Title: PLASTIC HOLLOW HBER CONTAINING A SHEAR-THICKENING FLUID FOR HIGH TENSILE STRENGTH FIBERS

Abstract: A method of forming a multi-component structure, the method including co-extruding at least one polymer and a shear-thickening fluid to form a multi-component structure, wherein an interior region of the multi-component structure includes the shear-thickening fluid, and wherein an outer region of the multi-component structure includes the at least one polymer. Also disclosed is a multi-component structure including at least one polymer, and a shear-thickening fluid, wherein an interior region of the multi-component structure comprises the shear-thickening fluid, and wherein an outer region of the multi-component structure comprises the at least one polymer.
Embodiments disclosed herein relate generally to fibers incorporating shear-thickening liquids. More specifically, embodiments disclosed herein relate to polymeric hollow fibers containing a shear-thickening liquid.

Background

Fluids may exhibit various flow behaviors, including Newtonian, shear-thinning, and shear-thickening. Most hydrocarbons and aqueous solutions exhibit Newtonian behavior, where the viscosity of the fluid depends primarily on temperature and pressure, and does not change significantly due to forces acting on the fluid, such as shear stress. Most polymeric solutions exhibit shear-thinning behavior, where the application of shear to the solution decreases the viscosity of the solution.

Some solutions, however, are known to exhibit shear-thickening behavior. The application of shear to a shear-thickening fluid increases the viscosity of solution. Shear-thickening fluids may also be referred to as dilatant materials, increasing in viscosity and setting to a solid as a result of deformation by expansion pressure, shear forces, or agitation.

Several uses have been developed for shear-thickening fluids (STF's), including: various oil production applications, such as well control fluids, viscosifiers, fracturing fluids, and the like; anti-misting additives for jet fuel; grease additives; pastes for printing; and in consumer products such as toothpaste.

Shear-thickening fluids have also been used in torque converters for all wheel drive systems. On high traction road surfaces, the relative motion between primary and secondary drive wheels is similar, resulting in low shear and negligible power transfer. When the primary drive wheels slip, the shear increases, causing the fluid to thicken, resulting in torque transfer to the secondary drive wheels. Shear-thickening fluids have also been used in energy dissipative devices, such as shock absorbers, as described in U.S. Patent No. 4,503,952. U.S. Patent Application Publication Nos. 20020171067 and 20060231357 disclose the use of shear-thickening fluids in other
automotive control devices, including dampers, mounts, brakes, valves, and similar devices.

[0006] U.S. Patent Application Publication No. 20060260210 discloses a temporary barrier that includes an inflatable fabric bag that is permeated with a shear-thickening fluid. U.S. Patent Nos. 5,599,290 and 5,545,128 disclose garments useful for preventing hip fracture that include one or more envelopes made of a flexible material, where the envelopes contain a shear-thickening fluid.

[0007] In addition to the above described end-use applications, shear-thickening fluids have also been used in various energy absorbing materials, such as body armor. For example, U.S. Patent Application Publication No. 20040173422 discloses an energy absorbing material comprising a cellular solid or fibrous matrix impregnated with a shear-thickening fluid. Body armor has also been produced using shear-thickening fluids, where the body armor is made of fiber or yarn, and where the fibers are impregnated with a shear-thickening fluid.


[0009] Other composites containing shear-thickening fluids are disclosed in U.S. Patent Application Publication No. 20060234572. One composite disclosed includes impregnating the shear-thickening fluid into a porous solid scaffold material, such as fabric-like or textile-based solid materials. A second composite disclosed is formed by mixing a shear-thickening fluid with a liquid or fluid-like component that can subsequently be converted to a solid through heating, cooling, chemical reactions, etc.

[0010] The above described applications for combining shear-thickening fluids and fibers or fabrics involve impregnating or soaking the fabrics in the shear-thickening fluid. The shear-thickening fluid is thus exposed to the surface of the fabric, which
may result in the degradation of the fabric properties over time due to frictional wear, washings, and other environmental attacks.

[0011] Accordingly, there exists a need for improved films, fibers, and fabrics incorporating shear-thickening fluids.

SUMMARY OF DISCLOSURE

[0012] In one aspect, embodiments disclosed herein relate to a method of forming a multi-component structure, the method including: co-extruding at least one polymer and a shear-thickening fluid to form a multi-component structure; wherein an interior region of the multi-component structure includes the shear-thickening fluid; and wherein an outer region of the multi-component structure includes the at least one polymer.

[0013] In another aspect, embodiments disclosed herein relate to a multi-component structure including: at least one polymer; and a shear-thickening fluid; wherein an interior region of the multi-component structure comprises the shear-thickening fluid; and wherein an outer region of the multi-component structure comprises the at least one polymer.

[0014] Other aspects and advantages will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0015] Figures IA-IC illustrate cross-sections of various embodiments of the multi-component fibers disclosed herein.

[0016] Figure 2 graphically illustrate the shear response of a shear-thickening fluid at various temperatures.

[0017] Figures 3A and 3B illustrate die heads useful for incorporating a shear-thickening fluid into a fiber according to embodiments disclosed herein.

[0018] Figure 4 is a flow chart illustrating a method for forming a multi-component structure according to embodiments disclosed herein.

[0019] Figure 5 illustrates a process to form a multi-component fiber from a multi-layered film according to embodiments disclosed herein.

[0020] Figure 6 illustrates a multi-layered film according to embodiments disclosed herein.
DETAILED DESCRIPTION

[0022] In one aspect, embodiments disclosed herein relate generally to multi-component structures and methods to form multi-component structures. More specifically, embodiments disclosed herein relate to co-extruding at least one polymer and a shear-thickening fluid to form a multi-component structure, wherein an interior region of the multi-component structure may include the shear-thickening fluid, and wherein an outer region of the multi-component structure may include the at least one polymer. In some embodiments, multi-component structures may include multi- or bicomponent fibers. In other embodiments, multi-component structures may include multi-layered films.

[0023] In some aspects, embodiments disclosed herein relate to fibers incorporating shear-thickening fluids. More specifically, embodiments disclosed herein relate to hollow polymeric fibers encapsulating or containing a shear-thickening fluid. In other aspects, embodiments disclosed herein relate to bicomponent or multi-component fibers, films, and foams having an interior region that includes a shear-thickening fluid and an outer region that includes a polymeric component.

[0024] As discussed above, shear-thickening fluid impregnated fibers have the disadvantage that the shear-thickening fluid is exposed to the elements, and the fabric performance may suffer as the shear-thickening fluid dries or wears out. In contrast, the multi-component structures described herein, encapsulating a shear-thickening fluid region, may protect the shear-thickening fluid from externalities, preventing the degradation of the fabric performance under impact or load conditions.

[0025] The multi-component or bicomponent fibers, films, and foams disclosed herein may have one or more distinct polymeric regions or domains encapsulating or containing one or more regions that include a shear-thickening fluid. The polymer and shear-thickening fluid regions may be arranged in substantially distinct zones across the cross-section of the multi-component or bicomponent fibers, films, and foams, and usually extend continuously along the length of the multi-component or bicomponent fiber, film, or foam.
In some embodiments, a shear-thickening fluid may form the core of a core-sheath bicomponent or multi-component fiber. In other embodiments, a shear-thickening fluid may be contained in an annular space between two polymeric layers of a multi-component fiber.

In some embodiments, a shear-thickening fluid may form the innermost layer of a multi-layer film. In other embodiments, a shear-thickening fluid may be sandwiched between an inner layer and an outer layer of a multi-layer film.

Fibers useful in embodiments disclosed herein may be formed from any natural or synthetic materials. In other embodiments, fibers may be formed from any thermoplastic or polymeric material. Fibers may include any natural or synthetic cellulosic fibers including cotton, abaca, kenaf, sabai grass, flax, esparto grass, straw, jute hemp, bagasse, milkweed floss fibers, and pineapple leaf fibers; and woody fibers.

Synthetic fibers may include rayon, polyolefin fibers, polyester fibers, ethylene vinyl alcohol copolymer fibers, multi-component binder fibers, and the like. Synthetic cellulose fiber types include rayon in all its varieties and other fibers derived from viscose or chemically-modified cellulose. Some suitable polymers that may be used to form the synthetic fibers include, but are not limited to: polyolefins, such as, polyethylene, polypropylene, polybutylene, and the like; polyesters, such as polyethylene terephthalate, poly(glycolic acid) (PGA), poly(lactic acid) (PLA), poly(β-malic acid) (PMLA), poly(ε-caprolactone) (PCL), poly(p-dioxanone) (PDS), poly(3-hydroxybutyrate) (PHB), and the like; polyamides, such as nylons (nylon-6, nylon-6.6, nylon-6,12, and others); polyaramids, such as KEVLAR®, NOMEX®, and the like, TEFLON®, and polyester nylons (EP). Synthetic or natural cellulose polymers, including but not limited to: cellulosic esters; cellulosic ethers; cellulosic nitrates; cellulosic acetates; cellulosic acetate butyrates; ethyl cellulose; regenerated celluloses, such as viscose, rayon, and the like; cotton; flax; silk; hemp; and mixtures thereof may be used in embodiments disclosed herein.

Other polymers suitable for use may include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. In various embodiments, the fabric layer may include polymers such as ethylene-vinyl acetate.
(EVA), ethylene/ vinyl alcohol copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), and thermoplastic polyurethanes. Suitable polyolefins may include linear or low density polyethylene, polypropylene (including atactic, isotactic, syndiotactic and impact modified versions thereof) and poly (4-methyl-1-pentene). Suitable styrenic polymers may include polystyrene, rubber modified polystyrene (HIPS), styrene/acrylonitrile copolymers (SAN), rubber modified SAN (ABS or AES) and styrene maleic anhydride copolymers.

Examples of the resins that may be used as fibers in the present disclosure include homopolymers and copolymers (including elastomers) of an alpha-olefin such as ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-heptene, 1-hexene, 1-octene, 1-decene, and 1-dodecene, as typically represented by polyethylene, polypropylene, poly-1-butene, poly-3-methyl-1-butene, poly-3-methyl-1-pentene, poly-4-methyl-1-pentene, ethylene-propylene copolymer, ethylene-1-butene copolymer, and propylene-1-butene copolymer; copolymers (including elastomers) of an alpha-olefin with a conjugated or non-conjugated diene, as typically represented by ethylene-butadiene copolymer and ethylene-ethyldiene norbornene copolymer; and polyolefins (including elastomers) such as copolymers of two or more alpha-olefins with a conjugated or non-conjugated diene, as typically represented by ethylene-propylene-butadiene copolymer, ethylene-propylene-dicyclopentadiene copolymer, ethylene-propylene-1,5-hexadiene copolymer, and ethylene-propylene-ethyldiene norbornene copolymer; ethylene-vinyl compound copolymers such as ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymer, ethylene-vinyl chloride copolymer, ethylene acrylic acid or ethylene-(meth)acrylic acid copolymers, and ethylene-(meth)acrylate copolymer; styrenic copolymers (including elastomers) such as polystyrene, ABS, acrylonitrile-styrene copolymer, α-methylstyrene-styrene copolymer, styrene vinyl alcohol, styrene acrylates such as styrene methylacrylate, styrene butyl acrylate, styrene butyl methacrylate, and styrene butadienes and crosslinked styrene polymers; and styrene block copolymers (including elastomers) such as styrene-butadiene copolymer and hydrate thereof, and styrene-isoprene-styrene tri-block copolymer; polyvinyl compounds such as polyvinyl chloride, polyvinylidene chloride, vinyl chloride-vinylidene chloride copolymer, polymethyl
acrylate, and polymethyl methacrylate; polyamides such as nylon 6, nylon 6,6, and nylon 12; thermoplastic polyesters such as polyethylene terephthalate and polybutylene terephthalate; polycarbonate, polyphenylene oxide, and the like; and glassy hydrocarbon-based resins, including poly-dicyclopentadiene polymers and related polymers (copolymers, terpolymers); saturated mono-olefins such as vinyl acetate, vinyl propionate and vinyl butyrate and the like; vinyl esters such as esters of monocarboxylic acids, including methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, phenyl acrylate, methyl methacrylate, ethyl methacrylate, and butyl methacrylate and the like; acrylonitrile, methacrylonitrile, acrylamide, mixtures thereof; resins produced by ring opening metathesis and cross metathesis polymerization and the like. These resins may be used either alone or in combinations of two or more.

[0033] Embodiments disclosed herein may also include a polymeric fiber that may include at least one multi-block olefin interpolymer. Suitable multi-block olefin inter polymers may include those described in U.S. Provisional Patent Application No. 60/818,911, for example. The term "multi-block copolymer" or "multi-block inter polymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") preferably joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined endto-end with respect to polymerized ethylenic functionality, rather than in pendant or grafted fashion. In certain embodiments, the blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, or any other chemical or physical property.

[0034] As another suitable resin, the esterification products of a di- or poly-carboxylic acid and a diol comprising a diphenol may be used. These resins are illustrated in U.S. Patent No. 3,590,000, which is incorporated herein by reference. Other specific examples of resins include styrene/methacrylate copolymers, and styrene/butadiene copolymers; suspension polymerized styrene butadienes; polyester resins obtained from the reaction of bisphenol A and propylene oxide followed by the reaction of
the resulting product with fumaric acid; and branched polyester resins resulting from
the reaction of dimethylterephthalate, 1,3-butanediol, 1,2-propanediol, and
pentaerythritol, styrene acrylates, and mixtures thereof.

Further, specific embodiments of the present disclosure may employ ethylene-
based polymers, propylene-based polymers, propylene-ethylene copolymers, and
styrenic copolymers as one component of a composition. Other embodiments of the
present disclosure may use polyester resins, including those containing aliphatic
diols such as UNOXOL 3,4 diol, available from The Dow Chemical Company
(Midland, MI).

In specific embodiments, polyolefins such as polypropylene, polyethylene,
copolymers thereof, and blends thereof, as well as ethylene-propylene-diene
terpolymers, may be used. In some embodiments, preferred olefinic polymers
include homogeneous polymers, as described in U.S. Patent No. 3,645,992 issued to
Elston; high density polyethylene (HDPE), as described in U.S. Patent No.
4,076,698 issued to Anderson; heterogeneously branched linear low density
polyethylene (LLDPE); heterogeneously branched ultra low linear density
polyethylene (ULDPE); homogeneously branched, linear ethylene/alpha-olefin
copolymers; homogeneously branched, substantially linear ethylene/alpha-olefin
polymers, which can be prepared, for example, by processes disclosed in U.S. Patent
Nos. 5,272,236 and 5,278,272, the disclosures of which are incorporated herein by
reference; and high pressure, free radical polymerized ethylene polymers and
copolymers such as low density polyethylene (LDPE) or ethylene vinyl acetate
polymers (EVA).

Polymer compositions, and blends thereof, described in U.S. Patent Nos.
6,566,446, 6,545,088, 6,538,070, 6,448,341, 6,316,549, 6,111,023, 5,869,575,
5,844,045, or 5,677,383, each of which is incorporated herein by reference in its
entirety, may also be suitable in some embodiments. In some embodiments, the
blends may include two different Ziegler-Natta polymers. In other embodiments,
the blends may include blends of a Ziegler-Natta polymer and a metallocene
polymer. In still other embodiments, the polymer used herein may be a blend of two
different metallocene polymers. In other embodiments, single site catalyst polymers
may be used.
The olefin polymers, copolymers, interpolymers, and multi-block interpolymers may be functionalized by incorporating at least one functional group in its polymer structure. Exemplary functional groups may include, for example, ethylenically unsaturated mono- and di-functional carboxylic acids, ethylenically unsaturated mono- and di-functional carboxylic acid anhydrides, salts thereof and esters thereof. Such functional groups may be grafted to an olefin polymer, or it may be copolymerized with ethylene and an optional additional comonomer to form an interpolimer of ethylene, the functional comonomer and optionally other comonomer(s). Means for grafting functional groups onto polyethylene are described for example in U.S. Patents Nos. 4,762,890, 4,927,888, and 4,950,541, the disclosures of which are incorporated herein by reference in their entirety. One particularly useful functional group is maleic anhydride.

In other particular embodiments, the thermoplastic resin may be ethylene vinyl acetate (EVA) based polymers. In other embodiments, the thermoplastic resin may be ethylene-methyl acrylate (EMA) based polymers. In other particular embodiments, the ethylene-alpha olefin copolymer may be ethylene-butene, ethylene-hexene, or ethylene-octene copolymers or interpolymers. In other particular embodiments, the propylene-alpha olefin copolymer may be a propylene-ethylene or a propylene-ethylene-butene copolymer or interpolimer.

Shear-Thickening Fluids

Shear-thickening fluids useful in embodiments disclosed herein may include any useful shear-thickening fluid. Dilatant or shear-thickening fluids show a reversible increase in viscosity with increase of deformation or shear rate. These fluids are generally stable dispersions of colloidal particles. The critical deformation rate at which the system switches into the high viscosity state may be adjusted by varying the particle size, volume concentration, or other parameters. In accordance with embodiments disclosed herein, such shear-thickening fluids may be used to fill the core of a hollow fiber to make a material that progressively stiffens with increasing deformation rate.

The shear-thickening fluid may be a surfactant solution exhibiting a shear-thickening transition, or may be any fluid which exhibits an increase in viscosity with increasing applied shear stress or shear rate. Shear-thickening fluids may be formed
using water-based or oil-based solvents or liquid carriers, and may include those having a mineral oil or silicon oil base fluid. In some embodiments, the liquid carrier may include polyethylene glycol having a molecular weight ranging from 200 to 400 Daltons. The viscosity of the liquid carrier may range from 0.5 to 1,000,000 centipoise in some embodiments; and from 10 to 100,000 centipoise in other embodiments.

Shear-thickening fluids may be formed by suspending solids in a liquid carrier. The particles may be made of various materials including, but not limited to, inorganic oxides, silicon dioxide, calcium carbonate, polymers such as polyurethane, polyvinylchloride, polystyrene or polymethylmethacrylate, or other polymers from emulsion polymerizations, and starches, such as corn starch.

The shear-thickening fluids may be concentrated dispersions of particulates within a fluid medium that exhibit an increase in viscosity with increasing applied stress. The particles within the fluid may have a smallest dimension of less than 10 microns in some embodiments; less than 1 micron in other embodiments; and less than 100 nm in the smallest dimension in other embodiments. Particles may be of any solid material, including spherical amorphous silica such as that produced via Stober type synthesis, synthetic inorganic particles synthesized via solution precipitation processes such as precipitated calcium carbonate, or synthesized by gel-sol techniques (hematite, TiO₂), or fumed silica, or carbon black. Natural inorganic particulates such as montmorillonite and kaolin clays may be dispersed in solvents and have been shown to exhibit shear-thickening behavior. Ground mineral powders, such as quartz, calcite, talc, gypsum, and mica may be dispersed in liquid mediums and exhibit shear-thickening behavior. The solid dispersed phase may also be polymeric in nature, such as plastisols generated through emulsion polymerization processes such as poly(methyl methacrylate) (PMMA), and polystyrene (PS) microspheres.

The solids used may have a particle size less than that of the fiber core diameter or annular thickness in which the thickening fluid will be contained. In some embodiments, the particles may have an average particle size of 100 microns or less; 20 microns or less in other embodiments; 10 microns or less in other embodiments; 5 microns or less in other embodiments; and 2 microns or less in yet other embodiments. In other embodiments, the particles may have an average particle size ranging from 0.1 to 10 microns; from 0.2 to 5 microns in other embodiments; and
from 0.5 to 2 microns in yet other embodiments. In other embodiments, the particles may have an average particle size ranging from 0.1 to 1 microns; from 0.2 to 0.8 microns in other embodiments; and from 0.4 to 0.6 microns in yet other embodiments.

The particles may be stabilized in solution or dispersed by charge, Brownian motion, adsorbed surfactants, and adsorbed or grafted polymers, polyelectrolytes, polyampholytes, or oligomers. Particle shape is not limited, and may include rods, spherical particles, elliptical particles, and disk-like or clay particles. The particles may be synthetic and/or naturally occurring minerals. Also, the particles may be monodisperse, bidisperse, or polydisperse in size and shape.

The volume occupied by the solid particles may be 10 to 80 percent of the total volume of the shear-thickening fluid in some embodiments. In other embodiments, the volume occupied by the solid particles may be 20 to 70 percent of the total volume of the shear-thickening fluid; from 30 to 60 percent in other embodiments; and from 35 to 53 percent in yet other embodiments.

The shear rate at which the shear-thickening fluids may undergo the shear-thickening transition may range from 1 to 10,000 s⁻¹ in some embodiments. In other embodiments, the shear-thickening transition may occur in the range from 1 to 100 s⁻¹.

Fiber Formation

The multi-component or bicomponent fibers disclosed herein include fibers that have one or more distinct polymer regions or domains encapsulating or containing one or more regions that include a shear-thickening fluid. The polymer and shear-thickening fluid regions may be arranged in substantially distinct zones across the cross-section of the multi-component or bicomponent fibers, and usually extend continuously along the length of the bicomponent fiber. In some embodiments, an interior of the multi-component fibers may include the shear-thickening fluid, and an outer region of the multi-component fiber may include a polymer.

The configuration of a multi-component or bicomponent fiber may be, for example, a sheath/core arrangement, as illustrated in Figure 1A, where a polymeric sheath 1 encapsulates a shear-thickening fluid core 2. In other embodiments, a multi-component fiber may be, for example, a sheath/core arrangement, as illustrated in Figure 1B, where a shear-thickening fluid region 4 is contained in an annular region.
between two polymeric regions 5a, 5b. Polymeric regions 5a, 5b may be the same or different polymers. In other embodiments, as illustrated in Figure 1C, a multi- or bicomponent fiber may have an "islands-in-the sea" arrangement, where two or more shear-thickening fluid regions 7 are encapsulated or contained within a polymeric region 8. Other configurations for multi- or bicomponent fibers may also be used where a polymeric regions encapsulates or contains a shear-thickening fluid region. Bicomponent fibers are further described in U.S. Patent Nos. 6,225,243, 6,140,442, 5,382,400, 5,336,552 and 5,108,820.

[0052] The multi- or bicomponent fibers having a shear-thickening fluid region encapsulated by a polymeric region may show softness to the touch, and may develop high rigidity under impact or load conditions. The outer polymeric region may provide for the soft feel, and the inner shear-thickening fluid region may provide support or impact resistance when placed under load.

[0053] Currently, body armor is formed by immersing a fibrous substrate in a shear-thickening fluid, impregnating the substrate with the shear-thickening fluid. Impregnated fibers have the disadvantage that the shear-thickening fluid is exposed to the elements, and the fabric performance may suffer as the shear-thickening fluid dries or wears out. In contrast, the multi- or bicomponent fibers described herein, encapsulating a shear-thickening fluid region, may protect the shear-thickening fluid from externalities, preventing the degradation of the fabric performance under impact or load conditions.

[0054] The multi- and bicomponent fibers disclosed herein may be of any thickness, may include one or more polymeric components, and may include one or more shear-thickening fluids. Post-filling a hollow fiber with a shear-thickening fluid would be cumbersome due to the response of the fluid under shear. Thus, the shear-thickening fluid would have to be extruded into the middle of a fiber during fiber production. However, shear-thickening fluids, by their nature, are not easily pumped. It has been found that, by pumping the shear-thickening fluid through a hot die, the shear response of the shear-thickening fluid decreases, allowing the shear-thickening fluid to be incorporated into the fiber core. For example, Figure 2 illustrates the response of a 1:1 mixture, based on volume, of porous silica powder and polyethylene glycol (PEG), having an M_w of 200, as a function of temperature. At 25°C, the viscosity of the silica-PEG shear-thickening fluid increases rapidly at a shear rate of
approximately 20 s⁻¹. In contrast, at 100°C, the viscosity of the silica-PEG shear-thickening fluid does not increase, but rather decreases, up to shear rates as high as 1000 s⁻¹, and only increases slightly at shear rates above 1000 s⁻¹.

Any process which provides for the extrusion of multi-component fibers and filaments, such as that set forth in U.S. Patent No. 5,290,626, may be used to form the shear-thickening fluid containing fibers described herein. Methods for making multi-component fibers are well known and need not be described here in detail. Generally, the multi-component fibers may be prepared using conventional multi-component textile fiber spinning processes and apparatus and utilizing mechanical drawing techniques as known in the art. Processing conditions for the melt extrusion and fiber-formation may vary depending upon the polymers used to form the fibers, and may be determined by those skilled in the art. Bicomponent fibers may be formed in some embodiments by meltblowing or meltspinning processes.

One example of a system useful for forming the fibers disclosed may be described as follows. Fiber production may be performed by introducing the shear-thickening fluid into a line via a pressure assisted gravity feed system. Incorporation of the shear-thickening fluid into the fiber may be accomplished by utilizing a die structure, examples of which are illustrated in cross-section in Figures 3A and 3B. Referring now to Figure 3A, as shear-thickening fluid 12 meets die 14, the shear-thickening fluid 12 is heated, reducing the shear-thickening response of shear-thickening fluid 12, allowing fluid 12 to be pumped into core 16 of the fiber 18 during spinning. Polymeric material 20 is extrudated through flow channel 22, encapsulating shear-thickening fluid 12 as the fiber 18 is drawn. In some embodiments, a needle (not shown) may extend from die 14. The needle tip in some embodiments may extend up to 5 mm past the assembled die. Figure 3B illustrates a disassembled die structure, where AA indicates the flow channels for the fiber material, and BB indicates the injection needle through which the shear-thickening fluid is fed during fiber drawing. The ratio of the polymeric sheath to the shear-thickening fluid core may be adjusted by controlling the feed rate of the shear-thickening fluid relative to the extrusion rate of the polymeric sheath.

Referring now to Figure 4, a process for forming the multi-component fibers described herein is illustrated. If required to reduce the shear response of a shear-thickening fluid, the shear-thickening fluid may be heated in step 30. The shear-
thickening fluid and a polymer may then be co-extruded in step 32 to form a multi-
component structure, wherein an interior region of the multi-component structure
includes the shear-thickening fluid, and wherein an outer region of the multi-
component structure includes the polymer. Following co-extrusion, the multi-
component structure may be quenched or cooled in step 34, solidifying or increasing
the viscosity of the polymeric layer and increasing the shear response of the shear-
thickening fluid. The multi-component structure may then be further processed in
step 36 to form manufactured articles incorporating the multi-component structure.

The overall diameter of fibers used in embodiments disclosed herein may be
widely varied. The fiber denier, however, may be adjusted to suit the capabilities of
the finished article. Fiber diameter may be measured and reported in a variety of
fashions. Generally, fiber diameter is measured in denier per filament. Denier is a
textile term which is defined as the grams of the fiber per 9000 meters of that fiber's
length. Monofilament generally refers to an extruded strand having a denier per
filament greater than 15, usually greater than 30. Fine denier fiber generally refers to
fiber having a denier of about 15 or less. Microdenier (or microfiber) generally refers
to fiber having a diameter not greater than about 100 micrometers. Fibers useful in
embodiments disclosed herein may include fibers having a diameter corresponding to
monofilament, fine denier, and microdenier fibers. In some embodiments, the fiber
diameter may range from about 0.5 to about 20,000 denier/filament. The sheath
thickness and average particle size of any solids in the shear-thickening fluid may be
selected based upon the desired filament diameter or denier.

In some embodiments, the sheath thickness may range from about 0.1 to about
200 microns. In other embodiments, the sheath thickness may range from about 0.1
to about 100 microns; from about 0.5 to about 50 microns in other embodiments; and
from about 1 to about 20 microns in yet other embodiments.

In some embodiments, the cross-sectional area of the shear-thickening fluid
containing regions may be from 1 to 99 percent of the total cross sectional area of the
fiber. In other embodiments, the cross-sectional area of the shear-thickening fluid
containing regions may be from 1 to 90 percent of the total cross section area of the
fiber; from 5 to 75 percent in other embodiments; and from 10 to 50 percent in yet
other embodiments.
In some embodiments, the cross-sectional area of the polymeric regions may be from 1 to 99 percent of the total cross-sectional area of the fiber. In other embodiments, the cross-sectional area of the polymeric regions may be from 10 to 99 percent of the total cross section area of the fiber; from 25 to 95 percent in other embodiments; and from 50 to 90 percent in yet other embodiments.

The multi-component fibers may have shear-thickening fluid regions that comprise 5 to 80 percent by weight of the fiber. In other embodiments, the shear-thickening fluid regions may be from 10 to 70 percent by weight of the fiber. The multi-component fibers may have polymeric regions that comprises from about 20 to about 95 percent by weight of the fiber. In other embodiments, the polymeric regions may comprise from about 30 to about 90 percent by weight of the fiber.

The shape of the fiber is not limited. For example, in some embodiments the fibers may have a circular or elliptical cross-sectional shape. In other embodiments, the fibers may have different shapes, such as a trilobal shape, or a flat (i.e., "ribbon" like) shape. The multi-component fibers disclosed herein are not limited by the shape of the fiber.

Films and Foams

Suitable films and foams may be formed from the polymers used to form the above described fibers. Similar to the fiber forming process, multi-layer foams, films, and microcapillary films may be formed by co-extruding a shear-thickening fluid and at least one polymer. A multilayered film may be formed where an interior layer of the multilayered film structure includes the shear-thickening fluid, and where outer layers of the multilayered film are formed from one or more polymers. For example, a shear-thickening fluid may be sandwiched between two polymeric layers, forming a multilayered sheet. In some embodiments, a shear-thickening fluid may be contained within the cavity of a microcapillary film.

Similar to the fibers described above, in some embodiments, the cross-sectional area of the shear-thickening fluid containing regions may be from 1 to 99 percent of the total cross-sectional area of the multi-layered films or foams. In other embodiments, the cross-sectional area of the shear-thickening fluid containing regions may be from 1 to 90 percent of the total cross section area of the multi-layered films.
or foams; from 5 to 75 percent in other embodiments; and from 10 to 50 percent in yet other embodiments.

[0067] In some embodiments, the cross-sectional area of the polymeric regions may be from 1 to 99 percent of the total cross-sectional area of the multi-layered films or foams. In other embodiments, the cross-sectional area of the polymeric regions may be from 10 to 99 percent of the total cross section area of the multi-layered films or foams; from 25 to 95 percent in other embodiments; and from 50 to 90 percent in yet other embodiments.

[0068] The multi-layered films and foams may have shear-thickening fluid regions that comprise 5 to 80 percent by weight of the multi-layered films or foams. In other embodiments, the shear-thickening fluid regions may be from 10 to 70 percent by weight of the multi-layered films or foams. The multi-layered films or foams may have polymeric regions that comprises from about 20 to about 95 percent by weight of the multi-layered films or foams. In other embodiments, the polymeric regions may comprise from about 30 to about 90 percent by weight of the multi-layered films or foams.

[0069] In some embodiments, fibers may be formed from the multi-layered films having a shear-thickening fluid region. For example, as illustrated in Figure 5, a multi-layer film 40 may have a first polymeric layer 41, a shear-thickening fluid layer 42, and a second polymeric layer 43. The multi-layer film may undergo a rolling process 45, resulting in fiber 47 having an inner polymeric region 41a, a shear-thickening fluid region 42a, and an outer polymeric region 43a. Although fibers illustrated herein are depicted as circular, fibers may be of any of a wide variety of shapes.

[0070] In some embodiments, the films used in multi-layered films disclosed herein may be fibrous films. For example, as illustrated in Figure 6, a multi-layered film may have a first fibrous layer 51, a shear-thickening fluid layer 52, and a second fibrous layer 53. Fibrils 55, hook-shaped fibrils in some embodiments, may extend from one or more of the fibrous layers 51, 53.

[0071] In some embodiments, fibrils 55 may extend from both fibrous layers 51, 53, and the fibrils may form a link between first fibrous layer 51 and second fibrous layer 53. In this manner, the fibrils may act as a barrier between shear-thickening fluid volumes. Additionally, the interconnected fibrils may provide for increased film
strength, providing improved performance under shear. As described above with respect to Figure 5, the multi-layered films having fibrils extending between the layers may also be rolled to form fibers, where the fibrils interconnect the outer polymeric sheath layer with the inner polymeric core layer.

[0072] End-Use Applications

[0073] The shear-thickening fluid containing bicomponent and multi-component fibers disclosed herein may be used in various applications, including textiles, ropes, fabrics, and others. Fabrics made from the multi- and bicomponent fibers disclosed herein include woven, non-woven, and knit fabrics. Non-woven fabrics can be made by various methods, e.g., spunlaced (or hydrodynamically entangled) fabrics as disclosed in U.S. Patent Nos. 3,485,706 and 4,939,016, carding and thermally bonding staple fibers; spunbonding continuous fibers in one continuous operation; or by melt blowing fibers into fabric and subsequently calendering or thermally bonding the resultant web. These various non-woven fabric manufacturing techniques are well known to those skilled in the art and the scope of the present disclosure is not limited to any particular method. Other structures made from such fibers are also included within the scope of the disclosure, including, for example, blends of the fibers of the present disclosure with other fibers (e.g., PET, cotton, etc.). Continuous filaments as described herein may also be used in woven applications where high resilience is desired.

[0074] Materials formed from fibers disclosed herein may also be rendered pervious or "breathable" by any method well known in the art including by aperturing, slitting, microperforating, mixing with fibers or foams, or the like and combinations thereof. Examples of such methods include U.S. Patent Nos. 3,156,242, 3,881,489, 3,989,867, and 5,085,654, each of which is herein incorporated by reference in their entirety.

[0075] Embodiments of the shear-thickening fluid containing fibers disclosed herein may be used in applications such as body armor and KEVLAR® replacement applications (such as hovercraft skirting, blast protection sheets, and sports wear). Other embodiments of the STF-filled fibers may be used as fibers in medical and hygiene applications. STF-filled fibers may also be used in mid-range tenacity applications, such as climbing ropes and seat belts.
Examples

A shear-thickening fluid (STF) is made by mixing a porous silica powder (NIPPON SHOKUBAI KE-P50, an amorphous silica powder with an average particle diameter of 450 nm) with a 200 molecular weight polyethylene glycol (PEG) (Dow Carbowax PEG 200E) at a ratio of 1:1 based on volume, optionally while simultaneously heating the STF, the silica powder, and the PEG. To blend 100 grams of the STF, 35 grams of PEG is transferred to a beaker together with 35 grams of silica. This is mixed utilizing a Heidolph STI high power rotary mixer at speed step 3 until a uniform consistency is reached. The remaining 30 grams of silica is added to the mixture and the mixing is continued. The final liquid is mixed until a uniform consistency is achieved. The beaker is placed under vacuum at 50 mbar for at least 5 hours at 25°C to remove entrapped air.

Fiber production is performed on an Extrusion Center using homopolymer polypropylene having a melt flow rate of 25 g/10 minutes at 2.16 kg and 230°C as the fiber material, available from The Dow Chemical Company, Midland, Michigan. The polymer is extruded using a temperature profile in the extruder as shown in Table 1, an extruder speed of 27 rpm, twin-screw speed of 43 rpm, fiber speed 33 rpm. A water bath is used to stabilize the fiber before stretching. The die pressure is approximately 17 bar, and the quench temperature is approximately 16°C. The die diameter is 5 mm and a 3 mm thick pin, effectively resulting in a 1 mm concentric extrudate.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Temperature (°C)</th>
<th>Zone</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>158</td>
<td>5</td>
<td>195</td>
</tr>
<tr>
<td>2</td>
<td>179</td>
<td>6</td>
<td>195</td>
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<tr>
<td>3</td>
<td>190</td>
<td>7</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>195</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The STF is introduced into the line via a pressure assisted gravity feed system at 1.8 bar. As the STF meets the die, it is heated, reducing the shear-thickening response, as shown in Figure 2, allowing the STF to be pumped into the core of the fiber during spinning. Incorporation of the liquid into the fiber is done by utilizing a die structure as shown in Figure 3 and described above. The needle tip extending from the die is approximately 4 mm longer than the assembled die.
The tensile performance of the fiber is tested using ASTM D3822-96, using various test speeds (50 mm/min, 100 mm/min, 500 mm/min, and 800 mm/min). For comparative purposes, a full PP fiber, a hollow PP fiber, and a PEG filled fiber were also tested for tensile performance. The results of the tensile tests are shown in Figure 7 and in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pull Rate (mm/min)</th>
<th>Tensile Strength at 5% (MPa)</th>
<th>Tensile Strength at 10% (MPa)</th>
<th>Tensile Strength at 15% (MPa)</th>
<th>Tensile Strength at 20% (MPa)</th>
<th>Tensile Strength at 30% (MPa)</th>
<th>Maximum Force (MPa)</th>
<th>Maximum Force (MPa/dex)</th>
<th>Elongation at Maximum Force (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow</td>
<td>50</td>
<td>10.76</td>
<td>9.53</td>
<td>8.85</td>
<td>8.77</td>
<td>8.76</td>
<td>8.72</td>
<td>19.04</td>
<td>0.00396</td>
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<tr>
<td>Hollow</td>
<td>100</td>
<td>12.10</td>
<td>10.13</td>
<td>9.13</td>
<td>8.59</td>
<td>8.60</td>
<td>8.60</td>
<td>21.51</td>
<td>0.00447</td>
</tr>
<tr>
<td>Hollow</td>
<td>500</td>
<td>11.90</td>
<td>8.86</td>
<td>9.06</td>
<td>9.08</td>
<td>9.14</td>
<td>8.93</td>
<td>21.79</td>
<td>0.00453</td>
</tr>
<tr>
<td>Hollow</td>
<td>800</td>
<td>9.70</td>
<td>7.46</td>
<td>7.28</td>
<td>7.40</td>
<td>7.39</td>
<td>7.41</td>
<td>19.20</td>
<td>0.00399</td>
</tr>
<tr>
<td>Full fiber</td>
<td>50</td>
<td>13.61</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>13.70</td>
<td>0.00251</td>
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<tr>
<td>Full fiber</td>
<td>100</td>
<td>17.61</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>17.33</td>
<td>0.00318</td>
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<tr>
<td>Full fiber</td>
<td>500</td>
<td>18.94</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>18.31</td>
<td>0.00336</td>
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<tr>
<td>Full fiber</td>
<td>800</td>
<td>22.78</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>21.54</td>
<td>0.00395</td>
</tr>
<tr>
<td>PEG-filled</td>
<td>50</td>
<td>13.94</td>
<td>11.46</td>
<td>11.49</td>
<td>11.34</td>
<td>11.45</td>
<td>11.61</td>
<td>23.89</td>
<td>0.00365</td>
</tr>
<tr>
<td>PEG-filled</td>
<td>100</td>
<td>10.02</td>
<td>8.61</td>
<td>8.43</td>
<td>8.51</td>
<td>8.63</td>
<td>8.57</td>
<td>17.81</td>
<td>0.00272</td>
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<tr>
<td>PEG-filled</td>
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<td>9.09</td>
<td>8.38</td>
<td>8.19</td>
<td>8.21</td>
<td>8.32</td>
<td>8.47</td>
<td>17.47</td>
<td>0.00267</td>
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<tr>
<td>PEG-filled</td>
<td>800</td>
<td>17.32</td>
<td>16.09</td>
<td>13.47</td>
<td>12.14</td>
<td>12.12</td>
<td>12.20</td>
<td>19.76</td>
<td>0.00302</td>
</tr>
<tr>
<td>STF-filled</td>
<td>50</td>
<td>24.44</td>
<td>27.81</td>
<td>27.39</td>
<td>19.34</td>
<td>18.76</td>
<td>18.98</td>
<td>34.17</td>
<td>0.00287</td>
</tr>
<tr>
<td>STF-filled</td>
<td>100</td>
<td>31.53</td>
<td>36.96</td>
<td>37.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>37.40</td>
<td>0.00314</td>
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<tr>
<td>STF-filled</td>
<td>500</td>
<td>33.54</td>
<td>42.11</td>
<td>37.64</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>42.27</td>
<td>0.00355</td>
</tr>
<tr>
<td>STF-filled</td>
<td>800</td>
<td>37.47</td>
<td>44.61</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>44.82</td>
<td>0.00376</td>
</tr>
</tbody>
</table>

The results illustrated in Figure 7 and in Table 2 show a slight increase in tensile strength for PEG-filled fibers as compared to hollow fibers. The results also indicate a substantial increase in tensile strength for shear-thickening fluid filled fibers. Tensile strength for all samples is dependent upon pull rate, where a higher pull rate yields a higher tensile strength. The tensile strength of the STF filled fibers is more than two times that of a full fiber, a hollow fiber, or a hollow fiber filled with PEG when tested at a pull rate of 800 mm/min.

At a pull rate of 50 mm/min, the shear-thickening fluid had an elongation of 881%, similar to hollow and PEG-filled fibers. At higher shear rates, elongation values for the shear-thickening fluid filled fibers decreased. The decrease in
elongation of the shear-thickening fluid at higher pull rates is a result of the shear-
thickening response of the shear-thickening fluid. At higher pull rates, higher shear is
placed on the shear-thickening fluid, resulting in a hardening of the fluid. As the fluid
hardens, the fiber becomes less flexible, breaking after only a short elongation.

These results are indicative of a fabric that is flexible during normal activity,
but stiffens upon impact or deformation. The STF-filled fibers may provide high
toughness and high shear strength when under a load, yet the fiber may remain
flexible when the stress or load is not present.

Advantageously, embodiments disclosed herein may provide for one or more
of the following. Fibers having a shear-thickening fluid core may have enhanced
tensile strength compared to neat fibers. Fibers encapsulating a shear-thickening fluid
may protect the shear-thickening fluid from environmental degradation, such as
factional wear and washings. Additionally, incorporating the shear-thickening fluid
into the core of the fiber during the production of the fibers may reduce the number of
steps required to manufacture the fibers and articles made from the fibers.

While the disclosure has been limited to a number of embodiments, those
skilled in the art, having benefit of this disclosure, will appreciate that other
embodiments can be devised which do not depart from the scope of the embodiments
as disclosed herein. Accordingly, the scope of the disclosure should be limited only
by the attached claims.

All priority documents are herein fully incorporated by reference for all
jurisdictions in which such incorporation is permitted. Further, all documents cited
herein, including testing procedures, are herein fully incorporated by reference for all
jurisdictions in which such incorporation is permitted to the extent such disclosure is
consistent with the description of the present invention.
CLAIMS

What is claimed:

1. A method of forming a multi-component structure, comprising:
   - co-extruding at least one polymer and a shear-thickening fluid to form a multi-component structure;
   - wherein an interior region of the multi-component structure comprises the shear-thickening fluid; and
   - wherein an outer region of the multi-component structure comprises the at least one polymer.

2. The method of claim 1, further comprising heating the shear-thickening fluid.

3. The method of claim 1, wherein the multi-component structure is a multi-component fiber.

4. The method of claim 3, wherein the multi-component fiber has a core-sheath configuration.

5. The method of claim 3, wherein the multi-component fiber has an islands-in-the-sea configuration.

6. The method of claim 1, wherein the multi-component structure is a multi-layered film.

7. The method of claim 6, further comprising rolling the multi-layered film to form a multi-component fiber.

8. The method of claim 6, wherein the multi-layered film comprises:
   - an outer region comprising a first fibrous film disposed on a first side of the interior region; and
   - an outer region comprising a second fibrous film disposed on a second side of the interior region.

9. The method of claim 8, wherein at least one of the first and second fibrous films comprise fibrils extending into the interior region.

10. The method of claim 9, wherein fibrils extending from the first fibrous film interconnect with fibrils extending from the second fibrous film.

11. The method of claim 1, wherein the at least one polymer comprises at least one of an ethylene-based homopolymer, copolymer, or multi-block interpolymer and a propylene-based homopolymer, copolymer, or multi-block interpolymer.

12. The method of claim 1, wherein the shear-thickening fluid comprises a liquid carrier and a particulate component.
13. The method of claim 12, wherein the liquid carrier comprises at least one of mineral oil, silicon oil, and polyethylene glycol.

14. The method of claim 12, wherein the particulate component comprises at least one inorganic oxide, silicone dioxide, silica, calcium carbonate, corn starch, polyurethane particles, polyvinylchloride particles, polystyrene particles, and polymethylmethacrylate particles.

15. The method of claim 12, wherein the particulate component has an average particle size equal to or less than 10 microns.

16. The method of claim 12, wherein the particulate component has an average particle size within the range from about 0.1 microns to about 1 micron.

17. The method of claim 12, wherein the particulate component comprises from 20 to 70 volume percent of a total volume of the shear-thickening fluid.

18. A multi-component structure comprising:
   at least one polymer; and
   a shear-thickening fluid;
   wherein an interior region of the multi-component structure comprises the shear-thickening fluid; and
   wherein an outer region of the multi-component structure comprises the at least one polymer.

19. The multi-component structure of claim 18, wherein the multi-component structure is a multi-component fiber.

20. The multi-component structure of claim 19, wherein the multi-component fiber has a core-sheath configuration.

21. The multi-component structure of claim 19, wherein the multi-component fiber has an islands-in-the-sea configuration.

22. The multi-component structure of claim 18, wherein the multi-component structure is a multi-layered film.

23. The multi-component structure of claim 22, wherein the multi-layered film comprises:
   an outer region comprising a first fibrous film disposed on a first side of the interior region; and
   an outer region comprising a second fibrous film disposed on a second side of interior region.
24. The multi-component structure of claim 23, wherein at least one of the first and second fibrous films comprise fibrils extending into the interior region.

25. The multi-component structure of claim 24, wherein fibrils extending from the first fibrous film interconnect with fibrils extending from the second fibrous film.

26. The multi-component structure of claim 18, wherein the at least one polymer comprises at least one of an ethylene-based homopolymer, copolymer, or multi-block interpolymer and a propylene-based homopolymer, copolymer, or multi-block interpolymer.

27. The multi-component structure of claim 18, wherein the shear-thickening fluid comprises a liquid carrier and a particulate component.

28. The multi-component structure of claim 27, wherein the liquid carrier comprises at least one of mineral oil, silicon oil, and polyethylene glycol.

29. The multi-component structure of claim 27, wherein the particulate component comprises at least one inorganic oxide, silicone dioxide, silica, calcium carbonate, corn starch, polyurethane particles, polyvinylchloride particles, polystyrene particles, and polymethylmethacrylate particles.

30. The multi-component structure of claim 27, wherein the particulate component has an average particle size equal to or less than 10 microns.

31. The method of claim 27, wherein the particulate component has an average particle size within the range from about 0.1 microns to about 1 micron.

32. The multi-component structure of claim 27, wherein the particulate component comprises from 20 to 70 volume percent of a total volume of the shear-thickening fluid.

33. A manufactured article comprising the structure of claim 18.
Figure 4

Further Process

Quench or cool

Co-extrude

Heat to reduce shear response