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**Polymeric material with a multimodal pore size distribution**

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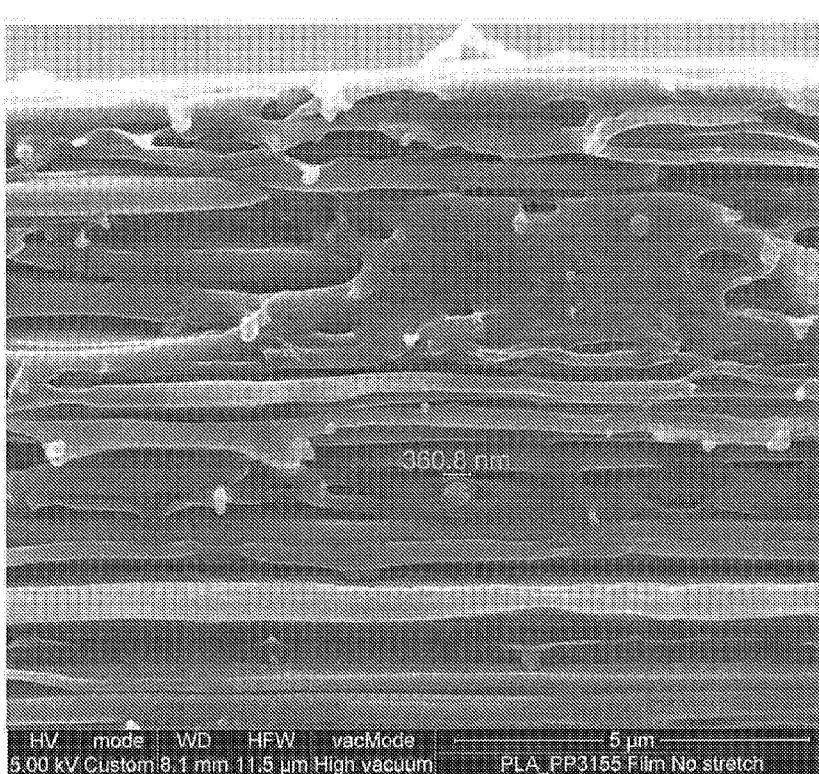
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(54) Title: POLYMERIC MATERIAL WITH A MULTIMODAL PORE SIZE DISTRIBUTION



(57) Abstract: A polymeric material having a multimodal pore size distribution is provided. The material is formed by applying a stress to a thermoplastic composition that contains first and second inclusion additives dispersed within a continuous phase that includes a matrix polymer. Through the use of particular types of inclusion additives and careful control over the manner in which such additives are dispersed within the polymer matrix, the present inventors have discovered that a unique, multimodal porous structure can be achieved.



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## **POLYMERIC MATERIAL WITH A MULTIMODAL PORE SIZE DISTRIBUTION**

### **Related Applications**

The present application claims priority to U.S. provisional applications serial nos. 81/833,983, filed on June 12, 2013, and 61/907,566, filed on November 22, 2013, which are incorporated herein in their entirety by reference thereto.

### **Background of the Invention**

Significant efforts have been made to produce low density polymeric materials to improve the use of natural resources and reduction of the carbon footprint in finished products. A typical approach to producing such low density materials is by foaming the polymer using physical or chemical blowing agents, which create gas-filled pores through the bulk. Chemical blowing agents are compounds that undergo chemical reaction liberating gas that creates the pore structure through the bulk of the polymer. Physical blowing agents are typically compressed gases that are dispersed in the polymer and expand creating the pores. Regardless, typical foaming processes induce low molecular orientation because the pore formation happens when the polymer is in the molten state. This prevents the polymer from strain hardening, which typically occurs at temperatures well above the melting temperature or glass transition temperature of the polymer, yielding products with low mechanical strength. Furthermore, typical foaming processes generate large cell sizes, such as greater than 100  $\mu\text{m}$ . This reduces the melt strength, thus leading to breaks in high speed production processes with high deformation rates (e.g., fiber spinning, film formation, molding, etc.).

As such, a need currently exists for an improved polymeric material that is porous.

### **Summary of the Invention**

In accordance with one embodiment of the present disclosure, a porous polymeric material is disclosed that contains a thermoplastic composition. The thermoplastic composition includes a continuous phase in which a first inclusion additive and second inclusion additive are dispersed in the form of discrete domains, the continuous phase including a matrix polymer. A plurality of micropores are formed at and/or around the first domains that have an average cross-sectional dimension of from about 0.5 to about 30 micrometers, and a plurality of nanopores are

formed at and/or around the second domains that have an average cross-sectional dimension of from about 50 to about 500 nanometers.

According to a first aspect of the present invention there is provided a porous polymeric material that contains a thermoplastic composition, the thermoplastic composition including a continuous phase in which a first inclusion additive and second inclusion additive are dispersed in the form of discrete domains, the continuous phase including a matrix polymer, wherein the first inclusion additive is polymeric and is present in the thermoplastic composition in an amount of from about 1 wt.% to about 20 wt.% and wherein the second inclusion additive is polymeric and is present in the thermoplastic composition in an amount of from about 0.01 wt.% to about 15 wt.%, wherein a plurality of micropores are formed at and/or around the first domains that have an average cross-sectional dimension of from about 0,5 to about 30 micrometers, and wherein a plurality of nanopores are formed at and/or around the second domains that have an average cross-sectional dimension of from about 50 to about 500 nanometers.

According to a second aspect of the present invention there is provided a method for forming the porous polymeric material of the first aspect of the invention, the method comprising drawing the thermoplastic composition while in a solid state to form the porous network.

Other features and aspects of the present invention are discussed in greater detail below.

### **Brief Description of the Drawings**

A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, which makes reference to the appended figures in which:

Figs. 1-2 are SEM microphotographs of the unstretched film of Example 1 (film was cut parallel to machine direction orientation);

Figs. 3-4 are SEM microphotographs of the stretched film of Example 1 (film was cut parallel to machine direction orientation);

Figs. 5-6 are SEM microphotographs of the unstretched film of Example 2, where the film was cut perpendicular to the machine direction in Fig. 5 and parallel to the machine direction in Fig. 8;

Figs. 7-8 are SEM microphotographs of the stretched film of Example 2 (film was cut parallel to machine direction orientation);

Fig. 9 is an SEM photomicrograph of the unstretched injection molded sample of Example 3 (polypropylene, polylactic acid, and polyepoxide) after freeze fracturing in liquid nitrogen;

Fig. 10 is an SEM photomicrograph of the stretched injection molded sample of Example 3 (polypropylene, polylactic acid, and polyepoxide) after freeze fracturing in liquid nitrogen;

Fig. 11 is a stress-strain curve for the stretched sample of Example 3;

Fig. 12 is an SEM photomicrograph (1,000X) of the fiber of Example 4 (polypropylene, polylactic acid, and polyepoxide) after freeze fracturing in liquid nitrogen;

Fig. 13 is an SEM photomicrograph (5,000X) of the fiber of Example 4 (polypropylene, polylactic acid, and polyepoxide) after freeze fracturing in liquid nitrogen; and

Fig. 14 is an SEM photomicrograph (10,000X) of the fiber surface of Example 4 (polypropylene, polylactic acid, and polyepoxide).

Repeat use of references characters in the present specification and drawings is intended to represent same or analogous features or elements of the invention.

#### Detailed Description of Representative Embodiments

5 Reference now will be made in detail to various embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations may be made in the present invention without departing from the scope 10 or spirit of the invention. For instance, features illustrated or described as part of one embodiment, may be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention covers such modifications and variations as come within the scope of the appended claims and their equivalents.

15 Generally speaking, the present invention is directed to a polymeric material having a multimodal pore size distribution. The material is formed by applying a stress to a thermoplastic composition that contains first and second inclusion additives dispersed within a continuous phase that includes a matrix polymer. The first and second inclusion additives are generally selected so that they are partially 20 incompatible (e.g., different modulus of elasticity) with the matrix polymer. In this manner, the inclusion additives can be more readily dispersed within the polymer matrix in the form of discrete domains.

25 The first inclusion additive is typically dispersed within the polymer matrix in the form of discrete first domains of a relatively large size. These first domains may have an average cross-sectional dimension of from about from about 0.05 to about 50 micrometers, in some embodiments from about 0.2 to about 10 micrometers, and in some embodiments, from 0.5 to about 5 micrometers. The term "cross-sectional dimension" generally refers to a characteristic dimension 30 (e.g., width or diameter) of a domain, which is substantially orthogonal to its major axis (e.g., length) and also typically substantially orthogonal to the direction of the stress applied during drawing. The first domains also have an average axial dimension of from about 0.5 to about 250 micrometers, in some embodiments from about 1 to about 100 micrometers, in some embodiments from about 2 to about 50

micrometers, and in some embodiments, from about 5 to about 25 micrometers. The "axial dimension" is the dimension in the direction of the major axis (e.g., length), which is typically in the direction of drawing. This may result in an aspect ratio for the first domains (the ratio of the axial dimension to a dimension orthogonal to the axial dimension) of from about 2 to about 150, in some embodiments from about 3 to about 100, and in some embodiments, from about 4 to about 50. Likewise, the second inclusion additive is typically dispersed within the polymer matrix in the form of second discrete domains, which have a smaller size than the first domains. For example, the second domains may have an average cross-sectional dimension of from about 50 to about 500 nanometers, in some embodiments from about 60 to about 400 nanometers, and in some embodiments from about 80 to about 300 nanometers. Due to their small size, the second domains are not typically elongated in the same manner as the micro-scale domains. For example, the second domains may be substantially spherical in nature. Additional inclusion additives may also be employed that have a size that is the same, larger, or smaller than the first or second domains.

Through the use of particular types of inclusion additives and careful control over the manner in which such additives are dispersed within the polymer matrix, the present inventors have discovered that a unique porous structure can be achieved. Namely, when the composition is subjected to an external applied stress (e.g., mechanical drawing), stress intensification areas can be created at and around the domains, the location of which are dependent upon the particular nature of the additives. When the inclusion additives have a higher modulus than the matrix polymer, for instance, the maximum stress intensification areas are located at the pole of the domains and aligned in the direction of applied stress. Notably, the stress intensification areas created by the first inclusion additive can overlap those created by the second inclusion additive. In this manner, a dramatic increase in local stresses (i.e., stress amplification) can occur at and around the inclusion boundaries, with the smaller inclusion additives located in the stress intensification areas of the first inclusion additive exhibiting the largest stress amplification. The present inventors have discovered that this stress amplification phenomenon can initiate a controlled and cascading process of debonding and pore formation at or around the inclusion additives, beginning with the smaller

second domains exhibiting the largest stress amplification and propagating to the larger first domains as externally applied stress increases. In addition, because the pores are located adjacent to the discrete domains, a bridge can be formed between the boundaries of the pores that act as internal structural hinges to help prevent the pores from collapsing.

The cascading manner in which pore formation is initiated allows for the formation of a porous network with a multimodal distribution. For instance, a plurality of micropores may be formed at and/or around the first domains that have an average cross-sectional dimension (e.g., width or diameter) of from about 0.5 to about 30 micrometers, in some embodiments from about 1 to about 20 micrometers, and in some embodiments, from about 2 micrometers to about 15 micrometers. In addition, a plurality of first nanopores may be formed at and/or around the second domains that have an average cross-sectional dimension (e.g., width or diameter) of from about 50 to about 500 nanometers, in some embodiments from about 60 to about 450 nanometers, and in some embodiments, from about 100 to about 400 nanometers. It should also be understood that pores of different sizes can also be formed at and/or around the inclusion additives. For example, in certain cases, a plurality of second nanopores may also be formed at and/or around the second domains, which have an average cross-sectional dimension of from about 1 to about 50 nanometers, in some embodiments from about 2 to about 45 nanometers, and in some embodiments from about 5 to about 40 nanometers. The micropores and/or nanopores may have any regular or irregular shape, such as spherical, elongated, etc., and may also have an aspect ratio (the ratio of the axial dimension to the cross-sectional dimension) of from about 1 to about 30, in some embodiments from about 1.1 to about 15, and in some embodiments, from about 1.2 to about 5.

The present inventors have also discovered that the pores (e.g., micropores, nanopores, or both) can be distributed in a substantially homogeneous fashion throughout the material. For example, the pores may be distributed in columns that are oriented in a direction generally perpendicular to the direction in which a stress is applied. These columns may be generally parallel to each other across the width of the material. Without intending to be limited by theory, it is believed that the presence of such a homogeneously distributed porous network

can result in a high thermal resistance as well as good mechanical properties (e.g., energy dissipation under load and impact strength). This is in stark contrast to conventional techniques for creating pores that involve the use of blowing agents, which tend to result in an uncontrolled pore distribution and poor mechanical properties. Notably, the formation of the porous network by the process described above does not necessarily result in a substantial change in the cross-sectional size (e.g., width) of the material. In other words, the material is not substantially necked, which may allow the material to retain its initial cross-sectional dimension and a greater degree of strength properties.

The average percent volume occupied by the micropores and nanopores within a given unit volume of the material may be from about 15% to about 80% per  $\text{cm}^3$ , in some embodiments from about 20% to about 70%, and in some embodiments, from about 30% to about 60% per cubic centimeter of the material. In certain cases, nanopores can be present in a relatively high amount. For example, the nanopores may constitute from about 15 vol.% to about 99 vol.%, in some embodiments from about 20 vol.% to 95 vol.%, and in some embodiments, from about 40 vol.% to about 90 vol.% of the total pore volume in the polymeric material. Likewise, the micropores may constitute from about 1 vol.% to about 85 vol.%, in some embodiments from about 5 vol.% to 80 vol.%, and in some embodiments, from about 10 vol.% to about 60 vol.% of the total pore volume in the polymeric material. Of course, additional classes of pores may also be present in the polymeric material. Regardless, with such a high pore volume, the resulting polymeric material may have a relatively low density, such as about 1.2 grams per cubic centimeter ("g/cm<sup>3</sup>") or less, in some embodiments about 1.0 g/cm<sup>3</sup> or less, in some embodiments from about 0.2 g/cm<sup>3</sup> to about 0.8 g/cm<sup>3</sup>, and in some embodiments, from about 0.1 g/cm<sup>3</sup> to about 0.5 g/cm<sup>3</sup>.

Besides a reduced density, the unique multimodal pore structure may also provide a variety of functional benefits to the resulting polymeric material. For example, such a structure can help restrict the flow of fluids through the material and be generally impermeable to fluids (e.g., liquid water), thereby allowing the material to insulate a surface from water penetration. In this regard, the polymeric material may have a relatively high hydrohead value of about 50 centimeters ("cm") or more, in some embodiments about 100 cm or more, in some

embodiments, about 150 cm or more, and in some embodiments, from about 200 cm to about 1000 cm, as determined in accordance with ATTCC 127-2008. Other beneficial properties may also be achieved. For example, the resulting polymeric material may be generally permeable to water vapors. The permeability of the material to water vapor may be characterized by its relatively high water vapor transmission rate ("WVTR"), which is the rate at which water vapor permeates through a material as measured in units of grams per meter squared per 24 hours (g/m<sup>2</sup>/24 hrs). For example, the polymeric material may exhibit a WVTR of about 300 g/m<sup>2</sup>-24 hours or more, in some embodiments about 500 g/m<sup>2</sup>-24 hours or more, in some embodiments about 1,000 g/m<sup>2</sup>-24 hours or more, and in some embodiments, from about 3,000 to about 15,000 g/m<sup>2</sup>-24 hours, such as determined in accordance with ASTM E96/96M-12, Procedure B or INDA Test Procedure IST-70.4 (01). The polymeric material can also act as a thermal barrier that exhibits a relatively low thermal conductivity, such as about 0.40 watts per meter-kelvin ("W/m-K") or less, in some embodiments about 0.20 W/m-K or less, in some embodiments about 0.15 W/m-K or less, in some embodiments from about 0.01 to about 0.12 W/m-K, and in some embodiments, from about 0.02 to about 0.10 W/m-K. Notably, the material is capable of achieving such low thermal conductivity values at relatively low thicknesses, which can allow the material to possess a greater degree of flexibility and conformability, as well as reduce the space it occupies in an article. For this reason, the polymeric material may also exhibit a relatively low "thermal admittance", which is equal to the thermal conductivity of the material divided by its thickness and is provided in units of watts per square meter-kelvins ("W/m<sup>2</sup>K"). For example, the material may exhibit a thermal admittance of about 1000 W/m<sup>2</sup>K or less, in some embodiments from about 10 to about 800 W/m<sup>2</sup>K, in some embodiments from about 20 to about 500 W/m<sup>2</sup>K, and in some embodiments, from about 40 to about 200 W/m<sup>2</sup>K. The actual thickness of the polymeric material may depend on its particular form, but typically ranges from about 5 micrometers to about 100 millimeters, in some embodiments from about 10 micrometers to about 50 millimeters, in some embodiments from about 200 micrometers to about 25 millimeters.

Various embodiments of the present invention will now be described in more detail.

## I. Thermoplastic Composition

### A. Matrix Polymer

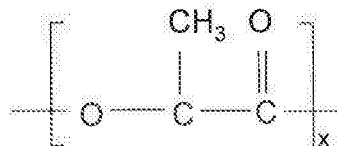
As indicated above, the thermoplastic composition contains a continuous phase within which the first and second inclusion additives are dispersed. The continuous phase contains one or more matrix polymers, which typically constitute from about 60 wt.% to about 99 wt.%, in some embodiments from about 75 wt.% to about 98 wt.%, and in some embodiments, from about 80 wt.% to about 95 wt.% of the thermoplastic composition. The nature of the matrix polymer(s) used to form the continuous phase is not critical and any suitable polymer may generally be employed, such as polyesters, polyolefins, styrenic polymers, polyamides, etc. In certain embodiments, for example, polyesters may be employed in the composition to form the polymer matrix. Any of a variety of polyesters may generally be employed, such as aliphatic polyesters, such as polycaprolactone, polyesteramides, polylactic acid (PLA) and its copolymers, polyglycolic acid, polyalkylene carbonates (e.g., polyethylene carbonate), poly-3-hydroxybutyrate (PHB), poly-3-hydroxyvalerate (PHV), poly-3-hydroxybutyrate-co-4-hydroxybutyrate, poly-3-hydroxybutyrate-co-3-hydroxyvalerate copolymers (PHBV), poly-3-hydroxybutyrate-co-3-hydroxyhexanoate, poly-3-hydroxybutyrate-co-3-hydroxyoctanoate, poly-3-hydroxybutyrate-co-3-hydroxydecanoate, poly-3-hydroxybutyrate-co-3-hydroxyoctadecanoate, and succinate-based aliphatic polymers (e.g., polybutylene succinate, polybutylene succinate adipate, polyethylene succinate, etc.); aliphatic-aromatic copolymers (e.g., polybutylene adipate terephthalate, polyethylene adipate terephthalate, polyethylene adipate isophthalate, polybutylene adipate isophthalate, etc.); aromatic polyesters (e.g., polyethylene terephthalate, polybutylene terephthalate, etc.); and so forth.

In certain cases, the thermoplastic composition may contain at least one polyester that is rigid in nature and thus has a relatively high glass transition temperature. For example, the glass transition temperature ("T<sub>g</sub>") may be about 0°C or more, in some embodiments from about 5°C to about 100°C, in some embodiments from about 30°C to about 80°C, and in some embodiments, from about 50°C to about 75°C. The polyester may also have a melting temperature of from about 140°C to about 300°C, in some embodiments from about 150°C to about 250°C, and in some embodiments, from about 160°C to about 220°C. The

melting temperature may be determined using differential scanning calorimetry ("DSC") in accordance with ASTM D-3417. The glass transition temperature may be determined by dynamic mechanical analysis in accordance with ASTM E1640-09.

5 One particularly suitable rigid polyester is polylactic acid, which may generally be derived from monomer units of any isomer of lactic acid, such as levorotatory-lactic acid ("L-lactic acid"), dextrorotatory-lactic acid ("D-lactic acid"), meso-lactic acid, or mixtures thereof. Monomer units may also be formed from anhydrides of any isomer of lactic acid, including L-lactide, D-lactide, meso-lactide, or mixtures thereof. Cyclic dimers of such lactic acids and/or lactides may also be employed. Any known polymerization method, such as polycondensation or ring-opening polymerization, may be used to polymerize lactic acid. A small amount of 10 a chain-extending agent (e.g., a diisocyanate compound, an epoxy compound or an acid anhydride) may also be employed. The polylactic acid may be a homopolymer or a copolymer, such as one that contains monomer units derived 15 from L-lactic acid and monomer units derived from D-lactic acid. Although not required, the rate of content of one of the monomer unit derived from L-lactic acid and the monomer unit derived from D-lactic acid is preferably about 85 mole% or more, in some embodiments about 90 mole% or more, and in some embodiments, 20 about 95 mole% or more. Multiple polylactic acids, each having a different ratio between the monomer unit derived from L-lactic acid and the monomer unit derived from D-lactic acid, may be blended at an arbitrary percentage. Of course, polylactic acid may also be blended with other types of polymers (e.g., polyolefins, 25 polyesters, etc.).

25 In one particular embodiment, the polylactic acid has the following general structure:



One specific example of a suitable polylactic acid polymer that may be used in the present invention is commercially available from Biomer, Inc. of Krailling, 30 Germany) under the name BIOMER™ L9000. Other suitable polylactic acid

polymers are commercially available from Natureworks LLC of Minnetonka, Minnesota (NATUREWORKS®) or Mitsui Chemical (LACEA™). Still other suitable polylactic acids may be described in U.S. Patent Nos. 4,797,468; 5,470,944; 5,770,682; 5,821,327; 5,880,254; and 6,326,458.

5 The polylactic acid typically has a number average molecular weight ("M<sub>n</sub>") ranging from about 40,000 to about 180,000 grams per mole, in some embodiments from about 50,000 to about 160,000 grams per mole, and in some embodiments, from about 80,000 to about 120,000 grams per mole. Likewise, the polymer also typically has a weight average molecular weight ("M<sub>w</sub>") ranging from about 80,000 to about 250,000 grams per mole, in some embodiments from about 100,000 to about 200,000 grams per mole, and in some embodiments, from about 110,000 to about 160,000 grams per mole. The ratio of the weight average molecular weight to the number average molecular weight ("M<sub>w</sub>/M<sub>n</sub>"), i.e., the "polydispersity index", is also relatively low. For example, the polydispersity index typically ranges from about 1.0 to about 3.0, in some embodiments from about 1.1 to about 2.0, and in some embodiments, from about 1.2 to about 1.8. The weight and number average molecular weights may be determined by methods known to those skilled in the art.

20 The polylactic acid may also have an apparent viscosity of from about 50 to about 600 Pascal seconds (Pa·s), in some embodiments from about 100 to about 500 Pa·s, and in some embodiments, from about 200 to about 400 Pa·s, as determined at a temperature of 190°C and a shear rate of 1000 sec<sup>-1</sup>. The melt flow rate of the polylactic acid (on a dry basis) may also range from about 0.1 to about 40 grams per 10 minutes, in some embodiments from about 0.5 to about 20 grams per 10 minutes, and in some embodiments, from about 5 to about 15 grams per 10 minutes, determined at a load of 2160 grams and at 190°C.

25 Some types of neat polyesters (e.g., polylactic acid) can absorb water from the ambient environment such that it has a moisture content of about 500 to 600 parts per million ("ppm"), or even greater, based on the dry weight of the starting polylactic acid. Moisture content may be determined in a variety of ways as is known in the art, such as in accordance with ASTM D 7191-05, such as described below. Because the presence of water during melt processing can hydrolytically degrade the polyester and reduce its molecular weight, it is sometimes desired to

dry the polyester prior to blending. In most embodiments, for example, it is desired that the polyester have a moisture content of about 300 parts per million ("ppm") or less, in some embodiments about 200 ppm or less, in some embodiments from about 1 to about 100 ppm prior to blending with the first and second inclusion additives. Drying of the polyester may occur, for instance, at a temperature of from about 50°C to about 100°C, and in some embodiments, from about 70°C to about 80°C.

5           B.     First Inclusion Additive

The particular nature of the first inclusion additive is not critical, and may include liquids, semi-solids, or solids (e.g., amorphous, crystalline, or semi-crystalline). In certain embodiments, the first inclusion additive is polymeric in nature and possesses a relatively high molecular weight to help improve the melt strength and stability of the thermoplastic composition. Typically, the first inclusion additive polymer may be generally incompatible with the matrix polymer. In this manner, the additive can better become dispersed as discrete phase domains within a continuous phase of the matrix polymer. The domains may have a variety of different shapes, such as elliptical, spherical, cylindrical, plate-like, tubular, etc. In one embodiment, for example, the domains have a substantially elliptical shape. The physical dimension of an individual domain is typically small enough to minimize the propagation of cracks through the polymeric material upon the application of an external stress, but large enough to initiate microscopic plastic deformation and allow for shear and/or stress intensity zones at and around particle inclusions.

20           While the polymers may be incompatible, the first inclusion additive may nevertheless be selected to have a solubility parameter that is relatively similar to that of the matrix polymer. This can improve the interfacial compatibility and physical interaction of the boundaries of the discrete and continuous phases, and thus reduces the likelihood that the composition will fracture. In this regard, the ratio of the solubility parameter for the matrix polymer to that of the additive is typically from about 0.5 to about 1.5, and in some embodiments, from about 0.8 to about 1.2. For example, the first inclusion additive may have a solubility parameter of from about 15 to about 30 MJoules<sup>1/2</sup>/m<sup>3/2</sup>, and in some embodiments, from about 18 to about 22 MJoules<sup>1/2</sup>/m<sup>3/2</sup>, while polylactic acid may have a solubility

parameter of about 20.5 MJoules<sup>1/2</sup>/m<sup>3/2</sup>. The term "solubility parameter" as used herein refers to the "Hildebrand Solubility Parameter", which is the square root of the cohesive energy density and calculated according to the following equation:

$$\delta = \sqrt{(\Delta H_v - RT)/V_m}$$

5

where:

$\Delta H_v$  = heat of vaporization

$R$  = Ideal Gas constant

$T$  = Temperature

$V_m$  = Molecular Volume

10

The Hildebrand solubility parameters for many polymers are also available from the Solubility Handbook of Plastics, by Wyeych (2004), which is incorporated herein by reference.

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The first inclusion additive may also have a certain melt flow rate (or viscosity) to ensure that the discrete domains and resulting pores can be adequately maintained. For example, if the melt flow rate of the additive is too high, it tends to flow and disperse uncontrollably through the continuous phase. This results in lamellar, plate-like domains or co-continuous phase structures that are difficult to maintain and also likely to prematurely fracture. Conversely, if the melt flow rate of the additive is too low, it tends to clump together and form very large elliptical domains, which are difficult to disperse during blending. This may cause uneven distribution of the additive through the entirety of the continuous phase. In this regard, the present inventors have discovered that the ratio of the melt flow rate of the first inclusion additive to the melt flow rate of the matrix polymer is typically from about 0.2 to about 8, in some embodiments from about 0.5 to about 6, and in some embodiments, from about 1 to about 5. The first inclusion additive may, for example, have a melt flow rate of from about 0.1 to about 250 grams per 10 minutes, in some embodiments from about 0.5 to about 200 grams per 10 minutes, and in some embodiments, from about 5 to about 150 grams per 10 minutes, determined at a load of 2160 grams and at 190°C.

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In addition to the properties noted above, the mechanical characteristics of the first inclusion additive may also be selected to achieve the desired porous network. For example, when a blend of the matrix polymer and first inclusion

additive is applied with an external force, stress concentrations (e.g., including normal or shear stresses) and shear and/or plastic yielding zones may be initiated at and around the discrete phase domains as a result of stress concentrations that arise from a difference in the elastic modulus of the additive and matrix polymer.

5 Larger stress concentrations promote more intensive localized plastic flow at the domains, which allows them to become significantly elongated when stresses are imparted. These elongated domains can allow the composition to exhibit a more pliable and softer behavior than the matrix polymer, such as when it is a rigid polyester resin. To enhance the stress concentrations, the first inclusion additive 10 may be selected to have a relatively low Young's modulus of elasticity in comparison to the matrix polymer. For example, the ratio of the modulus of elasticity of the matrix polymer to that of the additive is typically from about 1 to about 250, in some embodiments from about 2 to about 100, and in some 15 embodiments, from about 2 to about 50. The modulus of elasticity of the first inclusion additive may, for instance, range from about 2 to about 1000 Megapascals (MPa), in some embodiments from about 5 to about 500 MPa, and in some embodiments, from about 10 to about 200 MPa. To the contrary, the modulus of elasticity of polylactic acid, for example, is typically from about 800 MPa to about 3000 MPa.

20 While a wide variety of first inclusion additives may be employed that have the properties identified above, particularly suitable examples of such additives may include synthetic polymers, such as polyolefins (e.g., polyethylene, polypropylene, polybutylene, etc.); styrenic copolymers (e.g., styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene-propylene-styrene, styrene-ethylene-butadiene-styrene, etc.); polytetrafluoroethylenes; polyesters (e.g., recycled polyester, polyethylene terephthalate, etc.); polyvinyl acetates (e.g., poly(ethylene vinyl acetate), polyvinyl chloride acetate, etc.); polyvinyl alcohols (e.g., polyvinyl alcohol, poly(ethylene vinyl alcohol), etc.); polyvinyl butyrals; acrylic 25 resins (e.g., polyacrylate, polymethylacrylate, polymethylmethacrylate, etc.); polyamides (e.g., nylon); polyvinyl chlorides; polyvinylidene chlorides; polystyrenes; polyurethanes; etc. Suitable polyolefins may, for instance, include ethylene polymers (e.g., low density polyethylene ("LDPE"), high density polyethylene ("HDPE"), linear low density polyethylene ("LLDPE"), etc.), propylene 30

homopolymers (e.g., syndiotactic, atactic, isotactic, etc.), propylene copolymers, and so forth.

In one particular embodiment, the polymer is a propylene polymer, such as homopolypropylene or a copolymer of propylene. The propylene polymer may, for instance, be formed from a substantially isotactic polypropylene homopolymer or a copolymer containing equal to or less than about 10 wt.% of other monomer, i.e., at least about 90% by weight propylene. Such homopolymers may have a melting point of from about 160°C to about 170°C.

In still another embodiment, the polyolefin may be a copolymer of ethylene or propylene with another  $\alpha$ -olefin, such as a C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefin or C<sub>3</sub>-C<sub>12</sub>  $\alpha$ -olefin. Specific examples of suitable  $\alpha$ -olefins include 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. Particularly desired  $\alpha$ -olefin comonomers are 1-butene, 1-hexene and 1-octene. The ethylene or propylene content of such copolymers may be from about 60 mole% to about 99 mole%, in some embodiments from about 80 mole% to about 98.5 mole%, and in some embodiments, from about 87 mole% to about 97.5 mole%. The  $\alpha$ -olefin content may likewise range from about 1 mole% to about 40 mole%, in some embodiments from about 1.5 mole% to about 15 mole%, and in some embodiments, from about 2.5 mole% to about 13 mole%.

Exemplary olefin copolymers for use in the present invention include ethylene-based copolymers available under the designation EXACT™ from ExxonMobil Chemical Company of Houston, Texas. Other suitable ethylene copolymers are available under the designation ENGAGE™, AFFINITY™, DOWLEX™ (LLDPE) and ATTANE™ (ULDPE) from Dow Chemical Company of Midland, Michigan. Other suitable ethylene polymers are described in U.S. Patent Nos. 4,937,299 to Ewen et al.; 5,218,071 to Tsutsui et al.; 5,272,236 to Lai, et al.; and 5,278,272 to Lai, et al. Suitable propylene copolymers are also commercially available under the designations VISTAMAXX™ from ExxonMobil Chemical Co. of Houston, Texas; FINA™ (e.g., 8573) from Atofina Chemicals of Feluy, Belgium;

TAFMER™ available from Mitsui Petrochemical Industries; and VERSIFY™ available from Dow Chemical Co. of Midland, Michigan. Suitable polypropylene homopolymers may likewise include Exxon Mobil 3155 polypropylene, Exxon Mobil Achieve™ resins, and Total M3661 PP resin. Other examples of suitable propylene polymers are described in U.S. Patent Nos. 6,500,563 to Datta, et al.; 5,539,056 to Yang, et al.; and 5,596,052 to Resconi, et al.

Any of a variety of known techniques may generally be employed to form the olefin copolymers. For instance, olefin polymers may be formed using a free radical or a coordination catalyst (e.g., Ziegler-Natta). Preferably, the olefin polymer is formed from a single-site coordination catalyst, such as a metallocene catalyst. Such a catalyst system produces ethylene copolymers in which the comonomer is randomly distributed within a molecular chain and uniformly distributed across the different molecular weight fractions. Metallocene-catalyzed polyolefins are described, for instance, in U.S. Patent Nos. 5,571,619 to McAlpin et al.; 5,322,728 to Davis et al.; 5,472,775 to Obijeski et al.; 5,272,236 to Lai et al.; and 6,090,325 to Wheat, et al. Examples of metallocene catalysts include bis(n-butylcyclopentadienyl)titanium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)scandium chloride, bis(indenyl)zirconium dichloride, bis(methylcyclopentadienyl)titanium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, cobaltocene, cyclopentadienyltitanium trichloride, ferrocene, hafnocene dichloride, isopropyl(cyclopentadienyl,-1-flourenyl)zirconium dichloride, molybdocene dichloride, nickelocene, niobocene dichloride, ruthenocene, titanocene dichloride, zirconocene chloride hydride, zirconocene dichloride, and so forth. Polymers made using metallocene catalysts typically have a narrow molecular weight range. For instance, metallocene-catalyzed polymers may have polydispersity numbers ( $M_w/M_n$ ) of below 4, controlled short chain branching distribution, and controlled isotacticity.

Regardless of the materials employed, the relative percentage of the first inclusion additive in the thermoplastic composition is selected to achieve the desired properties without significantly impacting the base properties of the composition. For example, the first inclusion additive is typically employed in an amount of from about 1 wt.% to about 30 wt.%, in some embodiments from about

2 wt.% to about 25 wt.%, and in some embodiments, from about 5 wt.% to about 20 wt.% of the thermoplastic composition, based on the weight of the continuous phase (matrix polymer(s)). The concentration of the first inclusion additive in the entire thermoplastic composition may likewise constitute from about 0.1 wt.% to about 30 wt.%, in some embodiments from about 0.5 wt.% to about 25 wt.%, and in some embodiments, from about 1 wt.% to about 20 wt.%.

5 **C. Second Inclusion Additive**

The second inclusion additive is typically employed in an amount of from about 0.05 wt.% to about 20 wt.%, in some embodiments from about 0.1 wt.% to about 10 wt.%, and in some embodiments, from about 0.5 wt.% to about 5 wt.% of the thermoplastic composition, based on the weight of the continuous phase (matrix polymer(s)). The concentration of the second inclusion additive in the entire thermoplastic composition may likewise be from about 0.01 wt.% to about 15 wt.%, in some embodiments from about 0.05 wt.% to about 10 wt.%, and in some embodiments, from about 0.1 wt.% to about 8 wt.% of the thermoplastic composition.

10 The particular state or form of the second inclusion additive is not critical so long as the desired domains can be formed. For example, in some embodiments, the second inclusion additive can be in the form of a liquid or semi-solid at room temperature (e.g., 25°C). Such a liquid can be readily dispersed in the matrix to form a metastable dispersion, and then quenched to preserve the domain size by reducing the temperature of the blend. In yet other embodiments, the second inclusion additive is in the form of a solid, which may be amorphous, crystalline, or semi-crystalline. For example, the second inclusion additive may be polymeric in nature and possess a relatively high molecular weight to help improve the melt 15 strength and stability of the thermoplastic composition.

20 To enhance its ability to become dispersed into nano-scale domains, the second inclusion additive may contain a polar component that is compatible with a portion of the matrix polymer and/or the first inclusion additive. This may be particularly useful when the matrix polymer or the first inclusion additive possesses 25 a polar moiety, such as a polyester. One example such a second inclusion additive is a functionalized polyolefin. The polar component may, for example, be provided by one or more functional groups and the non-polar component may be

provided by an olefin. The olefin component of the second inclusion additive may generally be formed from any linear or branched  $\alpha$ -olefin monomer, oligomer, or polymer (including copolymers) derived from an olefin monomer, such as described above.

5 The functional group of the second inclusion additive may be any group, molecular segment and/or block that provides a polar component to the molecule and is not compatible with the matrix polymer. Examples of molecular segment and/or blocks not compatible with polyolefin may include acrylates, styrenics, polyesters, polyamides, etc. The functional group can have an ionic nature and comprise charged metal ions. Particularly suitable functional groups are maleic anhydride, maleic acid, fumaric acid, maleimide, maleic acid hydrazide, a reaction product of maleic anhydride and diamine, methylnadic anhydride, dichloromaleic anhydride, maleic acid amide, etc. Maleic anhydride modified polyolefins are particularly suitable for use in the present invention. Such modified polyolefins are typically formed by grafting maleic anhydride onto a polymeric backbone material. Such maleated polyolefins are available from E. I. du Pont de Nemours and Company under the designation Fusabond®, such as the P Series (chemically modified polypropylene), E Series (chemically modified polyethylene), C Series (chemically modified ethylene vinyl acetate), A Series (chemically modified

10 ethylene acrylate copolymers or terpolymers), or N Series (chemically modified ethylene-propylene, ethylene-propylene diene monomer ("EPDM") or ethylene-octene). Alternatively, maleated polyolefins are also available from Chemtura Corp. under the designation Polybond® and Eastman Chemical Company under the designation Eastman G series.

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20 In certain embodiments, the second inclusion additive may also be reactive. One example of such a reactive second inclusion additive is a polyepoxide that contains, on average, at least two oxirane rings per molecule. Without intending to be limited by theory, it is believed that such polyepoxide molecules can induce reaction of the matrix polymer (e.g., polyester) under certain conditions, thereby improving its melt strength without significantly reducing glass transition temperature. The reaction may involve chain extension, side chain branching, grafting, copolymer formation, etc. Chain extension, for instance, may occur through a variety of different reaction pathways. For instance, the modifier may

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enable a nucleophilic ring-opening reaction via a carboxyl terminal group of a polyester (esterification) or via a hydroxyl group (etherification). Oxazoline side reactions may likewise occur to form esteramide moieties. Through such reactions, the molecular weight of the matrix polymer may be increased to counteract the degradation often observed during melt processing. While it may be desirable to induce a reaction with the matrix polymer as described above, the present inventors have discovered that too much of a reaction can lead to crosslinking between polymer backbones. If such crosslinking is allowed to proceed to a significant extent, the resulting polymer blend can become brittle and difficult to process into a material with the desired strength and elongation properties.

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In this regard, the present inventors have discovered that polyepoxides having a relatively low epoxy functionality are particularly effective, which may be quantified by its "epoxy equivalent weight." The epoxy equivalent weight reflects the amount of resin that contains one molecule of an epoxy group, and it may be calculated by dividing the number average molecular weight of the modifier by the number of epoxy groups in the molecule. The polyepoxide of the present invention typically has 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. The polyepoxide may contain less than 50, in some embodiments from 5 to 45, and in some embodiments, from 15 to 40 epoxy groups. In turn, the epoxy equivalent weight may be less than about 15,000 grams per mole, in some embodiments from about 200 to about 10,000 grams per mole, and in some embodiments, from about 500 to about 7,000 grams per mole.

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The polyepoxide may be a linear or branched, homopolymer or copolymer (e.g., random, graft, block, etc.) containing terminal epoxy groups, skeletal oxirane units, and/or pendent epoxy groups. The monomers employed to form such polyepoxides may vary. In one particular embodiment, for example, the polyepoxide contains at least one epoxy-functional (meth)acrylic monomeric component. As used herein, the term "(meth)acrylic" includes acrylic and methacrylic monomers, as well as salts or esters thereof, such as acrylate and

methacrylate monomers. For example, suitable epoxy-functional (meth)acrylic monomers 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.

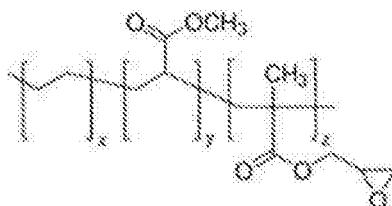
The polyepoxide typically has a relatively high molecular weight, as indicated above, so that it may not only result in chain extension, but also help to achieve the desired blend morphology. The resulting melt flow rate of the polymer is thus typically within a range of from about 10 to about 200 grams per 10 minutes, in some embodiments from about 40 to about 150 grams per 10 minutes, and in some embodiments, from about 60 to about 120 grams per 10 minutes, determined at a load of 2160 grams and at a temperature of 190°C.

If desired, additional monomers may also be employed in the polyepoxide to help achieve the desired molecular weight. Such monomers may vary and include, for example, ester monomers, (meth)acrylic monomers, olefin monomers, amide monomers, etc. In one particular embodiment, for example, the polyepoxide includes at least one linear or branched  $\alpha$ -olefin monomer, such as those having from 2 to 20 carbon atoms and preferably 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. Particularly desired  $\alpha$ -olefin comonomers are ethylene and propylene.

Another suitable monomer may include a (meth)acrylic monomer that is not epoxy-functional. Examples of such (meth)acrylic monomers may include methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, s-butyl acrylate, i-butyl acrylate, t-butyl acrylate, n-amyl acrylate, i-amyl acrylate, isobornyl acrylate, n-hexyl acrylate, 2-ethylbutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, methylcyclohexyl acrylate, cyclopentyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, 2-hydroxyethyl

methacrylate, n-propyl methacrylate, n-butyl methacrylate, i-propyl methacrylate, i-butyl methacrylate, n-amyl methacrylate, n-hexyl methacrylate, i-amyl methacrylate, s-butyl-methacrylate, t-butyl methacrylate, 2-ethylbutyl methacrylate, methylcyclohexyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, isobornyl methacrylate, etc., as well as combinations thereof.

In one particularly desirable embodiment of the present invention, the polyepoxide is a terpolymer formed from an epoxy-functional (meth)acrylic monomeric component,  $\alpha$ -olefin monomeric component, and non-epoxy functional (meth)acrylic monomeric component. For example, the polyepoxide may be poly(ethylene-co-methylacrylate-co-glycidyl methacrylate), which has the following structure:



wherein, x, y, and z are 1 or greater.

The epoxy functional monomer may be formed into a polymer using a variety of known techniques. For example, a monomer containing polar functional groups may be grafted onto a polymer backbone to form a graft copolymer. Such grafting techniques are well known in the art and described, for instance, in U.S. Patent No. 5,179,164. In other embodiments, a monomer containing epoxy 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.

The relative portion of the monomeric component(s) may be selected to achieve a balance between epoxy-reactivity and melt flow rate. More particularly, high epoxy monomer contents can result in good reactivity with the matrix polymer, but too high of a content may reduce the melt flow rate to such an extent that the polyepoxide adversely impacts the melt strength of the polymer blend. Thus, in most embodiments, the epoxy-functional (meth)acrylic monomer(s) constitute from about 1 wt.% to about 25 wt.%, in some embodiments from about 2 wt.% to about

20 wt.%, and in some embodiments, from about 4 wt.% to about 15 wt.% of the copolymer. The  $\alpha$ -olefin monomer(s) may likewise constitute from about 55 wt.% to about 95 wt.%, in some embodiments from about 60 wt.% to about 90 wt.%, and in some embodiments, from about 65 wt.% to about 85 wt.% of the copolymer.

5 When employed, other monomeric components (e.g., non-epoxy functional (meth)acrylic monomers) may constitute from about 5 wt.% to about 35 wt.%, in some embodiments from about 8 wt.% to about 30 wt.%, and in some embodiments, from about 10 wt.% to about 25 wt.% of the copolymer. One specific example of a suitable polyepoxide that may be used in the present 10 invention is commercially available from Arkema under the name LOTADER® AX8950 or AX8900. LOTADER® AX8950, for instance, has a melt flow rate of 70 to 100 g/10 min and has a glycidyl methacrylate monomer content of 7 wt.% to 11 wt.%, a methyl acrylate monomer content of 13 wt.% to 17 wt.%, and an ethylene monomer content of 72 wt.% to 80 wt.%. Another suitable polyepoxide is 15 commercially available from DuPont under the name ELVALOY® PTW, which is a terpolymer of ethylene, butyl acrylate, and glycidyl methacrylate and has a melt flow rate of 12 g/10 min.

In addition to controlling the type and relative content of the monomers used 20 to form the polyepoxide, the overall weight percentage may also be controlled to achieve the desired benefits. For example, if the modification level is too low, the desired increase in melt strength and mechanical properties may not be achieved. The present inventors have also discovered, however, that if the modification level is too high, processing may be restricted due to strong molecular interactions (e.g., crosslinking) and physical network formation by the epoxy functional groups. 25 Thus, the polyepoxide is typically employed in an amount of from about 0.05 wt.% to about 10 wt.%, in some embodiments from about 0.1 wt.% to about 8 wt.%, in some embodiments from about 0.5 wt.% to about 5 wt.%, and in some embodiments, from about 1 wt.% to about 3 wt.%, based on the weight of the matrix polymer employed in the composition. The polyepoxide may also constitute 30 from about 0.05 wt.% to about 10 wt.%, in some embodiments from about 0.05 wt.% to about 8 wt.%, in some embodiments from about 0.1 wt.% to about 5 wt.%, and in some embodiments, from about 0.5 wt.% to about 3 wt.%, based on the total weight of the composition.

Other reactive second inclusion additives may also be employed in the present invention, such as oxazoline-functionalized polymers, cyanide-functionalized polymers, etc. When employed, such reactive second inclusion additives may be employed within the concentrations noted above for the polyepoxide. In one particular embodiment, an oxazoline-grafted polyolefin may be employed that is a polyolefin grafted with an oxazoline ring-containing monomer. The oxazoline may include a 2-oxazoline, such as 2-vinyl-2-oxazoline (e.g., 2-isopropenyl-2-oxazoline), 2-fatty-alkyl-2-oxazoline (e.g., obtainable from the ethanolamide of oleic acid, linoleic acid, palmitoleic acid, gadoleic acid, erucic acid and/or arachidonic acid) and combinations thereof. In another embodiment, the oxazoline may be selected from ricinoloxazoline maleinate, undecyl-2-oxazoline, soya-2-oxazoline, ricinus-2-oxazoline and combinations thereof, for example. In yet another embodiment, the oxazoline is selected from 2-isopropenyl-2-oxazoline, 2-isopropenyl-4,4-dimethyl-2-oxazoline and combinations thereof.

#### D. Other Inclusion Additives

As indicated above, the pores of the present invention can be formed through a cascading process of debondings created by differently sized inclusion additives. In this regard, it may be desired to employ additional inclusion additives to even further facilitate this debonding process. In one particular embodiment, for instance, a third inclusion additive may be dispersed within the polymer matrix in the form of discrete third domains. These third domains may be even smaller than the second domains and, for instance, have an average cross-sectional dimension of from about 1 to about 50 nanometers, in some embodiments from about 2 to about 45 nanometers, and in some embodiments from about 5 to about 40 nanometers. A plurality of nanopores may also be formed at and/or around the third domains that have a dimension in the cross-sectional dimension of from about 1 to about 50 nanometers, in some embodiments from about 2 to about 45 nanometers, and in some embodiments from about 5 to about 40 nanometers. The nanopores may have any regular or irregular shape, such as spherical, elongated, etc. The nanopores can be distributed in a substantially homogeneous fashion throughout the material. For example, the nanopores may be distributed in columns that are oriented in a direction generally perpendicular to the direction in

which a stress is applied. These columns may be generally parallel to each other across the width of the material.

The material used for the third inclusion additive is not particular critical. In certain embodiments, for example, nanofillers may be employed, such as carbon black, carbon nanotubes, carbon nanofibers, nanoclays, metal nanoparticles, nanosilica, nanoalumina, etc. Nanoclays are particularly suitable for the third inclusion additive. The term "nanoclay" generally refers to nanoparticles of a clay material (a naturally occurring mineral, an organically modified mineral, or a synthetic nanomaterial), which typically have a platelet structure. Examples of nanoclays include, for instance, montmorillonite (2:1 layered smectite clay structure), bentonite (aluminium phyllosilicate formed primarily of montmorillonite), kaolinite (1:1 aluminosilicate having a platy structure and empirical formula of  $Al_2Si_2O_5(OH)_4$ ), halloysite (1:1 aluminosilicate having a tubular structure and empirical formula of  $Al_2Si_2O_5(OH)_4$ ), etc. An example of a suitable nanoclay is Cloisite®, which is a montmorillonite nanoclay and commercially available from Southern Clay Products, Inc. Other examples of synthetic nanoclays include but are not limited to a mixed-metal hydroxide nanoclay, layered double hydroxide nanoclay (e.g., sepiocite), laponite, hectorite, saponite, indonite, etc. If desired, the nanoclay may contain a surface treatment to help improve compatibility with the matrix polymer (e.g., polyester). The surface treatment may be organic or inorganic. In one embodiment, an organic surface treatment is employed that is obtained by reacting an organic cation with the clay. Suitable organic cations may include, for instance, organoquaternary ammonium compounds that are capable of exchanging cations with the clay, such as dimethyl bis[hydrogenated tallow] ammonium chloride (2M2HT), methyl benzyl bis[hydrogenated tallow] ammonium chloride (MB2HT), methyl tris[hydrogenated tallow alkyl] chloride (M3HT), etc. Examples of commercially available organic nanoclays may include, for instance, Dellite® 43B (Laviosa Chimica of Livorno, Italy), which is a montmorillonite clay modified with dimethyl benzylhydrogenated tallow ammonium salt. Other examples include Cloisite® 25A and Cloisite® 30B (Southern Clay Products) and Nanofil 919 (Süd Chemie).

When employed, the third inclusion additive typically constitutes from about 0.05 wt.% to about 20 wt.%, in some embodiments from about 0.1 wt.% to about

10 wt.%, and in some embodiments, from about 0.5 wt.% to about 5 wt.% of the thermoplastic composition, based on the weight of the continuous phase (matrix polymer(s)). The concentration of the third inclusion additive in the entire thermoplastic composition may likewise be from about 0.01 wt.% to about 15 wt.%, in some embodiments from about 0.05 wt.% to about 10 wt.%, and in some embodiments, from about 0.1 wt.% to about 8 wt.% of the thermoplastic composition.

If desired, the third inclusion additive (e.g., nanoclay) can be blended with a carrier resin to form a masterbatch that enhances the compatibility of the additive with the other polymers in the composition. Particularly suitable carrier resins include, for instance, polyesters (e.g., polylactic acid, polyethylene terephthalate, etc.); polyolefins (e.g., ethylene polymers, propylene polymers, etc.); and so forth, as described in more detail above. In some cases, the carrier resin can become dispersed in the form of domains of a micro-scale size, such as an average cross-sectional dimension of from about 0.5 to about 30 micrometers, in some embodiments from about 1 to about 20 micrometers, and in some embodiments, from about 2 micrometers to about 15 micrometers. Nevertheless, at least a portion of the third inclusion additive can migrate from the internal regions to form discrete domains of a nano-scale size, such as an average cross-sectional dimension of from about 1 to about 50 nanometers, in some embodiments from about 2 to about 45 nanometers, and in some embodiments from about 5 to about 40 nanometers. In this manner, the carrier resin can result in the formation of a plurality of micropores, such as within the size ranges noted above, while the migrated inclusion additive can result in the formation of a plurality of nanopores, such as within the size ranges noted above. For this reason, the polymer used to form the masterbatch for the third inclusion additive may, if so desired, simultaneously serve as both as the first inclusion additive and as a carrier resin for the third inclusion additive. Of course, it should be understood that this is by no means required, and that a separate carrier resin and first inclusion additive may be employed.

#### E. Other Components

A wide variety of ingredients may be employed in the composition for a variety of different reasons. For instance, in one particular embodiment, an

interphase modifier may be employed in the thermoplastic composition to help reduce the degree of friction and connectivity between the inclusion additive(s) and matrix polymer, and thus enhance the degree and uniformity of debonding. In this manner, the pores can become distributed in a more homogeneous fashion throughout the composition. The modifier may be in a liquid or semi-solid form at room temperature (e.g., 25°C) so that it possesses a relatively low viscosity, allowing it to be more readily incorporated into the thermoplastic composition and to easily migrate to the polymer surfaces. In this regard, the kinematic viscosity of the interphase modifier is typically from about 0.7 to about 200 centistokes ("cs"), in some embodiments from about 1 to about 100 cs, and in some embodiments, from about 1.5 to about 80 cs, determined at 40°C. In addition, the interphase modifier is also typically hydrophobic so that it has an affinity for the first inclusion additive, for example, resulting in a change in the interfacial tension between the matrix polymer and the additive. By reducing physical forces at the interfaces between the matrix polymer and the inclusion additives, it is believed that the low viscosity, hydrophobic nature of the modifier can help facilitate debonding. As used herein, the term "hydrophobic" typically refers to a material having a contact angle of water in air of about 40° or more, and in some cases, about 60° or more. In contrast, the term "hydrophilic" typically refers to a material having a contact angle of water in air of less than about 40°. One suitable test for measuring the contact angle is ASTM D5725-99 (2008).

Suitable hydrophobic, low viscosity interphase modifiers may include, for instance, silicones, silicone-polyether copolymers, aliphatic polyesters, aromatic polyesters, alkylene glycols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, polybutylene glycol, etc.), alkane diols (e.g., 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pantanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6 hexanediol, 1,3-cyclohexanediethanol, 1,4-cyclohexanediethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, etc.), amine oxides (e.g., octyldimethylamine oxide), fatty acid esters, fatty acid amides (e.g., oleamide, erucamide, stearamide, ethylene bis(stearamide), , etc.), mineral, and vegetable oils, and so forth. One particularly suitable liquid or semi-solid is polyether polyol, such as commercially available under the trade name Pluriol® WI

from BASF Corp. Another suitable modifier is a partially renewable ester, such as commercially available under the trade name HALLGREEN® IM from Hallstar.

When employed, the interphase modifier may constitute from about 0.1 wt.% to about 20 wt.%, in some embodiments from about 0.5 wt.% to about 15 wt.%, and in some embodiments, from about 1 wt.% to about 10 wt.% of the thermoplastic composition, based on the weight of the continuous phase (matrix polymer(s)). The concentration of the interphase modifier in the entire thermoplastic composition may likewise constitute from about 0.05 wt.% to about 20 wt.%, in some embodiments from about 0.1 wt.% to about 15 wt.%, and in some embodiments, from about 0.5 wt.% to about 10 wt.%.

The interphase modifier has a character that enables it to readily migrate to the interfacial surface of the polymers and facilitate debonding without disrupting the overall melt properties of the thermoplastic composition. For example, the interphase modifier does not typically have a plasticizing effect on the polymer by reducing its glass transition temperature. Quite to the contrary, the present inventors have discovered that the glass transition temperature of the thermoplastic composition may be substantially the same as the initial matrix polymer. In this regard, the ratio of the glass temperature of the composition to that of the matrix polymer is typically from about 0.7 to about 1.3, in some embodiments from about 0.8 to about 1.2, and in some embodiments, from about 0.9 to about 1.1. The thermoplastic composition may, for example, have a glass transition temperature of from about 35°C to about 80°C, in some embodiments from about 40°C to about 80°C, and in some embodiments, from about 50°C to about 65°C. The melt flow rate of the thermoplastic composition may also be similar to that of the matrix polymer. For example, the melt flow rate of the composition (on a dry basis) may be from about 0.1 to about 70 grams per 10 minutes, in some embodiments from about 0.5 to about 50 grams per 10 minutes, and in some embodiments, from about 5 to about 25 grams per 10 minutes, determined at a load of 2160 grams and at a temperature of 190°C.

Compatibilizers may also be employed that improve interfacial adhesion and reduce the interfacial tension between the domain and the matrix, thus allowing the formation of smaller domains during mixing. Examples of suitable compatibilizers may include, for instance, copolymers functionalized with epoxy or

maleic anhydride chemical moieties. An example of a maleic anhydride compatibilizer is polypropylene-grafted-maleic anhydride, which is commercially available from Arkema under the trade names Orevac™ 18750 and Orevac™ CA 100. When employed, compatibilizers may constitute from about 0.05 wt.% to about 10 wt.%, in some embodiments from about 0.1 wt.% to about 8 wt.%, and in some embodiments, from about 0.5 wt.% to about 5 wt.% of the thermoplastic composition, based on the weight of the continuous phase matrix.

Other suitable materials that may also be used in the thermoplastic composition, such as catalysts, antioxidants, stabilizers, surfactants, waxes, solid solvents, fillers, nucleating agents (e.g., calcium carbonate, etc.), and other materials added to enhance the processability and mechanical properties of the thermoplastic composition. Nevertheless, one beneficial aspect of the present invention is that good properties may be provided without the need for various conventional additives, such as blowing agents (e.g., chlorofluorocarbons, hydrochlorofluorocarbons, hydrocarbons, carbon dioxide, supercritical carbon dioxide, nitrogen, etc.) and plasticizers (e.g., solid or semi-solid polyethylene glycol). In fact, the thermoplastic composition may be generally free of blowing agents and/or plasticizers. For example, blowing agents and/or plasticizers may be present in an amount of no more than about 1 wt.%, in some embodiments no more than about 0.5 wt.%, and in some embodiments, from about 0.001 wt.% to about 0.2 wt.% of the thermoplastic composition. Further, due to its stress whitening properties, as described in more detail below, the resulting composition may achieve an opaque color (e.g., white) without the need for conventional pigments, such as titanium dioxide. In certain embodiments, for example, pigments may be present in an amount of no more than about 1 wt.%, in some embodiments no more than about 0.5 wt.%, and in some embodiments, from about 0.001 wt.% to about 0.2 wt.% of the thermoplastic composition.

## II. Blending

Prior to initiating pores in the composition, the components are typically blended together using any of a variety of known techniques. In one embodiment, for example, the components may be supplied separately or in combination. For instance, the components may first be dry mixed together to form an essentially homogeneous dry mixture, and they may likewise be supplied either

simultaneously or in sequence to a melt processing device that dispersively blends the materials. Batch and/or continuous melt processing techniques may be employed. For example, a mixer/kneader, Banbury mixer, Farrel continuous mixer, single-screw extruder, twin-screw extruder, roll mill, etc., may be utilized to blend and melt process the materials. Particularly suitable melt processing devices may be a co-rotating, twin-screw extruder (e.g., ZSK-30 extruder available from Werner & Pfleiderer Corporation of Ramsey, New Jersey or a Thermo Prism™ USALAB 16 extruder available from Thermo Electron Corp., Stone, England). Such extruders may include feeding and venting ports and provide high intensity distributive and dispersive mixing. For example, the components may be fed to the same or different feeding ports of the twin-screw extruder and melt blended to form a substantially homogeneous melted mixture. If desired, other additives may also be injected into the polymer melt and/or separately fed into the extruder at a different point along its length.

Regardless of the particular processing technique chosen, the resulting melt blended composition typically contains domains of the inclusion additives as described above. The degree of shear/pressure and heat may be controlled to ensure sufficient dispersion, but not so high as to adversely reduce the size of the domains so that they are incapable of achieving the desired properties. For example, blending typically occurs at a temperature of from about 180°C to about 300°C, in some embodiments from about 185°C to about 250°C, and in some embodiments, from about 190°C to about 240°C. Likewise, the apparent shear rate during melt processing may range from about 10 seconds<sup>-1</sup> to about 3000 seconds<sup>-1</sup>, in some embodiments from about 50 seconds<sup>-1</sup> to about 2000 seconds<sup>-1</sup>, and in some embodiments, from about 100 seconds<sup>-1</sup> to about 1200 seconds<sup>-1</sup>. The apparent shear rate may be equal to  $4Q/\pi R^3$ , where  $Q$  is the volumetric flow rate ("m<sup>3</sup>/s") of the polymer melt and  $R$  is the radius ("m") of the capillary (e.g., extruder die) through which the melted polymer flows. Of course, other variables, such as the residence time during melt processing, which is inversely proportional to throughput rate, may also be controlled to achieve the desired degree of homogeneity.

To achieve the desired shear conditions (e.g., rate, residence time, shear rate, melt processing temperature, etc.), the speed of the extruder screw(s) may

be selected with a certain range. Generally, an increase in product temperature is observed with increasing screw speed due to the additional mechanical energy input into the system. For example, the screw speed may range from about 50 to about 600 revolutions per minute ("rpm"), in some embodiments from about 70 to about 500 rpm, and in some embodiments, from about 100 to about 300 rpm. This may result in a temperature that is sufficient high to disperse the first inclusion additive without adversely impacting the size of the resulting domains. The melt shear rate, and in turn the degree to which the additives are dispersed, may also be increased through the use of one or more distributive and/or dispersive mixing elements within the mixing section of the extruder. Suitable distributive mixers for single screw extruders may include, for instance, Saxon, Dulmage, Cavity Transfer mixers, etc. Likewise, suitable dispersive mixers may include 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 (VIP) mixers.

### III. Pore Initiation

To initiate pore formation, the polymeric material is subjected to an external applied stress as described above. If desired, the material may be drawn in-line as it is being formed. Alternatively, the material may be drawn in its solid state after being formed, before and/or after lamination to any other optional materials, such as by a mechanical drawing process (e.g., bending, stretching, twisting, etc.) that imparts energy to the interface of the continuous phase and inclusion additives. By "solid state" drawing, it is generally meant that the composition is kept at a temperature ("drawing temperature") below the melting temperature of the matrix polymer. Among other things, this helps to ensure that the polymer chains are not altered to such an extent that the porous network becomes unstable. For example, the material may be drawn at a temperature of from about -50°C to about 125°C, in some embodiments from about -25°C to about 100°C, and in some embodiments, from about -20°C to about 50°C. The drawing temperature may also be below the glass transition temperature of the component having the highest glass transition temperature (e.g., matrix polymer, first inclusion additive, etc.). For example, the drawing temperature may be at least about 10°C, in some

embodiments at least about 20°C, and in some embodiments, at least about 30°C below the glass transition temperature of the matrix polymer and/or first inclusion additive.

5 Drawing may occur in any direction, such as the longitudinal direction (e.g., machine direction), transverse direction (e.g., cross-machine direction), etc., as well as combinations thereof. To perform the desired drawing, the thermoplastic composition may be formed into a precursor shape, drawn, and thereafter converted into the desired material (e.g., film, fiber, etc.). In one embodiment, the precursor shape may be a film having a thickness of from about 1 to about 5000 micrometers, in some embodiments from about 2 to about 4000 micrometers, in some embodiments from about 5 to about 2500 micrometers, and in some embodiments, from about 10 to about 500 micrometers. As an alternative to forming a precursor shape, the thermoplastic composition may also be drawn in situ as it is being shaped into the desired form for the polymeric material. In one embodiment, for example, the thermoplastic composition may be drawn as it is being formed into a film or fiber.

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Various drawing techniques may be employed. One suitable mechanical drawing technique, for instance, is a nip roll process in which the material is passed between a nip defined between two rolls, at least one of which is rotatable. 20 In one embodiment, at least one of the rolls contains a pattern of raised embossing elements, which can create a local deformation in the material. The other roll may likewise be patterned or smooth (e.g., anvil roll). If the deformed areas are stressed to a level above the cavitation yield stress, these areas can form initial pores. When subjected to further drawing stress, the pores areas will grow in size before the remaining material cavitates. Another suitable nip roll process involves 25 the use of a grooved roll through which the polymeric material is able to course. Besides the use of a nip, the rotational velocity of the rolls themselves may also be utilized to help impart the desired degree of mechanical stress. In one embodiment, for example, the material is passed over a series of rolls that 30 progressively draw the material. One such suitable method for accomplishing such drawing is through the use of a machine direction orienter ("MDO"). MDO units typically have a plurality of rolls (e.g., from 5 to 8) that can progressively draw and the polymeric material in the machine direction. The material may be drawn in

either single or multiple discrete drawing operations. It should be noted that some of the rolls in an MDO apparatus may not be operating at progressively higher speeds. To draw the material in the manner described above, it is typically desired that the rolls of the MDO are not heated. Nevertheless, if desired, one or more rolls may be heated to a slight extent to facilitate the drawing process so long as the temperature of the composition remains below the ranges noted above.

Of course, it should be understood that rotatable rolls are by no means required to mechanically draw the polymeric material. Die drawing, for instance, may be employed to mechanically draw the material. In a typical die drawing process, the material is initially extruded into a precursor shape (e.g., profile) and quenched. The precursor is then mechanically drawn through a converging die while in a solid state. One particularly suitable die drawing process is pultrusion, during which the material is drawn or pulled through the die to form an engineered profile or shape determined by the shape of the die. Apart from die drawing, other mechanical drawing techniques may also be employed. In one embodiment, for instance, sheet drawing may be employed, such as tenter frame drawing, brake drawing, etc. In one particular embodiment, for instance, the polymeric material may be mechanically drawn in the form of a sheet using a mechanical, electrical, hydraulic or pneumatic brake assembly. The brake assembly may include a surface where the material is initially placed, a clamping bar, and a bending member that is lifted to create a bend in the material. More particularly, the brake assembly may include a plurality of generally c-shaped members that each present opposing clamping surfaces for receiving a polymeric material. Furthermore, a socket connection may be employed to rotatably support the bending member for bending the material disposed between the clamping surfaces. The socket connection generally includes a male portion and a female portion in sliding engagement with one another or connected by a pin hinge connection to one another. Such brake assemblies are known in the art and described in more detail in, for instance, U.S. Patent No. 4,282,735 to Break; 4,557,132 to Break, and to 6,389,864 to Chubb.

Yet another technique for mechanically drawing the polymeric material involves the use of a fluidic medium (e.g., gas) to impart the desired degree of energy and stress to the material. One such process is, for instance, aspiration,

which typically involves the use of blown air to draw the material. For example, a fiber draw aspirator may be employed, such as a linear fiber aspirator of the type shown in U.S. Patent Nos. 3,802,817 and 3,423,255. A fiber draw aspirator generally includes an elongated vertical passage through which the fibers are drawn by aspirating air entering from the sides of the passage and flowing downwardly through the passage. A heater or blower may supply the aspirating air, which causes the fibers to draw or attenuate.

Regardless of the particular technique employed, the polymeric material is typically drawn (e.g., in the machine direction) to a draw ratio of from about 1.1 to about 3.5, in some embodiments from about 1.2 to about 3.0, and in some embodiments, from about 1.3 to about 2.5. The draw ratio may be determined by dividing the length of the drawn material by its length before drawing. The draw rate may also vary to help achieve the desired properties, such as within the range of from about 5% to about 1500% per minute of deformation, in some embodiments from about 20% to about 1000% per minute of deformation, and in some embodiments, from about 25% to about 850% per minute of deformation. In addition to forming a porous network, mechanical drawing can also significantly increase the axial dimension of the domains so that they have a generally linear, elongated shape. For example, the first domains may have an average axial dimension that is about 10% or more, in some embodiments from about 20% to about 500%, and in some embodiments, from about 50% to about 250% greater than the axial dimension of the domains prior to drawing. Prior to drawing, for instance, the first domains may have an average axial dimension (e.g., length) of from about 0.05 to about 30 micrometers, in some embodiments from about 0.1 to about 25 micrometers, in some embodiments from about 0.5 to about 20 micrometers, and in some embodiments from about 1 to about 10 micrometers.

As a result of the unique porous and domain structure, the present inventors have discovered that the resulting polymeric material can expand uniformly in volume when drawn in longitudinal direction, which is reflected by a low "Poisson coefficient", as determined according to the following equation:

$$\text{Poisson coefficient} = - E_{\text{transverse}} / E_{\text{longitudinal}}$$

where  $E_{\text{transverse}}$  is the transverse deformation of the material and  $E_{\text{longitudinal}}$  is the longitudinal deformation of the material. More particularly, the Poisson

coefficient of the material can be approximately 0 or even negative. For example, the Poisson coefficient may be about 0.1 or less, in some embodiments about 0.08 or less, and in some embodiments, from about -0.1 to about 0.04. When the  
5 Poisson coefficient is zero, there is no contraction in transverse direction when the material is expanded in the longitudinal direction. When the Poisson coefficient is negative, the transverse or lateral dimensions of the material are also expanding when the material is drawn in the longitudinal direction. Materials having a negative Poisson coefficient can thus exhibit an increase in width when drawn in the longitudinal direction, which can result in increased energy absorption in the  
10 cross direction.

If desired, the polymeric material of the present invention may be subjected to one or more additional processing steps, before and/or after being drawn. Examples of such processes include, for instance, groove roll drawing, embossing, coating, etc. In certain embodiments, the polymeric material may also be  
15 annealed to help ensure that it retains the desired shape. Annealing typically occurs at or above the glass transition temperature of the polymer matrix, such as at from about 40° to about 120°C, in some embodiments from about 50°C to about 100°C, and in some embodiments, from about 70°C to about 90°C. The polymeric material may also be surface treated using any of a variety of known techniques to  
20 improve its properties. For example, high energy beams (e.g., plasma, x-rays, e-beam, etc.) may be used to remove or reduce any skin layers, to change the surface polarity, porosity, topography, to embrittle a surface layer, etc. If desired, such surface treatment may be used before and/or drawing of the thermoplastic composition.

25 **IV. Articles**

The polymeric material of the present invention may generally have a variety of different forms depending on the particular application, such as films, fibrous materials, molded articles, profiles, etc., as well as composites and  
30 laminates thereof. In one embodiment, for example, the polymeric material is in the form of a film or layer of a film. Multilayer films may contain from two (2) to fifteen (15) layers, and in some embodiments, from three (3) to twelve (12) layers. Such multilayer films normally contain at least one base layer and at least one additional layer (e.g., skin layer), but may contain any number of layers desired.

For example, the multilayer film may be formed from a base layer and one or more skin layers, wherein the base layer and/or skin layer(s) are formed from the polymeric material of the present invention. It should be understood, however, that other polymer materials may also be employed in the base layer and/or skin layer(s), such as polyolefin polymers.

The thickness of the film may be relatively small to increase flexibility. For example, the film may have a thickness of from about 1 to about 200 micrometers, in some embodiments from about 2 to about 150 micrometers, in some embodiments from about 5 to about 100 micrometers, and in some embodiments, from about 10 to about 60 micrometers. Despite having such a small thickness, the film may nevertheless be able to retain good mechanical properties during use. For example, the film may be relatively ductile. One parameter that is indicative of the ductility of the film is the percent elongation of the film at its break point, as determined by the stress strain curve, such as obtained in accordance with ASTM Standard D638-10 at 23°C. For example, the percent elongation at break of the film in the machine direction ("MD") may be about 10% or more, in some embodiments about 50% or more, in some embodiments about 80% or more, and in some embodiments, from about 100% to about 600%. Likewise, the percent elongation at break of the film in the cross-machine direction ("CD") may be about 15% or more, in some embodiments about 40% or more, in some embodiments about 70% or more, and in some embodiments, from about 100% to about 400%. Another parameter that is indicative of ductility is the tensile modulus of the film, which is equal to the ratio of the tensile stress to the tensile strain and is determined from the slope of a stress-strain curve. For example, the film typically exhibits a MD and/or CD tensile modulus of about 2500 Megapascals ("MPa") or less, in some embodiments about 2200 MPa or less, in some embodiments from about 50 MPa to about 2000 MPa, and in some embodiments, from about 100 MPa to about 1000 MPa. The tensile modulus may be determined in accordance with ASTM D638-10 at 23°C.

Although the film is ductile, it can still be relatively strong. One parameter that is indicative of the relative strength of the film is the ultimate tensile strength, which is equal to the peak stress obtained in a stress-strain curve, such as obtained in accordance with ASTM Standard D638-10. For example, the film may

exhibit an MD and/or CD peak stress of from about 5 to about 65 MPa, in some embodiments from about 10 MPa to about 60 MPa, and in some embodiments, from about 20 MPa to about 55 MPa. The film may also exhibit an MD and/or CD break stress of from about 5 MPa to about 60 MPa, in some embodiments from about 10 MPa to about 50 MPa, and in some embodiments, from about 20 MPa to about 45 MPa. The peak stress and break stress may be determined in accordance with ASTM D638-10 at 23°C.

In addition to a film, the polymeric material may also be in the form of a fibrous material or a layer or component of a fibrous material, which can include individual staple fibers or filaments (continuous fibers), as well as yarns, fabrics, etc. formed from such fibers. Yarns may include, for instance, multiple staple fibers that are twisted together ("spun yarn"), filaments laid together without twist ("zero-twist yarn"), filaments laid together with a degree of twist, single filament with or without twist ("monofilament"), etc. The yarn may or may not be texturized. Suitable fabrics may likewise include, for instance, woven fabrics, knit fabrics, nonwoven fabrics (e.g., spunbond webs, meltblown webs, bonded carded webs, wet-laid webs, airlaid webs, coform webs, hydraulically entangled webs, etc.), and so forth.

Fibers formed from the thermoplastic composition may generally have any desired configuration, including monocomponent and multicomponent (e.g., sheath-core configuration, side-by-side configuration, segmented pie configuration, island-in-the-sea configuration, and so forth). In some embodiments, the fibers may contain one or more additional polymers as a component (e.g., bicomponent) or constituent (e.g., biconstituent) to further enhance strength and other mechanical properties. For instance, the thermoplastic composition may form a sheath component of a sheath/core bicomponent fiber, while an additional polymer may form the core component, or *vice versa*. The additional polymer may be a thermoplastic polymer such as polyesters, e.g., polylactic acid, polyethylene terephthalate, polybutylene terephthalate, and so forth; polyolefins, e.g., polyethylene, polypropylene, polybutylene, and so forth; polytetrafluoroethylene; polyvinyl acetate; polyvinyl chloride acetate; polyvinyl butyral; acrylic resins, e.g., polyacrylate, polymethylacrylate, polymethylmethacrylate, and so forth; polyamides, e.g., nylon; polyvinyl chloride; polyvinylidene chloride; polystyrene;

polyvinyl alcohol; and polyurethanes.

When employed, the fibers can deform upon the application of strain, rather than fracture. The fibers may thus continue to function as a load bearing member even after the fiber has exhibited substantial elongation. In this regard, the fibers of the present invention are capable of exhibiting improved "peak elongation properties, i.e., the percent elongation of the fiber at its peak load. For example, the fibers of the present invention may exhibit a peak elongation of about 50% or more, in some embodiments about 100% or more, in some embodiments from about 200% to about 1500%, and in some embodiments, from about 400% to about 800%, such as determined in accordance with ASTM D638-10 at 23°C. Such elongations may be achieved for fibers having a wide variety of average diameters, such as those ranging from about 0.1 to about 50 micrometers, in some embodiments from about 1 to about 40 micrometers, in some embodiments from about 2 to about 25 micrometers, and in some embodiments, from about 5 to about 15 micrometers.

While possessing the ability to extend under strain, the fibers of the present invention can also remain relatively strong. For example, the fibers may exhibit a peak tensile stress of from about 25 to about 500 Megapascals ("MPa"), in some embodiments from about 50 to about 300 MPa, and in some embodiments, from about 60 to about 200 MPa, such as determined in accordance with ASTM D638-10 at 23°C. Another parameter that is indicative of the relative strength of the fibers of the present invention is "tenacity", which indicates the tensile strength of a fiber expressed as force per unit linear density. For example, the fibers of the present invention may have a tenacity of from about 0.75 to about 6.0 grams-force ("gr") per denier, in some embodiments from about 1.0 to about 4.5 gr per denier, and in some embodiments, from about 1.5 to about 4.0 gr per denier. The denier of the fibers may vary depending on the desired application. Typically, the fibers are formed to have a denier per filament (i.e., the unit of linear density equal to the mass in grams per 9000 meters of fiber) of less than about 6, in some embodiments less than about 3, and in some embodiments, from about 0.5 to about 3.

Due to its unique and beneficial properties, the resulting polymeric material of the present invention is well suited for use in a variety of different types of

articles, such as an absorbent article, packaging film, barrier film, medical product (e.g., gown, surgical drape, facemask, head covering, surgical cap, shoe covering, sterilization wrap, warming blanket, heating pad, etc.), and so forth. For example, the polymeric material may be incorporated into an “absorbent article” that is capable of absorbing water or other fluids. Examples of some absorbent articles include, but are not limited to, personal care absorbent articles, such as diapers, training pants, absorbent underpants, incontinence articles, feminine hygiene products (e.g., sanitary napkins), swim wear, baby wipes, mitt wipe, and so forth; medical absorbent articles, such as garments, fenestration materials, underpads, bedpads, bandages, absorbent drapes, and medical wipes; food service wipers; clothing articles; pouches, and so forth. Materials and processes suitable for forming such articles are well known to those skilled in the art. Absorbent articles, for instance, typically include a substantially liquid-impermeable layer (e.g., outer cover), a liquid-permeable layer (e.g., bodyside liner, surge layer, etc.), and an absorbent core. In one embodiment, for example, the polymeric material may be in the form of a fibrous material (e.g., nonwoven web) and used to form an outer cover of an absorbent article. If desired, the nonwoven web may be laminated to a liquid-impermeable film that is either vapor-permeable or vapor-impermeable. The polymeric material may likewise be in the form of a film that is used in an absorbent article, such as a liquid-impermeable film of the outer cover, which is either vapor-permeable or vapor-impermeable.

The polymeric material may also be employed in a wide variety of other types of articles. Non-limiting examples include, for instance, insulation materials for refrigeration units (e.g., refrigerators, freezers, vending machines, etc.); automotive components (e.g., front and rear seats, headrests, armrests, door panels, rear shelves/package trays, steering wheels and interior trim, dashboards, etc.); building panels and sections (e.g., roofs, wall cavities, under floors, etc.); apparel (e.g., coats, shirts, pants, gloves, aprons, coveralls, shoes, boots, headware, sock liners, etc.); furniture and bedding (e.g., sleeping bags, comforters, etc.); fluid storage/transfer systems (e.g., pipes or tankers for liquid/gas hydrocarbons, liquid nitrogen, oxygen, hydrogen, or crude oil); extreme environments (e.g., underwater or space); food and beverage products (e.g., cups, cup holders, plates, etc.); containers and bottles; and so forth. The polymeric

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material may also be used in a "garment", which is generally meant to include any article that is shaped to fit over a portion of a body. Examples of such articles include, without limitation, clothing (e.g., shirts, pants, jeans, slacks, skirts, coats, activewear, athletic, aerobic, and exercise apparel, swimwear, cycling jerseys or shorts, swimsuit/bathing suit, race suit, wetsuit, bodysuit, etc.), footwear (e.g., shoes, socks, boots, etc.), protective apparel (e.g., firefighter's coat), clothing accessories (e.g., belts, bra straps, side panels, gloves, hosiery, leggings, orthopedic braces, etc.), undergarments (e.g., underwear, t-shirts, etc.), compression garments, draped garments (e.g., kilts loinloths, togas, ponchos, cloaks, shawls, etc.), and so forth.

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The polymeric material may be employed in a wide variety of articles within any particular application. For example, when considering automotive applications, the polymeric material may be employed in fibrous articles or as solid moldings. By way of example, fibers of the polymeric material may be beneficially employed in articles that can enhance comfort and/or aesthetics of a vehicle (e.g., coverings and/or paddings for sun visors, speaker housings and coverings, seat coverings, seal slip agents, and backings for seat coverings, carpeting and carpet reinforcement including carpet backing, car mats and backings for car mats, coverings for seat belts and seat belt anchorages, trunk floor coverings and liners, rear shelf panels, headliner facings and backings, upholstery backings, general decorative fabrics, etc.), materials that can provide general temperature and/or noise insulation (e.g., column padding, door trim pads, hood liners, general sound proofing and insulation materials, muffler wraps, bodywork parts, windows, saloon roofs, and sunroofs, tire reinforcements, etc.), and filtration/engine materials (e.g., fuel filters, oil filters, battery separators, cabin air filters, transmission tunnel materials, fuel tanks, etc.).

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Solid moldings including the polymeric material can be utilized to enhance automotive safety components. For instance, the polymeric material can be encompassed in passive safety components such as crumple zones on the rear, front, and/or sides of a vehicle; within the safety cell of the automobile, as a component of the airbag or steering wheel (e.g., a collapsible steering column); as a cargo barrier; or as a component of a pedestrian safety system (e.g., as a component of the bumpers, hood, window frame, etc.).

The low density of the polymeric material can provide weight saving benefits in automotive applications. For example, the polymeric material can be a component of the structure of an automobile including, without limitation, the hood, bumpers and/or bumper supports, the trunk lid and/or compartment, and the underbody of the vehicle.

Such broad-based application of the polymeric material is applicable to a wide variety of fields, and is not intended to be in any way limited to the automotive industry. For instance, the polymeric material can be used in the transportation industry in any suitable application including, without limitation, air and space applications (e.g., airplanes, helicopters, space transports, military aerospace devices, etc.), marine applications (boats, ships, recreational vehicles), trains, and so forth. The polymeric material can be utilized in transportation applications in any desired fashion, e.g., in fibrous articles or solid moldings, in aesthetic applications, for temperature and/or noise insulation, in filtration and/or engine components, in safety components, etc.

The present invention may be better understood with reference to the following examples.

#### Test Methods

##### *Melt Flow Rate:*

The melt flow rate ("MFR") is the weight of a polymer (in grams) forced through an extrusion rheometer orifice (0.0825-inch diameter) when subjected to a load of 2160 grams in 10 minutes, typically at 190°C, 210°C, or 230°C. Unless otherwise indicated, melt flow rate is measured in accordance with ASTM Test Method D1239 with a Tinius Olsen Extrusion Plastometer.

##### *Thermal Properties:*

The glass transition temperature ( $T_g$ ) may be determined by dynamic mechanical analysis (DMA) in accordance with ASTM E1640-09. A Q800 instrument from TA Instruments may be used. The experimental runs may be executed in tension/tension geometry, in a temperature sweep mode in the range from -120°C to 150°C with a heating rate of 3°C/min. The strain amplitude frequency may be kept constant (2 Hz) during the test. Three (3) independent samples may be tested to get an average glass transition temperature, which is defined by the peak value of the  $\tan \delta$  curve, wherein  $\tan \delta$  is defined as the ratio

of the loss modulus to the storage modulus ( $\tan \delta = E''/E'$ ).

The melting temperature may be determined by differential scanning calorimetry (DSC). The differential scanning calorimeter may be a DSC Q100 Differential Scanning Calorimeter, which may be outfitted with a liquid nitrogen cooling accessory and with a UNIVERSAL ANALYSIS 2000 (version 4.6.6) analysis software program, both of which are available from T.A. Instruments Inc. of New Castle, Delaware. To avoid directly handling the samples, tweezers or other tools may be used. The samples may be placed into an aluminum pan and weighed to an accuracy of 0.01 milligram on an analytical balance. A lid may be crimped over the material sample onto the pan. Typically, the resin pellets may be placed directly in the weighing pan.

The differential scanning calorimeter may be calibrated using an indium metal standard and a baseline correction may be performed, as described in the operating manual for the differential scanning calorimeter. A material sample may be placed into the test chamber of the differential scanning calorimeter for testing, and an empty pan may be used as a reference. All testing may be run with a 55-cubic centimeter per minute nitrogen (industrial grade) purge on the test chamber. For resin pellet samples, the heating and cooling program is a 2-cycle test that began with an equilibration of the chamber to -30°C, followed by a first heating period at a heating rate of 10°C per minute to a temperature of 200°C, followed by equilibration of the sample at 200°C for 3 minutes, followed by a first cooling period at a cooling rate of 10°C per minute to a temperature of -30°C, followed by equilibration of the sample at -30°C for 3 minutes, and then a second heating period at a heating rate of 10°C per minute to a temperature of 200°C. For fiber samples, the heating and cooling program may be a 1-cycle test that begins with an equilibration of the chamber to -25°C, followed by a heating period at a heating rate of 10°C per minute to a temperature of 200°C, followed by equilibration of the sample at 200°C for 3 minutes, and then a cooling period at a cooling rate of 10°C per minute to a temperature of -30°C. All testing may be run with a 55-cubic centimeter per minute nitrogen (industrial grade) purge on the test chamber.

The results may be evaluated using the UNIVERSAL ANALYSIS 2000 analysis software program, which identifies and quantifies the glass transition

temperature ( $T_g$ ) of inflection, the endothermic and exothermic peaks, and the areas under the peaks on the DSC plots. The glass transition temperature may be identified as the region on the plot-line where a distinct change in slope occurred, and the melting temperature may be determined using an automatic inflection calculation.

5

#### *Film Tensile Properties*

Films may be tested for tensile properties (peak stress, modulus, strain at break, and energy per volume at break) on a MTS Synergie 200 tensile frame.

The test may be performed in accordance with ASTM D638-10 (at about 23°C).

10

Film samples may be cut into dog bone shapes with a center width of 3.0 mm before testing. The dog-bone film samples may be held in place using grips on the MTS Synergie 200 device with a gauge length of 18.0 mm. The film samples may be stretched at a crosshead speed of 5.0 in/min until breakage occurred. Five samples may be tested for each film in both the machine direction (MD) and the cross direction (CD). A computer program (e.g., TestWorks 4) may be used to collect data during testing and to generate a stress versus strain curve from which a number of properties may be determined, including modulus, peak stress, elongation, and energy to break.

15

#### *Fiber Tensile Properties:*

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Fiber tensile properties may be determined in accordance with ASTM 638-10 at 23°C. For instance, individual fiber specimens may initially be shortened (e.g., cut with scissors) to 38 millimeters in length, and placed separately on a black velvet cloth. 10 to 15 fiber specimens may be collected in this manner. The fiber specimens may then be mounted in a substantially straight condition on a rectangular paper frame having external dimension of 51 millimeters x 51 millimeters and internal dimension of 25 millimeters x 25 millimeters. The ends of each fiber specimen may be operatively attached to the frame by carefully securing the fiber ends to the sides of the frame with adhesive tape. Each fiber specimen may be measured for its external, relatively shorter, cross-fiber dimension employing a conventional laboratory microscope, which may be properly calibrated and set at 40X magnification. This cross-fiber dimension may be recorded as the diameter of the individual fiber specimen. The frame helps to mount the ends of the sample fiber specimens in the upper and lower grips of a

constant rate of extension type tensile tester in a manner that avoids excessive damage to the fiber specimens.

A constant rate of extension type of tensile tester and an appropriate load cell may be employed for the testing. The load cell may be chosen (e.g., 10N) so that the test value falls within 10-90% of the full scale load. The tensile tester (i.e., MTS SYNERGY 200) and load cell may be obtained from MTS Systems Corporation of Eden Prairie, Michigan. The fiber specimens in the frame assembly may then be mounted between the grips of the tensile tester such that the ends of the fibers may be operatively held by the grips of the tensile tester. Then, the sides of the paper frame that extend parallel to the fiber length may be cut or otherwise separated so that the tensile tester applies the test force only to the fibers. The fibers may be subjected to a pull test at a pull rate and grip speed of 12 inches per minute. The resulting data may be analyzed using a TESTWORKS 4 software program from the MTS Corporation with the following test settings:

Calculation Inputs		Test Inputs	
Break mark drop	50%	Break sensitivity	90%
Break marker elongation	0.1 in	Break threshold	10 gr
Nominal gage length	1 in	Data Acq. Rate	10 Hz
Slack pre-load	1 lbf	Denier length	9000 m
Slope segment length	20%	Density	1.25 g/cm <sup>3</sup>
Yield offset	0.20%	Initial speed	12 in/min
Yield segment length	2%	Secondary speed	2 in/min

The tenacity values may be expressed in terms of gram-force per denier.

Peak elongation (% strain at break) and peak stress may also be measured.

#### *Expansion Ratio, Density, and Percent Pore Volume*

To determine expansion ratio, density, and percent pore volume, the width ( $W_i$ ) and thickness ( $T_i$ ) of the specimen may be initially measured prior to drawing. The length ( $L_i$ ) before drawing may also be determined by measuring the distance between two markings on a surface of the specimen. Thereafter, the specimen may be drawn to initiate voiding. The width ( $W_f$ ), thickness ( $T_f$ ), and length ( $L_f$ ) of the specimen may then be measured to the nearest 0.01 mm utilizing Digimatic Caliper (Mitutoyo Corporation). The volume ( $V_i$ ) before drawing may be calculated by  $W_i \times T_i \times L_i = V_i$ . The volume ( $V_f$ ) after drawing may also be calculated by  $W_f \times T_f \times L_f = V_f$ . The expansion ratio ( $\Phi$ ) may be calculated by  $\Phi = V_f/V_i$ ; the density

( $P_f$ ) may be calculated by:  $P_f = P_i / \Phi$ , where  $P_i$  is density of precursor material; and the percent pore volume (%  $V_v$ ) may be calculated by:  $\%V_v = (1 - 1/\Phi) \times 100$ .

*Hydrostatic Pressure Test ("Hydrohead"):*

The hydrostatic pressure test is a measure of the resistance of a material to penetration by liquid water under a static pressure and is performed in accordance with AATCC Test Method 127-2008. The results for each specimen may be averaged and recorded in centimeters (cm). A higher value indicates greater resistance to water penetration.

*Water Vapor Transmission Rate ("WVTR")*

The test used to determine the WVTR of a material may vary based on the nature of the material. One technique for measuring the WVTR value is ASTM E96/96M-12, Procedure B. Another method involves the use of INDA Test Procedure IST-70.4 (01). The INDA test procedure is summarized as follows. A dry chamber is separated from a wet chamber of known temperature and humidity by a permanent guard film and the sample material to be tested. The purpose of the guard film is to define a definite air gap and to quiet or still the air in the air gap while the air gap is characterized. The dry chamber, guard film, and the wet chamber make up a diffusion cell in which the test film is sealed. The sample holder is known as the Permatran-W Model 100K manufactured by Mocon/Modem Controls, Inc., Minneapolis, Minnesota. A first test is made of the WVTR of the guard film and the air gap between an evaporator assembly that generates 100% relative humidity. Water vapor diffuses through the air gap and the guard film and then mixes with a dry gas flow that is proportional to water vapor concentration. The electrical signal is routed to a computer for processing. The computer calculates the transmission rate of the air gap and the guard film and stores the value for further use.

The transmission rate of the guard film and air gap is stored in the computer as CalC. The sample material is then sealed in the test cell. Again, water vapor diffuses through the air gap to the guard film and the test material and then mixes with a dry gas flow that sweeps the test material. Also, again, this mixture is carried to the vapor sensor. The computer then calculates the transmission rate of the combination of the air gap, the guard film, and the test material. This information is then used to calculate the transmission rate at which moisture is

transmitted through the test material according to the equation:

$$TR_{test\ material} = TR_{test\ material, guardfilm, airgap} - TR_{guardfilm, airgap}$$

The water vapor transmission rate ("WVTR") is then calculated as follows:

$$WVTR = \frac{F\rho_{sat}(T)RH}{AP_{sat}(T)(1-RH)}$$

5 wherein,

F = the flow of water vapor in  $\text{cm}^3$  per minute;

$\rho_{sat}(T)$  = the density of water in saturated air at temperature T;

RH = the relative humidity at specified locations in the cell;

A = the cross sectional area of the cell; and

10  $P_{sat}(T)$  = the saturation vapor pressure of water vapor at temperature T.

#### Conductive Properties

Thermal conductivity ( $\text{W}/\text{mK}$ ) and thermal resistance ( $\text{m}^2\text{K}/\text{W}$ ) may be determined in accordance with ASTM E-1530-11 ("Resistance to Thermal Transmission of Materials by the Guarded Heat Flow Meter Technique") using an Anter Unitherm Model 2022 tester. The target test temperature may be 25°C and the applied load may be 0.17 MPa. Prior to testing, the samples may be conditioned for 40+ hours at a temperature of 23°C ( $\pm 2^\circ\text{C}$ ) and relative humidity of 50% ( $\pm 10\%$ ). Thermal admittance ( $\text{W}/\text{m}^2\text{K}$ ) may also be calculated by dividing 1 by the thermal resistance.

#### 20 Moisture Content

Moisture content may be determined using an Arizona Instruments Compütrac Vapor Pro moisture analyzer (Model No. 3100) in substantial accordance with ASTM D 7191-05, which is incorporated herein in its entirety by reference thereto for all purposes. The test temperature (§X2.1.2) may be 130°C, the sample size (§X2.1.1) may be 2 to 4 grams, and the vial purge time (§X2.1.4) may be 30 seconds. Further, the ending criteria (§X2.1.3) may be defined as a "prediction" mode, which means that the test is ended when the built-in programmed criteria (which mathematically calculates the end point moisture content) is satisfied.

### EXAMPLE 1

The ability to form films from a blend of 85.3 wt.% polylactic acid (PLA 6201D, Natureworks®), 9.5 wt.% of a first inclusion additive, 1.4 wt.% of a second inclusion additive, and 3.8 wt.% of an internal interfacial modifier was demonstrated. The first inclusion additive was Vistamaxx™ 2120 (ExxonMobil), which is a polypropylene-polyethylene copolymer elastomer with a melt flow rate of 29 g/10 min (190°C, 2160 g) and a density of 0.866 g/cm<sup>3</sup>. The second inclusion additive was poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (Lotader® AX8900, Arkema) having a melt flow rate of 5-6 g/10 min (190°C/2160 g), a glycidyl methacrylate content of 7 to 11 wt.%, methyl acrylate content of 13 to 17 wt.%, and ethylene content of 72 to 80 wt.%. The internal interfacial modifier was PLURIOL® WI 285 Lubricant from BASF, which is a polyalkylene glycol functional fluid. The polymers were fed into a co-rotating, twin-screw extruder (ZSK-30, diameter of 30 mm, length of 1328 millimeters) for compounding that was manufactured by Werner and Pfleiderer Corporation of Ramsey, New Jersey. The extruder possessed 14 zones, numbered consecutively 1-14 from the feed hopper to the die. The first barrel zone #1 received the resins via gravimetric feeder at a total throughput of 15 pounds per hour. The PLURIOL® WI285 was added via injector pump into barrel zone #2. The die used to extrude the resin had 3 die openings (6 millimeters in diameter) that were separated by 4 millimeters. Upon formation, the extruded resin was cooled on a fan-cooled conveyor belt and formed into pellets by a Conair pelletizer. The extruder screw speed was 200 revolutions per minute ("rpm"). The pellets were then flood fed into a signal screw extruder heated to a temperature of 212°C where the molten blend exited through 4.5 inch width slit die and drawn to a film thickness ranging from 36 µm to 54 µm. The films were stretched in the machine direction to about 100% to initiate cavitation and void formation.

The morphology of the films was analyzed by scanning electron microscopy (SEM) before and after stretching. The results are shown in Figs. 1-4. As shown in Figs. 1-2, the first inclusion additive was initially dispersed in domains having an axial size (in machine direction) of from about 2 to about 30 micrometers and a transverse dimension (in cross-machine direction) of from about 1 to about 3 micrometers, while the second inclusion additive was initially dispersed as

spherical or spheroidal domains having an axial size of from about 100 to about 300 nanometers. Figs. 3-4 show the film after stretching. As indicated, pores formed around the first and second inclusion additives. The micropores formed around the first inclusion additive generally had an elongated or slit-like shape with a broad size distribution ranging from about 2 to about 20 micrometers in the axial direction. The nanopores associated with the second inclusion additive generally had a size of from about 50 to about 500 nanometers.

#### EXAMPLE 2

The compounded pellets of Example 1 were dry blended with a third inclusion additive, which was a halloysite clay masterbatch (MacroComp MNH-731-36, MacroM) containing 22 wt.% of a styrenic copolymer modified nanoclay and 78 wt.% polypropylene (Exxon Mobil 3155). The mixing ratio was 90 wt.% of the pellets and 10 wt.% of the clay masterbatch, which provided a total clay content of 2.2%. The dry blend was then flood fed into a single screw extruder heated to a temperature of 212°C, where the molten blend exited through 4.5 inch width slit die and drawn to a film thickness ranging from 51 to 58 µm. The films were stretched in the machine direction to about 100% to initiate cavitation and void formation.

The morphology of the films was analyzed by scanning electron microscopy (SEM) before and after stretching. The results are shown in Figs. 5-8. As shown in Figs. 5-6, some of the nanoclay particles (visible as brighter regions) became dispersed in the form of very small domains – i.e., axial dimension ranging from about 50 to about 300 nanometers. The masterbatch itself also formed domains of a micro-scale size (axial dimension of from about 1 to about 5 micrometers). Also, the first inclusion additive (Vistamax™) formed elongated domains, while the second inclusion additive (Lotader®, visible as ultrafine dark dots) and third inclusion additive (nanoclay masterbatch, visible as bright platelets) formed spheroidal domains. The stretched film is shown in Figs. 7-8. As shown, the voided structure is more open and demonstrates a broad variety of pore sizes. In addition to highly elongated micropores formed by the first inclusions (Vistamaxx™), the nanoclay masterbatch inclusions formed more open spheroidal micropores with an axial size of about 10 microns or less and a transverse size of about 2 microns. Spherical nanopores are also formed by the second inclusion additive (Lotader®) and third inclusion additive (nanoclay particles).

Various tensile properties (machine direction) of the films of Example 1 and 2 were also tested. The results are provided below in Table 1.

**Table 1**

Example	Avg. Thickness (μm)	Avg. Modulus (MPa)	Avg. Yield Stress (MPa)	Avg. Break Stress (MPa)	Avg. Strain at Break (%)	Avg. Energy per Vol. (J/cm <sup>3</sup> )
1	49	2066	48.1	35	236	73
2	56	1945	41.3	36	299	65

5 As shown, the addition of the nanoclay filler resulted in a slight increase in break stress and a significant increase in elongation at break.

**EXAMPLE 3**

A precursor blend was formed from 91.8 wt.% polypropylene (M3661, Total Petrochemicals) 7.4 wt.% of a first inclusion additive (PLA 6252), and 0.7 wt.% of a second inclusion additive. The second inclusion additive was poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (LOTADER® AX8900, Arkema) having a melt flow rate of 6 g/10 min (190°C/2160 g), a glycidyl methacrylate content of 8 wt.%, methyl acrylate content of 24 wt.%, and ethylene content of 68 wt.%. The components were compounded in a co-rotating twin-screw extruder (Werner and Pfleiderer ZSK-30 with a diameter of 30 mm and a L/D=44). The extruder had seven heating zones. The temperature in the extruder ranged from 180°C to 220°C. The polymer was fed gravimetrically to the extruder at the hoper at 15 pounds per hour and the liquid was injected into the barrel using a peristaltic pump. The extruder was operated at 200 revolutions per minute (RPM). In the last section of the barrel (front), a 3-hole die of 6 mm in diameter was used to form the extrudate. The extrudate was air-cooled in a conveyor belt and pelletized using a Conair Pelletizer. Injection molded specimens (ASTM D638 Type 1) were made of the precursor blend using a Boy 22D injection molding machine with 3 heating sections. The temperature in the heating sections ranged from 185 to 220°C. The injection holding pressure time ranged from 14s to 24s, the cooling time from 12 to 23s, cycle time ranged from 22s to 43s, and the mold temperature was set at about 21°C. Once formed, the molded specimens were stretched in an 810 Material Test System tension tester at a cross-head speed of 25 mm/min at 25°C.

To analyze the material morphology, both the unstretched and stretched injection molded bars were freeze fractured in liquid nitrogen. The fractured surfaces were sputter coated with gold-palladium alloy, and analyzed via Scanning Electron Microscope Jeol 6490LV at high vacuum. The results are shown in Figs. 5 9-10. As indicated in Fig. 9, the blend exhibited a relatively small domain size. Upon stretching, as shown in Fig. 10, the small domain sizes of the blend tended to form relatively small pores. A stress-strain curve was also generated for the stretched sample and is shown in Fig. 11. As shown, the blend showed good mechanical properties, similar to that of neat polypropylene. Also, a section of the 10 necked region of the stretched molded bar was cut and then submerged in hexane (density of 0.65 g/cc). It was observed that the necked region of the stretched molded bars floated in hexane, which suggested that the density is lower than 0.65 g/cc.

#### EXAMPLE 4

Fiber was produced from the precursor blend of Example 3 using a Davis-Standard fiber spinning line equipped with a 0.75-inch single screw extruder and 16 hole spinneret with a diameter of 0.6 mm. The fibers were collected at different draw down ratios. The take up speed ranged from 1 to 1000 m/min. The 20 temperature of the extruder ranged from 175°C to 220°C. The fibers were stretched in a tensile tester machine at 300 mm/min up to 400% elongation at 25°C. To analyze the material morphology, the fibers were freeze fractured in liquid nitrogen and analyzed via Scanning Electron Microscope Jeol 6490LV at high vacuum. The results are shown in Fig. 12-14. As shown, spheroidal pores 25 are formed that are highly elongated in the stretching direction. Both nanopores (~50 nanometers in width, ~500 nanometers in length) and micropores (~0.5 micrometers in width, ~4 micrometers in length) were formed.

While the invention has been described in detail with respect to the specific 30 embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

**CLAIMS:**

1. A porous polymeric material that contains a thermoplastic composition, the thermoplastic composition including a continuous phase in which a first inclusion additive and second inclusion additive are dispersed in the form of discrete domains, the continuous phase including a matrix polymer, wherein the first inclusion additive is polymeric and is present in the thermoplastic composition in an amount of from about 1 wt.% to about 20 wt.% and wherein the second inclusion additive is polymeric and is present in the thermoplastic composition in an amount of from about 0.01 wt.% to about 15 wt.%, wherein a plurality of micropores are formed at and/or around the first domains that have an average cross-sectional dimension of from about 0.5 to about 30 micrometers, and wherein a plurality of nanopores are formed at and/or around the second domains that have an average cross-sectional dimension of from about 50 to about 500 nanometers.

2. The porous polymeric material of claim 1, wherein the nanopores have an average cross-sectional dimension of from about 60 to about 450 nanometers, and preferably from about 100 to about 400 nanometers and/or wherein the micropores have an average cross-sectional dimension of from about 1 to about 20 micrometers, and preferably from about 2 micrometers to about 15 micrometers.

3. The porous polymeric material of any one of the foregoing claims, wherein the first domains have an average cross-sectional dimension of from about 0.05 to about 50 micrometers, in some embodiments from about 0.2 to about 10 micrometers, and in some embodiments, from 0.5 to about 5 micrometers and/or wherein the second domains have an average cross-sectional dimension of from about 50 to about 500 nanometers, preferably from about 60 to about 400 nanometers, and more preferably from about 80 to about 300 nanometers.

4. The porous polymeric material of any one of the foregoing claims, wherein the porous network further comprises a plurality of second nanopores that are formed at and/or around the second domains.

5. The porous polymeric material of claim 4, wherein the second nanopores have an average cross-sectional dimension of from about 1 to about 50 nanometers, preferably from about 2 to about 45 nanometers, and more preferably from about 5 to about 40 nanometers.

6. The porous polymeric material of any one of the foregoing claims, wherein the total pore volume of the polymeric material is from about 15% to about 80%, preferably about 20% to about 70%, and more preferably, from about 30% to about 60% per cubic centimeter of the material.

7. The porous polymeric material of any one of the foregoing claims, wherein the polymeric material has a density of about 1.2 g/cm<sup>3</sup> or less, preferably about 1.0 g/cm<sup>3</sup> or less, more preferably from about 0.2 g/cm<sup>3</sup> to about 0.8 g/cm<sup>3</sup>, and even more preferably about 0.1 g/cm<sup>3</sup> to about 0.5 g/cm<sup>3</sup>.

8. The porous polymeric material of any one of the foregoing claims, wherein the continuous phase constitutes from about 60 wt.% to about 99 wt.% of the thermoplastic composition, the first inclusion additive constitutes from about 5 wt.% to about 20 wt.% of the composition based on the weight of the continuous phase, and the second inclusion additive constitutes from about 0.1 wt.% to about 10 wt.% of the composition based on the weight of the continuous phase.

9. The porous polymeric material of any one of the foregoing claims, wherein the matrix polymer includes a polyester or polyolefin.

10. The porous polymeric material of any one of the foregoing claims, wherein the matrix polymer has a glass transition temperature of about 0°C or more.

11. The porous polymeric material of any one of the foregoing claims, wherein the first inclusion additive includes a polyolefin.

12. The porous polymeric material of any one of the foregoing claims, wherein the second inclusion additive is a functionalized polyolefin.

13. The porous polymeric material of claim 12, wherein the second inclusion additive is a polyepoxide.

14. The porous polymeric material of any one of the foregoing claims, wherein the thermoplastic composition further contains a third inclusion additive that is dispersed within the continuous phase in the form of discrete third domains.

15. The porous polymeric material of claim 14, wherein the third domains have an average cross-sectional dimension of from about 1 to about 50 nanometers, preferably from about 2 to about 45 nanometers, and more preferably from about 5 to about 40 nanometers.

16. The porous polymeric material of claim 14 or 15, wherein the network further comprises a plurality of nanopores formed at and/or around the third domains that have an average cross-sectional dimension of from about 1 to about 50 nanometers, preferably from about 2 to about 45 nanometers, and more preferably from about 5 to about 40 nanometers,

17. The porous polymeric material of any one of claims 14 to 16, wherein the third inclusion additive includes a nanoclay.

18. The porous polymeric material of claim 17, wherein the third inclusion additive is blended with a carrier resin.

19. The porous polymeric material of claim 18, wherein the carrier resin is dispersed in the continuous phase in the form of domains having an average cross-sectional dimension of from about 0.5 to about 30 micrometers, preferably from about 1 to about 20 micrometers, and more preferably from about 2 micrometers to about 15 micrometers.

20. The porous polymeric material of any one of claims 14 to 19, wherein the third inclusion additive constitutes from about 0.05 wt.% to about 20 wt.%, preferably from about 0.1 wt.% to about 10 wt.%, and more preferably from about 0.5 wt.% to about 5 wt.% of the thermoplastic composition, based on the weight of the continuous phase.

21. The porous polymeric material of any one of the foregoing claims, wherein the thermoplastic composition further comprises an interphase modifier.

22. The porous polymeric material of any one of the foregoing claims, wherein the polymeric material is generally free of gaseous blowing agents.

23. The porous polymeric material of any one of the foregoing claims, wherein the micropores are elongated and the nanopores are generally spherical.

24. The porous polymeric material of any one of the foregoing claims, wherein the porous network is distributed in a substantially homogeneous fashion throughout the material and/or wherein the micropores and/or nanopores are distributed in generally parallel columns.

25. A method for forming the porous polymeric material of any one of the foregoing claims, the method comprising drawing the thermoplastic composition while in a solid state to form the porous network.

26. The method of claim 25, wherein the composition is drawn at a temperature of from about -50°C to about 50°C, more preferably at a temperature of from about -25°C to about 40°C, and even more preferably at a temperature of from about -20°C to about 30°C and/or wherein the composition is drawn at a temperature that is at least about 10°C, preferably at least about 20°C, and more preferably at least about 30°C below the glass transition temperature of the matrix polymer and/or the first inclusion additive.

27. The method of claim 25 or 26, wherein the composition is mechanically drawn.

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**Patent Attorneys for the Applicant/Nominated Person**

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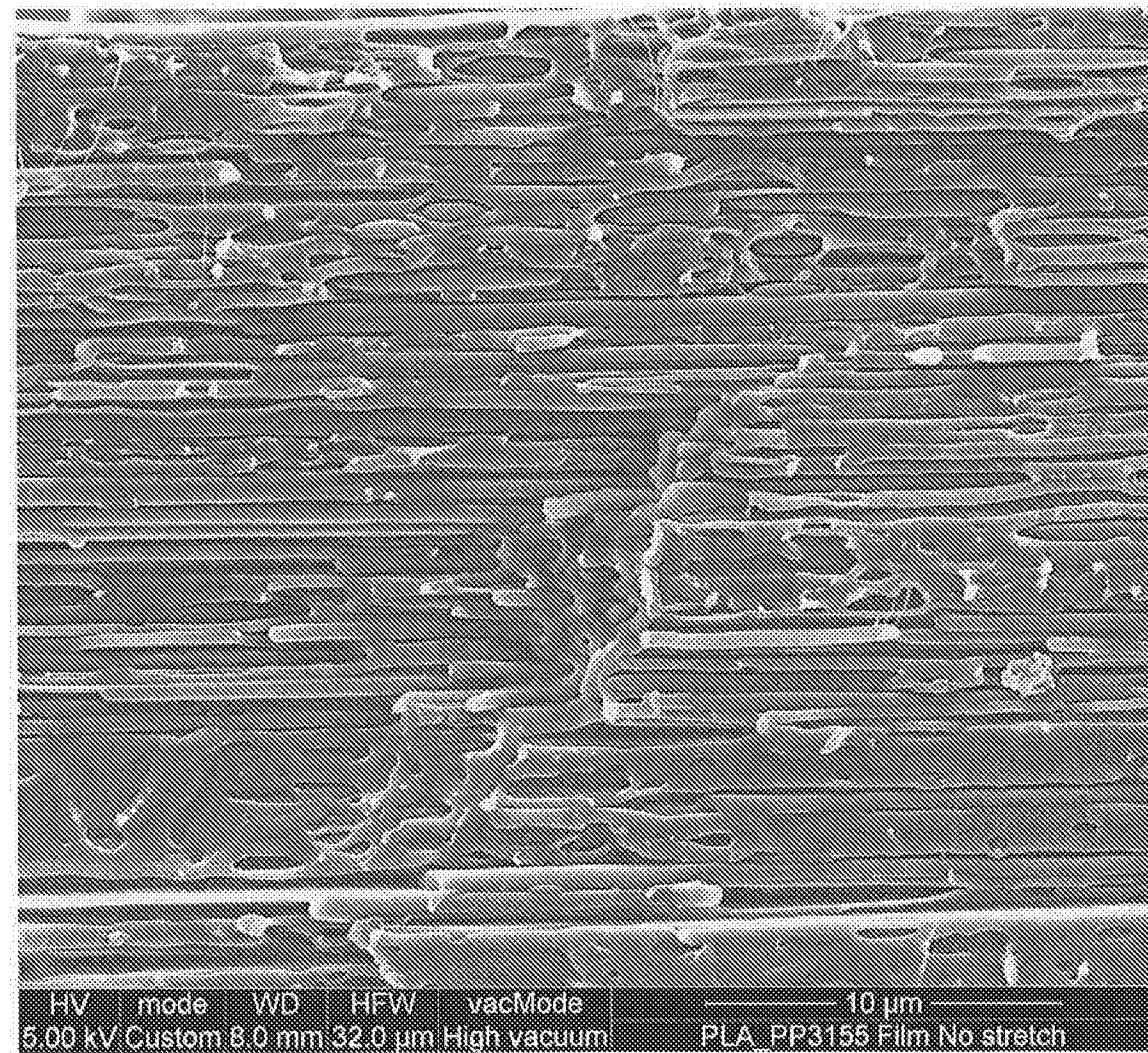


Fig. 1

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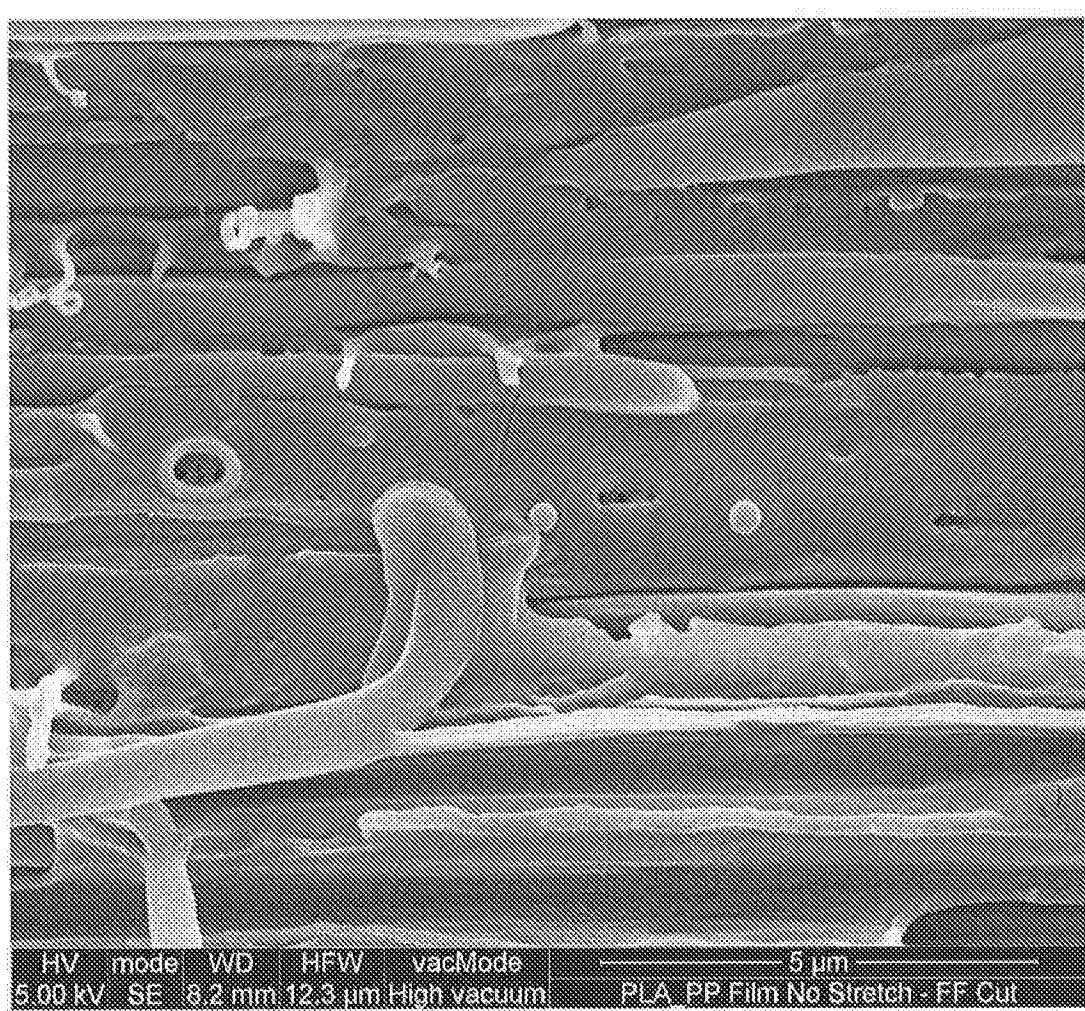


Fig. 2

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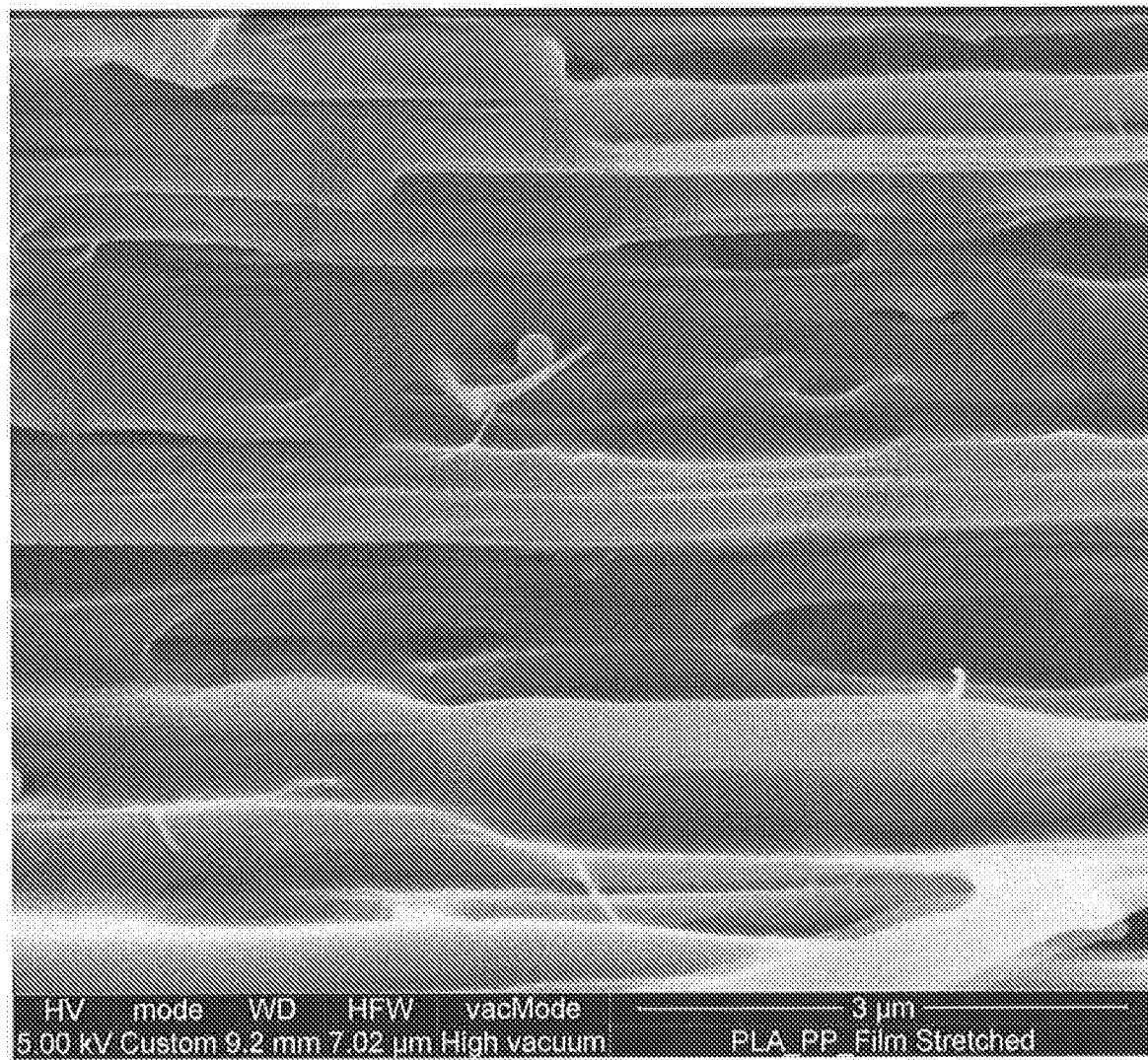


Fig. 3

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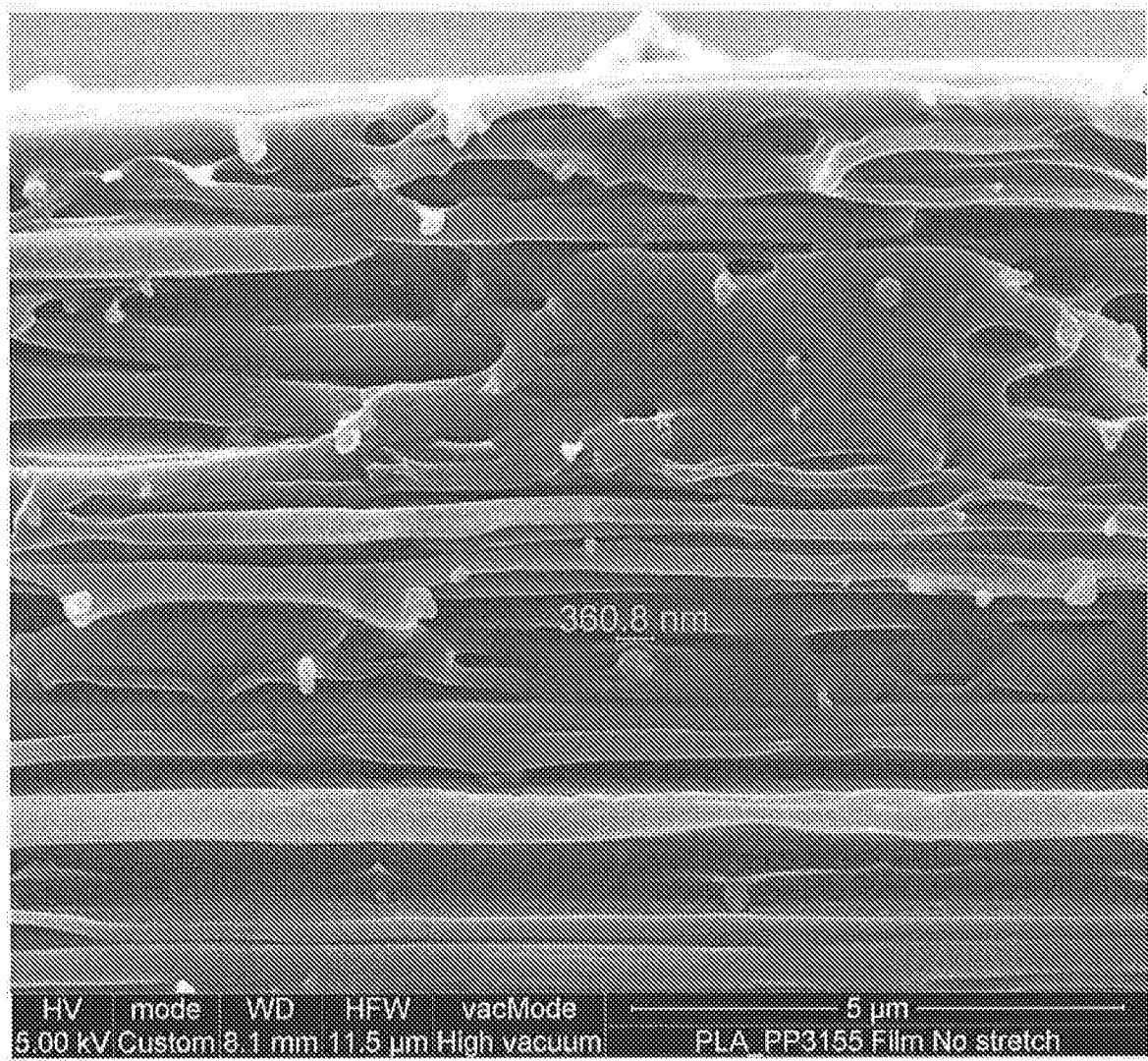


Fig. 4

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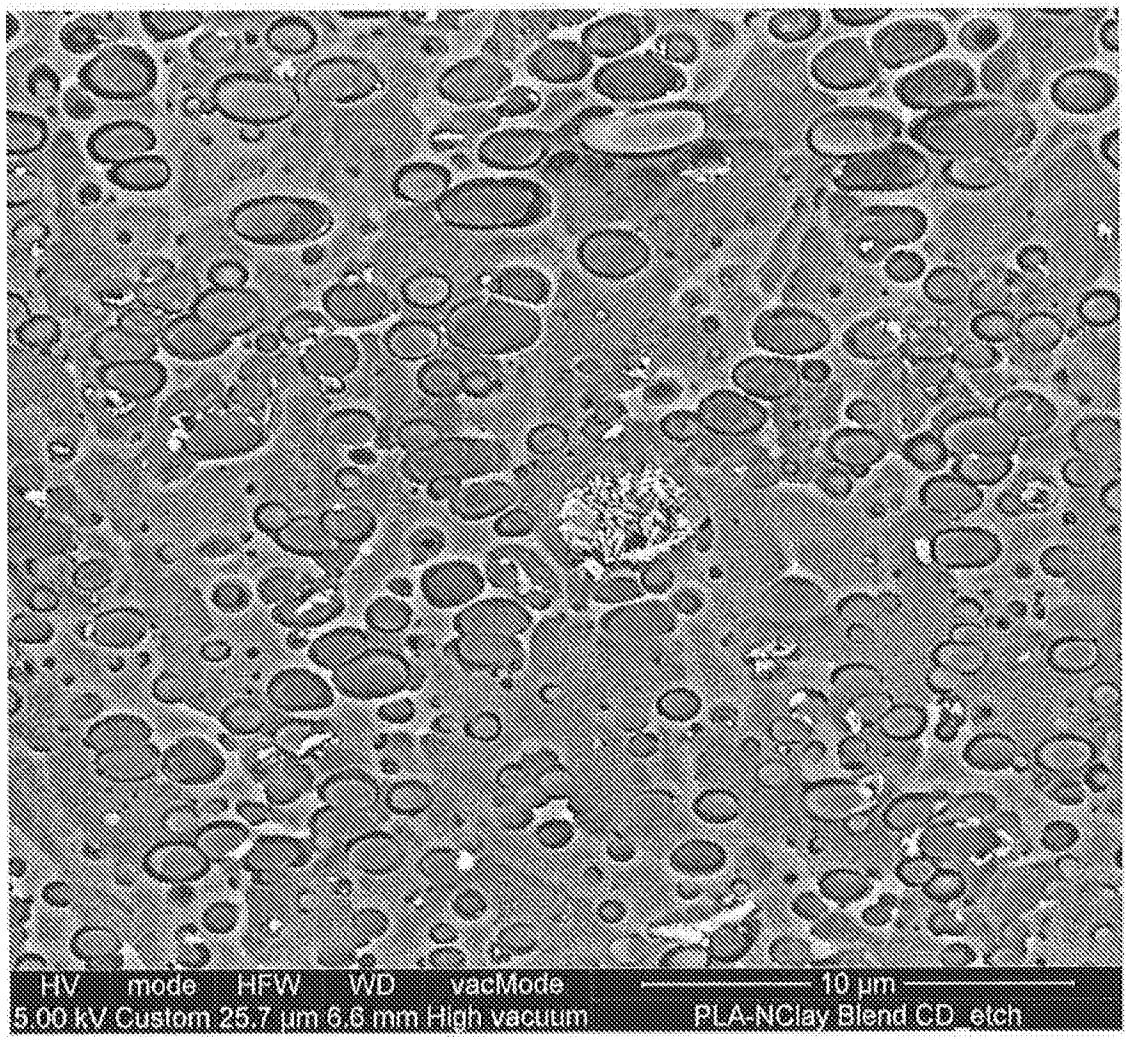


Fig. 5

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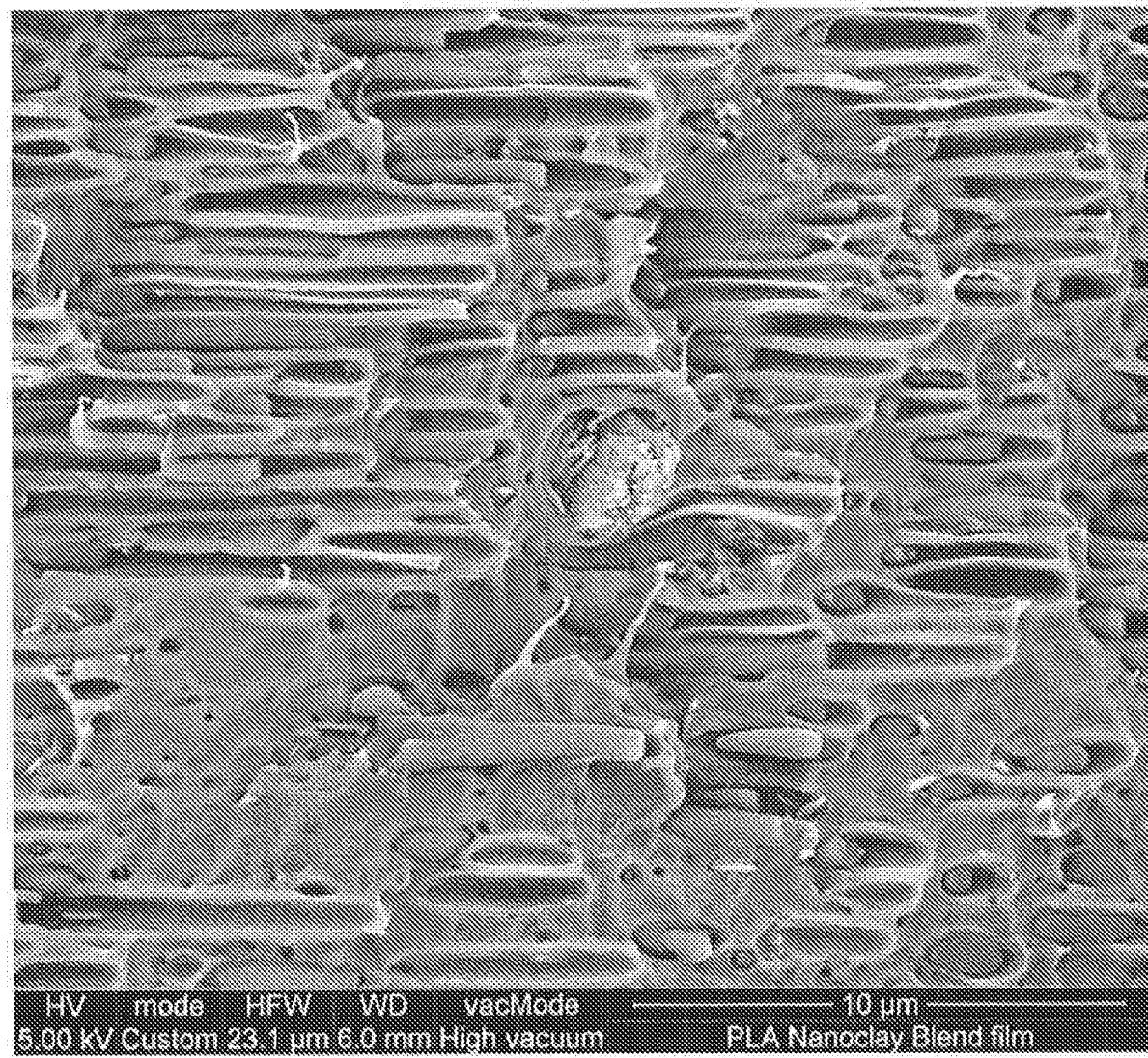


Fig. 6

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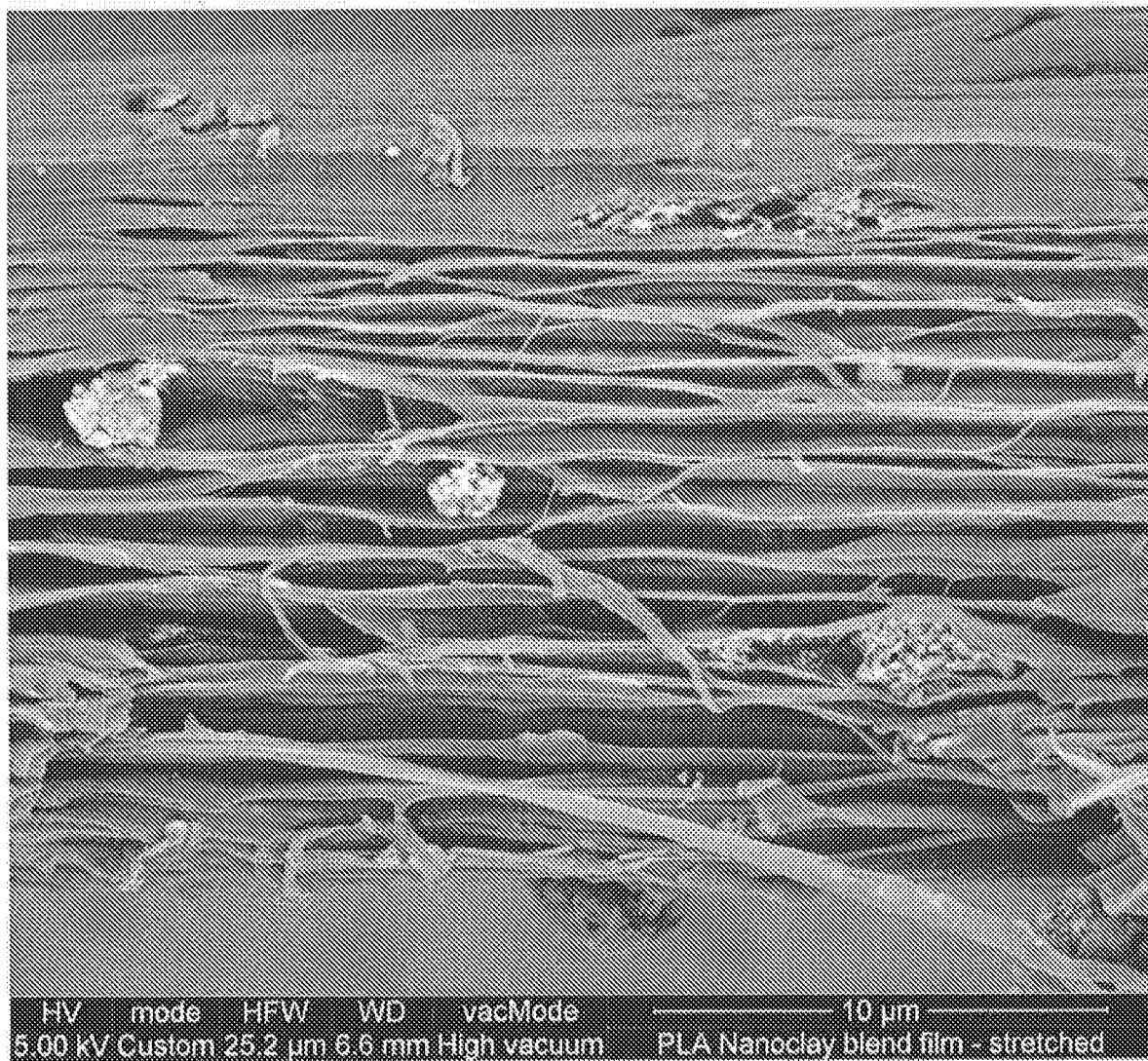


Fig. 7

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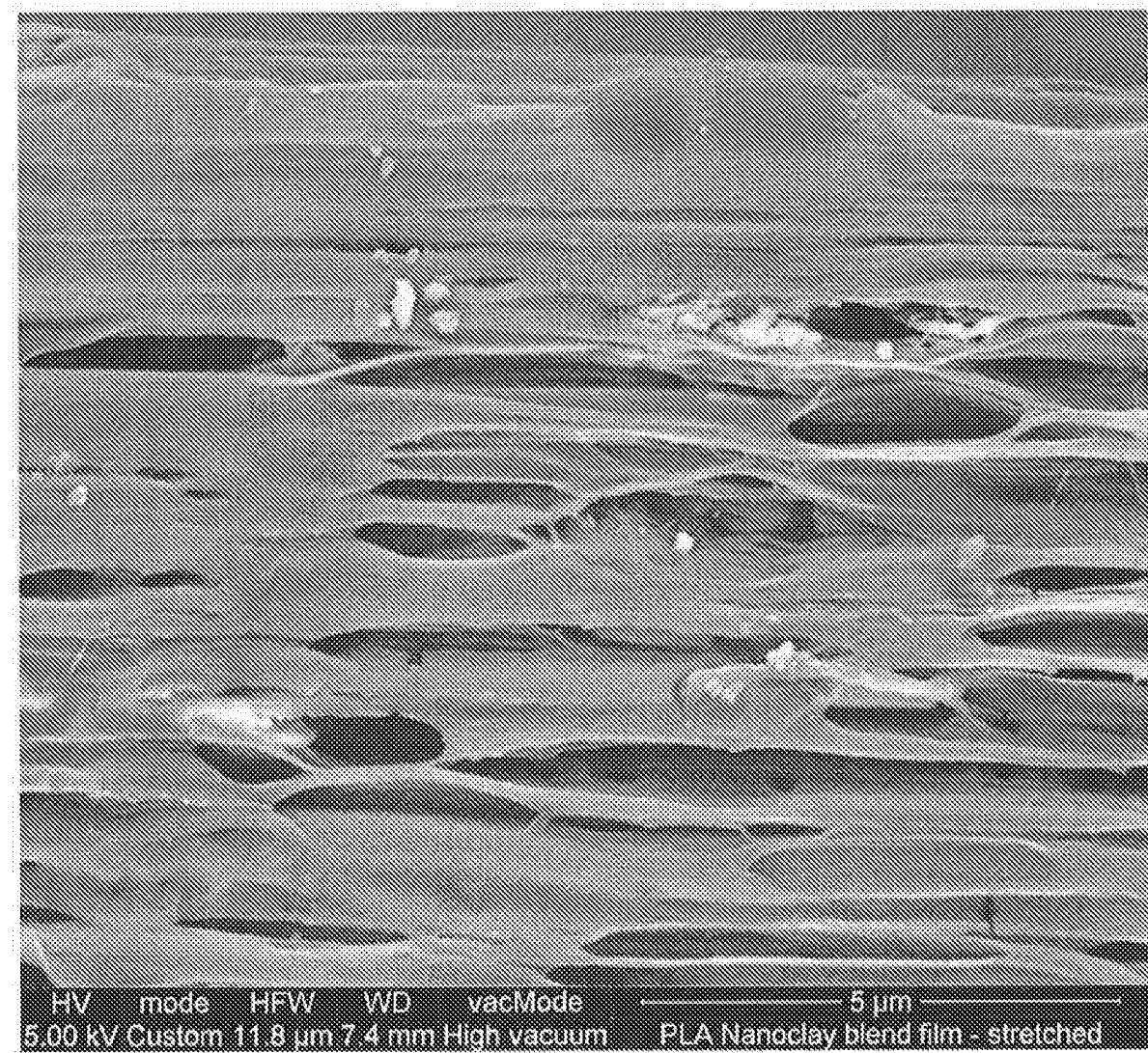


Fig. 8

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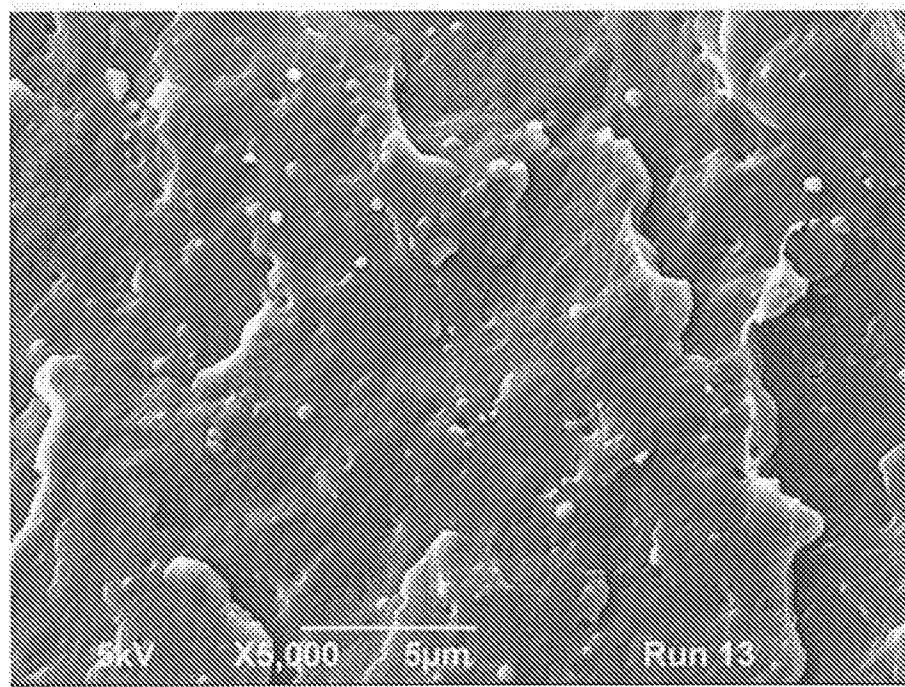


Fig. 9

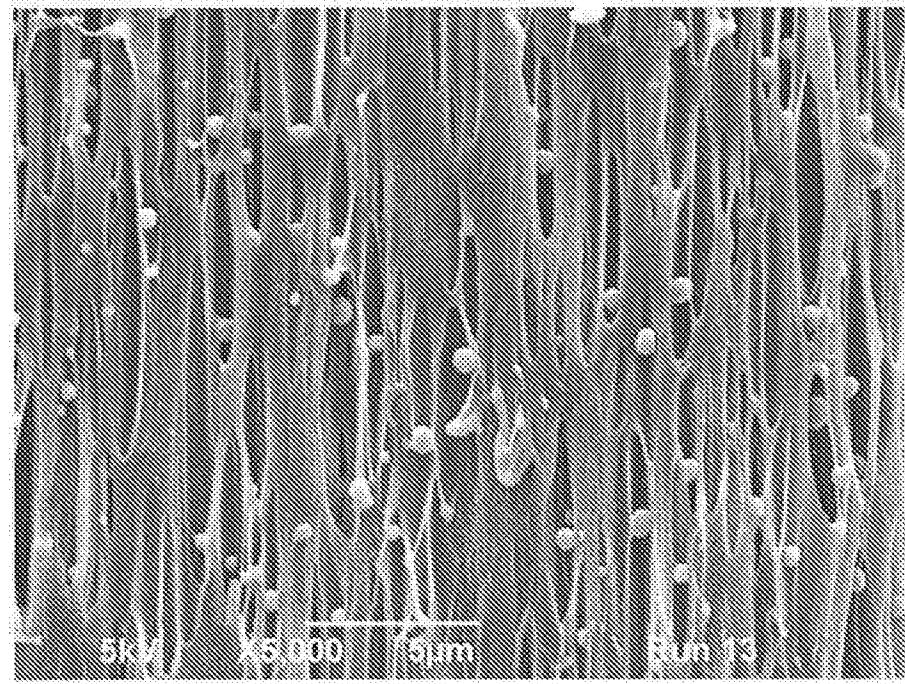


Fig. 10

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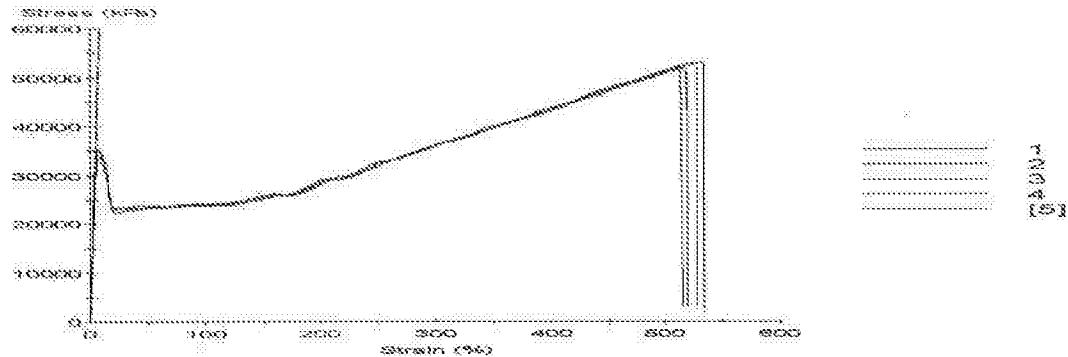


Fig. 11

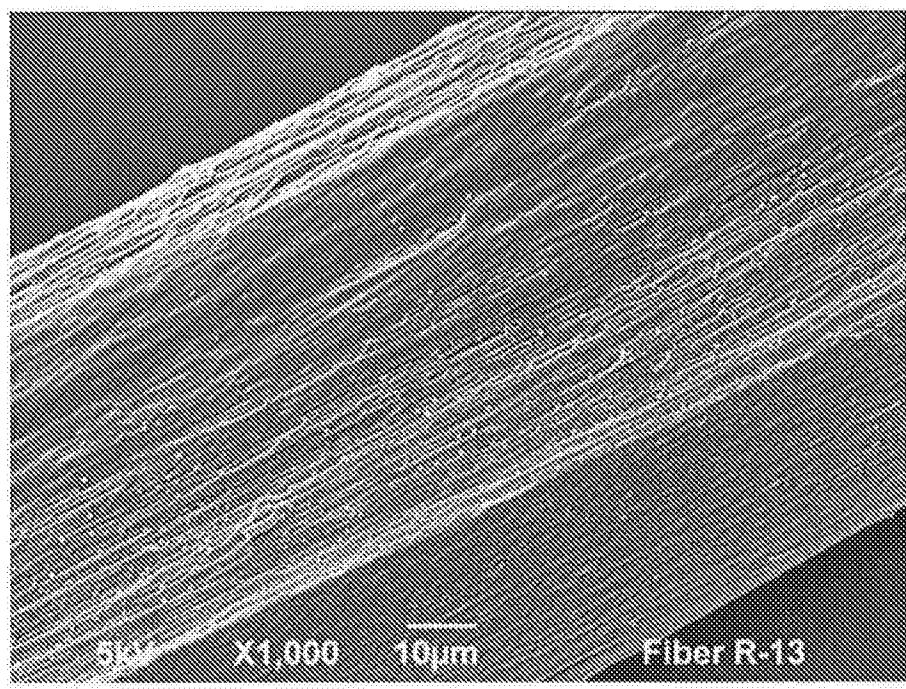


Fig. 12

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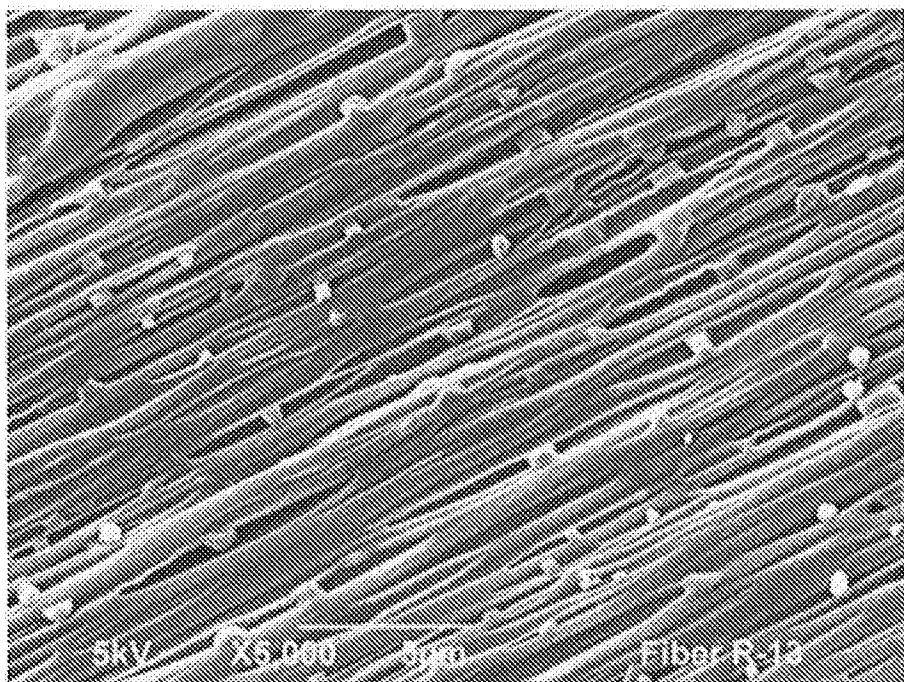


Fig. 13

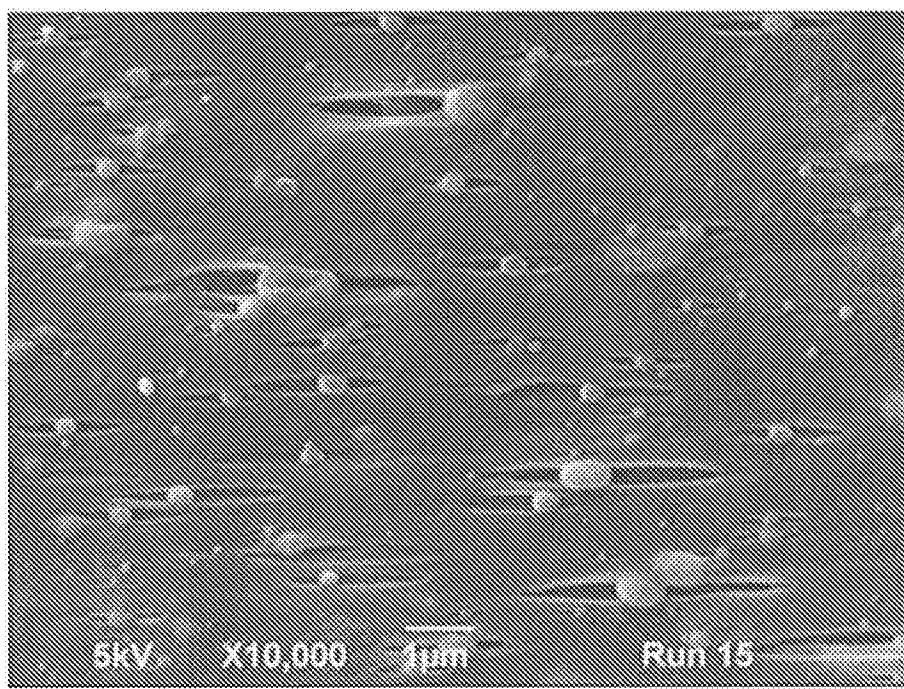


Fig. 14