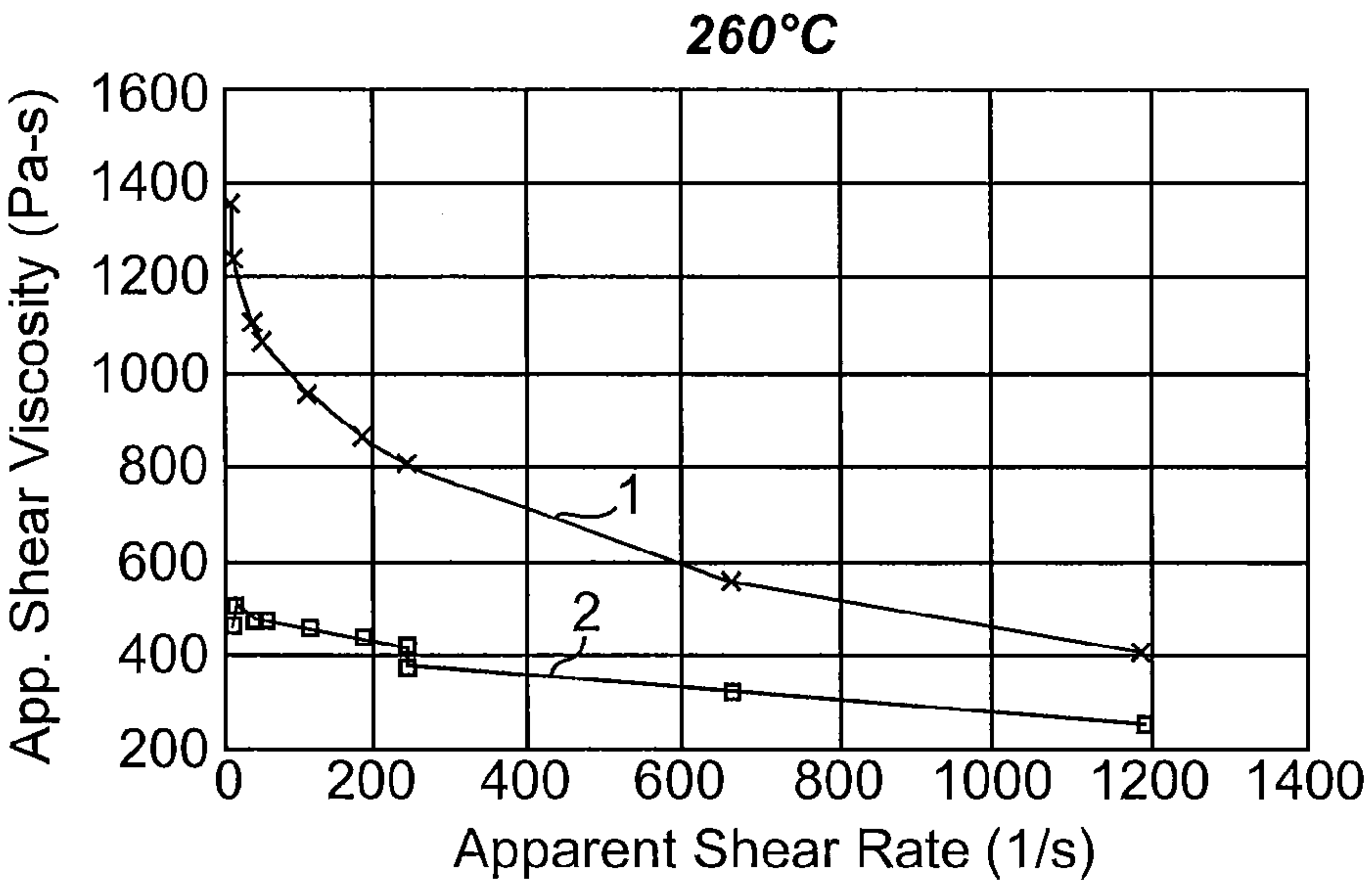

260°C
App. Shear Viscosity (Pa-s)
1600
1400
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
Apparent Shear Rate (1/s)
1
2

Fig. 1

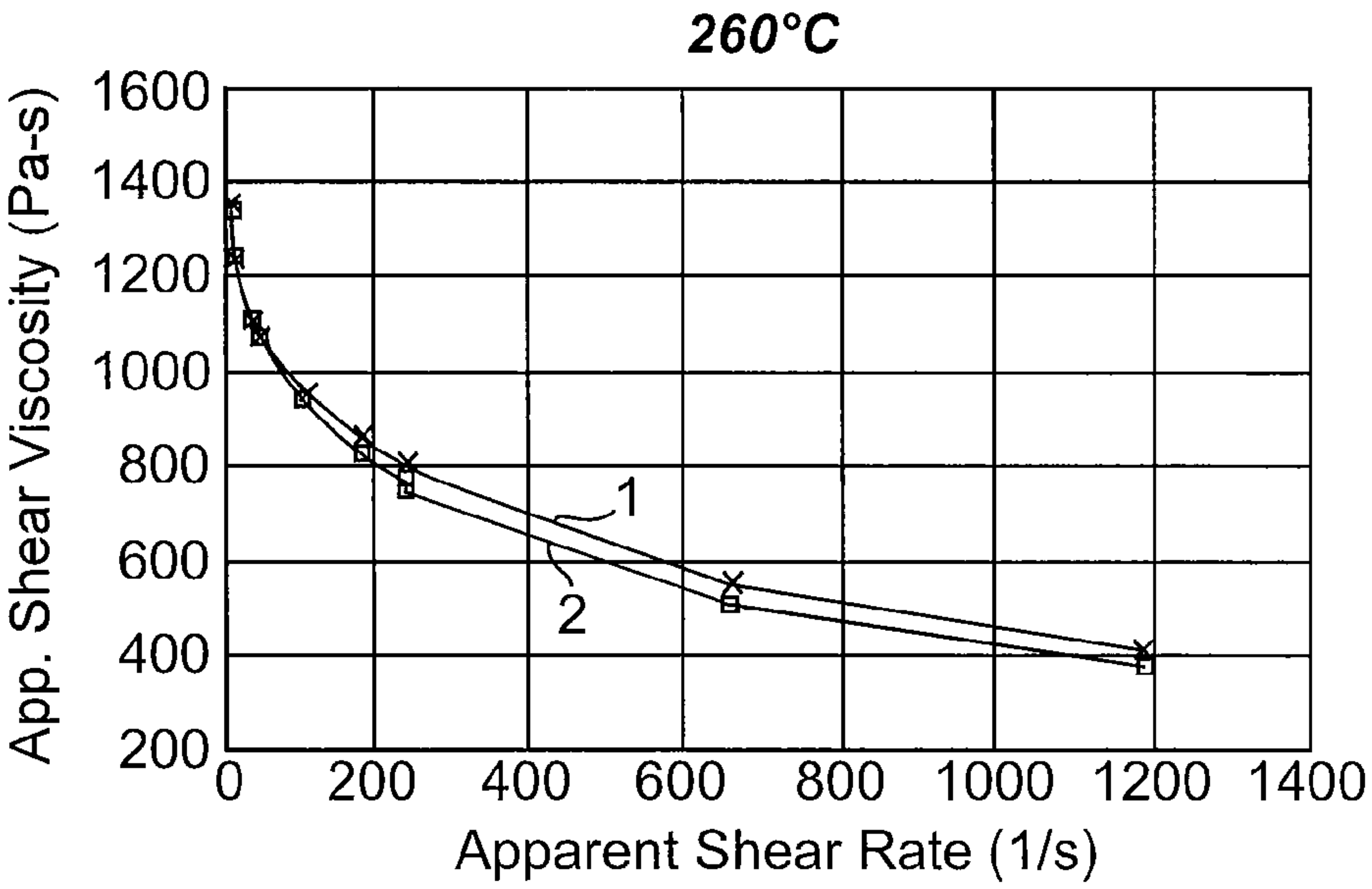

260°C
App. Shear Viscosity (Pa-s)
1600
1400
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
Apparent Shear Rate (1/s)
1
2

Fig. 2

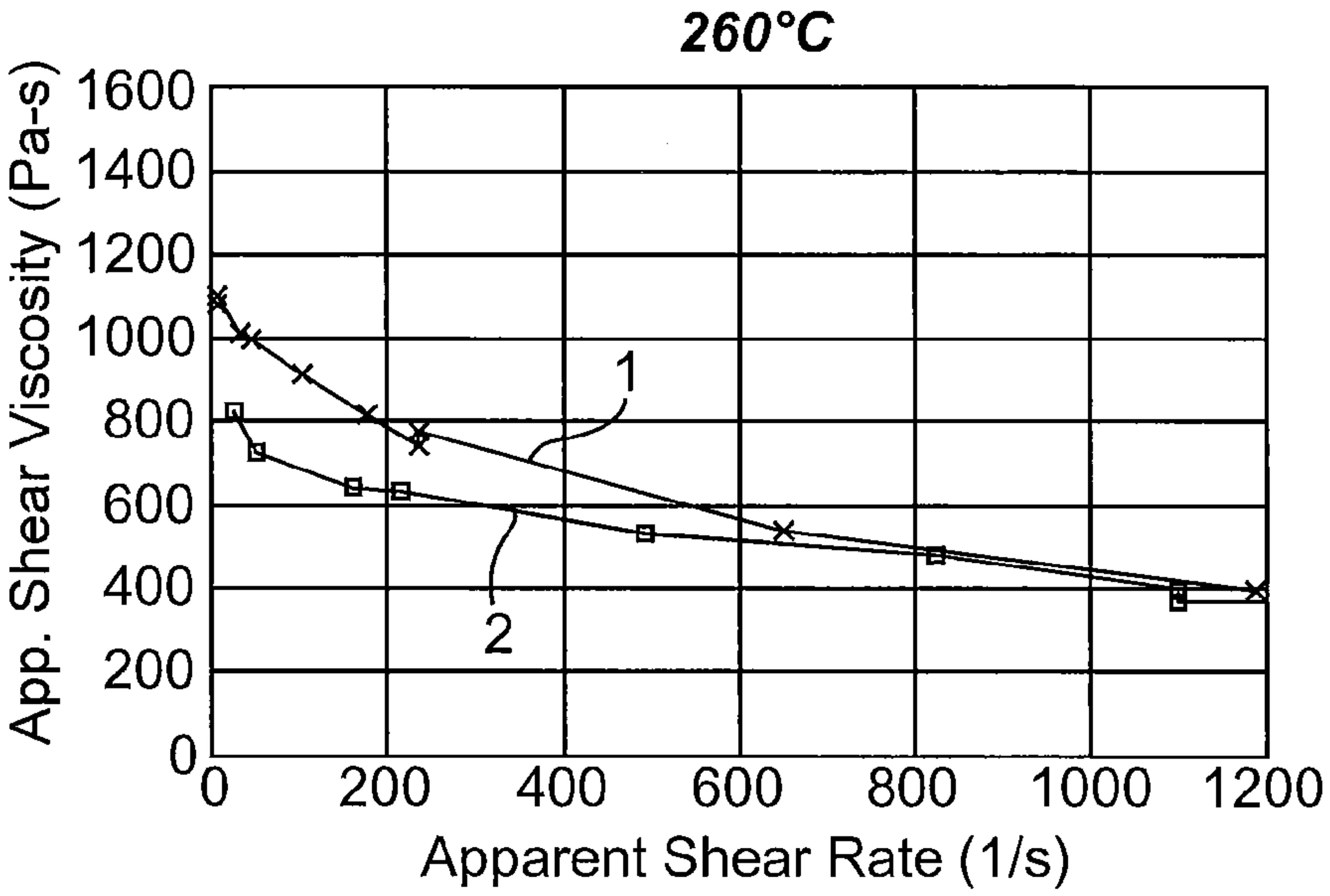

260°C
App. Shear Viscosity (Pa-s)
1600
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Apparent Shear Rate (1/s)
1
2

Fig. 3

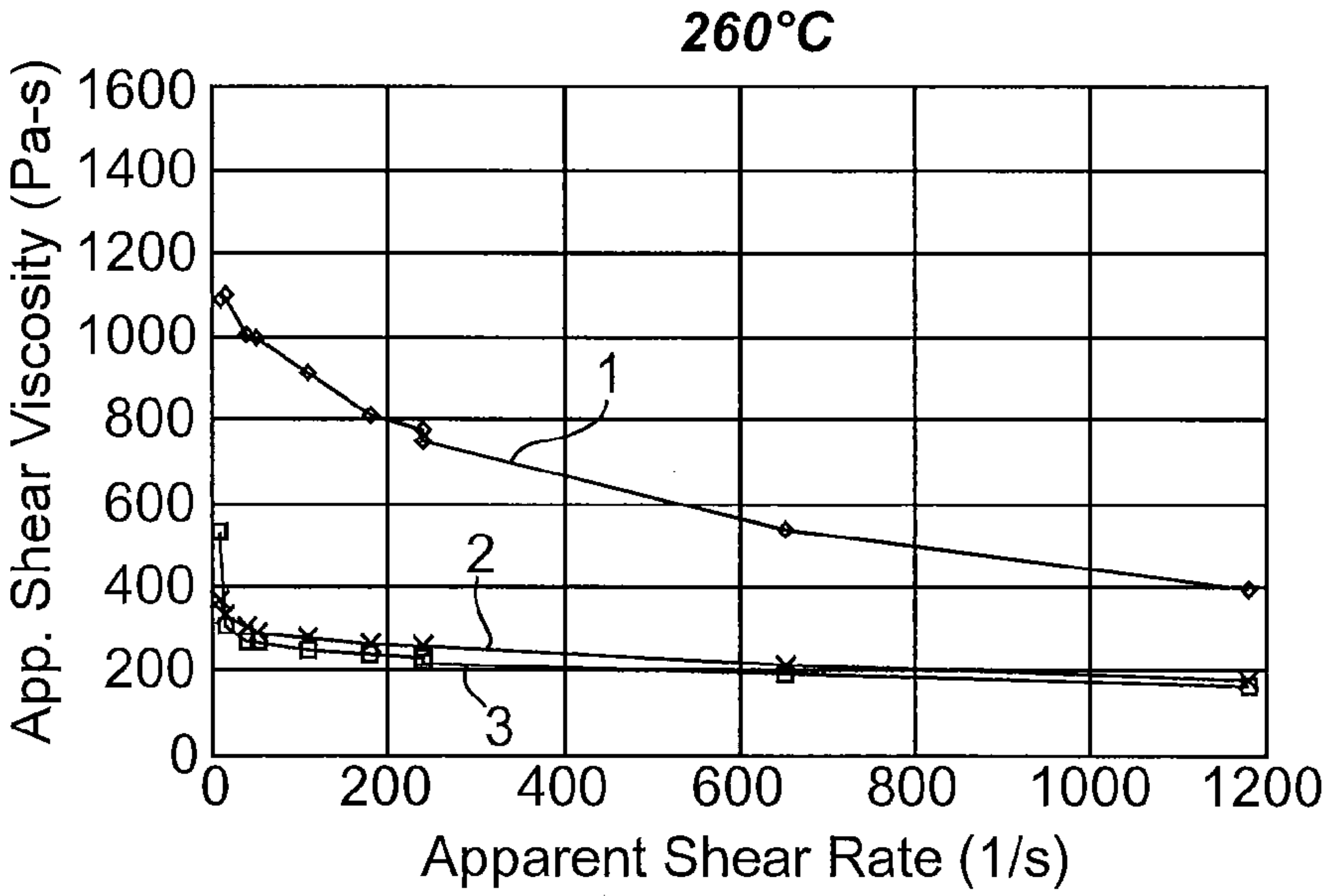

260°C
App. Shear Viscosity (Pa-s)
1600
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Apparent Shear Rate (1/s)
1
2
3

Fig. 4

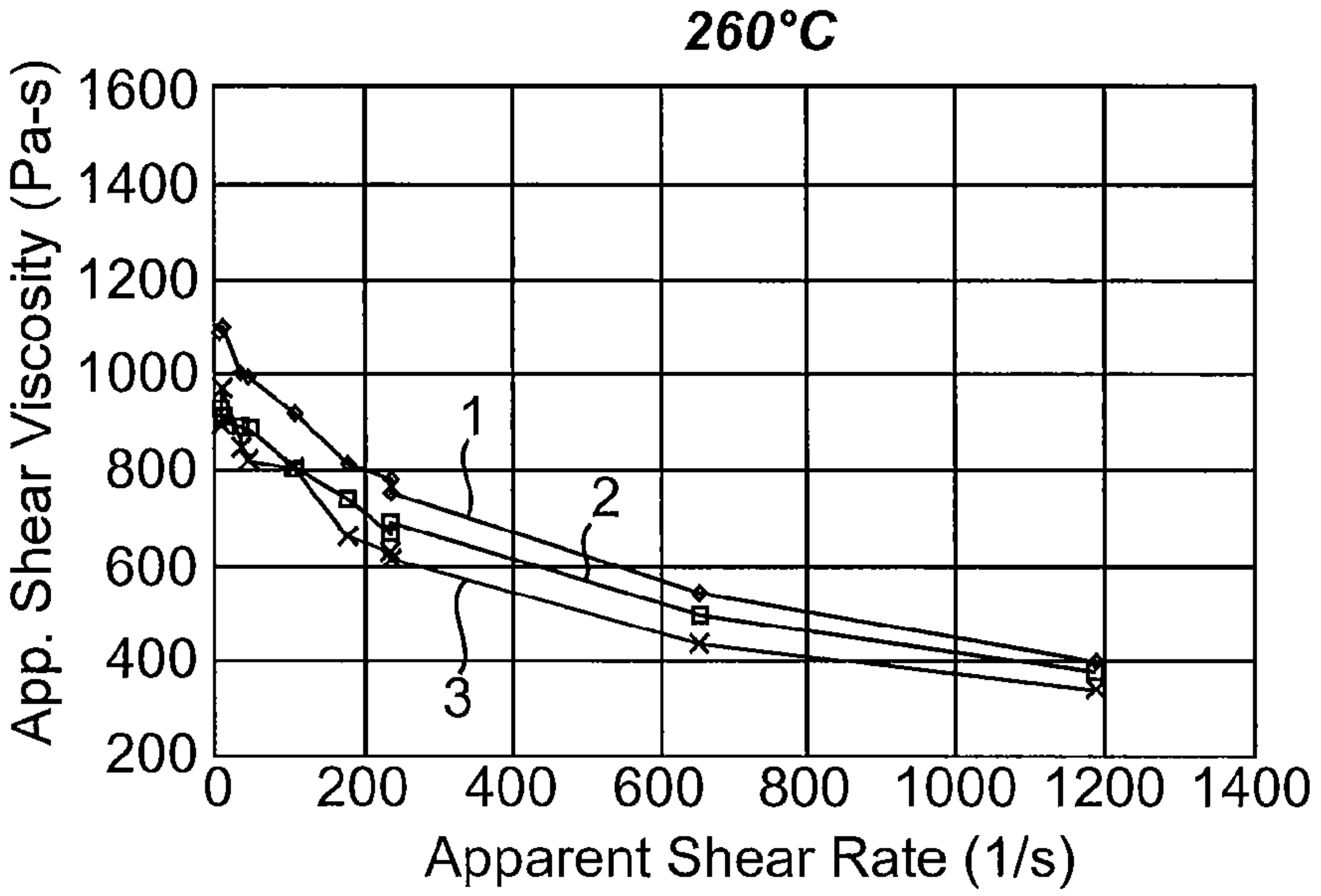

260°C
App. Shear Viscosity (Pa-s)
1600
1400
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
Apparent Shear Rate (1/s)
1
2
3

Fig. 5

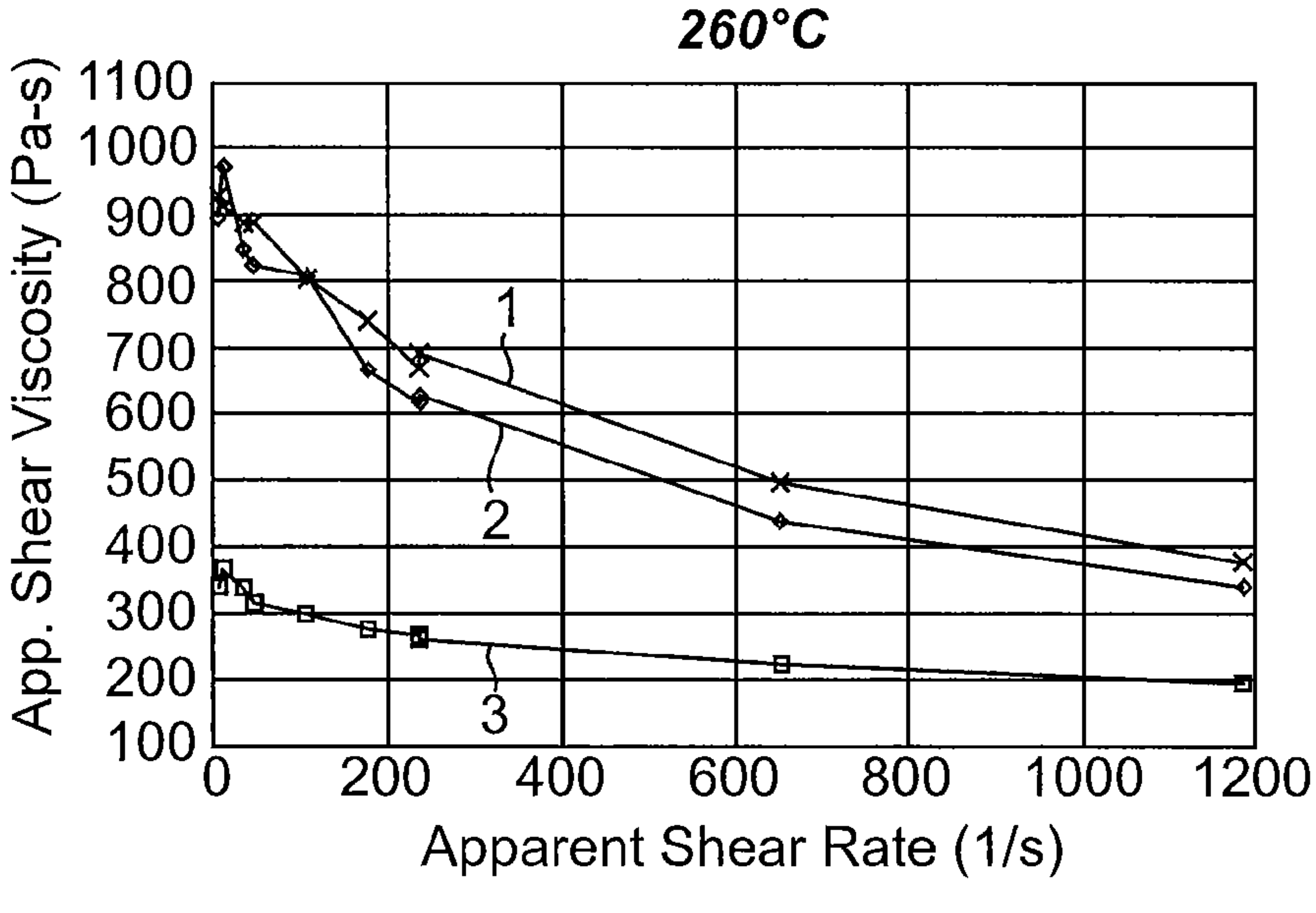
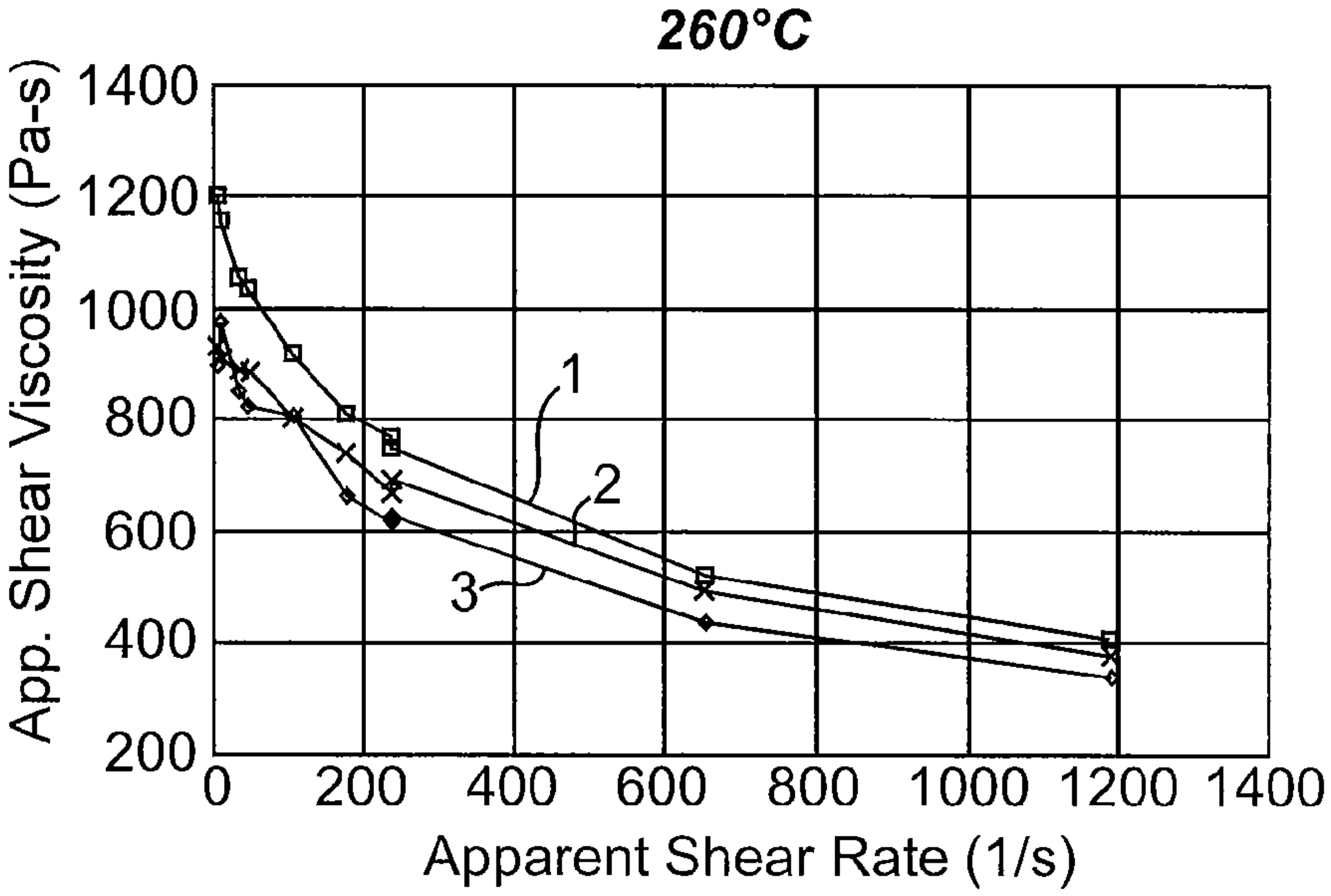

260°C
App. Shear Viscosity (Pa-s)
1100
1000
900
800
700
600
500
400
300
200
100
0
200
400
600
800
1000
1200
Apparent Shear Rate (1/s)
1
2
3

Fig. 6


260°C
App. Shear Viscosity (Pa-s)
1400
1200
1000
800
600
400
200
0
200
400
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800
1000
1200
1400
Apparent Shear Rate (1/s)
1
2
3

Fig. 7

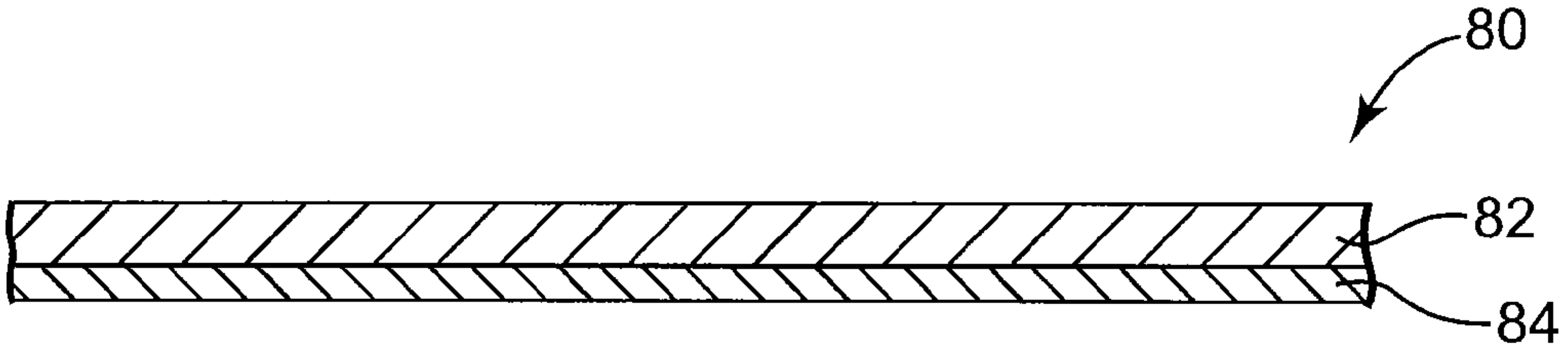


Fig. 8

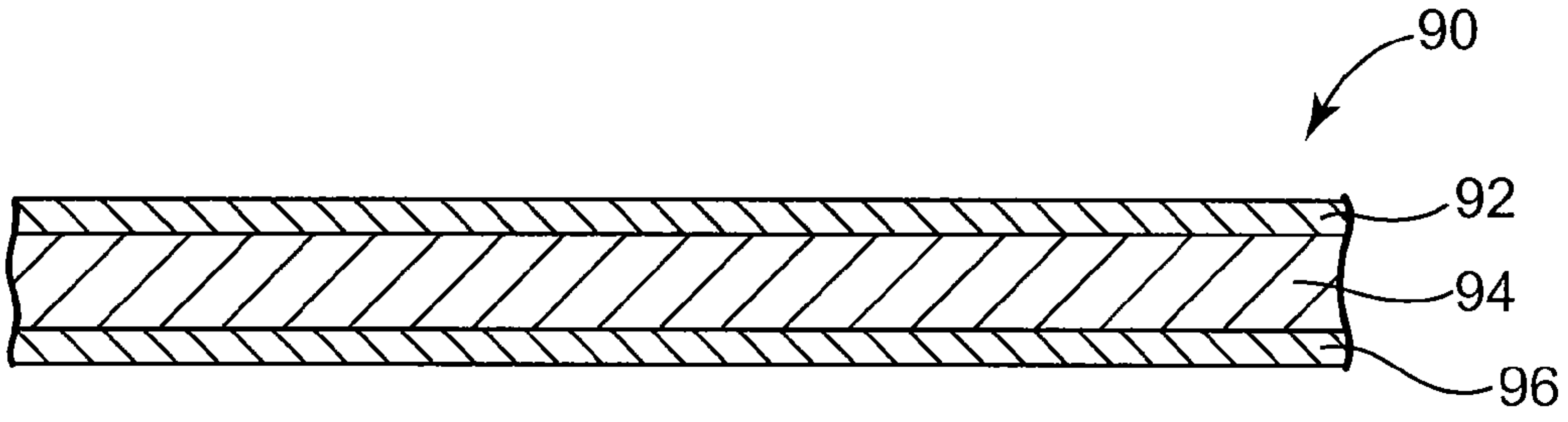
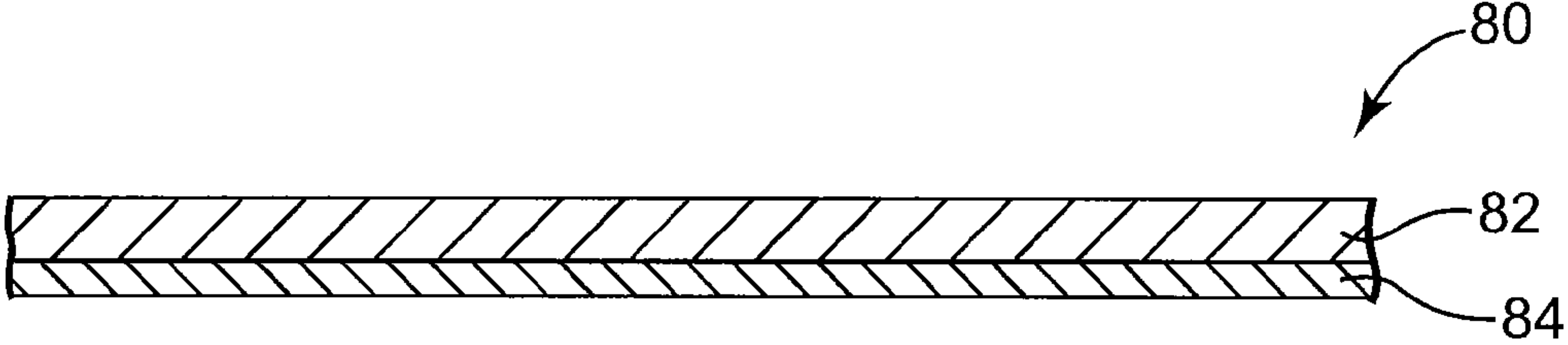


Fig. 9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