A unique multilayer composite / "smart pellet" system was introduced as a method for producing reinforced matrix polymers with superior mechanical properties. Ethylene-octene copolymer / polysulfone and polypropylene / inorganic fiber were chosen as model systems with which to test this concept. The reinforcing agents were present in the multilayer composite and mixed with the matrix polymer in injection-molding. Mechanical properties of the resulting matrix polymer products were studied by performing tensile, flexural, and impact strength tests. The morphology behaviors of the multilayer composites and matrix polymer products were investigated by scanning electron microscopy, atomic force microscopy, and optical microscopy. In one experiment, the polysulfone layers resembled clay platelet morphology dispersed in a matrix polymer.
MULTILAYER COMPOSITE USEFUL AS A POLYMER ADDITIVE

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS
This application claims, pursuant to 35 U.S.C. § 119(e), the benefit of the filing date of provisional U.S. Patent Application No. 61/274,239, which was filed on August 14, 2009, and is hereby incorporated by reference.

TECHNICAL FIELD OF THE INVENTION
This invention is directed to a multilayer polymer composite, which may be provided in the form of a pellet, and incorporated in a matrix polymer, to improve one or more of the physical, chemical or electrical properties of the matrix polymer.

BACKGROUND OF THE INVENTION
Reinforcement of polymer products is well known to be successfully accomplished using a range of inorganic fillers, including glass fibers and flakes, smectite clays, talc and many other minerals. While such fillers can substantially increase the moduli and thermal properties (heat deflection temperature, glass transition temperature, onset of thermal degradation), these property enhancements generally come at the expense of ductility and processability. Inorganic fillers used to reinforce organic polymers also often require the use of specialized compatibilizing agents, dispersing agents, and surface modification. Additionally, treatments to create an intercalated material, which will exfoliate to form platelets, typically require a processing step to introduce a polymer layer between inorganic filler layers.

Beall et al., US Patent No. 5,552,469, disclose exfoliated layered silicate material derived from intercalates formed by contacting the layer material, e.g., a phyllosilicate, with an intercalant polymer to sorb or intercalate the polymer between adjacent platelets of the layered material. Sufficient intercalant polymer is sorbed between adjacent platelets to expand the adjacent platelets to a spacing of at least about 10 Å (as measured after water removal), up to about 100 Å and preferably in the range of about 30-45 Å, so that the intercalate easily can be exfoliated, e.g.,
when mixed with a thermoplastic or thermosetting matrix polymer melt, to provide a matrix polymer/platelet nanocomposite material - the platelets being exfoliated from the intercalate.

Bagrodia et al., US Patent No. 6,395,386 B2 disclose multilayer formed articles including, but not limited to containers such as bottles, tubes, pipes, preforms and films (including oriented films such as biaxially oriented) comprising a melt processible resin having dispersed therein a platelet filler. Suitable platelet particles are derived from clay materials, such as mica-type layered phyllosilicates, including clays, smectite clays, sodium montmorillonite, sodium hectorite, bentonites, nontronite, beidellite, volkonskoite, saponite, sauconite, magadiite, kenyaita, synthetic sodium hectorites, and the like. Generally, it was found to be desirable to treat the selected clay material to separate the agglomerates of platelet particles to individual platelet particles and small tactoids prior to introducing the platelet particles into the matrix polymer.

Techniques for fabricating multilayer polymer structures, having uniform layers with a thickness ranging from 5 nm to 5 μm, are known. For example, Baer et al., US Patent No. 6,582,807 B2 disclose a multilayer polymer assembly process for fabricating nonlinear, optical structures, useful as optical switches and optical limiters. Baer et al., US Patent No. 7,002,754 B2 disclose multilayer polymer gradient index (GRIN) lenses, fabricated by layering composite polymer films in a hierarchical structure.

The coextrusion of multilayer sheets and other articles wherein individual layer thicknesses are on the order of microns is known in the art. For example, Schrenk, U.S. Pat. Nos. 3,773,882 and 3,884,606, teaches devices which prepare multilayered coextruded thermoplastic polymeric materials having substantially uniform layer thicknesses. The feedblock of the coextrusion device receives streams of the diverse thermoplastic polymeric materials from sources such as heat plastifying extruders. The streams of resinous materials are passed to a mechanical manipulating section within the feedblock. This section serves to rearrange the
original streams into a multilayered stream having the number of layers desired in
the final body.

Optionally, this multilayered stream may be subsequently passed through a
series of layer multiplying means (sometimes termed interfacial surface generators)
in order to further increase the number of layers in the final body as is described in
Schrenk et al, U.S. Pat. No. 3,759,647. The multilayered stream is then passed into
an extrusion die which is so constructed and arranged that streamlined flow is
maintained therein. Such an extrusion device is described in Chisholm et al., U.S.
Pat. No. 3,557,265. The resultant product is extruded to form a multilayered body in
which each layer is generally parallel to the major surface of adjacent layers. This
technology may be termed microlayer coextrusion technology because of the
thinness of the layers which are formed. Microlayer coextrusion is to be distinguished
from conventional multilayer coextrusion which typically involves the production of
less than about fifteen layers each having thicknesses which may be from one to two
orders of magnitude greater than the layer thicknesses produced in microlayer
coextrusion.

The potential replacement of high aspect ratio inorganic platelets with organic
platelets might offer improved phase compatibility, and potentially could lessen the
negative impact upon polymer processability.

SUMMARY OF THE INVENTION

The present invention includes a multilayer composite, a method of improving
the properties of a matrix polymer by mixing the multilayer composite and matrix
polymer together, followed by melt extruding the mixture, and a matrix polymer
composition obtained from incorporating the multilayer composite in the matrix
polymer according to the foregoing method.

The multilayer composite is comprised of at least eight layers of one or more
polymers. Each polymer layer is contiguous with at least one other polymer layer,
that is, each polymer layer is in contact with at least one adjacent polymer layer, as
distinguished from prior art additives such as clays having a layer of a polymer disposed between alternating inorganic layers. The components of the various alternating layers may be the same or different, as long as at least one component includes a polymer that can melt when extruded with a matrix polymer, i.e. the target polymer that is intended to be modified by incorporation of the multilayer composite. The number of organic polymer layers in the composite may be 16, 32, 64, 128, 256, 512 or more. For example, multilayer composites having as many as 5000 layers may be fabricated by those skilled in art.

The multilayer composite may be fabricated by a multilayer coextrusion forced assembly process, as described in greater detail herein. Briefly, the process employs coextrusion using multiple extruders to create a multilayer film structure, that is, one layer for each of the extruders. The original film structure is then split in two, the two sections are stacked together, and the stacked sections are compressed and spread, resulting in a film having double the number of layers, with the thickness of the individual layers decreased. The process can be repeated to fabricate a composite with the desired number of layers and layer thicknesses. The thickness of each of the layers of the composite need not be the same. Thus, it is possible using two, three, four or more extruders to create a composite having alternating structures comprised of two, three, four or more layers, respectively, throughout the multilayer composite. It has been found to be advantageous in creating a composite with thin layers having a consistent thickness to use organic polymers that have a similar melt viscosity. By way of example, all of the polymers in the composite may be selected to have a melt viscosity within a factor of four of each other, as measured by melt rheometry.

The thickness of the polymer layers in the composite may range from 15 nm to 100 µm, as measured perpendicular to the plane of the layer. In particular, polymer layers having a thickness ranging from 200 nm to 10 µm, or from 400 nm to 1,500 nm are believed to be useful. The final shape of the multilayer composite particles may be selected to provide individual layers with an aspect ratio that optimizes the performance of the composite when the composite is mixed with a matrix polymer and melt extruded. For example, platelets of one or more of the
organic polymers that comprise the layers of the composite may have an aspect ratio of at least 4, particularly at least 10, and more particularly having ranges from 50 to 20,000, or from 100 to 10,000, as determined by comparing the thickness of an individual layer to its maximum dimension parallel to the plane of such layer.

The multilayer composite may be provided in the shape of a pellet, having a diameter of from 2 mm to 6 mm, determined by the maximum width measured parallel to the plane of the layers. Alternatively, after the multi-layer composite structure exits the multiplier block assembly of the extruder, the composite is not stranded and cut into pellets, but collected in sheet, tape or strand form. In such a case, the layers of the composite would exist as tapes or ribbons, but not platelets. These sheets, tapes or strands can then be fed into the throat of the matrix polymer extruder or alternatively fed downstream into a port on the matrix polymer extruder. In one example, the sheet, tape or strand is fed into the throat or downstream port on an injection molder, thermoformer or extrusion blow molder. In another embodiment of the invention, the multi-layer composite structure, which exits the multiplier block assembly of the extruder, is fed directly into the matrix polymer extruder as described above, with or without partial cooling. Comminution of the multilayer composite structure occurs during melt extruding.

In one aspect of the present invention, the multilayer composite has at least two alternating layers, identified as first and second polymer layers. When the multilayer composite is employed as an additive to improve the properties of a matrix polymer, the first polymer softens and flows readily during the melt extrusion process, whereas the second polymer does not flow readily. Thus, the multilayer composite can be understood to undergo an exfoliation process, whereby the individual layers of the second polymer or platelets are dispersed throughout the matrix polymer, forming a two-phase system, when the layers of the first polymer soften and flow readily. Thus, the use of the multilayer composite as an additive provides a method to disperse layers (platelets) of the second polymer and thereby improve the properties of the matrix polymer. The first polymer is also dispersed throughout the matrix polymer as well, during the melt extrusion step. The first polymer may be miscible, partially miscible or immiscible in the matrix polymer. By
way of example, the first polymer and the matrix polymer may be the same class of polymers, for example polyolefins, and the first polymer of the composite is miscible in the matrix polymer.

The multilayer composite may be mixed with the matrix polymer to provide a concentration of the composite of from 3 to 33 weight %, based on the total weight of the mixture, and thus in the final product.

\[ T_f \] is the temperature above which a polymer will readily flow under normal shear rates experienced during typical processing conditions. \( T_f \) is defined as the larger of either the \( T_g \) or the \( T_m \) of a polymer. \( T_m \) is defined as the polymer melting point. \( T_g \) is defined as the glass transition temperature. For amorphous polymers that do not melt, a polymer can flow above its \( T_g \), so \( T_f = T_g \). However, for semicrystalline polymers that do melt, \( T_f = T_m \). To promote exfoliation and dispersion of the second polymer layer throughout the matrix polymer, the \( T_f \) of the polymer in the first layer of the composite is selected to be relatively close to or less than the processing temperature of the matrix polymer, for example, the \( T_f \) of the first polymer is not greater than the processing temperature of the matrix polymer. Conversely, the polymer in the second layer is not intended to flow and preferably retains its shape, so the \( T_f \) of the second polymer should be selected to be greater than the processing temperature of the matrix polymer, for example, by at about 10 °C or more. In terms of the multilayer composite, the difference in the \( T_f \) of the polymers in the first and second layers should be such that the first polymer will readily melt or flow during melt extrusion and the second polymer will not. By way of example, the difference between the \( T_f \) of the first and the second polymers may be at least 10 °C. In other embodiments of the invention, the difference in \( T_f \) is at least 20 °C or 30 °C.

The polymer of the second layer may have one or more additives incorporated therein to improve the stiffness of the polymer, which has the effect of minimizing distortion during processing, as well as positively affecting the properties of the matrix polymer.

In one embodiment of the invention, the first and second polymers comprising layers of the multilayer composite are characterized by the second layer having a
flexural modulus that is at least 2 times greater, preferably 5 times greater, than the flexural modulus of the first layer, as measured by ASTM D-790.

The multilayer composite is mixed with the matrix polymer to provide a concentration of the layers of the second polymer (platelets), as is desired to improve the properties in the matrix polymer. By way of example, the layers of the second polymer may be present in a concentration of 1 to 50 weight %, or 3 to 33 weight %, based on the weight of the matrix polymer and multilayer composite mixture.

In another aspect of the invention, the polymer layers comprising the multilayer composite are selected to provide layers of first and second polymer that both flow, when the multilayer composite and matrix polymer are melt extruded. For example, when the multilayer composite is fabricated from two polymers that are stacked in alternating layers, then both layers of the composite material are melted and dispersed in the matrix polymer. In this aspect of the invention, at least one of the polymer layers has an additive incorporated therein, which is released into the matrix polymer, when that layer of the composite softens and flows. The present invention is particularly useful in regard to additives that function as a reinforcing agent in the matrix polymer, such as high aspect ratio, inorganic additives, including reinforcing agents in the form of whiskers, fibers, platelets and the like. By way of further example, additives having an aspect ratio of at least 4, which neither dissolve nor melt in the matrix polymer during melt extrusion with the matrix polymer, may be employed as additives to improve the performance of the matrix material. Without being bound to a particular theory, it is believed that certain fabrication processes for creating multilayer composite materials, such as the multilayer coextrusion forced assembly process, orient high aspect ratio additives that are dispersed in one or more of the polymer layers. After the layer of the composite melts during the extrusion step, the additive dispersed in the matrix polymer retains at least some of the orientation, resulting in improved properties in the matrix polymer, as compared to traditional methods of mixing and melt extruding the additive and matrix polymer.

Thus, the multilayer composite functions as a means for delivering and dispersing an additive in the matrix polymer.
The multilayer composite is mixed with the matrix polymer to provide a desired concentration of the additive, which is dispersed in one or more of the polymer layers of the composite, to improve the properties in the matrix polymer. By way of example, the concentration of the additive, which is dispersed in one or more of the polymer layers of the composite, may be present in a concentration of 3 to 33 weight %, based on the weight of the matrix polymer and multilayer composite mixture. Accordingly, in one embodiment, the concentration of the additive in at least one of the layers of the polymer in the multilayer composite may range from 5 to 80 weight % of such polymer, typically from 10 to 30 weight %. Alternatively measured, the concentration of the additive in at least one of the layers of the polymer in the multilayer composite may range from 3 to 50 volume %.

Various properties of the matrix polymer may be improved by practicing the methods outlined above, such as the tensile modulus, elongation at break and flexural modulus of the matrix polymer. For example, by selecting various combinations of polymers in the multilayer composite, additives in the polymer layers and concentrations relative to the matrix polymer, the tensile modulus and flexural modulus of the matrix polymer may be increased by at least 50%, 75% or 100%. The elongation at break of the matrix polymer may also be increased by at least 25% or more.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of a multilayer coextrusion forced assembly process for a two polymer system.

Figures 2A, 2B, 2C, and 2D are a series of cross-sectional views illustrating the manner in which coextruded polymer melts can be divided and combined in a multilayer extrusion process.

Figures 3A, 3B, and 3C are atomic force microscopy images of the multilayer film produced in Example 1 taken at various levels of magnification.

Figures 4A and 4B are scanning electron micrographs of the multilayered extrudate produced in Example 1 taken in the flow direction.
Figures 4C and 4D are scanning electron micrographs of the multilayered extrudate produced in Example 1 taken in the transverse direction (i.e., perpendicular to the flow direction).

DETAILED DESCRIPTION OF THE INVENTION

Without limiting the scope of the invention, the preferred embodiments and features are hereinafter set forth. All of the United States patents, which are cited in the specification, are hereby incorporated by reference. Unless otherwise indicated, conditions are 25 °C, 1 atmosphere of pressure and 50% relative humidity, concentrations are by weight, and molecular weight is based on weight average molecular weight.

The term "polymer" or "polymeric material" as used in the present application denotes a material having a weight average molecular weight (Mw) of at least 5,000. Such polymeric materials can be amorphous, crystalline or elastomeric polymeric materials. The term "polymer" as used in the present application is not intended to include inorganic materials, such as clays, silicates, metals, metal oxides, aluminosilicates, graphitic materials, hydrotalcites, and metal nitrides. One or more of the polymer layers comprising the multilayer composite may, however, contain a finely-divided inorganic material dispersed throughout, as a reinforcing agent. The term "oligomer" or "oligomeric material" as used in the present application denotes a material with a weight average molecular weight of from 1,000 to less than 5,000.

Multilayer Composite

The multilayer composite of the present invention is comprised of at least eight layers of one or more organic polymers. In one aspect of the invention, a film comprising two, three, four or more organic polymers forms an alternating structure throughout the multilayer composite. The multilayer composite may have as may as 5000 layers. Typically, all of the layers in the multilayer composite will be comprised of one or more polymers. By way of example, multilayer composites having from 20 to 5000 layers are believed to be particularly useful.
In one aspect of the invention, substantially all of the polymer layers, for example, at least 90%, are contiguous with two polymer layers, or even all of the polymer layers, except the end layers, are contiguous with two polymer layers.

In another aspect of the invention, the multilayer composite is comprised of repeating film structures having at least two different polymer layers in each structure. The layers may differ in one or more of the following characteristics: type of polymer, additives within the polymer, flexural modulus, processing temperature, T_g and tensile strength. At least one of the polymers is selected to be processable, that is, it melts, when the multilayer composite is melt extruded with a matrix polymer.

In one aspect of the invention, the multilayer film can be made of two alternating layers (e.g. ABABA . . .) of a first polymer referred to as a polymer "(a)" and a second polymer referred to as polymer "(b)". The components (a) and (b), may be the same or different and form a multilayer structure represented by formula (AB)x, where x=(2)^n, and n is the number of multiplier elements. It can be understood that the multilayer structure of the invention may include additional types of layers. For instance, a three component structure of alternating layers (ABCBABCBABA . . .) of components (a), (b) and (c) is represented by (ABC)x, where x is as defined above and (c) is a third material. The components of the various alternating layers may be the same or different, as long as at least one component includes a polymer that can melt when extruded with a matrix polymer, i.e. the target polymer that is intended to be modified by incorporation of the multilayer composite.

In one aspect of the invention, a film comprising three or more layers can be made, wherein the layers may be the same or different in composition. The film may be used to fabricate the multilayer composite of the present invention. One of the layers, for example, may be a compatibilizing or decompatibilizing layer. For example, in the case of a decompatibilizing layer, the third layer can act to
destabilize the adhesion between layers one and two and thus facilitate the separation of the layers when mixed into the matrix polymer.

Multilayer extrusion, especially as it pertains to the production of polymer films, sheet and bottles, is a well-known method which is widely used to produce products, such as decorative packaging films, vacuum-packed packages of goods, such as coffee, and bottles used to store products, such as catsup.

Those skilled in the art will recognize that while such multilayer extrusions are in common practice, the use of simple extrusion dies through which molten polymers flow to produce the desired layered structures suffer from practical issues of polymer rheology which limit the number of layers that may be incorporated into an extruded film or sheet of fixed overall thickness, to a relatively low number, and hence limit the degree to which the thickness of an individual layer within such a multilayered structure may be reduced.

In order to produce extruded films or sheets in which the number of layers for a given overall thickness can exceed the normal practical limit (and therefore in which the thickness of an individual layer can be reduced to less than that attainable using traditional multilayer extrusion technology), a method known as layer multiplication has been developed.

The multilayer composite of the present invention can be fabricated using a multilayer coextrusion forced assembly technique. A typical multilayer coextrusion apparatus is illustrated in Fig. 1. The two component (AB) coextrusion system consists of two \( rac{3}{4} \) inch single screw extruders each connected by a melt pump to a coextrusion feedblock. The feedblock for this two component system combines polymeric material (a) and polymeric material (b) in an (AB) layer configuration or film. The melt pumps control the two melt streams that are combined in the feedblock as two parallel layers. By adjusting the melt pump speed, the relative layer thickness, that is, the ratio of A to B can be varied. From the feedblock, the melt goes through a series of multiplying elements. A multiplying element first slices
the AB structure vertically, and subsequently spreads the melt horizontally. The
flowing streams recombine, doubling the number of layers. An assembly of n
multiplier elements produces an extrudate with the layer sequence (AB)x where x is
equal to (2)n and n is the number of multiplier elements. It is understood by those
skilled in the art that the number of extruders used to fabricate the structure of the
invention equals the number of components. Thus, a three-component multilayer
(ABC . . . ), requires three extruders.

Multilayer extrusion offers a means by which two or more polymers can be
easily arrayed in an alternating structure. This extrusion process can operate at
standard polymer film line throughputs, making use of commercial polymers and
composite materials as its constituents, subject to melt temperature/rheological
match requirements. By way of further explanation, the multilayer coextrusion forced
assembly process is shown below in the following figures.

In layer multiplication, two or more polymeric materials (referred to as "A" and
"B" in Figures 2A-2D) are melt coextruded into a channel (commonly rectangular in
cross section) to produce a molten flow that appears as depicted in Figure 2A. While
still in molten flow, the polymer is divided "cut" into two halves, as depicted in Figure
2B. The cut layers are then directed to flow (are "stretched") back to their original
widths, with reduced thicknesses, as depicted in Figure 2C. The stretched layers are
then assembled through flow channels so they are "stacked" upon one another to
produce a "layer doubled" structure, as depicted in Figure 2D.

Repeating the cut/stretch/stack process will increase the theoretical number of
layers by powers of two, i.e. 2,4,8,16,32,64,... and can in fact be used to produce
hundreds or even thousands of layers in a film or sheet of less than about 10 mm in
overall thickness, and more ideally less than about 5 mm in overall thickness, and
even less than about 1 mm in overall thickness. By this method it is possible to
produce multilayered structures with individual layer thicknesses (A or B in the above
Figures) of less than about 5000 nm, more preferably less than about 500 nm. In
some cases it may be preferable to produce multilayered structures with individual
layers less than about 100 nm in thickness, or even as low as about 15-20 nm in thickness.

For ease of handling, it is sometimes advantageous to encase a multilayered structure produced by layer multiplying with an outside "skin layer" which serves to protect the product from physical damage in handling. Such a skin layer may be left in place, or peeled away from the multilayered structure, depending on the circumstances of its use.

A layer multiplication technology useful in conjunction with the present invention is disclosed in Baer et al., US Patent No. 6,582,807 B2 and Baer et al., US Patent No. 7,002,754 B2, and in "Processing and Properties of Polymer Multilayered Systems", by E. Baer, J. Kerns, and A. Hiltner, in Structure Development During Polymer Processing, A. M. Cunha and S. Fakirov, eds., pp 327-344, 2000, Kluwer Academic Publishers, The Netherlands. Details of the extrusion process and layer multiplication dies used in the examples which follow in this application are therefore understood to be equivalent to those shown in the above-mentioned reference, which, along with references cited therein, is hereby incorporated into the present application in its entirety.

Those skilled in the art will understand that while the examples and claims of this application were obtained using the specific layer multiplication technology described in the above-mentioned reference, the claims are in no way bound by use of that specific methodology. Alternative layer multiplication methodologies which allow for production of alternating layered structures which meet the requirements set forth in the claims of this application are understood to be part of the present invention as well.

By altering the relative flow rates or the number of layers, while keeping the film or sheet thickness constant, the individual layer thickness can be controlled. By way of example, the thickness of the individual layers can range from 15 nm to 100 \( \mu m \), 20 nm to 50 \( \mu m \), or 50 nm to 10 \( \mu m \). The multilayer film or sheet has an overall
thickness ranging from 10 nanometers to 1000 mils, preferably from 0.1 mils to 125 mils and any increments therein. Further, through the use of forming dies, the multilayer films may be formed into a variety of useful shapes including pellets, profiles, tubes and the like. A polymer "skin" may be added to either side of the multilayer composite, as is known in the art.

The foregoing aspects of the invention have been described in terms of a multilayer composite formed by repeatedly dividing, restacking and spreading the layers. The invention is not intended to be limited to a particular fabrication process, and other process for fabricating a multilayer film, meeting the parameters identified herein for the number of layers, layer thickness and performance of the polymers comprising the multilayer composite may be used.

The multilayer composite may be fabricated from thermoplastic polymers, thermosetting polymers, or a combination thereof. Thermoplastic polymers are particularly useful for fabricating the multilayer composite. Useful polymers include, but are not limited to, melt processible synthetic polymeric materials, such as polyesters (including, but not limited to PET, PBT, PTT, PLA, polyglycolic acid, polycaprolactone, wholly aromatic polyesters and water dispersible polyesters), polyamides (i.e. nylon 6,6, 6, 11, 12, 6,12, MXD6®), copolymers of ethylene and vinyl alcohol, ethyl-vinyl acetate copolymer, polyimides, polycarbonate, polystyrene, polyvinylchloride (PVC), polyacrylates, polymethacrylates, polyvinylethers, thermoplastic fluoro-based polymers (FEP, PFA, ETFE, EFEP), polyolefins, polysulfones, polyether ketones, polysulfides (such as PPS), polyamide-imides, polyacetals, recycled polymers and mixtures thereof.

Examples of olefin polymers are polymers and copolymers of aliphatic monoolefins containing 2 to about 8 carbon atoms which have an average molecular weight of from about 10,000 to about 2,000,000, preferably from about 30,000 to about 300,000, such as, without limitation, polyethylene, linear low density polyethylene, isotactic polypropylene, syndiotactic polypropylene, crystalline ethylene propylene copolymer, poly(i-butene), poly(4-methyl)pentene, 1-hexene, 1-
octene, homo and copolymer of norbornene such as COC and COP polymers, ethylene-octene copolymers, SEBS, and vinyl cyclohexane. The polyolefin polymers may include aliphatic polyolefins and copolymers made from at least one aliphatic olefin and one or more ethylenically unsaturated co-monomers. Generally, the co-monomers, if present, will be provided in a minor amount, e.g., about 10 percent or less or even about 5 percent or less, based upon the weight of the polyolefin (e.g. random copolymer polypropylene), but copolymers containing up to 25% or more of the co-monomer (e.g., impact copolymers) are also envisaged. Other polymers (such as acrylic acids and vinyl acetate) or rubber (such as EPDM, SBS, SEBS or EPR) may also be compounded with the polyolefin to obtain desired characteristics. The polyolefins of the present invention may be described as basically linear, regular polymers that may optionally contain side chains such as are found, for instance, in conventional low density polyethylene.

Thermosetting polymers or a combination of thermoplastic and thermosetting polymers may be used to fabricate the multilayer composite. During the fabrication process, such as by multilayer coextrusion forced assembly, the thermosetting polymer may be provided uncured, for example, without cross-linking, and then cured after fabrication is complete. For example, the thermosetting polymer may be cured prior to melt extruding the multilayer composite and a matrix polymer.

Examples of thermosetting polymers that may be used include photocrosslinkable polymers, such as (but not limited to) acrylic copolymers, epoxy resins, and unsaturated polyester resins.

The "polymer" comprising a particular layer of the composite may be a mixture of one or more individual polymers. Although not required, additives normally used in any of the above polymers may be used if desired. Such additives include, but are not limited to colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, acetaldehyde reducing compounds, oxygen scavaging compounds and the like. Furthermore, reinforcing agents, as described below in more detail, may be incorporated into one or more of the polymers comprising repeating layers of the multilayer composite.
Applications of the Multilayer Composite

The multilayer composite can be mixed with a matrix polymer, and the mixture can be melt extruded, to improve one or more of the properties of the matrix polymer. A wide range of thermoplastic polymers may be employed as the matrix polymer. For example, the thermoplastic polymers listed above may be employed, especially the polymers having a T\textsubscript{f} and processing temperature below 350°C. Particularly useful as the matrix polymers are polyolefins, for example, the polyolefins listed above.

In selecting the multilayer composite / matrix polymer system, one should bear in mind whether it is desirable for one or more of the polymers comprising layers of the composite not to melt during melt extrusion with the matrix polymer, or whether it is desirable for all of the polymers comprising the layers of the composite to melt during melt extrusion with the matrix polymer. Persons skilled in the art of injection molding of polymers will be able to select materials that are consistent with the intended mechanism and desired properties of the resulting product.

As noted above, the multilayer composite may be provided with alternating structures, with each structure comprising a layer of first and second polymers.

In one aspect of the invention, the multilayer composite is employed as an additive to improve the properties of a matrix polymer, and the first polymer flows readily during the melt extrusion process, whereas the second polymer does not flow readily, whereby the individual layers of the second polymer or platelets are dispersed throughout the matrix polymer, forming a two-phase system, when the layers of the first polymer melt. Examples of useful polymer combinations include: for the matrix polymer: polyolefins; for the first polymer: polyethylene, polypropylene or their compolymers; and for the second polymer: polysulfone or poly(ether ketones).

In another aspect of the invention, the polymer layers comprising the multilayer composite are selected to provide layers of first and second polymer that both melt, when the multilayer composite and matrix polymer are melt extruded. In
this aspect of the invention, at least one of the polymer layers has an additive incorporated therein, which is released into the matrix polymer, when that layer of the composite melts. In an embodiment of the invention, both the first and second layers may have an additive incorporated therein, which is capable of improving the properties of a matrix polymer. Of particular interest, is the use of additives that function as reinforcing agents in the matrix polymer, for example, to increase the tensile strength, flexural modulus, heat deflection temperature ("HDT") and/or the elongation at break. By way of example, one or more of the following additives may be incorporated into the first or second polymer layer, or both, of the multilayer composite, as a reinforcing agent: glass fibers, carbon fibers, carbon nanotubes, boron fibers, basalt fibers, metal oxide fibers, inorganic fibers, such as metal fibers, inorganic whiskers, such as metal oxide whiskers, nanocrystalline cellulose, cellulosic fibers and cellulose whiskers, and textile fibers, such as aramid fibers.

Inorganic whiskers are largely a family composed of single crystal inorganic materials with rod-like, fiber-like, or ribbon-like morphologies. They are often characterized by high aspect ratios (>5), diameters from 10 nm to 10 microns and lengths from 50 nm to several hundred microns. Common examples include but are not limited to: magnesium oxysulfate, aragonite calcium carbonate, calcium sulfate, calcium silicic acid, calcium sodium metaphosphate, calcium silicate, boron nitride, zinc oxide, zinc oxide tetrapods, magnesium carbonate, magnesium hydroxide, magnesium oxide, magnesium borate, magnesium oxide-aluminum oxide, magnesium perborate, nickel borate, silicon carbide, silicon nitride, tin oxide, copper oxide, sodium titanate, potassium titanate, potassium hexatitanate, potassium octatitanate, calcium hydroxyapatite, aluminum nitride, aluminum oxide, aluminum borate, mulite, titanium dioxide, aluminum silicate, zirconia, alpha chitin, carbon whiskers such as Graskers™, aluminum zirconate, magnesium oxychloride, aluminophosphate zeolites, alumina, calcium metaphosphate, and others. Examples of preferred inorganic whiskers include magnesium oxysulfate, sold by Milliken Chemical as Hyperform® HPR-803, calcium carbonate aragonite whiskers, sold by Maruo Calcium of Japan, calcium sulfate whiskers, magnesium borate whiskers, and calcium silicate whiskers such as Zono Hige™ sold by Ube Materials.
Other useful reinforcing agents could include plate-like materials like talcs, clays, metal oxide flakes, graphite or graphene, nanocrystalline silica, glass plates, zirconium phosphate nanoplatelets, Beohmites, magnesium hydroxide nanomaterials, synthetic clays such as Perkalite® from Akzo Nobel and a wide range of other plate-like reinforcing agents. Reinforcing agents and fillers can be surface treated or blended with by a range of materials known by those skilled in the art to increase compatibility and/or dispersion or other properties. Examples include coupling agents, nucleating agents, compatibilizing agents, and others known to those skilled in the art.

It can be understood that the use of additives, particularly a reinforcing agent, may be employed in various ways to improve the performance of the multilayer composite, that is, in improving the properties of a matrix polymer. For example, the multilayer composite / matrix polymer system may be designed so that the first polymer layers melt and the second polymer layers of the composite do not melt, during melt extrusion with a matrix polymer. Nevertheless, it is possible to minimize distortion of the second polymer layer (typically a platelet), by incorporating a reinforcing agent into the second polymer. Thus, the exfoliated second polymer layer is able to perform at or near maximum level in the matrix polymer, because it less likely to lose its planar shape when heated and stressed during melt extrusion.

The invention may be further understood in view of the following examples.

**Examples**

**Materials**

For the examples presented below, two ethylene-octene copolymers: "EO" (Dow Engage 8100) and "EO*" (Dow Engage 8400) with MFI values of 1 and 30 respectively and identical densities of 0.87 g/cm³ were used. Polysulfone "PSF" (Solvay Udel-3703) with MFI=17g/10min, 2.16 kg at 343°C (ASTM D 1238) and a density of 1.24g/cm³ was used as well. All three of these commercial polymers were used as received without any chemical modification.
Another polymer used in the examples which follow was Domolen 2300K, a 4MF polypropylene impact copolymer. A "masterbatch" concentrate of the same PP was reinforced by 30 wt% magnesium-based inorganic whisker from Milliken Chemical Co. (Hyperform HPR-803) "MF", produced by melt compounding using a side-fed Leistritz 28 mm co-rotating twin screw extruder operated with the following temperature profile from feed to die: 230-230-220-220-210-210-200-200-200-220-220°C and a melt temperature of 223°C. This masterbatch will be referred to Fiber-PP (FP), and had a density of 2.3 g/cm³. The MFI of both PP and FP were 5 g/10 min, 3.7kg at 190°C.

Example 1

A multilayered composite film of PSF and EO, with 4096 alternating layers was melt extruded at 285°C on a laboratory scale coextrusion line, employing layer-multiplying technology as described above. Both polymer melts were controlled at the same temperature during this extrusion. The total extruded multilayer strand thickness measured 4 mm, including two protective 1.08 mm EO skin layers. The composition of PSF/EO alternative layers 50/50 was by volume (i.e. the same volumes of "A" and "B" layer polymers were used in these examples). The multilayer extruded strand was cut into pellet size (about 4mm x 5mm) using a Flexible Plastic Blade (Model 3001 EVO/13, Accucutter Company, Carlisle, PA). With such cutting into pellets, the multilayered material could be handled and processed in the normal manner of commercial polymers. These pellets are referred to as PSF/EO "Smart Pellets" below.

The thickness of individual PSF and EO layers in the extruded product of Example 1 were measured by atomic force microscopy (AFM, Nanoscope Ilia, Digital Instruments, Santa Barbara, CA). The cross section of the strand was microtomed perpendicular to the extrusion direction. AFM images were obtained in air, operating in tapping mode. The AFM images of the PSF/EO multilayered film are shown in the Figures 3A-3C.
It should be noted that some variation in layer thickness is unavoidable during an extrusion process. Those skilled in the art will understand that this level of thickness variation will be expected to be considerably less on a commercial multilayering production line, than that obtained on a laboratory-scale extrusion system. For the extrusion of Example 1, individual layer thicknesses in the 500-1500 nm thickness range were measured.

**Example 2**

A multilayered composite film of PP and FP, with 64 alternating layers was melt extruded at 195°C on a laboratory scale coextrusion line, employing layer-multiplying technology as described above. Both polymer melts were controlled at the same temperature during this extrusion. The total film thickness was targeted at 76.8 µm; the composition of FP/PP alternating layers was 50/50 by volume. The thickness of individual PP and FP layer was targeted at 1.2 µm and later measured by scanning electron microscopy microtomed samples using Philips XL scanning electron microscope. The samples were sputter coated with palladium to provide enhanced conductivity, and were studied with the microscope operating at 15 or 20 kV. Images of the alternating FP/PP multilayered extrudate are shown in the Figure 4 below. After extrusion, 20 individual multilayer films were stacked and compression molded using a Carver Model C Laboratory Press operating at 150°C/1.5 Kpsi for 5 min to make a thick sheet; the final sheet was cut into multilayer FP/PP pellets (FP/PP) for injection-molding by using a bandsaw (Ryobi Model BS902) and the Flexible Plastic Blade described above. These pellets are referred to as FP/PP "Smart Pellets" below.

**Examples - Injection molding conditions**

All specimens involved in following tests were molded on a Boy 22-S injection molding machine equipped with a family mold including an ASTM D-790 flex bar and an ASTM D-638 type IV tensile bar.

Before injection-molding, PSF was dried in vacuum at 150°C overnight. All the PP resins were dried in vacuum at 80°C overnight.
Conditions used for the specific matrix polymers that were injection molded are given in the Table 1 below:

**Table 1.** Injection molding processing parameters.

<table>
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<tr>
<th></th>
<th>EO</th>
<th>EO*</th>
<th>PP</th>
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<tbody>
<tr>
<td>Melt temperature (°C)</td>
<td>175</td>
<td>130</td>
<td>200</td>
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<td>Mold temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>25</td>
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<tr>
<td>Injection pressure (psi)</td>
<td>1800</td>
<td>1100</td>
<td>1800</td>
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<td>Cooling time (sec)</td>
<td>15</td>
<td>15</td>
<td>15</td>
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<td>Cycle time (sec)</td>
<td>60</td>
<td>60</td>
<td>60</td>
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<tr>
<td>Screw rotation speed (rpm)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**Comparative Example 1**
EO Polymer was injection molded using the Boy 22-S injection molding machine into the family mold described above according to the EO process conditions indicated in the above Table 1.

**Comparative Example 2**
Polymer pellets of PSF and EO (10/90 wt/wt% respectively) were melt-blended and pelletized using a twin-screw extruder (Haake Fisons Rheodrive 5000) at 280°C prior to injection-molding shaken to combine the two materials. The bended pellets were then injection molded under the same conditions as were used in Comparative Example 1.

**Example 3**
PSF/EO "Smart Pellets" of Example 1 were combined by shaking with EO polymer in a 10/90 wt/wt% ratio respectively, and were injection molded under the same conditions as were used in Comparative Examples 1 and 2.
Comparative Example 3

Pellets of EO and EO* polymers (27:73 wt/wt% respectively) were combined by shaking, then injection molded according to the EO* process conditions indicated in the above Table 1.

Example 4

PSF/EO Smart Pellets of Example 1 were combined by shaking with pellets of EO* polymer in a 10/90 wt/wt% ratio, respectively, then injection molded in the same manner as was used in Comparative Example 3.

Comparative Example 4

Pellets of PP were injection molded according to the PP processing conditions indicated in the above Table 1.

Comparative Example 5

FP Masterbatch pellets were combined by shaking with PP pellets in a 1:5 wt/wt% ratio respectively, to produce an overall fiber loading of 5 wt%. This blend of pellets was injection molded under the same conditions used for Comparative Example 4.

Example 5

The FP/PP smart pellets of Example 2 were combined by shaking with PP pellets in a 30:70 wt/wt% ratio respectively, to produce an overall fiber loading of 5 wt%. This blend of pellets was injection molded under the same conditions used for Comparative Examples 4 and 5.

The injection molded samples of Comparative Examples 1-5 and of Examples 3-5 are summarized in Table 2.
Table 2. Injection molded Samples.

<table>
<thead>
<tr>
<th>Example</th>
<th>Compositions</th>
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<tbody>
<tr>
<td>Comp. 1</td>
<td>EO</td>
</tr>
<tr>
<td>Comp. 2</td>
<td>PSF/EO blend (10% wt/wt)</td>
</tr>
<tr>
<td>Example 3</td>
<td>PSF/EO smart pellet system (10% wt/wt)</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>EO/EO* (27:73 wt/wt)</td>
</tr>
<tr>
<td>Example 4</td>
<td>PSF/EO smart pellet system/EO* (10% wt/wt)</td>
</tr>
<tr>
<td>Comp. 4</td>
<td>PP</td>
</tr>
<tr>
<td>Comp. 5</td>
<td>FP/PP blend (fiber 5% wt/wt)</td>
</tr>
<tr>
<td>Example 5</td>
<td>FP/PP smart pellet system (fiber 5% wt/wt)</td>
</tr>
</tbody>
</table>

Examples - Mechanical Property Testing

Tensile, flexural, and impact tests were performed according to ASTM D-638, ASTM D-790, and ASTM D-256 standards respectively. All the tests were carried out at room temperature (approximately 25°C) and an average of at least five test specimens are reported herein. Tensile tests were conducted using an Instron 5566 Universal testing machine at a crosshead speed of 40 mm/min. Bars of 40 mm x 6.45 mm x 3.2 mm were used. Three point static flexural tests were carried out using 125 mm x 12.7 mm x 3.2 mm bars and a 50 mm span length on the same testing machine mentioned above at a crosshead speed of 1 mm/min. Izod Impact tests were conducted on specimens using a QC-63 universal impact testing machine and 3.2 mm thick specimens with a V notch in the middle.

Results for tensile testing of injection molded bars from Comparative Examples 1 and 2, and from Example 3 are compared in Table 3 below. Use of the PSF/EO Smart Pellet system produced a product with noticeably higher tensile modulus than was obtained with the starting EO polymer or from a simple PSF/EO polymer blend.
Table 3. Tensile test results of PSF/EO injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>5% secant modulus/Mpa</th>
<th>Ultimate Strength/Mpa</th>
<th>Elongation at break /100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1 EO</td>
<td>9.4 ± 0.4</td>
<td>4.9 ± 1.4</td>
<td>230 ± 10</td>
</tr>
<tr>
<td>Comp. Ex. 2 PSF/EO blend</td>
<td>12.0 ± 1.2</td>
<td>7.6 ± 1.0</td>
<td>425 ± 25</td>
</tr>
<tr>
<td>Ex. 3 PSF/EO smart pellet system</td>
<td>21.8 ± 2.4</td>
<td>6.5 ± 1.4</td>
<td>135 ± 15</td>
</tr>
</tbody>
</table>

Results for tensile testing of injection molded bars from Comparative Example 3, and from Example 4 are compared in Table 4 below. Use of the PSF/EO Smart Pellet system in EO⁺ polymer produced a product with noticeably higher tensile modulus than was obtained with the starting EO⁺ polymer.

Table 4. Tensile test results of PSF/EO⁺ injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>5% secant modulus/Mpa</th>
<th>Ultimate Strength/Mpa</th>
<th>Elongation at break /100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1 EO/EO⁺</td>
<td>5.5 ± 0.3</td>
<td>6.7 ± 0.4</td>
<td>810 ± 60</td>
</tr>
<tr>
<td>Comp. Ex. 4 PSF/EO smart pellet system</td>
<td>9.1 ± 0.7</td>
<td>2.0 ± 0.2</td>
<td>160 ± 70</td>
</tr>
</tbody>
</table>

Results for tensile testing of injection molded bars from Comparative Examples 4 and 5, and from Example 5 are compared in Table 5 below. Use of the FP/PP Smart Pellet system produced a product with noticeably higher tensile modulus than was obtained with the starting PP polymer, and matched that obtained with a fiber masterbatch/PP blend.
Table 5. Tensile test results of FP/PP injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>1% secant modulus/Mpa</th>
<th>Yield Strength /Mpa</th>
<th>Elongation at break /100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 4 PP</td>
<td>860 ± 30</td>
<td>23 ± 2</td>
<td>320 ± 20</td>
</tr>
<tr>
<td>Comp. Ex. 5 FP/PP blend</td>
<td>1030 ± 40</td>
<td>19 ± 2</td>
<td>340 ± 15</td>
</tr>
<tr>
<td>Ex. 5 FP/PP smart pellet system</td>
<td>1070 ± 170</td>
<td>19 ± 4</td>
<td>320 ± 50</td>
</tr>
</tbody>
</table>

Results for flexural testing of injection molded bars from Comparative Examples 1 and 2, and from Example 3 are compared in Table 6 below. Use of the PSF/EO Smart Pellet system produced a product with higher flexural than was obtained with the starting EO polymer or from a simple PSF/EO polymer blend.

Table 6. Flexural test results of PSF/EO injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Flexural Modulus/Mpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 1 EO</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>Comp. Ex. 2 PSF/EO blend</td>
<td>23 ± 7</td>
</tr>
<tr>
<td>Ex. 3 PSF/EO smart pellet system</td>
<td>27 ± 5</td>
</tr>
</tbody>
</table>

Results for flexural testing of injection molded bars from Comparative Examples 3, and from Example 4 are compared in Table 7 below. Use of the PSF/EO Smart Pellet system produced a product with a noticeably higher flexural than was obtained with the starting EO* polymer.

Table 7. Flexural test results of PSF/EO* injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Flexural Modulus/Mpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Ex. 3 EO/EO*</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>Comp. Ex. 4 PSF/EO *smart pellet system</td>
<td>29 ± 6</td>
</tr>
</tbody>
</table>
Results for flexural testing of injection molded bars from Comparative Examples 4 and 5, and from Example 5 are compared in Table 8 below. Use of the PF/PP Smart Pellet system produced a product with noticeably higher flexural modulus than was obtained with the starting PP polymer or from a simple fiber filled polymer.

**Table 8.** Flexural test results of FP/PP injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Flexural Modulus/Mpa</th>
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<tr>
<td>Comp. Ex. 4 PP</td>
<td>1060 ± 80</td>
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<tr>
<td>Comp. Ex. 5 FP/PP blend</td>
<td>1640 ± 70</td>
</tr>
<tr>
<td>Ex. 5 FP/PP smart pellet system</td>
<td>2120 ± 170</td>
</tr>
</tbody>
</table>

Results for impact testing of injection molded bars from Comparative Examples 4 and 5, and from Example 5 are compared in Table 9 below. Use of the PF/PP Smart Pellet system did not appear to offer any advantage in impact properties over the simple fiber filled polymer.

**Table 9.** Impact test results of FP/PP injection-molding samples.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Impact Strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>186 ± 33</td>
</tr>
<tr>
<td>FP/PP blend</td>
<td>139 ± 25</td>
</tr>
<tr>
<td>FP/PP smart pellet system</td>
<td>134 ± 20</td>
</tr>
</tbody>
</table>

The invention may be further understood by reference to the following claims.
What we claim is:

1. A method of improving the properties of a matrix polymer, comprising the steps of providing a mixture of the matrix polymer and a multilayer composite to an extruder, wherein the multilayer composite is comprised of at least eight, organic polymer layers, wherein each organic polymer layer is contiguous with at least one other organic polymer layer, and extruding the mixture under conditions sufficient to melt the matrix polymer, and a plurality of the polymer layers of the composite.

2. The method of Claim 1, wherein the multilayer composite comprises at least sixteen layers.

3. The method of Claim 1, wherein the multilayer composite comprises at least thirty-two layers.

4. The method of Claim 1, wherein the multilayer composite comprises at least sixty-four layers.

5. The method of Claim 1, wherein the multilayer composite is selected from the group consisting of two alternating layers, three alternating layers and four alternating layers.

6. The method of Claim 5, wherein a first alternating composite layer is melted when the mixture is extruded.

7. The method of Claim 5, wherein a second alternating composite layer is not melted when the mixture is extruded, and the second alternating layer is dispersed throughout the matrix polymer.

8. The method of Claim 5, wherein a second alternating composite layer comprises an additive selected from the group consisting of glass fibers, carbon fibers, carbon nanotubes, metal oxide fibers and whiskers, and cellulose whiskers dispersed therein.
9. The method of Claim 8, wherein the second composite layer is melted when the mixture is extruded.

10. The method of Claim 8, wherein the second alternating composite layer is not melted when the mixture is extruded, and the second alternating layer is dispersed throughout the matrix polymer.

11. The method of Claim 1, wherein the multilayer composite material is exfoliated when the mixture is extruded.

12. The method of Claim 1, wherein the organic polymer layers of the composite have a thickness of from 15 nm to 100 µm.

13. The method of Claim 1, where platelets derived from the organic polymer layers of the composite have an aspect ratio of at least 4.

14. The method of Claim 1, where platelets derived from the organic polymer layers of the composite have an aspect ratio of from 50 to 20,000.

15. The method of Claim 1, wherein the organic polymers layers of the composite have a melt viscosity within a factor of 4 of each other.

16. The method of Claim 1, wherein the multilayer composite is fabricated by a multilayer coextrusion forced assembly process.

17. The method of Claim 1, wherein the multilayer composite is comprised of at least sixty-four layers, and the composite is comprised of first and second alternating layers, wherein the first alternating composite layer is melted when the mixture is extruded, and the second alternating composite layer is not melted when the mixture is extruded, and the second alternating layer is dispersed throughout the matrix polymer, wherein platelets derived from the second alternating layer have a thickness of 400 nm to 1,500 nm and an aspect ratio of from 100 to 10,000.

18. The method of Claim 17, wherein the matrix polymer is selected from the group consisting of polyethylene and its copolymers, and polypropylene and its
copolymers, and the organic polymer of the first layer is selected from the group
consisting of polyethylene and its copolymers, and polypropylene and its
copolymers, and the organic polymer of the second layer is selected from the group
consisting of polysulfone, poly(ether ketone) and liquid crystalline polyesters.

19. The method of Claim 1, wherein the multilayer composite is in the
shape of a pellet having a width of from 2 mm to 6 mm.

20. The method of Claim 1, wherein the tensile modulus of the matrix
polymer is increased by at least 50%.

21. The method of Claim 1, wherein the flexural modulus of the matrix
polymer is increased by at least 50%.

22. The method of Claim 1, wherein the elongation at break of the matrix
polymer is increased by at least 25%.

23. The method of Claim 1, wherein the mixture is comprised of from 3 to
33 weight % of the multilayer composite.

24. The method of Claim 10, wherein the mixture is comprised of from 3 to
33 weight % of the second polymer layer of the multilayer composite.

25. The method of Claim 1, wherein the matrix polymer is a polyolefin.

26. The composition obtained from any of the methods of Claims 1-25.

27. A multilayer composite comprising at least eight, contiguous, organic
polymer layers, wherein the multilayer composite is selected from the group
consisting of two alternating layers, three alternating layers and four alternating
layers, wherein a first alternating layer of the composite has a \( T_f \) and a second
alternating layer of the composite has a processing temperature wherein the
difference between the these temperatures is at least 10 °C.
28. A multilayer composite comprising at least eight, contiguous, organic polymer layers, wherein at least one of the layers comprises an additive selected from the group consisting of glass fibers, carbon fibers, carbon nanotubes, metal oxide fibers and whiskers, cellulose whiskers, dispersed therein.

29. A multilayer composite comprising at least eight, contiguous, organic polymer layers, wherein the composite is in the shape of a pellet, having a height and diameter each of about 2-6mm and the layers have an aspect ratio ranging from 100 to 10,000.

30. The composite of Claim 29, wherein a first layer of the composite has a first flexural modulus and a second layer of the composite has a second flexural modulus, and wherein the difference between the first and second flexural modulus is at least threefold.
INTERNATIONAL SEARCH REPORT

PCT/US2010/002250

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J3/22 C08L23/06 C08L23/10

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 C08F B29D B32B

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 Further documents are listed in the continuation of Box C

X See patent family annex

* Special categories of cited documents

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

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on novelty 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

*A* document member of the same patent family

Date of the actual completion of the international search

21 December 2010

Date of mailing of the international search report

29/12/2010

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2
NL - 2280 HV RUISWIJK
Tel (+31-70) 340-2040
Fax (+31-70) 340-3016

Authorized officer

oi de Scheper, Bernd

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</table>
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-26
   A method of improving properties of a matrix polymer and a composition obtained by said method.

2. claim: 27
   A multilayer composite

3. claim: 28
   A multilayer composite

4. claims: 29, 30
   A multilayer composite
### Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos [ ]
   - because they relate to subject matter not required to be searched by this Authority, namely...

2. Claims Nos [ ]
   - because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be earned out, specifically...

3. Claims Nos [ ]
   - because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

### Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

**see additional sheet**

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims [ ]

2. [x] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims, it is covered by claims Nos

### Remark on Protest

- [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee
- [ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation
- [ ] No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (April 2005)