starch can be made water-resistant by coating with biodegradable polyesters such as poly(beta-hydroxybutyrate-co-valerate) (PHBV), poly(lactic acid) (PLA), and poly(epsilon-caprolactone) (PCL). Adherence of the two dissimilar materials is achieved through the use of an intervening layer of a resinous material such as shellac or rosin which possesses a solubility parameter (hydrophobicity) intermediate to that of the starch and the polyesters. Coating is achieved by spraying an alcoholic solution of the shellac or rosin onto the starch-based article and subsequently coating with a solution of the polyester in an appropriate solvent. However, these products are not optimally designed for allowing a user to carry them easily while being in a physical activity. In addition, they are not designed to provide different liquid volumes that can be consumed according to instant needs.

[0010] All of the aforementioned prior art constructions are deficient with respect to their failure to provide a simple, efficient, and practical packaging arrangement for liquids that will provide the user with easy access to flexible compartmented packaging for liquids. Consequently, there is a need for a new and improved type of a biodegradable liquid receptacle.

SUMMARY

[0011] In one aspect, there is provided a multilayered biodegradable sheet, wherein at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles, ~~In some embodiments, the multilayered biodegradable sheet comprises~~ said at least one layer comprising a bridge between the surface treated nanoclay particles and the biodegradable polymer, ~~the~~said bridge comprising a functional moiety having at least two functional sites, wherein at least one of the functional sites is conjugated to the nanoclay surface with a covalent bond and at least another one of the functional sites is conjugated to the biodegradable polymer. In some embodiments of the disclosure, the multilayered biodegradable sheet comprises a bridge between the surface treated nanoclay particles and the biodegradable polymer, the bridge having a first end and a second end and comprising a plurality of functional moieties, each functional moiety having at least two functional sites, wherein at least one of the functional sites of one of the moieties on the first end of the bridge is conjugated to the nanoclay surface and at least one of the functional sites of another moiety on the second end of the bridge is conjugated to the biodegradable polymer, and wherein the functional moieties are conjugated to one another between the first and second ends of the bridge. In some embodiments of the disclosure, the surface treated nanoclay particles are a nanoclay concentrate. According to some embodiments, the nanoclay particles are 1-30%w/w of a nanoclay concentrate. In some

embodiments of the disclosure, the nanoclay concentrate was prepared by ring opening polymerization (ROP), wherein the ROP includes polymerizing ring bearing monomers selected from L-lactide, D-lactide, D,L-lactide and epsilon-caprolacton or a combination thereof.

[0012] In some embodiments of the disclosure, the surface treated nanoclay particles were pretreated to remove ions adsorbed on the surface of the nanoclay particles. In some embodiments of the disclosure, the functional moiety is 3-(dimethylamino)-1-propylamine (DMPA), a diisocyanante group, triethoxysilane substituted with an isocyanate group, aminopropyl triethoxysilane or any combination thereof. In some embodiments of the disclosure, the functional moiety comprises a functional group selected from the group consisting of a di-aldehyde selected from glutearaldehyde, diacrylate, meta-acrylate, or di-epoxide, or a diisocyanate group is selected from hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).

[0013] In one ~~aspect~~embodiment, there is provided a multilayered biodegradable sheet, wherein at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles, wherein the surface treated nanoclay particles are homogeneously dispersed in the at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles.

[0014] In one aspect, there is provided a multilayered biodegradable sheet, wherein at least one layer comprises PVOH grafted ~~and PBS or PBSA~~ with a crosslinker and PBS or PBSA. The w/w ratio between PVOH, the cross linker and PBS or PBSA is typically 10-90%:0.1-10%:90-10%.

[0015] In an embodiment of the disclosure, there is provided a multilayered biodegradable sheet, wherein at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles wherein the multilayered biodegradable sheet further comprising at least one layer that comprises PVOH grafted ~~and PBS or PBSA~~ with a crosslinker and PBS or PBSA, which maybe MAH. According to some embodiments the grafted PVOH is in a separate layer from the surface treated nanoclay particles. In some embodiments, the w/w ratio between PVOH, the crosslinker and PBS/PBSA is 10-90%:0.1-10%:90-10%

[0016] In one ~~aspect~~embodiment, there is provided a single layered biodegradable sheet comprising at least one biodegradable polymer and surface treated nanoclay particles.

[0017] In one aspect, there is provided a single layered biodegradable sheet comprising PVOH grafted with a cross linker and PBS or PBSA.

[0018] The multilayered biodegradable sheet of the disclosure may typically comprise 2, 3, 4, 5, 6, or 7 layers.

[0019] In one aspect, there is provided a method of preparing a PVOH grafted ~~and PBS or PBSA~~ with a cross linker and PBS or PBSA comprising the step of blending dried PBS or PBSA and PVOH with the cross linker and a radical initiator. The method may further comprise a step of pelletizing the blended dried PBS or PBSA and PVOH the crosslinker and the radical initiator. The radical initiator may be peroxide and azo- group free radical former. In some embodiments, the radial initiator is benzoyl peroxide (BPO), lauroyl peroxide (LP), azobisisobutyronitrile (AIBN), or Azobis(cyanocyclohexane), (ACHN) or any combination thereof.

[0020] The method may further comprising the step of drying the blended dried PBS or PBSA and PVOH with the cross linker and the radical initiator or the pellet thereof.

[0021] In one aspect, there is provided a method of preparing surface treated nanoclay particles, said method comprising: reacting nanoclay particles with a functional moiety comprising at least two functional sites to form a covalent bond between said nanoclay particles and said functional moiety, leaving at least one free functional site for further reaction; and reacting said at least one free functional site with a biodegradable polymer.

[0022] In one aspect, there is provided a method of preparing surface treated nanoclay particles, said method comprising: reacting nanoclay particles with a plurality of functional moieties to form a covalent bond between said nanoclay particle and said functional moieties, each comprising at least two functional sites, such that at least one functional site ties at least one functional moiety to said nanoclay particle and at least a second functional site on the same functional moiety ties to an additional functional moiety, which is attached to any remaining functional moieties, leaving at least one free functional site; and reacting said free functional site with a biodegradable polymer.

[0023] The method may further comprise pretreating the nanoclay particles with an acid, prior to the reaction thereof with a functional moiety.

[0024] In one ~~aspect~~embodiment, there is provided a method of preparing surface treated nanoclay particles, the method comprising: mixing the nanoclay particles in a solution of at least one ring-bearing monomer; and initiating a ring opening polymerization reaction between the nanoclay particles and the monomers, such that polymeric brushes are formed on the surface of the nanoclay particles. The step of mixing may include creating a dispersion of the nanoclay particles in a solution of at least one ring-bearing or double-bond or epoxide or di-amine monomer. In some embodiments of the disclosure, the ring opening polymerization reaction includes the use of a catalyst. In some embodiments of the disclosure, the ring opening polymerization reaction includes heating.

[0025] The crosslinker used is typically selected from the group consisting of 1,4-Butanediol dimethacrylate, hexamethylene dimethacrylate, maleic anhydride, polyethylene glycol-dimethacrylate, and polycaprolactone dimethacrylate or any combination thereof.

[0026] In one aspect, there is provided a multilayered biodegradable sheet comprises the following:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH, grafted with PBSA or PBS;

Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 4: consisting of about 100% w/w PVOH grafted with PBSA or PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0027] In one aspect, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH w/ or w/o a crosslinker;

Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 4: consisting of about 100% w/w PVOH w/ or w/o a crosslinker;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0028] In one ~~aspect~~embodiment, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH, grafted with PBSA or PBS;

Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 4: consisting of about 100% w/w PVOH grafted with PBSA or PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0029] In one ~~aspect~~embodiment, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 3: consisting of about 100% w/w PVOH w/ or w/o a crosslinker;

Layer 4: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0030] In one aspect, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% grafted PBSA or grafted PBS;

Layer 3: consisting of about 100% PVOH w/ or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PBSA or grafted PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0031] In one aspect, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% grafted PVOH with PBSA or PBS;

Layer 3: consisting of about 100% PVOH w/or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PVOH with PBSA or PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0032] In one aspect, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA;

Layer 2: consisting of about 100% grafted PVOH with PBS;

Layer 3: consisting of about 100% PVOH w/or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PVOH with PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

[0033] In one aspect, there is provided a multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

What is claimed is:

1. A multilayered biodegradable sheet, wherein at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles, said at least one layer comprising a bridge between the surface treated nanoclay particles and the biodegradable polymer, said bridge comprising a functional moiety having at least two functional sites, wherein at least one of the functional sites is conjugated to the nanoclay surface with a covalent bond and at least another one of the functional sites is conjugated to the biodegradable polymer.

~~2. The multilayered biodegradable sheet according to claim 1, comprising a bridge between the surface treated nanoclay particles and the biodegradable polymer, said bridge comprising a functional moiety having at least two functional sites, wherein at least one of the functional sites is conjugated to the nanoclay surface and at least another one of the functional sites is conjugated to the biodegradable polymer.~~

~~3~~2. The multilayered biodegradable sheet according to claim 1 ~~comprising a bridge between the surface treated nanoclay particles and the biodegradable polymer,~~ said bridge having a first end and a second end and comprising a plurality of said functional moieties, each functional moiety having at least two functional sites, wherein at least one of the functional sites of one of the moieties on the first end of the bridge is conjugated to the nanoclay surface with a covalent bond and at least one of the functional sites of another moiety on the second end of the bridge is conjugated to the biodegradable polymer, and wherein the functional moieties are conjugated to one another between the first and second ends of the bridge.

43. The multilayered biodegradable sheet according to claim 1, wherein the surface treated nanoclay particles are a nanoclay concentrate.

~~5. The multilayered biodegradable sheet according to claim 4, wherein the nanoclay concentrate was prepared by ring opening polymerization (ROP).~~

~~6. The multilayered biodegradable sheet according to claim 5, wherein the ROP includes polymerizing ring bearing monomers selected from L-lactide, D-lactide, D,L-lactide and epsilon-caprolacton or a combination thereof.~~

~~7~~4. The multilayered biodegradable sheet according to claim 1, wherein the surface treated nanoclay particles were pretreated to remove~~d~~ ions adsorbed on the surface of the nanoclay particles.

~~8. The multilayered biodegradable sheet according to any one of claims 2 or 3, wherein the functional moiety is 3-(dimethylamino)-1-propylamine (DMPA), a diisocyanante group, triethoxysilane substituted with an isocyanate group, aminopropyl triethoxysilane or any combination thereof.~~

~~9. The multilayered biodegradable sheet according to claim 8, wherein the functional moiety comprises a functional group selected from a di-aldehyde selected from gluteraldehyde, diacrylate, meta-acrylate, or di-epoxide, or a diisocyanate group is selected from~~

~~hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI).~~

~~10. A multilayered biodegradable sheet, wherein at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles, wherein the surface treated nanoclay particles are homogenously dispersed in the at least one layer comprises at least one biodegradable polymer and surface treated nanoclay particles.~~

~~11~~5. A multilayered biodegradable sheet, wherein at least one layer comprises PVOH grafted ~~and PBS or PBSA~~ with a crosslinker and PBS or PBSA.

~~12~~6. The multilayered biodegradable sheet according to claim 5~~11~~, wherein the w/w ratio between PVOH, the crosslinker and PBS or PBSA is 10-90%:0.1-10%:90-10%.

~~13~~7. The multilayered sheet according to claim 1, further comprising at least one layer that comprises PVOH grafted ~~and PBS or PBSA~~ with a crosslinker and PBS or PBSA.

~~14~~8. The multilayered sheet according to claim ~~11~~5, wherein the grafted PVOH is in a separate layer from ~~the~~a layer comprising surface treated nanoclay particles.

~~15~~9. The multilayered biodegradable sheet according to claim 7~~13~~, wherein the w/w ratio between PVOH, the crosslinker and PBS or PBSA is 10-90%:0.1-10%:90-10%.

~~16. A single layered biodegradable sheet comprising at least one biodegradable polymer and surface treated nanoclay particles.~~

~~17~~10. A single layered biodegradable sheet comprising PVOH grafted with a crosslinker and PBS or PBSA.

~~18~~11. The multilayered biodegradable sheet of claims 1, ~~11~~5 and 7~~13~~, wherein the multilayered biodegradable sheet comprises 2, 3, 4, 5, 6, or 7 layers.

~~19~~12. A method of preparing a PVOH grafted ~~and PBS or PBSA~~ with a crosslinker and PBS or PBSA comprising the step of blending dried PBS or PBSA and PVOH with the crosslinker and a radical initiator.

~~20~~13. The method of claim 12~~19~~ wherein method further comprises a step of pelletizing the blended dried PBS or PBSA and PVOH with the crosslinker and the radical initiator.

~~21~~14. The method of any one of claims 12~~19~~ or ~~20~~13, wherein the method further comprises the step of drying the blended dried PBS or PBSA and PVOH with the crosslinker and the radical initiator or the pellet thereof.

~~22~~15. A method of preparing surface treated nanoclay particles, the method comprising

reacting nanoclay particles with a functional moiety comprising at least two functional sites to form a covalent bond between said nanoclay particles and said functional moiety, leaving at least one free functional site for further reaction; and

reacting said at least one free functional site with a biodegradable polymer.

~~23~~16. A method of preparing surface treated nanoclay particles, the method comprising

reacting nanoclay particles with a plurality of functional moieties to form a covalent bond between said nanoclay particles and said functional moieties, each comprising at least two functional sites, such that at least one functional site ties at least one functional moiety to said nanoclay particle with said covalent bond and at least a second functional site on the same functional moiety ties to an additional functional moiety, which is attached to any remaining functional moieties, leaving at least one free functional site; and

reacting said free functional site with a biodegradable polymer.

~~24~~17. The method according to claim ~~22~~15 or 16~~23~~ further comprising pretreating the nanoclay particles with an acid, prior to the reaction thereof with a functional moiety.

~~25. A method of preparing surface treated nanoclay particles, the method comprising:~~

~~mixing the nanoclay particles in a solution of at least one ring-bearing monomer; and~~

~~initiating a ring opening polymerization reaction between the nanoclay particles and the monomers, such that polymeric brushes are formed on the surface of the nanoclay particles.~~

~~26. The method according to claim 25, wherein the mixing includes creating a dispersion of the nanoclay particles in a solution of at least one ring-bearing or double-bond or epoxide or di-amme monomer.~~

~~27. The method according to claim 25, wherein the ring opening polymerization reaction includes the use of a catalyst.~~

~~28. The method according to claim 25, wherein the ring opening polymerization reaction includes heating.~~

~~29~~18. The multilayered biodegradable sheet according to claim 43, wherein the sheet comprises 1-30% w/w of a nanoclay concentrate.

~~30~~19. The multilayered biodegradable sheet according to any one of ~~the previous claims~~claims 5, 6, or 9, the single layered biodegradable sheet according to claim 10, or the method according to any one of claims 12, 13 or 14 wherein the crosslinker is selected from the group consisting of 1,4-Butanediol dimethacrylate, hexamethylene dimethacrylate, maleic anhydride, polyethylene glycol-dimethacrylate, and polycaprolactone dimethacrylate and any combination thereof.

~~31~~20. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH, grafted with PBSA or PBS;

Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 4: consisting of about 100% w/w PVOH grafted with PBSA or PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~32~~21. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH w/ or w/o crosslinker;

Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 4: consisting of about 100% w/w PVOH w/ or w/o crosslinker;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~33~~. ~~A multilayered biodegradable sheet comprising:~~

~~Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;~~

~~Layer 2: consisting of about 100% w/w PVOH, grafted with PBSA or PBS;~~

~~Layer 3: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;~~

~~Layer 4: consisting of about 100% w/w PVOH grafted with PBSA or PBS;~~

~~Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.~~

~~34~~. ~~A multilayered biodegradable sheet according to claim 1 comprising:~~

~~Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;~~

~~Layer 2: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;~~

~~Layer 3: consisting of about 100% w/w PVOH w/ or w/o a crosslinker;~~

~~Layer 4: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;~~

~~Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.~~

~~35~~22. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% grafted PBSA or grafted PBS;

Layer 3: consisting of about 100% PVOH w/ or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PBSA or grafted PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~36~~23. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% grafted PVOH with PBSA or PBS;

Layer 3: consisting of about 100% PVOH w/or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PVOH with PBSA or PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~37~~24. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA;

Layer 2: consisting of about 100% grafted PVOH with PBS;

Layer 3: consisting of about 100% PVOH w/or w/o a crosslinker;

Layer 4: consisting of about 100% grafted PVOH with PBS;

Layer 5: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~38~~25. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH, grafted with PBSA or PBS;

Layer 3: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~39~~26. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 100% w/w PVOH w/ or w/o crosslinker;

Layer 3: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~40~~27. A multilayered biodegradable sheet comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 98-85% PBSA and about 2-15% w/w and surface treated nanoclay particles;

Layer 3: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~41~~28. A multilayered biodegradable sheet according to claim 1 comprising:

Layer 1: consisting about 25% w/w PLA and about 75% w/w PBSA or PBS;

Layer 2: consisting of about 98-85% w/w PVOH, grafted with PBSA or PBS and about 2-15% w/w and surface treated nanoclay particles;

Layer 3: consisting of about w/ or w/o 25% w/w PLA and about 75% or 100% w/w PBSA or PBS or PBAT.

~~42~~29. The method of claims ~~19~~12-~~142~~1, wherein the radical initiator is peroxide and azo- group free radical former.

~~43~~30. The method of claim ~~42~~29, wherein the ~~radial~~radical initiator is benzoyl peroxide (BPO), lauroyl peroxide (LP), azobisisobutyronitrile (AIBN), or Azobis(cyanocyclohexane), (ACHN) or any combination thereof.

31. The multilayered biodegradable sheet according to claim 13, wherein said crosslinker is selected from the group consisting of 1,4-Butanediol dimethacrylate, hexamethylene dimethacrylate, maleic anhydride, polyethylene glycol-dimethacrylate, and polycaprolactone dimethacrylate and any combination thereof.