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(57) Abstract: A thermoplastic blend comprising (a) a thermoplastic polymer matrix and (b) an amphiphilic block copolymer that includes: (i) a first block that is immiscible in the thermoplastic polymer matrix and (ii) a second block that is miscible in the thermoplastic polymer matrix. The blend has a microstructure in the form of a continuous phase comprising the thermoplastic polymer matrix and nanoscale-sized domains dispersed in the continuous phase. The thermoplastic polymer matrix and second block are selected such that when the thermoplastic polymer and a homopolymer of the first block are combined, they exhibit a negative χ ("chi") parameter.



Toughened Thermoplastic Blends

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of priority from U.S. Provisional Application Serial No. 62/156,383, filed on May 4, 2015.

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TECHNICAL FIELD

This invention relates to toughening thermoplastic polymers.

BACKGROUND

Thermoplastic polymers such as polyesters are useful in a number of applications, including packaging, textiles, and automotive parts. Although these polymers often have high strength and modulus, they are often brittle, thereby limiting their utility. Various strategies have been proposed to toughen such polymers. One approach involves adding a low molecular weight plasticizer to the polymer to lower the glass transition temperature of the polymer and thus enhance its flexibility. Another approach involves modifying the polymer itself by copolymerizing the monomer used to prepare the polymer with one or more toughening monomers to create a copolymer having a different molecular structure. A third approach involves blending the polymer with a toughening polymer such as an elastomer. The resulting blend features a multi-phase microstructure in which the toughening polymer forms domains that are dispersed throughout a continuous polymer matrix.

SUMMARY

In one aspect, a thermoplastic blend is described that includes: (a) a thermoplastic polymer matrix ("polymer C") and (b) an amphiphilic block copolymer. The block copolymer, in turn, includes: (i) a first block ("polymer A") that is miscible in the thermoplastic polymer matrix and (ii) a second block ("polymer B") that is immiscible in the thermoplastic polymer matrix. The blend A-B/C has a microstructure in the form of a

continuous phase comprising the thermoplastic polymer matrix C and nanoscale-sized domains comprising the block B dispersed in the continuous phase. The thermoplastic polymer matrix C and block A are selected such that when the thermoplastic polymer C and a homopolymer A are combined in a melt, they exhibit a negative χ ("chi")

5 parameter, i.e., $\chi(AC) < 0$. The χ parameter, also known as the polymer-polymer interaction parameter or Flory-Huggins (or simply Flory) parameter, reflects the exchange energy difference between molecules of different types. χ is the energy needed to extract one molecule of polymer A from the undiluted melt state, one molecule of polymer C from the undiluted melt state, and exchange them. $\chi(AA$ or BB or $CC)$ equals
10 zero, and $\chi(BC)$ is a positive number. A negative χ parameter, $\chi(AC)$, means that polymers A and C prefer to make contact with each other at the repeat unit length scale versus contact of A with A and C with C. A negative χ implies a negative excess Gibbs free-energy of mixing.

In a second aspect, there is described a thermoplastic blend that includes: (a) a
15 thermoplastic polyester matrix and (b) an amphiphilic block copolymer comprising (i) a first polyalkylene ether block that is miscible in the thermoplastic polymer matrix and (ii) a second polyalkylene ether block that is different from the first polyalkylene ether block and immiscible in the thermoplastic polymer matrix. The blend has a microstructure in the form of a continuous phase comprising the thermoplastic polyester matrix and
20 nanoscale-sized domains comprising the second block dispersed in the continuous phase.

In embodiments of the first and second aspects, the thermoplastic polymer matrix may be a homopolymer or copolymer that includes at least two different types of monomer units. The block copolymer includes at least two different blocks.

In some embodiments, the thermoplastic matrix is a polyester matrix and the
25 block copolymer includes a first polyalkylene ether block that is miscible in the polyester matrix and a second polyalkylene ether block, different from the first polyalkylene ether block, which is immiscible in the polyester matrix. The polyester may include units derived from a hydroxy carboxylic acid. For example, the polyester may be selected from the group consisting of poly-L-lactic acid, poly-D-lactic acid, poly-D,L-lactic acid,
30 and combinations thereof.

In some embodiments, the first block of the block copolymer includes a polyalkylene ether selected from the group consisting of polyethylene oxide, polypropylene oxide, and poly(ethylene-co-propylene oxide), and the second block of the block copolymer includes a polyalkylene ether selected from the group consisting of polybutylene oxide, polyhexylene oxide, and polydodecylene oxide. For example, the first block may include polyethylene oxide and the second block may include polybutylene oxide. The block copolymer may be present in an amount no greater than 20% by weight or no greater than 10% by weight based upon the weight of the blend. In some embodiments, the block copolymer is present in an amount no greater than 5% by weight based upon the weight of the blend, or no greater than 2.5% by weight based upon the weight of the blend.

Inclusion of the block copolymer improves the mechanical properties of the thermoplastic plastic matrix such as tensile toughness and breaking strain. For example, in some embodiments, the blend has a tensile toughness that is at least 20 MJ/m³. The tensile toughness of the blend may be at least 10 times higher than the tensile toughness of the thermoplastic polyester matrix alone. In some embodiments, the blend has a breaking strain that is at least 2, 3, 5, or 10 times higher than the breaking strain of the thermoplastic polyester matrix alone. The blend may also be transparent to visible light (i.e. the % transmission of a 1 mm thick sample of the blend is at least 84% to visible light). In some embodiments, the blends can be used to prepare blown films

The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1 is graph of stress v. strain for blends featuring polylactic acid blended with various amounts of a poly(ethylene oxide)-b-poly(butylene oxide) block copolymer.

FIGS 2(a)-(d) are representative TEM images of a blend featuring polylactic acid blended with 5 wt.% of a poly(ethylene oxide)-b-poly(butylene oxide) block copolymer.

FIG. 3 is a graph of stress v. strain for blends featuring polylactic acid blended with 5 wt.% of a poly(ethylene oxide)-*b*-poly(butylene oxide) and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) block copolymers.

FIGS 4(a)-(d) are representative TEM images of a blend featuring polylactic acid
5 blended with 5 wt.% of a poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) block copolymer.

FIG. 5 is a graph of stress v. strain for a blown film prepared from blends featuring polylactic acid blended with 2.5 wt.% of a poly(ethylene oxide)-*b*-poly(propylene oxide) block copolymer.

10 FIGS. 6(a)-(d) are representative TEM images of a blown film prepared from blends featuring polylactic acid blended with 2.5 wt.% of a poly(ethylene oxide)-*b*-poly(propylene oxide) block copolymer.

FIGS. 7(a)-(b) are representative TEM images of a blend featuring polylactic acid blended with 2.5 wt.% of a poly(ethylene oxide)-*b*-poly(butylene oxide) block
15 copolymer.

FIGS. 7(c)-(d) are representative TEM images of a blown film along the machine direction prepared from blends featuring polylactic acid blended with 2.5 wt.% of a poly(ethylene oxide)-*b*-poly(propylene oxide) block copolymer.

20 Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION

Thermoplastic blends are prepared that feature a thermoplastic polymer (“C”) matrix and an amphiphilic block copolymer (“A-B”). The block copolymer includes at least two blocks. One of the blocks (“A”) is miscible in the thermoplastic polymer matrix
25 and one of the blocks (“B”) is immiscible in the thermoplastic polymer matrix. The microstructure of the blend is characterized by a continuous phase that includes the thermoplastic polymer matrix (C) and the miscible block (A), and nanoscale-sized domains dispersed in the continuous phase that include the immiscible block (B).

Examples of suitable thermoplastic polymers and block copolymers that may be used to prepare blends having the above-described microstructure are those in which the thermoplastic polymer matrix (C) and a homopolymer of the miscible block (A) exhibit a negative χ ("chi") parameter when they are combined in the melt, i.e., $\chi(AC) < 0$. The measurement of a χ parameter can be conducted in several different ways. One approach is to isotopically label polymer A or C with deuterium and use Small Angle Neutron Scattering (SANS) techniques. Based on the Random Phase Approximation (RPA) theory, $\chi(AC)$ can be evaluated from the intermolecular component of the scattering from binary mixtures of A and C. Russell *et al.* clearly demonstrated the utility of SANS for measuring negative χ values for mixtures of poly(ethylene oxide) with protio- and deuterio-poly(meth methacrylate). H. Ito, T. P. Russell, G. D. Wignall, *Macromolecules*, 1987, 20, 2213-2220. An alternative to SANS are thermal measurement techniques based on the melting point depression of a crystalline phase in a miscible blend. Lin *et al.* estimated χ parameters for blends of poly-L-lactic acid and poly(ethylene glycol)s with different end groups. W. C. Lai, W. B. Liao, T. T. Lin, *Polymer*, 2004, 45, 3073-3080.

Specific examples of matrix/block copolymer combinations that can be used to prepare blends having the above-described microstructure include polyester matrix polymers and polyalkylene ether-based block copolymers. Examples of suitable polyesters include polyesters prepared from hydroxy-carboxylic acid monomers, including alpha-, beta-, and gamma-hydroxy carboxylic acid monomers. Specific examples include poly-L-lactic acid, poly-D-lactic acid, poly-D,L-lactic acid. Also suitable are polyacrylates and polymethacrylates, e.g., polyalkyl acrylates and methacrylates such as poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), and poly(ethyl methacrylate). The matrix polymer is generally brittle or has a glass transition temperature higher than 55°C. Its number average molecular weight generally exceeds 10^5 g/mol, higher than the associated entanglement molecular weight of that polymer and much higher than the block copolymer molecular weight. In addition, the matrix polymer typically is amorphous. In some embodiments, the matrix polymer has a crystallinity no greater than 10% or no greater than 5% by weight.

The block copolymer may be a diblock, linear triblock, linear tetrablock, or higher order multi-block structure. Also suitable are branched and starblock structures. The number average molecular weight of the block copolymer generally ranges from 1,000 to 30,000 (e.g., 3,000 to 20,000) g/mol. Representative examples include block copolymers in which one of the blocks is a polyalkylene ether that is miscible in the thermoplastic polymer matrix and one of the blocks is a different polyalkylene ether that is immiscible in the thermoplastic polymer matrix. Specific examples of suitable polyalkylene ether block copolymers include block copolymers in which the miscible block is polyethylene oxide, polypropylene oxide, or poly(ethylene-co-propylene oxide), and the immiscible block is polybutylene oxide, polyhexylene oxide, and polydodecylene oxide. For example, the first block may include polyethylene oxide and the second block may include polybutylene oxide. Other useful examples are described in U.S. 7,670,649, which is incorporated by reference in its entirety.

Additional examples of suitable block copolymers include block copolymers in which the matrix-immiscible block is a rubber (i.e. a homopolymer of the block has a glass transition temperature less than the use temperature). Examples that are particularly useful for blends in which the polyester matrix is derived from a hydroxyl carboxylic acid, e.g., a polylactide include poly(β -methyl-valerolactone) and other substituted poly(lactones), poly(isoprene), poly(butadiene), poly(dimethylsiloxane), poly(alkyl methacrylates) such as poly(n-butyl methacrylate), poly(alkyl acrylates) such as poly(butyl acrylate), and poly(ethylene-propylene).

Other examples of useful matrix-immiscible blocks include poly(ethylene), poly(styrene), poly(methyl methacrylate), and poly(propylene).

Additional examples of combinations of a miscible block and matrix polymer in which the block has a negative χ ("chi") parameter when they are combined in the melt, i.e., $\chi(AC) < 0$, including the following:

Poly(styrene)/poly(vinyl methyl ether (PS/PVME),
Poly(vinyl acetate)/poly(ethylene oxide (PVAc/PEO),
Poly(vinyl pyridine)/poly(hydroxystyrene) (PVP/PHS),
Poly(acrylic acid)/poly(vinyl pyridine) (PAA/PVP),

Poly(acrylic acid)/poly(ethylene oxide) (PAA/PEO),

Poly(vinyl sulfonic acid)/poly(vinyl pyridine) (PVSA/PVP), and

Poly(dimethylamino ethyl methacrylate)/poly(acrylic acid) (PDMAEM/PAA).

The pairs can be interchanged, i.e. the first member can serve as the A block and
5 the second member as the C matrix, or the first member can serve as the C matrix and the
second member as the A block.

The relative amounts of matrix polymer and block copolymer are selected to
maximize the toughening effect of the block copolymer while at the same time retaining a
microstructure featuring a continuous phase and dispersed nanoscale domains dispersed
10 throughout the continuous phase. In general, the block copolymer is present in an
amount no greater than 10% by weight based upon the weight of the blend. For example,
the block copolymer is present in an amount no greater than 5% by weight based upon
the weight of the blend, or no greater than 2.5% by weight based upon the weight of the
blend.

15 The blends may be prepared by either solvent blending or melt blending. In the
case of solvent blending, the matrix polymer and block copolymer are dissolved in a
mutually compatible solvent, after which the solvent is removed, e.g., by drying in a
vacuum oven. Examples of useful solvents for blends of polyesters and polyalkylene
oxide-based block copolymers include chloroform and acetone. In the case of melt
20 blending, the matrix polymer and block copolymer are combined in a twin-screw
extruder under an inert atmosphere (e.g., a nitrogen atmosphere) at a temperature
sufficiently high to melt the matrix polymer and block copolymer.

EXAMPLES

Example 1

25 Blends featuring polylactic acid polymer (Ingeo™ 2003D from NatureWorks
LLC) and a poly(ethylene oxide)-*b*-poly(butylene oxide) diblock copolymer (Fortegra™
100 from Dow Chemical) were prepared by dissolving the polylactic acid pellets and
block copolymer liquid in chloroform at room temperature with stirring for 24 hours. At
30 the end of the 24 hour period, the chloroform was removed by heating the sample in a

vacuum oven at 100°C). Samples were prepared containing 2.5 wt.%, 5 wt.%, and 10 wt.% of the copolymer based upon the total weight of the blend.

Following removal of the solvent, each sample was placed in a metal mold and annealed at 190°C for 3 minutes, followed by 2000 pounds hot press for 2 minutes. Each sample was then immediately water-cooled (approximately 60-70°C/minute) to room temperature.

TEM images of the blends containing 5 wt. % copolymer are shown in FIGS. 2(a)-(d).

Dogbone-shaped tensile bars were prepared from each sample and aged in a room temperature vacuum oven for 2 days prior to testing. The tensile strength of each bar as a function of strain was then measured according to ASTM D1708. The results are shown graphically in Figure 1, as well as in Table 1 set forth below.

TABLE 1: SUMMARY OF UNIAXIAL TENSILE TEST RESULTS

Copolymer Loading (wt.%)	Yield stress (MPa)	Elastic modulus (GPa)	Breaking strain (%)	Tensile Toughness (MJ/m ³)
0	51.5 ± 3.3	2.20 ± 0.03	7 ± 2	2.1 ± 0.9
2.5	29.9 ± 2.5	1.45 ± 0.08	143 ± 30	27.7 ± 3.8
5	28.1 ± 3.7	1.41 ± 0.06	175 ± 28	26.4 ± 4.1
10	21.0 ± 3.5	1.32 ± 0.06	221 ± 18	20.1 ± 1.0

Each value represents an average over at least five identical specimens. Elastic modulus was determined by fitting the first linear region of each curve. Tensile toughness was determined from the integrated area under the engineering stress-strain curve shown in Fig. 1, from the zero strain point to the breaking strain point.

The results demonstrate that the inclusion of the block copolymer causes large drops in both the yield stress ($> 40\%$) and elastic modulus ($> 30\%$) of the matrix polymer. At the same time, both the ductility (as measured by breaking strain) and toughness of the matrix polymer are significantly improved. For example, with a copolymer loading as low as 2.5 wt.%, the blend exhibits an approximately twenty-fold increase in breaking strain and greater than ten-fold increase in tensile toughness relative to the matrix polymer.

Example 2

Blends featuring polylactic acid polymer (Ingeo™ 2003D from NatureWorks LLC) and a poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer (Pluronic™ L10 from BASF) were prepared in a twin-screw batch mixer. The mixing process was conducted at 180°C with 200 rpm for 5 min under inert nitrogen gas. Samples were quenched in liquid nitrogen. Samples were prepared containing 5 wt.% of the copolymer based upon the total weight of the blend.

TEM images of the blends containing 5 wt. % copolymer are shown in FIGS. 4(a)-(d).

The preparation of dogbone tensile bars and the uniaxial tensile tests were performed in a similar fashion as described above. A comparison between the results of modified polylactic acids containing 5 wt.% Pluronic L10 and Fortegra 100 are shown graphically in Figure 3, as well as in Table 2 set forth below.

TABLE 2: COMPARISON OF UNIAXIAL TENSILE TEST RESULTS
BETWEEN FORTEGRA 100 AND PLURONIC L10

Copolymer Loading	Yield stress (MPa)	Elastic modulus (GPa)	Breaking strain (%)	Tensile Toughness (MJ/m ³)
0	51.5 ± 3.3	2.20 ± 0.03	7 ± 2	2.1 ± 0.9
5 wt.% Pluronic L10	29.4 ± 2.4	1.43 ± 0.08	136 ± 21	20.9 ± 4.0
5 wt.% Fortegra 100	28.1 ± 3.7	1.41 ± 0.06	175 ± 28	26.4 ± 4.1

Each value represents an average over at least five identical specimens. Elastic modulus was determined by fitting the first linear region of each curve. Tensile toughness was determined from the integrated area under the engineering stress-strain curve shown in Fig. 3, from the zero strain point to the breaking strain point.

5 The results demonstrate that the modification with two different block copolymers leads to similar mechanical properties. Pluronic L10 is as effective as Fortegra 100 in toughening PLA, giving a twentyfold increase in ductility and a tenfold increment in tensile toughness relative to the unmodified matrix polymer.

Example 3

10 This example describes the preparation of blown films.

Poly-D,L-lactic acid ("PDLLA) homopolymer (Ingeo™ 4060D from NatureWorks®), having a similar molecular weight and molecular weight distribution ($M_n = 118$ kg/mol, $\bar{D} = 1.89$), relative to the PLLA homopolymer (Ingeo™ 2003D) described in Example 1, was used. The only difference is that PDLLA cannot crystallize. For the
15 modifier, a poly(ethylene oxide)-*b*-poly(butylene oxide) diblock copolymer having the same chemical composition as the FORTEGRA-100® modifier described in Example 1 was used.

Blends of PDDL A and the block copolymer were prepared by melt-blending. In the melt-blending process, large sample batches (300 – 500 g) were created using a 16 mm
20 twin-screw extruder (PRISM, L:D 24:1, four heating zones at 180 °C and a feed zone at 140 °C, 40 rpm screw speed, 3.2 feeder screw speed). The mass flow rate and residence time distribution were measured to be 2 – 9 g/min and 2 – 7 min for all blends, respectively. Outlet pressure ranged from 50 – 160 psi and torques from 3 – 10 N·m. After steady state polymer flow was achieved, a syringe pump was used to dispense
25 liquid block copolymer modifier (diluted in acetone to reduce viscosity, roughly 50 wt.% block polymer solution) at a controlled rate. Extrudate was chilled in a water bath, dried by air blower, pelletized, and stored in a vacuum oven for at least 48 h before further processing.

Blown films were prepared from the pellets as follows.

Pellets with different loadings of block copolymer were fed into a lab scale extruder with a blown film die and attachment. The single-screw extruder had a diameter of 1 inch and a length of 25:1, L:D. The metering zone was 10:1, L:D and had a square pitch with a depth of 0.065 inch, a flight thickness of 0.14 inch and a helix angle of 17.7
5 degrees. The annular die had an outer diameter of 1 inch. The apparatus was operated under steady state conditions to maintain a stable bubble formation. The films produced were approximately 0.2 mm in thickness.

TEM images of blown films containing 2.5 wt.% block copolymer are shown in FIGS. 6(a)-(d). FIGS. 6(a) and 6(b) depict films stretched in the machine direction (MD),
10 i.e. the direction in which the films were stretched during the blown-film process, as denoted by the arrow in FIG. 6(a). FIGS. 6(c) and (d) depict films stretched in the transverse (TD) direction, i.e. the direction perpendicular to the machine direction.

TEM images of bulk compositions containing 2.5% block copolymer are shown in FIGS. 7(a)-(b). TEM images of blown films having the same composition stretched in
15 the machine direction are shown in FIGS. 7(c)-(d). FIGS. 7(c)-(d) show features (“micelles”) stretched and aligned along the machine direction.

A RSA-G2 solids analyzer (TA Instruments) was used for uniaxial tensile tests. A punch was used to prepare dog-bone samples with a total length of 25 mm, a gauge length of 6 mm, a width of 3.2 mm, and a thickness of approximately 0.2 mm. The dog-
20 bone specimens were aged at room temperature under vacuum to remove residual moisture for 48 h before testing. Samples were pulled at a rate of 0.1 mm/s until failure. The engineering stress ($\sigma = F/A_0$) was calculated from the measured force (F) and the initial cross-section area (A_0). Strain ($\epsilon = (\Delta l)/l_0$) was obtained from the change in grip-to-grip distance (Δl) and gauge length (l_0). Young’s modulus ($E = \sigma/\epsilon$) was determined
25 from the linear portion of the stress-strain curve. Toughness was taken as the area under the stress-strain curve. For each sample, the data reported are the average and standard deviation of at least five specimens.

The results of the tensile testing are shown graphically in FIG. 5, as well as in Table 3 set forth below. “4060” refers to the PDLLA alone. “MD” refers to films
30 stretched in the machine direction. “TD” refers to films stretched in the transverse

direction. Data for a compression-molded blend having the same chemical composition is also included in Table 3.

Table 3. Summary of the tensile properties of modified blown films.

Sample	E [MPa]	ϵ_b [%]	σ_b [MPa]	σ_{yield} [MPa]	Toughness MJ/m ³
Neat 4060D - MD	1280 ± 380	20 ± 13	18 ± 11	44 ± 11	5.6 ± 3.9
Neat 4060D - TD	1610 ± 300	5.9 ± 3.1	31 ± 15	2.9 ± 0.3	1.6 ± 1.1
Blend - MD	1380 ± 150	150 ± 30	12 ± 7	43 ± 4	46 ± 8
Blend - TD	1240 ± 160	60 ± 19	23 ± 4	29 ± 2	14 ± 4
Blend - Compression Molded, Fast Quench	1160 ± 290	49 ± 21	16 ± 6	41 ± 6	15 ± 8

5 As shown in Figure 5 and Table 3, in the MD, only 2.5 wt% block copolymer can impart a 700% increase in the breaking strain, and a 800% increase in the tensile toughness. Meanwhile, the tensile modulus and yield strength are not affected. There is a significant difference in the tensile properties for films in the machine direction (MD) and transverse direction (TD). As shown in Table 3, at the same block copolymer loading, films in MD have a toughness that is more than 300% higher than that of films in TD.

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

- 1 1. A thermoplastic blend comprising:
 - 2 (a) a thermoplastic polyester matrix and
 - 3 (b) an amphiphilic block copolymer comprising:
 - 4 (i) a first polyalkylene ether block that is miscible in the thermoplastic polymer
 - 5 matrix and
 - 6 (ii) a second polyalkylene ether block that is different from the first polyalkylene
 - 7 ether block and immiscible in the thermoplastic polymer matrix,
 - 8 the blend having a microstructure in the form of a continuous phase comprising
 - 9 the thermoplastic polyester matrix and nanoscale-sized domains comprising the second
 - 10 block dispersed in the continuous phase.
- 1 2. The blend of claim 1 wherein the polyester comprises units derived from a hydroxy
- 2 carboxylic acid.
- 1 3. The blend of claim 2 wherein the polyester is selected from the group consisting of
- 2 poly-L-lactic acid, poly-D-lactic acid, poly-D,L-lactic acid, and combinations thereof.
- 1 4. The blend of claim 1 wherein the first block of the block copolymer comprises a
- 2 polyalkylene ether selected from the group consisting of polyethylene oxide,
- 3 polypropylene oxide, and poly(ethylene-co-propylene oxide), and the second block of
- 4 the block copolymer comprises a polyalkylene ether selected from the group
- 5 consisting of polybutylene oxide, polyhexylene oxide, and polydodecylene oxide.
- 1 5. The blend of claim 1 wherein the first block of the block copolymer comprises
- 2 polyethylene oxide and the second block of the block copolymer comprises
- 3 polybutylene oxide.
- 1 6. The blend of claim 1 wherein the block copolymer is present in an amount no greater
- 2 than 10% by weight based upon the weight of the blend.

1 7. The blend of claim 1 wherein the block copolymer is present in an amount no greater
2 than 5% by weight based upon the weight of the blend.

1 8. The blend of claim 1 wherein the block copolymer is present in an amount no greater
2 than 2.5% by weight based upon the weight of the blend.

1 9. The blend of claim 1 wherein the blend has a tensile toughness that is at least 20
2 MJ/m³.

1 10. The blend of claim 1 wherein the blend has a tensile toughness that is at least 10
2 times higher than the tensile toughness of the thermoplastic polyester matrix alone.

1 11. The blend of claim 1 wherein the blend has a breaking strain that is at least 3 times
2 higher than the breaking strain of the thermoplastic polyester matrix alone.

1 12. The blend of claim 1 wherein the blend has a breaking strain that is at least 5 times
2 higher than the breaking strain of the thermoplastic polyester matrix alone.

1 13. The blend of claim 1 wherein the blend has a breaking strain that is at least 10 times
2 higher than the breaking strain of the thermoplastic polyester matrix alone.

1 14. The blend of claim 1 wherein the blend is transparent to visible light.

1 15. A thermoplastic blend comprising:

2 (a) a thermoplastic polymer matrix selected from the group consisting of poly-L-
3 lactic acid, poly-D-lactic acid, poly-D,L-lactic acid, and combinations thereof; and

4 (b) no greater than 10% by weight, based upon the weight of the blend, of an
5 amphiphilic block copolymer comprising:

6 (i) a polyethylene oxide block that is miscible in the thermoplastic polymer matrix
7 and

8 (ii) a polybutylene oxide block that is immiscible in the thermoplastic polymer
9 matrix,

the blend having a microstructure in the form of a continuous phase comprising the thermoplastic polymer matrix and nanoscale-sized domains comprising the second block dispersed in the continuous phase,

wherein the blend has a breaking strain that is at least 20 times higher than the breaking strain of the thermoplastic polymer matrix alone and a tensile toughness that is at least 10 times higher than the tensile toughness of the thermoplastic polymer matrix alone.

16. A thermoplastic blend comprising:

(a) a thermoplastic polymer matrix and

(b) an amphiphilic block copolymer comprising:

(i) a first block that has a negative Flory-Huggins interaction parameter (χ) with the thermoplastic polymer matrix and

(ii) a second block that is immiscible in the thermoplastic polymer matrix, the blend having a microstructure in the form of a continuous phase comprising the thermoplastic polymer matrix and nanoscale-sized domains comprising the second block dispersed in the continuous phase,

wherein the thermoplastic polymer matrix and first block are selected such that when the thermoplastic polymer and a homopolymer of the first block are combined in a melt, they exhibit a negative χ ("chi") parameter.

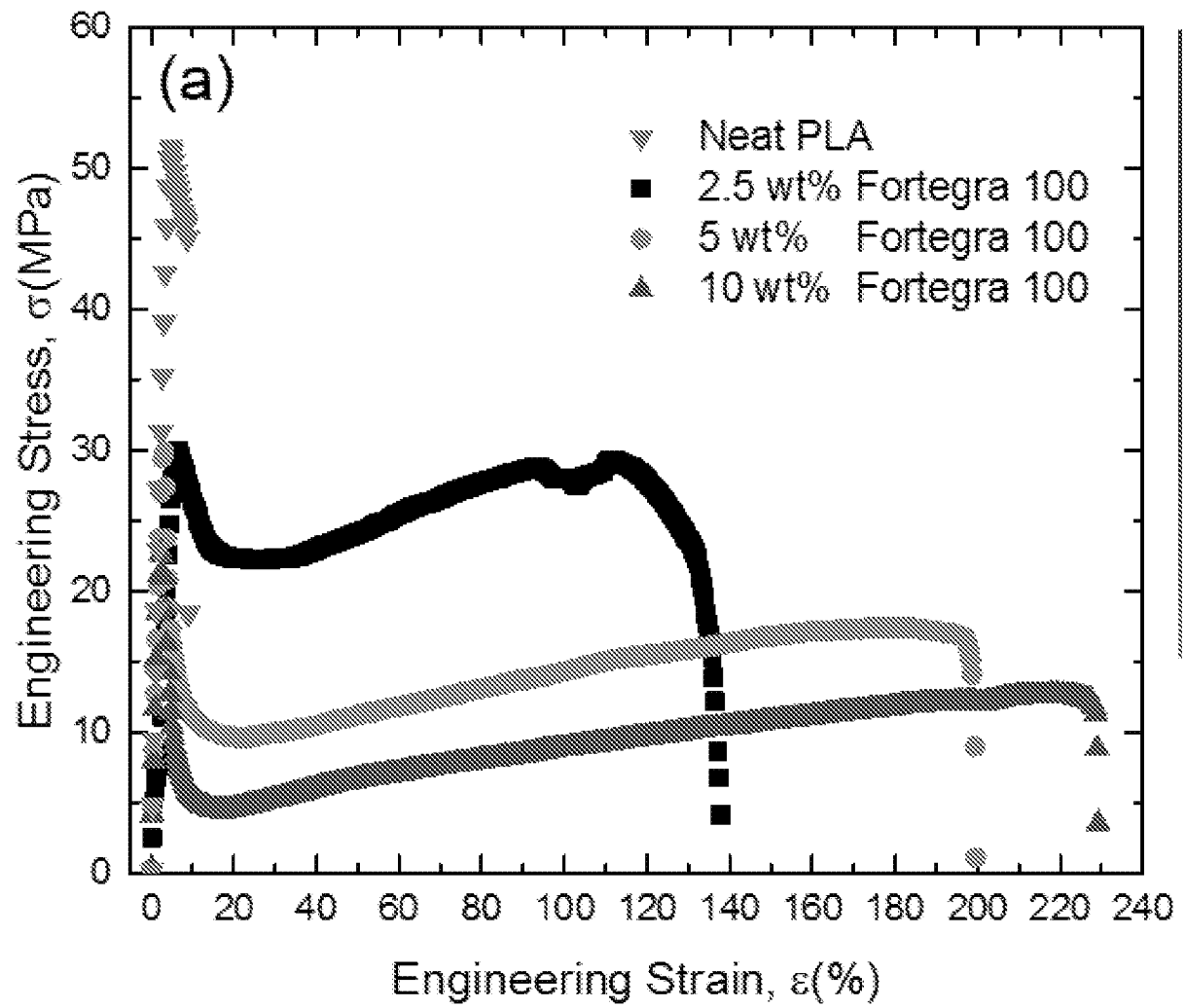


FIG. 1

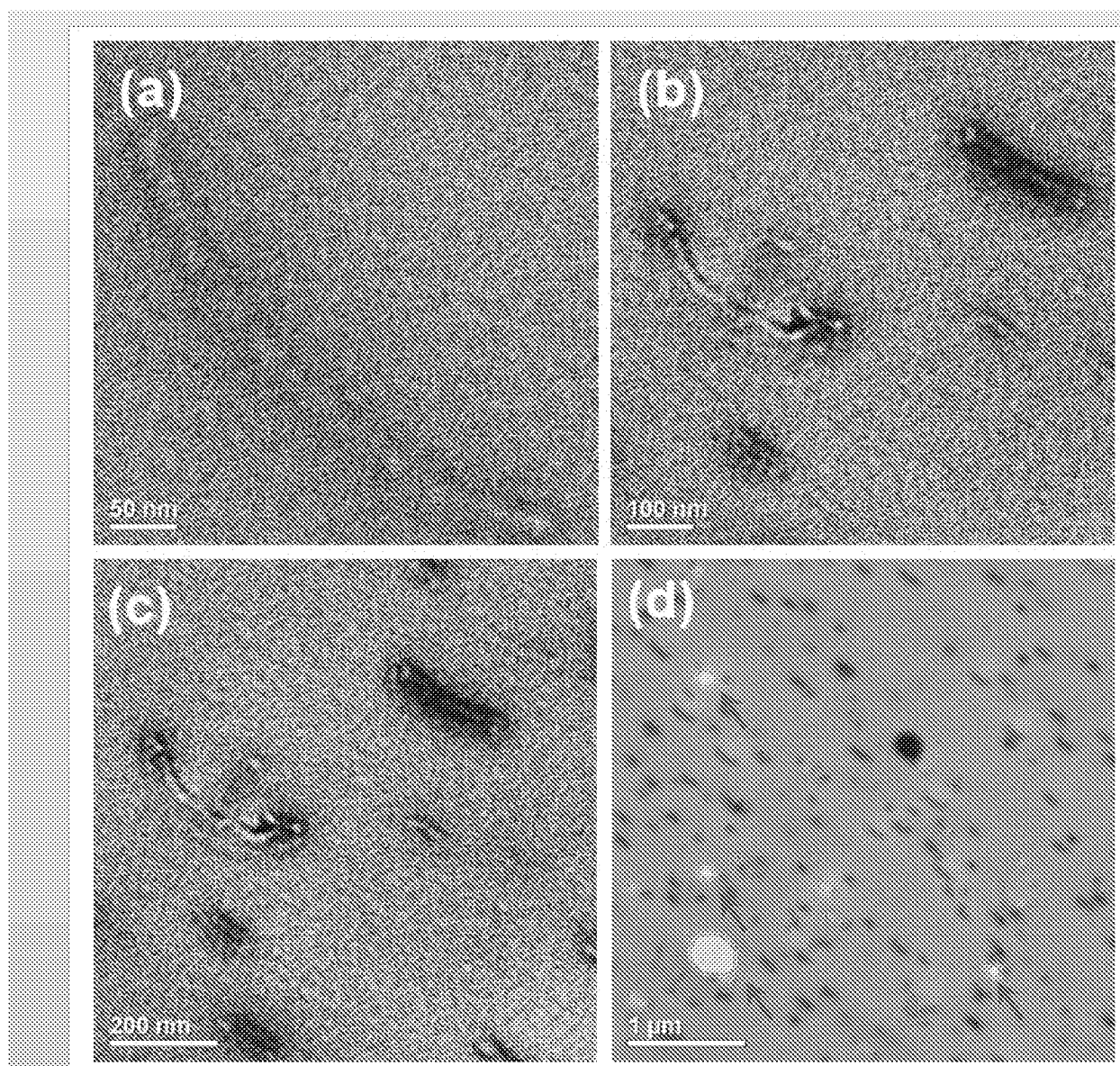


FIG. 2

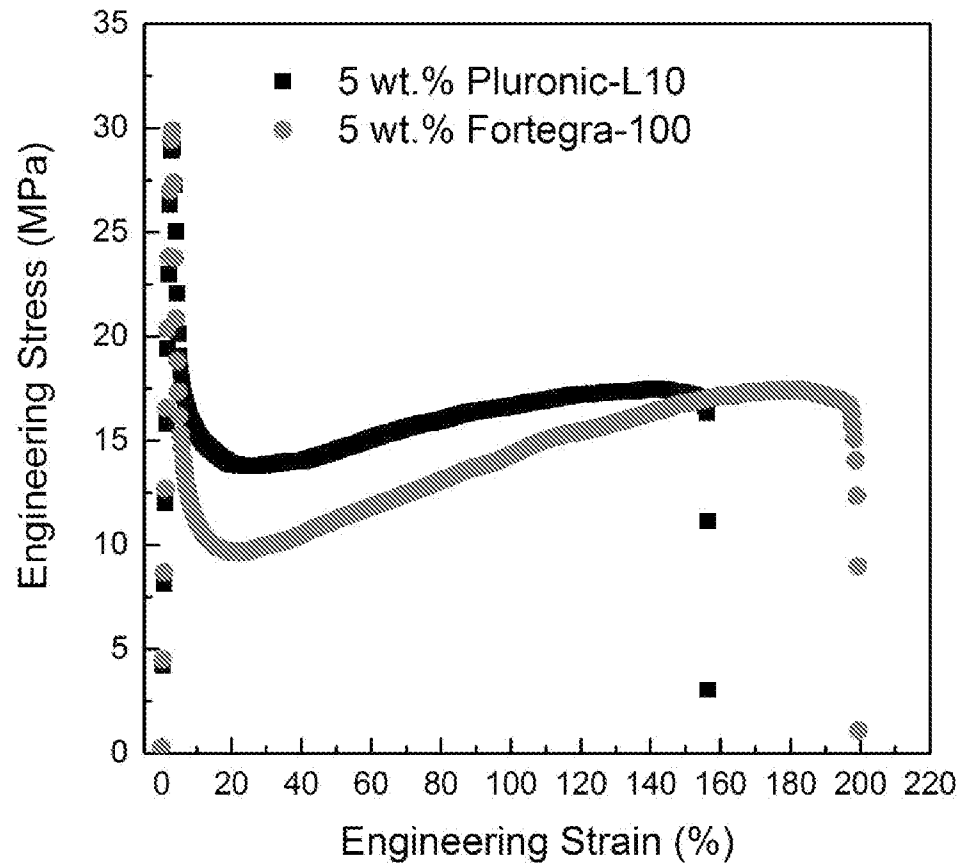


FIG. 3

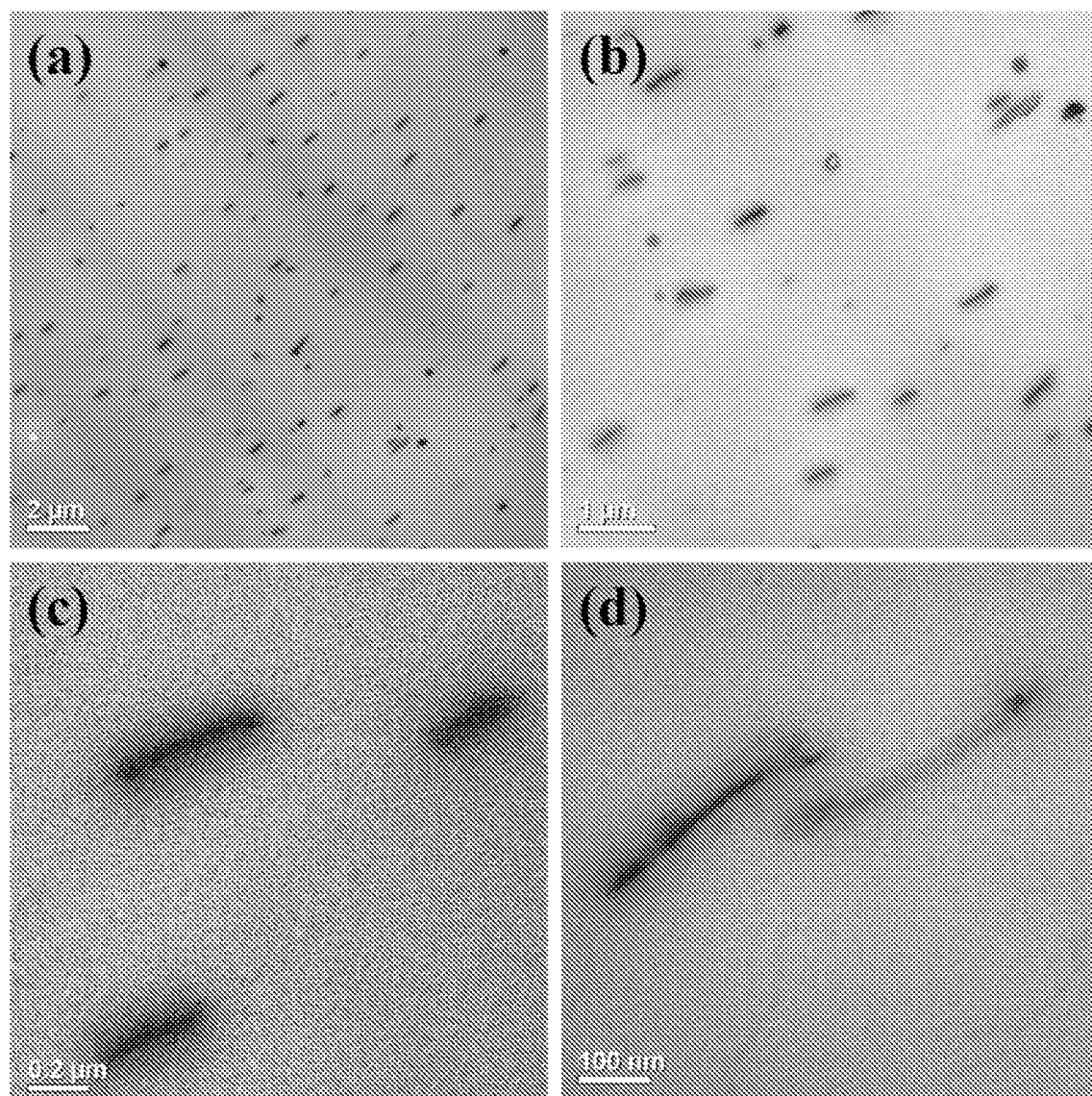


FIG. 4

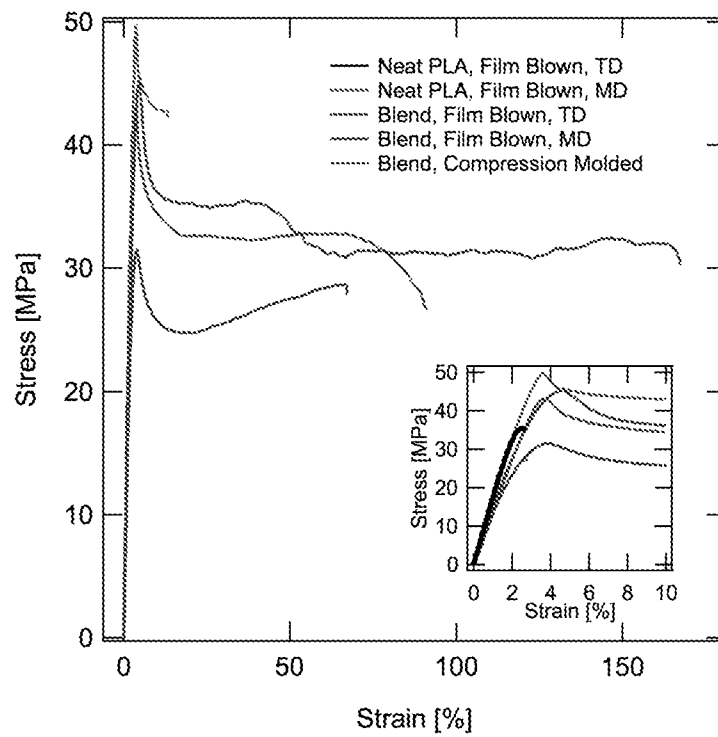


FIG. 5

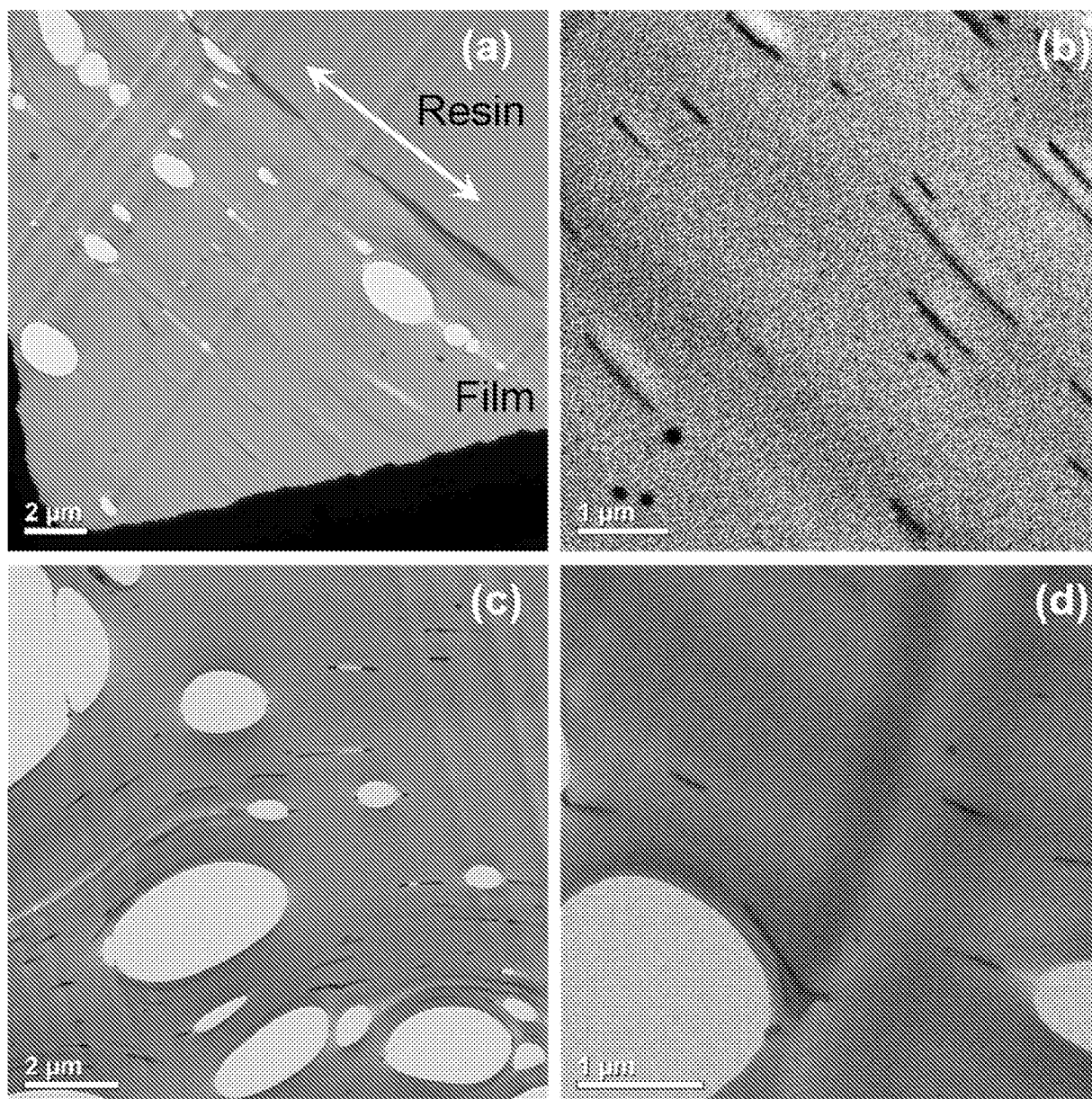


FIG. 6

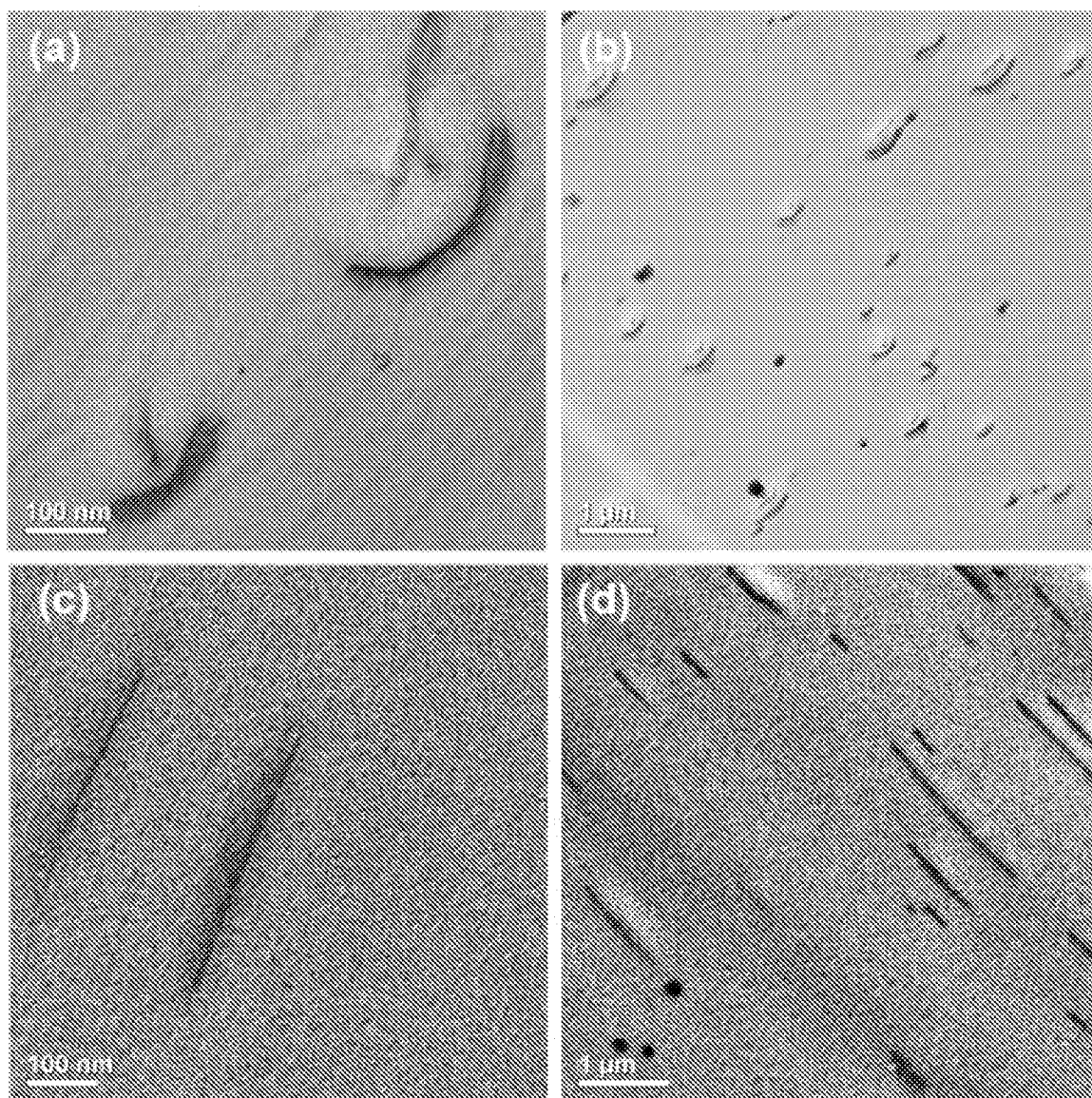


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/30354

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08L 53/00; C08L 67/04; C08L 71/02 (2016.01)

CPC - C08L 53/00; C08L 67/04; C08L 71/02; B29K 2067/046; B29K 2071/02; C08G 2261/126

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C08L 53/00; C08L 67/04; C08L 71/02 (2016.01)

CPC: C08L 53/00; C08L 67/04; C08L 71/02; B29K 2067/046; B29K 2071/02; C08G 2261/126

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 525/55; 525/64; 525/69

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

Google Scholar, Google Patents, PatBase

Keywords used: polyester, polylactic acid, thermoplastic, thermosoft, matrix, block copolymer, polyethylene oxide, polyethylene glycol, polybutylene oxide, nano, micro, disperse

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2007/0265373 A1 (Bates et al.) 15 November 2007 (15.11.2007); para [0001], para [0016], para [0017], para [0025], para [0035], para [0047], see table 2, comparative example B and example 4, table 3 comparative example D and examples 7 and 8	1; 4-13 ----- 2-3; 14-15
X --- Y	US 2013/0210983 A1 (Topolkaraev et al.) 15 August 2013 (15.08.2013); entire document, but especially: para [0003], para [0021], para [0039]	16 ----- 2-3; 14-15
X -- A	US 2009/0239433 A1 (Kurihara et al.) 24 September 2009 (24.09.2009); entire document, but especially: para [0012], para [0013], para [0025], para [0028], para [0144]	16 ----- 1-15
A	US 4,753,980 A (Deyrup) 28 June 1988 (28.06.1988); entire document, but especially: col 2 lines 4-10	1-16
A	Sinturel et al. "Nanostructured Polymers Obtained from Polyethylene-block-poly(ethylene oxide) Block Copolymer in Unsaturated Polyester" Macromolecules, Vol 40 Issue 7 (15 February 2007): pages 2532-2538; entire document, but especially: abstract, conclusion	1-16
A	US 5,393,837 A (Kinoshita et al.) 28 February 1995 (28.02.1995); entire document	1-16

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 June 2016 (16.06.2016)

Date of mailing of the international search report

29 AUG 2016

Name and mailing address of the ISA/US

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