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(54) Title: POLYOLEFIN NANOCOMPOSITES

(57) Abstract: The present invention relates to methods for the preparation of clay/polymer nanocomposites. The methods include combining an organophilic clay and a polymer, each having a recrystallization temperature, wherein the organophilic clay recrystallization temperature sufficiently matches the polymer recrystallization temperature such that the nanocomposite formed has less permeability to a gas than the polymer. Such nanocomposites exhibit 5, 10, or even 100 fold or greater reductions in permeability to, e.g., oxygen compared to the polymer. The invention also provides a method of preparing a nanocomposite that includes combining an amorphous organophilic clay and an amorphous polymer, each having a glass transition temperature, wherein the organophilic clay glass transition temperature sufficiently matches the polymer glass transition temperature such that the nanocomposite formed has less permeability to a gas than the polymer.



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POLYOLEFIN NANOCOMPOSITES

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0001] The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the United States Department of Energy and the University of Chicago representing Argonne National Laboratory.

FIELD OF THE INVENTION

[0002] This invention relates to a method for preparing organoclays for use in clay/polymer nanocomposites. More particularly, the invention relates to methods for the surface modification of clays to provide solid-state compatibility between the organoclay and semi-crystalline polymers like the polyolefins and waxes.

BACKGROUND OF THE INVENTION

[0003] Since the late 1980s a great deal of research around the world has focused on developing methods to incorporate fully exfoliated smectite clays into polymers to increase mechanical and barrier properties. The approach relies on organoclay technology developed by Jordan in the 1950s, wherein the clay surface is treated to render it compatible with hydrophobic materials like the polyolefins and waxes. This surface treatment consists of an adsorbed monolayer of a high-molecular-weight quaternary amine, such as dimethyl dihydrogenated tallow amine. The surfactant adsorption takes place via an ion-exchange reaction involving the negatively charged basal surface of the clay platelets.

[0004] The simple mechanism by which the organoclays can improve barrier properties relies on the high aspect ratio of the exfoliated clay platelets to impart a tortuous path that retards the transport of diffusing species like oxygen or water vapor. In a strictly tortuous path mechanism, all diffusing species would be retarded to the

same degree. The tortuosity factor can be as high as several-hundred-fold for impermeable platelets with aspect ratios of 100-500 and at modest mineral loadings of 5-10 volume percent. Unfortunately, nanocomposite performance has not always lived up to expectations, and barrier improvements of two- to four-fold or less are more typical.

[0005] To overcome the difficulties in exfoliating organoclays in hydrophobic polymers like the polyolefins, researchers have used functionalized polymers, like maleated polyethylene and polypropylene, as dispersants. While polar functional groups can interact with the organoclay surface and compatibilizing agents can promote exfoliation, this approach to nanocomposite formation has provided only modest improvements in the mechanical properties of polyolefins. Moreover, there have not been any published results that show increased barrier toward oxygen or water vapor in polyolefins or waxes.

[0006] Accordingly, there is a need for a rational approach to the design of new organoclay chemistries that provide both melt- and solid-state miscibility and enable the preparation of nanocomposites demonstrating significant improvements in the control of polymer nucleation, crystal growth, and physical properties such as increased mechanical and barrier performance.

SUMMARY OF THE INVENTION

[0007] This invention provides a method to prepare clay/polymer nanocomposites with improved control over the dispersion of the organoclay yielding increased barrier properties. Specifically, the method comprises combining an organophilic clay and a polymer, each having a recrystallization temperature, wherein the organophilic clay recrystallization temperature sufficiently matches the polymer recrystallization temperature such that the nanocomposite formed has less permeability to a gas than the polymer. Such nanocomposites exhibit 5, 10, or even 100 fold or greater reductions in permeability to, e.g., oxygen compared to the polymer. Where the recrystallization temperatures of the organophilic clay and the polymer are not sufficiently matched, the mixture will show little or no improved barrier properties, and may exhibit partial or substantial phase-separation. Similarly,

the invention provides a method for preparing a nanocomposite comprising combining an amorphous organophilic clay and an amorphous polymer, each having a glass transition temperature, wherein the organophilic clay glass transition temperature sufficiently matches the polymer glass transition temperature such that the nanocomposite formed has less permeability to a gas than the polymer.

[0008] Invention methods for the preparation of nanocomposites further include the preparation of the organophilic clay by treating a clay with at least one surfactant to yield an organophilic clay having a recrystallization temperature higher than the polymer recrystallization temperature. Such an organophilic clay may function as a nucleating agent during formation of the nanocomposite. In addition, by use of such an organoclay the growth of polymer spherulites is lessened or prevented.

[0009] The nanocomposites formed by the present method include organophilic clays that are partially or completely exfoliated. Such organophilic clays may be prepared by surface treatment of a clay with a surfactant, such as a quaternary amine, and are compatible with hydrophobic materials such as polyolefins and waxes. Additionally, the surface of the clay is modified to produce an isotropic surface coating so that the polymer will wet and bond to the organoclay. This is achievable by using surfactants with sufficiently long alkyl chains so that they can become a part of the polymer crystal phase. Alternatively, if the polymer is amorphous, such as an elastomer, the surfactant used to produce the organoclay will require alkyl chains that also remain amorphous throughout the temperature range of intended use. Typically, the organoclays are surface treated with a high-molecular-weight quaternary amine together with high-molecular-weight hydrotrope and/or an edge modifying surfactant to render the clay surface organophilic. Suitable clays include phyllosilicates that are able to undergo ion exchange, such as smectites or mica. Natural or synthetic clays may be used in the present invention. Talcs may also be used in the invention but will normally require treatment with an appropriate edge-modifying surfactant.

[0010] In one embodiment, the method of the present invention employs a surface-treated clay such as one including a nonionic polymeric hydrotrope adsorbed onto a basal surface thereof, and/or an edge modifying surfactant adsorbed onto an edge thereof. The process used to produce hydrotrope-modified organoclays is described in detail in co-pending United States Patent Application, 10/078992, filed

on February 20, 2002. The process used to make organoclays incorporating both basal surface modification with a hydrotrope and edge treatment is described in detail in co-pending United States Patent Application, 10/100,381, filed on March 18, 2002.

[0011] Various processes may be used to prepare the organoclays. By way of non-limiting example, the smectite clay may be dispersed in water with the use of a pressure vessel to enable heating above the boiling point of the water. The clay slurry is heated to a temperature sufficient to melt the quaternary amine and allow ion exchange with the basal surface of the clay. The product of the reaction being an organoclay that exhibits melt/freeze transitions that match those of the polymer sufficiently so that the clay is able to remain dispersed in both the liquid and solid states. The solids concentration of the slurry may range from less than 1 weight percent to approximately 60 to 70 weight percent. At high solids concentration, sufficient mixing can be accomplished by use of a helical paddle mixer or alternatively, the mixing can be done using a single-screw extruder with a pressurized feeder to eliminate boiling of the water and thereby maintain the clay slurry at the desired water to solids ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1. DSC curve for the organoclay of Example 1. The peak transition from the crystal phase to the lamellar liquid crystal (LLC) phase occurs at about 40°C, while the recrystallization transition occurs at about 34.4°C with a heat of crystallization of -4.4 J/g.

[0013] FIG. 2. Cooling curves for a paraffin reference and the nanocomposite of Example 1 containing 10 weight percent organoclay. The peak freeze transitions occur at 45° and 28°C. The peak freeze transition for the pure organoclay is no longer present in the nanocomposite.

[0014] FIG. 3. Cooling curves for the polyethylene-*block*-poly(ethylene glycol) cosurfactant and the nanocomposite of Example 4 containing 70 weight percent organoclay. The presence of the organoclay reduced the peak recrystallization temperature of the block copolymer from 92.6° to 84°C.

[0015] FIG. 4. DSC heating curve for the nanocomposite of Example 4 showing the presence of the melt transitions for the quaternary amine on the organoclay and the cosurfactant [polyethylene-*block*-poly(ethylene glycol)].

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention provides organoclay/polymer nanocomposites having improved barrier properties and methods for making the same. More specifically, the invention permits the preparation of organoclay/polymer nanocomposites with improved barrier properties, that are explained by simple tortuosity effects, which result from the formation of a nanocomposite phase. The nanocomposite phase may be demonstrated by the presence of a new set of thermal transitions that are intermediate between the individual thermal transitions of the organoclay and the polymer.

[0017] The present invention provides for the preparation of polyolefin nanocomposites wherein the organophilic clay is homogeneously dispersed throughout the polymer matrix. Such nanocomposites exhibit superior dispersion stability such that the organoclay is dispersed in the polymer melt and is capable of maintaining the homogenous dispersion as the polymer cools to a semi-crystalline solid. Inventive methods also provide for organoclays that act as nucleating agents by virtue of their high specific surface areas and appropriately designed recrystallization temperatures.

[0018] Thus, to prepare clay/polymer nanocomposites according to the present invention, the recrystallization temperature of the organophilic clay must be sufficiently matched with the polymer recrystallization temperature to promote the formation of the nanocomposite phase. The phrase "sufficiently matched" does not require that the recrystallization temperatures be identical. Indeed, a wide range of recrystallization temperatures is possible. In some embodiments, the organoclay recrystallization temperature is within $\pm 100\%$ of the polymer recrystallization temperature, and is preferably within $\pm 50\%$. Even more preferably the organoclay recrystallization temperature is within $\pm 25\%$ of the polymer recrystallization temperature, and still more preferably is within $\pm 10\%$. Typically, the barrier

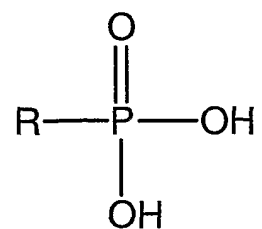
properties of a nanocomposite will improve the more closely matched are the recrystallization temperatures of the organoclay and polymer.

[0019] Other additives such as antioxidants, anticorrosion agents, reactive scavengers, such as colloidal metal oxides for improved acid barrier capabilities, oxygen scavengers for improved oxygen barrier capabilities, UV stabilizers, and colorants such as dyes and pigments may be incorporated into the compositions by admixing with the nanocomposite or by incorporating the additives directly onto the organoclay surface. For example, organoclays may be combined with water-soluble dyes and then dispersed in waxes or polyolefins. In this unique application, the organoclays aid the dispersion of the dyes. Water-soluble dyes which would not be expected to be dispersible in polyolefins may be used.

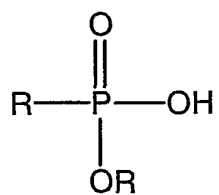
[0020] The present invention also encompasses embodiments wherein the organoclay has been modified on its basal surfaces with nonionic polymeric hydrotropes and on its edges with anionic surfactants that include organophosphorous and organosulfur compounds. The process used to produce hydrotrope-modified organoclays is described in detail in co-pending United States Patent Application, 10/078992, filed on February 20, 2002, and co-pending United States Patent Application, 10/100,381, filed on March 18, 2002. Both applications are herein incorporated by reference in their entirety. Briefly, adsorption of a polymeric hydrotrope on the basal surface of an edge modified clay is achieved by dispersing and/or dissolving a polymeric hydrotrope in the clay dispersion and allowing the hydrotrope to adsorb onto the surface of the dispersed, edge modified clay. The edge modification of the dispersed clay is carried out using an appropriate organic surfactant modifier.

[0021] Suitable organic surfactant edge modifiers for use in the present invention include organophosphorous and organosulfur compounds, particularly the following:

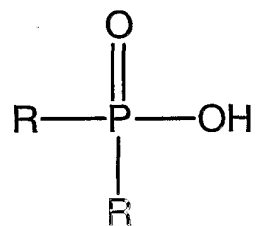
- a) phosphonic acids with the formula



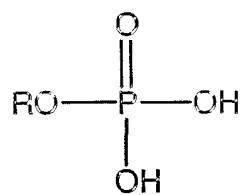
- b) phosphonic acids with the formula



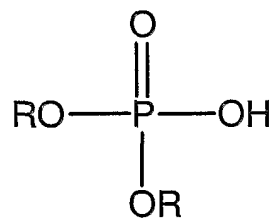
- c) phosphinic acids with the formula



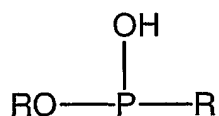
- d) phosphoric acid esters with the formula



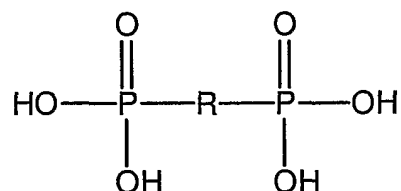
- e) phosphoric acid diesters with the formula



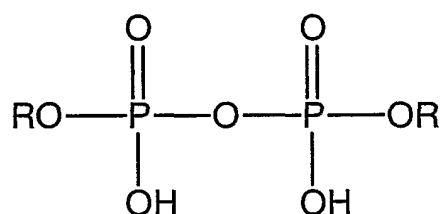
- f) phosphorous acid diesters with the formula



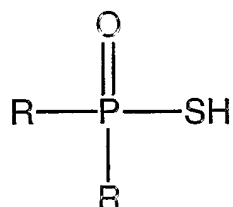
- g) diphosphonic acids with the formula



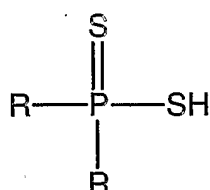
- h) pyrophosphoric acid diesters with the formula



- i) thiophosphonic acids with the formula



- j) dithiophosphonic acids with the formula



where R is an alkyl or hydroxyalkyl group with 1 to 50 carbon atoms or an aryl or hydroxyaryl group with 6 to 12 carbon atoms. Additionally, the R group may include oligomers comprised of two or more chemical species. Nonlimiting examples include polyethylene/poly(ethylene glycol)/polyethylene, Polypropylene/poly(ethylene glycol)/polypropylene, polypropylene/poly(ethylene glycol), polyethylene/poly(ethylene glycol), polyethylene/polypropylene,

poly(dimethylsiloxane)/poly(alkylmethylsiloxane), polyethylene/polybutylene, polyethylene/polybutene, polypropylene/polybutene, polystyrene/polybutadiene.

[0022] Suitable nonionic polymeric hydrotropes include, but are not limited to, polyvinyl alcohol, polyvinylpyrrolidone, polypropylene glycol, polybutylene glycol, methoxypolyethylene glycol, dimethoxypolyethylene glycol, polyethylene glycol, polyethylene glycol derivatives such as, polyethylene glycol acrylate, polyethylene glycol diacrylate, polyethylene glycol methyl ether acrylate, polyethylene glycol methacrylate, polyethylene glycol dimethacrylate, polyethylene glycol methyl ether methacrylate, polyethylene glycol methyl ether epoxide, polyethylene glycol diglycidyl ether, polyethylene glycol phenyl ether acrylate, polyethylene glycol bisphenol A diglycidyl ether, polyethylene glycol dibenzoate, polyethylene glycol bis(3-aminopropyl ether), polyethylene glycol butyl ether, polyethylene glycol dicarboxymethyl ether, polyethylene glycol divinyl ether, as well as copolymers of polyethylene glycol/polypropylene glycol, and polyethylene glycol/polybutylene glycol, and mixtures thereof.

[0023] Other nonlimiting examples of polymeric hydrotropes include polyethylene-*block*-poly(ethylene glycol)-*block*-polyethylene, Polypropylene-*block*-poly(ethylene glycol)-*block*-polypropylene, polypropylene-*block*-poly(ethylene glycol), polyethylene glycol-*block*-polypropylene glycol-*block*-polyethylene glycol, polyethylene glycol-*ran*-polypropylene glycol, polyethylene glycol-*ran*-polypropylene glycol monobutyl ether, polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol, polypropylene glycol monobutyl ether, polytetrahydrofuran, polytetrahydrofuran bis(3-aminopropyl), polyethylene-*block*-polyethylene glycol and polypropylene glycol, and mixtures thereof.

[0024] In some embodiments where the surface treated clay has been modified on both basal surfaces and edges, the melt comprises about 1-99 weight percent of the nanocomposite. In other embodiments, the surface treated clay comprises about 1-15 weight percent and preferably about 3-10 weight percent of the nanocomposite.

[0025] In embodiments wherein the phyllosilicates are subject to cation exchange, the phyllosilicates are exposed to enough cationic surfactant to approximately satisfy the cationic exchange capacity of the phyllosilicates. For

dispersions in aliphatic solvents, waxes, and polyolefins, the amount of cation in the dispersion should be enough to satisfy between about 50 and 100 percent of the cation exchange capacity of the phyllosilicates. This includes embodiments where the amount of cation is sufficient to satisfy between about 75 and 100 percent of the exchange capacity of the phyllosilicate. This has the advantage that it substantially eliminates excess cationic surfactant which is only loosely bound to the phyllosilicate surface and easily separates during processing and composite material formation, degrading the quality of the composite materials. In preparing organoclays for polyolefin nanocomposites, the cation exchange will be carried out at temperatures at least equal to or above the melting point of the surfactant. For surfactants that melt at temperatures above 100°C, the exchange will be carried out in a reactive extruder that is pressurized to prevent the evaporative loss of water from the clay slurry.

[0026] Suitable clays for use in the invention include phyllosilicate clays, such as mica and smectite clays. Exemplary smectite clays include montmorillonite, hectorite, saponite, sauconite, beidellite, nontronite and synthetic smectites such as Laponite®. As will be well understood by one skilled in the art, the clays discussed herein inherently have basal surfaces and are arranged in layers of particles which are stacked on top of one another. The stacking of the clay platelets provides interlayers, or galleries, between the clay layers. These galleries are normally occupied by cations, typically comprising sodium, potassium, calcium, magnesium ions and combinations thereof, that balance the charge deficiency generated by the isomorphous substitution within the clay layers. Typically, water is also present in the galleries and tends to associate with the cations. The distance between the basal surfaces of adjacent clay layers is referred to as the basal spacing.

[0027] To obtain useful nanocomposite properties in clay/polymer mixtures, the organoclay must be compatible with the polymer. Compatibility between polymer/polymer and polymer/wax blends is known from prior art to be a function of the freezing points of the two components. If one component freezes at a significantly higher temperature than the other, the result upon cooling is a phase separated mixture that does not improve the properties of either component. For example, a paraffin wax that freezes at about 45°C is not compatible with either low density polyethylene which freezes at about 87°C or with high density polyethylene which freezes above

100°C. The effect of the organoclay on the recrystallization temperatures of the polymer must also be considered in the design of a useful nanocomposite system. Melt and shear histories of polymer systems are also important factors. For example, the recrystallization temperature of a polymer can be increased 15-20°C if the temperature of the polymer melt is insufficient to ensure complete crystal melting or if the polymer melt contains locally entangled segments originating from the polymer crystallites.

[0028] In a similar manner, amorphous polymers, such as atactic polypropylene, ethylene propylene random copolymers, ethylene vinyl acetate copolymers, polyisoprene, polybutadiene, polychloroprene, polyisobutylene, poly(styrene-butadiene-styrene), silicones, polyurethanes, poly(methyl methacrylate), poly(methacrylate), poly(ethyl methacrylate), poly(propyl methacrylate), poly(butyl methacrylate), atactic polystyrene, would not be compatible with organoclays that possess a surface crystallization temperature. Organoclay compatibility with amorphous polymers would require sufficiently matching the T_g (glass transition temperature) of the surfactant coating with that of the polymer if the nanocomposite is to be used at temperatures below the T_g of the polymer.

[0029] The nanocomposites prepared according to the present invention display unexpectedly high gas barrier capabilities in comparison to previous clay/wax and clay/polymer nanocomposites. The nanocomposites disclosed herein can routinely reduce the oxygen permeability of wax coatings by a factor of ten to one hundred or more. At sufficient clay concentrations, the permeability may be reduced by one thousand to ten thousand or more. Combinations of wax nanocomposites with polyolefins can in turn result in significant reductions in gas permeability relative to the pure polymer. Reductions in oxygen permeability of ten to one-hundred fold or more relative to the pure polymer can be achieved with the present invention.

[0030] While not wishing to be bound by theory and without limiting the scope of the invention, it is believed that invention methods improve the barrier properties of clay/polymer nanocomposites by taking into account the effect of the semi-crystalline structure of polymers on nanocomposite morphology and performance. The polyolefins, consist of a mixture of crystalline and amorphous phases at temperatures above the T_g and below T_m (melting transition temperature)

The hydrocarbon chains fold in on themselves to form crystallites which in turn stack upon themselves to form spherulites. The crystallites are generally on the order of 10-20 nm, while the spherulites can be as large as 50-100 microns or larger as in the case of waxes. The crystallites are held together by amorphous polymer segments which contribute to the strength of the material. If the hydrocarbon chain length is shortened sufficiently, as in the case of the waxes, the chains become less and less able to bridge the gap between the crystallites, and the material becomes brittle. Gas diffusion can take place at the interfaces between the crystallites and at the surfaces of the spherulites. Thus, a tortuous diffusion path is an inherent component of all semi-crystalline polymer systems.

[0031] Despite the chemical similarity between paraffin wax and low-density polyethylene (LDPE), they are not compatible because of the large difference in their freezing points – that is, their mixtures phase-separate upon cooling from the melt. By extension, organoclay that is prepared with paraffin-like surfactants is unlikely to be compatible with either LDPE or the other polyolefins. During cooling of the polymer, if the interaction energy between the organoclay surface and the polymer chains is insufficient to disrupt the normal crystallization process, the organoclay will be pushed aside by the growing polymer crystallites, along with any other impurities that happen to be present in the polymer melt. In fact, there is no prior art showing an increase in barrier properties for any olefin-based nanocomposites, including waxes. In these systems, the addition of organoclays, according to prior art, actually results in a decrease of barrier properties. The lack of significant commercial nanocomposite barrier materials, despite years of research since the first publications in the field (see, e.g., Okada, F., et al., U.S. Patent No. 4,739,007 (1988)) illustrates just how difficult these problems are to solve.

[0032] Thus, it is not enough that the melted polymer wet the surface of the organoclay; the cohesion energy of the organoclay coating must be close to that of the wax or polyolefin crystal phase. In other words, the freezing points of the surfactant chains on the clay surface and the polyolefin must be close enough to enable the exfoliated organoclay to enter solid solution as the nanocomposite phase freezes. It is reasonable to expect that this requirement will be true of all semi-crystalline materials, such as nylons, polyesters, and polyolefins. Because of supercooling effects,

recrystallization temperatures will be lower than the melting temperatures. In addition, the presence of the organoclay may affect the recrystallization temperature, especially if the organoclay is capable of acting as a nucleating agent. Therefore, the recrystallization temperature is expected to be a better predictor of solid-state miscibility than is the melting point.

[0033] The following non-limiting examples serve to further illustrate advantages of the disclosed invention.

EXAMPLES

EXAMPLE 1

[0034] In this example, the superior barrier performance that can be achieved when the melt/freeze transitions of the organoclay and a paraffin wax are close enough to generate a new nanocomposite phase. An organophilic clay was prepared from a commercially available, water-washed montmorillonite (Cloisite Na[®] which is a product of Southern Clay Products). The clay was dispersed in 40°C tap water at a solids concentration of 2.5 weight percent by high-shear mixing for 40 minutes. The edge of the clay was modified by addition of an aqueous solution of the ammonium salt of 1-hydroxydodecane-1,1-diphosphonic acid. The amount of ammonium alkylidiphosphonate added was 3 weight percent relative to the weight of the dry clay. Following equilibration for 30 minutes, the temperature of the slurry was increased to 70°C and an amount of dimethyl dihydrogenated tallow ammonium chloride (Arquad 2HT-75, a quaternary amine salt commercially available from Alzo Nobel) equivalent to 110 milliequivalents per 100 g clay was added over a period of one hour. Combined with the quaternary amine was an amount of poly(propylene glycol) equivalent to 4 weight percent relative to the dry weight of the clay. The molecular weight of the poly(propylene glycol) was 1000. Also combined with the quaternary amine solution was an antioxidant, Irganox[®] B225 (a product of Ciba Specialty Chemicals Corp.) at a concentration of 1000 ppm relative to the weight of the organoclay. Mixing of the clay suspension was continued for one hour after all of the quaternary amine salt was added. The suspension was vacuum filtered, redispersed in deionized water at 60°C and refiltered. The organoclay was dried under vacuum at 70°C to produce a fine powder with less than 1 weight percent moisture. The basal

spacing of the organoclay product, as measured by x-ray diffraction, was approximately 36.5 Å.

[0035] Wax nanocomposites with organoclay concentrations of 5, 10, and 15 weight percent were prepared by mixing the organoclay powder into the melted wax with stirring at approximately 80°C. The paraffin used to prepare the samples was purchased from Aldrich Chemical Co. The wax nanocomposites were applied to a silicone release paper using a smooth coating rod from R. D. Specialties, Inc.

[0036] The oxygen transmission rate was measured on films with thickness of approximately 2 mils. The measured film thickness was used to calculate oxygen permeability from the measured oxygen transmission rate. The results for three different organoclay loadings are shown in Table 1 along with the reference value for zero clay addition. (A control experiment in which 5 weight percent Cloisite 15A was dispersed in the wax showed no reduction in oxygen permeability.) There is a dramatic decrease in oxygen permeability with increasing organoclay concentration until 15 weight percent organoclay loading. Microscopic examination of the film with 15 weight percent organoclay revealed extensive cracking that looked identical to that in the reference film with no added organoclay. With only 5 weight percent organoclay the oxygen permeability dropped by approximately 62 fold, while with 10 weight percent organoclay addition, the oxygen permeability dropped by 330 fold. This performance is well beyond what has been found in nylon nanocomposites where reduction in oxygen permeability of 2-5 fold is found for 2-5 weight percent organoclay loading. See, e.g., A. Usuki, N. Hasegawa, H. Kadoura, and T. Okamoto, Nano Lett, 1, No. 5, 271 (2001). No reduction in oxygen permeability has been reported for wax nanocomposites.

TABLE 1. Oxygen Permeability of clay/wax nanocomposite films.

Organoclay, Wt %	O ₂ Permeability*
0	4629 x 10 ⁻¹⁷
5	75 x 10 ⁻¹⁷
10	14 x 10 ⁻¹⁷
15	4629 x 10 ⁻¹⁷

* units are mol O₂/m²•s•Pa

[0037] The levels of reduction in gas permeability found in nylon nanocomposites are consistent with a tortuosity mechanism in which the permeability is proportional to clay loading (i.e., Nielsen model). If the gas permeability is limited by diffusion through narrow gaps between the oriented clay platelets, the relative permeability is a function of the aspect ratio (α) and the clay loading (ϕ) as shown in equation (1):

$$P_o/P_c = 1 + 1/2 \alpha \cdot \phi \quad (1)$$

where P_o and P_c are the permeability of the pure polymer and the nanocomposite, respectively. In this case the relative permeability is proportional to the clay loading. If the permeability is limited by gas diffusion around impermeable clay platelets, the relative permeability becomes proportional to the square of the clay loading:

$$P_o/P_c = 1 + \alpha^2 \cdot \phi^2 / (1 - \phi) \quad (2)$$

[0038] If we attempt to fit the data of Table 1 with the Nielsen equation (Eq. 1) in which the gas permeability is a function of both the volume fraction of the mineral filler and the aspect ratio of the filler platelets, we can calculate an effective aspect ratio for the organoclay platelets in our wax nanocomposites at 5 and 10 weight percent organoclay. The calculated aspect ratios turn out to be approximately 3,000 and 9,500 for 5 weight percent and 10 weight percent clay loading, respectively. These values are well beyond the typical aspect ratios for montmorillonite which are reported to be between 100-500. If, on the other hand, we use Eq 2 to back calculate an effective aspect ratio, we obtain values of 250 and 240 at 5 and 10 weight percent loading, respectively. These values are well within the physically acceptable range of

aspect ratios for montmorillonite in nanocomposite systems. Clearly, the mechanism by which the oxygen permeability in the wax nanocomposites is reduced is by a tortuous path in which the permeability is limited by diffusion around the clay platelets, as described in Eq 2.

[0039] In this example, the melt/freeze transitions of the organoclay and the wax are close enough to produce a nanocomposite phase in which the organoclay remains in solid solution after the freezing of the wax takes place. The DSC data in Figure 1 show the peak of the melt and freeze transitions of the pure organoclay which occur at 39.6° and 34.4°C, respectively. In Figure 2, the DSC cooling curves for the paraffin wax and the nanocomposite containing 10 weight percent organoclay are shown. The peak freeze transitions for the paraffin wax occur at 45.7°C and 28.4°C with ΔH values of -136.8 J/g and -26.6 J/g, respectively. The presence of two freeze temperatures indicates that the paraffin wax consists of a bimodal distribution of molecular weights. The cooling curve for the nanocomposite is almost identical to the pure paraffin wax, but differs in a significant way when the total thermal transition energy is considered. The freeze transition of the organoclay at 35°C is no longer present in the nanocomposite because of the formation of a new nanocomposite phase. The peak freeze transitions of the nanocomposite occur at 45.2 and 28.1°C with ΔH values of -127.0 J/g and -27.5 J/g, respectively. From a measurement of normalized peak areas (i.e., normalized for sample weight), the total heat of crystallization for the pure paraffin is -0.99 J while for the nanocomposite the value is -1.66 J. These data show that the degree of crystallization in the nanocomposite is higher than the paraffin reference. Thus, it may be concluded that the organoclay acts as a nucleating agent.

EXAMPLE 2

[0040] In this example, the effect of using a paraffinic wax with increased melt/freeze temperature on nanocomposite performance is illustrated. The organoclay of Example 1 was dispersed in Parafint H-1 (a product of Moore & Munger). This is a high melting wax that is miscible with low density polyethylene (LDPE) at low wax/polymer ratios. The melt and freeze transitions of the wax are almost identical with that of LDPE. The nanocomposite was prepared with 10 weight percent organoclay loading and the oxygen permeability of the pure wax and the

nanocomposite were measured. The permeability of the reference wax was 3404×10^{-17} mol O₂/m•s•Pa, while that of the nanocomposite was 2393×10^{-17} mol O₂/m•s•Pa. In this case the oxygen permeability was reduced only 30 percent relative to the pure wax. This is in contrast to the paraffin wax nanocomposite of Example 1 which demonstrated a 98.4 percent reduction in oxygen permeability at 10 weight percent organoclay loading. This example illustrates the point that as the freeze transitions of the organoclay and the wax are further separated from one another, the ability to form an effective nanocomposite phase is diminished.

EXAMPLE 3

[0041] While maintaining the organoclay in an exfoliated state is important to nanocomposite performance, it may not be the only determining factor affecting barrier performance. Without wishing to be limited to any specific theory, it is believed that the inability of an isotropic polymer phase to wet and bond with an anisotropic organoclay surface is also a contributing factor responsible for the poor barrier performance observed in polyolefin systems, and in polymer systems in general. In other words, while it may be relatively easy for a paraffin molecule to suffer the loss in entropy necessary to adopt a favorable orientation to interact with the organoclay surface, it is unlikely that the significantly greater loss in entropy accompanying the uncoiling of a high-molecular-weight polymer could be compensated sufficiently by changes in enthalpy. This hypothesis is supported by the data in Table 2, which show the effects of freezing points and molecular weight on oxygen barrier. As the olefin chain length is increase from paraffin to LDPE, we see a steady decline in the influence of the organoclay on oxygen transmission rate. This can be partially explained by the fact that an increase in chain length is accompanied by an increase in recrystallization temperature, which would lead to phase separation of the clay during cooling of the melt. However, while the recrystallization temperatures of Paraflint H-1 and LDPE are virtually identical, the wax nanocomposite still exhibits some improvement in barrier properties while the LDPE system shows no change in oxygen permeability.

TABLE 2. Relationship between oxygen barrier, molecular weight, and recrystallization temperature.

System*	Olefin MW	Peak Freezing Temperature, °C	% Reduction in O ₂ Permeability
Paraffin	~400	45.5	98.4
Paraflint H-1	785	87	36.9
LDPE	>40,000	86.6	0

*The nanocomposite systems all contain 5 weight percent organoclay as prepared in Example 1.

EXAMPLE 4

[0042] To overcome the difficulties in exfoliating organoclays in hydrophobic polymers like the polyolefins, researchers have used functionalized polymers, like maleated polyethylene and polypropylene, as dispersants. While polar functional groups can interact with the organoclay surface and compatibilizing agents can promote exfoliation, the presence of organoclay thermal transitions would still be present and, if not matched to the polymer, would create a highly permeable interphase surrounding the organoclay. While this approach to nanocomposite formation has been shown to provide modest improvements in the mechanical properties of polyolefins, there is no prior art that shows increased barrier toward oxygen or water vapor in polyolefins or waxes.

[0043] In Example 1, the poly(propylene glycol) was used to introduce disorder within the quaternary amine monolayer. In this example a cosurfactant is used to increase the interaction between the organoclay surface and LDPE by increasing the effective freeze temperature of the organoclay surface and to introduce a degree of isotropy to the organoclay surface. An organoclay was prepared in the same manner as in Example 1 except without the addition of poly(propylene glycol). Furthermore, the quaternary amine loading was reduced to 90 meq per 100 g of clay to accommodate the adsorption of the cosurfactant. The organoclay filter cake was mixed with polyethylene-*block*-poly(ethylene glycol) (Aldrich Chemical Co.) at a weight ratio of 70 percent organoclay to 30 percent cosurfactant, on a dry basis. The

cosurfactant, which has an HLB value of 4, a 50-carbon alkyl chain, and a melting and freezing point that closely matches that of LDPE is miscible with LDPE at low loading levels.

[0044] The DSC data in Figure 3 are the cooling curves for the polyethylene-*block*-poly(ethylene glycol) and the clay nanocomposite containing 70 weight percent organoclay. The presence of the organoclay reduced the peak freeze temperature of the block copolymer from 92.6°C to 84°C, indicating the presence of a nanocomposite phase having thermal transitions that are intermediate to those of the individual components. However, the thermal transitions present in the pure organoclay of Example 1 were still detectable in the nanocomposite. In Figure 4 the melt transitions of the quaternary amine and the cosurfactant are detectable at 42.1° and 97.1°C, respectively. The broad melt/freeze transitions of the cosurfactant are also noteworthy and problematic. The broad thermal transitions mean that at least a portion of the organoclay surface will be in the melt state while the polymer is recrystallizing. This raises the possibility of forming interfacial defects between the organoclay and the polymer as the system cools to room temperature. The ideal surfactant for preparing an organoclay would display narrow melt/freeze transitions at temperatures near or slightly above the thermal transitions of the polymer.

[0045] The x-ray diffraction pattern of the nanocomposite showed a broad reflection from the basal surface without any discrete basal spacing (D. J. Chaiko in *Affordable Materials Technology – Platform to Global Value and Performance*, B. M. Pasmussen, L. A. Pilato, and H. S. Kliker, EDS., SAMPE: Covinal, CA, 2002, 1064). The organoclay concentrate was diluted with LDPE to a final organoclay concentration of about 8 weight percent by compounding in a Brabender mixer for 30 min. at 130°C at a temperature of 170°C. The nanocomposite was compression molded to produce transparent films of 125 microns thick. The oxygen permeability of the nanocomposite was measured and found to be 14x lower than the LDPE reference. This represents an approximate 93 percent reduction in oxygen transmission relative to the pure LDPE film.

[0046] While the performance of the nanocomposite is very good, the relative reduction in oxygen permeability is less than what was observed in the paraffin system of Example 1. This is believed to be due to the fact that the melt/freeze

transitions of the organoclay surface were still detectable (see FIG. 4). Increasing the recrystallization temperature of the organoclay by use of a higher freezing quaternary amine would be expected to improve the barrier properties even further.

[0047] This example highlights the fact that while coupling agents or compatibilizing agents (e.g., maleated polyolefins) may help disperse the organoclay and aid in the formation of nanoscale dispersions, the fact remains that the phase transitions of the quaternary amine are likely to still be present, and can be expected to lead to grain boundary defects that would provide an unimpeded path for gas transport, thereby limiting the barrier performance of the nanocomposite.

COMPARATIVE EXAMPLE 1

[0048] In the previous examples, the quaternary amine used to prepare the organoclay exhibited a melting point below 40°C. In the present comparative example, an organoclay is prepared using cetyltrimethyl ammonium bromide, which has a decomposition temperature in excess of 230°C.

[0049] The organoclay was prepared by dispersing Cloisite Na® in deionized water at 40°C. The clay was dispersed with high shear mixing at a solids concentration of 2 weight percent. The edge of the clay was treated with the ammonium salt of 1-hydroxydodecane-1,1-diphosphonic acid. The amount of ammonium alkylidiphosphonate added was 0.5 weight percent relative to the weight of the dry clay. Following equilibration for 30 minutes, the temperature of the slurry was raised to 70°C and an amount of cetyltrimethyl ammonium bromide (Aldrich) was added equivalent to 100 meq per 100 g clay over a period of one half hour. Combined with the quaternary amine was an amount of poly(ethylene glycol) equivalent to 4 weight percent relative to the weight of the dry clay. The molecular weight of the poly(ethylene glycol) was 1500. Mixing of the clay suspension was continued for one hour after all of the quaternary amine salt was added. The suspension was filtered, redispersed in deionized water at 70°C and refiltered. The organoclay was dried crushed and examined by DSC. The organoclay did not show a melt transition. Furthermore, the organoclay failed to disperse in LDPE by melt compounding. This example illustrates the importance of preparing organoclays with

surfactants that exhibit melt/freeze transitions near those of the polymer if dispersion and exfoliation are to be achieved.

[0050] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above.

[0051] All references cited herein are specifically incorporated by reference in their entirety into the disclosure of this application.

[0052] While preferred embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the invention in its broader aspects as defined in the following claims.

CLAIMS

What is claimed:

- 1 1. A method of preparing a nanocomposite comprising combining
2 an organophilic clay and a polymer, each having a recrystallization temperature,
3 wherein the organophilic clay recrystallization temperature sufficiently matches the
4 polymer recrystallization temperature such that the nanocomposite formed has less
5 permeability to a gas than the polymer.
- 1 2. The method according to claim 1, wherein the gas is oxygen.
- 1 3. The method according to claim 2, wherein the nanocomposite
2 formed has at least ten fold less permeability to oxygen than the polymer.
- 1 4. The method according to claim 1, wherein the organophilic
2 clay is a phyllosilicate.
- 1 5. The method according to claim 1, wherein the organophilic
2 clay is a smectite or mica.
- 1 6. The method according to claim 1, wherein the organophilic
2 clay is a smectite selected from the group consisting of montmorillonite, hectorite,
3 saponite, sauconite, beidellite, nontronite, Laponite, and combinations of two or more
4 thereof.
- 1 7. The method according to claim 1, wherein the organophilic
2 clay is a surface-treated clay.
- 1 8. The method according to claim 7, wherein the surface-treated
2 clay includes an edge modifying surfactant adsorbed onto an edge thereof.
- 1 9. The method according to claim 7, wherein the surface-treated
2 clay includes a nonionic polymeric hydrotrope adsorbed onto the basal surface
3 thereof.

1 10. The method according to claim 1, wherein the organophilic
2 clay recrystallization temperature is within $\pm 100\%$ of the polymer peak
3 recrystallization temperature.

1 11. The method according to claim 1, wherein the organophilic
2 clay recrystallization temperature is within $\pm 50\%$ of the polymer peak
3 recrystallization temperature.

1 12. The method according to claim 1, wherein the organophilic
2 clay recrystallization temperature is within $\pm 25\%$ of the polymer peak
3 recrystallization temperature.

1 13. The method according to claim 1, wherein the organophilic
2 clay recrystallization temperature is within $\pm 10\%$ of the polymer peak
3 recrystallization temperature.

1 14. The method according to claim 1 further comprising preparing
2 the organophilic clay by treatment of a clay with at least one surfactant to yield an
3 organophilic clay having a recrystallization temperature higher than the polymer
4 recrystallization temperature.

1 15. The method according to claim 14, wherein the organophilic
2 clay may function as a nucleating agent during formation of the nanocomposite.

1 16. The method according to claim 14, whereby the growth of
2 polymer spherulites is lessened.

1 17. The method according to claim 14, whereby the growth of
2 polymer spherulites is prevented.

1 18. A method of preparing a nanocomposite comprising combining
2 an amorphous organophilic clay and an amorphous polymer, each having a glass
3 transition temperature, wherein the organophilic clay glass transition temperature
4 sufficiently matches the polymer glass transition temperature such that the
5 nanocomposite formed has less permeability to a gas than the polymer.

FIG. 1

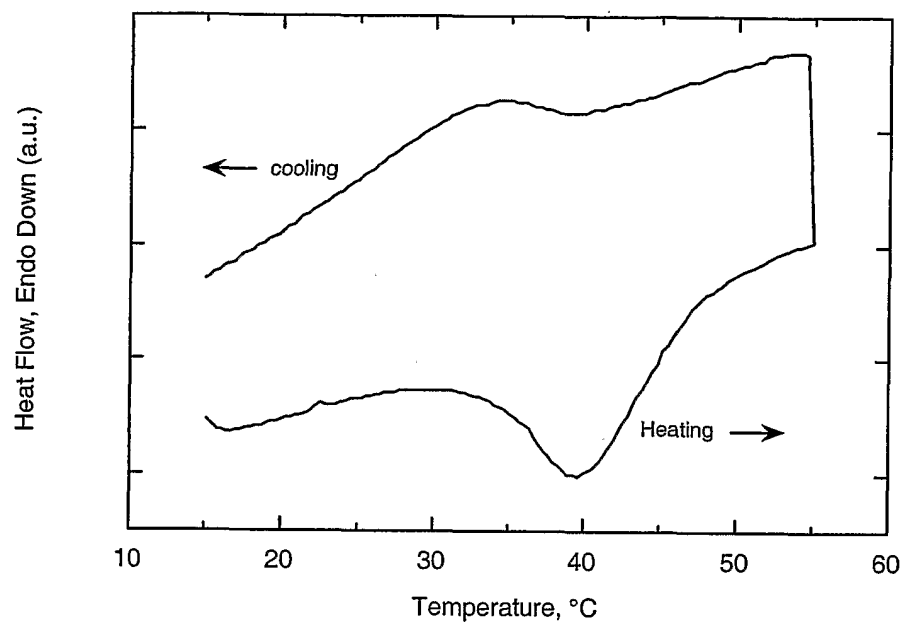


FIG. 2

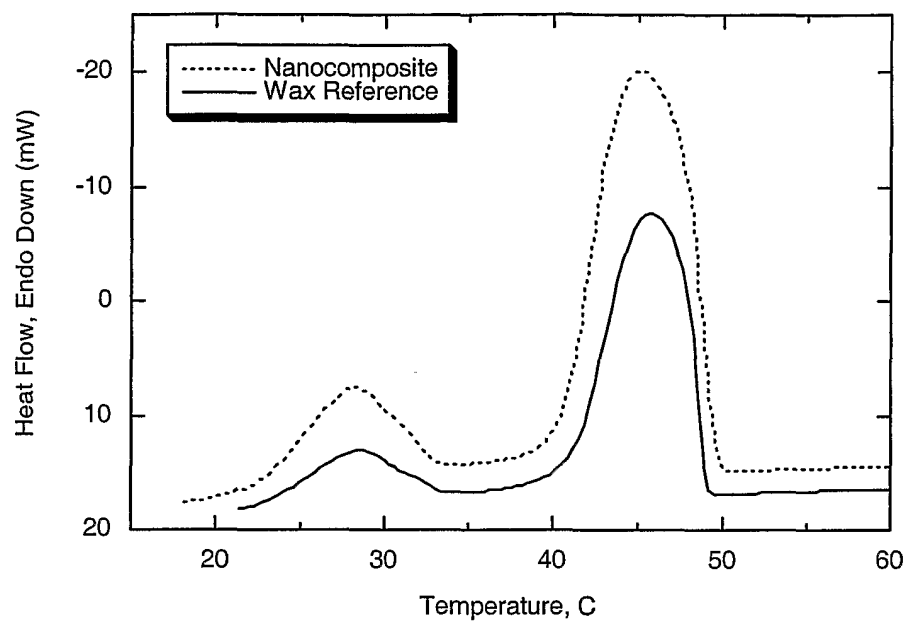


FIG. 3.

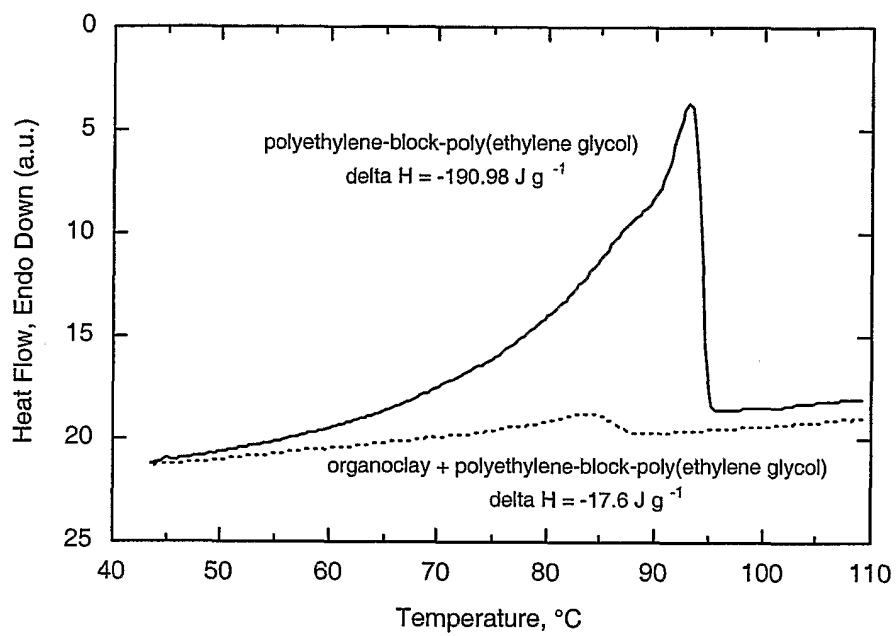


FIG. 4

