



US 20070032585A1

(19) **United States**

(12) **Patent Application Publication**
Giannelis et al.

(10) **Pub. No.: US 2007/0032585 A1**

(43) **Pub. Date: Feb. 8, 2007**

(54) **COMPOSITE OF HIGH MELTING POLYMER
AND NANOCCLAY WITH ENHANCED
PROPERTIES**

(75) Inventors: **Emmanuel P. Giannelis**, Ithaca, NY
(US); **Jin Zhu**, New Brunswick, NJ
(US); **Byoungkyeu Park**, Suncheon-Si
(KR); **Kyung Hoon Seo**, Gwanak-ku
(KR)

Correspondence Address:
BACON & THOMAS, PLLC
625 SLATERS LANE
FOURTH FLOOR
ALEXANDRIA, VA 22314

(73) Assignee: **Cornell Research Foundation, Inc.**, Ith-
aca, NY (US)

(21) Appl. No.: **11/545,452**

(22) Filed: **Oct. 11, 2006**

Related U.S. Application Data

(63) Continuation of application No. 10/739,534, filed on
Dec. 19, 2003, now Pat. No. 7,148,282.

Publication Classification

(51) **Int. Cl.**
C08K 9/04 (2006.01)

(52) **U.S. Cl.** **524/445; 524/449**

(57) **ABSTRACT**

Composite of high melting polymer and nanoclay converted
so the balancing cation is quaterized copolymer of styrene
and 2-(dimethylamine)ethyl methacrylate provides transpar-
ent form without coloration and enhanced modulus and
strength without loss of elongation and toughness.

COMPOSITE OF HIGH MELTING POLYMER AND NANOCLAY WITH ENHANCED PROPERTIES

TECHNICAL FIELD

[0001] This invention is directed at composites of high melting polymers and nanoclays.

BACKGROUND OF THE INVENTION

[0002] Nanoclays are known to be added to polymers to improve some properties of the polymers.

[0003] For this purpose, the nanoclays must be modified to be hydrophobic so as to be miscible with the polymers by conversion of the nanoclays to ammonium or phosphonium form.

[0004] Conventional ammonium form nanoclays when used to form composites with high melting polymers, while providing modest increase in modulus, because of low thermal stability begin to decompose at around 200° C. resulting in composites with significant coloration (so their use is limited to forming dark colored objects) and have poor elongation and toughness (impact resistance).

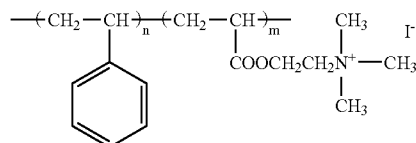
[0005] Conventional phosphonium form nanoclays when used to form composites with high melting polymers, while having acceptable thermal stability, have defective modulus and elongation properties and may be immiscible with the polymers.

SUMMARY OF THE INVENTION

[0006] It has been discovered herein that ammonium form nanoclays can be prepared that will form composites with high melting polymers that have enhanced modulus and strength without loss in elongation and toughness, and can provide formed objects which are transparent and without coloration

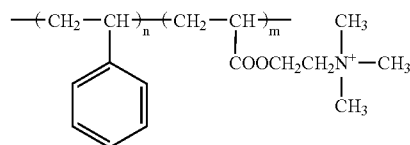
[0007] In a first embodiment herein, these advantages are provided by a composite of polymer that requires a temperature of 200° C. or more for forming, with from 0.1 to 10% by weight of a nanoclay which has been modified to contain an ammonium cation that is stable at the temperature required for forming the polymer and which provides a modified nanoclay which is compatible (miscible) with the polymer.

[0008] In a second embodiment herein, there is provided a copolymer for use for modifying cationic form nanoclay so the nanoclay contains ammonium cation that is stable at a temperature of at least 200° C. and is miscible with high melting polymers. In one case the copolymer has the structure:



where n ranges from 10 to 200 and m ranges from 1 to 5.

[0009] In a third embodiment herein, there is provided a 2,1-layered silicate that is modified to contain organic cation which is



where n ranges from 10 to 200 and m ranges from 1 to 5.

[0010] The exemplified case of the second embodiment is useful to modify cation form 2,1-layered silicate to provide the third embodiment.

DETAILED DESCRIPTION

[0011] We turn now to the first embodiment of the invention herein.

[0012] The polymer requires a temperature of 200° C. or more for forming. This polymer can be, for example, a polycarbonate or other polyester. A polycarbonate of melt index of 10-12, commercially available from Aldrich Chemical Company, is used in the working example herein.

[0013] Nanoclays are known as nanoclays because of 1 nanometer spacing between layers. The modified nanoclays herein are 2:1 layered silicates modified to contain an ammonium cation that is stable at the temperature required for forming the polymer and which provides a modified nanoclay which is compatible (miscible) with the polymer.

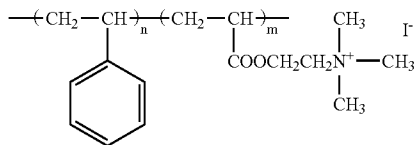
[0014] The term "2:1 layered silicates" is a known term and describes silicates containing lattice layers containing two tetrahedral sheets that share an edge with an octahedral sheet of either aluminum or magnesium hydroxide. The stacking of the layers provides interlayers or galleries between the layers. The galleries are normally occupied by cations that balance the charge deficiency that is generated by the isomorphous substitution within the layers. Besides the charge-balancing cations, water is also present in the galleries where it tends to associate with the cations. The silicates may be referred to as gallery-containing to describe this characteristic of 2:1 layered silicates which allows for intercalation therein of polymers. The silicates may be either natural or synthetic. The natural silicates include, for example, smectite clay minerals (e.g., montmorillonite, saponite, beidellite, nontronite, hectorite and stevensite), vermiculite and halloysite. The synthetic silicates include for example, laponite, fluoromica, fluorohectorite, hydroxyl hectorite, boron fluophlogopite, hydroxyl boron phlogopite, and solid solutions among those and between those and structurally compatible natural silicates selected from the group consisting of talc, fluorotalc, polyolithionite, fluoropolyolithionite, phlogopite, and fluorophlogopite. These normally are associated with, i.e., in the pristine state contain, charge balancing cations selected from the group consisting of sodium ions, potassium ions, lithium ions, calcium ions and magnesium ions. The 2,1-layered silicate preferably has a cationic chain capacity of 60-190 meq/100 grams. To provide the modified nanoclays herein, charge-balancing ammonium cation that is stable at the temperature required for forming the polymer and which provides a modified nanoclay which is compatible (miscible) with the

polymer, is exchanged for those that are normally associated with the nanoclays. The exchange constitutes ion exchange and may be carried out as taught in Okada et al U.S. Pat. No. 4,739,007, Okada et al U.S. Pat. No. 4,849,411 or Kawasumi et al U.S. Pat. No. 4,810,734. Suitable exchange may be carried out, for example, by suspending the clay in a solution of modifying agent or by passing solution of modifying agent through a column containing the nanoclay in particulate form. Suitable exchange in the specific case of the working example is carried out by dispensing particulate clay into a coater containing solvent for the modifying agent, adding the modifying agent to form a solution of the modifying agent in admixture with the particulate clay, with the admixture at 50° C. mixing to form a suspension of the clay in the solution, then recovering the modified clay and washing and drying. A suitable modifying quaternary ammonium salt to provide modified nanoclay herein is that of the second embodiment herein. A modified 2,1-layered silicate where the cation is stable at a temperature for forming the polymer and which is compatible (miscible) with the polymer is where, for example, the modification is to convert pristine cationic form silicate to quaternary ammonium form where the quaternary ammonium substituent is quaternized copolymer of styrene and 2-(dimethylamine) ethyl methacrylate. Preferably, the modified 2,1-layered silicate is the modified 2,1-layered silicate of the third embodiment herein.

[0015] Composite of the first embodiment is readily prepared by melting the polymer and blending the melted polymer with modified nanoclay, e.g., ground to through 250 mesh, in an extruder whereby extruded product is constituted of the composite.

[0016] We turn now to the second embodiment herein that is directed to a copolymer for use for modifying cationic form nanoclay so that the nanoclay contains an ammonium cation that is stable at a temperature of at least 200° C. and is miscible with the polymer that requires a temperature of 200° C. or more for forming.

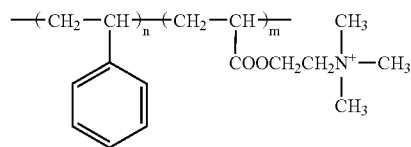
[0017] The copolymer of the second embodiment has the structure



where n ranges from 10 to 200 and m ranges from 1 to 5.

[0018] The copolymer of the second embodiment can be prepared from styrene and 2-(dimethylamine) ethyl methacrylate by reacting these in the presence of a vinyl polymerization catalyst, e.g., azobisisobutyronitrile, in suitable solvent, e.g., tetrahydrofuran, e.g., at 70° C., to produce the amine corresponding to the above structure and then quaternizing with methyl iodide, e.g., in tetrahydrofuran at 60° C.

[0019] We turn now to the third embodiment which is directed to a 2,1-layered silicate modified to contain the organic cation

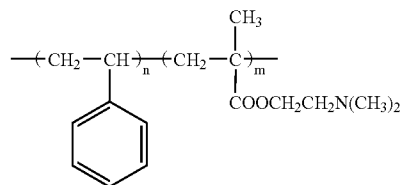


where n ranges from 10 to 200 and m ranges from 1 to 5. 2,1-Layered silicates so modified in the working example herein are montmorillonite and fluoromica. Modification is carried out by ion exchange with the composition of the second embodiment.

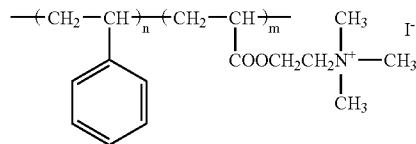
[0020] The invention is illustrated by the following working example:

EXAMPLE

[0021] Styrene (9.5 g) and 2-(dimethylamine) ethyl methacrylate (0.5 g) were dissolved in tetrahydrofuran together with azobisisobutyronitrile (1 gram in 20 ml tetrahydrofuran) and the solution was heated at 70° C. overnight to cause polymerization and form

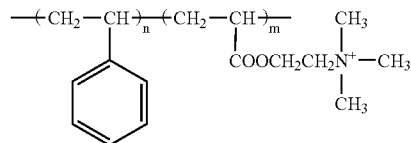


where n is 50 and m is 1. The polymerization product was quaternized using 1 gram methyl iodide (in excess) in solution in tetrahydrofuran at 60° C. for 4 hours to produce



where n is 50 and m is 1.

[0022] Montmorillonite (cationic form) and fluoromica (cationic form) was modified as described above. The montmorillonite and fluoromica were obtained commercially. In each case a modified nanoclay was obtained where the balancing organic cation was



where n is 50 and m is 1.

[0023] Composites were prepared from polycarbonate of melt index of 10-12 (available from Aldrich Chemical Company) and in one case, the modified montmorillonite and in a second the modified fluoromica. In each case the composite contained 3% by weight modified nanoclay. The composites were prepared by melting the polycarbonate and blending it with modified nanoclay (ground to through 250 mesh) in a twin screw microextruder at 270° C. and 130 rpm for 5 min. This caused the polycarbonate to intercalate between layers in the modified nanoclays.

[0024] The absence of a decomposition peak in x-ray diffraction for the modified nanoclay upon blending with polycarbonate showed the modified nanoclays possess much higher thermal stability compared to conventional nanoclays. Even after injection molding the composites did not show a decomposition peak. Transmission electron microscopy images showed well dispersed hybrids were obtained (thereby demonstrating compatibility and good miscibility). Injection molded forms of the composites were transparent and without coloration.

[0025] Mechanical properties obtained on polycarbonate (PC), composite of polycarbonate and 3% by weight modified montmorillonite (PCN-M) and composite of polycarbonate and 3% modified fluoromica (PCN-FM) were measured, and results are shown in the table below.

TABLE

Sample	Modulus (GPa)	Elongation (%)	Yield Strength (MPa)	Tensile Strength (MPa)	Toughness (Mpa)
PC	1.3	150	62	73	80
PCN-M	1.5	140	67	74	81
PCN-FM	1.6	170	70	82	104

Modulus, elongation, strength and toughness were all measured by tensile testing.

[0026] The results show the composites have enhanced modulus and strength without loss of elongation and toughness.

Variations

[0027] Variations of the above will be evident to those skilled in the art. Therefore, the scope of the invention is defined by the claims.

1-7. (canceled)

8. Composite of(a) polycarbonate with (b) from 1% to 10% by weight of the composite of polycarbonate-compatible 2,1 layered silicate, the composite having enhanced modulus and strength without loss in elongation and toughness compared to the polycarbonate.

9. The composite of claim 8 which is transparent and without coloration on injection molding.

10. The composite of claim 9 where the silicate has been converted to quaternary ammonium form, to effect polycarbonate-compatibility thereof.

11. The composition of claim 10 where the polycarbonate-compatible 2,1 layered silicate is a polycarbonate-compatible cationic form fluoromica and the composite has enhanced elongation and toughness compared to the polycarbonate.

12. The composite of claim 8 where the polycarbonate is intercalated between layers of the silicate.

13. The composite of claim 12 which is transparent and without coloration or injection molding.

14. The composite of claim 13 where the silicate has been converted to quaternary ammonium form, to effect polycarbonate-compatibility thereof.

15. The composite of claim 14 where the polycarbonate-compatible 2,1 layered silicate is a polycarbonate-compatible cationic form fluorimica and the composite has enhanced elongation and toughness compared to the polycarbonate.

* * * * *