Title: PROCESS FOR THE PRODUCTION OF POLYESTER NANO COMPOSITE SITES AND SHAPED ARTICLES MADE THEREOF

Abstract: Polyester nanocomposites with improved mechanical properties are prepared by melt-compounding a mixture of fibrous clay, sodium salt, optionally at least one linear polyester oligomer, and at least one polyester polymer; and, optionally, subjecting the nanocomposite composition to solid state polymerization to increase polyester molecular weight. The polyester nanocomposites can also be prepared from a melt-compounded masterbatch, containing a greater concentration of fibrous clay than is desired in the final resin composition.
PROCESS FOR THE PRODUCTION OF POLYESTER NANOCOMPOSITES AND SHAPED ARTICLES MADE THEREOF

FIELD OF THE INVENTION

The present disclosure relates to methods of forming polyester nanocomposites comprising a fibrous clay nanofiller and a polyester.

BACKGROUND OF THE INVENTION

Nanocomposites are polymers reinforced with nanometer sized particles, i.e., particles with a dimension on the order of 1 to several hundred nanometers.

Polymer-layered silicate nanocomposites incorporate a layered clay mineral filler in a polymer matrix. Layered silicates are made up of several hundred thin platelet layers stacked into an orderly packet known as a tactoid. Each of these platelets is characterized by a large aspect ratio (diameter/thickness on the order of 100-1,000). Accordingly, when the clay is dispersed homogeneously and exfoliated as individual platelets throughout the polymer matrix, dramatic increases in strength, flexural and Young's modulus, and heat distortion temperature are observed at very low filler loadings (<10% by weight) because of the large surface area contact between polymer and filler. In addition, barrier properties are greatly improved because the large surface area of the platelets greatly increases the tortuosity of the path a diffusing species must follow in permeating through the polymeric material.

Co-pending U. S. Patent Application Publication 20080315453, herein incorporated by reference in its entirety, discloses a method for dispersing fibrous clay particles in a polyester matrix by melt-compounding a mixture of: fibrous clay, at least one linear polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition; and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase polyester molecular weight. Further described is a method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: fibrous clay, at
least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition containing a greater concentration of fibrous clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.

A process is desired for producing polyester/fibrous clay nanocomposite materials with improved mechanical properties.

**SUMMARY OF THE INVENTION**

The invention is directed a method for preparing a polyester nanocomposite, comprising melt-mixing a mixture of:

a. fibrous clay,

b. at least one sodium salt

c. optionally, at least one linear polyester oligomer, and
d. at least one polyester polymer

to produce a nanocomposite composition; and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase polyester molecular weight.

The invention is further directed to a method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: fibrous clay, at least one sodium salt, optionally at least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition containing a greater concentration of fibrous clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.

**DETAILED DESCRIPTION OF THE INVENTION**

In the context of this disclosure, a number of terms shall be utilized.
As used herein, the term "nanocomposite" or "polymer nanocomposite" means a polymeric material which contains particles, dispersed throughout the polymeric material, having at least one dimension in the 0.1 to 100 nm range ("nanoparticles"). The polymeric material in which the nanoparticles are dispersed is often referred to as the "polymer matrix." The term "polyester composite" refers to a nanocomposite in which the polymeric material includes at least one polyester.

As used herein, the term "fibrous clay" refers to naturally-occurring and synthetic clays which are predominantly characterized by long, slender fibers (which can be hollow), as opposed to plates or grainy structures.

The term "exfoliate" literally refers to casting off in scales, laminae, or splinters, or to spread or extend by or as if by opening out leaves. In the case of smectic clays, "exfoliation" refers to the separation of platelets from the smectic clay and dispersion of these platelets throughout the polymer matrix. As used herein, for fibrous clays, "exfoliation" or "exfoliated" means the separation of fiber bundles or aggregates into nanometer diameter fibers which are then dispersed throughout the polymer matrix.

As used herein, the term "TSPP" means tetrasodium pyrophosphate. "TSPP decahydrate" refers specifically to Na₄P₂O₇·10H₂O. TSPP is also available in an anhydrous form, Na₄P₂O₇.

As used herein, "polyester" means a condensation polymer in which more than 50 percent of the groups connecting repeat units are ester groups. Thus polyesters may include polyesters, poly(ester-amides) and poly(ester-imides), so long as more than half of the connecting groups are ester groups. Preferably at least 70% of the connecting groups are esters, more preferably at least 90% of the connecting groups are ester, and especially preferably essentially all of the connecting groups are esters. The proportion of ester connecting groups can be estimated to a first approximation by the molar ratios of monomers used to make the polyester.
As used herein, "PET" means a polyester in which at least 80, more preferably at least 90, mole percent of the diol repeat units are from ethylene glycol and at least 80, more preferably at least 90, mole percent of the dicarboxylic acid repeat units are from terephthalic acid.

As used herein, "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

As used herein, "linear polyester oligomer" means oligomeric material, excluding macrocyclic polyester oligomers, which by itself or in the presence of monomers can polymerize to a higher molecular weight polyester.

As used herein, "polyester component" refers to the total of all polyester moieties present in the nanocomposite, i.e., linear oligomers plus polymer(s).

As used herein, "resin" means a composition comprising a polymer and at least one additional ingredient (for example, a filler, flame retardant, toughener, plasticizer, etc.).

As used herein, the term "melt mixing" means applying shear stress to a melt to mix the ingredients comprising the melt. One or more ingredients (e.g., clay, glass fiber) may remain unmelted during the melt mixing process as long as at least one ingredient is molten. The terms "melt mixing," "compounding," and "melt compounding" as used herein are synonymous.

As used herein, the term "dry blend" means to mix together unmelted ingredients, typically prior to melt mixing.

As used herein, the term "staged feeding" indicates that ingredients are separately fed at different stages of a melt mixing process. For example, two different ingredients may be fed into one feed port of an extruder and a third ingredient into a second feed port downstream of the first one.

As used herein, the term "split feeding" indicates that the total amount of an ingredient has been split into two or more portions and the portions are separately fed at different stages of a melt mixing process. For example, an ingredient may be split into three portions, each of which
is fed into a different feed port of an extruder. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

One aspect of the invention described herein is directed to a method for preparing a polyester nanocomposite, comprising melt-compounding a mixture of: fibrous clay, at least one sodium salt, optionally at least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition; and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight.

Another aspect of the invention described herein is a method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: fibrous clay, at least one sodium salt, optionally at least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition containing a greater concentration of fibrous clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.

Preparing the Polyester Nanocomposite

Fibrous Clays

The nanocomposite composition contains about 0.1 to about 40 wt% of fibrous clay. Fibrous clays include naturally-occurring and synthetic clays which are predominantly characterized by long, slender fibers (which can be hollow), as opposed to plates or grainy structures. The individual fibers generally range from about 0.2 to 5 micrometers in length and have a diameter ranging from about 5 to 200 nanometers. Such fibrous clays generally occur as aluminosilicates, magnesium silicates and aluminomagnesium silicates. Examples of fibrous clays
include but are not limited to: attapulgite (palygorskite), sepiolite, halloysite, endellite, chrysotile asbestos, and imogolite. Sepiolite and attapulgite, separately or as a mixture, are attractive because of a combination of high length-to-diameter ratio, ready availability, and low cost.

Sepiolite [Mg₄Si₆O₁₅(OH)₂·G(H₂O)] is a hydrated magnesium silicate filler that exhibits a high aspect ratio due to its fibrous structure. Unique among the silicates, sepiolite is composed of long lath-like crystallites in which the silica chains run parallel to the axis of the fiber. The material has been shown to consist of two forms, an α and a β form. The α form is known to be long bundles of fibers and the β form is present as amorphous aggregates.

Attapulgite (also known as palygorskite) is almost structurally and chemically identical to sepiolite except that attapulgite has a slightly smaller unit cell. As used herein, the term "fibrous clay" includes attapulgite as well as sepiolite itself.

Fibrous clays are layered fibrous materials in which each layer is made up of two sheets of tetrahedral silica units bonded to a central sheet of octahedral units containing magnesium ions (see, e.g., Figures 1 and 2 in L. Bokobza et al., Polymer International, 53, 1060-1 065 (2004)). The fibers stick together to form fiber bundles, which in turn can form agglomerates. These agglomerates can be broken apart by industrial processes such as micronization or chemical modification (see, e.g., European Patent 170,299 to Tolsa, S.A.) to produce nanometer diameter fibers, i.e., exfoliated fibrous clay.

The amount of fibrous clay used in the present invention ranges from about 0.1 to about 40 wt% based on the fibrous clay and polyester component of the composition. The specific amount chosen will depend on the intended use of the nanocomposite, as is well understood in the art.

Fibrous clays are available in a high purity ("rheological grade"), uncoated form (e.g., PANGEL® S9 sepiolite clay from the Tolsa Group, Madrid, Spain) or, more commonly, treated with an organic material to make the clay more "organophilic," i.e., more compatible with systems of low-to-medium polarity (e.g., PANGEL® B20 sepiolite clay from the Tolsa
An example of such a coating for fibrous clay is a quaternary ammonium salt such as dimethylbenzylalkylammonium chloride, as disclosed in European Patent Application 221,225.

The fibrous clay used in the process described herein is typically unmodified; i.e., the surface of the fibrous clay has not been treated with an organic compound (such as anonium compound, for example, to make its surface less polar). Such onium compounds tend to degrade at the temperatures used to process polyesters such as PET.

In an embodiment, the fibrous clay is rheological grade, such as described in European patent applications EP-A-0454222 and EP-A-0170299 and marketed under the trademark Pangel® by Tolsa, S.A., Madrid, Spain. As described therein, "rheological grade" denotes a fibrous clay with a specific surface area greater than 120 m²/g (N₂, BET), and typical fiber dimensions: 200 to 2000 nm long, 10-30 nm wide, and 5-10nm thick.

Rheological grade sepiolite is obtained from natural sepiolite by means of special micronization processes that substantially prevent breakage of the sepiolite fibers, such that the sepiolite disperses easily in water and other polar liquids, and has an external surface with a high degree of irregularity, a high specific surface, greater than 300 m²/g and a high density of active centers for adsorption, that provide it a very high water retaining capacity upon being capable of forming, with relative ease, hydrogen bridges with the active centers. The microfibrous nature of the rheological grade sepiolite nanoparticles makes sepiolite a material with high porosity and low apparent density.

Additionally, rheological grade sepiolite has a very low cationic exchange capacity (10-20 meq/1 00 g) and the interaction with electrolytes is very weak, which in turn causes rheological grade sepiolite not to be practically affected by the presence of salts in the medium in which it is found, and therefore, it remains stable in a broad pH range.

The above-mentioned qualities of rheological grade sepiolite can also be attributed to rheological grade attapulgite with particle sizes smaller than 40 microns, such as for example the range of ATTAGEL.
goods (for example ATTAGEL 40 and ATTAGEL 50) manufactured and marketed by the firm Engelhard Corporation, United States, and the MIN-U-GEL range of Flohdin Company.

Typically, the amount of fibrous clay used in the present invention ranges from about 0.1 to about 40 wt% based on the fibrous clay and polyester component of the composition. The specific amount chosen will depend on the intended use of the nanocomposite composition, as is well understood in the art. For example, in film, it may be advantageous to use as little fibrous clay as possible, so as to retain desired optical properties.

The method described herein is particularly useful in preparing "masterbatches" of the nanocomposite composition, which contain relatively high concentrations of fibrous clay, typically 15 to 30 wt%. The masterbatch can then be mixed with additional polyester (let down), and optionally other ingredients to produce a resin composition that contains a desired lower concentration of fibrous clay. Let-down ratios are selected so that the desired level of dispersed filler particles is present in the final product. For example, a nanocomposite composition masterbatch containing 30% by weight of the fibrous clay may be used. Then, if a composition having 3 weight percent of the fibrous clay is needed, the composition containing the 3 weight percent may be made by melt mixing 1 part by weight of the 30% masterbatch with 9 parts by weight of the "pure" polyester, i.e., a let-down ratio of 9 parts additional polymer to 1 part masterbatch. A let-down weight ratio of from about 0.5-20 parts of additional polymer or polymerizable material to 1 part masterbatch, especially about 1-1 0:1 or even about 2-6:1 is often convenient. This is conveniently done by melting the components and mixing them, or by forming a dry blend followed by heating and melt mixing. During melt mixing, other ingredients can also be added to form a final desired composition.

The amount of fibrous clay in the nanocomposite is preferably about 0.1 to about 35 wt% based on the weight of fibrous clay plus polyester component. In some embodiments, the, fibrous clay is present
in the amount between (and optionally including) any two of the following weight percentages: 0.1, 5, 10, 15, 20, 25, 30, 35 and 40.

**Sodium salt**

At least one sodium salt is added in an amount ranging from about 0.5 to about 12 wt% based on the weight of fibrous clay, where "wt% based on the weight of fibrous clay" is defined as 100 times the weight of sodium salt divided by the weight of fibrous clay; e.g., 4 grams sodium salt plus 50 grams fibrous clay would be 2 wt% sodium salt based on the weight of fibrous clay. In some embodiments, the sodium salt is present in the amount between (and optionally including) any two of the following weight percentages: 0.5, 1, 3, 5, 7, 9, 11, and 12 weight percent of the weight of the fibrous clay. Examples of suitable sodium salts include without limitation: tetrasodium pyrophosphate ("TSPP"), trisodium phosphate ("TSP", Na₃PO₄), sodium carbonate (Na₂CO₃), and mixtures thereof. The TSPP may be the anhydrous form, Na₄P₂O₇ [CAS Reg. No. 7722-88-5], or the hydrated form, "TSPP decahydrate," Na₄P₂O₇·10H₂O [CAS Reg. No. 13472-36-1]. It may be used as-received (flake) or ground to a powder as desired.

**Polyesters**

Linear polyester oligomers and polyester polymers suitable for use in the process described herein are described below. The molecular weight of the polyester polymer will depend on the eventual use of the final composition. Typically, the number average molecular weight (Mₙ) will be from about 12,000 to about 50,000.

Linear polyester oligomers include, for example, oligomers of linear polyesters and oligomers of polymerizable polyester monomers. For example, reaction of dimethyl terephthalate or terephthalic acid with ethylene glycol, when carried out to remove methyl ester or carboxylic groups, usually yields a mixture of bis(2-hydroxyethyl) terephthalate and a variety of oligomers: oligomers of bis(2-hydroxyethyl) terephthalate, oligomers of mono(2-hydroxyethyl) terephthalate (which contain carboxyl groups), and polyester oligomers capable of being further extended. Typically, such oligomers will have an average degree of polymerization...

Linear polyester oligomers obtained by these processes are likely to have a broad molecular weight distribution and to contain measurable amounts of monomeric species. Linear polyester oligomer could also be produced in situ in the process described herein by adding monomeric species (e.g., ethylene glycol, bis-hydroxyterephthalic acid) to a mixture of polyester polymer and fibrous clay and then melt mixing.

Polyesters (which have mostly or all ester linking groups) are normally derived from one or more dicarboxylic acids and one or more diols. They can also be produced from polymerizable polyester monomers or from macrocyclic or linear polyester oligomers as described in copending U. S. Patent Application 11/31 2068 herein incorporated by reference in its entirety.

Polyesters for use in practicing the invention described herein may be amorphous, crystalline, semicrystalline, anisotropic (i.e., liquid crystalline), or isotropic or may contain a mixture of these morphologies. Polyesters most suitable for use in practicing the invention comprise isotropic thermoplastic polyester homopolymers and copolymers (both block and random).
The production of polyesters from reaction mixtures containing diols and hydrocarbyl diacids or esters of such diacids is well known in the art, as described by A. J. East, M. Golden, and S. Makhija in the *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, J. r.

Kroschwitz exec. ed., M. Howe-Grant, ed., 4th edition (1996), vol. 19, 609-653. Among suitable diacids (and their corresponding esters) are those selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acids, cyclohexane dicarboxylic acids, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, fumaric acid, maleic acid, and the derivatives thereof, such as, for example, the dimethyl, diethyl, or dipropyl esters.

Some representative examples of glycols that can be utilized as the diol component include ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propane diol, 2,2-dimethyl-1,3-propane diol, 2-ethyl-2-butyl-1,3-propane diol, 2-ethyl-2-isobutyl-1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 2,2,4-trimethyl-1,6-hexane diol, 1,2-cyclohexane dimethanol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, isosorbide, naphthalene glycols, biphenols, diethylene glycol, theethylene glycol, resorcinol, hydroquinone, t-butyl-hydroquinone, and longer chain diols and polyols, such as pollytetramethylene ether glycol, which are the reaction products of diols or polyols with alkylene oxides. Alkyl-substituted and chloro-substituted versions of these species may also be used.

Polyesters suitable for use in the present invention can also be produced directly from reaction mixtures containing polymerizable polyester monomers. Some representative examples of said polymerizable polyester monomers hydroxyacids such as hydroxybenzoic acids, hydroxynaphthoic acids and lactic acid; bis(2-hydroxyethyl)terephthalate, bis(4-hydroxybutyl)terephthalate, bis(2-hydroxyethyl)naphthalenedioate, bis(2-hydroxyethyl)isophthalate, bis[2-(2-hydroxyethoxy)ethyl]terephthalate, bis[2-(2-hydroxyethoxy)ethyl]isophthalate, bis[(4-
hydroxymethylcyclohexyl)ethyl]terephthalate, and bis[(4-hydroxymethylcyclohexyl)ethyl]isophthalate, mono(2-hydroxyethyl)terephthalate, bis(2-hydroxyethyl)sulfoisophthalate, and lactide. Alkyl-substituted and chloro-substituted versions of these species may also be used.

Polyester polymers can also be produced directly from reaction mixtures containing macrocyclic polyester oligomers. Examples of suitable macrocyclic polyester oligomers include without limitation macrocyclic polyester oligomers of 1,4-butylene terephthalate (CBT); 1,3-propylene terephthalate (CPT); 1,4-cyclohexylenedimethylene terephthalate (CCT); ethylene terephthalate (CET); 1,2-ethylene 2,6-naphthalenedicarboxylate (CEN); the cyclic ester dimer of terephthalic acid and diethylene glycol (CPEOT); and macrocyclic co-oligoesters comprising two or more of the above structural repeat units. Alkyl-substituted and chloro-substituted versions of these species may also be used.

The polyesters may be branched or unbranched, and may be homopolymers or copolymers or polymeric blends comprising at least one such homopolymer or copolymer.

Examples of specific polyesters include without limitation poly(ethylene terephthalate) (PET), poly(1,3-propylene terephthalate) (PPT), poly(1,4-butylene terephthalate) (PBT), a thermoplastic elastomeric polyester having poly(1,4-butylene terephthalate) and poly(tetramethylene ether)glycol blocks (available as HYTREL® from E. I. du Pont de Nemours & Co., Inc., Wilmington, DE 19898 USA), poly(1,4-cyclohexyldimethylene terephthalate) (PCT), and polylactic acid (PLA).

The polyester component is about 0 to about 99 wt% linear oligomer and about 100 to about 1 wt% polyester polymer. In some embodiments, the linear oligomer is present in the amount between (and optionally including) any two of the following weight percentages of the polyester component: 0, 5, 10, 13, 15, 17, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 99. In some embodiments, the polyester polymer is present in the amount between (and optionally
including) any two of the following weight percentages of the polyester component: 100, 95, 90, 87, 85, 83, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, and 1.

Melt-mixing Process Conditions

In the process described herein, a mixture is formed comprising fibrous clay, at least one sodium salt, at least one polyester polymer, and optionally at least one linear polyester oligomer. The mixture is melt-mixed (i.e., a shear stress is applied to the molten mixture) and, optionally, subjected to solid phase polymerization to raise the polyester molecular weight. Process equipment typical for melt-mixing thermoplastics in a batchwise or continuous fashion may be used. Examples of such equipment include without limitation kneaders (e.g., a Buss Co-Kneader from Buss AG, Pratteln, Switzerland), extruders (single screw, twin-screw, multi-screw), Banbury® Mixers, Farrel® Continuous Mixers (Banbury® and Farrel® are registered trademarks of Farrel Corporation, Ansonia, Connecticut, USA), and the like. Twin-screw extruders, such as ZSK machines from Werner & Pfleiderer (now part of Coperion Werner & Pfleiderer GmbH & Co. KG, Stuttgart, Germany) are commonly used. For processing using a twin-screw extruder, the screw design encompasses the typical polyester processing operations of conveying, melting, mixing, homogenization, dispersion, devolatilization (i.e., off-gassing), stranding, and peptization. The optimum mixing intensity depends on the configuration of the mixer, the temperatures, compositions, etc. being mixed, and is readily determined by one skilled in the art.

The ingredients of the nanocomposite may be introduced to an extruder in a number of different ways. A mixture of the ingredients may be fed at once into a rear feed port. In some embodiments, separate ingredients may be fed into separate feed ports ("staged feeding"; for example, one ingredient fed into one port, two other ingredients into a second). In other embodiments, feeds of any single component (linear polyester oligomer, polyester polymer, fibrous clay, sodium salt, optional ingredients) may be split into two or more streams and fed into multiple
feed ports ("split feeding"). In yet other embodiments, both staged feeding and split feeding processes may be used.

In another embodiment, two or more extruders in series can be employed, each to perform one or more compounding steps. Alternatively, some or all of the extruded composition, also, known as "output" of an extruder can be re-fed one or more times through the same extruder to produce the final composition.

Extrusion conditions are adjusted depending on the specific composition, i.e., specific materials and relative amounts. For example, extrusion temperatures may need to be adjusted to maintain adequate melt strength depending on the concentration of linear polyester oligomer and whether the oligomer is solid or molten when added. Such considerations are well-understood by a practitioner of the art and can readily be adapted for different compositions.

The molecular weight of the polymer material in the resulting nanocomposite may be increased by any of a number of known approaches, or by a combination of any of these approaches, e.g., chain extension, reactive extrusion, extrusion let-down, solid state polymerization or annealing, annealing under a flow of inert gas, vacuum annealing, let-down in a melt reactor, etc. The productivity of such processes for increasing molecular weight is enhanced by the presence of the end groups on the linear polyester oligomer. Solid state polymerization ("SSP," also referred to as "solid phase polymerization") is typically used (see, e.g., A. East, "Polyesters, Thermoplastic," *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, A. Seidel ed., 5th edition, vol. 20, 31-95 (2006)).

Optional ingredients to be melt-mixed with the nanocomposite composition

Nanocomposites may contain additional ingredients, including but not limited to stabilizers, antioxidants, tougheners, pigments, other fillers, plasticizers, lubricants, mold release agents, flame retardants, and other polymers.
Nanocomposite compositions containing ingredients in addition to polyester and fibrous clay can be prepared in a variety of ways. A polyester nanocomposite masterbatch with a high concentration of fibrous clay could be prepared using the process described herein, then let down by melt mixing with additional polyester, then melt mixed with the desired added ingredients (process A). Alternatively, and more economically, the masterbatch could simply be melt-mixed with the additional polyester and desired additional ingredients at once (process B). In another variation (process C), a polyester nanocomposite could be prepared at the desired final fibrous clay concentration and melt-mixed in a separate step with the desired additional ingredients, or (process D) the final composition could be prepared by including all ingredients when the nanocomposite is made. Other variations might combine these approaches; for example, a stabilizer might be included when a nanocomposite masterbatch is prepared and flame retardant added when the masterbatch is let down with additional polyester. Which of these or other processes is used will depend on factors such as economics and the nature of the additional ingredients and is readily determined by one of ordinary skill in the art. For example, process B is more economical than process A because it has two processing steps while A has three. Process D may be convenient in some circumstances, for example, when the additional ingredients are relatively volatile or borderline in thermal stability. Process C allows the manufacturer some flexibility in composition formulation, while use of a masterbatch in process A or B is more flexible by allowing easy variation of clay content over a wide range.

If deemed appropriate, ingredients may be added at one or more downstream points in the extruder instead of into a rear feed port for one or more of a variety of reasons, for example, to decrease attrition of solids such as fillers, improve dispersion, decrease equipment wear, decrease the thermal history of relatively thermally unstable ingredients, and/or decrease losses by evaporation of volatile ingredients.
Solid particulate fillers exclusive of the fibrous clay

Other solid fillers can be added during the extrusion of the fibrous clay/sodium salt/polyester mixture or melt mixed with a formed nanocomposite composition in a separate step.

Such fillers must be finely divided enough to be dispersed under melt mixing conditions into the composition. Typically, the solid particulate filler will be a material which may already be used in thermoplastic compositions, such as pigments, reinforcing agents, and fillers. The solid particulate filler may or may not have a coating on it, for example, a sizing and/or a coating to improve adhesion of the solid particulate filler to the polymers of the composition. The solid particulate filler may be organic or inorganic. Useful solid particulate fillers include minerals such as clay (other than sepiolite and attapulgite), talc, wollastonite, mica, and calcium carbonate; glass in various forms such as fibers, milled glass, solid or hollow spheres; carbon as carbon black, carbon fiber, graphene sheets (exfoliated graphite, graphite oxide), carbon nanotubes or nano-diamond; titanium dioxide; aramide in the form of short fibers, fibrils or fibrils; and flame retardants such as antimony oxide, sodium antimonate, and appropriate infusible organic compounds.

The solid particulate material may be conventionally melt mixed with the nanocomposite, for example in a twin-screw extruder or Buss kneader. However the particulate material may also be added to the process for forming the polyester nanocomposite, i.e., added as part of the formation of the polymer/fibrous clay/linear oligomer/sodium salt mixture. It may be added at the same time as the fibrous clay, although if a great deal of particulate material is added it may increase the viscosity of the material undergoing the melt mixing process, and care should be taken not to increase the viscosity so much that the material is difficult to process.

Plasticizers

Plasticizers can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step.
A plasticizer is a compound that, when added to a polymer, makes it more pliable, typically by lowering its glass transition temperature. A plasticizer is typically a compound or mixture of compounds with a melting point of about 50°C or less with an (average) molecular weight of 2000 or less. Typically, the plasticizer is 0 to about 5 weight percent of the weight of polyester in the composition. Specific useful plasticizers include poly(ethylene glycol 400) di-2-ethylhexanoate and poly(ethylene glycol) dilaurate with a number average molecular weight of approximately 946.

Toughening Agents

Toughening agents can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step.


One optional ingredient in the compositions of the present invention is a polymeric toughening agent. This is a polymer, typically which is an elastomer or has a relatively low melting point, generally <200°C, preferably <150°C, which has attached to it functional groups which can react with the polyester (and optionally other polymers present), as described in copending U.S. Patent Application 11/312065, herein incorporated by reference in its entirety. Typically the amount of polymeric toughening agent containing functional groups present is about 1 to about 20 percent based on the weight of the polyester. Examples of suitable tougheners include those listed in U.S. Patent 4,753,980, which is hereby incorporated by reference, such as copolymers of ethylene, ethyl acrylate or n-butyl acrylate, and glycidyl methacrylate.

The polymeric toughener typically will contain about 0.5 to about 20 weight percent of monomers containing functional groups, often about 1.0
to about 15 weight percent, or even about 7 to about 13 weight percent of monomers containing functional groups.

Other polymers

Other polymers can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step.

The polyester nanocomposites can be blended with a wide variety of other polymers, as described in copending U. S. Patent Application 11/6421 82, herein incorporated by reference in its entirety. Such other polymers include olefin homopolymers and copolymers, thermoplastic polyurethanes, polyvinyl chloride, polyvinylidene chloride copolymers, liquid crystalline polymers, fluoroelastomers, polyamides, polyimides, polyphenylene sulfide, polyphenylene oxide, polysulfones, polyethersulfones, rubbers, polycarbonate, polyacrylates, terpene resins, polyacetal, styrene-containing copolymers, coumarone/indene copolymers, and the like and combinations thereof.

EDOXV compounds or resins

Another type of other ingredient is an epoxy compound or resin. It is believed that in some instances the epoxy compound or resin stabilizes melt viscosity and/or improves color stability of the composition. Typically such a compound or resin has an average molecular weight of less than about 1000. This epoxy material is normally present at a level of 0 to about 1.0 weight percent of the entire composition. It can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step.

Examples of useful epoxy compounds or resins include without limitation Epon® 1002F, 1009F or 1031 (Resolution Performance Products, Houston, Texas); and Araldite® GT7099 or GT6099 (Huntsman Advanced Materials Americas Inc., Los Angeles, California).
**Hydrolysis stabilizers**

Hydrolysis stabilizers can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step.

The polyester nanocomposites can be stabilized with an effective amount of any hydrolysis stabilization additive, particularly when it is to be used to form monofilament. The hydrolysis stabilization additive can be any known material that enhances the stability of the polyester nanocomposite to hydrolytic degradation. Examples of the hydrolysis stabilization additive can include: diazomethane, carbodiimides, epoxides, cyclic carbonates, oxazolines, aziridines, keteneimines, isocyanates, alkoxy end-capped polyalkylene glycols, and the like, as described in copending U. S. Patent Application 11/642182, herein incorporated by reference in its entirety.

In general, the amount of hydrolysis stabilization additive used is from 0.1 to 10.0 weight percent based on the polyester nanocomposite. Typically the amount of the hydrolysis stabilization additive used is in the range of 0.2 to 4.0 weight percent.

**Other Additives**

Other ingredients can be added during the extrusion of the fibrous clay/linear polyester oligomer/polyester polymer or melt mixed with a formed nanocomposite composition in a separate step. Such ingredients may be added to the present composition in amounts commonly used in thermoplastics as needed for the desired end use. Examples of such materials include without limitation antioxidants, lubricant, mold release agents, flame retardants, (paint) adhesion promoters, thermal stabilizers, UV absorbers, UV stabilizers, processing aids, waxes, color stabilizers, pigments, nucleants, dyes, delusterants such as titanium dioxide and zinc sulfide, antiblocks such as silica, antistats, brighteners, silicon nitride, metal ion sequestrants, anti-staining agents, silicone oil, surfactants, soil repellants, viscosity modifiers, and zirconium acid.
It is to be understood that any ingredient and/or ingredient amount may be combined with any other ingredient and/or ingredient amount herein.

The process described herein for making polyester nanocomposite compositions can also be integrated with additional forming processes, for example, by feeding the product, or co-feeding with an additional polymer stream, directly into an additional forming device, such as an extruder, extruder to form shaped articles, including but not limited to monofilament, multifilament yarn, film, sheet, pellets, and tubing. One example is an integrated continuous process for making monofilament in which the output of the extruder is fed directly into a filament extruder or co-fed into a filament extruder with an additional polymer stream.

**USES**

Articles comprising the nanocomposite compositions produced by the present invention may be prepared by any means known in the art, such as, but not limited to, methods of injection molding, extrusion, blow molding, thermoforming, solution casting, or film blowing. They are particularly useful in appearance parts, packaging, monofilament, and other applications in which engineering plastics are typically used.

**Appearance parts**

The compositions described herein (often when having additional optional ingredients present) are particularly useful as "appearance parts", that is parts in which the surface appearance is important. Such parts include automotive body panels such as fenders, fascia, hoods, tank flaps and other exterior parts; interior automotive panels; automotive lighting fixtures (e.g., bezels); parts for appliances (e.g., refrigerators, dishwashers, washing machines, clothes driers, food mixers, hair driers, coffee makers, toasters, and cameras), such as handles, control panels, chassis (cases), washing machine tubs and exterior parts, interior or exterior refrigerator panels, and dishwasher front or interior panels; power tool housings such as drills and saws; electronic cabinets and housings.
such as personal computer housings, printer housings, peripheral housings, server housings; exterior and interior panels for vehicles such as trains, tractors, lawn mower decks, trucks, snowmobiles, aircraft, and ships; decorative interior panels for buildings; furniture such as office and/or home chairs and tables; and telephones and other telephone equipment. As mentioned above these parts may be painted or they may be left unpainted in the color of the composition.

**Nonappearance parts**

Nonappearance parts may also be made with these compositions. These are parts whose surface appearance is not critical. Such parts include those now made with so-called engineering thermoplastics, especially those which are filled with materials which are designed to enhance the composition's physical properties, such as stiffness, toughness, and tensile strength. Examples include but are not limited to electrical connectors, covers for switchboxes or fuses, radiator grille supports, printed circuit boards, plugs, switches, keyboard components, small electric motor components, distributor caps, bobbins, coil-formers, rotors, windshield wiper arms, headlight mountings, other fittings, and conveyor-belt links.

Where at least one polyester is a thermoplastic elastomer, the nanocomposites will find use in applications that involve some type of repeated mechanical movement, such as bending, flexing, pushing, rotating, pulsing, impacting, or recoiling, since they have a desirable combination of they have an excellent combination of strength, toughness, flexibility and recovery from deformation (see East, *op. cit.*). Examples of uses include but are not limited to hydraulic hosing, rail car couplers, release binders, auto vacuum control tubing, door lock bumpers, railroad car shock absorbers, headphones; specialty fibers, films, and sheets; jacketing, automotive shock absorbers, diaphragms for railroad cars, corrugated plastic tubing, railroad draft gear, auto electric window drive tapes, CVJ boots, recreational footwear, conductive rubbers, wire coatings, energy management devices, telephone handset cords,
compression spring pads, wire clamps, gun holsters, drive belts, run-flat tire inserts, and medical films.

Packaging

Nanocomposite compositions made by the process described herein can be formed into shaped articles useful in packaging applications, such as film, sheet, container, membrane, laminate, pellet, coating, and foam. Articles may be prepared by any means known in the art, such as, but not limited to, methods of injection molding, (co)extrusion, blow molding, thermoforming, solution casting, lamination, and film blowing. The article may be an injection stretch blow molded bottle.

Examples of articles comprising nanocomposite compositions prepared by the process described herein include without limitation packaging for food, personal care (health and hygiene) items, and cosmetics. Packaging refers to either an entire package or a component of a package. Examples of packaging components include, but are not limited to, packaging film, liners, shrink bags, shrink wrap; trays such as but not limited to "CPET" (crystalline polyethylene terephthalate) trays, including but not limited to frozen food trays; tray/container assemblies, replaceable and nonreplaceable caps, lids, and drink bottle necks. The package may be in any form appropriate for the particular application, such as a can, box, bottle, jar, bag, cosmetics package, or closed-ended tube. Other examples of packaging for food include without limitation hot fill bottles and jars for, e.g., juices and sports drinks; and plastic cans for, e.g., vegetables, soup, canned stews, meats, and beans.

The packaging may be fashioned by any means known in the art, such as, but not limited to, extrusion, coextrusion, thermoforming, injection molding, lamination, or blow molding.

Some specific examples of packaging for personal care items and cosmetics include, but are not limited to, bottles, jars, and caps for food and for prescription and non-prescription capsules and pills; solutions, creams, lotions, powders, shampoos, conditioners, deodorants,
antiperspirants, and suspensions for eye, ear, nose, throat, vaginal, urinary tract, rectal, skin, and hair contact; and lip product.

**Monofilament fiber and multifilament yarn**

Polymeric monofilaments are used as reinforcements for rubber articles, fishing lines, toothbrush bristles, paintbrush bristles and the like. In addition, woven fabrics produced from monofilaments are used, for example, in industrial belts and paper machine clothing. Poly(ethylene terephthalate) ("PET") filaments are also employed in industrial applications such as tire cords, composites, belts, and textiles.

Multifilament yarns can be produced comprising the polyester nanocomposites described herein using any of the typical processes well known in the art for making multifilament polyester yarns (see, e.g., Reese, Glen, "Polysters, Fibers" in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc. (2002), vol. 3, 652-678; U. S. Patents 3,409,496, 4,933,427, 4,929,698, 5,061,422, 5,277,858; British Patent 1,162,506). Textile filament yarns are continuous yarns produced at high speeds and are used for fabrics with silk-like esthetics. Industrial filament yarns are used for rubber reinforcement and high strength industrial fabrics.

**EXAMPLES**

The present invention is further defined in the following Examples. It should be understood that these Examples, while indicating preferred embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions.

The meaning of abbreviations is as follows: "bk" means break(s), "h" means hour(s), "IV" means intrinsic viscosity, "kg" means kilogram(s), "Ib" means pound(s), "MB" means masterbatch(es), "mm" means
millimeter(s), "MPa" means megapascal(s), "N" means newton(s), "PET" means poly(ethylene terephthalate), "pph" means pound(s) per hour, "RPM" means revolutions per minute, "SD" means standard deviation, "TSP" means trisodium phosphate, "TSPP" means tetrasodium pyrophosphate, and "wt%" means weight percent(age).
Characterization Methods.

Intrinsic viscosity of polyester polymers was determined at a concentration of 0.5 g/100 ml of a 50:50 weight % thfluroacetic acid:dichloromethane acid solvent system at room temperature by a Goodyear R-103B method.

ISO 1A multipurpose bars (4 mm thick) were molded from dried polyester nanocomposite resins on a Nissei 3000 injection molding machine with temperatures of 265-280°C and a mold temperature of 120°C. Tensile properties of the molded bars were measured according to the procedures of ISO 527 with an extension rate of 5 mm/min. A minimum of 5 bars per condition were tested.

Sample preparation

Masterbatch

Except as indicated, a 30 mm Werner & Pfleiderer 13-barrel twin-screw extruder (Coperion Werner & Pfleiderer GmbH & Co. KG, Stuttgart, Germany) was used to make polyester nanocomposite masterbatches. The sodium salt was compounded into a combination of Pangel® S-9 sepiolite, dried Crystar® PET pellets and, where present, linear PET oligomers in the amounts indicated in the Tables. The ingredients were added simultaneously using two separate calibrated weight-loss feeders (K-Tron T-35 Twin-Screw for sodium salt, sepiolite, and oligomer flake; and K-Tron S-200 for PET pellets, K-Tron International, Pitman, New Jersey, USA) into a rear feed port of the extruder. The appropriate quantities of sodium salt, as indicated in the tables, sepiolite (20 wt%), and, where present, oligomers (16 wt%) were first blended together in a polyethylene bag and then added to the K-Tron T-35 feeder. Barrel temperatures ranged from 240 to 280°C and the screw speed was 300 RPM. A 45-degree-1/8 inch (3.2 mm) single hole die was used. The resulting strand was quenched in a water bath and pelletized with a Conair 304 pelletizer (The Conair Group, Inc., Pittsburgh, Pennsylvania, USA).

The resins were then solid-phase polymerized in an oven with circulating nitrogen (Blue M Model 336, General Signal Co.). The
temperature was increased from room temperature to 235°C over 3 h and then held constant for 24 h. The heaters then turned off and the pellets were removed after cooling.

Let-down with additional PET to achieve desired resin composition

These solid-phase polymerized masterbatch pellets were then dry-blended in a polyethylene bag with dried Crystar® PET, Licowax® PE520 (Clahant), and Irganox® 1010 to prepare a polyester nanocomposite with final concentrations 3 wt% sepiolite, 1 wt% Licowax®, and 0.25 wt% Irganox® 1010. Each of these dry blends was then fed with a single K-Tron S-200 feeder into a rear feed port of a 30 mm Werner & Pfleiderer 13-barrel twin-screw extruder at 30 pph (13.6 kg/h) with a screw speed of 250 RPM. Barrel temperatures ranged were set at 270°C. A 3/16 inch (4.8 mm) single hole die was used. The resulting strand was quenched in a water bath and pelletized with a Conair 304 pelletizer. The resulting pellets were then dried.

In the Examples, all parts are parts by weight.

EXAMPLES 1-2. COMPARATIVE EXAMPLE A

Examples 1 and 2 demonstrate the preparation of polyester nanocomposites from masterbatches containing sepiolite and TSPP decahydrate powder. In Comparative Example A, a control polyester nanocomposite was prepared from a masterbatch containing no TSPP decahydrate.

Nanocomposite resins and test bars were prepared as described above using Crystar® 3905 PET for both masterbatch and let-down and TSPP decahydrate as the sodium salt. The TSPP decahydrate was introduced as ground powder, having been ground from as-received flake with a Reitz Hammer Mill (12,000 RPM, 1/16 inch (1.59 mm) die hole screen). The masterbatch contained 16 wt% linear oligomer and 20 wt% sepiolite. The total masterbatch compounding rate for the examples was 20 lb/h (9.1 kg/h) and 30 lb/h (13.6 kg/h) for Comparative Example A. Compositions and tensile properties of test bars are presented in Table 1.
The tensile testing results show a significant monotonic increase in both tensile strength and elongation-to-break, with no significant change in modulus, upon the addition of TSPP decahydrate.

<table>
<thead>
<tr>
<th>Example</th>
<th>Ground TSPP decahydrate Concentration, wt% of sepiolite</th>
<th>Tensile Strength, MPa (SD)</th>
<th>Strain at Break, % (SD)</th>
<th>Modulus, MPa (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative</td>
<td>0</td>
<td>47.9 (0.8)</td>
<td>1.36 (0.05)</td>
<td>3863 (116)</td>
</tr>
<tr>
<td>Example A</td>
<td>1</td>
<td>56.5 (4.7)</td>
<td>1.70 (0.17)</td>
<td>3809 (109)</td>
</tr>
<tr>
<td>Example 1</td>
<td>5</td>
<td>61.1 (3.9)</td>
<td>1.95 (0.17)</td>
<td>3659 (145)</td>
</tr>
</tbody>
</table>

**EXAMPLES 3-4, COMPARATIVE EXAMPLE B**

Examples 3 and 4 demonstrate the preparation of polyester nanocomposites from masterbatches containing sepiolite and TSPP decahydrate flake (i.e., unground). In Comparative Example B, a control polyester nanocomposite was prepared from a masterbatch containing no TSPP decahydrate.

Resins and test bars were prepared as described above, using Crystar® 3905 PET for both masterbatch and let-down and TSPP decahydrate as the sodium salt, except that the TSPP decahydrate was introduced as the as-received larger flake, rather than as ground powder. The masterbatch contained 16 wt% linear oligomer and 20 wt% sepiolite, in addition, the masterbatch compounding extruder used a die with a screen pack, employing screens of 20 and 40 mesh surrounding a Dynalloy® Filter Medium X5 (Pall Inc.) with filter ratings of 7 micrometer mean and 10 micrometer absolute. The total masterbatch compounding rate was 20 pph (9.1 kg/h). Compositions and tensile properties of test bars are presented in Table 2. The tensile testing results in Table 2 show
a significant monotonic increase in both tensile strength and elongation-to-break, with no significant change in modulus, upon the addition of TSPP decahydrate.

Table 2

<table>
<thead>
<tr>
<th>Example</th>
<th>TSPP decahydrate Flake Concentration (wt% of sepiolite)</th>
<th>Tensile Strength, MPa (SD)</th>
<th>Strain at Break, % (SD)</th>
<th>Modulus, MPa (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. B</td>
<td>0</td>
<td>45.3 (4.9)</td>
<td>1.29 (0.17)</td>
<td>3789 (193)</td>
</tr>
<tr>
<td>Example 3</td>
<td>1</td>
<td>50.1 (4.8)</td>
<td>1.48 (0.17)</td>
<td>3761 (152)</td>
</tr>
<tr>
<td>Example 4</td>
<td>5</td>
<td>61.2 (3.4)</td>
<td>1.93 (0.176)</td>
<td>3753 (71)</td>
</tr>
</tbody>
</table>

EXEMPLARY 5-10, COMPARATIVE EXAMPLE C

Examples 5 through 10 are additional examples of the preparation of polyester nanocomposites from masterbatches containing sepiolite and TSPP decahydrate flake (i.e., unground) or powder. In Comparative Example C, a control polyester nanocomposite was prepared from a masterbatch containing no TSPP decahydrate.

Resins and test bars were prepared as described above using Crystar® 3905 PET for both masterbatch and let-down and TSPP decahydrate as the sodium salt. TSPP decahydrate was introduced at levels of 5, 7.5, or 10 wt% (based on sepiolite) as either ground powder or flake, as indicated in Table 3. The masterbatch contained 16 wt% linear oligomer and 20 wt% sepiolite. The total masterbatch compounding rate was 40 pph (18.2 kg/h). The tensile testing results in Table 3 show a significant increase in both tensile strength and elongation-to-break, with no significant change in modulus, upon the addition of TSPP decahydrate, regardless of the physical form of the TSPP decahydrate.
Example 1 illustrates the improved properties resulting from adding TSPP decahydrate to a polyester nanocomposite composition without added linear oligomer. In Comparative Example D, a control polyester nanocomposite was prepared from a masterbatch containing no TSPP decahydrate and no added linear oligomer. The same procedures as above were followed. The total masterbatch compounding rate was 40 pph (18.2 kg/h).

Table 4

<table>
<thead>
<tr>
<th>Example-</th>
<th>wt% TSPP decahydrate (based on sepiolite)</th>
<th>TSPP decahydrate State</th>
<th>Tensile Strength, MPa (SD)</th>
<th>Strain at Break, % (SD)</th>
<th>Modulus, MPa (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example C</td>
<td>0</td>
<td>Ground</td>
<td>41.8 (3.0)</td>
<td>1.13 (0.11)</td>
<td>3975 (254)</td>
</tr>
<tr>
<td>Example 5</td>
<td>5</td>
<td>Ground</td>
<td>55.9 (8.0)</td>
<td>1.65 (0.30)</td>
<td>3812 (90)</td>
</tr>
<tr>
<td>Example 6</td>
<td>7.5</td>
<td>Ground</td>
<td>60.6 (2.3)</td>
<td>1.85 (0.06)</td>
<td>3771 (147)</td>
</tr>
<tr>
<td>Example 7</td>
<td>10</td>
<td>Ground</td>
<td>58.9 (5.6)</td>
<td>1.73 (0.23)</td>
<td>3919 (55)</td>
</tr>
<tr>
<td>Example 8</td>
<td>5</td>
<td>Unground</td>
<td>58.5 (2.1)</td>
<td>1.73 (0.08)</td>
<td>3796 (147)</td>
</tr>
<tr>
<td>Example 9</td>
<td>7.5</td>
<td>Unground</td>
<td>56.3 (2.8)</td>
<td>1.65 (0.10)</td>
<td>3814 (58)</td>
</tr>
<tr>
<td>Example 10</td>
<td>10</td>
<td>Unground</td>
<td>57.7 (7.1)</td>
<td>1.73 (0.28)</td>
<td>3847 (84)</td>
</tr>
</tbody>
</table>

EXAMPLE 11, COMPARATIVE EXAMPLE D

Examples 12 through 20 demonstrate the effects of PET molecular weight and sodium salt type on nanocomposite properties.

Resins and test bars were prepared as described above, except that TSPP decahydrate when used was introduced as as-received flake,
the oligomers were introduced at either 0 or 16 wt.%, as indicated in Table 5, the total masterbatch compounding rate was 40 pph (18.2 kg/h), a range of sodium salts was used, as indicated in Table 5: TSPP decahydrate, trisodium phosphate (TSP), and sodium carbonate, $\text{Na}_2\text{CO}_3$, and the PET grade used for both compounding and let-down was either Crystar® 3905 (IV=0.62) or Crystar® 5005 (IV=0.85), a higher molecular weight PET grade. In Comparative Example E, a control polyester nanocomposite was prepared from a masterbatch containing Crystar® 5005, 16 wt% linear oligomer, and no sodium salt. In Comparative Example F, a control polyester nanocomposite was prepared from a masterbatch containing Crystar® 5005, no added linear oligomer, and no sodium salt.

### Table 5

<table>
<thead>
<tr>
<th>Example</th>
<th>Crystar® PET grade</th>
<th>PET Oligomer Concentration (wt.%)</th>
<th>Sepiolite Concentration (wt.%)</th>
<th>Sodium Salt Concentration (wt.%, based-on-sepiolite)</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example E</td>
<td>5005</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Example 12</td>
<td>5005</td>
<td></td>
<td></td>
<td>5</td>
<td>TSP</td>
</tr>
<tr>
<td>Example 13</td>
<td>5005</td>
<td></td>
<td></td>
<td>4.9</td>
<td>$\text{Na}_2\text{CO}_3$</td>
</tr>
<tr>
<td>Example 14</td>
<td>5005</td>
<td>16</td>
<td>20</td>
<td>6.1</td>
<td>TSPP decahydrate</td>
</tr>
<tr>
<td>Example 15</td>
<td>5005</td>
<td></td>
<td></td>
<td>5</td>
<td>TSPP decahydrate</td>
</tr>
<tr>
<td>Example 16</td>
<td>3905</td>
<td></td>
<td></td>
<td>5</td>
<td>TSPP decahydrate</td>
</tr>
<tr>
<td>Example 17</td>
<td>3905</td>
<td>0</td>
<td>20</td>
<td>5</td>
<td>TSPP decahydrate</td>
</tr>
<tr>
<td>Example 18</td>
<td>5005</td>
<td></td>
<td></td>
<td>5</td>
<td>TSPP</td>
</tr>
</tbody>
</table>

30
As shown in Table 6, the use of the higher molecular weight grade Crystar® 5005 led to ductile breaks (i.e., the bars yielded) during the tensile testing, rather than the brittle breaks observed when using Crystar® 3905. Thus, the strains-to-break are reported in two ways: an average strain-to-break for the bars that broke in a brittle fashion (i.e., when the stress decreased to zero because the specimen broke as the testing machine continued to increase the jaw distance; the strains in this case were measured with an extensometer) and an average nominal strain-to-break for the bars that broke in a ductile fashion (i.e., when the stress decreased to a finite value while the testing machine continued to increase the jaw distance; the strains-to-break were measured from the jaw separation). In addition, an average overall energy-to-break was calculated as the area under the stress-strain curve. The results demonstrate that the each salt was effective at increasing the strains and overall energy-to-break with 16% oligomers and with no oligomers.

Table 6

<table>
<thead>
<tr>
<th>Example</th>
<th>Nomin</th>
<th>Stress at Break, Strain at Break, Overall Energy To Break, tensile strength, modulus of elasticity</th>
<th>N* m/m</th>
<th>6.1</th>
<th>5</th>
<th>4.9</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 19</td>
<td>5005</td>
<td>TSPP decahydrated</td>
<td></td>
<td>6.1</td>
<td>5</td>
<td>4.9</td>
<td>0</td>
</tr>
<tr>
<td>Example 20</td>
<td>5005</td>
<td>TSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 21</td>
<td>5005</td>
<td>Na₂CO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example F</td>
<td>5005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparative 0 64.0 63.8 2.62 3596 2,196


**EXAMPLES 22-33**

Examples 22 through 33 demonstrate the effects of PET molecular weight and sodium salt type on nanocomposite properties.

Resins and test bars were prepared as described above, except that either TSPP decahydrate or anhydrous TSPP was introduced as as-received flake at a level of 5 wt% (based on sepiolite), no oligomers were used, different molecular weight grades of PET (IV=0.85 or 0.95) were used for the making of the masterbatches and the subsequent let-downs, and some of the masterbatches were not solid-phase polymerized before let-down. The total masterbatch compounding rate was 40 lb/h (18.2 kg/h). The specific conditions are listed in Table 7 ("MB" means...
masterbatch). The tensile results listed in Table 8 indicate that there is no significant difference in efficacy between the TSPP decahydrate and the anhydrous TSPP; solid-phase polymerization of the masterbatch increases the strain-to-break without affecting the modulus; and a range of PET molecular weights can be used in either masterbatch production or let-downs without significantly affecting the results.

Table 7

<table>
<thead>
<tr>
<th>Example #</th>
<th>Let-Down Resin IV</th>
<th>Solid Phased? #</th>
<th>MB Screw Design (barrels)</th>
<th>MB Resin IV</th>
<th>MB TSPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 22</td>
<td>0.85</td>
<td>No</td>
<td>13</td>
<td>0.85</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Example 23</td>
<td>0.85</td>
<td>No</td>
<td>13</td>
<td>0.85</td>
<td>Decahydrate</td>
</tr>
<tr>
<td>Example 24</td>
<td>0.85</td>
<td>Yes</td>
<td>13</td>
<td>0.85</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Example 25</td>
<td>0.85</td>
<td>Yes</td>
<td>13</td>
<td>0.85</td>
<td>Decahydrate</td>
</tr>
<tr>
<td>Example 26</td>
<td>0.85</td>
<td>No</td>
<td>13</td>
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<th>Modulus, MPa (SD)</th>
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33
EXAMPLES 34-37, COMPARATIVE EXAMPLES G AND H

Examples 34 through 37 demonstrate the effects of PET molecular weight, solid-phase polymerization, and extruder barrel length on nanocomposite properties.

The same procedures as described above were used to produce the masterbatches. However, rather than a 13-barrel machine, a 9-barrel 30 mm Werner & Pfleiderer twin-screw extruder (Copehon Werner & Pfleiderer GmbH & Co. KG, Stuttgart, Germany) was used. As indicated in Table 9, different molecular weight PET grades (IV=0.85 and 0.95) were used to make the masterbatches and let-downs, and some masterbatches were solid-phase polymerized before let-down. The total masterbatch compounding rate was 40 lb/h (18.2 kg/h). Anhydrous TSPP was introduced at the 5 wt% level (based on sepiolite) in the as-received flake form. In Comparative Examples G and H, control polyester nanocomposites were prepared from masterbatches containing no sodium salts and compounded with identical conditions.

The results in Table 10 indicate that there is a significant improvement in strain-to-break upon the addition of anhydrous TSPP in this different extruder configuration.
Where a range of numerical values is recited herein, the range includes the endpoints thereof and all the individual integers and fractions within the range, and also includes each of the narrower ranges therein formed by all the various possible combinations of those endpoints and internal integers and fractions to form subgroups of the larger group of values within the stated range to the same extent as if each of those narrower ranges was explicitly recited. Where a range of numerical values is stated herein as being greater than a stated value, the range is nevertheless finite and is bounded on its upper end by a value that is operable within the context of the invention as described herein. Where a range of numerical values is stated herein as being less than a stated value, the range is nevertheless bounded on its lower end by a non-zero value.
In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, where an embodiment of the subject matter hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of the subject matter hereof, however, may be stated or described as consisting essentially of certain features or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter hereof may be stated or described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage,

(a) amounts, sizes, ranges, formulations, parameters, and other quantities and characteristics recited herein, particularly when modified by the term "about", may but need not be exact, and may also be approximate and/or larger or smaller (as desired) than stated, reflecting tolerances, conversion factors, rounding off, measurement error and the like, as well as the inclusion within a stated value of those values outside it that have, within the context of this invention, functional and/or operable equivalence to the stated value;

(b) all numerical quantities of parts, percentage or ratio are given as parts, percentage or ratio by weight;

(c) use of the indefinite article "a" or "an" with respect to a statement or description of the presence of an element or feature of this invention, does not limit the presence of the element or feature to one in number; and
(d) the words "include", "includes" and "including" are to be read and interpreted as if they were followed by the phrase "without limitation" if in fact that is not the case.
CLAIMS

What is claimed is:

1. A method for preparing a polyester nanocomposite composition, comprising melt-mixing a mixture of:
   (a) fibrous clay;
   (b) sodium salt;
   (c) at least one polyester polymer; and
   (d) optionally, at least one linear polyester oligomer; and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase polyester molecular weight.

2. The method of claim 1 wherein the fibrous clay is sepiolite, attapulgite, or a mixture thereof.

3. The method of claim 1 wherein the ratio of the at least one linear polyester oligomer to the at least one polyester polymer is from about 0:1 to about 99:1 by weight.

4. The method of claim 1 wherein the amount of fibrous clay is from about 0.1 to about 40 wt% based on the weight of the fibrous clay and the optional at least one linear polyester oligomer and the at least one polyester polymer.

5. The method of claim 1 wherein the amount of sodium salt is from about 0.5 to about 12 wt% based on the weight of the fibrous clay.

6. The method of claim 1 wherein the sodium salt is anhydrous tetrarsodium pyrophosphate, tetrarsodium pyrophosphate decahydrate, thsodium phosphate, or sodium carbonate.

7. The method of claim 1 wherein the optional at least one linear polyester oligomer and/or the at least one polyester polymer is branched or unbranched, a homopolymer or copolymer, or a polymeric blend comprising at least one such homopolymer or copolymer.

8. The method of claim 1 wherein the optional at least one linear polyester oligomer and/or the at least one polyester polymer is selected from the group consisting of the following:
(a) polyesters produced from reaction mixtures containing one or more diols and one or more hydrocarbyl diacids or esters of such diacids, wherein the diols are selected from the group consisting of ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propane diol, 2,2-dimethyl-1,3-propane diol, 2-ethyl-2-butyl-1,3-propane diol, 2-ethyl-2-isobutyl-1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 2,2,4-thmethyl-1,6-hexane diol, 1,2-cyclohexane dimethanol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, isosorbide, naphthalene glycols, biphenols, diethylene glycol, thethylene glycol, resorcinol, hydroquinone, t-butyl-hydroquinone, polytetramethylene ether glycol and other longer chain diols and polyols which are the reaction products of diols or polyols with alkylene oxides, and alkyl-substituted and chloro-substituted versions of said diols; and the diacids are selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acids, cyclohexane dicarboxylic acids, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecane dioic acid, fumaric acid, maleic acid, and alkyl-substituted and chloro-substituted versions of said diacids;

(b) polyesters produced from reaction mixtures containing one or more polymehzable polyester monomers selected from the group consisting of hydroxybenzoic acids, hydroxynaphthoic acids, lactic acid, bis(2-hydroxyethyl) terephthalate, bis(4-hydroxybutyl) terephthalate, bis(2-hydroxyethyl)naphthalenedioate, bis(2-hydroxyethyl)isophthalate, bis[2-(2-hydroxyethoxy)ethyl]terephthalate, bis[2-(2-hydroxyethoxy)ethyl]isophthalate, bis[(4-hydroxymethyl)cyclohexyl]methyl]terephthalate, and bis[(4-
hydroxymethylcyclohexyl)methyl]isophthalate, mono(2-hydroxyethyl)terephthalate, bis(2-hydroxyethyl)sulfoisophthalate, lactide, and alkyl-substituted and chloro-substituted versions of said polymerizable polyester monomers; and
(c) polyesters produced directly from reaction mixtures containing macrocyclic polyester oligomers selected from the group consisting of macrocyclic polyester oligomers of: 1,4-butylene terephthalate, 1,3-propylene terephthalate, 1,4-cyclohexylenedimethylene terephthalate, ethylene terephthalate, 1,2-ethylene 2,6-naphthalenedicarboxylate, the cyclic ester dimer of terephthalic acid and diethylene glycol, macrocyclic co-oligoesters comprising two or more of the above structural repeat units, and alkyl-substituted and chloro-substituted versions of said macrocyclic polyester oligomers.

9. The method of claim 1 wherein the at least one linear polyester oligomer and/or the at least one polyester polymer is selected from the group consisting of the following: poly(ethylene terephthalate), poly(1,3-propylene terephthalate), poly(1,4-butylene terephthalate), a thermoplastic elastomeric polyester having poly(1,4-butylene terephthalate) and poly(tetramethylene ether)glycol blocks, poly(1,4-cyclohexyldimethylene terephthalate), and polylactic acid.

10. The method of claim 1 wherein the fibrous clay is unmodified.

11. The method of claim 1 wherein the melt-mixing of the composition is carried out using at least one twin-screw extruder forming an extruded composition.

12. The method of claim 11 wherein some or all of the extruded composition of the one twin-screw extruder is re-fed one or more times through the same extruder.

13. The method of claim 11 further comprising staged feeding.
14. The method of claim 11 further comprising split feeding at least one ingredient.

15. The method of claim 11 further comprising the step of feeding the extruded composition of the extruder, or co-feeding said extruded composition with an additional polymer stream, into an additional forming device to form a shaped article.

16. The method of claim 15 wherein the additional forming device is an extruder.

17. The method of claim 15 wherein the shaped article is selected from the group consisting of monofilament, multifilament yarn, film, sheet, tubing, and pellets.

18. A method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: fibrous clay, sodium salt, optionally at least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition containing a greater concentration of fibrous clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.

19. A shaped article comprising the polyester nanocomposite composition produced by the method of claim 1 or claim 18, wherein the article is formed using at least one method selected from the group consisting of injection molding, (co)extrusion, blow molding, thermoforming, solution casting, lamination, and film blowing.

20. The shaped article of claim 19 wherein said shaped article is selected from the group consisting of:

(a) appearance parts selected from the group consisting of automotive body panels, fenders, fascia, hoods, tank flaps and other exterior parts; interior automotive panels; automotive lighting fixtures (bezels); appliance handles,
control panels, chassis (cases), washing machine tubs and exterior parts, interior or exterior refrigerator panels, and dishwasher front or interior panels; power tool housings; electronic cabinets and housings; exterior and interior panels for vehicles; decorative interior panels for buildings; office and home furniture; telephones and other telephone equipment;

(b) non-appearance parts selected from the group
   i) consisting of electrical connectors, covers for switchboxes or fuses, radiator grille supports, headlamp mountings, printed circuit boards, plugs, switches, keyboard components, small electric motor components, distributor caps, bobbins, coil-formers, rotors, windshield wiper arms, headlight mountings, other fittings, conveyor-belt links, hydraulic hosing, rail car couplers, release binders, auto vacuum control tubing, door lock bumpers, railroad car shock absorbers, headphones; specialty fibers, films, and sheets; jacketing, automotive shock absorbers, diaphragms for railroad cars, corrugated plastic tubing, railroad draft gear, auto electric window drive tapes, CVJ boots, recreational footwear, conductive rubbers, wire coatings, energy management devices, telephone handset cords, compression spring pads, wire clamps, gun holsters, drive belts, run-flat tire inserts, and medical films;

(c) packaging selected from the group consisting of packaging film, liners, shrink bags, shrink wrap, frozen food trays, CPET trays, other trays, tray/container assemblies, replaceable and nonreplaceable caps, lids, drink bottle necks, cans, boxes, bottles, jars, bags, cosmetics packages, and closed-ended tubes, hot fill bottles and jars, plastic cans; and

(d) monofilaments, multifilament yarn, fishing lines, toothbrush bristles, paintbrush bristles, industrial belts and paper
machine clothing comprising woven fabrics produced from monofilaments, tire cords, composites, belts, textiles, reinforced rubber, and high strength industrial fabrics.
REPLACEMENT CLAIMS

1. A method for preparing a polyester nanocomposite composition, comprising melt-mixing a mixture of:
   (a) fibrous clay;
   (b) at least one sodium salt wherein the sodium salt is selected from the group consisting of: anhydrous tetradsodium pyrophosphate, tetradsodium pyrophosphate decahydrate, trisodium phosphate, sodium carbonate; or a mixture thereof;
   (c) at least one polyester polymer; and
   (d) optionally, at least one linear polyester oligomer;

and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase polyester molecular weight.

2. The method of claim 1 wherein the fibrous clay is sepiolite, attapulgite, or a mixture thereof.

3. The method of claim 1 wherein the ratio of the at least one linear polyester oligomer to the at least one polyester polymer is from about 0:100 to about 99:1 by weight.

4. The method of claim 1 wherein the amount of fibrous clay is from about 0.1 to about 40 wt% based on the weight of the fibrous clay and the optional at least one linear polyester oligomer and the at least one polyester polymer.

5. The method of claim 1 wherein the amount of sodium salt is from about 0.5 to about 12 wt% based on the weight of the fibrous clay.

6. The method of claim 1 wherein the optional at least one linear polyester oligomer and/or the at least one polyester polymer is branched or unbranched, a homopolymer or copolymer, or a polymeric blend comprising at least one such homopolymer or copolymer.

7. The method of claim 1 wherein the optional at least one linear polyester oligomer and/or the at least one polyester polymer is selected from the group consisting of the following:
   (a) polyesters produced from reaction mixtures containing one or more diols and one or more hydrocarbyl diacids or esters of such diacids, wherein the diols are selected from the group consisting of ethylene
glycol, 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propane diol, 2,2-dimethyl-1,3-propane diol, 2-ethyl-2-butyl-1,3-propane diol. 2-ethyl-2-isobutyl-1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 2,2,4-trimethyl-1,6-hexane diol, 1,2-cyclohexane dimethanol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutane diol, isosorbide, naphthalene glycols, biphenols, diethylene glycol, triethylene glycol, resorcinol, hydroquinone, t-butyl-hydroquinone, polytetramethylene ether glycol and other longer chain diols and polyols which are the reaction products of diols or polyols with alkylene oxides, and alkyl-substituted and chloro-substituted versions of said diols; and the diacids are selected form the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acids, cyclohexane dicarboxylic acids, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, fumaric acid, maleic acid, and alkyl-substituted and chloro-substituted versions of said diacids; (b) polyesters produced from reaction mixtures containing one or more polymerizable polyester monomers selected from the group consisting of hydroxybenzoic acids, hydroxynaphthoic acids, lactic acid, bis(2-hydroxyethyl) terephthalate, bis(4-hydroxybutyl) terephthalate, bis(2-hydroxyethyl)naphthalenedioate, bis(2-hydroxyethyl)isophthalate, bis[2-(2-hydroxyethoxy)ethyl]terephthalate, bis[2-(2-hydroxyethoxy)ethyl]isophthalate, bis[(4-hydroxymethylcyclohexyl)methyl]terephthalate, and bis[(4-hydroxymethylcyclohexyl)methyl]isophthalate, mono(2-hydroxyethyl)terephthalate, bis(2-hydroxyethyl)sulfoisophthalate, lactidθ, and alkyl-substituted and chloro-substituted versions of said polymerizable polyester monomers; and (c) polyesters produced directly from reaction mixtures containing macrocyclic polyester oligomers selected from the group consisting of macrocyclic polyester oligomers of: 1,4-butylene terephthalate, 1,3-propylene terephthalate, 1,4-cyclohexylenedimethylene terephthalate, ethylene terephthalate, 1,2-ethylene 2,6-naphthalenedicarboxylate, the
cyclic ester dimer of terephthalic acid and diethylene glycol, macrocyclic co-oligoesters comprising two or more of the above structural repeat units, and alkyl-substituted and chloro-substituted versions of said macrocyclic polyester oligomers.

9. The method of claim 1 wherein the at least one linear polyester oligomer and/or the at least one polyester polymer is selected from the group consisting of the following: poly(ethylene terephthalate), poly(1,3-propylene terephthalate), poly(1,4-butylene terephthalate), a thermoplastic elastomeric polyester having poly(1,4-butylene terephthalate) and poly(tetramethylene ether)glycol blocks, poly(1,4-cylohexyldimethylene terephthalate), and polylactic acid.

10. The method of claim 1 wherein the fibrous clay is unmodified.

11. The method of claim 1 wherein the melt-mixing of the composition is carried out using at least one twin-screw extruder forming an extruded composition.

12. The method of claim 11 wherein some or all of the extruded composition of the one twin-screw extruder is re-fed one or more times through the same extruder.

13. The method of claim 11 further comprising staged feeding.

14. The method of claim 11 further comprising split feeding at least one ingredient.

15. The method of claim 11 further comprising the step of feeding the extruded composition of the extruder, or co-feeding said extruded composition with an additional polymer stream, into an additional forming device to form a shaped article.

16. The method of claim 15 wherein the additional forming device is an extruder.

17. The method of claim 15 wherein the shaped article is selected from the group consisting of monofilament, multifilament yarn, film, sheet, tubing, and pellets.

18. A method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: fibrous clay, sodium salt, optionally at least one polyester oligomer, and at least one
polyester polymer to produce a nanocomposite composition containing a greater concentration of fibrous clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.

19. A shaped article comprising the polyester nanocomposite composition produced by the method of claim 1 or claim 18, wherein the article is formed using at least one method selected from the group consisting of injection molding, (co)extrusion, blow molding, thermoforming, solution casting, lamination, and film blowing.

20. The shaped article of claim 19 wherein said shaped article is selected from the group consisting of:
   (a) appearance parts selected from the group consisting of automotive body panels, fenders, fascia, hoods, tank flaps and other exterior parts; interior automotive panels; automotive lighting fixtures (bezels); appliance handles, control panels, chassis (cases), washing machine tubs and exterior parts, interior or exterior refrigerator panels, and dishwasher front or interior panels; power tool housings; electronic cabinets and housings; exterior and interior panels for vehicles; decorative interior panels for buildings; office and home furniture; telephones and other telephone equipment;
   (b) non-appearance parts selected from the group
      i) consisting of electrical connectors, covers for switchboxes or fuses, radiator grille supports, headlamp mountings, printed circuit boards, plugs, switches, keyboard components, small electric motor components, distributor caps, bobbins, coil-formers, rotors, windshield wiper arms, headlight mountings, other fittings, conveyor-belt links, hydraulic hosing, rail car couplers, release binders, auto vacuum control tubing, door lock bumpers, railroad car shock absorbers, headphones; specialty fibers, films, and sheets; jacketing, automotive shock absorbers, diaphragms for railroad cars, corrugated plastic tubing, railroad
draft gear, auto electric window drive tapes, CVJ boots,
recreational footwear, conductive rubbers, wire coatings, energy
management devices, telephone handset cords, compression
spring pads, wire clamps, gun holsters, drive belts, run-flat tire
inserts, and medical films;
(c) packaging selected from the group consisting of packaging film,
liners, shrink bags, shrink wrap, frozen food trays, CPET trays, other
trays, tray/container assemblies, replaceable and nonreplaceable caps,
lids, drink bottle necks, cans, boxes, bottles, jars, bags, cosmetics
packages, and closed-ended tubes, hot fill bottles and jars, plastic
cans; and
(d) monofilaments, multifilament yarn, fishing lines, toothbrush bristles,
paintbrush bristles, industrial belts and paper machine clothing
comprising woven fabrics produced from monofilaments, tire cords,
composites, belts, textiles, reinforced rubber, and high strength
industrial fabrics,
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J5/00 C08K3/34
ADD.

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)
C08J C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X See patent family annex

Further documents are listed in the continuation of Box C

Date of the actual completion of the international search 30 September 2010

Date of mailing of the international search report 07/10/2010

Name and mailing address of the ISA/Authorized officer
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NL - 2280 HV Hilversum
Tel (+31-70) 340-2040,
Fax (+31-70) 340-3016
Kaul-Buchberger, Eva
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