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(54) Title: POLYARYLENE SULFIDE COMPONENTS FOR AUTOMOTIVE APPLICATIONS

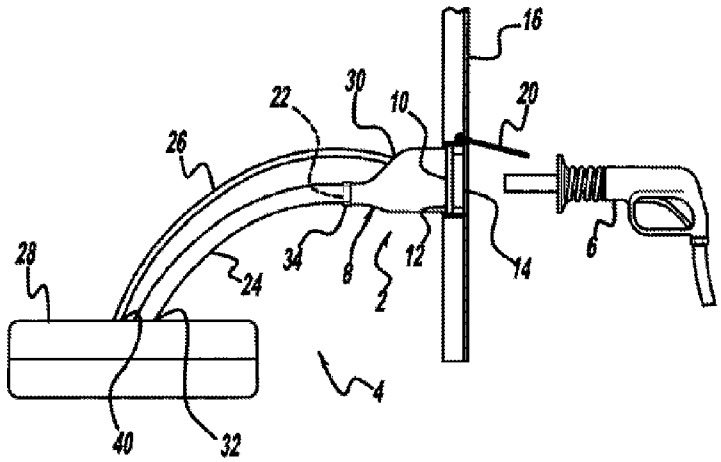


FIG. 7

(57) Abstract: Components for automobiles are described that exhibit high strength and flexibility. The components are formed from a polyarylene sulfide that exhibits high strength and flexibility characteristics. Methods for forming the components are also described. Formation methods include dynamic vulcanization of a polyarylene sulfide composition that includes an impact modifier dispersed throughout the polyarylene sulfide. A crosslinking agent is combined with the other components of the composition following dispersal of the impact modifier throughout the composition. The automotive components can include tubular member such as pipes and hoses that can be utilized in exhaust systems, charge air systems, urea tanks, fuel systems, and so forth.

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POLYARYLENE SULFIDE COMPONENTS FOR AUTOMOTIVE APPLICATIONS

Background of the Invention

[0001] The formation of components for automotive applications presents many unique challenges as automotive components should withstand harsh working conditions over a long lifetime while ideally also being light weight and relatively inexpensive to produce. For example, Vehicles that have been designed to carry large cargo loads face unique operating conditions due to the circumstances that can be expected during use. For instance, the engines of heavy duty trucks, which include those trucks having a gross vehicle weight range of over about 9,000 kg (about 19,800 pounds), operate at high temperatures, particularly when carrying a load. In addition, heavy duty truck components will encounter high mechanical stresses, large vibrations, and environmental assaults (e.g., dirt and rocks, extreme heat and cold, chemical assaults, etc.) on a regular basis. The day-to-day operating conditions for a heavy duty truck are more extreme in almost every respect as compared to a typical passenger vehicle and the components used to form the heavy duty truck should provide the desired strength characteristics and resistance to degradation in the face of the expected operation conditions over the life of the vehicle.

[0002] In addition, cost and revenue associated with transport of goods are influenced by the weight and durability of the transport vehicles. Exemplary costs include fuel and maintenance. Each pound weight of a vehicle increases fuel consumption and wear on a vehicle. Revenue is also affected by weight. Each pound of additional cargo that may be transported leads to increased revenue. As such, transportation companies attempt to reduce the weight of vehicles while simultaneously retaining durability of replaced parts.

[0003] Specific vehicle components that could benefit from improved materials design include automotive fuel line tubing and hoses including both monolayer and multilayer components. Traditionally, metals were used to form many automotive components including fuel lines, but automotive manufacturers have been replacing metals wherever possible to reduce weight and CO_2 emissions. More recently, fuel line tubing and hoses have been formed of aliphatic

polyamide (PA), high-heat rubber composites, and braided polytetrafluoroethylene (PTFE). Unfortunately, these materials have often provided less than ideal performance and/or required complex and costly formation techniques. For example, while braided PTFE and high heat rubber composites can be used in high heat environments, the constructions are often complex and costly. The use of aliphatic polyamide also has limitations. For instance, PA12 has limitations with regard to both permeation of fuel and long term heat aging at the higher temperatures present in newer vehicles. Thus, automotive components formed of these materials often require a heat shield at added weight and cost. In addition, multi-layer constructions of these materials are often subject to delamination, especially where fluoropolymer layers are present, and generally require special chemical bonding between layers.

[0004] There are multiple different requirements for automotive components such as lines in the fuel system, some of them varying depending upon the final application. For example, in a vapor line, a good barrier property must be provided to prevent vapors from escaping into the environment. In addition, there are thermal and mechanical requirements that should be maintained over a long lifetime. Included in the mechanical requirements are sufficient flexibility and impact strength for both fabrication and safety. In addition to the requirements for vapor lines, liquid lines must also meet the requirement that essentially no materials used in forming the fuel line contaminate the fuel, which could lead to problems such as clogged fuel injectors. Thus, the lines must be chemically resistant to the liquids to be carried by the lines. Many polymers that have been examined for use in forming fuel lines to date have leached oligomers that can clog the fuel system and reduce engine performance.

[0005] Polyarylene sulfides are high-performance polymers that may withstand high thermal, chemical, and mechanical stresses and are beneficially utilized in a wide variety of applications. Polyarylene sulfides have often been blended with other polymers to improve characteristics of the product composition. For example, elastomeric impact modifiers have been found beneficial for improvement of the physical properties of a polyarylene sulfide composition.

[0006] Unfortunately, elastomeric polymers generally considered useful for impact modification are not compatible with polyarylene sulfides and phase separation has been a problem in forming compositions of the two. Attempts have

been made to improve the composition formation, for instance through the utilization of compatibilizers. However, even upon such modifications, compositions including polyarylene sulfides in combination with impact modifying polymers still fail to provide product performance as desired, particularly in applications that require both high heat resistance and high impact resistance as may be encountered by heavy duty truck components.

[0007] What are needed in the art are automotive components such as heavy duty truck components and automotive fuel lines formed of polyarylene sulfide compositions that exhibit light weight and excellent barrier properties in conjunction with high strength characteristics and resistance to degradation, even in extreme operating conditions as may be expected for heavy duty trucks.

Summary of the Invention

[0008] Disclosed in one embodiment is an automotive component formed of a polyarylene sulfide composition. The polyarylene sulfide composition includes a polyarylene sulfide and a crosslinked impact modifier. The automotive component exhibits high strength and good flexibility. For instance, the polyarylene sulfide composition used to form the component can exhibit a notched Charpy impact strength of greater than about 3 kJ/m^2 as measured according to ISO Test No. 179-1 at a temperature of 23°C and a notched Charpy impact strength of greater than about 8 kJ/m^2 as measured according to ISO Test No. 179-1 at a temperature of -30°C.

[0009] Also disclosed is a method for forming an automotive component that includes shaping a polyarylene sulfide composition that includes a polyarylene sulfide and a crosslinked impact modifier. For instance, the polyarylene sulfide composition can be injection molded, blow molded, or otherwise molded to form the automotive component. In one embodiment, a method can include first forming the polyarylene sulfide composition according to a process that includes feeding a polyarylene sulfide, an impact modifier, and a cross linking agent to a melt processing unit. More specifically, the cross linking agent can be fed to the processing unit following combination of the impact modifier and the polyarylene sulfide and following distribution of the impact modifier throughout the polyarylene sulfide.

[0010] Also disclosed are automotive components that can beneficially incorporate the polyarylene sulfide composition including, without limitation, tubular

members. Tubular members can encompass both single layer and multi-layer members such as pipes and hoses suitable for carrying water, oil, gasoline, diesel, air, exhaust, urea, etc. Vehicles such as heavy duty trucks incorporating the components are also disclosed herein.

Brief Description of the Figures

[0011] The present disclosure may be better understood with reference to the following figures:

[0012] FIG. 1 is a single layer tubular member as may be formed from the polyarylene sulfide composition.

[0013] FIG. 2 is a single layer tube as may be formed from the polyarylene sulfide composition

[0014] FIG. 3 is a multi-layer tubular member, one or more layers of which may be formed from the polyarylene sulfide composition.

[0015] FIG. 4 is a two layer hose, one or more layers of which may be formed from the polyarylene sulfide composition.

[0016] FIG. 5 is a three layer hose, one or more layers of which may be formed from the polyarylene sulfide composition.

[0017] FIG. 6 is another multi-layer tubular member, one or more layers of which may be formed from the polyarylene sulfide composition.

[0018] FIG. 7 illustrates a portion of a fuel system that can incorporate one or more fuel lines that include the polyarylene sulfide composition.

[0019] FIG. 8 illustrates an engine for a heavy duty truck including tubular members as may be formed from the polyarylene sulfide composition.

[0020] FIG. 9 illustrates a charge air system coupling for a heavy duty truck as may be formed of the polyarylene sulfide composition.

[0021] FIG. 10 illustrates a urea tank for a heavy duty truck as may incorporate components including the polyarylene sulfide composition.

[0022] FIG. 11 illustrates a fitting of the urea tank of FIG. 10.

[0023] FIG. 12 illustrates another embodiment of a urea tank for a heavy duty truck as may incorporate components including the polyarylene sulfide composition.

[0024] FIG. 13 illustrates a heavy duty truck exhaust system as may incorporate components formed of the polyarylene sulfide composition.

[0025] FIG. 14 illustrates a coiled air brake hose assembly as may

incorporate the polyarylene sulfide composition.

[0026] FIG. 15 illustrates an exemplary heavy duty truck incorporating the air brake hose assembly of FIG. 10.

[0027] FIG. 16 is a schematic representation of a process for forming the polyarylene sulfide composition as disclosed herein.

[0028] FIG. 17 illustrates a continuous blow molding process as may be utilized in forming a fuel line from the polyarylene sulfide composition

[0029] FIG. 18 illustrates the sample used in determination of melt strength and melt elongation of polyarylene sulfide compositions described herein.

[0030] FIG. 19 illustrates the effect of temperature change on the notched Charpy impact strength of a polyarylene sulfide composition as described herein and that of a comparison composition.

[0031] FIG. 20 is a scanning electron microscope image of a polyarylene sulfide composition as described herein (FIG. 20B) and a comparison polyarylene sulfide (FIG. 20A).

[0032] FIG. 21 compares the effect of sulfuric acid exposure on strength characteristics of polyarylene sulfide compositions as described herein and a comparison composition.

[0033] FIG. 22 provides the log of the complex viscosity obtained for polyarylene sulfide compositions described herein as a function of the shear rate.

[0034] FIG. 23 provides the melt strength of polyarylene sulfide compositions described herein as a function of the Hencky strain.

[0035] FIG. 24 provides the melt elongation for polyarylene sulfide compositions described herein as a function of Hencky strain.

[0036] FIG. 25 illustrates a blow molded container formed of the polyarylene sulfide composition.

[0037] FIG. 26A and FIG. 26B are cross sectional images of the container shown in FIG. 25.

[0038] FIG. 27 illustrates the daily weight loss for testing samples in determination of permeation resistance of polyarylene sulfide compositions to CE10 fuel blend.

[0039] FIG. 28 illustrates the daily weight loss for testing samples in determination of permeation resistance of polyarylene sulfide compositions to CM15A fuel blend.

[0040] FIG. 29 illustrates the daily weight loss for testing samples in determination of permeation resistance of polyarylene sulfide compositions to methanol.

Detailed Description

[0041] It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present disclosure.

[0042] The present disclosure is generally directed to automotive components formed of polyarylene sulfide compositions that exhibit excellent toughness and flexibility characteristics as well as resistance to chemical degradation due to contact with, e.g., water, oil, gas, synthetic or natural chemicals, etc. For instance, the automotive components can be utilized in heavy duty trucks or as fuel lines for any type of automobile. Beneficially, the polyarylene sulfide composition can maintain good physical characteristics even when utilized in extreme temperature applications such as may be encountered during the lifetime of the automotive component. The polyarylene sulfide can also maintain good physical characteristics under conditions in which the materials are subjected to extreme temperature fluctuations.

[0043] The polyarylene sulfide composition used to form the automotive components can be formed according to a melt processing technique that includes combining a polyarylene sulfide with an impact modifier to form a mixture and subjecting the mixture to dynamic vulcanization. More specifically, the polyarylene sulfide can be combined with the impact modifier and this mixture can be subjected to shear conditions such that the impact modifier becomes well distributed throughout the polyarylene sulfide. Following formation of the mixture, a polyfunctional crosslinking agent can be added. The polyfunctional crosslinking agent can react with the components of the mixture to form crosslinks in the composition, for instance within and between the polymer chains of the impact modifier.

[0044] Without being bound to any particular theory, it is believed that by adding the polyfunctional crosslinking agent to the polyarylene sulfide composition following distribution of the impact modifier throughout the polyarylene sulfide, interaction between the polyarylene sulfide, the impact modifier, and the crosslinking agent within the melt processing unit can be improved, leading to

improved distribution of the crosslinked impact modifier throughout the composition. The improved distribution of the crosslinked impact modifier throughout the composition can improve the strength and flexibility characteristics of the composition, e.g., the ability of the composition to maintain strength under deformation, as well as provide a composition with good processibility that can be utilized to form a heavy duty truck component that can exhibit excellent resistance to degradation under a variety of conditions.

[0045] The high strength and flexibility characteristics of the polyarylene sulfide composition can be evident by examination of the tensile, flexural, and/or impact properties of the materials. For example, the polyarylene sulfide composition can have a notched Charpy impact strength of greater than about 3 kJ/m^2, greater than about 3.5 kJ/m^2, greater than about 5 kJ/m^2, greater than about 10 kJ/m^2, greater than about 15 kJ/m^2, greater than about 30 kJ/m^2, greater than about 33 kJ/m^2, greater than about 40 kJ/m^2, greater than about 45 kJ/m^2, or greater than about 50 kJ/m^2 as determined according to ISO Test No. 179-1 (technically equivalent to ASTM D256, Method B) at 23°C. The unnotched Charpy samples do not break under testing conditions of ISO Test No. 180 at 23°C (technically equivalent to ASTM D256).

[0046] Beneficially, the polyarylene sulfide composition can maintain good physical characteristics even at extreme temperatures, including both high and low temperatures. For instance, the polyarylene sulfide composition can have a notched Charpy impact strength of greater than about 8 kJ/m^2, greater than about 9 kJ/m^2, greater than about 10 kJ/m^2, greater than about 14 kJ/m^2, greater than about 15 kJ/m^2, greater than about 18 kJ/m^2 , or greater than about 20 kJ/m^2 as determined according to ISO Test No. 179-1 at -30°C; and can have a notched Charpy impact strength of greater than about 8 kJ/m^2, greater than about 9 kJ/m^2, greater than about 10 kJ/m^2, greater than about 11 kJ/m^2, greater than about 12 kJ/m^2, or greater than about 15 kJ/m^2 as determined according to ISO Test No. 179-1 at -40°C.

[0047] Moreover, the effect of temperature change on the polyarylene sulfide composition can be surprisingly small. For instance, the ratio of the notched Charpy impact strength as determined according to ISO Test No. 179-1 at 23°C to that at -30°C can be greater than about 3.5, greater than about 3.6, or greater than about 3.7. Thus, and as described in more detail in the example

section below, as the temperature increases the impact strength of the polyarylene sulfide composition also increases, as expected, but the rate of increase of the impact strength is very high, particularly as compared to a composition that does not include the dynamically crosslinked impact modifier. Accordingly, the polyarylene sulfide composition can exhibit excellent strength characteristics at a wide range of temperatures.

[0048] The polyarylene sulfide composition can exhibit very good tensile characteristics. For example, the polyarylene sulfide composition can have a tensile elongation at yield of greater than about 4.5%, greater than about 6%, greater than about 7%, greater than about 10%, greater than about 25%, greater than about 35%, greater than about 50%, greater than about 70%, greater than about 75%, greater than about 80%, or greater than about 90%. Similarly, the tensile elongation at break can be quite high, for instance greater than about 10%, greater than about 25%, greater than about 35%, greater than about 50%, greater than about 70%, greater than about 75%, greater than about 80%, or greater than about 90%. The strain at break can be greater than about 5%, greater than about 15%, greater than about 20%, or greater than about 25%. For instance the strain at break can be about 90%. The yield strain can likewise be high, for instance greater than about 5%, greater than about 15%, greater than about 20%, or greater than about 25%. The yield stress can be, for example, greater than about 50% or greater than about 53%. The polyarylene sulfide composition may have a tensile strength at break of greater than about 30 MPa, greater than about 35 MPa, greater than about 40 MPa, greater than about 45 MPa, or greater than about 70 MPa.

[0049] In addition, the polyarylene sulfide composition can have a relatively low tensile modulus. For instance, the polyarylene sulfide composition can have a tensile modulus less than about 3000 MPa, less than about 2300 MPa, less than about 2000 MPa, less than about 1500 MPa, or less than about 1100 MPa as determined according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min.

[0050] The polyarylene sulfide composition can exhibit good characteristics after annealing as well. For instance, following annealing at a temperature of about 230°C for a period of time of about 2 hours, the tensile modulus of the composition can be less than about 2500 MPa, less than about 2300 MPa, or less

than about 2250 MPa. The tensile strength at break after annealing can be greater than about 50 MPa, or greater than about 55 MPa, as measured according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min.

[0051] The polyarylene sulfide composition can also be utilized continuously at high temperature, for instance heavy duty truck components formed of the polyarylene sulfide composition may be utilized at a continuous use temperature of up to about 150°C, about 160°C, or about 165°C without loss of tensile strength. For example, the polyarylene sulfide composition can maintain greater than about 95%, for instance about 100% of the original tensile strength after 1000 hours of heat aging at 165°C and can maintain greater than about 95%, for instance about 100% of the original tensile elongation at yield after 1000 hours heat aging at 135°C.

[0052] Tensile characteristics can be determined according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min or 50 mm/min (technically equivalent to ASTM D623 at 23°C).

[0053] The flexural characteristics of the composition can be determined according to ISO Test No. 178 (technically equivalent to ASTM D790 at a temperature of 23°C and a testing speed of 2 mm/min. For example, the flexural modulus of the composition can be less than about 2500 MPa, less than about 2300 MPa, less than about 2000 MPa, less than about 1800 MPa, or less than about 1500 MPa. The polyarylene sulfide composition may have a flexural strength at break of greater than about 30 MPa, greater than about 35 MPa, greater than about 40 MPa, greater than about 45 MPa, or greater than about 70 MPa.

[0054] The deflection temperature under load of the polyarylene sulfide composition can be relatively high. For example, the deflection temperature under load of the polyarylene sulfide composition can be greater than about 80°C, greater than about 90°C, greater than about 100°C, or greater than about 105°C, as determined according to ISO Test No. 75-2 (technically equivalent to ASTM D790) at 1.8 MPa.

[0055] The Vicat softening point can be greater than about 200°C or greater than about 250°C, for instance about 270°C as determined according to the Vicat A test when a load of 10 N is used at a heating rate of 50 K/hr. For the Vicat B test, when a load of 50 N is used at a heating rate of 50 K/hr, the Vicat softening

point can be greater than about 100°C, greater than about 150°C greater than about 175°C, or greater than about 190°C, for instance about 200°C. The Vicat softening point can be determined according to ISO Test No. 306 (technically equivalent to ASTM D1525).

[0056] The polyarylene sulfide composition can also exhibit excellent stability during long term exposure to harsh environmental conditions. For instance, under long term exposure to an acidic environment, the polyarylene sulfide composition can exhibit little loss in strength characteristics. For instance, following 500 hours exposure to a strong acid (e.g., a solution of about 5% or more strong acid such as sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, etc.), the polyarylene sulfide composition can exhibit a loss in Charpy notched impact strength of less than about 17%, or less than about 16% following exposure of about 500 hours to a strong acid solution at a temperature of about 40°C, and can exhibit a loss in Charpy notched impact strength of less than about 25%, or less than about 22% following exposure of about 500 hours to a strong acid solution at a temperature of about 80°C. Even under harsher conditions, for instance in a 10% sulfuric acid solution held at a temperature of about 80°C for 1000 hours, the polyarylene sulfide composition can maintain about 80% or more of the initial Charpy notched impact strength. The polyarylene sulfide composition can also maintain desirable strength characteristics following exposure to other potentially degrading materials, such as salts, e.g., road salts as may be encountered by heavy trucks.

[0057] Permeation resistance can be important for a wide variety of applications for the polyarylene sulfide composition, for instance when utilizing the composition in formation of heavy duty truck components such as fuel lines, storage tanks, or the like. The polyarylene sulfide composition can exhibit excellent permeation resistance to a wide variety of materials. For instance, a shaped product formed of the polyarylene sulfide composition can exhibit a permeation resistance to a fuel or a fuel source (e.g., gasoline, diesel fuel, jet fuel, unrefined or refined oil, etc.) of less than about 3 g-mm/m^2-day, less than about 2 g-mm/m^2-day, less than about 1 g-mm/m^2-day, or less than about 0.5 g-mm/m^2-day. By way of example, the polyarylene sulfide composition (or a product formed of the polyarylene sulfide composition) can exhibit a permeation resistance to an ethanol blend of ethanol/iso-octane/toluene at a weight ratio of 10:45:45 at 40°C of

less than about 3 g-mm/m^2-day, less than about 2.5 g-mm/m^2-day, less than about 1 g-mm/m^2-day, or less than about 0.1 g-mm/m^2-day. The permeation resistance to a blend of 15 wt.% methanol and 85 wt.% oxygenated fuel (CM15A) at 40°C can be less than about 3 g-mm/m^2-day, less than about 2.5 g-mm/m^2-day, less than about 1 g-mm/m^2-day, less than about 0.5 g-mm/m^2-day, less than about 0.3 g-mm/m^2-day, or less than about 0.15 g-mm/m^2-day. The permeation resistance to methanol at 40°C can be less than about 1 g-mm/m^2-day, less than about 0.5 g-mm/m^2-day, less than about 0.25 g-mm/m^2-day, less than about 0.1 g-mm/m^2-day, or less than about 0.06 g-mm/m^2-day. Permeation resistance can be determined according to SAE Testing Method No. J2665. In addition, the polyarylene sulfide composition can maintain original density following long term exposure to hydrocarbons. For example, the composition can maintain greater than about 95% of original density, greater than about 96% of original density, such as about 99% of original density following long term (e.g., greater than about 14 days) exposure to hydrocarbons such as heptane, cyclohexane, toluene, and so forth, or combinations of hydrocarbons.

[0058] The polyarylene sulfide composition can exhibit good heat resistance and flame retardant characteristics. For instance, the composition can meet the V-0 flammability standard at a thickness of 0.2 millimeters. The flame retarding efficacy may be determined according to the UL 94 Vertical Burn Test procedure of the "Test for Flammability of Plastic Materials for Parts in Devices and Appliances", 5th Edition, Oct. 29, 1996. The ratings according to the UL 94 test are listed in the following table:

Rating	**Afterflame Time (s)**	**Burning Drips**	Burn to Clamp
V-0	< 10	No	No
V-1	< 30	No	No
V-2	< 30	Yes	No
Fail	< 30		Yes
Fail	> 30		No

[0059] The "afterflame time" is an average value determined by dividing the total afterflame time (an aggregate value of all samples tested) by the number of samples. The total afterflame time is the sum of the time (in seconds) that all the

samples remained ignited after two separate applications of a flame as described in the UL-94 VTM test. Shorter time periods indicate better flame resistance, i.e., the flame went out faster. For a V-0 rating, the total afterflame time for five (5) samples, each having two applications of flame, must not exceed 50 seconds. Using the flame retardant of the present invention, articles may achieve at least a V-1 rating, and typically a V-0 rating, for specimens having a thickness of 0.2 millimeters.

[0060] The polyarylene sulfide composition can also exhibit good processing characteristics, for instance as demonstrated by the melt viscosity of the composition. For instance, the polyarylene sulfide composition can have a melt viscosity of less than about 2800 poise as measured on a capillary rheometer at 316°C and 400 sec^{-1} with the viscosity measurement taken after five minutes of constant shear. Moreover, the polyarylene sulfide composition can exhibit improved melt stability over time as compared to polyarylene sulfide compositions that do not include crosslinked impact modifiers, i.e., while polyarylene sulfide compositions that do not include a crosslinked impact modifier tend to exhibit an increase in melt viscosity over time, disclosed compositions can maintain or even decrease in melt viscosity over time.

[0061] The polyarylene sulfide composition can have a complex viscosity as determined at low shear (0.1 radians per second (rad/s)) and 310°C of greater than about 10 kPa/sec, greater than about 25 kPa/sec, greater than about 40 kPa/sec, greater than about 50 kPa/sec, greater than about 75 kPa/sec, greater than about 200 kPa/sec, greater than about 250 kPa/sec, greater than about 300 kPa/sec, greater than about 350 kPa/sec, greater than about 400 kPa/sec, or greater than about 450 kPa/sec. Higher value for complex viscosity at low shear is indicative of the crosslinked structure of the composition and the higher melt strength of the polyarylene sulfide composition. In addition, the polyarylene sulfide composition can exhibit high shear sensitivity, which indicates excellent characteristics for use in formation processes such as blow molding and extrusion processing.

[0062] The polyarylene sulfide composition may be utilized in forming all manner of components as may be incorporated in an automobile. In one embodiment, the polyarylene sulfide composition may be utilized in forming tubular members that may be subject to extreme temperatures as well as large

temperature fluctuations during use. For instance, tubular members may be used in cooling air systems, gasoline lines, diesel lines, air brake lines, urea tanks, exhaust systems, and the like. Components as may be formed from the polyarylene sulfide composition are not limited to tubular members, however, and other heavy duty truck components such as flanges, valves, valve seats, seals, sensor housings, thermostats, thermostat housings, diverters, linings, propellers, and so forth, may be formed of the polyarylene sulfide composition.

[0063] The tubular members formed from the polyarylene sulfide composition may be single-layered or multi-layered. In operation, a tubular member may be a component of, e.g., a hose assembly or a fuel line assembly or a fluid transfer system. A fluid transfer system generally includes a tubular member such as a hose and at one or more ends of the hose, one or more clamps, couplings, connectors, tubing, nozzles, and/or fittings, fluid handling devices, and the like.

[0064] A component can include the polyarylene sulfide composition throughout the entire component or only a portion of the component. For instance, when considering a component having a large aspect ratio (L/D > 1), such as a tubular member, the component can be formed such that the polyarylene sulfide composition extends along a section of the component and an adjacent section can be formed of a different composition, for instance a different polyarylene sulfide composition. Such a component can be formed by, e.g., altering the material that is fed to a molding device during a formation process. The component can include an area in which the two materials are mixed that represents a border region between a first section and a second section formed of different materials. A component can include a single section formed of the polyarylene sulfide composition or a plurality of sections, as desired. Moreover, other sections of a component can be formed of multiple different materials. By way of example, when considering a tubular component such as a fluid conduit, both ends of the tubular component can be formed of the polyarylene sulfide composition and a center section can be formed of a less flexible composition. Thus, the more flexible ends can be utilized to tightly affix the component to other components of a system. Alternatively, a center section of a component could be formed from the polyarylene sulfide composition, which can improve flexibility of the component in that section, making installation of the component easier.

[0065] Referring to FIG. 1, one embodiment of a tubular member 110 formed from the polyarylene sulfide composition is shown. As shown, the tubular member 110 extends in multiple directions leading to a relatively complex shape. For instance, during formation and before the polyarylene sulfide composition can solidify, the angular displacements as shown in FIG. 1 can be formed into the part. The tubular member 110 includes angular displacement changes at 112, 114 and 116. The tubular member 110 may comprise, for instance, a part that may be used in the exhaust system of a heavy duty truck.

[0066] FIG. 2 illustrates a perspective view of a single layer tube 150 formed of the polyarylene sulfide composition. A single layer tube can be utilized, for example, in forming a vent line and/or a fuel line. A single layer tube 150 can generally have a wall thickness of less than about 3 millimeters, for instance from about 0.5 to about 2.5 millimeters, or from about 0.8 to about 2 millimeters. Single layer tube 150 can generally have a cross sectional diameter of less than about 10 millimeters, or less than about 5 millimeters in one embodiment. The length of a single layer tube can vary depending on the specific application and can be relatively long, for instance about 1 meter long or more, or can be short, for instance less than about 50 centimeters, or less than about 10 centimeters. Additionally, a single layer tube 50 can have a corrugated surface or a smooth surface.

[0067] A tubular member that incorporates the polyarylene sulfide composition can be a multi-layered tubular member. FIG. 3 illustrates a multi-layered tubular member 210 as may incorporate the polyarylene sulfide composition in one or more layers of the tubular member. For example, the inner layer 212 can include the polyarylene sulfide composition. The outer layer 214 and the intermediate layer 216 can include a polyarylene sulfide composition that is the same or different than the polyarylene sulfide composition utilized to form the inner layer. Alternatively, layers of the multilayer tubular member may be formed of different materials. For example, in one embodiment the intermediate layer 216 can be formed of polyamides from the group of homopolyamides, co-polyamides, their blends or mixtures with each other or with other polymers. Alternatively, layer 216 can be formed of a fiber reinforced material such as a fiber-reinforced resin composite or the like. For example, a polyaramid (e.g., Kevlar®) woven mat can

be utilized to form an intermediate layer 216 that is highly resistant to mechanical assaults.

[0068] Outer layer 214 can provide protection from external assaults as well as provide insulative or other desirable characteristics to the tubular member. For example, a multi-layer hose can include an outer layer 214 formed from an adequate kind of rubber material. Examples of such materials include thermoplastic elastomer such as polyamide thermoplastic elastomer, polyester thermoplastic elastomer, polyolefin thermoplastic elastomer, and styrene thermoplastic elastomer. Other possible materials for outer layer 214 include, without limitation, ethylene-propylene-diene terpolymer rubber, ethylene-propylene rubber, chlorosulfonated polyethylene rubber, a blend of acrylonitrile-butadiene rubber and polyvinyl chloride, a blend of acrylonitrile-butadiene rubber and ethylene-propylene-diene terpolymer rubber, and chlorinated polyethylene rubber.

[0069] Outer layer 214 can alternatively be formed of a harder, less flexible material, such as a polyolefin, polyvinylchloride, or a high density polyethylene, a fiber reinforced composite material such as a glass fiber composite or a carbon fiber composite, or a metal material such as a steel jacket.

[0070] Of course, a multi-layer tubular member is not limited to three layers, and may include two, four, or more distinct layers.

[0071] FIG. 4 illustrates a two-layered fuel line 160 and FIG. 5 illustrates a three-layered fuel line 70 as may incorporate the polyarylene sulfide composition in one or more layers of the fuel line 160, 70. Multi-layer fuel lines, similar to single layer fuel tubes, can be formed to have a wide variety of cross sectional and length dimensions, as is known in the art. In general, each layer of a multi-layer fuel line can have a wall thickness of less than about 2 millimeters, or less than about 1 millimeter; and the inner diameter of the multi-layer fuel line can generally be less than about 100 millimeters, less than about 50 millimeters, or less than about 30 millimeters.

[0072] As can be seen, two-layered fuel line 160 includes an inner layer 61 and an outer layer 62. Three-layered fuel line 70 includes an inner layer 71, an intermediate layer 72, and an outer layer 73. The excellent barrier properties of the polyarylene sulfide composition combined with the chemical resistance properties of the polyarylene sulfide composition make it suitable for use in forming an inner layer of a multi-layer fuel line. For example, the inner layers 61, 71 of the

illustrated fuel lines 160, 70 can be formed of the polyarylene sulfide composition.

[0073] The polyarylene sulfide composition is not limited to utilization as an inner layer of a multi-layer fuel line. The high strength characteristics of the polyarylene sulfide composition combined with the excellent barrier properties and good flexibility make the polyarylene sulfide composition suitable for use in forming outer layers and/or intermediate layers of a multi-layer fuel line in addition to or alternative to forming the inner layer of the multi-layer fuel line.

[0074] In those embodiments in which the polyarylene sulfide composition forms a layer of the multi-layer hose, additional layers can be formed of a material that is the same or different than the polyarylene sulfide composition that forms the layer of the multi-layer hose. For example, when considering a fuel line that includes three layers as illustrated in FIG. 5, an intermediate layer 72 and outer layer 73 can be formed of materials as discussed above with reference to FIG. 3. Such materials may also be utilized to form an inner layer of a fuel hose in those embodiments in which the polyarylene sulfide composition is utilized for one or more layers other than the inner layer of the fuel hose. An intermediate layer may be formed over the pre-formed inner layer or may be formed first, and the inner layer may be formed on the interior surface of the first-formed layer, for instance according to a blow molding method.

[0075] Referring to FIG. 6, a multi-layer tubular member including five layers is illustrated. Tubular member 511 includes an inner tube 512, intermediate barrier layer 514, and outer cover 516. Tubular member 511 also includes a reinforcement layer 518 positioned between a tie layer 520 and the outer cover 516, though the reinforcement layer may optionally be located between different layers of the tubular member 511. For example, the reinforcement layer may be located between the inner tube 512 and the intermediate barrier layer 514. Tubular member 511 may also include one or more tie layers and/or adhesive coatings between various layers.

[0076] In general, the inner tube 512 may include the polyarylene sulfide composition. Thus, the inner surface material of the tube may be chosen to withstand the fluids and environmental conditions expected within the hose. The barrier layer 514 may be formed of a material that can exhibit low permeability to materials to be carried by the tubular member, e.g., diesel fuel, gasoline, etc. For example, the barrier layer may be formed of a polyamide such as PA6, PA11,

PA12, PA66, PA 610, PA46, etc., as well as blends of polymers.

[0077] In general, tie layer 520 may be used to facilitate bonding between the barrier layer 514 and other layers such as a reinforcement layer 518. A tie layer may include a rubber composition based on, e.g., epichlorohydrin rubber, nitrile rubber, butadiene rubber/poly(vinyl chloride) blends, hydrogenated nitrile rubber, thermoplastic elastomers, or the like. The tie layer could be an adhesive coating.

[0078] In general, cover 516 may be made of one or more suitable flexible elastomeric or plastic materials designed to withstand the exterior environment encountered. For instance, the cover 516 may be formed of a polyarylene sulfide composition that is the same or different as the polyarylene sulfide composition utilized in forming the inner tube 512. According to another embodiment, the outer cover 516 can be based on a rubber formulation such as, without limitation, hydrogenated nitrile rubber, chlorosulfonated polyethylene, polychloroprene, epichlorohydrin rubber, ethylene/vinylacetate copolymers, polyacrylic rubber, ethylene alkene copolymer, butadiene rubber/poly(vinyl chloride) blends, chlorinated polyethylene, and the like, which may be formulated with other ingredients in accordance with known methods of rubber compounding.

[0079] A reinforcement layer 518 may be present in the tubular member 511. The reinforcement may be applied directly onto intermediate layer 514 and thereby at least a portion of the reinforcement layer 518 may be in contact with the intermediate layer 514. For instance, a spiraled, knitted or braided layer of textile or wire can be utilized as a reinforcement layer 518. In a spiral construction, for example, the spiraled layer may comprise two layers, each applied at or near the so-called lock angle or neutral angle of about 54° with respect to the longitudinal axis of the tubular member 511 but with opposite spiral directions. However, the tubular member 511 is not limited to spiral constructions. A textile or wire reinforcement layer 518 may be knit, braided, wrapped, woven, or non-woven fabric.

[0080] A multi-layer tubular member may further contain one or more adhesive layers formed from adhesive materials such as, for example, polyester polyurethanes, polyether polyurethanes, polyester elastomers, polyether elastomers, polyamides, polyether polyamides, polyether polyimides, functionalized polyolefins, and the like.

[0081] FIG. 7 illustrates a portion of a fuel system that can include a fuel line that includes the polyarylene sulfide composition. FIG. 7 illustrates the intake portion generally of a fuel system and includes a fuel filler neck 2, a filler tube 24, a fuel tank 28, a vent tube 26, and a gas cap 14, and is supported by an automobile body 16, which includes a movable cover 20 to conceal the gas cap 14. The filler neck 2 generally includes a funnel-shaped member 8. The filler neck 2 may receive a nozzle receptor 12, which is an insert adapted to receive a fuel nozzle 6 during fueling. The member 8 is defined at one end by an inlet opening 10 adapted to receive the gas cap 14, which screws directly into threads 36 integrally formed in the member 8.

[0082] An opposite end of the member 8 is defined by an outlet opening 22, which is coupled to a first end 34 of a fuel line 24. The fuel line 24 can be a single layer tube or a multi-layer hose formed of the polyarylene sulfide composition. At a second end 32, the fuel line 24 is coupled to the fuel tank 28. The fuel tank system 4 may also include a vent line 26 that connects to the member 8 at funnel vent opening 30 and to the fuel tank 28 at fuel tank opening 40. The vent line 26 allows displaced vapors in the fuel tank 28 to be vented during fueling. The vent line 26 may also be a single layer tube or a multi-layer hose that can be formed from the polyarylene sulfide composition.

[0083] Any fuel line that has a generally tubular shape and includes a hollow passage through the line (i.e., in the axial direction of the tubular member) as may be included in a vehicle engine, including both gasoline and diesel engines, may include one or more layers formed of the polyarylene sulfide composition, and it should be understood that the fuel lines are not in any way limited to the in-take portion of the fuel system as illustrated in FIG. 7. For example, fuel lines encompassed herein include fuel feed lines that carry fuel from the fuel tank to the engine and can be located downstream and/or upstream of the fuel filter. Other fuel lines as may incorporate the polyarylene sulfide composition can include, without limitation, fuel return lines, fuel bypass lines, fuel crossover lines, breather lines, evaporation lines, etc.

[0084] A tubular member including the polyarylene sulfide composition can exhibit excellent flexibility and heat resistance, which can be of benefit if forming a tubular member for the charge air system of a heavy duty truck. For example, FIG. 8 illustrates an engine block 30 that can include tubular members 32, 33 that can

be formed of the polyarylene sulfide composition and utilized in the air handling system. A heat resistant tubular member for use in the air handling system can include an inner layer that includes the polyarylene sulfide composition and an outer layer formed on an outer peripheral surface of the tubular inner layer that can include a flame retardant. For example, the outer layer can be formed by using a material containing non-halogen flame retardant.

[0085] FIG. 9 illustrates a charge air system coupling 35 as may be formed from the polyarylene sulfide composition. A charge air system coupling 35 can provide a connection between various charge components of the charge air system including, without limitation, at the compressor inlet and discharge, at the charge air cooler, and/or at the turbine inlet and discharge. The flexibility and strength of the polyarylene sulfide composition can provide for a charge air system coupling that can handle slight misalignments between components of the system as well as isolate vibration between ends of the coupling. In addition, the resistance characteristics of the polyarylene sulfide composition can improve the coupling with regard to ozone resistance and increase the life of the component.

[0086] The polyarylene sulfide composition can be beneficially utilized in urea tanks of heavy duty trucks. For example, the urea tank 310 schematically depicted in FIG. 10 includes a container 312 with a bottom wall 314 and a top wall 316. In the top wall 316 there is an opening 318 for the accommodation of a set of fittings 330. The container 312 further comprises a filling opening 317.

[0087] The set of fittings 330 comprises a head 332 arranged to be connected fluid-tightly to the opening 318 in the top wall 316. This may be achieved in many different ways, e.g. by a flange connection between a radial flange 320 (FIG. 11) of the opening 318 and a radial flange 334 of the head 332. The head 332 may also take the form of a screw cap with internal or external threads adapted to engaging with complementary threads (not depicted) of the opening 318. A multiplicity of fittings 336 extend from the head 332 into the container 312. The fittings 336 may include a suction pipe for urea/water solution, a return pipe for unconsumed solution, a heating coil for thawing the solution when the latter is frozen by low ambient temperature, and a level sensor for the solution in the container. Beneficially, one or more of the suction pipe, the return pipe and the heating coil and/or a protective cover 340 may be formed of the polyarylene sulfide composition.

[0088] The excellent strength characteristics of the polyarylene sulfide composition can protect the components of the fittings 336 from harmful mechanical effects due to icing in the container 312, and the fittings 336 can sustain affect from movements of ice in the container 312.

[0089] Another exemplary urea tank assembly 410 is shown in FIG. 12. The urea tank assembly includes a reservoir 412 having a cavity 414 configured for receiving and holding a liquid, such as urea solution 416. The assembly further includes a tubular member 418 that can be formed of the polyarylene sulfide composition having one or more, or plurality of, openings 420 formed therethrough for providing fluid communication between a hollow portion 422 of the hollow member and the cavity of the reservoir. The assembly further includes a heater 424 located proximate to or formed by the hollow portion to heat the urea solution within and about the hollow member. The assembly also includes a pump 426 for causing fluid from within the cavity 414, and in some exemplary embodiments from within the hollow portion, to be pumped to an exhaust gas stream for dispensing therein.

[0090] In operation, the urea solution 416 is pumped, injected or otherwise placed into the cavity 414 through suitable urea input conduit 428 or through other means such as a capped opening 450. The urea solution is heated through heater 424 and pumped through a urea outlet conduit 430 through pump 426. Optionally, pumping of the urea solution may be achieved through a fluid level switch 432, 456 and heating may be based upon temperature reading from a temperature sensor 434. The urea solution travels along the urea outlet conduit to a port in fluid communication with an exhaust gas conduit from an engine. The port provides means, such as an injector, for delivery into an exhaust gas stream and more particularly upstream from an exhaust gas treatment device.

[0091] The polyarylene sulfide composition may also be beneficially utilized in forming components of an exhaust system such as the diesel exhaust system 900 illustrated in FIG. 13 for venting exhaust from an exhaust manifold 905 of a diesel engine 907 as depicted by directional arrow 916. The exhaust system 900, as shown, includes an exhaust line 902 with inlet end 901 and outlet end 903. All or a portion of the exhaust line 902 can be formed of the polyarylene sulfide composition. The inlet end 901 is coupled to the diesel engine 907 through an exhaust manifold 905. The inlet end 901 may include a connection device 904,

which may take on any suitable form. For example, the connection device 904 may be a flange that can be coupled to a similar flange on a connection portion 909 of the exhaust manifold 905. Although the exhaust line 902 is shown as being generally straight, in practice it may take on other profiles and may include straight and curved sections and/or sections of differing diameter.

[0092] The exhaust system 900 includes a first particulate filter 906 disposed adjacent to the inlet end 901 of the exhaust line 902 so as to be in a "close-coupled" position with respect to the engine 907 and, of course, also the exhaust manifold 905. A turbocharger 911 is positioned in the exhaust line 902 and the first particulate filter 906 upstream of the turbocharger 911 such that the hot gases directly impinge upon the first filter 906. The exhaust system 900 of FIG. 9 further includes a second particulate filter 908 positioned in the exhaust line 902. The exhaust system 900 may further include devices such as diffusion and expansion cones 910, 912 at the inlet and outlet ends of the particulate filters 906, 908 to aid in achieving desired exhaust flow distribution in the particulate filters, and/or size and weight reductions in the exhaust line 902.

[0093] The air brake system of a heavy duty truck may also include components formed of the polyarylene sulfide composition. FIG. 14 illustrates an exemplary embodiment of a coiled air brake hose assembly 700. The coiled air brake hose assembly 700 includes a coiled hose 702 having a plurality of coils and a straight terminal end 720. The hose 702 may be a single layer hose or a multi-layer hose as described above in which at least one layer includes the polyarylene sulfide composition.

[0094] The coiled air brake hose assembly 700 also includes a fitting 706 molded over the end of hose 702. In addition, the coiled air brake hose may include a strain relief component 704, embodied in FIG. 14 as a spring. In the exemplary embodiment illustrated, the hose 702 defines a lumen 716 that is accessible via the fitting 706. The overmolded fitting 706 is a single monolithic component and is formed to bond to and conform to the shape of the hose 702 and, optionally, the strain relief component 704.

[0095] FIG. 15 illustrates an exemplary heavy duty truck including a tractor truck and trailer. The coiled air brake hose assembly 700 may be used to couple air brake systems between vehicles or within a vehicle, as shown. Utilization of the polyarylene sulfide composition in forming the air brake hose assembly can be

particularly advantageous. For example, the coiled air brake hose assembly can exhibit considerable leak resistance and protection from external exposure to corrosive chemicals, such as road salts including, without limitation, zinc chloride, calcium chloride, copper chloride, and magnesium chloride. In addition, the assembly can exhibit considerable tensile strength when exposed to longitudinal forces due to the excellent physical characteristics of the polyarylene sulfide composition.

[0096] Of course, heavy duty trucks as may include one or more components formed from a polyarylene sulfide composition are not limited to those as illustrated in FIG. 15. Any heavy duty truck having a gross vehicle weight range over about 9,000 kg is encompassed herein. Such trucks can include trucks have two, three, four, or more axles and can include both tractors and trailers that may be pulled by tractors. By way of example, contractor's trucks, delivery trucks, dump trucks, panel trucks, mix-in-transit trucks, truck tractors, and so forth are encompassed herein.

[0097] According to one embodiment, a method for forming the automotive components can include formation of the polyarylene sulfide composition. FIG. 16 illustrates a schematic of a process that can be used in forming the polyarylene sulfide composition. As illustrated, the components of the polyarylene sulfide composition may be melt-kneaded in a melt processing unit such as an extruder 50. Extruder 50 can be any extruder as is known in the art including, without limitation, a single, twin, or multi-screw extruder, a co-rotating or counter rotating extruder, an intermeshing or non-intermeshing extruder, and so forth. In one embodiment, the composition may be melt processed in an extruder 50 that includes multiple zones or barrels. In the illustrated embodiment, extruder 50 includes 10 barrels numbered 51-60 along the length of the extruder 50, as shown. Each barrel 51-60 can include feed lines 54, 66, vents 52, temperature controls, etc. that can be independently operated. A general purpose screw design can be used to melt process the polyarylene composition. By way of example, a polyarylene sulfide composition may be melt mixed using a twin screw extruder such as a Coperion co-rotating fully intermeshing twin screw extruder.

[0098] In forming a polyarylene sulfide composition, the polyarylene sulfide can be fed to the extruder 50 at a main feed throat 54. For instance, the polyarylene sulfide may be fed to the main feed throat 54 at the first barrel 51 by

means of a metering feeder. The polyarylene sulfide can be melted and mixed with the other components of the composition as it progresses through the extruder 50. The impact modifier can be added to the composition in conjunction with the polyarylene sulfide composition at the main feed throat 54 or downstream of the main feed throat, as desired.

[0099] At a point downstream of the main feed throat 54, and following addition of the impact modifier to the composition, the crosslinking agent can be added to the composition. For instance, in the illustrated embodiment, a second feed line 56 at barrel 56 can be utilized for addition of the crosslinking agent. The point of addition for the crosslinking agent is not particularly limited. However, the crosslinking agent can be added to the composition at a point after the polyarylene sulfide has been mixed with the impact modifier under shear such that the impact modifier is well distributed throughout the polyarylene sulfide.

[00100] The polyarylene sulfide may be a polyarylene thioether containing repeat units of the formula (I):

$$-[(Ar^1)_n\text{-}X]_m\text{-}[(Ar^2)_i\text{-}Y]_j\text{-}[(Ar^3)_k\text{-}Z]_l\text{-}[(Ar^4)_o\text{-}W]_p- \qquad (I)$$

wherein Ar^1, Ar^2, Ar^3, and Ar^4 are the same or different and are arylene units of 6 to 18 carbon atoms; W, X, Y, and Z are the same or different and are bivalent linking groups selected from $–SO_2–$, –S–, –SO–, –CO–, –O–, –COO– or alkylene or alkylidene groups of 1 to 6 carbon atoms and wherein at least one of the linking groups is –S–; and n, m, i, j, k, l, o, and p are independently zero or 1, 2, 3, or 4, subject to the proviso that their sum total is not less than 2. The arylene units Ar^1, Ar^2, Ar^3, and Ar^4 may be selectively substituted or unsubstituted. Advantageous arylene systems are phenylene, biphenylene, naphthylene, anthracene and phenanthrene. The polyarylene sulfide typically includes more than about 30 mol%, more than about 50 mol%, or more than about 70 mol% arylene sulfide (–S–) units. In one embodiment the polyarylene sulfide includes at least 85 mol% sulfide linkages attached directly to two aromatic rings.

[00101] In one embodiment, the polyarylene sulfide is a polyphenylene sulfide, defined herein as containing the phenylene sulfide structure $–(C_6H_4–S)_n–$ (wherein n is an integer of 1 or more) as a component thereof.

[00102] The polyarylene sulfide may be synthesized prior to forming the

polyarylene sulfide composition, though this is not a requirement of a process, and a polyarylene sulfide can be purchased from known suppliers. For instance Fortron® polyphenylene sulfide available from Ticona of Florence, Kentucky, USA can be purchased and utilized as the polyarylene sulfide.

[00103] When employed, synthesis techniques that may be used in making a polyarylene sulfide are generally known in the art. By way of example, a process for producing a polyarylene sulfide can include reacting a material that provides a hydrosulfide ion, e.g., an alkali metal sulfide, with a dihaloaromatic compound in an organic amide solvent.

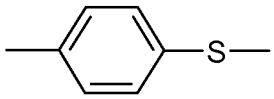
[00104] The alkali metal sulfide can be, for example, lithium sulfide, sodium sulfide, potassium sulfide, rubidium sulfide, cesium sulfide or a mixture thereof. When the alkali metal sulfide is a hydrate or an aqueous mixture, the alkali metal sulfide can be processed according to a dehydrating operation in advance of the polymerization reaction. An alkali metal sulfide can also be generated *in situ*. In addition, a small amount of an alkali metal hydroxide can be included in the reaction to remove or react impurities (e.g., to change such impurities to harmless materials) such as an alkali metal polysulfide or an alkali metal thiosulfate, which may be present in a very small amount with the alkali metal sulfide.

[00105] The dihaloaromatic compound can be, without limitation, an o-dihalobenzene, m-dihalobenzene, p-dihalobenzene, dihalotoluene, dihalonaphthalene, methoxy-dihalobenzene, dihalobiphenyl, dihalobenzoic acid, dihalodiphenyl ether, dihalodiphenyl sulfone, dihalodiphenyl sulfoxide or dihalodiphenyl ketone. Dihaloaromatic compounds may be used either singly or in any combination thereof. Specific exemplary dihaloaromatic compounds can include, without limitation, p-dichlorobenzene; m-dichlorobenzene; o-dichlorobenzene; 2,5-dichlorotoluene; 1,4-dibromobenzene; 1,4-dichloronaphthalene; 1-methoxy-2,5-dichlorobenzene; 4,4'-dichlorobiphenyl; 3,5-dichlorobenzoic acid; 4,4'-dichlorodiphenyl ether; 4,4'-dichlorodiphenylsulfone; 4,4'-dichlorodiphenylsulfoxide; and 4,4'-dichlorodiphenyl ketone.

[00106] The halogen atom can be fluorine, chlorine, bromine or iodine, and 2 halogen atoms in the same dihalo-aromatic compound may be the same or different from each other. In one embodiment, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene or a mixture of 2 or more compounds thereof is used as the dihalo-aromatic compound.

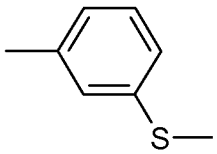
[00107] As is known in the art, it is also possible to use a monohalo compound (not necessarily an aromatic compound) in combination with the dihaloaromatic compound in order to form end groups of the polyarylene sulfide or to regulate the polymerization reaction and/or the molecular weight of the polyarylene sulfide.

[00108] The polyarylene sulfide may be a homopolymer or may be a copolymer. By a suitable, selective combination of dihaloaromatic compounds, a polyarylene sulfide copolymer can be formed containing not less than two different units. For instance, in the case where p-dichlorobenzene is used in combination with m-dichlorobenzene or 4,4'-dichlorodiphenylsulfone, a polyarylene sulfide copolymer can be formed containing segments having the structure of formula (II):



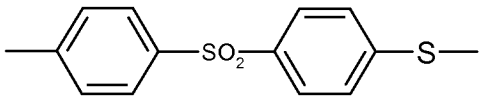
(II)

and segments having the structure of formula (III):



(III)

or segments having the structure of formula (IV):



(IV)

[00109] In general, the amount of the dihaloaromatic compound(s) per mole of the effective amount of the charged alkali metal sulfide can generally be from 1.0 to 2.0 moles, from 1.05 to 2.0 moles, or from 1.1 to 1.7 moles. Thus, the polyarylene sulfide can include alkyl halide (generally alkyl chloride) end groups.

[00110] A process for producing the polyarylene sulfide can include carrying out the polymerization reaction in an organic amide solvent. Exemplary organic amide solvents used in a polymerization reaction can include, without limitation, N-methyl-2-pyrrolidone; N-ethyl-2-pyrrolidone; N,N-dimethylformamide; N,N-dimethylacetamide; N-methylcaprolactam; tetramethylurea; dimethylimidazolidinone; hexamethyl phosphoric acid triamide and mixtures thereof. The amount of the organic amide solvent used in the reaction can be,

e.g., from 0.2 to 5 kilograms per mole (kg/mol) of the effective amount of the alkali metal sulfide.

[00111] The polymerization can be carried out by a step-wise polymerization process. The first polymerization step can include introducing the dihaloaromatic compound to a reactor, and subjecting the dihaloaromatic compound to a polymerization reaction in the presence of water at a temperature of from about 180°C to about 235°C, or from about 200°C to about 230°C, and continuing polymerization until the conversion rate of the dihaloaromatic compound attains to not less than about 50 mol % of the theoretically necessary amount.

[00112] In a second polymerization step, water is added to the reaction slurry so that the total amount of water in the polymerization system is increased to about 7 moles, or to about 5 moles, per mole of the effective amount of the charged alkali metal sulfide. Following, the reaction mixture of the polymerization system can be heated to a temperature of from about 250°C to about 290°C, from about 255°C to about 280°C, or from about 260°C to about 270°C and the polymerization can continue until the melt viscosity of the thus formed polymer is raised to the desired final level of the polyarylene sulfide. The duration of the second polymerization step can be, e.g., from about 0.5 to about 20 hours, or from about 1 to about 10 hours.

[00113] The polyarylene sulfide may be linear, semi-linear, branched or crosslinked. A linear polyarylene sulfide includes as the main constituting unit the repeating unit of –(Ar–S) –. In general, a linear polyarylene sulfide may include about 80 mol% or more of this repeating unit. A linear polyarylene sulfide may include a small amount of a branching unit or a cross-linking unit, but the amount of branching or cross-linking units may be less than about 1 mol% of the total monomer units of the polyarylene sulfide. A linear polyarylene sulfide polymer may be a random copolymer or a block copolymer containing the above-mentioned repeating unit.

[00114] A semi-linear polyarylene sulfide may be utilized that may have a cross-linking structure or a branched structure provided by introducing into the polymer a small amount of one or more monomers having three or more reactive functional groups. For instance between about 1 mol% and about 10 mol% of the polymer may be formed from monomers having three or more reactive functional groups. Methods that may be used in making semi-linear polyarylene sulfide are

generally known in the art. By way of example, monomer components used in forming a semi-linear polyarylene sulfide can include an amount of polyhaloaromatic compounds having 2 or more halogen substituents per molecule which can be utilized in preparing branched polymers. Such monomers can be represented by the formula $R'X_n$, where each X is selected from chlorine, bromine, and iodine, n is an integer of 3 to 6, and R' is a polyvalent aromatic radical of valence n which can have up to about 4 methyl substituents, the total number of carbon atoms in R' being within the range of 6 to about 16. Examples of some polyhaloaromatic compounds having more than two halogens substituted per molecule that can be employed in forming a semi-linear polyarylene sulfide include 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3-dichloro-5-bromobenzene, 1,2,4-triiodobenzene, 1,2,3,5-tetrabromobenzene, hexachlorobenzene, 1,3,5-trichloro-2,4,6-trimethylbenzene, 2,2',4,4'-tetrachlorobiphenyl, 2,2',5,5'-tetra-iodobiphenyl, 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethylbiphenyl, 1,2,3,4-tetrachloronaphthalene, 1,2,4-tribromo-6-methylnaphthalene, and the like, and mixtures thereof.

[0100] Following polymerization, the polyarylene sulfide may be washed with liquid media. For instance, the polyarylene sulfide may be washed with water and/or organic solvents that will not decompose the polyarylene sulfide including, without limitation, acetone, N-methyl-2-pyrrolidone, a salt solution, and/or an acidic media such as acetic acid or hydrochloric acid prior to combination with other components while forming the mixture. The polyarylene sulfide can be washed in a sequential manner that is generally known to persons skilled in the art. Washing with an acidic solution or a salt solution may reduce the sodium, lithium or calcium metal ion end group concentration from about 2000 ppm to about 100 ppm.

[0101] A polyarylene sulfide can be subjected to a hot water washing process. The temperature of a hot water wash can be at or above about 100°C, for instance higher than about 120°C, higher than about 150°C, or higher than about 170°C.

[0102] The polymerization reaction apparatus for forming the polyarylene sulfide is not especially limited, although it is typically desired to employ an apparatus that is commonly used in formation of high viscosity fluids. Examples of such a reaction apparatus may include a stirring tank type polymerization reaction apparatus having a stirring device that has a variously shaped stirring blade, such

as an anchor type, a multistage type, a spiral-ribbon type, a screw shaft type and the like, or a modified shape thereof. Further examples of such a reaction apparatus include a mixing apparatus commonly used in kneading, such as a kneader, a roll mill, a Banbury mixer, etc. Following polymerization, the molten polyarylene sulfide may be discharged from the reactor, typically through an extrusion orifice fitted with a die of desired configuration, cooled, and collected. Commonly, the polyarylene sulfide may be discharged through a perforated die to form strands that are taken up in a water bath, pelletized and dried. The polyarylene sulfide may also be in the form of a strand, granule, or powder.

[0103] The polyarylene sulfide composition may include the polyarylene sulfide component (which also encompasses a blend of polyarylene sulfides) in an amount from about 10 wt.% to about 99 wt.% by weight of the composition, for instance from about 20% wt.% to about 90 wt.% by weight of the composition.

[0104] The polyarylene sulfide may be of any suitable molecular weight and melt viscosity, generally depending upon the final application intended for the polyarylene sulfide composition. For instance, the melt viscosity of the polyarylene sulfide may be a low viscosity polyarylene sulfide, having a melt viscosity of less than about 500 poise, a medium viscosity polyarylene sulfide, having a melt viscosity of between about 500 poise and about 1500 poise, or a high melt viscosity polyarylene sulfide, having a melt viscosity of greater than about 1,500 poise, as determined in accordance with ISO Test No. 11443 at a shear rate of 1200 s^{-1} and at a temperature of 310°C.

[0105] According to one embodiment, the polyarylene sulfide can be functionalized to further encourage bond formation between the polyarylene sulfide and the impact modifier. For instance, a polyarylene sulfide can be further treated following formation with a carboxyl, acid anhydride, amine, isocyanate or other functional group-containing modifying compound to provide a functional terminal group on the polyarylene sulfide. By way of example, a polyarylene sulfide can be reacted with a modifying compound containing a mercapto group or a disulfide group and also containing a reactive functional group. In one embodiment, the polyarylene sulfide can be reacted with the modifying compound in an organic solvent. In another embodiment, the polyarylene sulfide can be reacted with the modifying compound in the molten state.

[0106] In one embodiment, a disulfide compound containing the desired functional group can be incorporated into the polyarylene sulfide composition formation process, and the polyarylene sulfide can be functionalized in conjunction with formation of the composition. For instance, a disulfide compound containing the desired reactive functional groups can be added to the melt extruder in conjunction with the polyarylene sulfide or at any other point prior to or in conjunction with the addition of the crosslinking agent.

[0107] Reaction between the polyarylene sulfide polymer and the reactively functionalized disulfide compound can include chain scission of the polyarylene sulfide polymer that can decrease melt viscosity of the polyarylene sulfide. In one embodiment, a higher melt viscosity polyarylene sulfide having low halogen content can be utilized as a starting polymer. Following reactive functionalization of the polyarylene sulfide polymer by use of a functional disulfide compound, a relatively low melt viscosity polyarylene sulfide with low halogen content can be formed. Following this chain scission, the melt viscosity of the polyarylene sulfide can be suitable for further processing, and the overall halogen content of the low melt viscosity polyarylene sulfide can be quite low. A polyarylene sulfide composition that exhibits excellent strength and degradation resistance in addition to low halogen content can be advantageous as low halogen content polymeric materials are becoming increasingly desired due to environmental concerns. In one embodiment, the polyarylene sulfide composition can have a halogen content of less than about 1000 ppm, less than about 900 ppm, less than about 600 ppm, or less than about 400 ppm as determined according to an elemental analysis using Parr Bomb combustion followed by Ion Chromatography.

[0108] The disulfide compound can generally have the structure of:

$$R^1–S–S–R^2$$

wherein R^1 and R^2 may be the same or different and are hydrocarbon groups that independently include from 1 to about 20 carbons. For instance, R^1 and R^2 may be an alkyl, cycloalkyl, aryl, or heterocyclic group. R^1 and R^1 may include reactive functionality at terminal end(s) of the disulfide compound. For example, at least one of R^1 and R^2 may include a terminal carboxyl group, hydroxyl group, a substituted or non-substituted amino group, a nitro group, or the like. In general, the reactive functionality can be selected such that the reactively functionalized polyarylene sulfide can react with the impact modifier. For example, when

considering an epoxy-terminated impact modifier, the disulfide compound can include carboxyl and/or amine functionality.

[0109] Examples of disulfide compounds including reactive terminal groups as may be encompassed herein may include, without limitation, 2,2'-diaminodiphenyl disulfide, 3,3'-diaminodiphenyl disulfide, 4,4'-diaminodiphenyl disulfide, dibenzyl disulfide, dithiosalicyclic acid, dithioglycolic acid, α,α'-dithiodilactic acid, β,β'-dithiodilactic acid, 3,3'-dithiodipyridine, 4,4'dithiomorpholine, 2,2'-dithiobis(benzothiazole), 2,2'-dithiobis(benzimidazole), 2,2'-dithiobis(benzoxazole) and 2-(4'-morpholinodithio)benzothiazole.

[0110] The ratio of the amount of the polyarylene sulfide to the amount of the disulfide compound can be from about 1000:1 to about 10:1, from about 500:1 to about 20:1, or from about 400:1 to about 30:1.

[0111] In addition to the polyarylene sulfide polymer, the composition also includes an impact modifier. More specifically, the impact modifier can be an olefinic copolymer or terpolymer. For instance, the impact modifier can include ethylenically unsaturated monomer units have from about 4 to about 10 carbon atoms.

[0112] The impact modifier can be modified to include functionalization so as to react with the crosslinking agent. For instance, the impact modifier can be modified with a mole fraction of from about 0.01 to about 0.5 of one or more of the following: an α, β unsaturated dicarboxylic acid or salt thereof having from about 3 to about 8 carbon atoms; an α, β unsaturated carboxylic acid or salt thereof having from about 3 to about 8 carbon atoms; an anhydride or salt thereof having from about 3 to about 8 carbon atoms; a monoester or salt thereof having from about 3 to about 8 carbon atoms; a sulfonic acid or a salt thereof; an unsaturated epoxy compound having from about 4 to about 11 carbon atoms. Examples of such modification functionalities include maleic anhydride, fumaric acid, maleic acid, methacrylic acid, acrylic acid, and glycidyl methacrylate. Examples of metallic acid salts include the alkaline metal and transitional metal salts such as sodium, zinc, and aluminum salts.

[0113] A non-limiting listing of impact modifiers that may be used include ethylene-acrylic acid copolymer, ethylene-maleic anhydride copolymers, ethylene-alkyl (meth)acrylate-maleic anhydride terpolymers, ethylene-alkyl (meth)acrylate-glycidyl (meth)acrylate terpolymers, ethylene-acrylic ester-methacrylic acid

terpolymer, ethylene-acrylic ester-maleic anhydride terpolymer, ethylene-methacrylic acid-methacrylic acid alkaline metal salt (ionomer) terpolymers, and the like. In one embodiment, for instance, an impact modifier can include a random terpolymer of ethylene, methylacrylate, and glycidyl methacrylate. The terpolymer can have a glycidyl methacrylate content of from about 5% to about 20%, such as from about 6% to about 10%. The terpolymer may have a methylacrylate content of from about 20% to about 30%, such as about 24%.

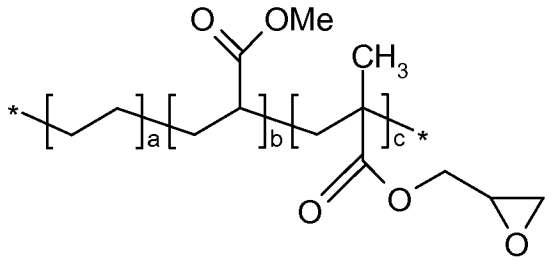
[0114] According to one embodiment, the impact modifier may be a linear or branched, homopolymer or copolymer (e.g., random, graft, block, etc.) containing epoxy functionalization, e.g., terminal epoxy groups, skeletal oxirane units, and/or pendent epoxy groups. For instance, the impact modifier may be a copolymer including at least one monomer component that includes epoxy functionalization. The monomer units of the impact modifier may vary. In one embodiment, for example, the impact modifier can include epoxy-functional methacrylic monomer units. As used herein, the term methacrylic generally refers to both acrylic and methacrylic monomers, as well as salts and esters thereof, e.g., acrylate and methacrylate monomers. Epoxy-functional methacrylic monomers as may be incorporated in the impact modifier may include, but are not limited to, those containing 1,2-epoxy groups, such as glycidyl acrylate and glycidyl methacrylate. Other suitable epoxy-functional monomers include allyl glycidyl ether, glycidyl ethacrylate, and glycidyl itoconate.

[0115] Other monomer units may additionally or alternatively be a component of the impact modifier. Examples of other monomers may include, for example, ester monomers, olefin monomers, amide monomers, etc. In one embodiment, the impact modifier can include at least one linear or branched α-olefin monomer, such as those having from 2 to 20 carbon atoms, or from 2 to 8 carbon atoms. Specific examples include ethylene; propylene; 1-butene; 3-methyl-1-butene; 3,3-dimethyl-1-butene; 1-pentene; 1-pentene with one or more methyl, ethyl or propyl substituents; 1-hexene with one or more methyl, ethyl or propyl substituents; 1-heptene with one or more methyl, ethyl or propyl substituents; 1-octene with one or more methyl, ethyl or propyl substituents; 1-nonene with one or more methyl, ethyl or propyl substituents; ethyl, methyl or dimethyl-substituted 1-decene; 1-dodecene; and styrene.

[0116] Monomers included in an impact modifier that includes epoxy

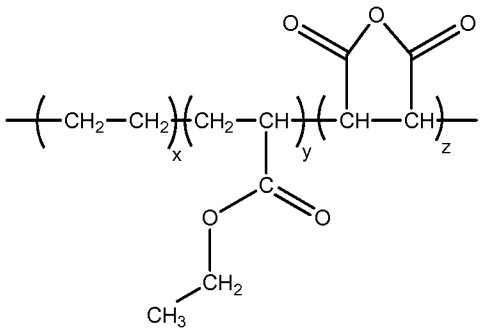
functionalization can include monomers that do not include epoxy functionalization, as long as at least a portion of the monomer units of the polymer are epoxy functionalized.

[0117] In one embodiment, the impact modifier can be a terpolymer that includes epoxy functionalization. For instance, the impact modifier can include a methacrylic component that includes epoxy functionalization, an α-olefin component, and a methacrylic component that does not include epoxy functionalization. For example, the impact modifier may be poly(ethylene-co-methylacrylate-co-glycidyl methacrylate), which has the following structure:



wherein, a, b, and c are 1 or greater.

[0118] In another embodiment the impact modifier can be a random copolymer of ethylene, ethyl acrylate and maleic anhydride having the following structure:



wherein x, y and z are 1 or greater.

[0119] The relative proportion of the various monomer components of a copolymeric impact modifier is not particularly limited. For instance, in one embodiment, the epoxy-functional methacrylic monomer components can form from about 1 wt. % to about 25 wt. %, or from about 2 wt. % to about 20 wt % of a copolymeric impact modifier. An a-olefin monomer can form from about 55 wt. % to about 95 wt. %, or from about 60 wt. % to about 90 wt. %, of a copolymeric impact modifier. When employed, other monomeric components (e.g., a non-epoxy functional methacrylic monomers) may constitute from about 5 wt. % to about 35

wt. %, or from about 8 wt. % to about 30 wt. %, of a compolymeric impact modifier.

[0120] An impact modifier may be formed according to standard polymerization methods as are generally known in the art. For example, a monomer containing polar functional groups may be grafted onto a polymer backbone to form a graft copolymer. Alternatively, a monomer containing functional groups may be copolymerized with a monomer to form a block or random copolymer using known free radical polymerization techniques, such as high pressure reactions, Ziegler-Natta catalyst reaction systems, single site catalyst (e.g., metallocene) reaction systems, etc.

[0121] Alternatively, an impact modifier may be obtained on the retail market. By way of example, suitable compounds for use as an impact modifier may be obtained from Arkema under the name Lotader®.

[0122] The molecular weight of the impact modifier can vary widely. For example, the impact modifier can have a number average molecular weight from about 7,500 to about 250,000 grams per mole, in some embodiments from about 15,000 to about 150,000 grams per mole, and in some embodiments, from about 20,000 to 100,000 grams per mole, with a polydispersity index typically ranging from 2.5 to 7.

[0123] In general, the impact modifier may be present in the composition in an amount from about 0.05% to about 40% by weight, from about 0.05% to about 37% by weight, or from about 0.1% to about 35% by weight.

[0124] Referring again to FIG. 12, the impact modifier can be added to the composition in conjunction with the polyarylene sulfide composition at the main feed throat 54 of the melt processing unit. This is not a requirement of the composition formation process, however, and in other embodiments, the impact modifier can be added downstream of the main feed throat. For instance, the impact modifier may be added at a location downstream from the point at which the polyarylene sulfide is supplied to the melt processing unit, but yet prior to the melting section, i.e., that length of the melt processing unit in which the polyarylene sulfide becomes molten. In another embodiment, the impact modifier may be added at a location downstream from the point at which the polyarylene sulfide becomes molten.

[0125] If desired, one or more distributive and/or dispersive mixing elements may be employed within the mixing section of the melt processing unit. Suitable

distributive mixers for single screw extruders may include but are not limited to, for instance, Saxon, Dulmage, Cavity Transfer mixers, etc. Likewise, suitable dispersive mixers may include but are not limited to Blister ring, Leroy/Maddock, CRD mixers, etc. As is well known in the art, the mixing may be further improved by using pins in the barrel that create a folding and reorientation of the polymer melt, such as those used in Buss Kneader extruders, Cavity Transfer mixers, and Vortex Intermeshing Pin mixers.

[0126] In addition to the polyarylene sulfide and the impact modifier, the polyarylene composition can include a crosslinking agent. The crosslinking agent can be a polyfunctional compound or combination thereof that can react with functionality of the impact modifier to form crosslinks within and among the polymer chains of the impact modifier. In general, the crosslinking agent can be a non-polymeric compound, i.e., a molecular compound that includes two or more reactively functional terminal moieties linked by a bond or a non-polymeric (non-repeating) linking component. By way of example, the crosslinking agent can include but is not limited to di-epoxides, poly-functional epoxides, diisocyanates, polyisocyanates, polyhydric alcohols, water-soluble carbodiimides, diamines, diaminoalkanes, polyfunctional carboxylic acids, diacid halides, and so forth. For instance, when considering an epoxy-functional impact modifier, a non-polymeric polyfunctional carboxylic acid or amine can be utilized as a crosslinking agent.

[0127] Specific examples of polyfunctional carboxylic acid crosslinking agents can include, without limitation, isophthalic acid, terephthalic acid, phthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, 4,4'-bisbenzoic acid, 1,4- or 1,5-naphthalene dicarboxylic acids, decahydronaphthalene dicarboxylic acids, norbornene dicarboxylic acids, bicyclooctane dicarboxylic acids, 1,4-cyclohexanedicarboxylic acid (both cis and trans), 1,4-hexylenedicarboxylic acid, adipic acid, azelaic acid, dicarboxyl dodecanoic acid, succinic acid, maleic acid, glutaric acid, suberic acid, azelaic acid and sebacic acid. The corresponding dicarboxylic acid derivatives, such as carboxylic acid diesters having from 1 to 4 carbon atoms in the alcohol radical, carboxylic acid anhydrides or carboxylic acid halides may also be utilized.

[0128] Exemplary diols useful as crosslinking agents can include, without limitation, aliphatic diols such as ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 2,2-dimethyl-1,3-propane diol, 2-ethyl-2-methyl-1,3-propane diol,

1,4-butane diol, 1,4-but-2-ene diol, 1,3-1,5-pentane diol, 1,5-pentane diol, dipropylene glycol, 2-methyl-1,5-pentane diol, and the like. Aromatic diols can also be utilized such as, without limitation, hydroquinone, catechol, resorcinol, methylhydroquinone, chlorohydroquinone, bisphenol A, tetrachlorobisphenol A, phenolphthalein, and the like. Exemplary cycloaliphatic diols as may be used include a cycloaliphatic moiety, for example 1,6-hexane diol, dimethanol decalin, dimethanol bicyclooctane, 1,4-cyclohexane dimethanol (including its cis- and trans-isomers), triethylene glycol, 1,10-decanediol, and the like.

[0129] Exemplary diamines that may be utilized as crosslinking agents can include, without limitation, isophorone-diamine, ethylenediamine, 1,2-, 1,3-propylene-diamine, N-methyl-1,3-propylene-diamine, N,N'-dimethyl-ethylene-diamine, and aromatic diamines, such as, for example, 2,4- and 2,6-toluoylene-diamine, 3,5-diethyl-2,4- and/or -2,6-toluoylene-diamine, and primary ortho- di-, tri- and/or tetra-alkyl-substituted 4,4'-diaminodiphenyl-methanes. (cyclo)aliphatic diamines, such as, for example, isophorone-diamine, ethylenediamine, 1,2-, 1,3-propylene-diamine, N-methyl-1,3-propylene-diamine, N,N'-dimethyl-ethylene-diamine, and aromatic diamines, such as, for example, 2,4- and 2,6-toluoylene-diamine, 3,5-diethyl-2,4- and/or -2,6-toluoylene-diamine, and primary ortho- di-, tri- and/or tetra-alkyl-substituted 4,4'-diaminodiphenyl-methanes.

[0130] In one embodiment, the composition can include a disulfide-free crosslinking agent. For example, the crosslinking agent can include carboxyl and/or amine functionality with no disulfide group that may react with the polyarylene sulfide. A crosslinking agent that is disulfide-free can be utilized so as to avoid excessive chain scission of the polyarylene sulfide by the crosslinking agent during formation of the composition. It should be understood, however, that the utilization of a disulfide-free crosslinking agent does not in any way limit the utilization of a reactively functionalized disulfide compound for functionalizing the polyarylene sulfide. For instance, in one embodiment, the composition can be formed according to a process that includes addition of a reactively functionalized disulfide compound to the melt processing unit that can reactively functionalize the polyarylene sulfide. The crosslinking agent utilized in this embodiment can then be a disulfide-free crosslinking agent that can include functionality that is reactive with the impact modifier as well as with the reactively functionalized polyarylene sulfide.

Thus, the composition can be highly crosslinked without excessive scission of the polyarylene sulfide polymer chains.

[0131] In another embodiment the crosslinking agent and the polyarylene sulfide functionalization compound (when present) can be selected so as to encourage chain scission of the polyarylene sulfide. This may be beneficial, for instance, which chain scission is desired to decrease the melt viscosity of the polyarylene sulfide polymer.

[0132] The polyarylene sulfide composition may generally include the crosslinking agent in an amount from about 0.05 wt.% to about 2 wt.% by weight of the polyarylene sulfide composition, from about 0.07 wt.% to about 1.5 wt.% by weight of the polyarylene sulfide composition, or from about 0.1 wt.% to about 1.3 wt.%.

[0133] The crosslinking agent can be added to the melt processing unit following mixing of the polyarylene sulfide and the impact modifier. For instance, as illustrated in FIG. 12, the crosslinking agent can be added to the composition at a downstream location 66 following addition of polyarylene sulfide and the impact modifier (either together or separately) to the melt processing unit. This can ensure that the impact modifier has become dispersed throughout the polyarylene sulfide prior to addition of the crosslinking agent.

[0134] To help encourage distribution of the impact modifier throughout the melt prior to addition of the crosslinking agent, a variety of different parameters may be selectively controlled. For example, the ratio of the length ("L") to diameter ("D") of a screw of the melt processing unit may be selected to achieve an optimum balance between throughput and impact modifier distribution. For example, the L/D value after the point at which the impact modifier is supplied may be controlled to encourage distribution of the impact modifier. More particularly, the screw has a blending length ("L_B") that is defined from the point at which both the impact modifier and the polyarylene sulfide are supplied to the unit (i.e., either where they are both supplied in conjunction with one another or the point at which the latter of the two is supplied) to the point at which the crosslinking agent is supplied, the blending length generally being less than the total length of the screw. For example, when considering a melt processing unit that has an overall L/D of 40, the L_B/D ratio of the screw can be from about 1 to about 36, in some embodiments from about 4 to about 20, and in some embodiments, from about 5

to about 15. In one embodiment, the L/L_B ratio can be from about 40 to about 1.1, from about 20 to about 2, or from about 10 to about 5.

[0135] Following addition of the crosslinking agent, the composition can be mixed to distribute the crosslinking agent throughout the composition and encourage reaction between the crosslinking agent, the impact modifier, and, in one embodiment, with the polyarylene sulfide.

[0136] The composition can also include one or more additives as are generally known in the art. For example, one or more fillers can be included in the polyarylene sulfide composition. One or more fillers may generally be included in the polyarylene sulfide composition an amount of from about 5 wt.% to about 70 wt.%, or from about 20 wt.% to about 65 wt.% by weight of the polyarylene sulfide composition.

[0137] The filler can be added to the polyarylene sulfide composition according to standard practice. For instance, the filler can be added to the composition at a downstream location of the melt processing unit. For example, a filler may be added to the composition in conjunction with the addition of the crosslinking agent. However, this is not a requirement of a formation process and the filler can be added separately from the crosslinking agent and either upstream or downstream of the point of addition of the crosslinking agent. In addition, a filler can be added at a single feed location, or may be split and added at multiple feed locations along the melt processing unit.

[0138] In one embodiment, a fibrous filler can be included in the polyarylene sulfide composition. The fibrous filler may include one or more fiber types including, without limitation, polymer fibers, glass fibers, carbon fibers, metal fibers, basalt fibers, and so forth, or a combination of fiber types. In one embodiment, the fibers may be chopped fibers, continuous fibers, or fiber rovings (tows).

[0139] Fiber sizes can vary as is known in the art. In one embodiment, the fibers can have an initial length of from about 3 mm to about 5 mm. In another embodiment, for instance when considering a pultrusion process, the fibers can be continuous fibers. Fiber diameters can vary depending upon the particular fiber used. The fibers, for instance, can have a diameter of less than about 100 μm, such as less than about 50 μm. For instance, the fibers can be chopped or continuous fibers and can have a fiber diameter of from about 5 μm to about 50 μm, such as from about 5 μm to about 15 μm.

[0140] The fibers may be pretreated with a sizing as is generally known. In one embodiment, the fibers may have a high yield or small K numbers. The tow is indicated by the yield or K number. For instance, glass fiber tows may have 50 yield and up, for instance from about 115 yield to about 1200 yield.

[0141] Other fillers can alternatively be utilized or may be utilized in conjunction with a fibrous filler. For instance, a particulate filler can be incorporated in the polyarylene sulfide composition. In general, particulate fillers can encompass any particulate material having a median particle size of less than about 750 μm, for instance less than about 500 μm, or less than about 100 μm. In one embodiment, a particulate filler can have a median particle size in the range of from about 3 μm to about 20 μm. In addition, a particulate filler can be solid or hollow, as is known. Particulate fillers can also include a surface treatment, as is known in the art.

[0142] Particulate fillers can encompass one or more mineral fillers. For instance, the polyarylene sulfide composition can include one or more mineral fillers in an amount of from about 1 wt.% to about 60 wt.% of the composition. Mineral fillers may include, without limitation, silica, quartz powder, silicates such as calcium silicate, aluminum silicate, kaolin, talc, mica, clay, diatomaceous earth, wollastonite, calcium carbonate, and so forth.

[0143] A filler can be an electrically conductive filler such as, without limitation, carbon black, graphite, graphene, carbon fiber, carbon nanotubes, a metal powder, and so forth. In those embodiments in which the polyarylene sulfide composition includes electrically conductive fillers, for instance when the polyarylene sulfide composition is utilized in forming a fuel line, adequate electrically conductive filler can be included such that the composition has a volume specific resistance of equal to or less than about 10^9 ohms cm.

[0144] When incorporating multiple fillers, for instance a particulate filler and a fibrous filler, the fillers may be added together or separately to the melt processing unit. For instance, a particulate filler can be added to the main feed with the polyarylene sulfide or downstream prior to addition of a fibrous filler, and a fibrous filler can be added further downstream of the addition point of the particulate filler. In general, a fibrous filler can be added downstream of any other fillers such as a particulate filler, though this is not a requirement.

[0145] In one embodiment, the polyarylene sulfide composition can include a UV stabilizer as an additive. For instance, the polyarylene sulfide composition can include a UV stabilizer in an amount of between about 0.5 wt.% and about 15 wt.%, between about 1 wt.% and about 8 wt.%, or between about 1.5 wt.% and about 7 wt.% of a UV stabilizer. One particularly suitable UV stabilizer that may be employed is a hindered amine UV stabilizer. Suitable hindered amine UV stabilizer compounds may be derived from a substituted piperidine, such as alkyl-substituted piperidyl, piperidinyl, piperazinone, alkoxypiperidinyl compounds, and so forth. For example, the hindered amine may be derived from a 2,2,6,6-tetraalkylpiperidinyl. The hindered amine may, for example, be an oligomeric or polymeric compound having a number average molecular weight of about 1,000 or more, in some embodiments from about 1000 to about 20,000, in some embodiments from about 1500 to about 15,000, and in some embodiments, from about 2000 to about 5000. Such compounds typically contain at least one 2,2,6,6-tetraalkylpiperidinyl group (e.g., 1 to 4) per polymer repeating unit. One particularly suitable high molecular weight hindered amine is commercially available from Clariant under the designation Hostavin® N30 (number average molecular weight of 1200). Another suitable high molecular weight hindered amine is commercially available from Adeka Palmarole SAS under the designation ADK STAB® LA-63 and ADK STAB® LA-68.

[0146] In addition to the high molecular hindered amines, low molecular weight hindered amines may also be employed. Such hindered amines are generally monomeric in nature and have a molecular weight of about 1000 or less, in some embodiments from about 155 to about 800, and in some embodiments, from about 300 to about 800.

[0147] Other suitable UV stabilizers may include UV absorbers, such as benzotriazoles or benzopheones, which can absorb UV radiation.

[0148] An additive that may be included in a polyarylene sulfide composition is one or more colorants as are generally known in the art. For instance, the polyarylene sulfide composition can include from about 0.1 wt. % to about 10 wt.%, or from about 0.2 wt.% to about 5 wt.% of one or more colorants. As utilized herein, the term “colorant” generally refers to any substance that can impart color to a material. Thus, the term “colorant” encompasses both dyes, which exhibit

solubility in an aqueous solution, and pigments, that exhibit little or no solubility in an aqueous solution.

[0149] Examples of dyes that may be used include, but are not limited to, disperse dyes. Suitable disperse dyes may include those described in "Disperse Dyes" in the Color Index, 3rd edition. Such dyes include, for example, carboxylic acid group-free and/or sulfonic acid group-free nitro, amino, aminoketone, ketoninime, methine, polymethine, diphenylamine, quinoline, benzimidazole, xanthene, oxazine and coumarin dyes, anthraquinone and azo dyes, such as mono- or di-azo dyes. Disperse dyes also include primary red color disperse dyes, primary blue color disperse dyes, and primary yellow color dyes

[0150] Pigments that can be incorporated in a polyarylene sulfide composition can include, without limitation, organic pigments, inorganic pigments, metallic pigments, phosphorescent pigments, fluorescent pigments, photochromic pigments, thermochromic pigments, iridescent pigments, and pearlescent pigments. The specific amount of pigment can depends upon the desired final color of the product. Pastel colors are generally achieved with the addition of titanium dioxide white or a similar white pigment to a colored pigment.

[0151] Other additives that can be included in the polyarylene sulfide composition can encompass, without limitation, antimicrobials, lubricants, impact modifiers, antioxidants, other stabilizers (e.g., heat stabilizers including organophosphites such as Doverphos® products available from Dover Chemical Corporation), surfactants, flow promoters, solid solvents, and other materials added to enhance properties and processability. Such optional materials may be employed in the polyarylene sulfide composition in conventional amounts and according to conventional processing techniques, for instance through addition to the polyarylene sulfide composition at the main feed throat. For instance, colorants can be included so as to provide a heavy duty truck component, e.g., an air brake line that is of the proper color according to current regulations. Beneficially, the polyarylene sulfide composition can exhibit desirable characteristics without the addition of plasticizers. For instance, the composition can be free of plasticizers such as phthalate esters, trimellitates, sebacates, adipates, gluterates, azelates, maleates, benzoates, and so forth.

[0152] Following addition of all components to the polyarylene sulfide composition, the composition is thoroughly mixed in the remaining section(s) of the

extruder and extruded through a die. The final extrudate can be pelletized or other wise shaped as desired, for instance the final extrudate can be in the form of a pultruded tape or ribbon that can be wrapped to form a layer of a tubular member.

[0153] Conventional shaping processes can be used for forming heavy duty truck components of the polyarylene sulfide composition including, without limitation, extrusion, injection molding, blow-molding, thermoforming, foaming, compression molding, hot-stamping, fiber spinning and so forth. Shaped articles that may be formed may include structural and non-structural shaped parts. For instance thermoform sheets, foamed substrates, injection molded or blow molded components, and the like can be formed from the polyarylene sulfide composition.

[0154] By way of example, a single layer tubular member 110 as illustrated in FIG. 1 can formed according to a blow molding process. During blow molding, the polyarylene sulfide composition is first heated and extruded into a parison using a die attached to an extrusion device. When the parison is formed, the composition must have sufficient melt strength to prevent gravity from undesirably elongating portions of the parison and thereby forming non-uniform wall thicknesses and other imperfections. The parison is received into a molding device, generally formed of multiple sections that together form a three-dimensional mold cavity.

[0155] As can be appreciated, a certain period of time elapses from formation of the parison to moving the parison into engagement with the molding device. During this stage of the process, the melt strength of the polyarylene sulfide composition can be high enough such that the parison maintains its shape during movement. The polyarylene sulfide composition can also be capable of remaining in a semi-fluid state and not solidifying too rapidly before blow molding commences.

[0156] Once the molding device is closed, a gas, such as an inert gas is fed into the parison from a gas supply. The gas supplies sufficient pressure against the interior surface of the parison such that the parison conforms to the shape of the mold cavity. After blow molding, the finished shaped article is then removed. In one embodiment, cool air can be injected into the molded part for solidifying the polyarylene sulfide composition prior to removal from the molding device.

[0157] A fuel line can also be formed through utilization of a continuous blow molding process to form one or more layers of a fuel line. By way of example, FIG.

17 presents a schematic illustration of one method as may be utilized in forming a tubular member according to a continuous blow molding process. In a continuous process, a stationary extruder (not shown) can plasticize the molten polyarylene sulfide composition through a head to form a continuous parison 601. An accumulator 605 can be used to support the parison and prevent sagging prior to molding. The parison may be fed to a mold formed of articulated sections 602, 603 that travel in conjunction with the continuous parison on a mold conveyor assembly 604. Air under pressure is applied to the parison to blow mold the polyarylene sulfide composition within the mold. After the polyarylene sulfide composition has been molded and sufficiently cooled within the mold as the mold and composition travel together, the mold segments are separated from one another and the formed line 606 is removed from the conveyor and taken up, as on a take-up reel (not shown). The tubular member can then be cut to the desired length form.

[0158] Additional layers can be formed on a blow molded layer according to an extrusion process, for instance to form an outer layer on a pre-formed layer, or according to a second blow molding process, for instance to form an inner layer on a pre-formed layer.

[0159] Surface treatments can be carried out on pre-formed layers prior to formation of or attachment to an adjacent layer so as to improve adhesion between adjacent layers. For example, plasma treatment or corona treatment as is generally known can be carried out to improve adhesion between adjacent layers of a multi-layer fuel line.

[0160] Of course, any known tube-forming methods including blow molding in combination with other methods as well as alternative methods such as extrusion are employable. For instance, one or more layers of a multi-layered tubular member can be formed from a continuous tape, e.g., a fiber reinforced tape or ribbon formed according to a pultrusion formation method. A tape can be wrapped to form the tubular member or a layer of a multilayered tubular member according to known practices as are generally known in the art.

[0161] Multilayer tubular members may be made by use of one or more other conventional processes, such as, for example, co-extrusion, dry lamination, sandwich lamination, coextrusion coating, and the like. By way of example, in forming a three-layered tubular member 210 as illustrated in FIG. 3, the

polyarylene sulfide composition, a polyamide composition, and a thermoplastic elastomer composition can be separately fed into three different extruders. The separate extrusion melts from those three extruders can then be introduced into one die under pressure. While producing three different tubular melt flows, those melt flows can be combined in the die in such a manner that the melt flow of the polyarylene sulfide composition forms the inner layer 212, that of the polyamide composition forms the intermediate layer 216, and that of the thermoplastic elastomer composition forms the outer layer 214, and the thus-combined melt flows are co-extruded out of the die to produce a three-layered tubular member.

[0162] An automotive component including, without limitation, a pipe or a tube can be formed according to an extrusion process. For example, a simple or barrier type screw can be utilized and, in one embodiment, a mixing tip need not be utilized in the process. The compression ratio for an extrusion process can be between about 2.5:1 and about 4:1. For instance, the compression ratio can be about 25% feed, about 25% transition, and about 50% metering. The ratio of the barrel length to the barrel diameter (L/D) can be from about 16 to about 24. An extrusion process can also utilize other standard components as are known in the art such as, for example, breaker plates, screen packs, adapters, a die, and a vacuum tank. The vacuum tank can generally include a sizing sleeve/calibration ring, tank seals, and the like.

[0163] When forming an automotive component according to an extrusion process, the polyarylene sulfide composition can first be dried, for instance at a temperature of from about 90°C to about 100°C for about three hours. It may be beneficial to avoid drying for an extensive length of time so as to avoid discoloration of the composition. The extruder can exhibit different temperatures in different zones, as is known. For instance, in one embodiment, the extruder can include at least four zones, with the temperature of the first zone from about 276°C to about 288°C, the temperature of the second zone from about 282°C to about 299°C, the temperature of the third zone from about 282°C to about 299°C, and the temperature of the fourth zone from about 540°C to about 580°C. Meanwhile, the temperature of the die can be from about 293°C to about 310°C, and the vacuum tank water can be from about 20°C to about 50°C.

[0164] Typically, the head pressure can be from about 100 pounds per square inch (psi) (about 690 kPa) to about 1000 psi (about 6900 kPa), and the

head pressure can be adjusted to achieve a stable melt flow, as is known. For instance, the head pressure can be reduced by increasing the extruder zone temperature, by increasing the extruder screw rotations per minute, reducing the screen pack mesh size and/or the number of screens, and so forth. In general, the line speed can be from about 4 meters per minute to about 15 meters per minute. Of course, the actual line speed can depend upon the final dimension of the tubular member, the aesthetics of the final product and process stability.

[0165] The die swell during an extrusion process can generally be negligible. A draw down of about 1.2 to about 1.7 can generally be utilized, as a higher draw down can negatively affect the final properties of the tubular member, depending on other processing conditions. Die drool can generally be avoided by drying the resin adequately prior to extrusion as well as by maintaining the melt temperature at less than about 304°C.

[0166] In one embodiment, tubular members extruded from the polyarylene sulfide composition can have a wall thickness of between about 0.5 millimeters to about 5 millimeters, though tubular members having larger wall thickness can be formed from the composition as desired. The calibration ring inner diameter can decide the outer diameter of the tubular member and will generally be less than the outer diameter of the die, as is known. The inner diameter of the tubular member can be utilized to determine the desired outer diameter of the mandrel and the line speed, as is known.

[0167] Embodiments of the present disclosure are illustrated by the following examples that are merely for the purpose of illustration of embodiments and are not to be regarded as limiting the scope of the invention or the manner in which it may be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Formation and Test Methods

[0168] *Injection Molding Process:* Tensile bars are injection molded to ISO 527-1 specifications according to standard ISO conditions.

[0169] *Melt Viscosity*: All materials are dried for 1.5 hours at 150°C under vacuum prior to testing. The melt viscosity is measured on a capillary rheometer at 316°C and 400 sec^{-1} with the viscosity measurement taken after five minutes of constant shear.

[0170] *Tensile Properties*: Tensile properties including tensile modulus, yield stress, yield strain, strength at break, elongation at yield, elongation at break, etc. are tested according to ISO Test No. 527 (technically equivalent to ASTM D638). Modulus, strain, and strength measurements are made on the same test strip sample having a length of 80 mm, thickness of 10 mm, and width of 4 mm. The testing temperature is 23°C, and the testing speeds are 5 or 50 mm/min.

[0171] *Flexural Properties*: Flexural properties including flexural strength and flexural modulus are tested according to ISO Test No. 178 (technically equivalent to ASTM D790). This test is performed on a 64 mm support span. Tests are run on the center portions of uncut ISO 3167 multi-purpose bars. The testing temperature is 23°C and the testing speed is 2 mm/min.

[0172] *Deflection Temperature Under Load ("DTUL")*: The deflection under load temperature was determined in accordance with ISO Test No. 75-2 (technically equivalent to ASTM D648-07). More particularly, a test strip sample having a length of 80 mm, thickness of 10 mm, and width of 4 mm was subjected to an edgewise three-point bending test in which the specified load (maximum outer fibers stress) was 1.8 Megapascals. The specimen was lowered into a silicone oil bath where the temperature is raised at 2°C per minute until it deflects 0.25 mm (0.32 mm for ISO Test No. 75-2).

[0173] *Notched Charpy Impact Strength*: Notched Charpy properties are tested according to ISO Test No. ISO 179-1) (technically equivalent to ASTM D256, Method B). This test is run using a Type A notch (0.25 mm base radius) and Type 1 specimen size (length of 80 mm, width of 10 mm, and thickness of 4 mm). Specimens are cut from the center of a multi-purpose bar using a single tooth milling machine. The testing temperature is 23°C, -30°F, or -40°F as reported below.

[0174] *Unnotched Charpy Impact Strength*: Unnotched Charpy properties are tested according to ISO Test No. 180 (technically equivalent to ASTM D256). The test is run using a Type 1 specimen (length of 80 mm, width of 10 mm and thickness of 4 mm). Specimens are cut from the center of a multi-purpose bare using a single tooth milling machine. The testing temperature is 23°C.

[0175] *Izod Notched Impact Strength*: Notched Izod properties are tested according to ISO Test No. 180 (technically equivalent to ASTM D256, Method A).

This test is run using a Type A notch. Specimens are cut from the center of a multi-purpose bar using a single tooth milling machine. The testing temperature is 23°C.

[0176] *Density and Specific Gravity*: Density was determined according to ISO Test No. 1183 (technically equivalent to ASTM D792). The specimen was weighed in air then weighed when immersed in distilled water at 23°C using a sinker and wire to hold the specimen completely submerged as required.

[0177] *Vicat softening temperature*: Vicat Softening temperature was determined according to method A, with a load of 10 N and according to method B with a load of 50 N as described in ISO Test No. 306 (technically equivalent to ASTM D1525), both of which utilized a heating rate of 50 K/h.

[0178] *Water absorption* was determined according to ISO Test No. 62. The test specimens are immersed in distilled water at 23°C until the water absorption essentially ceases (23°C/sat).

[0179] *Complex viscosity:* Complex viscosity is determined by a Low shear sweep (ARES) utilizing an ARES-G2 (TA Instruments) testing machine equipped with 25 mm SS parallel plates and using TRIOS software. A dynamic strain sweep was performed on a pellet sample prior to the frequency sweep, in order to find LVE regime and optimized testing condition. The strain sweep was done from 0.1% to 100%, at a frequency 6.28 rad/s. The dynamic frequency sweep for each sample was obtained from 500 to 0.1 rad/s, with strain amplitude of 3%. The gap distance was kept at 1.5 mm for pellet samples. The temperature was set at 310°C for all samples.

[0180] *Melt strength and melt elongation* is performed on ARES-G2 equipped EVF fixture. The flame bar sample was cut as shown in FIG. 18. The same area of flame bar was used for each run, in order to keep the crystallinity of test sample same and thus to minimize the variation between replicates. A transient strain was applied to each sample at 0.2/s rate. At least triplicate run was done for each sample to obtain a representative curve.

[0181] *Permeation Resistance:* The fuel permeation studies were performed on samples according to SAE Testing Method No. J2665. For all samples, stainless-steel cups were used. Injection molded plaques with a diameter of 3 inches (7.6 centimeters) were utilized as test samples. The thickness of each sample was measured in 6 different areas. An O-ring Viton®

fluoroelastomer was used as a lower gasket between cup flange and sample (Purchased from McMaster-Carr, cat# 9464K57, A75). A flat Viton® fluoroelastomer (Purchased from McMaster-Carr, cat# 86075K52, 1/16" thickness, A 75) was die-cut to 3 inch (7.6 cm) OD and 2.5 inch (6.35 cm) ID, and used as the upper gasket between the sample and the metal screen. The fuel, about 200 ml, was poured into the cup, the cup apparatus was assembled, and the lid was finger-tightened. This was incubated in a 40°C oven for 1 hour, until the vapor pressure equilibrated and the lid was tightened to a torque 15 in-lb. The fuel loss was monitored gravimetrically, daily for the first 2 weeks followed by twice a week for the rest of the testing period. A blank run was done in the same manner with an aluminum disk (7.6 cm diameter, 1.5 mm thickness) and the result was subtracted from the samples. All samples were measured in duplicate. The normalized permeation rate was calculated following an equilibration period. The permeation rate for each sample was obtained from the slope of linear regression fitting of daily weight loss (gm/day). The normalized permeation rate was calculated by dividing the permeation rate by the effective permeation area and multiplying by average thickness of specimen. The average permeation rates are reported.

Example 1

[0182] Materials utilized to form the compositions included the following:

Polyarylene sulfide: Fortron® 0214 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

Impact Modifier: LOTADER® AX8840 - a random copolymer of ethylene and glycidyl methacrylate available from Arkema, Inc.

Crosslinking Agent: Terephthalic Acid

Disulfide: 2,2-dithiodibenzoic acid

Lubricant: Glycolube® P available from Lonza Group Ltd.

[0183] Materials were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. Upon melting and mixing of the above ingredients, the disulfide was fed using a gravimetric feeder at barrel 6. Materials were further

mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0184] Compositions of the samples are provided in Table 1, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 1

Component	Addition Point	Sample 1	Sample 2
Lubricant	main feed	0.3	0.3
Disulfide	barrel 6		1.0
Impact Modifier	main feed	25.0	25.0
Polyarylene Sulfide	main feed	74.7	73.7
Total		100.0	100.0

[0185] Following formation, samples were tested for a variety of physical characteristics. Results are provided in Table 2, below.

Table 2

	Sample 1	Sample 2
Melt Viscosity (poise)	3328	4119
Tensile Modulus (MPa)	1826	1691
Tensile Break Stress (MPa)	43.73	44.98
Tensile Break Strain (%)	96.37	135.12
Std. Dev.	39.07	34.40
Notched Charpy Impact Strength at 23°C (kJ/m^2)	61.03	53.00

[0186] Samples were annealed at 230°C for 2 hours and re-tested for physical characteristics. Results are provided in Table 3, below.

Table 3

	Sample 1	Sample 2
Tensile Modulus (MPa)	1994.00	1725.00
Tensile Break Stress (MPa)	45.04	45.20
Tensile Break Strain (%)	58.01	73.76
Std. Dev.	6.60	4.78

[0187] As can be seen, Sample 2 exhibited better tensile elongation and lower modulus before and after annealing. However, no improvement in impact strength was seen, which is believed to be due to a chain scission reaction between the disulfide and the polypropylene sulfide.

Example 2

[0188] Materials as described in Example 1 were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of

40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. The disulfide was fed using a gravimetric feeder at various locations in the extruder; at the main feed throat, at barrel 4 and barrel 6. The crosslinking agent was fed at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0189] Comparative Samples 3 and 4 were formed of the same composition and compounded by use of a different screw design.

Table 4

	Addition Point	3	4	5	6	7	8	9	10
Lubricant	main feed	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6	-	-	0.5	1.0	1.0	0.5	0.5	0.5
Disulfide	main feed	-	-	-	-	-	0.30	-	-
Disulfide	barrel 4	-	-	-	-	-	-	0.3	-
Disulfide	barrel 6	-	-	-	-	-	-	-	0.3
Impact Modifier	main feed	15.0	15.0	15.0	15.0	10.0	15.0	15.0	15.0
Polyarylene Sulfide	main feed	84.7	84.7	84.2	83.7	88.7	83.9	83.9	83.9
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0190] Following formation, tensile bars were formed and tested for a variety of physical characteristics. Results are provided in Table 5, below.

Table 5

	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Melt Viscosity (poise)	2423	-	2659	2749	2067	2349	2310	2763
Density (g/cm^3)	-	1.28	-	1.25	-	-	-	-
Tensile Modulus (MPa)	2076	2800	2177	2207	2551	1845	2185	2309
Tensile Break Stress (MPa)	46.13	-	45.40	48.27	51.71	46.47	47.16	47.65
Tensile Break Strain (%)	33.68	25	43.97	35.94	26.90	47.51	40.85	63.85
Elongation	5.17	5	5.59	7.49	4.5	11.78	6.94	7.00

at Yield (%)								
Yield Stress (MPa)	51.07	52	50.76	51.62	59.63	51.07	52.56	51.88
Notched Charpy Impact Strength at 23°C (kJ/m^2)	22.30	30	23.90	39.40	14.80	12.50	19.70	39.90
Notched Charpy Impact Strength at -30°C (kJ/m^2)	7.8	7	-	10	-	-	-	10.8
DTUL (°C)	-	100	-	102	-	-	-	-
Melt Temp. (°C)	280	280	280	280	280	280	280	280
Water absorption (%)	-	0.05	-	0.05	-	-	-	-

[0191] Samples were annealed at 230°C for 2 hours and re-tested for physical characteristics. Results are provided in Table 6, below.

Table 6

	Sample 3	**Sample** 4	**Sample 5**	**Sample 6**	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
Tensile Modulus (MPa)	2383	-	2339	2279	2708	2326	2382	2491
Tensile Break Stress (MPa)	52.70	-	53.96	53.11	61.10	56.74	54.81	55.25
Tensile Break Strain (%)	29.42	-	20.97	35.76	20.34	31.37	41.23	49.03
Std. Dev.	6.84	-	6.95	6.66	5.40	2.83	2.65	3.74

[0192] As can be seen, the highest tensile elongation and highest impact strength were observed for Sample 10, which includes both the crosslinking agent and the disulfide added at the same point downstream during processing.

[0193] FIG. 19 illustrates the relationship of notched Charpy impact strength

over temperature change for Sample 3 and for Sample 6. As can be seen, the polyarylene sulfide composition of Sample 6 exhibits excellent characteristics over the entire course of the temperature change, with a higher rate of increase in impact strength with temperature change as compared to the comparison material.

[0194] FIG. 20 is a scanning electron microscopy image of the polyarylene sulfide used in forming the sample 3 composition (FIG. 20A) and the Sample 6 composition (FIG. 20B). As can be seen, there is no clear boundary between the polyarylene sulfide and the impact modifier in the composition of FIG. 20B.

[0195] Tensile bar test specimens of samples 3, 6, and 10 were immersed in 10 wt.% sulfuric acid for 500 hours at either 40°C or 80°C. Tensile properties and impact properties were measured before and after the acid exposure. Results are summarized in Table 7 below.

Table 7

	Sample 3	Sample 6	Sample 10
Initial properties			
Tensile Modulus (MPa)	2076	2207	2309
Tensile Break Stress (MPa)	46.13	48.27	47.65
Tensile Break Strain (%)	33.68	35.94	63.85
Charpy notched impact strength at 23°C (kJ/m^2)	22.30	39.40	39.90
Properties after 500 hours exposure in sulfuric acid at 40 °C			
Tensile Modulus (MPa)	2368	2318	2327
Tensile Break Stress (MPa)	48.83	48.48	48.53
Tensile Break Strain (%)	10.99	28.28	30.05
Charpy notched impact strength at 23°C (kJ/m^2)	18.4	33.6	35.9
Loss in Charpy notched impact strength (%)	18	15	15
Properties after 500 hour exposure in sulfuric acid at 80 °C			
Tensile Modulus (MPa)	2341	2356	2354
Tensile Break Stress (MPa)	49.61	48.04	48.86
Tensile Break Strain (%)	10.60	19.88	26.32
Charpy notched impact strength at 23°C (kJ/m^2)	9.2	31.0	34.0
Loss in Charpy notched impact strength (%)	59	21	15

[0196] The results in the change in Charpy notched impact strength over time during exposure to the acid solution at an elevated temperature are illustrated in FIG. 21. As can be seen, the relative loss of strength of samples 6 and 10 is much less than the comparison sample.

Example 3

[0197] Materials as described in Example 1 were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the feed throat in the first barrel by means of a gravimetric feeder. The crosslinking agent was fed using a gravimetric feeder at the main feed throat and at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0198] Compositions of the samples are provided in Table 8, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 8

Component	Addition Point	Sample 11	Sample 12	Sample 13	Sample 14
Lubricant	main feed	0.3	0.3	0.3	0.3
Crosslinking Agent	main feed	-	0.5	1.0	-
Crosslinking Agent	barrel 6	-	-	-	1.0
Impact Modifier	main feed	15.0	15.0	15.0	15.0
Polyarylene Sulfide	main feed	84.7	84.2	83.7	83.7
Total		100.0	100.0	100.0	100.0

[0199] Following formation, tensile bars formed of the samples were tested for a variety of physical characteristics. Results are provided in Table 9, below.

Table 9

	Sample 11	Sample 12	Sample 13	Sample 14
Melt Viscosity (poise)	2649	2479	2258	3778
Tensile Modulus (MPa)	2387	2139	2150	1611
Tensile Break Stress (MPa)	46.33	49.28	51.81	42.44
Tensile Break Strain (%)	24.62	22.60	14.45	53.62
Std. Dev.	9.19	1.51	2.23	1.90
Notched Charpy Impact Strength at 23°C (kJ/m^2)	27.50	8.50	6.00	39.30

Std. Dev.	2.7	1.10	0.60	2.10

[0200] As can be seen, upstream feed of the crosslinking agent decreased the impact properties of the composition, while downstream feed increased the tensile elongation by 118% and room temperature impact strength by 43%.

Example 4

[0201] Materials as described in Example 1 were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the feed throat in the first barrel by means of a gravimetric feeder. The crosslinking agent was fed using a gravimetric feeder at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0202] Compositions of the samples are provided in Table 10, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 10

Component	Addition Point	Sample 15	Sample 16	Sample 17	Sample 18
Lubricant	main feed	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6	1.0	1.7	1.0	1.7
Impact Modifier	main feed	25.0	25.0	15.0	15.0
Polyarylene Sulfide	main feed	73.7	73.0	83.7	83.0
Total		100.0	100.0	100.0	100.0

[0203] Following formation, tensile bars formed of the samples were tested for a variety of physical characteristics. Results are provided in Table 11, below.

Table 11

	Sample 15	Sample 16	Sample 17	Sample 18
Melt Viscosity (poise)	4255	4198	2522	2733
Density (g/cm^3)	1.2	-	-	-
Tensile Modulus (MPa)	1582.00	1572.00	2183.00	2189.00
Tensile Break Stress (MPa)	45.59	46.29	48.98	49.26

Tensile Break Strain (%)	125.92	116.40	66.13	48.24
Std. Dev.	19.79	9.97	15.36	7.80
Elongation at Yield (%)	23	-	-	-
Yield Stress (MPa)	42	-	-	-
Flex Modulus (MPa)	1946.00	1935.00	2389.00	2408.00
Flexural Stress @3.5% (MPa)	48.30	48.54	68.55	68.12
Notched Charpy Impact Strength at 23°C (kJ/m^2)	55.60	51.80	43.60	19.10
Std. Dev.	1.00	1.40	1.50	1.50
Notched Charpy Impact Strength at -30°C (kJ/m^2)	13	-	-	-
Notched Charpy Impact Strength at -40°C (kJ/m^2)	13.30	12.10	11.26	8.70
Std. Dev.	1.50	0.90	0.26	0.50
DTUL (1.8 MPa) (°C)	97.20	97.60	101.70	100.90
Water absorption (%)	0.07	-	-	-

Example 5

[0204] Materials as described in Example 1 were utilized except for the polyarylene sulfide, which was Fortron® 0320 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky. Materials were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide and impact modifier were fed to the feed throat in the first barrel by means of a gravimetric feeder. The crosslinking agent was fed using a gravimetric feeder at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0205] Compositions of the samples are provided in Table 12, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 12

Component	Addition Point	Sample 19	Sample 20	Sample 21	Sample 22	Sample 23
Crosslinking Agent	barrel 6	-	-	-	0.1	0.2
Impact Modifier	main feed	-	1.5	3.0	1.5	3.0
Polyarylene Sulfide	main feed	100.0	98.5	97.0	98.4	96.8
Total		100.0	100.0	100.0	100.0	100.0

[0206] Following formation, tensile bars formed of the samples were tested for a variety of physical characteristics. Results are provided in Table 13, below.

Table 13

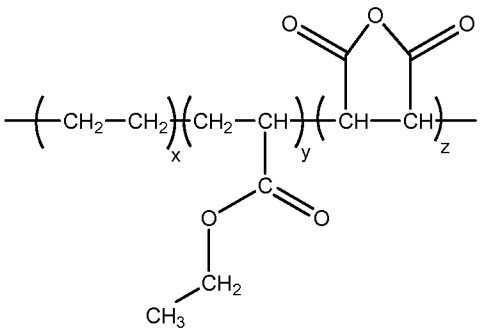
	Sample 19	Sample 20	Sample 21	Sample 22	Sample 23
Melt Viscosity (poise)	2435	2684	2942	2287	1986
Tensile Modulus (MPa)	3208	3207	3104	3245	3179
Tensile Break Stress (MPa)	67.20	72.94	59.06	63.95	60.80
Tensile Break Strain (%)	2.46	4.54	11.96	6.31	11.40
Std. Dev.	0.32	1.11	1.24	2.25	3.53
Flex Modulus (MPa)	3103.00	3173.00	3031.00	3284.00	3156.00
Flexural Stress @3.5% (MPa)	105.76	104.74	100.21	109.09	104.81
Notched Izod Impact Strength at 23°C (kJ/m^2)	2.90	5.20	5.60	4.10	4.30
Std. Dev.	0.40	0.40	0.40	0.20	0.20
DTUL (1.8 MPa) (°C)	105.60	104.00	103.70	104.20	104.80

Example 6

[0207] Materials utilized to form the compositions included the following:

Polyarylene sulfide: Fortron® 0214 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

Impact Modifier: LOTADER® 4720 - a random terpolymer of ethylene, ethyl acrylate and maleic anhydride available from Arkema, Inc.



Crosslinking Agent: Hydroquinone

Lubricant: Glycolube® P available from Lonza Group Ltd.

[0208] Materials were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. Upon melting and mixing of the above ingredients, the crosslinking agent was fed using a gravimetric feeder at the main feed for samples 24 and 25 and at barrel 6 for samples 26 and 27. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0209] Compositions of the samples are provided in Table 14, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 14

Component	Addition Point	Sample 24	Sample 25	Sample 26	Sample 27	Sample 28
Lubricant	main feed	0.3	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6	-	-	-	0.1	0.2
Crosslinking Agent	main feed	-	0.1	0.2	-	-
Impact Modifier	main feed	15.0	15.0	15.0	15.0	15.0
Polyarylene Sulfide	main feed	84.7	84.6	84.5	84.6	84.5
Total		100.0	100.0	100.0	100.0	100.0

[0210] Following formation, samples were tested for a variety of physical characteristics. Results are provided in Table 15, below.

Table 15

	Sample 24	Sample 25	Sample 26	Sample 27	Sample 28
Melt Viscosity (poise)	2435	2797	3251	2847	2918
Tensile Modulus (MPa)	2222	2164	2163	2184	2145
Tensile Break Stress (MPa)	52.03	45.17	46.53	45.47	46.39
Tensile Break Strain (%)	36.65	50.91	63.39	38.93	41.64
Std. Dev.	9.09	14.9	11.88	7.62	10.42
Elongation at Yield (%)	5.75	5.49	5.76	5.53	5.70
Yield Stress (MPa)	52.03	50.21	50.77	51.39	50.85
Flexural Modulus (MPa)	2358.00	2287.00	2286.00	2305.00	2281.00
Flexural Stress @3.5% (MPa)	70.51	68.25	68.03	69.23	68.23
Notched Charpy Impact Strength at 23°C (kJ/m^2)	29.80	44.60	50.60	42.30	45.90
Std. Dev.	4.10	2.40	1.90	1.90	1.60
Notched Charpy Impact Strength at -40°C (kJ/m^2)	5.90	9.30	11.00	9.60	9.80
Std. Dev.	1.00	0.90	1.20	0.80	1.30
DTUL (1.8 MPa) (°C)	99.10	93.90	98.20	100.10	99.00

Example 7

[0211] Materials utilized to form the compositions included the following:

Polyarylene sulfide:

PPS1 - Fortron® 0203 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

PPS2 – Fortron®0205 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

PPS3 - Fortron®0320 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

Impact Modifier: LOTADER® AX8840 - a random copolymer of ethylene and glycidyl methacrylate available from Arkema, Inc.

Crosslinking Agent: Terephthalic Acid

Lubricant: Glycolube® P available from Lonza Group Ltd.

[0212] Materials were melt mixed using a Coperion co-rotating, fully-

intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. Upon melting and mixing of the above ingredients, the crosslinking agent was fed using a gravimetric feeder at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0213] Compositions of the samples are provided in Table 16, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 16

Component	Addition Point	Sample 29	Sample 30	Sample 31	Sample 32	Sample 33	Sample 34
Lubricant	main feed	0.3	0.3	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6		1.0		1.0		1.0
Impact Modifier	main feed	15.0	15.0	15.0	15.0	15.0	15.0
PPS1	main feed	84.7	83.7				
PPS2	main feed			84.7	83.7		
PPS3	main feed					84.7	83.7
Total		100.0	100.0	100.0	100.0	100.0	100.0

[0214] Following formation, samples were tested for a variety of physical characteristics. Results are provided in Table 17, below.

Table 17

	Sample 29	Sample 30	Sample 31	Sample 32	Sample 33	Sample 34
Tensile Modulus (MPa)	2292	2374	2250	2427	2130	2285
Tensile Break Stress (MPa)	50.92	50.18	49.18	53.22	48.01	48.08
Tensile Break Strain (%)	5.79	2.84	23.79	34.73	23.55	45.42
Std. Dev.	0.99	0.18	11.96	4.01	18.57	18.94
Flexural Modulus (MPa)	2279.00	2382.00	2257.00	2328.00	2292.00	2294.00
Flexural Stress @3.5% (MPa)	71.11	74.94	69.72	72.39	67.95	68.95

Notched Charpy Impact Strength at 23°C (kJ/m^2)	5.70	3.70	9.10	12.80	19.40	45.40
Std. Dev.	0.90	0.70	0.80	1.00	2.70	7.70
Notched Charpy Impact Strength at -40°C (kJ/m^2)	3.00	2.50	5.10	5.00	5.10	8.00
Std. Dev.	0.70	0.30	0.60	0.30	0.40	1.00
DTUL (1.8 MPa) (°C)	101.00	105.50	100.00	102.90	99.90	100.40

Example 8

[0215] Materials utilized to form the compositions included the following:

Polyarylene sulfide: Fortron® 0214 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

Impact Modifier: LOTADER® AX8840 - a random copolymer of ethylene and glycidyl methacrylate available from Arkema, Inc.

Crosslinking Agent: Terephthalic Acid

Lubricant: Glycolube® P available from Lonza Group Ltd.

[0216] Materials were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. Upon melting and mixing of the above ingredients, the crosslinking agent was fed using a gravimetric feeder at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0217] Compositions of the samples are provided in Table 18, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 18

Component	Addition Point	Sample 35	Sample 36	Sample 37	Sample 38	Sample 39	Sample 40
Lubricant	main feed	0.3	0.3	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6		0.75		1.25		1.75
Impact Modifier	main feed	15.0	15.0	25.0	25.0	35.0	35.0
Polyarylene	main	84.7	83.95	74.70	73.45	64.70	62.95

Sulfide	feed						
Total		100.0	100.0	100.0	100.0	100.0	100.0

[0218] Following formation, samples were tested for a variety of physical characteristics. Results are provided in Table 19, below. Sample 39 was not injection moldable.

Table 19

	Sample 35	**Sample 36**	**Sample 37**	**Sample 38**	**Sample 39**	**Sample 40**
Melt Viscosity (poise)	2323	2452	2955	3821	2025	5462
Tensile Modulus (MPa)	2281	2298	2051	1721	-	1045
Tensile Break Stress (MPa)	47.09	49.09	47.29	46.18	-	39.81
Tensile Break Strain (%)	28.92	36.42	97.33	110.36	-	96.76
Std. Dev.	6.35	3.13	53.94	8.40	-	1.77
Elongation at Yield (%)	5.28	8.58	36.00	108.19	-	95.77
Yield Stress (MPa)	52.42	53.92	46.50	46.76	-	40.43
Flexural Modulus (MPa)	2388.00	2349.00	2210.00	1750.00	-	1209.00
Flexural Stress @3.5% (MPa)	71.52	71.70	63.15	50.52	-	34.41
Notched Charpy Impact Strength at 23°C (kJ/m^2)	35.15	38.40	57.00	52.70	-	52.10
Std. Dev.	6.22	1.50	1.40	3.40	-	2.10
Notched Charpy Impact Strength at -30°C (kJ/m^2)	8.20	10.70	8.70	18.10	-	14.10
Std. Dev.	1.50	1.60	0.20	0.90	-	0.80
Notched Charpy Impact Strength at -40°C (kJ/m^2)	7.26	9.20	8.00	16.80	-	12.47
Std. Dev.	1.54	2.30	0.60	0.40	-	0.92
DTUL (1.8 MPa) (°C)	99.90	103.60	98.10	99.30	-	92.70
Water absorption (%)	-	-	-	-	-	0.1

Example 9

[0219] Materials utilized to form the compositions included the following:

Polyarylene sulfide: Fortron® 0214 linear polyphenylene sulfide available from Ticona Engineering Polymers of Florence, Kentucky

Impact Modifier: LOTADER® AX8840 - a random copolymer of ethylene and

glycidyl methacrylate available from Arkema, Inc.

Crosslinking Agent: Terephthalic Acid

Lubricant: Glycolube® P available from Lonza Group Ltd.

[0220] Materials were melt mixed using a Coperion co-rotating, fully-intermeshing, twin-screw extruder with an overall L/D of 40 and ten temperature control zones including one at the die. A high shear screw design was used to compound the additives into a resin matrix. The polyarylene sulfide, impact modifier and lubricant were fed to the main feed throat in the first barrel by means of a gravimetric feeder. Upon melting and mixing of the above ingredients, the crosslinking agent was fed using a gravimetric feeder at barrel 6. Materials were further mixed then extruded through a strand die. The strands were water-quenched in a bath to solidify and granulated in a pelletizer.

[0221] Compositions of the samples are provided in Table 20, below. Amounts are provided as weight percentages based upon the weight of the sample.

Table 20

Component	Addition Point	Sample 41	Sample 42	Sample 43	Sample 44
Lubricant	main feed	0.3	0.3	0.3	0.3
Crosslinking Agent	barrel 6	1.0	1.1	1.25	1.25
Impact Modifier	main feed	15	20	25	30
Polyarylene Sulfide	main feed	83.7	78.6	73.45	68.45
Total		100.0	100.0	100.0	100.0

[0222] Following formation, samples were tested for a variety of physical characteristics. Results are provided in Table 21, below.

Table 21

	Sample 41	Sample 42	Sample 43	Sample 44
Specific Gravity (g/cm^3)	1.25	1.20	1.15	1.20
Tensile Modulus (MPa) (50 mm/min)	2200	1600	1200	1700
Tensile Break Strength (MPa) (50 mm/min)	50	42	40	46
Elongation at	40	100	90	75

Break (%) (50 mm/min)				
Yield Stress (MPa) (50 mm/min)	55	42	40	48
Yield Strain (%) (50 mm/min)	9	25	90	15
Flexural Modulus (MPa)	2200	1700	1300	1900
Flexural Strength @3.5% (MPa)	68	50	40	56
Notched Charpy Impact Strength at 23°C (kJ/m^2)	40	55	50	50
Notched Charpy Impact Strength at -30°C	10	24	20	20
Unnotched Charpy Impact Strength at 23°C	Not broken	Not broken	Not broken	Not broken
DTUL (1.8 MPa) (°C)	102	100	95	100
Water absorption (%)	0.05	0.07	0.1	0.05
Vicat softening temp. (A10N, °C)	270	270	270	270
Vicat softening temp. (B50N, °C)	200	160	110	180
Complex viscosity (0.1 rad/sec, 310°C) (kPa/sec)	79.994	289.27	455.19	-

[0223] Samples 41, 42, and 43 were tested to determine complex viscosity as well as melt strength and melt elongation as a function of Hencky strain. As a comparative material, Sample 3 as described in Example 2 was utilized. Samples 41, 42 and 43 were done at 310°C and sample 3 was done at 290°C. Results are shown in FIG. 22, FIG. 23, and FIG. 24.

Example 10

[0224] Sample 42 described in Example 9 was utilized to form a blow molded 1.6 gallon tank. The formed tank is illustrated in FIG. 25. Cross sectional views of the tank are presented in FIG. 26A and FIG. 26B. The formed tank had a good outer surface with regard to both visual inspection and feel. As shown in FIG. 26A, an even wall thickness (about 3 mm) was obtained and minimal sag was observed. As shown in FIG. 26B, the pinch-offs formed an excellent geometry.

Example 11

[0225] Samples 41, 42, and 43 described in Example 9 were tested to

determine permeation of various fuels including CE10 (10 wt.% ethanol, 45 wt.% toluene, 45 wt.% iso-octane), CM15A (15 wt.% methanol and 85 wt.% oxygenated fuel), and methanol. Sample No. 4 described in Example 2 was utilized as a comparison material. Two samples of each material were tested.

[0226] Table 22, below provides the average sample thickness and effective area for the samples tested with each fuel.

Table 22

Sample	Average Sample Thickness (mm)	Effective area (m^2)
CE10		
Aluminum blank – 1	1.50	0.00418
Aluminum blank – 2	1.50	0.00418
Sample No. 4 – 1	1.47	0.00418
Sample No. 4 – 2	1.45	0.00418
Sample No. 41 – 1	1.47	0.00418
Sample No. 41 – 2	1.49	0.00418
Sample No. 42 – 1	1.47	0.00418
Sample No. 42 – 2	1.46	0.00418
Sample No. 43 – 1	1.45	0.00418
Sample No. 43 – 2	1.47	0.00418
CM15A		
Aluminum blank – 1	1.50	0.00418
Aluminum blank – 2	1.50	0.00418
Sample No. 4 – 1	1.48	0.00418
Sample No. 4 – 2	1.49	0.00418
Sample No. 41 – 1	1.49	0.00418
Sample No. 41 – 2	1.50	0.00418
Sample No. 42 – 1	1.47	0.00418
Sample No. 42 – 2	1.48	0.00418
Sample No. 43 – 1	1.46	0.00418
Sample No. 43 – 2	1.47	0.00418
Methanol		
Aluminum blank – 1	1.50	0.00418
Aluminum blank – 2	1.50	0.00418
Sample No. 4 – 1	1.49	0.00418
Sample No. 4 – 2	1.49	0.00418
Sample No. 41 – 1	1.49	0.00418
Sample No. 41 – 2	1.51	0.00418
Sample No. 42 – 1	1.48	0.00418
Sample No. 42 – 2	1.47	0.00418
Sample No. 43 – 1	1.47	0.00418
Sample No. 43 – 2	1.48	0.00418

[0227] The daily weight losses for each material and each fuel are shown in FIGS. 27-29. Specifically, FIG. 27 shows the daily weight loss for the samples during the permeation test of CE10, FIG. 28 shows the daily weight loss for the samples during the permeation test of CM15A, and FIG. 29 shows the daily weight

loss for the samples during the permeation test of methanol.

[0228] The average permeation rates for each sample with each fuel are provided in Table 23. Note that Sample No. 43 takes a longer time to arrive at equilibrium, so the linear regression fitting was generated based on data between days 42 and 65 for this material, while the linear regress fitting was generated for the other materials between days 32 and 65. For methanol, the linear regression fitting was generated based on data between days 20 and 65, but with Sample No. 604, the methanol linear regression fitting was generated based on data between days 30 and 65. Some samples show negative permeability, which is because the weight loss of the sample was lower than that of the aluminum blank.

Table 23

Sample	Normalized permeation (g-mm/day-m^2)	Average Normalized permeation (g-mm/day-m^2)	Permeation – 3 mm thickness	Average Permeation – 3 mm thickness
CE10				
Sample No. 4–1	0.06	0.05±0.01	0.02	0.02±0
Sample No. 4–2	0.05		0.02	
Sample No. 41–1	0.07	0.04±0.04	0.02	0.01±0.01
Sample No. 41–2	0.01		0.00	
Sample No. 42–1	0.06	0.06±0	0.02	0.02±0
Sample No. 42–2	0.06		0.02	
Sample No. 43–1	2020	2.51±0.43	0.73	0.84±0.14
Sample No. 43–2	2.81		0.94	
CM15A				
Sample No. 4–1	0.49	0.18±0.44	0.16	0.06±0.15
Sample No. 4–2	-0.13		-0.04	
Sample No. 41–1	0.50	0.11±0.55	0.17	0.04±0.18
Sample No. 41–2	-0.27		-0.09	
Sample No. 42–1	-0.13	0.27±0.58	-0.04	0.09±0.19
Sample No. 42–2	0.68		0.23	
Sample No. 43–1	2.04	2.29±0.35	0.68	0.76±0.12
Sample No. 43–2	2.53		0.84	
Methanol				
Sample No. 4–1	0.37	0.25±0.18	0.12	0.08±0.06
Sample No. 4–2	0.13		0.04	
Sample No. 41–1	0.02	0.05±0.05	0.01	0.02±0.02
Sample No. 41–2	0.08		0.03	
Sample No. 42–1	0.28	0.25±0.05	0.09	0.08±0.02
Sample No. 42–2	0.21		0.07	
Sample No. 43–1	0.27	0.41±0.2	0.09	0.14±0.07
Sample No. 43–2	0.55		0.18	

The error was derived from the standard deviation of duplicates in each sample.

[0229] These and other modifications and variations to the present disclosure may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present disclosure. In addition, it should be

understood the aspects of the various embodiments may be interchanged, either in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the disclosure.

WHAT IS CLAIMED IS:

1. An automotive component comprising a polyarylene sulfide composition, the polyarylene sulfide composition including a polyarylene sulfide and a crosslinked impact modifier, wherein the automotive component is a component of a heavy duty truck or is an automotive fuel line.

2. The automotive component of claim 1, wherein the polyarylene sulfide composition has one or more of the following characteristics:

a notched Charpy impact strength of greater than about 3 kJ/m^2 as measured according to ISO Test No. 179-1 at a temperature of 23°C;

a notched Charpy impact strength of greater than about 8 kJ/m^2 as measured according to ISO Test No. 179-1 at a temperature of -30°C;

an elongation at yield of greater than about 4.5% as measured according to ISO Test No. 527 at a temperature of 23ºC and a test speed of 5 mm/min;

a tensile strength at break of greater than about 30 MPa as measured according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min;

a tensile modulus of less than about 3000 MPa as measured according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min;

exhibits a loss in Charpy notched impact strength as determined according to ISO Test no. 179-1 at 23°C of less than about 17% following exposure of about 500 hours to a strong acid solution at a temperature of about 40°C;

exhibits a loss in Charpy notched impact strength as determined according to ISO Test no. 179-1 at 23°C of less than about 25% following exposure of about 500 hours to a strong acid solution at a temperature of about 80°C;

a deflection temperature under load of greater than about 80°C as determined according to ISO Test No. 78 at 1.8 MPa;

a tensile break strain of greater than about 25% as measured according to ISO Test No. 527 at a temperature of 23°C and a test speed of 5 mm/min;

a halogen content of less than about 1000 ppm;

meets the V-0 flammability standard at a thickness of 0.2 millimeters;

exhibits a permeation resistance to a fuel or a fuel source of less than about

3 g-mm/m^2-day as determined according to SAE Testing Method No. J2665.

3. The automotive component of claim 1 or claim 2, wherein the automotive component is a multi-layer tubular member or a single-layer tubular member, for instance a multi-layer tubular member comprising the polyarylene sulfide composition in one or more of the layers.

4. The automotive component of any of the preceding claims, wherein the automotive component is a portion of a urea tank, a charge air system coupling, a component of an exhaust system, a single layer fuel tube, a multi-layer fuel hose, or a component of an air brake system.

5. The automotive component of any of the preceding claims, wherein the polyarylene sulfide is polypropylene sulfide or a functionalized polyarylene sulfide.

6. The automotive component of any of the preceding claims, the polyarylene sulfide composition further comprising one or more additives, for example one or more fillers, a UV stabilizer, a heat stabilizer, a lubricant, or a colorant.

7. The automotive component of any of the preceding claims, wherein the crosslinked impact modifier comprises the reaction product of an epoxy functionality of the impact modifier and a crosslinking agent or comprises the reaction product of maleic anhydride functionality of the impact modifier and a crosslinking agent.

8. The automotive component of any of the preceding claims, wherein a first section of the component comprises the polyarylene sulfide composition, the first section being adjacent to a second section of the component that does not comprise the polyarylene sulfide composition.

9. The automotive component of any of the preceding claims, wherein the polyarylene sulfide composition is free of plasticizers.

10. A heavy duty truck comprising the automotive component of any of the preceding claims.

11. A method for forming an automotive component comprising shaping a polyarylene sulfide composition to form the automotive component, the polyarylene sulfide composition comprising a polyarylene sulfide and a crosslinked impact modifier.

12. The method of claim 11, further comprising forming the polyarylene sulfide composition according to a process that includes:

feeding the polyarylene sulfide to a melt processing unit;

feeding the impact modifier to the melt processing unit, the polyarylene sulfide and the impact modifier mixing in the melt processing unit such that the impact modifier becomes distributed throughout the polyarylene sulfide, the impact modifier comprising a reactive functionality; and

feeding a crosslinking agent to the melt processing unit, the crosslinking agent being fed to the melt processing unit following distribution of the impact modifier throughout the polyarylene sulfide, the crosslinking agent comprising reactive functionality that is reactive to the reactive functionality of the impact modifier.

13. The method according to claim 14, wherein the melt processing unit has a length L and a blending length L_B, and wherein the ratio of L/L_B is from about 40 to about 1.1.

14. The method according to claim 13, further comprising feeding a disulfide compound to the melt processing unit, for example a disulfide-free crosslinking agent, the disulfide compound comprising reactive functionality at terminal end(s) of the disulfide compound, for instance disulfide compound and the crosslinking agent can be added in conjunction with one another and/or the reactive functionality of the disulfide compound can be the same as the reactive functionality of the crosslinking agent.

15. The method according to any of claims 12-14, wherein the impact modifier comprises an epoxy reactive functionality.

16. The method according to any of claims 12-15, wherein the step of shaping the polyarylene composition comprises a formation method including one or more of extrusion, injection molding, blow-molding, thermoforming, foaming, compression molding, hot-stamping, fiber spinning, and pultrusion.

17. The method according to any of claims 12-16, wherein the polyarylene sulfide composition is shaped to form a tubular member.

18. The method according to claim 12, wherein the shaping comprises utilization of an extrusion process having one or more of the following characteristics:

a compression ratio of between about 2.5:1 and about 4:1;

utilization of a barrel having a length and a diameter, the ratio of the barrel length to the barrel diameter being from about 16 to about 24;

utilization of a die, the temperature of the die being from about 293°C to about 310°C;

a head pressure that is from about 690 kPa to about 6900 kPa.

19. The method according to claim 12, where the shaping comprises an extrusion process utilizing an extruder having at least four zones, the temperature of the first zone being from about 276°C to about 288°C, the temperature of the second zone being from about 282°C to about 299°C, the temperature of the third zone being from about 282°C to about 299°C, and the temperature of the fourth zone being from about 540°C to about 580°C.

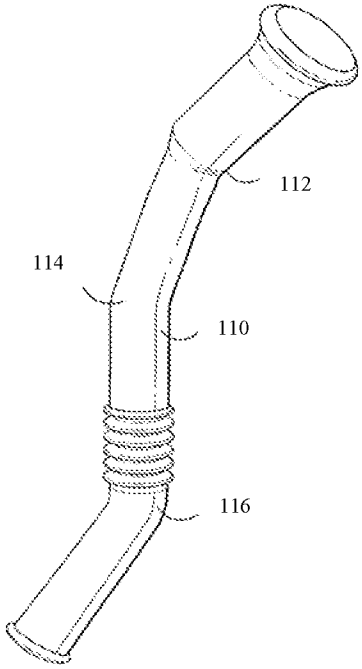


FIG. 1

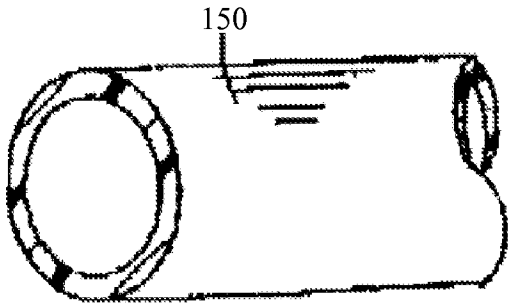


FIG. 2

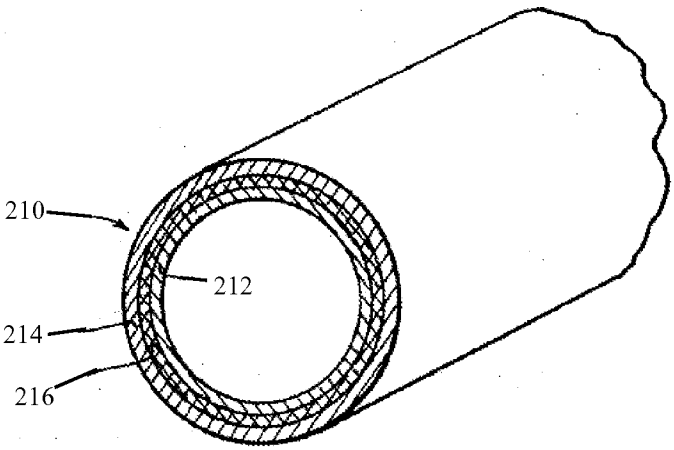


FIG. 3

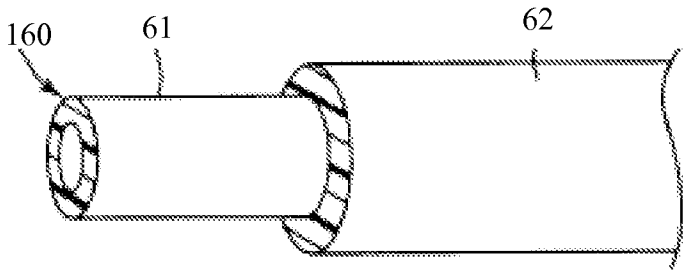


FIG. 4

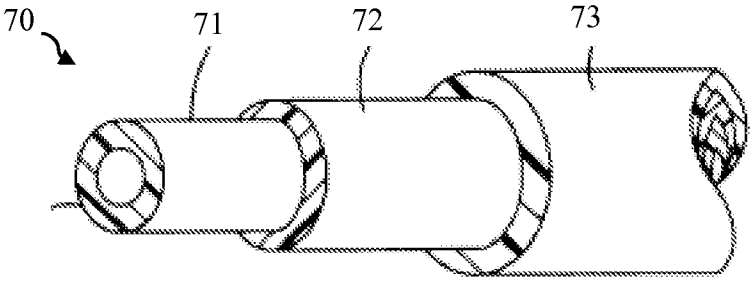


FIG. 5

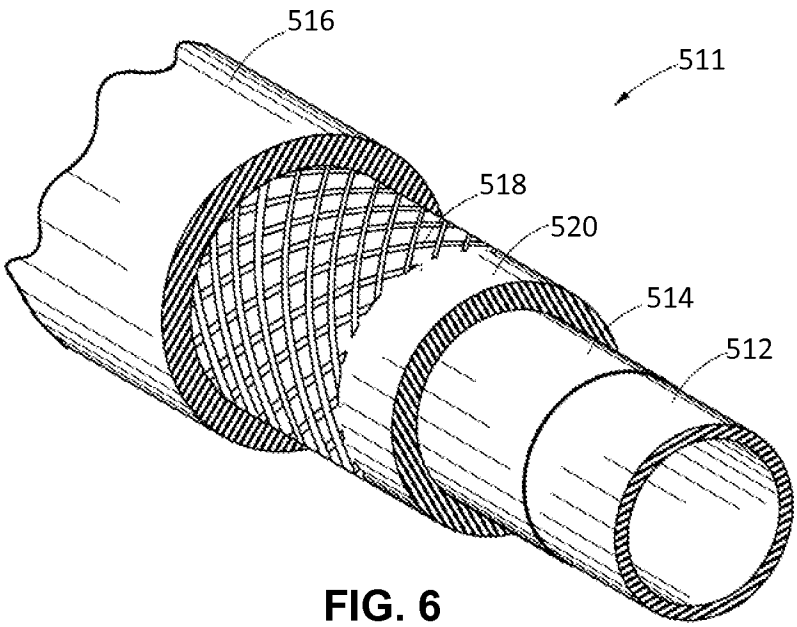


FIG. 6

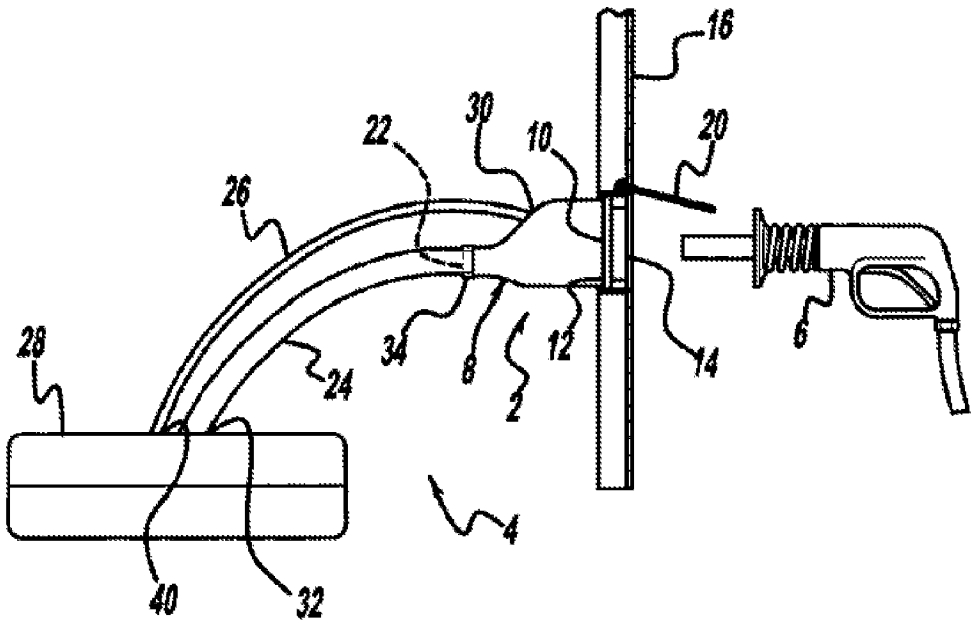


FIG. 7

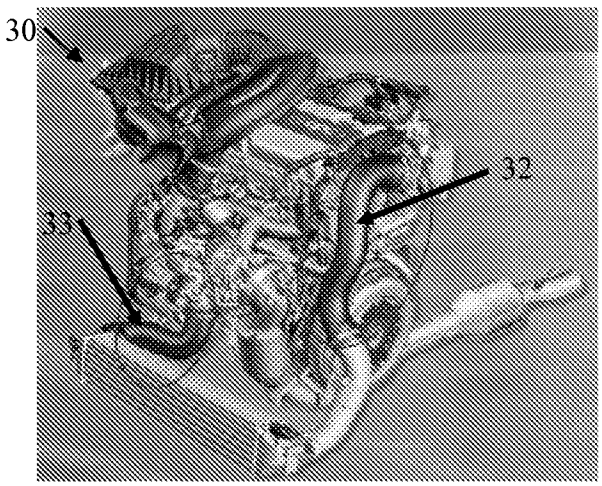


FIG. 8

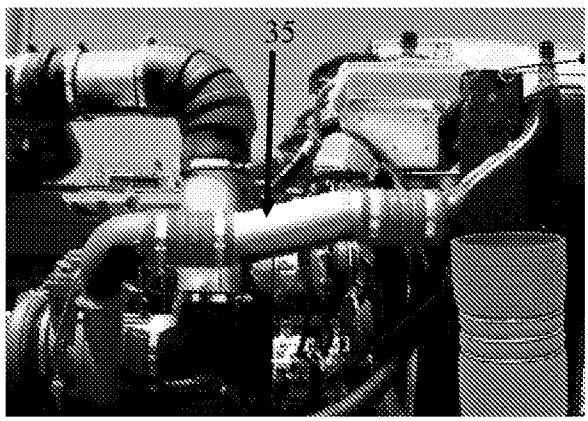


FIG. 9

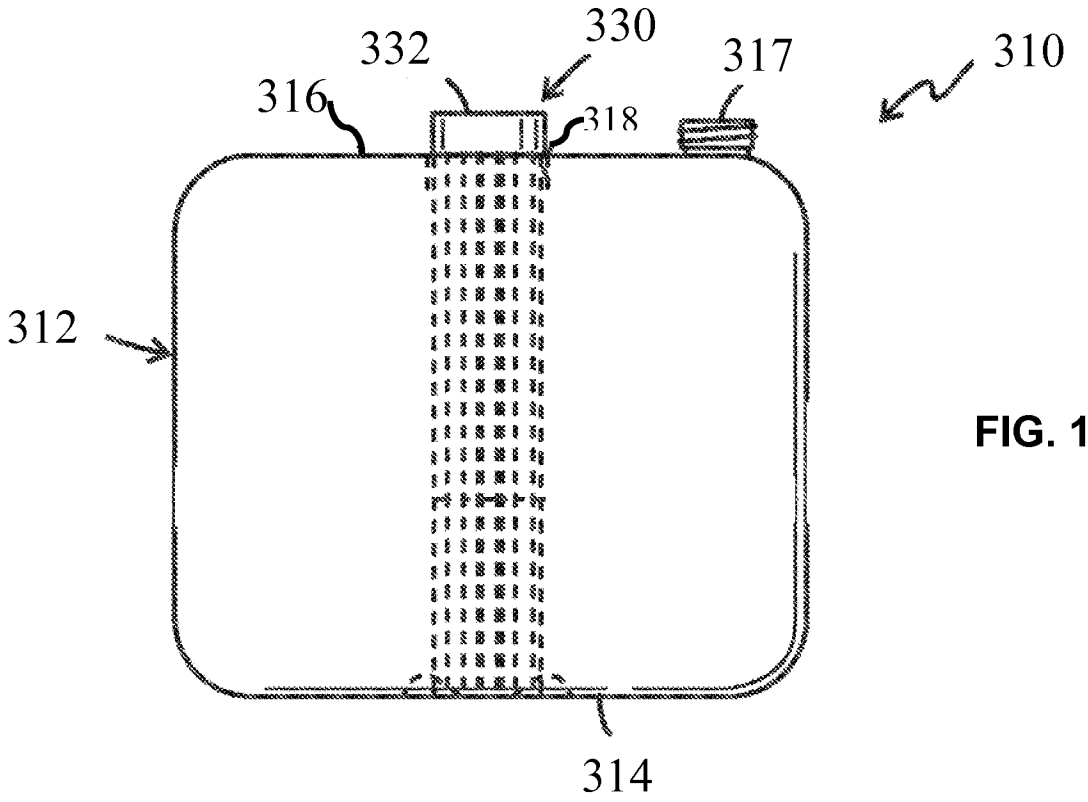


FIG. 10

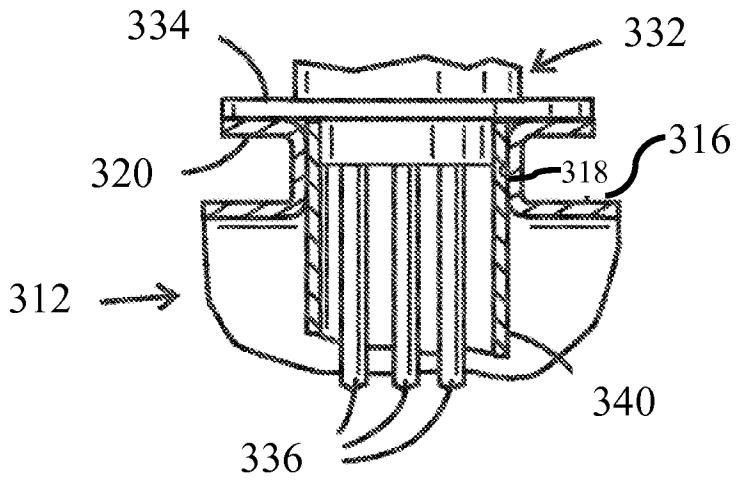


FIG. 11

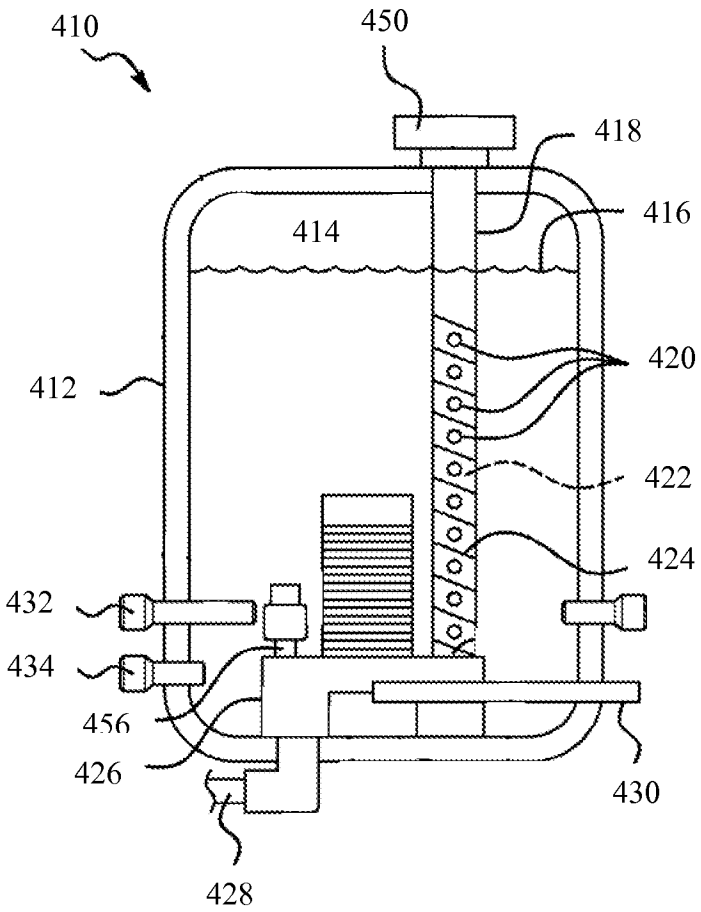

410
450
418
416
414
420
412
422
424
432
434
456
426
430
428

FIG. 12

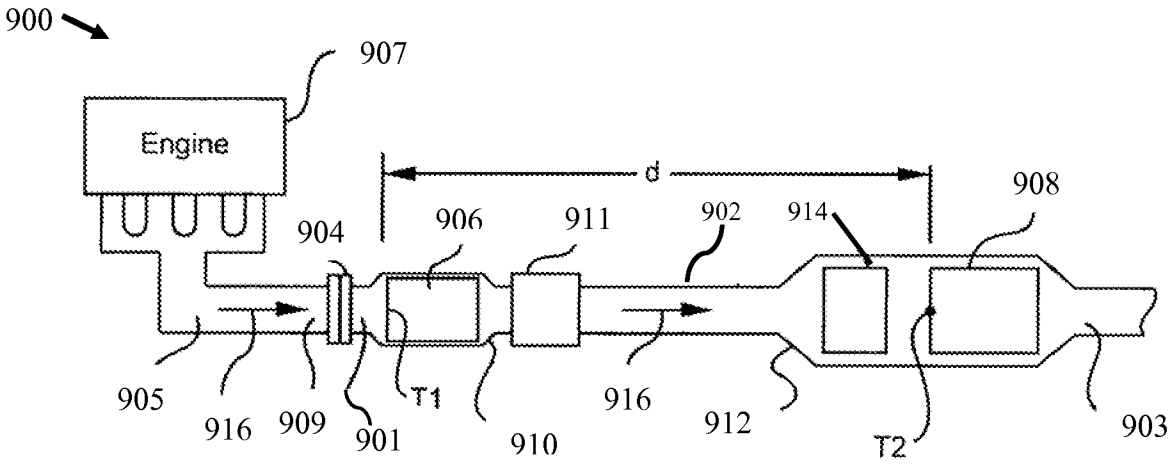

900
907
Engine
d
908
904
906
911
902
914
905
916
909
901
T1
910
916
912
T2
903

FIG. 13

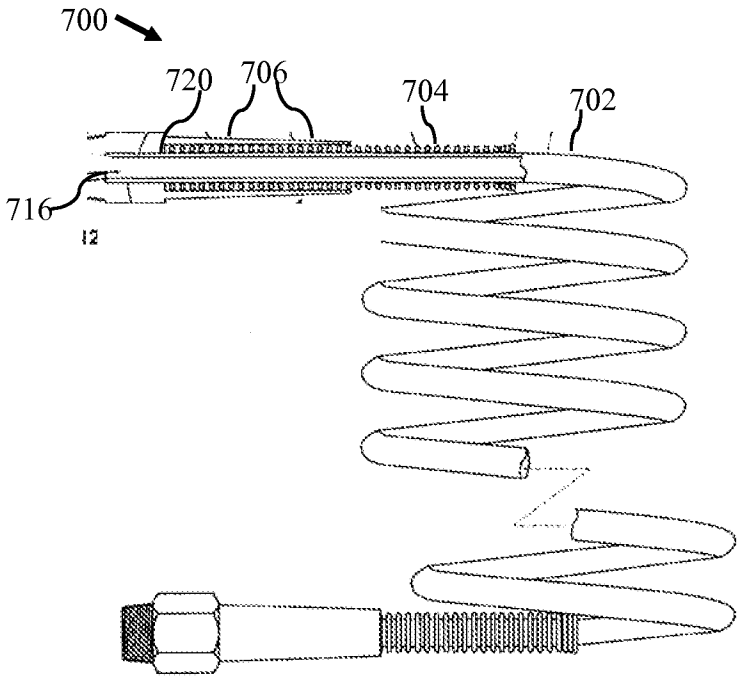


FIG. 14

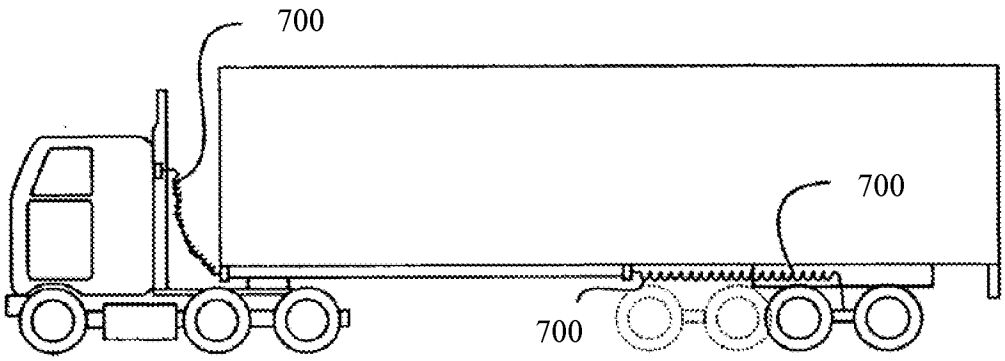


FIG. 15

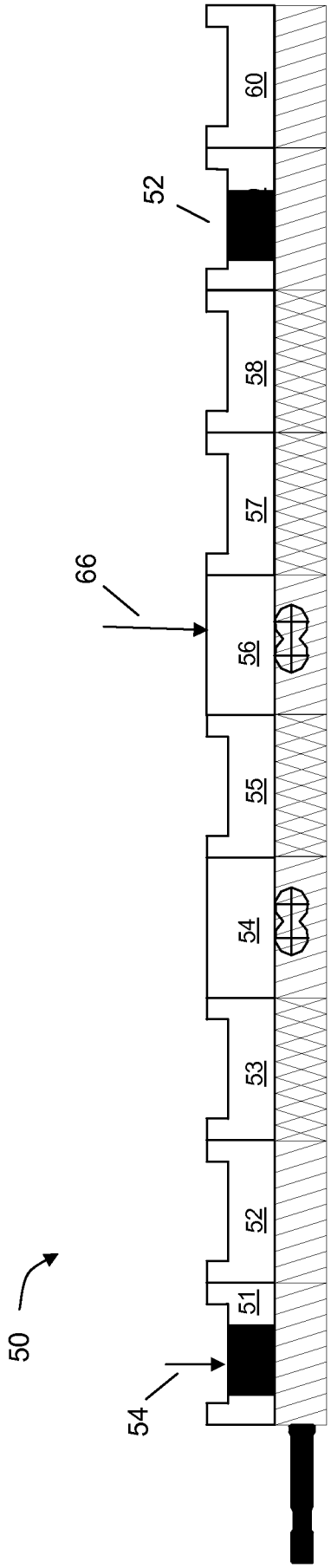


FIG. 16

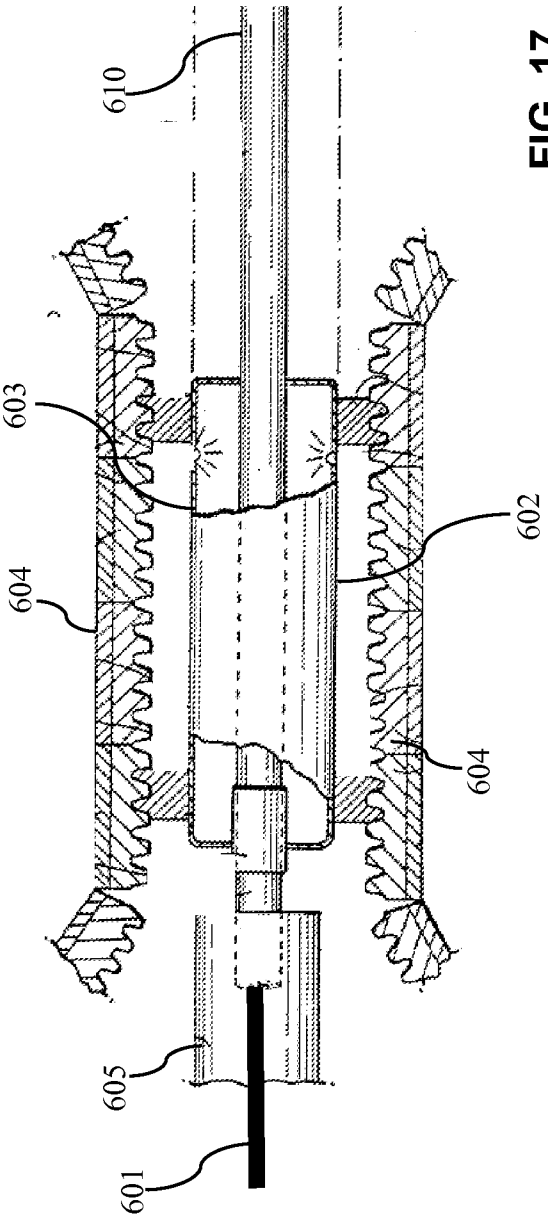


FIG. 17

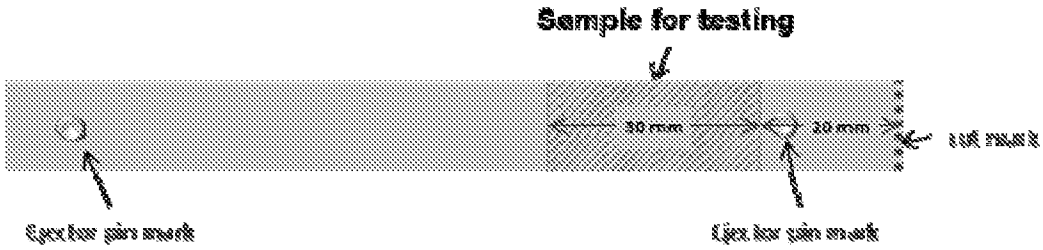

Sample for testing
50 mm
20 mm

FIG. 18

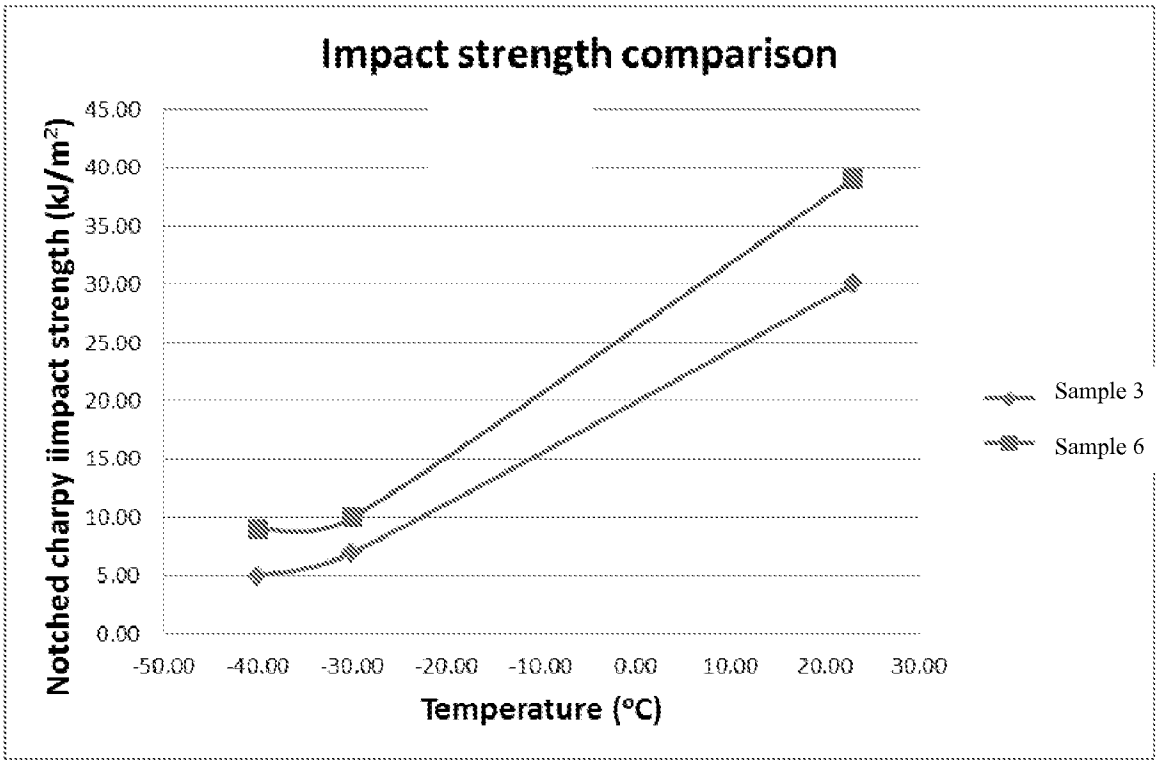

Impact strength comparison
Notched charpy iimpact strength (kJ/m²)
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
-50.00
-40.00
-30.00
-20.00
-10.00
0.00
10.00
20.00
30.00
Temperature (°C)
Sample 3
Sample 6

FIG. 19

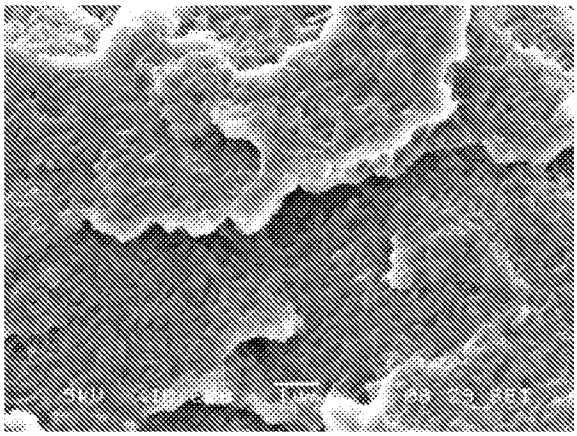


FIG. 20A (Sample 3)

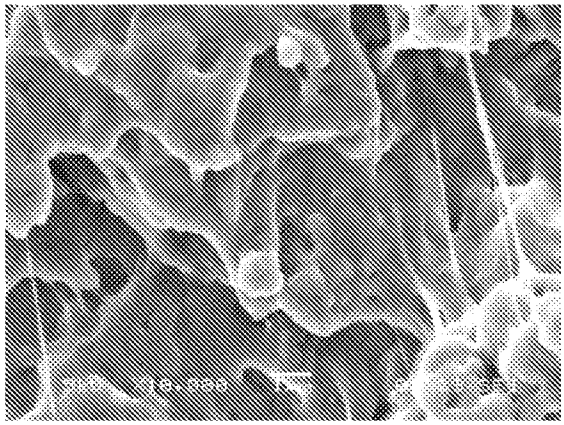


FIG. 20B (Sample 6)

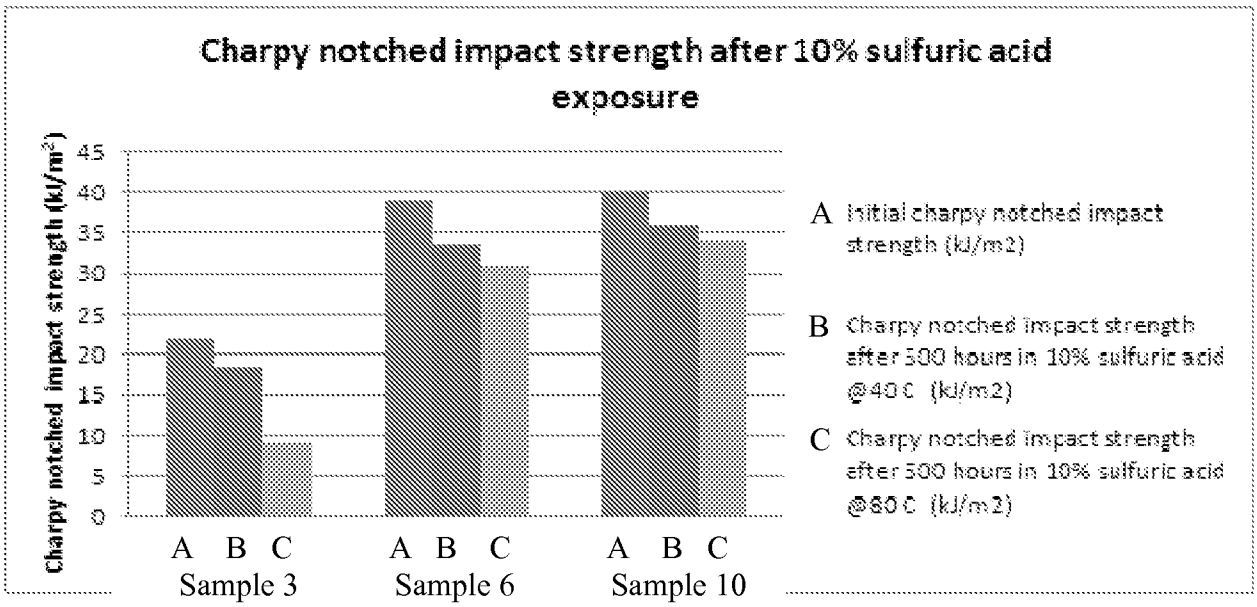


FIG. 21

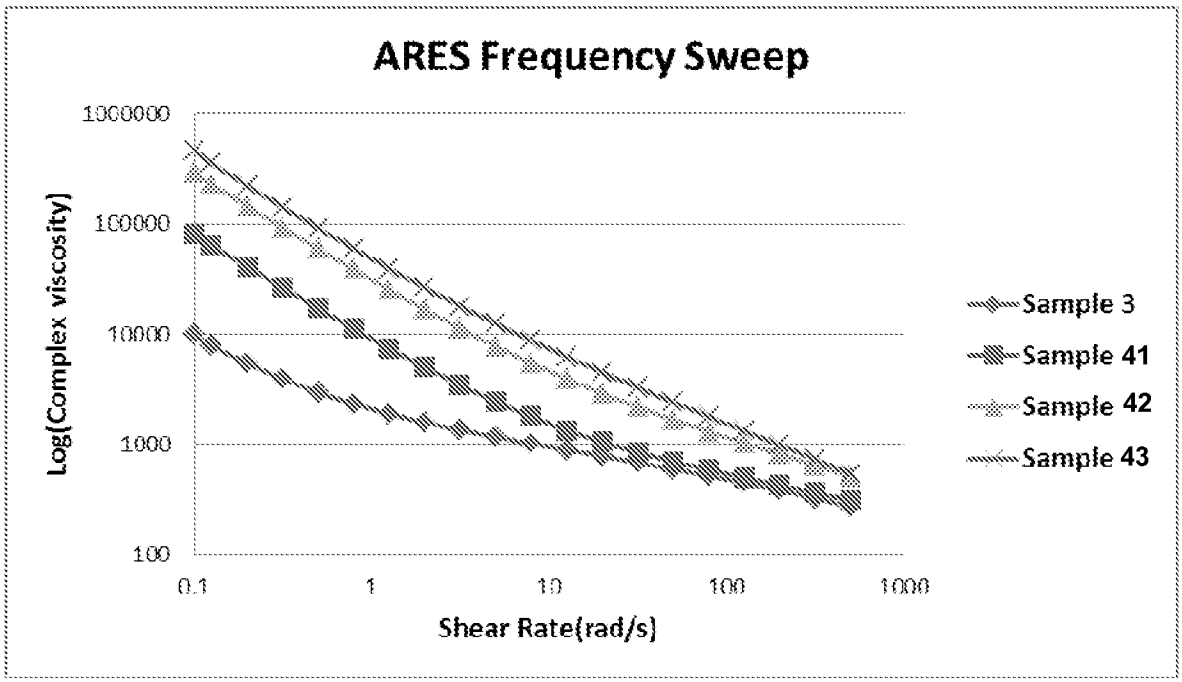

ARES Frequency Sweep
Log(Complex viscosity)
1000000
100000
10000
1000
100
0.1
1
10
100
1000
Shear Rate(rad/s)
Sample 3
Sample 41
Sample 42
Sample 43

FIG. 22

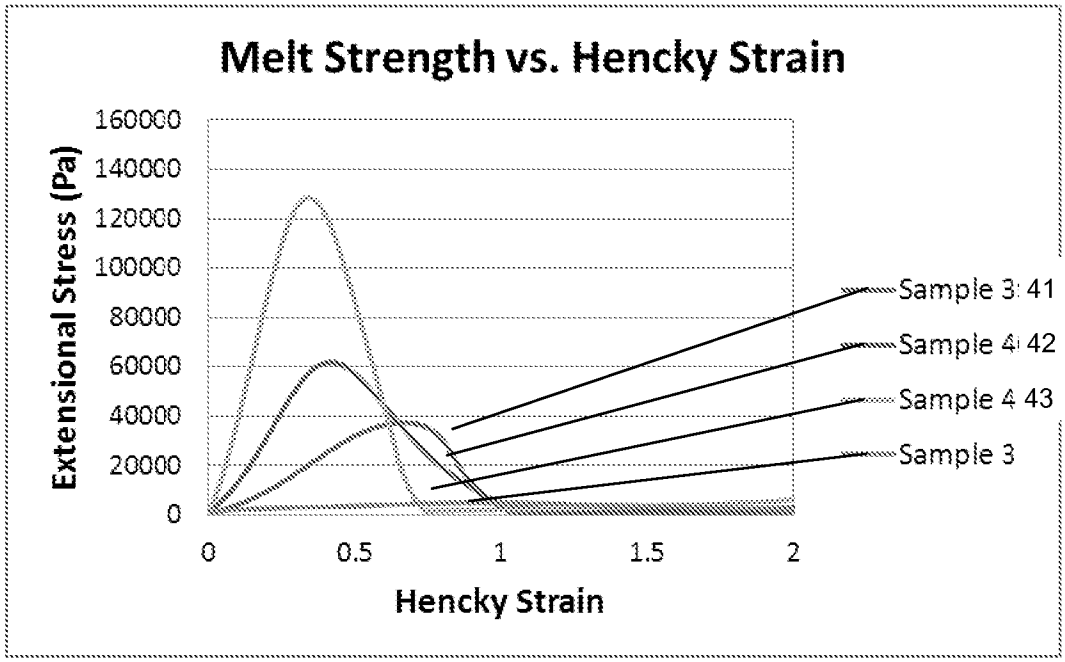

Melt Strength vs. Hencky Strain
Extensional Stress (Pa)
160000
140000
120000
100000
80000
60000
40000
20000
0
0
0.5
1
1.5
2
Hencky Strain
Sample 3: 41
Sample 4: 42
Sample 4 43
Sample 3

FIG. 23

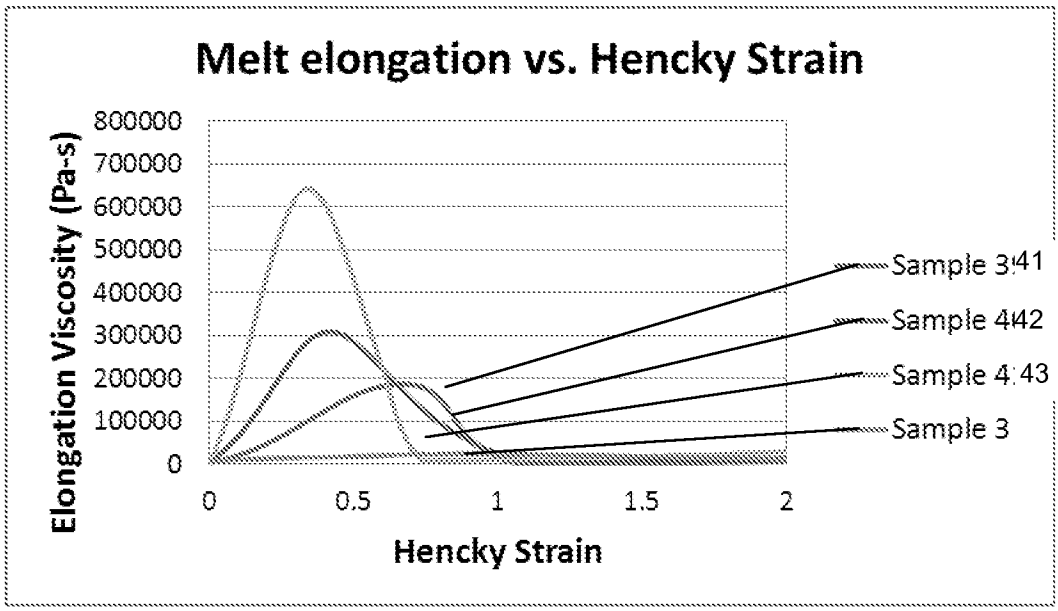

Melt elongation vs. Hencky Strain
Elongation Viscosity (Pa-s)
800000
700000
600000
500000
400000
300000
200000
100000
0
0
0.5
1
1.5
2
Hencky Strain
Sample 3:41
Sample 4:42
Sample 4:43
Sample 3

FIG. 24

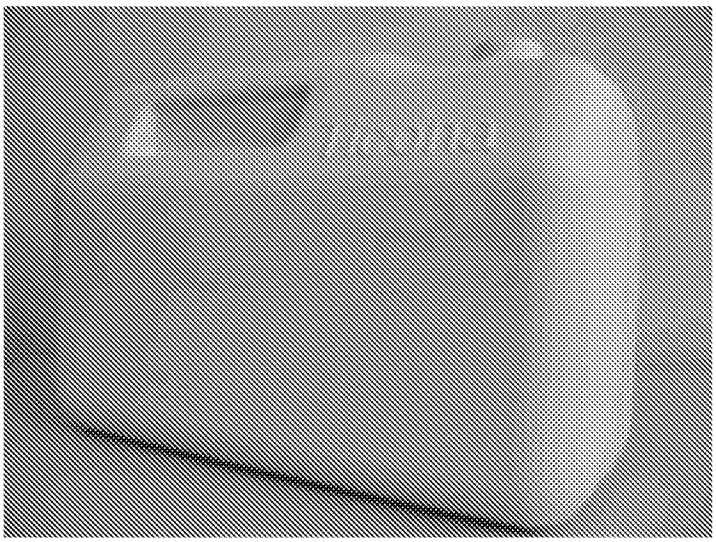


FIG. 25

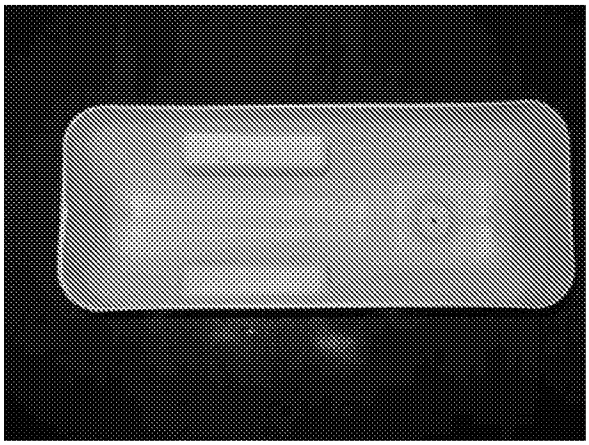


FIG. 26A

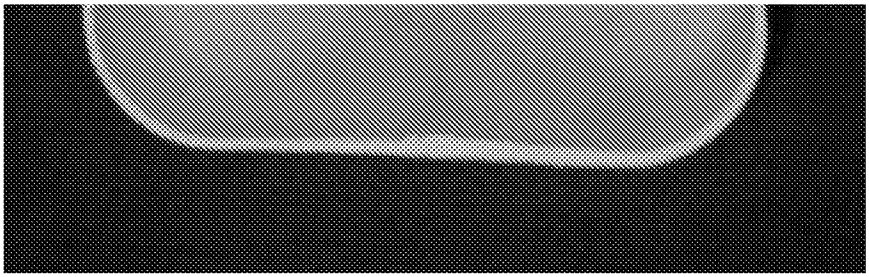
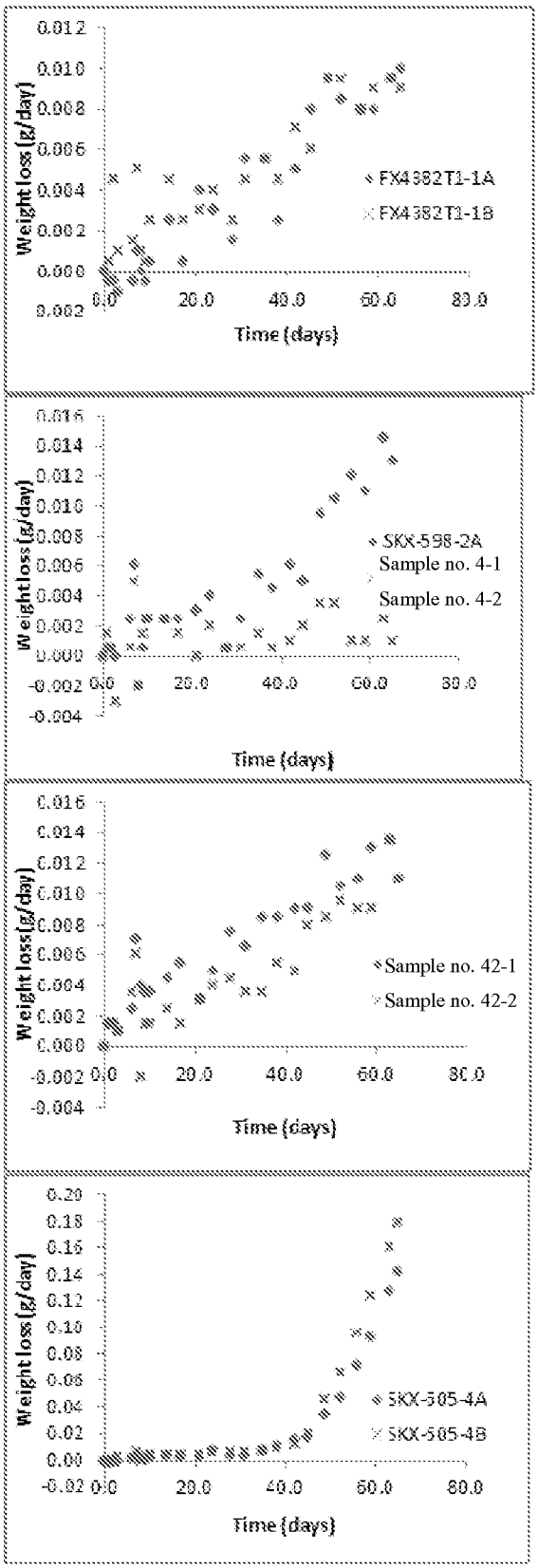


FIG. 26B



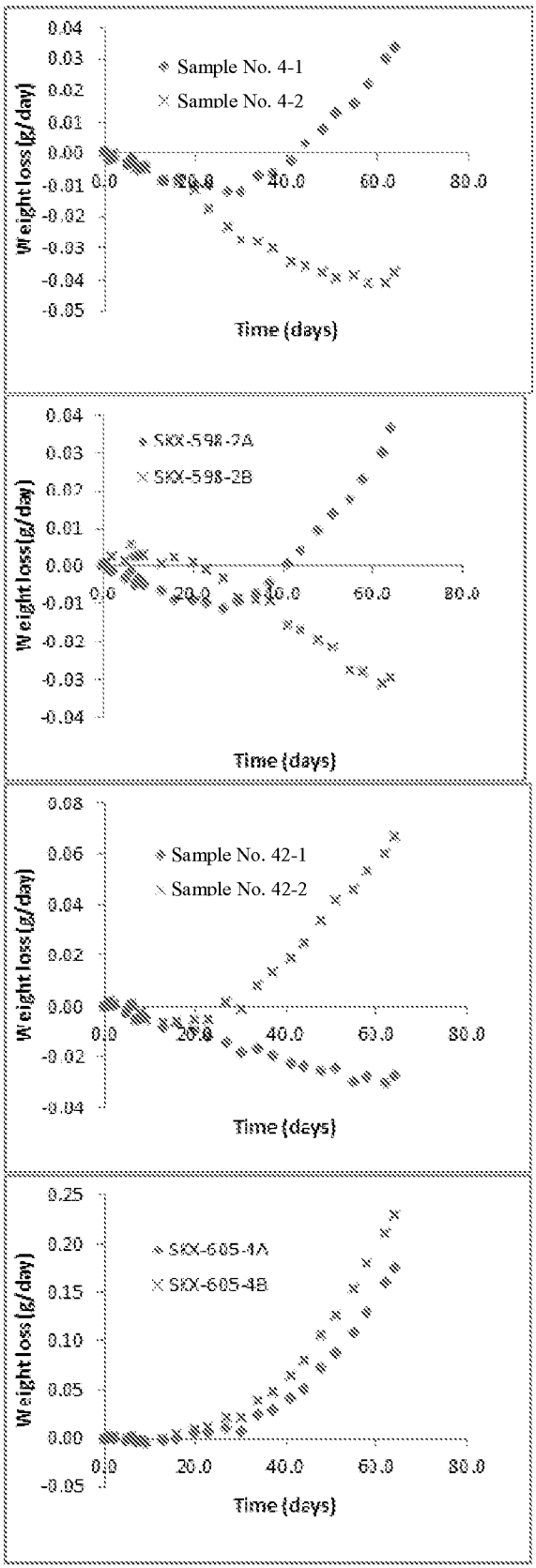
Sample no. 41-1

Sample no. 41-2

Sample no. 43-1

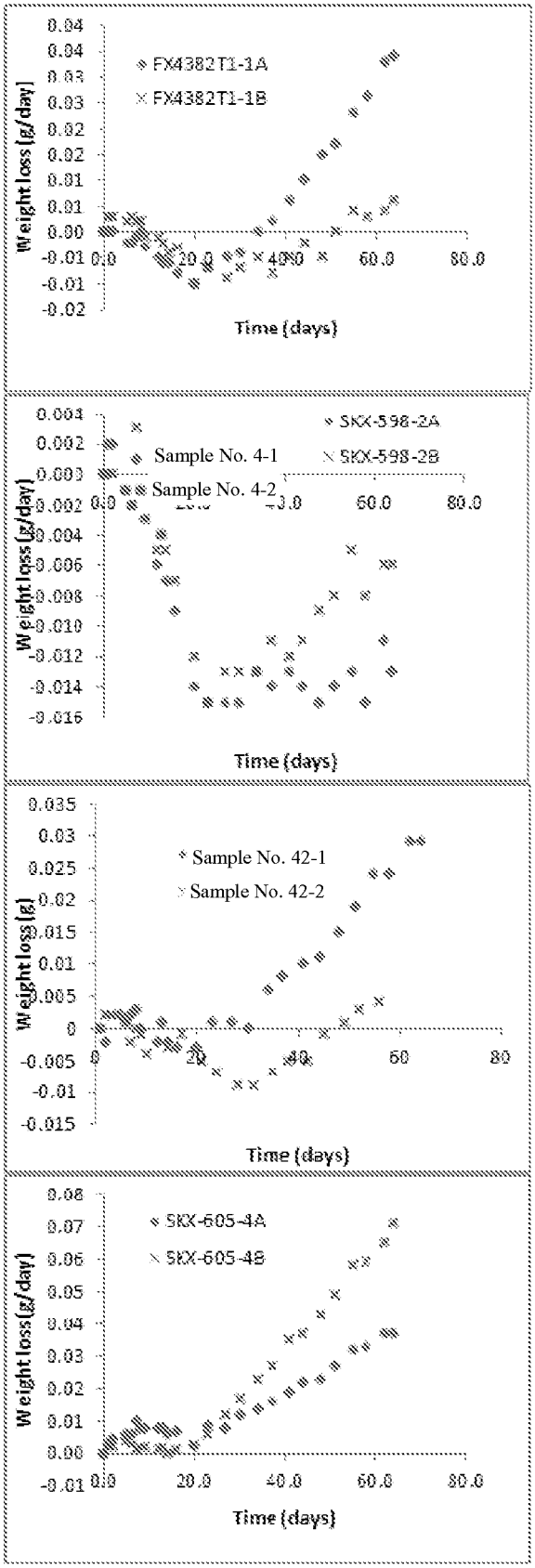
Sample no. 43-2

FIG. 27



Sample No. 41-1
Sample No. 41-2
Sample No. 43-1
Sample No. 43-2

FIG. 28



Sample No. 41-1

Sample No. 41-2

Sample No. 43-1

Sample No. 43-2

FIG. 29