



- (51) International Patent Classification:
B02C 17/00 (2006.01) *C08L 23/06* (2006.01)
C08K 3/00 (2006.01)
- (21) International Application Number:
PCT/US2012/065639
- (22) International Filing Date:
16 November 2012 (16.11.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/560,973 17 November 2011 (17.11.2011) US
- (71) Applicant: **TYSON FOODS, INC.** [US/US]; 2200 Don Tyson Parkway, Springdale, AR 72762 (US).
- (72) Inventor: **LIU, Yongcheng**; 1832 N. Buckley Drive, Fayetteville, AR 72701 (US).
- (72) Inventor: **WANG, Ke-Wei** (*deceased*).
- (72) Inventors: **BLANCHARD, Michael**; 11695 Effle Way, Farmington, AR 72730 (US). **LI, Clive**; 595 Broad Hollow Road, Farmingdale, NY 11735 (US). **METZGER, Gary**; 595 Broad Hollow Road, Farmingdale, NY 11735 (US).
- (74) Agents: **GIBSON, Matthew S.** et al.; McAfee & Taft, P.C., 10th Floor, Two Leadership Square, 211 North Robinson, Oklahoma City, OK 73102 (US).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: EGGSHELL POWDER COMPOSITIONS AND METHODS OF PRODUCING EGGSHELL POWDER COMPOSITIONS

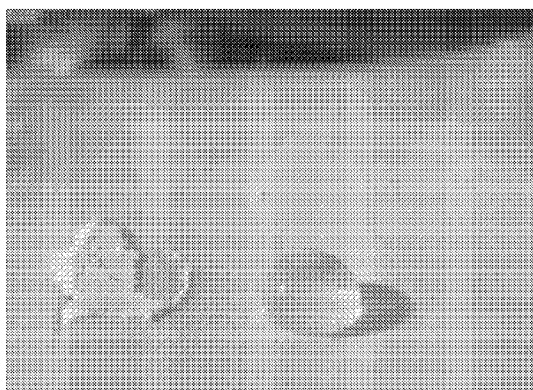


FIG. 1

(57) Abstract: A process for manufacturing eggshell powder for use in the production of bio-based products is provided. The process involves exposing a quantity of eggshell to high air speed at room temperatures to pulverize the eggshell and separate the eggshell component from the inner membrane component. Thus, the process avoids the use of high temperatures and other harsh chemical treatments to remove the inner membrane from the eggshell thereby resulting in an eggshell material that retains the original lipid-protein structure of the native eggshell from which the powder derives. Accordingly, an eggshell powder composition is provided that is substantially free of inner membrane material and possesses a lipid-protein structure substantially similar to that of the eggshell from which the powder is derived. A polymer composite composition comprising an eggshell component and a polymer component is also provided.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

EGGSHELL POWDER COMPOSITIONS AND METHODS OF PRODUCING EGGSHELL POWDER COMPOSITIONS

BACKGROUND

[0001] In order to provide more environmentally-responsible products, manufacturers are exploring alternative approaches to reduce the amount of polymer used to produce various polymer-based products. One such approach involves substituting a portion of the polymer content with a plant-based or “bio-based” filler such as wood flour, starch, or distilled grain. However, plant-based fillers absorb water and swell in a moist or humid environment and degrade at the high temperatures used during processing. This leads to poor product performance and undesirable characteristics.

[0002] Eggshell powder is an alternative to the standard plant-based materials. However, attempts to use eggshell powder as a filler in polymer composites has been problematic. First, the inner membrane associated with the eggshell, if left in association with the eggshell during the manufacturing process, produces a foul odor which can carry over into the ultimate product. The traditional methods used to remove the inner membrane from the eggshell involve the use of high-temperatures and/or harsh chemical treatments. This approach not only increases manufacturing costs, but also compromises the native lipid-protein surface structure of the eggshell. As a result, the interface between the eggshell powder and polymer is weakened resulting in sub-optimal product performance.

[0003] Therefore, a bio-based or environmentally-responsible filler material is needed for use in manufacturing polymer composites that maintain comparable or improved physical properties without undesirable characteristics and sub-optimal performance ratings.

SUMMARY

[0004] The processes and compositions described herein relate to an eggshell powder that possesses improved characteristics for use in polymer composites. To this end, the present invention solves the problems associated with the use of eggshell material as a bio-based filler by providing a process in which the inner membrane is removed from the eggshell without the use of high temperatures or harsh chemical treatments. As a result, the eggshell material retains its native lipid-protein structure thereby permitting a strong interaction with an associated polymer.

[0005] A process for producing an eggshell powder is provided. The process involves exposing the eggshell to air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated

inner membrane component. The separated eggshell component is then isolated from the inner membrane component by applying the bulk pulverized material to a first screen comprising a mesh size sufficient to retain the separated inner membrane component on the surface of the first screen while permitting passage of the eggshell component through the first screen. At this point, the collected eggshell component can either be applied to a second screen comprising a mesh size smaller than that of the first screen or re-exposed to the air flow at the same or an increased speed to further pulverize the material and then applied to the second screen. The pulverization step can be repeated additional times at the same or increased air flow speeds until the eggshell component is reduced to the desired particle size.

[0006] Additionally, an eggshell powder composition is provided. The eggshell powder composition is substantially free of the inner membrane and retains the lipid-protein structure present in the native eggshell material used to form the powder.

[0007] A polymer composite composition is also provided. The composite composition comprises a first component and a second component. The first component comprises a biobased filler consisting of eggshell powder that is void of the inner membrane and possesses the lipid-protein structure of the eggshell material used to form the powder. The second component comprises a polymer. In one aspect, the polymer is a thermoplastic polymer such as, but not limited to, polyolefin (e.g., polyethylene (PE)), polyesters (e.g., polyethylene terephthalate (PET)), polyamide (e.g., nylon), styrenic polymers (e.g., polystyrene), bio-degradable polymers (e.g., polylactic acid (PLA)), and engineering resins (e.g., polycarbonate). In another aspect, the polymer is a thermoset polymer such as, but not limited to, crosslink polymers (e.g., vulcanized rubber), melamine resin, epoxy resin, crosslink polyesters, and polyurethane. In yet another aspect, the composite composition further comprises a third component. The third component comprises one more additives such as, but not limited to, antioxidants, fiberglass fillers, color pigments (e.g., carbon black), and fragrances (e.g., citronella).

BREIF DESCRIPTIONS OF THE DRAWINGS

[0008] FIG. 1 is a photograph of a 22 μ g water drop on the surface of a sample of eggshell powder of the present invention.

DETAILED DESCRIPTION

[0009] The present application claims priority to U.S. provisional application no. 61/560,973 of the same title which is incorporated by reference in its entirety herein.

[0010] In one aspect, a process for producing an eggshell powder is provided. The process involves removal of the inner membrane from the eggshell prior to pulverization through a process that does not rely on a liquid carrier or high temperatures, but rather on air flow at low temperatures. Thus, in a preferred embodiment, the entire process of producing eggshell powder described herein can be performed without heating the eggshell material. As a result, an eggshell powder is yielded that retains the lipid/protein structure of the original eggshell surface from which the powder is derived, and is also substantially free of the eggshell inner membrane material.

[0011] In some applications, it may be desirable to sterilize the eggshell prior to processing. The sterilization step can be performed by a number of different methods which are generally known to those skilled in the art. For example, the eggshell can be exposed to a moist heat treatment of a temperature sufficient to eliminate various pathogens and microorganisms. Moist heat treatments include, but are not limited to passing steam infused water through a quantity of shells or simply steam treating the eggshells. Other potential methodologies include exposing the eggshells to UV light, high energy radiation, chemical treatment or reducing the available water (AW).

[0012] Following the optional sterilization step, one or more pulverization steps are performed to crush the eggshell to a desired particle size and to remove the inner membrane from the eggshell. Pulverization is preferably performed using high speed air flow at low temperatures. The determination of air speed will largely be dependent on the type of apparatus used, but regardless, should be sufficient to cause separation of the eggshell component from the inner membrane component. Example 1 provides an initial pulverization using an air speed of 3,500 rpm in a pulverdryer which provides a good basis to determine the air speed required to obtain the same result in related air flow equipment. The pulverization step can be performed using a vortex dryer, cyclone wind tunnel or any other apparatus that provides sufficient air speed to crush the eggshell and separate it from the inner membrane. The initial pulverization step should be sufficient to separate the eggshell from the inner membrane. Thus, any additional pulverization steps can be employed to further dry and reduce the particle size of the eggshell component. If a reduced particle size is desired, the air speed can be increased from about 3,500 rpm to about 10,000 rpm and any range therebetween.

[0013] The initial pulverization step results in the production of a bulk pulverized material consisting of an eggshell component and inner membrane component. The next

step is then to isolate the eggshell component from bulk pulverized material so that the resulting eggshell powder does not contain any of the inner membrane component. This can be performed by applying the bulk material to a mesh screen of a size sufficient to permit the eggshell component to pass through the screen while retaining the inner membrane component on the surface of the screen. For example, the bulk material can be applied to an ASTM 20 mesh screen. However, any number of approaches could be used by a skilled artisan to achieve the same ends as long as the eggshell component can be collected free from the inner membrane component.

[0014] The pulverization step can then be repeated for the entire eggshell component or only with respect to the large eggshell component particles (approximately greater than 100 μm) until a desired particle size is reached. The large eggshell component particles can be separated from the remaining eggshell component by using appropriately sized mesh screens. The subsequent pulverizing steps can be performed under the same conditions as the initial step or with higher air speeds for the same or longer time periods. If a specific particle size is desired, the pulverized eggshell component can be sifted through a screen having a particle size specific for the intended use of the eggshell powder. For example, an ASTM 270 mesh screen having a particle size of 53 μm .

[0015] The present process yields an improved eggshell powder that retains the lipid-protein structure of the original eggshell from which it is derived and is substantially free of eggshell inner membrane material. Thus, in another aspect of the present invention, an eggshell powder composition is provided. The eggshell powder composition possesses an ash content of about 90-95% and a moisture content from about 0.2% to about 5%, but is generally less than 1%. Of the ash content, approximately 33-36% is calcium in addition to less than 1% of each of magnesium, phosphorus, potassium, and sodium. The calcium content consists substantially of calcium oxide and other metal oxides rather than calcium carbonate. The fat content of the eggshell powder can be in the range of about 0.01% to about 3%, but is generally less than 1%. The protein content is generally less than 5% and more specifically, from about 0.2% to about 3%.

[0016] Furthermore, the present eggshell powder retains the original lipid/protein structure of the native eggshell surface from which the powder is derived. As a result, the present eggshell powder possesses hydrophobic properties. FIG. 1 demonstrates the hydrophobic properties of the eggshell powder by providing a photograph of a drop of water

(approximately 22 μg) being retained on the surface of the present eggshell powder. The drop possesses a water contact angle indicative of a hydrophobic material.

[0017] The hydrophobic, lipid/protein structure of the present eggshell powder is more similar to polymer structure than traditional minced calcium carbonate thereby providing an improved interaction with the polymer matrix. As a result, the use of the present eggshell powder in a polymer composite provides improved mechanical properties such as impact resistance and tensile strength as compared to polymer alone, which is demonstrated in Example 5 herein below.

[0018] The particle size of the present eggshell powder is, for example, generally less than 100 μm and can be from about 10 μm to about 100 μm . Depending on the intended use of the powder, the particle size is more preferably from about 20 μm to 50 μm . Particle size can be controlled by, for example, using screen filters with the desired mesh sizes and by repeating the pulverization step as described above. For example, the particle size yielded by using an ASTM 150 mesh screen is generally less than 104 μm whereas the particle size yielded by an ASTM 325 mesh screen is generally less than 44 μm .

[0019] Although the eggshell powder composition described herein is isolated from chicken eggs, it should be understood that other types of eggshells can be used to yield a similar powder such as, but not limited to, shells from turkey eggs, duck eggs, and other bird eggs.

[0020] In another aspect of the current invention, a polymer composite composition is provided. The composite composition comprises a first component consisting of a bio-based material, a second component consisting of a polymer, and in some instances a third component such as an additive or additional filler material. For example, the first component comprises eggshell powder that is substantially free of eggshell inner membrane and retains the original lipid-protein surface structure of the eggshell from which the powder was derived. The particle size of the eggshell powder can be any size desired and most effective for the particular polymer used in the composite. For example, the powder particle size can be from about 10 μm to about 100 μm and more specifically, from about 20 μm to 50 μm .

[0021] The second component comprises a polymer. In some instances, the polymer is a thermoplastic polymer such as, but not limited to, polyolefin (e.g., polyethylene, ethylene vinyl acetate, ethylene methyl acrylate, polypropylene, polybutylene, polymethyl pentene), styrenic polymers (e.g., general purpose polystyrene, impact modified polystyrene,

acrylonitrile butadiene styrene, butadiene styrene copolymer, styrene maleic anhydride copolymer, polystyrene methyl methacrylate copolymer), polyesters (e.g., polyethylene phthalate, polybutylene phthalate, polylactic acid), bio-degradable polymers (e.g., polylactic acid, polycaprolactone, polyvinyl alcohol, polyglycolic acid, polyalkene succinate, aliphatic-aromatic copolyesters, polyanhydrides, and polyhydroxyalkanoate), polyamides (e.g., nylons), and engineering resins (e.g., acetyls, allyl resins, cellulosic resins, chlorinated polyethylene, fluoropolymers, fluorocarbon polymers, liquid crystal polymers, phenolic resins, polyaryl sulfone, polyallomers, polyamide, polyacrylate, polyethersulfone, polymethyl methacrylate, polyphenyl sulfone, polyphenylene ether, polyphenylene oxide, polyphenylene sulfide, polysulfone, polyurethane, polyvinyl chloride and polycarbonate). In other instances, the polymer is a thermoset polymer such as, but not limited to crosslink polymers (e.g., vulcanized rubber), melamine resin, vinyl ester, epoxy resin, crosslink polyesters, phenolics, melamine resins, and polyurethane.

[0022] Additionally, the composite composition can further comprise a third component in some instances. The third component can comprise one or more additives such as, but not limited to, heat stabilizers, antioxidants, UV/light stabilizers, antistatic agents, antifogging agents, lubricants, processing aids, anti-blocking agents, slipping agents, mold-releasing agents, flame-retardant agents, chemical-blowing agents, crosslink agents, nucleating agents, antimicrobial agents, coupling agents, gas scavengers, acid and base scavengers, water scavengers, odor controlling agents, and food flavoring agents.

[0023] Alternatively, the third component can include a filler material such as, but not limited to calcium carbonate, dolomite, magnesium carbonate, calcium sulfate, barium sulfate, silica, carbon black, talc, mica, kaolin, clay, graphite, wollastonite, whiskers, glass fiber, carbon fiber, conductive filler, nano-filler, organic filler (including wood flour, cellulose fiber and distilled drained grain), and colorant (including pigment, dye, and fluorescent whitening agent).

[0024] The percentage of eggshell powder in the composite ranges from 1% to 90% by weight, from about 30% to 50% by weight, and in many applications is at least 25% by weight. A product made from a composite composition comprising 25% biobased material is suitable to label as "biobased" under USDA regulations. Moreover, the percentage of eggshell powder in the composite is a function of the type of polymer structure desired. The eggshell/polymer composites can be molded into a variety of commercial plastic products including, but not limited to chips, boxes, trays, barrels, golf tees, and disposable bins.

[0025] The eggshell powder described herein is integrated with the associated polymer by extrusion; a process in which polymeric resins, eggshell powder, and optionally, other ingredients such as additives and pigments are fed into an extruder barrel with one or more rotating screws. The screw forces the mixture forward in the extruder barrel which is heated to a melting temperature of the particular polymer, and then forces the molten mixture (composite) out of the extruder. The extruded composite is generally then cut into pellet form and subjected to further manufacturing processes such as injection molding, blow molding, extrusion and thermoforming.

[0026] In composites comprising thermoset polymers, the present eggshell powder is integrated with the thermoset polymers by first adding monomers to the powder, cross-linking agent and/or other fillers such as fiberglass or color pigment into a cavity of the mold. Pressure is then applied to force the mixture to the cavity voids. The mixture is then annealed at a temperature above the curing temperature to allow the monomer to cure.

[0027] Therefore, in one embodiment, the process for producing a composite of eggshell powder and a polymer is provided. The process includes following steps:

- (1) mixing eggshell powder with the polymer and in some instances other additives or fillers at various composition ratios either manually or in a mixing machine under conditions sufficient to produce a homogeneous mixture;
- (2) extruding the polymer/eggshell powder mixture in an extruder operating at an appropriate temperature profile for the die, metering zone, compression zone, and feed zone of the extruder suitable for the desired polymer;
- (3) pelletizing the extruded strand in an air bath or a water bath;
- (4) drying the pellets; and
- (5) subjecting the dried pellets of eggshell powder/polymer composite to various types of manufacturing processes including, for example, injection molding, final products at an injection pressure, speed, and a temperature profile for the feed zone, heated barrel zone, screw zone, heated chamber/melting zone, and injection nozzle appropriate for the particular polymer product desired.

[0028] The temperature profiles to be used in the extrusion and molding process for various polymers are set forth in Table 1. In instances in which polylactic acid, nylon 6, and nylon 66 are used as the polymer, an initial masterbatch is mixed and extruded under

the appropriate conditions followed by a second mixing step in which the masterbatch is mixed with the virgin polymer prior to the injection molding process.

Table 1: Temperature profiles for extrusion and injection molding of various polymers

Polymer	Extruding Temperature Range (°C)	Injection Molding Temperature Range (°C)
Polyethylene	120°-150°	140°-160°
High Density Polyethylene	130°-160°	140°-160°
Polypropylene	160°-190°	160°-200°
Polylactic Acid	170°-200°	160°-190°
High Impact Polystyrene	170°-250°	170°-250°
Acrylonitrile Butadiene Styrene	210°-250°	210°-250°
Nylon 6	140°-250°	140°-250°
Nylon 66	200°-250°	200°-250°

[0029] The following examples describe specific eggshell powder compositions and a process of producing such as well as polymer composite compositions formed using the processes described herein. The following examples are solely for purposes of illustrating certain aspects of the invention and not for the purpose of limitation.

EXAMPLE 1

Production of eggshell powder from white and brown eggs

[0030] In this example, a vortex dryer or pulverdryer was used to crush the eggshell material obtained from a group of white eggs and brown eggs and separate the eggshell material from the inner membrane material. In this instance, the initial pulverization was performed at the following conditions: (1) air speed - 3,500 rpm; (2) feeding time - 10 seconds; (3) cycling time - 0 seconds; (4) discharging time - 10 seconds; (5) feed rate - 8 kg/time; and (6) temperature - room temperature. This resulted in the production of a bulk pulverized material consisting of an eggshell component and an inner membrane component. The bulk pulverized material was then applied to an ATSM 20 mesh screen to separate the inner membrane component, which was retained on the screen, from the eggshell component, which passed through the mesh. The inner membrane component and eggshell component were each collected and the moisture content analyzed. The inner membrane component possessed a moisture content of approximately 36.4% whereas the eggshell component had a moisture content of 5.85%.

[0031] The pulverization procedure was then repeated to further dry and decrease the particle size of the eggshell component. Pulverization was performed under the following conditions: (1) air speed – 5,700 rpm; (2) feeding time - 10 seconds; (3) cycling time - 15 seconds; (4) discharging time – 10 seconds; (5) feed rate – 16 kg/time; (6) baghouse – 60%; and (7) temperature – room temperature. The eggshell component was collected and moisture determined to be 1.1%.

[0032] The eggshell component from the second pulverization run included some larger particle sizes so the pulverization was repeated for a third time. The third pulverization was performed under the following conditions: (1) air speed – 10,000 rpm; (2) feeding time - 10 seconds; (3) cycling time - 20 seconds; (4) discharging time – 10 seconds; (5) feed rate – 16 kg/time; (6) baghouse – 60%; and (7) temperature – room temperature. The eggshell component (powder) was collected and analyzed for content. The content analysis for each of the brown eggs and white eggs are provided in Table 2 below.

Table 2: Content of eggshell powder

	White eggshell powder	Brown eggshell powder
Moisture (%)	0.46	0.20
Protein (%)	3.92	5.04
Ash (%)	94.61	94.28
Fat (%)	0.35	0.08
Calcium (%)	34.12	33.13
Magnesium (%)	0.29	0.36
Phosphorous (%)	0.04	0.07
Potassium (%)	0.03	0.04
Sodium (%)	0.05	0.04
Copper (ppm)	<1ppm	<1ppm
Iron (ppm)	22ppm	<1ppm
Manganese (ppm)	<1ppm	<1ppm
Zinc (ppm)	<1 ppm	<1ppm

Example 2

Composition ratios and manufacturing conditions for various polymer composite plaques formed using the present eggshell powder composition

[0033] Tables 3A and 3B below provide composite composition ratios (Table 3A) and manufacturing conditions (Table 3B) to produce a number of specific polymer composite plaques using the present eggshell powder composition and methods. As used in the tables below, “N/A” denotes that for the specific composite, this step was not performed in this particular example and should not be interpreted to mean that this step cannot be used with

the particular composite. Specifically, composites 5 and 6 just proceeded through the extrusion process and in this particular example, did not undergo further manufacturing steps. Extrusion was performed by a twin screw extruder (Amco) for composites 1-4 and single screw extruder for composites 5-6.

Table 3A: Polymer/eggshell powder composite composition ratios

	Polymer	Additive	Masterbatch (MB)		
			% Eggshell Powder	% polymer	% Additive
Composite 1	polylactic acid	Citroflex A4 (plasticizer)	60%	39%	1%
Composite 2	High-impact polystyrene	mineral oil	30%	69.5%	.5%
Composite 3	acrylonitrile butadiene styrene (GP22)	mineral oil	30%	69.5%	.5%
Composite 4	nylon 6 & maleic anhydride modified ethyl methyl acrylate (copolymer)	INT-PA33FRK (processing aid)	60%	39.5% (MAMEMA)	.5%
Composite 5	polyethylene	Glycolube P (lubricant)	50%	49%	1%
Composite 6	polypropylene (copolymer pellet)	Polybond-300 (maleic anhydride modified polypropylene coupling agent)	50%	49%	<1% (approx. 230 grams)

Table 3B: Manufacturing conditions for the composite compositions described in Table 3A.

	Extruding Conditions (Temperature and screw speed)	Additional Masterbatch/Polymer Mix	Injection Molding Conditions
Composite 1	175°C and 60 rpm	50% MB w/50% virgin polylactic acid	182°
Composite 2	195°C and 60 rpm	N/A	200°
Composite 3	215°C and 60 rpm	N/A	220°
Composite 4	145°C and 60 rpm	50% MB w/50% virgin nylon 6	250°
Composite 5	130°C and 60 rpm	N/A	N/A
Composite 6	170°C and 60 rpm	N/A	N/A

Example 3

Comparison of strength variables between virgin nylon 66 and a nylon 66/eggshell polymer composite.

[0034] This example demonstrates that the use of eggshell powder to form a polymer composite plaque with nylon 66 results in improved properties as compared to a plaque formed of nylon 66 alone. The eggshell polymer composite plaque was produced according to the following procedure:

- (1) a masterbatch comprising 60.0% eggshell powder and 40.0% maleic anhydried modified polypropylene (MAPP) copolymer was mixed in a plastic bag by shaking;
- (2) the masterbatch of step 1 was applied to a twin screw extruder operating at 240 °C at a screw speed of 60 RPM screw speed. The product (strand) coming out of the extruder was then quenched in water, followed by grinding into small pellets;
- (3) the pellets from step 2 were then mixed with virgin Nylon 66 at a 1:1 ratio in a plastic bag by shaking; and
- (4) the mixture of step 3 was introduced into an injection molding machine (Amco) at 250 °C to form a nylon 66 composite plaque comprising 30% eggshell powder.

[0035] The plaque comprising nylon 66 and 30% eggshell powder was then tested for flexural modulus, tensile strength, and heat deflection at 0.45 MPa and 1.8 MPa. The results are shown in Table 4 below. Table 4 also includes the heat deflection and flexural modulus data of virgin nylon 66 (based on data provided by the manufacturer, BASF). As provided in Table 4, the plaque formed of the nylon 66/eggshell composite displays better properties than virgin nylon 66. Specifically, the composite of nylon 66 and eggshell powder presents higher flexural modulus (3270 Mpa) than nylon 66 itself (2920 Mpa). In other words, the composite of nylon 66 and eggshell powder is stiffer than virgin nylon 66. Furthermore, the composite of nylon 66 and eggshell powder exhibits higher heat deflection temperature at 1.80 MPa (78.3 °C) than nylon 66 (74 °C). This data implies that the composite of nylon and eggshell powder is more deform resistant and has a higher heat resistant capacity than virgin nylon 66. These properties are very important in, for example, automotive applications where resistance to heat is crucial. Therefore, the composite of

nylon 66 and eggshell powder may provide improved performance in automotive applications where virgin nylon 66 is traditionally used as it is stiffer and more heat resistant.

Table 4. Properties of nylon 66 and the composite of nylon 66 and eggshell powder

Property	Test Method	Units	Nylon 66 Control	Nylon 66 with 30% eggshell powder and 20% MAPP
Tensile Strength at Break	ISO 572	MPa	---	51.7
Flexural Modulus	ISO 178	MPa	2920	3270
Heat Deflection Temperature @ 0.45MPa	ISO 75	°C	---	138.1
Heat Deflection Temperature @ 1.80MPa	ISO 75	°C	74	78.3

[0036] Other embodiments of the current invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. Thus, the foregoing specification is considered merely exemplary of the current invention with the true scope thereof being defined by the following claims.

What is claimed is:

1. A polymer composite composition comprising:
an eggshell component, wherein the eggshell component possesses a lipid-protein structure substantially similar to that of the eggshell from which the eggshell component is derived, and wherein the eggshell component is substantially free of eggshell inner membrane material; and
a polymer component.
2. The composition of claim 1, wherein the polymer component is a thermoplastic polymer.
3. The composition of claim 1, wherein the polymer component is a thermoset polymer.
4. The composition of claim 1, wherein the polymer component is polyethylene.
5. The composition of any of claims 1-4, wherein the eggshell component constitutes 50% of the polymer composite composition.
6. The composition of claim 1, wherein the polymer component is polypropylene.
7. The composition of claim 6, wherein the eggshell component constitutes 50% of the polymer composite composition.
8. The composition of claim 1, wherein the polymer component is polylactic acid.
9. The composition of claim 8, wherein the eggshell component constitutes 50% of the polymer composite composition.
10. The composition of any of claims 1-9 further comprising an additive component selected from the group consisting of heat stabilizers, antioxidants, UV/light stabilizers, antistatic agents, antifogging agents, lubricants, processing aids, anti-blocking agents, slipping agents, mold-releasing agents, flame-retardant agents, chemical-blowing agents, crosslink agents, nucleating agents, antimicrobial agents, coupling agents, gas scavengers, acid and base scavengers, water scavengers, odor controlling agents, and food flavoring agents.
11. The composition of any of claims 1-10 further comprising a filler component selected from the group consisting of calcium carbonate, dolomite, magnesium carbonate, calcium sulfate, barium sulfate, silica, silicate, zeolite, carbon black, talc, mica, kaolin, clay,

graphite, wollastonite, whiskers, glass fiber, carbon fiber, conductive filler, nano-filler, wood flour, wood fiber, cellulose fiber, distilled drained grain, pigment, dye, and fluorescent whitening agent.

12. The composition of any of claims 1-11 wherein the eggshell component has a particle size from about 10 μm to about 100 μm .

13. The composition of any of claims 1-11 wherein the eggshell component has a particle size from about 20 μm to about 50 μm .

14. The composition of any of claims 1-13 wherein the eggshell component is hydrophobic.

15. A biobased product comprising:
an eggshell powder, wherein the eggshell powder retains the lipid-protein structure of the eggshell from which the eggshell powder is derived; and
a polymer.

16. The product of claim 15, wherein the polymer is a thermoplastic polymer.

17. The product of claim 15, wherein the polymer is a thermoset polymer.

18. The product of claim 15, wherein the polymer is polyethylene.

19. The product of any of claims 15-18, wherein the eggshell powder constitutes 25% by weight of the total weight of the product.

20. The product of claim 15, wherein the polymer is polypropylene.

21. The product of claim 20, wherein the eggshell powder constitutes 25% by weight of the total weight of the product.

22. The product of claim 15, wherein the polymer is polylactic acid.

23. The product of claim 22, wherein the eggshell powder constitutes 25% by weight of the total weight of the product.

24. The product of any of claims 15-23 further comprising an agent selected from the group consisting of heat stabilizers, antioxidants, UV/light stabilizers, antistatic agents, antifogging agents, lubricants, processing aids, anti-blocking agents, slipping agents, mold-releasing agents, flame-retardant agents, chemical-blowing agents, crosslink agents, nucleating agents, antimicrobial agents, coupling agents, gas scavengers, acid and base scavengers, water scavengers, odor controlling agents, and food flavoring agents.

25. The product of any of claims 15-24 further comprising an agent selected from the group consisting of calcium carbonate, dolomite, magnesium carbonate, calcium sulfate, barium sulfate, silica, silicate, zeolite, carbon black, talc, mica, kaolin, clay,

graphite, wollastonite, whiskers, glass fiber, carbon fiber, conductive filler, nano-filler, wood flour, wood fiber, cellulose fiber, distilled drained grain, pigment, dye, and fluorescent whitening agent.

26. The product of any of claims 15-25 wherein the eggshell powder has a particle size from about 20 μm to about 50 μm .

27. The product of any of claims 15-25 wherein the eggshell powder has a particle size from about 10 μm to about 100 μm .

28. The product of any of claims 15-27 wherein the eggshell powder is hydrophobic.

29. A process for producing an eggshell powder comprising the steps of:
exposing a quantity of eggshell to air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component;

applying the bulk pulverized material to a first screen comprising a mesh size sufficient to retain the separated inner membrane component on the surface of the first screen while permitting passage of the eggshell component through the first screen; and

collecting the eggshell component following passage through the first screen, wherein the eggshell component collected forms the eggshell powder of a first particle size, wherein the first particle size is less than or equal to that permitted to pass through the first screen.

30. The process of claim 29, wherein the first particle size is less than or equal to 100 μm .

31. The process of claim 29, further comprising the step of applying the eggshell powder to a second screen comprising a mesh size sufficient to permit passage of a second particle size, wherein the second particle size is less than the first particle size; and

collecting the eggshell powder that passes through the second screen, wherein the eggshell powder that passes through the second screen has a particle size less than or equal to the second particle size.

32. The process of claim 31, wherein the second particle size is less than or equal to 50 μm .

33. The process of claim 31, wherein the second particle size is less than or equal to 20 μm .

34. The process of claim 31, wherein the second particle size is greater than or equal to 10 μm .

35. The process of any of claims 31-34, further comprising the steps of:
collecting the eggshell powder that is retained on the second screen, wherein the eggshell powder retained on the second screen has a particle size greater than the second particle size;

re-exposing the eggshell powder retained on the second screen to air flow at a speed sufficient to further reduce the particle size; and

re-applying the eggshell powder to the second screen.

36. The process of claim 35 wherein the re-exposure of air flow is at a speed of 5,700 rpm for 10 seconds.

37. The process of claim 35 wherein the eggshell powder is exposed to air flow for a third time at a speed of 10,000 for 10 seconds.

38. The process of any of claims 29-37, further comprising the step of sterilizing the eggshell prior to pulverizing.

39. The process of any of claims 29-38, wherein the eggshell is not heated during the entire process.

40. The process of any of claims 29-39, wherein the air flow is at a speed of 3,500 rpm for 10 seconds.

41. The process of any of claims 29-40, wherein the step of exposing the eggshell to air flow is performed in a vortex dryer.

42. The process of any of claims 29-40, wherein the step of exposing the eggshell to air flow is performed in a cyclone wind tunnel.

43. A composition comprising an eggshell powder, wherein the eggshell powder possesses the lipid-protein structure of the eggshell from which the eggshell powder is derived, and wherein the eggshell powder is substantially free of eggshell inner membrane material.

44. The composition of claim 43 wherein the eggshell powder has a fat content from about 0.01% to about 3%.

45. The composition of claim 43 wherein the eggshell powder has a fat content of about 0.35%.

46. The composition of claim 43 wherein the eggshell powder has a fat content of about 0.08%.

47. The composition of claim 43 wherein the eggshell powder has a fat content of less than 1%.

48. The composition of any of claims 43-47 wherein the eggshell powder has a moisture content from about 0.2% to about 5%.

49. The composition of any of claims 43-47 wherein the eggshell powder has a moisture content of less than 1%.

50. The composition of any of claims 43-47 wherein the eggshell powder has a moisture content of about 0.46%.

51. The composition of any of claims 43-47 wherein the eggshell powder has a moisture content of about 0.2%.

52. The composition of any of claims 43-51 wherein the eggshell powder has a total ash content from about 90% to about 95%.

53. The composition of claim 52 wherein the total ash content comprises from about 33% to about 36% calcium.

54. The composition of claim 53 wherein the calcium is substantially calcium oxide.

55. The composition of any of claims 43-54 wherein the eggshell powder has a protein content of less than 5%.

56. The composition of any of claims 43-54 wherein the eggshell powder has a protein content from about 0.2% to about 3%.

57. The composition of any of claims 43-54 wherein the eggshell powder has a protein content of about 3.9%.

58. The composition of any of claims 43-54 wherein the eggshell powder has a protein content of about 5%.

59. The composition of any of claims 43-58 wherein the eggshell powder has a particle size from about 10 μm to about 100 μm .

60. The composition of any of claims 43-58 wherein the eggshell powder has a particle size from about 20 μm to about 50 μm .

61. The composition of any of claims 43-60 wherein the eggshell powder is crushed eggshell.

62. The composition of claims 43-61 wherein the eggshell powder is hydrophobic.

63. A polymer composite composition comprising:

an eggshell component, wherein the eggshell component is substantially free of eggshell inner membrane; and

a polymer component.

64. The composition of claim 63 wherein the polymer component is nylon 66.

65. The composition of claim 64 wherein the polymer component further comprises maleic anhydride modified polypropylene.

66. The composition of claim 65 wherein the composition possesses a flexural modulus of about 3270 Mpa.

67. The composition of any of claims 65-66 wherein the composition possesses a heat deflection temperature at 1.80MPa of about 78.3°C.

68. The composition of any of claims 65-67 wherein the eggshell component is about 30% by weight of the total weight of the composition.

69. The composition of any of claims 65-68 wherein the maleic anhydride modified polypropylene is about 20% by weight of the total weight of the composition.

70. The composition of any of claims 65-69 wherein the nylon 66 is about 50% by weight of the total weight of the composition.

71. The composition of any of claims 65-70 wherein the composition has a tensile strength at break of 51.7 MPa.

72. The composition of claim 63 wherein the polymer component is high-impact polystyrene.

73. The composition of claim 72 wherein the composition further comprises mineral oil.

74. The composition of claim 73 wherein the eggshell component is about 30% by weight of the total weight of the composition, wherein the nylon 66 is about 69.5% by weight of the total weight of the composition, and wherein the mineral oil is about 0.5% by weight of the total weight of the composition.

75. The composition of claim 63 wherein the polymer component is acrylonitrile butadiene styrene.

76. The composition of claim 75 wherein the composition further comprises mineral oil.

77. The composition of claim 76 wherein the eggshell component is about 30% by weight of the total weight of the composition, wherein the acrylonitrile butadiene styrene

is about 69.5% by weight of the total weight of the composition, and wherein the mineral oil is about 0.5% by weight of the total weight of the composition.

78. The composition of claim 63 wherein the polymer component is nylon 6.

79. The composition of claim 78 wherein the polymer component further comprises maleic anhydride modified ethyl methyl acrylate.

80. The composition of claim 79 wherein the composition further comprises a processing aid.

81. The composition of claim 80 wherein the eggshell component is about 30% by weight of the total weight of the composition, wherein the maleic anhydride modified ethyl methyl acrylate is about 69.75% by weight of the total weight of the composition, and wherein the processing aid is about 0.25% by weight of the total weight of the composition.

82. The composition of any of claims 63-81 wherein the eggshell component possesses the lipid-protein structure of the eggshell from which the eggshell component is derived.

83. The composition of any of claims 63-81 wherein the eggshell component is hydrophobic.

84. A process for producing an eggshell powder comprising the steps of:
exposing eggshell to an air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component; and
isolating the eggshell component from the bulk pulverized material.

85. The process of claim 84 wherein the eggshell component is exposed to an air flow at a speed greater than the initial exposure of the eggshell.

86. The process of claim 84 wherein the speed is about 3,500 rpm.

87. The process of claim 84 wherein the eggshell component is isolated from the bulk pulverized material by applying the bulk pulverized material to a screen having a mesh size sufficient to retain the inner membrane component on the surface of the screen while permitting passage of the eggshell component.

1/1



FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/65639

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B02C 17/00, C08K 3/00, C08L 23/06 (2012.01)

USPC - 241/24.12, 264/36.18, 524/10, 524/70, 524/581

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)

IPC(8)- B02C 17/00, C08K 3/00, C08L 23/06 (2012.01);

USPC- 241/24.12, 264/36.18, 524/10, 524/70, 524/581

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (USPTO, EPO, JPO, WIPO), GoogleScholar (PL, NPL), FreePatentsOnline (USPTO, EPO, JPO, WIPO, NPL);
search terms: egg, eggshell, lipid, protein, lipoprotein, polypropylene, polyethylene, polymer, pulverize, maleic, anhydride, flexural, modulus, heat, deflection, ethyl methyl acrylate, mineral, oil

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2011/0272502 A1 (NEW) 10 November 2011 (10.11.2011), para [0021], [0022], [0025]-[0027], [0032], [0034]	29, 31, 35/(31) ----- 30, 32-34, 35/(32-34), 36, 37, 85, 86
X -- Y	US 2011/0272858 A1 (TAMIR) 10 November 2011 (10.11.2011), para [0018], [0019], [0036], [0047], [0239], [0242], [0245], [0248], [0251]-[0255], [0258]-[0263], [0281], [0360]	63, 64, 72, 75, 78 ----- 1-9, 15-23, 43-51, 65-67, 71, 73, 74, 76, 77, 79-81
X -- Y	US 2003/0209617 A1 (MACNEIL) 13 November 2003 (13.11.2003), para [0056], [0019], [0021], [0025], [0056], [0058]	84, 87 ----- 30, 32-34, 35/(32-34), 36, 37, 85, 86
Y	US 2010/0254900 A1 (CAMPBELL et al.) 07 October 2010 (07.10.2010), para [0008], [0009], [0033], [0073], [0165], [0166], [0205]	1-9, 15-23, 43-51
Y	US 5,285,750 A (MOLIAN et al.) 15 February 1994 (15.02.1994), col 1, ln 39-54; col 2, ln 26-38	44-51
Y	US 6,221,928 B1 (KOZMA et al.) 24 April 2001 (24.04.2001), col 2, ln 63 to col 3, ln 4; col 8, ln 55 to col 9, ln 10; col 12, ln 32; col 23, ln 31; col 24, ln 7	65-67, 71, 73, 74, 76, 77, 79-81

☒ Further documents are listed in the continuation of Box C.



* 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 application or patent but published on or after the international filing date

"L" document which may throw doubts on priority 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

"&"

document member of the same patent family

Date of the actual completion of the international search

07 February 2013 (07.02.2013)

Date of mailing of the international search report

07 MAR 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/65639

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	WO 2012/036645 A2 (DURMUS et al.) 22 March 2012 (22.03.2012), pg 6-16	1-9, 15-23, 29-37, 43-51, 63-67, 72-81, 84-87
Y	US 2008/0166447 A1 (STROHBEHN et al.) 10 July 2008 (10.07.2008), para [0029]-[0146]	1-9, 15-23, 29-37, 43-51, 63-67, 72-81, 84-87
Y	US 2004/0180025 A1 (LONG et al.) 16 September 2004 (16.09.2004), para [0017]-[0184]	1-9, 15-23, 29-37, 43-51, 63-67, 72-81, 84-87

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/65639

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 carried out, specifically:
3. ☒ Claims Nos.: 10-14, 24-28, 38-42, 52-62, 68-71, 82, and 83
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:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-9, 15-23, 43-51, 63-67, and 72-81, drawn to a polymer composite comprising: an eggshell component, wherein the eggshell component is substantially free of eggshell inner membrane; and a polymer component.

Group II, claims 29-37 and 84-87, drawn to a process for producing an eggshell powder, comprising exposing eggshell to an air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component.

-- Please see extra sheet --

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying 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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/65639

Continued from Box No. III, Observations where unity of invention is lacking:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-9, 15-23, 43-51, 63-67, and 72-81, drawn to a polymer composite comprising: an eggshell component, wherein the eggshell component is substantially free of eggshell inner membrane; and a polymer component.

Group II, claims 29-37 and 84-87, drawn to a process for producing an eggshell powder, comprising exposing eggshell to an air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Group I does not include the special technical feature of an eggshell powder, comprising exposing eggshell to an air flow at a speed sufficient to pulverize the eggshell thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component, as required by Group II.

Group II does not include the special technical feature of a polymer composite comprising: an eggshell component, wherein the eggshell component is substantially free of eggshell inner membrane; and a polymer component, as required by Group I.

The special technical feature of an eggshell component (para [0016]), common to Groups I and II, is disclosed by US 2003/0209617 A1 (MacNeil), 13 November 2003 (13.11.2003).

MacNeil further discloses an eggshell powder (para [0056]), comprising exposing eggshell to an air flow at a speed sufficient to pulverize the eggshell (para [0019], [0021], [0056], [0058], Processed particle size using a pulverizer... for separate isolation of shell and membrane components... by forced air to separate membrane and shell components...) thereby rendering a bulk pulverized material comprising an eggshell component and a separated inner membrane component (para [0020], [0021], [0056], [0058], Isolated shell and membrane components (including outer membrane and inner membrane (para [0010]))... membrane components are collected using a conveyor belt... shell particles migrate to the cyclone wall where they slide to the bottom and into the collector... and a bulk disposal tank for removing significantly heavier pieces of shell.).

The special technical feature of an eggshell component (para [0019], [0248]), common to Groups I and II, is also disclosed by US 2011/0272858 A1 (Tamir), 10 November 2011 (10.11.2011).

Tamir further discloses a polymer composite comprising: an eggshell component, wherein the eggshell component is substantially free of eggshell inner membrane; and a polymer component (para [0018], [0019], [0047], [0239], [0248], [0281], Composite thermoplastic material comprising organic matter and plastic... wherein the plastic may be polyethylene or polypropylene... and/or a thermoset... and the organic matter may be egg shells.).

Furthermore, as separation of eggshell components into shells and membranes would have been known to one of ordinary skill in the art, as evidenced by MacNeil, the polymer composite comprising egg shell, as in Tamir, being substantially free of eggshell inner membrane cannot be considered an improvement over the art known in the field.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Groups I and II therefore lack unity under PCT Rule 13 because they do not share a corresponding special technical feature.