Food waste eggshell valorization through development of new composites: A review

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Abstract

The total amount of annual eggshell waste is similar as the amount of plastics waste input in the oceans every year. Hence, the management of this eggshell waste is a major challenge. The last five years have seen a dramatic increase in research dedicated to the use of eggshell waste as source materials for the development of novel sustainable composites. This paper provides a review of the broad range of eggshell waste use in polymer, metal and ceramic composites, and in other applications such as adsorbents, catalysts, additives and functional materials. The different types and sources of $CaCO_3$ are presented. An overview is given about the eggshell treatment methods and parameters, which fall broadly in two categories, low temperature treatment of $CaCO_3$ particles, and high temperature treatment involving carbonization or calcination. The mechanical properties of structural composites with eggshell derived particles are discussed for polymer, metal and ceramic matrix materials. A brief view on commercialization is presented, and the paper concludes with the main findings and suggestions for future research developments.

Keywords: eggshell, carbonate, calcite, food waste, circular economy, composite, sustainability

1. Introduction

The management of vast amounts of food waste is a major challenge. In the framework of circular economy, the aim is to eliminate waste and establish continual use of resources, such as using waste as a (renewable) resource to make value-added products. The use of waste from renewable resources in products is preferred over the use of finite resources for sustainability and environmental reasons. Therefore, research on plant fibre reinforced (biodegradable polymer) composites has gained much interest in recent years [1, 2]. In addition, inorganic food waste can provide a sustainable resource for the development of products. About 65.5 million metric tons of eggs are produced annually worldwide. This production has increased by 10% in Europe and by about 50% in China between 2000 and 2010. The largest egg producing country is China, with 45% of the total production (Fig. 1). It is estimated that global egg production will reach about 90 million tons by 2030 [3]. Considering that the eggshell is about 11% of the weight of an egg, it can be calculated that nearly 7.2 million tons of eggshell waste is created every year [4]. In comparison, this amount is about the same as the 8 million tons plastics waste input in the oceans each year, from a total of about 275 million tons plastic waste generated on land [5].

Eggshell waste is generally disposed of in landfills, and thus become a source of pollution with odor production and microbial growth [6]. To solve this challenge, optimal strategies of food waste treatment need to be developed, in particular because eggshell waste is considered a hazardous waste according to European Union regulations [7]. Eggshell waste from industrial processes can be used for agriculture, as an agent to increase soil pH. In this case, generally the shell $CaCO_3$ is calcined to obtain CaO, which is an energy-intensive process [8]. Despite this use, eggshell waste is still undervalued as a resource, and can be utilized as an alternative source for $CaCO_3$ [9], which is currently taken from non-renewable finite limestone natural resources. Eggshell $CaCO_3$ powder can replace conventional limestone derived $CaCO_3$ for 100% in final products. Recovery of food waste eggshells to produce new materials is thus an ideal recycling strategy. To fulfil the cradle-to-cradle sustainability concept, the final products may need to be materials that can either completely degrade and serve as nutrients in soil (e.g. composite with eggshell particles and biodegradable polymer matrix), or products that can be fully recycled.

Research on eggshell waste has gained rapidly more attention over the last five years. The reported studies with use of eggshell waste in new materials cover a range of applications, such as removal of toxic metals from contaminated water and soil [10], cosmetics [11], cement production [12], and polymer and metal composites. The driving factors behind the use of eggshell waste in composites include mainly the large size of the waste source and future projected increase, the environmental hazard of the waste source, the fact that this waste can be an alternative to finite natural resources, the fact that it is a common compound in composites, and that eggshell waste may present a potentially cheaper source and more environmentally friendly source especially at locations where limestone quarries are far away from the production site of the composites. Previous reviews on research involving eggshell waste have concentrated on ball milling of eggshells and mechanochemistry [13], and the use of eggshell and seafood shell waste in polymer composites [14]. The focus in the current paper is a review on eggshell treatment and a comprehensive overview of the wide range of different composites and applications with the use of eggshell and eggshell-derived material, e.g. the use of eggshell $CaCO_3$ particles as fillers in polymer composites, the use of eggshell treated material in metal composites or as a raw material for the production of hydroxyapatite materials and adsorbents and catalysts. The growing interest over the last years in this topic is also clear from the dramatic increase in the number of papers that have both “eggshell” and “composite” in the title based on the Web of Science database (Fig. 2).

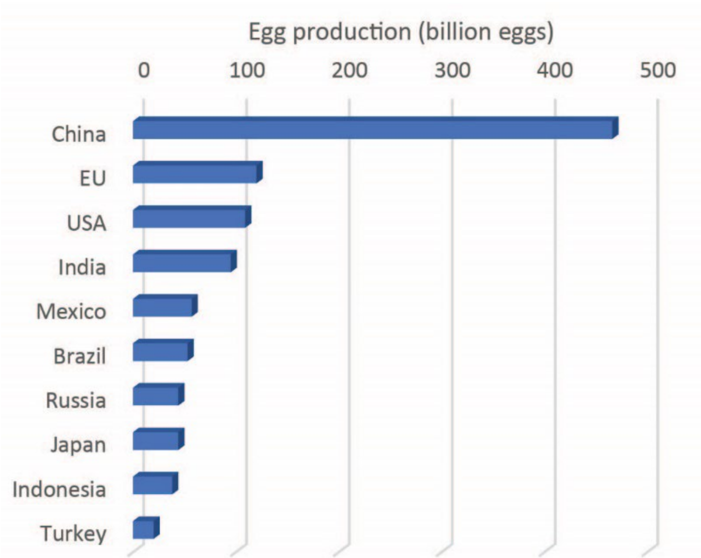

Fig. 1. The top ten egg producing countries (based on Food and Agriculture Organization database).

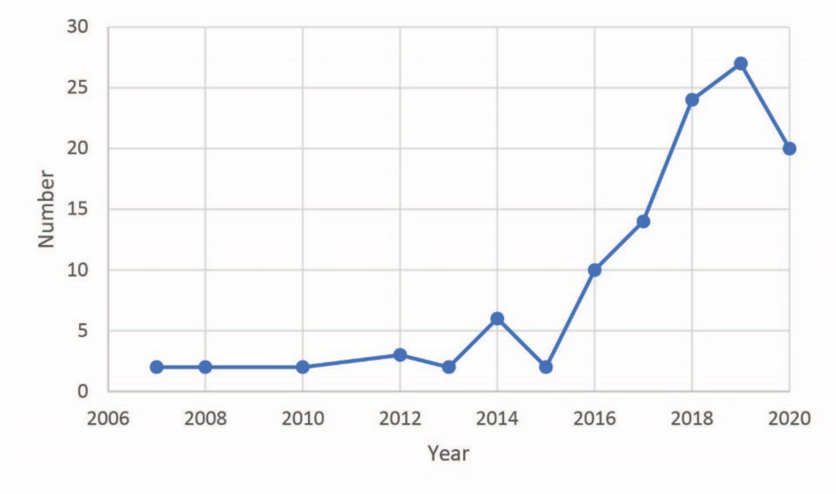

Fig. 2. Annual number of scientific publications that have both "composite" and "eggshell" in the title (based on Web of Science database), showing the massive increase over the last five years.

2. Carbonate types and sources

2.1. Types of carbonate

Several types of carbonate are formed via natural processes. The most abundant carbonate types found on Earth are natural rock resources, such as limestone and dolostone. Limestone is made up primarily of calcium carbonate [$CaCO_3$], whereas dolostone consists predominantly of calcium magnesium carbonate [$CaMg(CO_3)_2$ or dolomite]. There are also other carbonate minerals which are less common in natural mineral deposits, such as magnesite [$MgCO_3$], siderite [$FeCO_3$], witherite [$BaCO_3$], and rhodochrosite [$MnCO_3$]. Calcium carbonate can occur in the form of three different minerals (with different crystal structure) or polymorphs, namely (i) calcite with a trigonal crystal structure, (ii) aragonite with an orthorhombic crystal structure, and (iii) vaterite with a hexagonal crystal structure (Fig. 3). Calcite is the most common polymorph, especially in rocks, since calcite is more stable than aragonite and vaterite. Studies have also indicated that aragonite starting material changes to calcite at a temperature of around 400-450 °C when the material is subjected to heat treatment [15, 16]. Over geological time scale, vaterite and aragonite are converted to calcite. As a consequence, limestone derived $CaCO_3$ predominantly consists of calcite. In terms of origin and sedimentary rock formation, many limestone rocks are composed of debris material of marine organisms, such as molluscs, gastropods, corals, and carbonate mud which accumulated millions of years ago and subsequently lithified under burial of younger sediments. The density of calcite is 2.71 g/cm^3, that of aragonite is 2.93 g/cm^3, and that of vaterite is 2.54 g/cm^3. Calcium carbonate is a main source for the production of cement and mortar, and it is also a common filler in polymer composites. The type of $CaCO_3$ polymorph can influence the properties of polymer composites. For example, the crystallization temperature and crystallinity is higher for polypropene/$CaCO_3$ composites with vaterite as filler than with aragonite or calcite as filler; hence, vaterite is considered to be a better nucleating agent for polypropene [17]. The use of calcite whiskers in polypropene/$CaCO_3$ composites also leads to better mechanical properties and a higher degree of crystallinity than aragonite whiskers or calcite particles as filler [18].

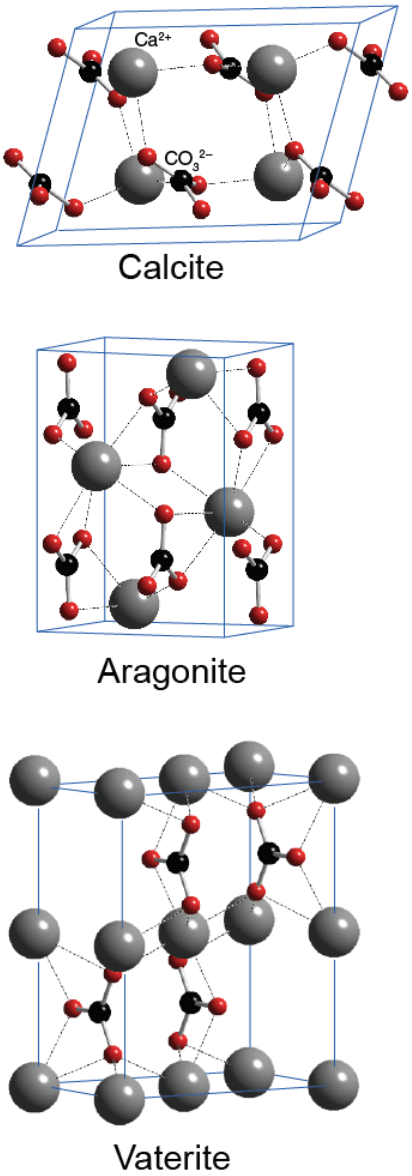

Fig. 3. The crystal structure of the three polymorphs of calcium carbonate, calcite, aragonite and vaterite (Chem3d).

2.2. Seafood waste $CaCO_3$ shells

Similar to ancient geological times, several living organisms still build shells of calcium carbonate. Several marine organisms have hard $CaCO_3$ shells. In contrast to lithified rocks, $CaCO_3$ from seafood waste, such as mussel, oyster and scallop shells, have not undergone physicochemical processes over geological time scales, such as conversion to the most stable minerals, compaction, lithification, recrystallization, corrosion and cementation. As a result, food waste shells have a more complex inorganic-organic structure and heterogeneous mineralogical composition than carbonate derived from rocks. Many organisms form a complex interlayered structure of organic and inorganic components, generally with a specific hierarchical three-dimensional build-up through which these organisms achieve shells with excellent mechanical strength and toughness [19]. These complex natural structures have inspired researchers to design biomimetic materials to obtain targeted or improved material properties [20]. A prominent example is biomimetic synthetic material inspired by nacre from seashells, consisting of crystalline calcium carbonate and organic biopolymer [21-24].

2.3. Avian food waste $CaCO_3$ eggshells

The focus in this review is on chicken eggshells, which consist also mainly of $CaCO_3$, but are very different from the shells of marine organisms that form limestone rocks. Chicken eggshells have a composition of 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic matter [25]. The eggshell forms by precipitation of calcium carbonate on the egg outer membrane fibres, in a supersaturated fluid with 6 to 10 mM calcium ions and 70 mM bicarbonate ions [26]. The polymorph calcite is formed rather than aragonite or vaterite due to the organic components in the fluid which promote nucleation of amorphous calcium carbonate which subsequently converts to calcite crystals [27]. The shell structure is composed of (from inside to outside): (i) mammillary cones, (ii) palisade calcite, (iii) a transitional crystal layer, and (iv) a cuticle coating with hydroxyapatite [28] (Fig. 4; [29]). A typical chicken egg has a biomineralized shell thickness of 0.3-0.4 mm [30].

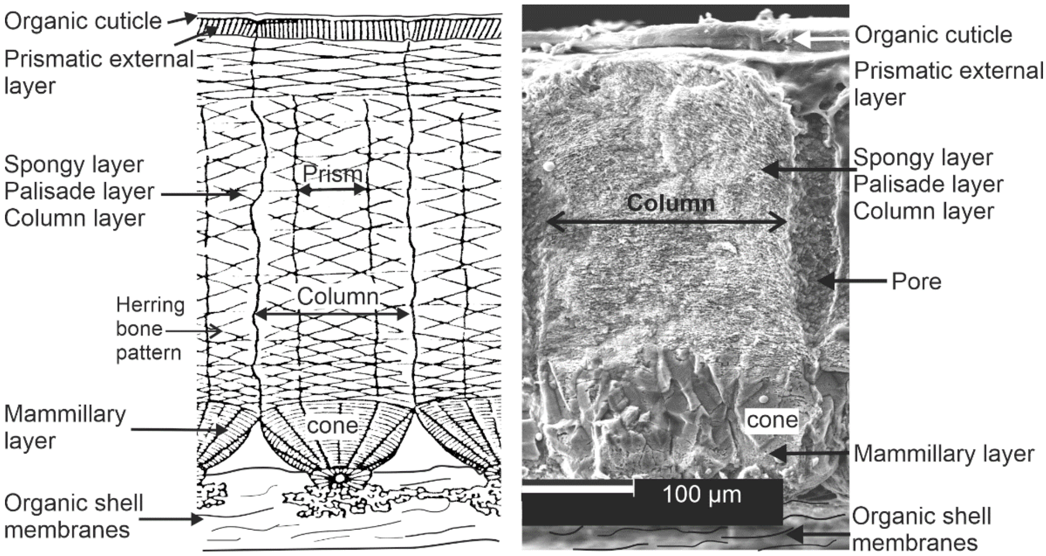

Fig. 4. Structure of an avian eggshell with schematic sketch and scanning electron microscope picture with labelled terminology of the different parts. Figure from Pérez-Huerta and Dauphin [29], reprinted with permission from Elsevier.

3. Eggshell treatment methods for use in composites

A wide range of eggshell treatment methods are reported in studies on eggshell-derived composites. Two main categories can be distinguished, namely (i) methods for composites that use eggshell $CaCO_3$ without high temperature treatment, and (ii) methods where the eggshells are treated at high temperature for carbonization or calcination to obtain CaO.

3.1. Preparation of eggshell $CaCO_3$ particles without high temperature treatment

An overview of the different preparation method parameters for eggshell $CaCO_3$ as filler in composites is presented in Table 1. The different parameters encompass type of washing agent, membrane removal, drying temperature, drying time, sieving mesh size, and particle surface modification. First, the food waste eggshells are cleaned to remove any potential egg white or dirt. In about 40% of the studies, it is reported that the inner membrane of the eggshell is removed. This is generally done manually by using hot water. The type of agent being used for the washing process is tap water, distilled water, deionized water, or ultrapure water in two thirds of the reported studies. The other works report washing the eggshells with a NaClO solution, NaCl solution, NaOH solution, methanol, acetone or dimethylformamide, and in some cases, the eggshells are first washed with water, followed by ethanol or acetone and methanol. After washing, the eggshells are dried at room temperature or in an oven (either in air or under vacuum) at elevated temperature, generally between 50 and 110 °C, and there are a few studies that report drying at 200 or 250 °C. The drying time varies from half an hour to several days, but is often not specified in the studies. The milled eggshell powder is sieved to obtain a specific size distribution, which varies amongst the reported studies. In almost half of the studies, a particle size of 50 μm or smaller is used, and about one fifth of the studies report a particle size smaller than 63, 75 or 100 μm. The smallest particle size of 10 nm was achieved by first grinding eggshells to a fine powder, and then using sonochemical methods with DMF for five hours [31]. In many cases, no additional chemical treatment or functionalization of the particles is conducted, and the powder is stored in a desiccator until use. Some studies describe treatment of the milled eggshell particles with acid, pimelic acid, stearic acid, acetic acid or phenylphosphonic acid, and polypropylene glycol, terpolymer and nanosized titanium dioxide.

Table 1

Overview of preparation method parameters for the production of eggshell $CaCO_3$ particles for composites.

Membrane removed	Washing solvent	Drying temperature (°C)	Particle size (μm)*	Surface modifier	Reference
yes	NaOH solution	60	-	none	[32]
no	NaOH solution	80	<63	none	[33]
no	acetone	25	<149	pimelic acid	[34]
yes	water	25	<125	none	[35]
no	water	110	-	stearic acid	[36]
no	DMF	25	<0.01	none	[31]
yes	water, ethanol	25	<2-0	acetic acid	[37]
no	water	25		none	[38]
yes	distilled water	50	<74	none	[39]
no	hot distilled water	70	<75, 75-150, 150-212	none	[40]
no	deionized water	110	2	none	[41]
no	water, ethanol	25	-	polypropylene glycol	[42]
no	methanol	100	<25	none	[43]
yes	water	105	<32, 32-63	none	[44]
no	deionized water	-	2	pimelic acid	[45]
yes	tap water	80	45-125	none	[46]
no	water	-	<74	none	[47]
no	NaClO solution	-	<45	none	[48]
yes	hot distilled water	50	-	none	[49]
no	-	80	-	acid	[50]
yes	tap water	80	<125	none	[51]
no	distilled water	80	<600	none	[52]
no	water	50	<44	none	[53]
no	deionized water	110	2	none	[54]
no	-	-	2	phenylphosphonic acid	[55]
yes	tap water	80	7	none	[56]
no	tap water	-	300	none	[57]
no	-	80	-	terpolymer	[58]

no	water, acetone, methanol	25	<75	none	[59]
yes	1M NaOH solution	25	<100	none	[60]
no	-	110	<106, 106-149, 149-250	none	[61]
no	NaClO solution	250	<25	nanosized titanium dioxide	[62]
yes	water	80	1.1	none	[63]
yes	hot water	100	0.3-20	none	[64]
yes	NaClO solution	100	<44, 44-150	none	[65]
yes	distilled water	105	45	none	[66]
yes	-	110	<300	none	[67]
no	-	80	<500	none	[68]
no	distilled water	200	<50	none	[69]
yes	NaClO solution	100	<44, 44-150	none	[70]
yes	NaCl solution	100	<100	none	[71]
no	deionized water	25	<25	none	[72]
no	deionized water	80	-	none	[73]
yes	tap water	25	<300	none	[74]
yes	clean water	80	<100	none	[75]
no	-	80	<25	none	[76]

* Particle size after grinding

3.2. Preparation of eggshell powder treated at high temperature

Chicken eggshell carbonate was also used as a source material subjected to high temperature heat treatment. For this process, the chicken eggshells were first washed with water and ground to powder. The different appearance of eggshells having undergone different degrees of heat treatment is presented in Fig. 5 [8]. In 40% of the reported studies, the eggshell membrane was removed before grinding the material. In terms of heat treatment, about one quarter of the studies report heating to 500 or 600 °C for a duration of one to three hours. This heat treatment is conducted to remove carbonaceous materials such as dirt and the protein membrane [77, 78], even though the membrane is removed before heat treatment in several studies [79, 80]. Analyses with Fourier Transform InfraRed spectrometry (FTIR) and X-ray diffraction (XRD) confirm that the eggshell powder upon such heat treatment has a $CaCO_3$ composition [77], and that amine functionalities from the organic part of the eggshell disappeared [80]. Moreover, thermogravimetric analysis (TGA) shows that the organic proteins in the calcified layers are decomposed at a temperature from 250 to 380 °C with a weight loss of 3.0% [80]. Scanning electron microscopy (SEM) data indicate that the carbonized eggshell particles have irregular sizes and shapes, and have a porous structure on the surface [78, 80]. Many studies conduct heat treatment of eggshells at even higher temperatures, generally between 800 and 1000 °C for calcination to obtain calcium oxide (CaO) [81-83]. The CaO is then converted to hydroxyapatite using the wet precipitation method with orthophosphoric acid for some applications [84-86]. The eggshells start to decompose at 650 °C and are completely decomposed at 800 °C [87], and TGA analysis confirms decomposition between 630 and 850 °C with a weight loss of 58% due to conversion of $CaCO_3$ to CaO [80]. Analyses of the calcined material using FTIR and XRD showed the presence of $Ca(OH)_2$ due to uptake of moisture from the air, as well as some carbonation triggered by CO_2 adsorption by CaO [82, 83]. The highest temperature reported for heat treatment of eggshell carbonate is 1200 °C whereby the dried eggshell powder is packed in a graphite crucible and heated in an electric resistance furnace [88]. In some cases, the eggshell material was heat treated while being mixed with another material for a targeted composite, e.g. with anthill powder [89, 90] or with Al matrix [91].

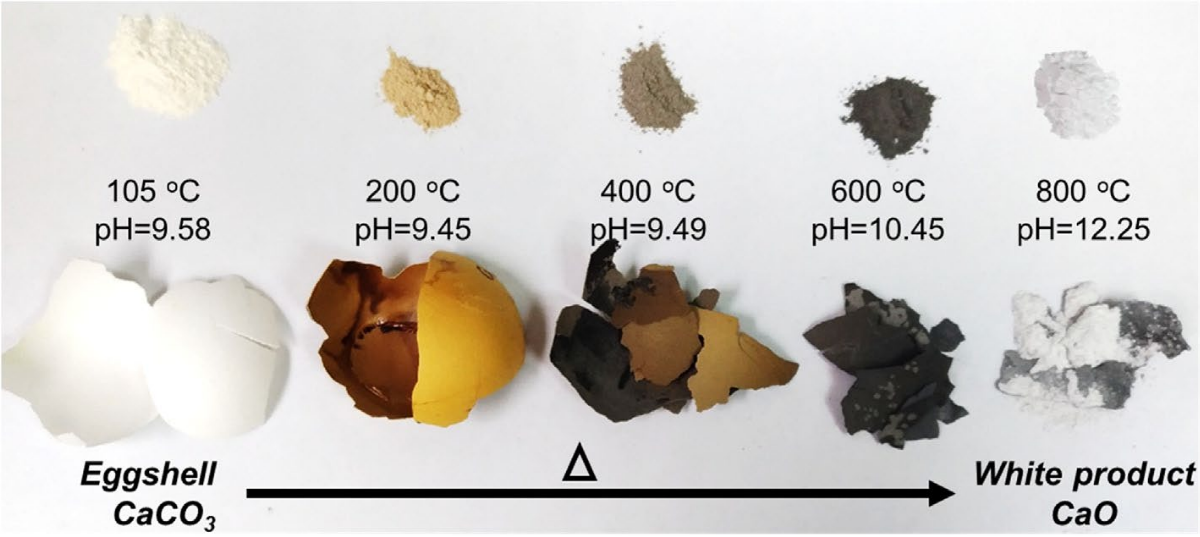

Fig. 5. Appearance of avian eggshells upon heat treatment at different temperatures. Figure from Lee et al. [8], reprinted with permission from Elsevier.

Table 2

Overview of preparation method parameters for the production of heat treated eggshell particles.

Membrane removed	Heating temperature (°C)	Heating time (hours)	Particle size (µm)*	Reference
yes	600	2	<37	[80]
no	500	1	100-120	[92]
no	500	2	100-350	[77]
no	500	3	25	[93, 94]
yes	800	2	<210	[81]
no	1000	4	-	[95]
yes	800	3	<53	[96]
yes	500	3	-	[79]
no	1000	5	-	[97]
no	900	8	-	[82]
no	900	2	-	[98]
yes	1000	4	150-220	[89]
yes	864	4	<300	[99]
yes	1200	-	<63	[88]
no	900	8	-	[83]
no	900	2	-	[100]
no	500	5	<50	[101]
yes	900	48	-	[102]
no	800	2	<250	[87]
yes	1000	1	-	[84]
yes	800	2	<210	[103]
no	800	3	<75	[104]
no	900	3	-	[85]
yes	700-900	-	125-300	[67]
no	500	3	-	[78]
no	1100	2	-	[105]

no	500	2	<75	[106]
no	900	2	-	[107]

* Particle size after grinding and heating

4. Application of food waste eggshells in structural composite materials

4.1. Thermoplastic polymer composites

Chicken eggshell was introduced as a new bio-filler in polymer composites in 2007 by Toro et al. [108]. This study showed that polypropene (PP) composite with 40% eggshell filler has a higher Young's modulus than PP composite with 40% conventional calcium carbonate filler of either smaller or larger particle size. This finding was attributed to a better eggshell-matrix interfacial bonding [108]. The Young's modulus of eggshell/PP composites increases with increasing filler loading from 0 to 60%, and with decreasing mean particle size from 90 to 8 μm. The impact strength and deformation at break decrease with increasing filler loading [109]. Subsequent studies on eggshell/PP composites focused on modification of the eggshell filler. Lin et al. [34] modified eggshell fillers with pimelic acid before melt compounding with PP, and this resulted in eggshell/β-PP composite. The modification by pimelic acid improved dispersion of eggshell particles and the interfacial bonding with the polymer matrix. However, the addition of eggshell filler (up to 5%) modified with pimelic acid to PP caused a slight decrease in the tensile and flexural strength of the material, but an increase in the impact strength [34]. Ghabeer et al. [36] modified eggshell particles with stearic acid in the preparation of eggshell/PP composite via melt extrusion. The Young's modulus of the composite increased with increasing eggshell filler loading up to 30%, but the tensile strength and strain at break decreased. The general trends are similar but more pronounced than for unmodified eggshell/PP composite [36]. A study highlighted the cost of grinding-sieving and/or chemical modification, and proposed direct processing of PP with up to 40% unmodified cm-scale eggshell shards using continuous, single-step solid-state shear pulverization [110]. An 87% increase in Young's modulus was achieved in 40% eggshell/PP composite in comparison to neat PP thanks to the very good dispersion of eggshell particles in the PP matrix, and a decrease in yield strength, elongation at break, and impact strength. The composite also has a higher thermal degradation temperature compared to neat PP [110]. Another study investigated the incorporation (5%) of a compatibilizer, maleic anhydride grafted PP, to improve dispersion of 30% eggshell powder in PP [77]. The results showed an increase in Young's modulus and flexural modulus.

Eggshell fillers have also been used in polyethene thermoplastic polymers. Supri et al. [33] investigated the effect of polyethene-grafted maleic anhydride added as a compatibilizer (6% of the eggshell filler loading) to improve the interfacial adhesion between eggshell fillers and low-density polyethene (LDPE). The Young's modulus increases, whereas the tensile strength and elongation at break decreases with an increase of the content of eggshell filler (5 to 25%) in the eggshell/LDPE composite with and without compatibilizer. The elongation at break is smaller for the composites containing the compatibilizer [33]. Also high-density polyethene (HDPE) composite with eggshell filler was studied [56]. This study adopted a silane coupling agent to modify the eggshell filler. Young's modulus increased and the tensile strength and elongation at break decreased with higher filler content (0 to 70%). The tensile strength, Young's modulus and thermal stability of the composite improved by this filler modification which enhanced the interfacial interaction and adhesion between HDPE and eggshell particles. The elongation at break was also shorter for the composite with silane coupling agent [56].

A few studies report eggshell fillers in other thermoplastic polymers. Murugan et al. [46] made composites with eggshell particles in poly(vinyl chloride) (PVC). Stearic acid, dibutyltin maleate and a plasticizer were added during compounding the eggshell/PVC composite. This study indicated a higher tensile modulus and lower elongation at break with increasing filler loading from 0 to 40% (Fig. 6; [46]). The change in mechanical properties with eggshell filler loading was more pronounced for a smaller particle size, 0.2 μm in comparison to 7 μm, due to better dispersion and improved filler-matrix interfacial adhesion [46]. Sharmeeni et al. [51] showed that the blending sequence of eggshell/PVC composite compounding has an effect on the processing, mechanical properties, morphology and thermal decomposition of the composite. The composite showed improved tensile strength and thermal stability when PVC, stearic acid and dibutyltin maleate were mixed first, and subsequently a mixture of eggshell and plasticizer was added [51]. Composites with eggshell filler have also been investigated with a polystyrene (PS) matrix. Hayeemasae et al. [111] compared composites with 20% eggshell filler (with a particle size of 75 μm) and different proportions of recycled and virgin PS. The results showed that the tensile strength, elongation at break, Young's modulus and impact strength increase for composites with a higher proportion of virgin PS [111]. In another study, eggshell filler (with a particle size of 74 μm) was used alongside bagasse fibers in extruded PS foam [47]. Acetate anhydride was added as a compatibilizer, and dioctyl phthalate as a stabilizer. The flexural strength and the toughness of the composite increase more than double for higher bagasse and eggshell filler loading (from 10% to 25% for each) [47].

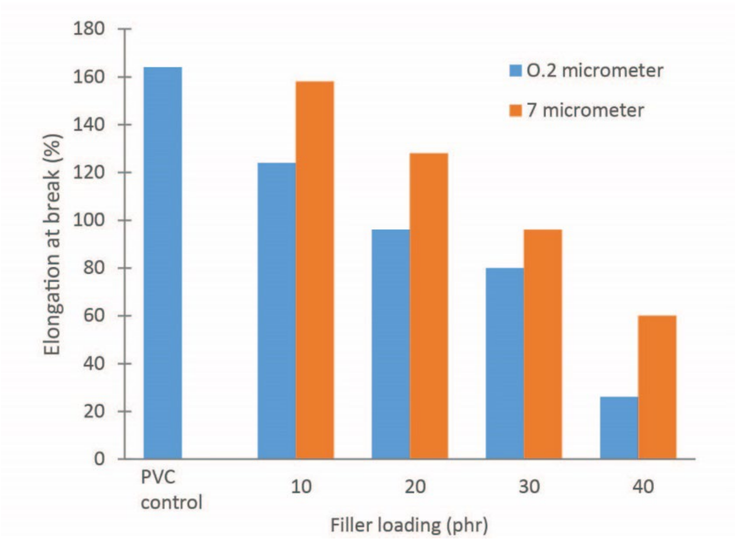

Fig. 6. Plot of the percentage elongation at break versus eggshell filler loading for PVC/eggshell composites for two different eggshell particles sizes of 0.2 and 7 μm. Figure adapted from Murugan et al. [46].

Bio-based polymers are also attractive as matrix in composites with eggshell filler. Xu and Hanna [112] made composite foams with corn starch and eggshell filler with particle sizes of 4-5 μm and 8-10 μm. They showed that the foam cell size, foam unit density, expansion ratio and compressibility decrease and the cell population and spring index increases with higher eggshell filler content (0 to 6%). Biodegradation of thermoplastic starch with eggshell fillers was investigated and it was shown that eggshell filler delays the biodegradation, but the biodegradation of the composite is faster in comparison with thermoplastic starch containing commercial calcium carbonate [113]. The study also presented that the eggshell particles were better dispersed in the matrix than the commercial calcium carbonate particles which showed more agglomeration. It was interpreted that the improved dispersion was caused by the eggshell organic membrane enhancing interaction with the thermoplastic starch. Furthermore, the eggshell/starch composite has a higher thermal stability and lower water adsorption [113]. The study by Jiang et al. [53] showed that the addition of up to 3% eggshell filler in corn starch increased the tensile strength, macroscopic rigidity and thermal stability of the composite films prepared by solution casting. Similar to the study by Bootklad and Kaewtatip [113], they interpreted that the organic compounds in the eggshell powder enhanced the interfacial interaction between the filler and the matrix [53]. Rahman et al. [37] developed a nanocomposite of soy protein with up to 10% eggshell nanoparticles. The particles were well dispersed with the aid of an anionic dispersant sodium polyacrylate (10% of the eggshell nanoparticles). Young's modulus and tensile strength was highest, and fracture strain lowest, for the composite with 5% eggshell nanofillers [37].

Biodegradable polypropene carbonate (PPC) was used with eggshell filler (up to 5% filler loading, with a particle size of <40 μm) in composite film via the solution-casting method by Feng et al. [4]. The tensile strength and modulus increased (up to 81% and 67% respectively) and the elongation at break decreased (by up to 36%) for PPC composite with increasing eggshell particle loading up to 4%. The thermal stability was higher by incorporation of eggshell filler in PPC composite. They suggested that compatibility between the eggshell particles and PPC was enhanced by dipole-dipole interaction and weak hydrogen bonding [4]. Hassan et al. [31] used a mechanochemical and ultrasonic irradiation technique to produce nanoscale eggshell particles and used those as filler to make a nanocomposite with thermoplastic polymer Bioplast GS2189 by solution mixing. The nanocomposite with 2% eggshell filler loading showed an increase of 35.3% and 30.5% in flexural strength and modulus, respectively, in comparison to the neat Bioplast. Similarly, the nanocomposite showed an increase of 33.3% in the strain at break [31]. Bacterial cellulose was also used as matrix in composites with eggshell filler [43]. The composites showed a decrease in Young's modulus and tensile strength with increasing eggshell filler loading (up to 5%). In contrast, the water adsorption capacity and vegetable oil adsorption capacity of the composite increased with eggshell filler loading [43]. Prabhakar et al. [114] prepared composite film from wheat protein matrix with eggshell filler particles. Both tensile strength and elongation at break increased with an increase in eggshell filler loading (up to 40%). The good dispersion and matrix-filler adhesion was attributed to the presence of organic compounds on the surface of the eggshell powder. The eggshell powder also improved the thermal stability [114]. Epichlorohydrin cross-linked chitosan/eggshell composites were prepared and studied by Rahmi et al. [49]. Up to 13.4% eggshell filler was used, and it was shown that the tensile strength increased by up to 60% with eggshell filler loading [49]. Wu et al. [76] investigated the effect of eggshell filler (up to 50%) in polyvinyl alcohol (PVA) prepared by solution blending and casting to films. The eggshell particles (<25 μm) were well dispersed, and a good adhesion with the matrix was attributed to the organic compounds on the eggshell surface. The results have shown an increase in Young's modulus of the composite with increasing eggshell filler (up to 50%). The composite tensile strength and elongation at break increased with increase in filler content up to 30% [76].

Polylactid acid (PLA) is one of the most studied bio-based biodegradable thermoplastic polymers, and was also used as a matrix in composites with eggshell filler. Ashok et al. [115] reported that the tensile strength and modulus of PLA/eggshell composite films increased with filler loading up to 4%, whereas the elongation at break decreased. The incorporation of eggshell filler increased the thermal stability and crystallinity of the composite [115]. Betancourt and Cree [44] investigated different loading and particle sizes of eggshell filler in PLA/eggshell composite and compared the results with PLA/limestone composite. The results showed that the incorporation of limestone particles or eggshell particles (up to 20%) in PLA composite both led to a decrease in tensile strength and an increase in tensile modulus for a filler loading of more than 5%. The tensile strength and modulus results were very similar for the two particle size distributions tested (<32 μm and 32-63 μm). In contrast, the impact strength was lower for PLA/eggshell composite than for PLA/limestone composite. The decrease in impact strength was most pronounced for the larger particle size [44]. Incorporation of eggshell filler (up to 20%) modified with phenylphosphonic acid in poly L-lactic acid (PLLA) matrix resulted in an increase of the tensile modulus of the composite [41]. Neat PLLA has smooth surfaces, whereas PLLA with eggshell filler has much rougher surfaces (Fig. 7; [41]). Li et al. [116] tested the properties of hot stretched (up to stretch ratio of 6) PLLA/eggshell filler (up to 30%) composite. The tensile strength of PLLA with 10% eggshell filler hot stretched to a stretch ratio of 6 was more than double that of neat PLLA, and the Young's modulus was more than triple that of neat PLLA [116].

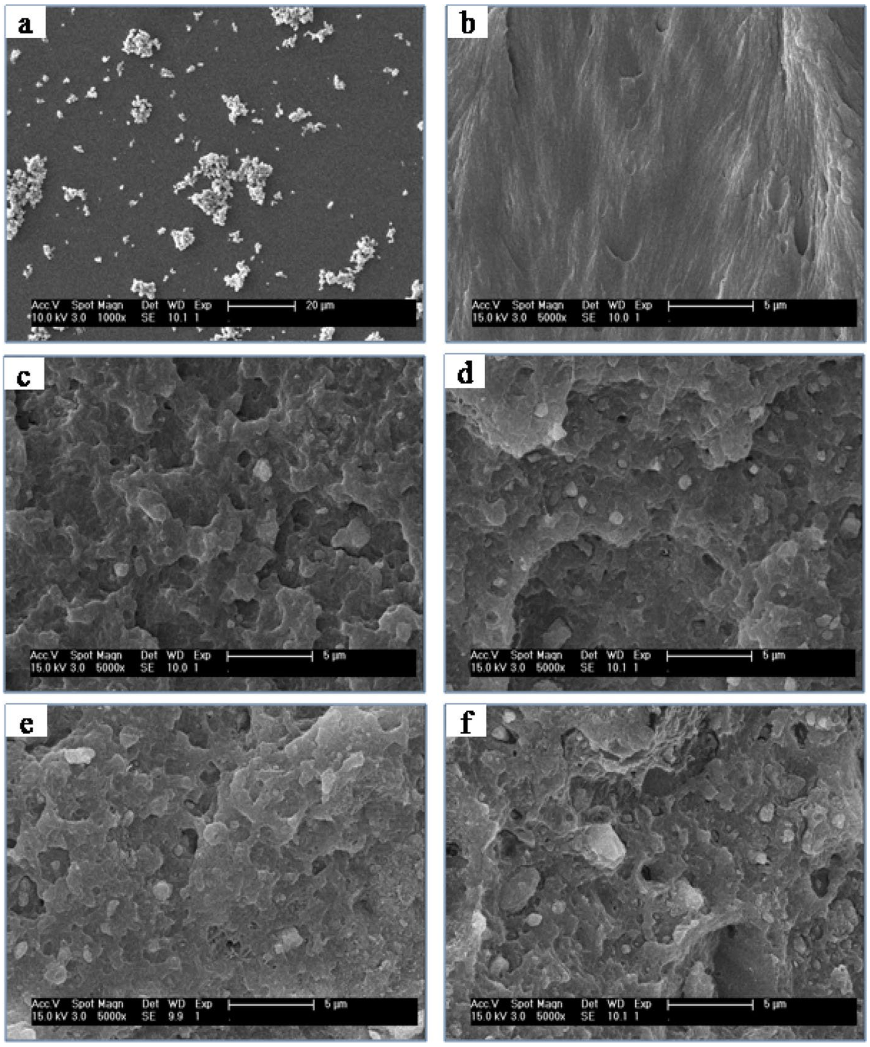

Fig. 7. Scanning electron microscope pictures of (A) eggshell (ES) particles, (b) neat PLLA, (c) PLLA with 5% ES, (d) PLLA with 10% ES, (e) PLLA with 15% ES, (f) PLLA with 20% ES. Figure from Li et al. [41], reprinted with permission from Elsevier.

Given the brittle nature of PLA, blends were prepared with compounds that can increase toughness and elongation at break of PLA composites. Somdee and Hasook [96] prepared PLA composite with 90% PLA, 3 to 10% natural rubber (NR) and 1 to 7% modified eggshell filler (modified by heating to 800 °C). The tensile strength and the elongation at break of PLA/NR/eggshell composites decreased with increasing eggshell filler loading, and were lower than those of neat PLA. The Young's modulus of the PLA/NR/eggshell composites increased with increasing eggshell filler loading, but only the one with 7% eggshell filler content had a higher Young's modulus than that of neat PLA. The impact strength decreases with higher eggshell filler content in the composites [96]. Tiimob et al. [117] studied the effect of eggshell/silver nanomaterial loading (up to 2%) on the mechanical properties of 70/30 poly(butene-*co*-adipate terephthalate) / polylactid acid (PBAT/PLA) immiscible blends. The toughness of the composite was better than that of PLA, but the strength was in between that of PBAT and PLA. The tensile strength decreased by incorporation of the eggshell/silver nanomaterial, probably because of poor interaction between the nanomaterial and the matrix [117]. Kong et al. [54] reported the synthesis of a novel polyester poly(diethylene glycol succinate) (PDEGS) for use as a plasticizer in PLA composites with functionalized eggshell powder. The addition of PDEGS resulted in a massive increase of the elongation at break from 6% to more than 200%. Moreover, it helped inhibiting aggregation of functionalized eggshell particles. The eggshell powder with a surface layer of phenylphosphonate acted as a nucleating agent and helped in PLA crystallization. The incorporation of eggshell particles in PLA limited the reduction in modulus caused by plasticization, and it contributed thermal stability [54]. In a similar study, 10% epoxidized soybean oil was used in PLA composites with different amounts of functionalized eggshell powder [118]. The elongation at break of this composite was 160%, and the tensile modulus was similar to that of neat PLA [118].

Table 3

Overview of preparation method parameters for the production of eggshell $CaCO_3$ particles for composites.

Matrix	Particle size (μm)	Filler loading (%)	Filler treatment	Tensile strength (MPa)	Young's modulus (MPa)	Strain (%)	Reference
PP	90.0	0	-	31	1077	260	[109]
PP	90.0	10	none	32	990	39	
PP	90.0	20	none	31	1016	38	
PP	90.0	30	none	31	1080	12	
PP	90.0	40	none	32	1106	7	
PP	90.0	50	none	31	1220	4	
PP	90.0	60	none	30	1310	3	
PP	50.0	0	-	31	1077	260	
PP	50.0	10	none	29	1037	40	
PP	50.0	20	none	26	1150	37	
PP	50.0	30	none	23	1250	11	
PP	50.0	40	none	29	1667	5	
PP	50.0	50	none	27	1745	3	
PP	50.0	60	none	28	1810	2	
PP	8.4	0	-	31	1077	260	
PP	8.4	10	none	31	1100	37	
PP	8.4	20	none	31	1510	35	
PP	8.4	30	none	31	1740	10	
PP	8.4	40	none	27	2000	6	
PP	8.4	50	none	15	2150	3	
PP	8.4	60	none	13	2220	3	
PP	-	0	-	33.4	-	15.6	[34]
PP	-	1.0	none	33.4	-	7.1	
PP	-	2.9	none	32.7	-	6.7	
PP	-	4.8	none	32.3	-	6.6	
PP	-	1.0	0.98E-4 pimelic acid	30.8	-	7.6	
PP	-	2.9	2.88E-4 pimelic acid	30.1	-	6.7	
PP	-	4.8	4.71E-4 pimelic acid	29.3	-	6.4	
PP	-	4.8	2.37E-4 pimelic acid	29.3	-	6.2	
PP	-	4.8	9.34E-4 pimelic acid	29.6	-	6.5	
PP	-	4.8	79.36E-4 pimelic acid	32.7	-	5.8	
PP	-	0	-	33	1030	700	[110]
PP	-	5	none	33	1230	60	
PP	<1	10	none	32	1320	30	
PP	<1	20	none	31	1420	20	
PP	<1	30	none	29	1600	10	
PP	-	40	none	28	1900	7	
corn starch	-	0	-	2.37	-	70.25	[53]
corn starch	-	1	none	3.97	-	97.38	
corn starch	-	1.5	none	4.13	-	103.63	
corn starch	-	2	none	4.69	-	108.38	
corn starch	-	2.5	none	4.17	-	106.42	
corn starch	-	3	none	3.81	-	98.13	

PPC	-	0	-	12.8	823	821	[4]
PPC	<40	1	none	13.1	974	705	
PPC	<40	2	none	14.2	1008	619	
PPC	<40	3	none	17.6	1206	586	
PPC	<40	4	none	23.2	1378	525	
PPC	<40	5	none	13.8	983	785	
Bioplast GS2189	-	0	-	-	-	6.3	[31]
Bioplast GS2189	<0.010	1	none	-	-	4.8	
Bioplast GS2189	<0.010	2	none	-	-	8.4	
Bioplast GS2189	<0.010	3	none	-	-	6.8	
bacterial cellulose	-	0	-	13.2	4.16	3.17	[43]
bacterial cellulose	-	0.5	none	7.05	3.89	1.81	
bacterial cellulose	-	1	none	2.53	0.4	6.29	
bacterial cellulose	-	2	none	1.47	0.42	3.5	
bacterial cellulose	-	5	none	0.78	0.12	6.37	
wheat protein	-	0	-	3.908	-	81.004	[114]
wheat protein	-	5	none	3.981	-	92.284	
wheat protein	-	10	none	4.079	-	102.568	
wheat protein	-	20	none	4.131	-	111.346	
wheat protein	-	30	none	5.223	-	112.341	
wheat protein	-	40	none	8.432	-	116.514	
PLA	-	0	-	16.8	1152	402	[115]
PLA	<25	1	none	17.7	1171	352	
PLA	<25	2	none	21.1	1433	213	
PLA	<25	3	none	25.5	1767	173	
PLA	<25	4	none	30.6	1964	143	
PLA	<25	5	none	22.5	1389	286	
PLA	-	0	-	61.1	1240	6	[54]
PLA	2	10	phenylphosphonate	49.4	1470	5	
PLA	2	20	phenylphosphonate	46.9	1740	3.8	
PLA	2	30	phenylphosphonate	44.3	2150	2.9	
PLA/PDEGS	2	0	-	24.9	550	491.7	
PLA/PDEGS	2	10	phenylphosphonate	20.2	590	334.4	
PLA/PDEGS	2	20	phenylphosphonate	18.4	630	320	
PLA/PDEGS	2	30	phenylphosphonate	16.7	810	218.8	
PLA	-	0	-	61.1	1240	6	[118]
PLA/soy bean oil	-	0	-	31.5	1190	159.2	
PLA/soy bean oil	-	10	phenylphosphonate	25.6	1520	122.7	
PLA/soy bean oil	-	20	phenylphosphonate	22.7	1750	116.8	
PLA/soy bean oil	-	30	phenylphosphonate	18.6	1790	70.4	
PLLA	-	0	-	58.5	1880	4.5	[41]
PLLA	2	5	phenylphosphonate	56.7	2020	4.6	
PLLA	2	10	phenylphosphonate	55.6	2200	3.5	
PLLA	2	15	phenylphosphonate	53.9	2320	3.2	
PLLA	2	20	phenylphosphonate	53.4	2460	2.5	
PLLA	-	0	-	56.8	1312	5.8	[116]
PLLA	-	10	none	53.7	1905	4.2	
PLLA	-	20	none	49.7	1987	3.4	
PLLA	-	30	none	45.6	2033	2.5	

PVA		0	-	33.52	1138	128.9	[76]
PVA	<25	10	none	34.51	1731	136.2	
PVA	<25	20	none	35.63	2474	145.4	
PVA	<25	30	none	38.78	2633	165.9	
PVA	<25	40	none	31.36	2804	118.7	
PVA	<25	50	none	29.71	3341	66.4	

Polymer matrix: polypropene (PP), Polypropene carbonate (PPC), Polylactic acid (PLA), poly(diethylene glycol succinate) (PDEGS), polyvinyl alcohol (PVA)

4.2. Thermoset polymer composites

Eggshell particles have also been investigated as filler in thermoset polymers, such as epoxy resin, to improve toughness [32]. This study showed that the eggshell particles (1 μm) have a larger surface area than conventional $CaCO_3$ particles of similar grain size distribution. The impact strength of epoxy resin was improved by 72% due to incorporation of 5% eggshell filler in the absence of silane coupling agent and without NaOH treatment of the eggshell particles [32]. Tiimob et al. [42] studied the effect of incorporation of eggshell nanoparticles (up to 10%) in bio-based epoxy resin. The flexural strength, modulus and toughness of the epoxy/eggshell composite increased with increasing eggshell filler loading up to 4% [42]. Also Azman et al. [68] used chicken eggshell particles (<500 μm) as a biofiller (up to 20%) in epoxy composites. The results showed that tensile strength decreased, and tensile modulus and thermal stability increased with eggshell filler loading, with an optimal loading of 15%. The epoxy composite with eggshell filler showed better mechanical, thermal stability and morphological properties than the composite with conventional $CaCO_3$ particles. The study also found that the dispersion of eggshell particles in the epoxy matrix was not homogeneous and that the interaction between the particles and the matrix was poor [68]. The addition of eggshell particles in epoxy composite decreased water uptake of the composite, but increased impact strength and tensile strength and modulus [69].

Several other studies on eggshell filler in epoxy resin reported properties other than the mechanical ones. Eggshell filler was investigated as a potential cure modifier because eggshell contains peptide functional groups and proteins [50, 58]. Also Souza et al. [65] tested eggshell filler in epoxy resin as a potential cure improver. The study showed that the eggshell membrane increased the curing rate. Also Jacques et al. [70] presented eggshell membrane as a suitable catalyzer for the crosslinking reaction of epoxy resin because of its amines, hydroxyl and sulphur. However, it was shown that eggshell membrane was not as efficient as the synthetic catalyzer DEH 35 [119]. Hamdi and Habubi [120] investigated epoxy/eggshell composite as potential thermal insulation. Similarly, Abdelmalik et al. [59] reported that the incorporation of eggshell powder in epoxy composite increased the thermal conductivity and the dielectric constant, and decreased the conductance, making the epoxy/eggshell composite a better electric insulation material. Panchal et al. [57] compared moisture absorption in epoxy composites with boiled and unboiled eggshell filler (up to 12%). The study showed that the highest water absorption occurred in the composite with 12% boiled eggshell filler [57]. The erosion wear behaviour of epoxy composites with boiled and unboiled eggshell filler was also studied [121]. The epoxy composite with 4% unboiled eggshell filler had the highest wear resistance in dry conditions [121]. The effect of eggshell filler in epoxy-based intumescent fire-retardant coatings with ammonium polyphosphate, pentaerythritol and melamine on thermal stability, flame retarding and smoke suppression properties was studied by Xu et al. [66]. The composite with 3% eggshell filler showed the best results with enhanced thermal stability and char-forming ability, and reduction in mass loss, heat release and smoke production.

Bhoopathi and Ramesh [122] investigated the addition of eggshell nanoparticles (up to 21%) in hemp fibre reinforced epoxy composites. The flexural strength and impact strength of the composite increased with increasing eggshell particle loading, but the tensile strength and the shear strength were lower for the composites with eggshell filler. Water absorption was lower in composites with a higher eggshell filler loading [122]. Eggshell filler (up to 40%) was also used in glass fibre reinforced epoxy composite laminates [75]. The study showed that tensile and compressive strength of the composite increased by 18% and 30%, respectively, with addition of 10% eggshell particles of 100 μm [75]. Besides epoxy composites, eggshell filler (50 to 65%) was also studied in polyester resin composites [61]. The flexural strength of the composite increases with increasing eggshell filler loading from 50 to 60% for each of the three different particle size distributions tested. Water absorption increases also with eggshell filler loading from 50 to 60% for the largest size distributions, 60 mesh and 100 mesh, but the trend is the opposite for the 150 mesh [61].

4.3. Elastomer polymer composites

Eggshell particles have also been used as filler in rubber materials. Intharapat et al. [80] studied the effect of incorporation of eggshell particles in natural rubber ENR-25 on the mechanical properties of the composite. The results were compared with natural rubber composite with treated eggshell carbonate heated to 600 °C and with commercial $CaCO_3$. The study showed that natural rubber/eggshell composite had the shortest cure time, which was interpreted by the enhancing effect of eggshell membrane protein on the vulcanization process. This composite also had the best tensile strength, tear strength, hardness and swelling resistance properties (Fig. 8; [80]). It was interpreted that the improved properties were a consequence of better dispersion and interfacial adhesion between eggshell particles and the rubber matrix because of the organic components in eggshell particles [80]. Natural rubber was also used as a matrix with eggshell filler and chlorinated polyethene as a flame retardant and curing agent to make thermal insulation composite rubber foams [38]. The composite foams had similar properties as those made with commercial $CaCO_3$ particles. Also Moonlek and Saenboonruang [63] found that natural rubber latex composites with 4% eggshell filler had similar tensile properties as those with 4% commercial $CaCO_3$ filler. Moreover, they showed that incorporation of more eggshell filler (tested up to 6%) in the composite increased the swelling resistance [63]. Ren and Cornish [123] replaced bifunctionally silanized silica partially or completely by eggshell filler in guayule natural rubber composites, and this improved the dynamic mechanical properties and ozone resistance of the composite. In a study by Roy et al. [124], eggshell nanoparticles were used as filler in natural rubber composites with and without compatibilizer maleated natural rubber. The results showed that the composite with compatibilizer had improved torque difference, tensile and thermal properties. The addition of compatibilizer improved the uniform dispersion of eggshell nanoparticles and the interaction between the eggshell filler and the matrix [124]. Bhagavatheswaran et al. [125] functionalized eggshell particles with terpolymer polyvinyl 2-pyrrolidone-*co*-maleic acid-*co*-acrylic acid for incorporation as filler in acrylonitrile butadiene rubber composite. The surface modification had no or only a limited effect on the tensile modulus and elongation at break of the composite at low filler loading of up to 15%.

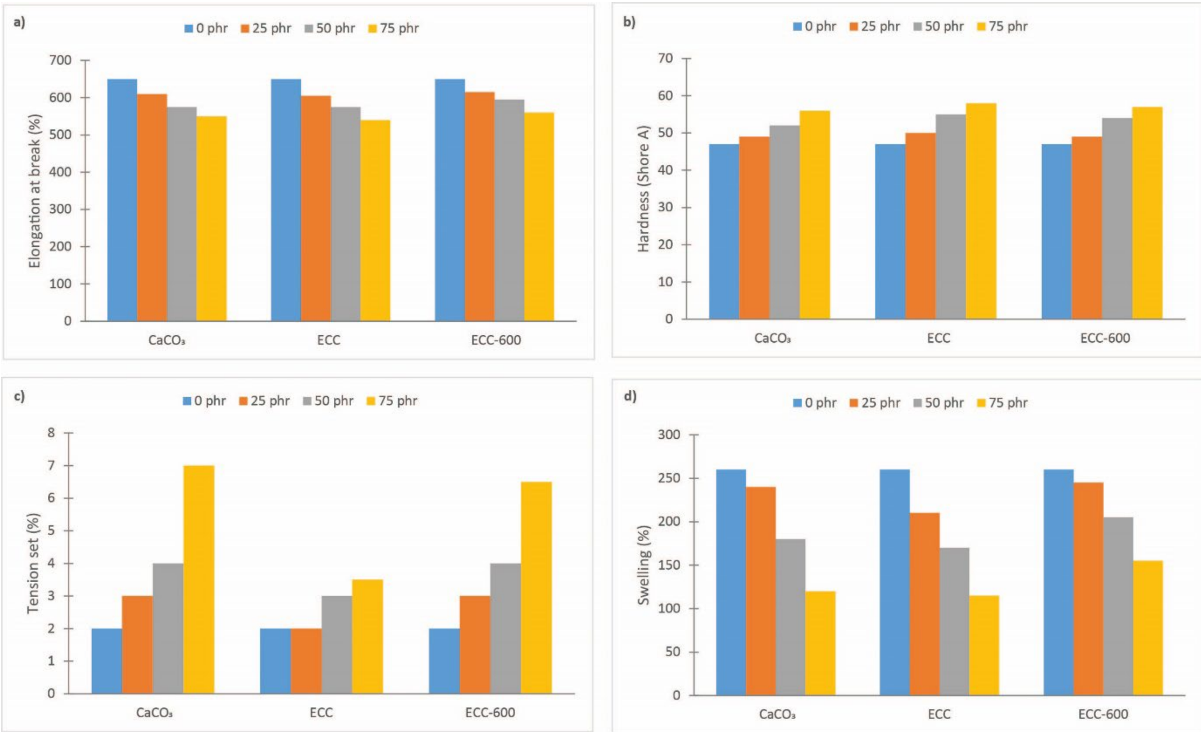

Fig. 8. Comparison of properties of natural rubber ENR-25 composites with commercial $CaCO_3$ filler ($CaCO_3$), eggshell carbonate filler (ECC) and eggshell treated at 600 °C (ECC-600) for different filler loadings, elongation at break (a), hardness (b), tension set (c) and swelling resistance (d). Figure adapted from Intharapat et al. [80].

4.4. Metal matrix composites

The incorporation of (carbonized) eggshell powder as reinforcement filler in metal matrix composites was studied. Uncarbonized eggshell, carbonized eggshell and commercial $CaCO_3$ particles were used in AA2014 matrix alloy composites [126]. The hardness, tensile strength, and fatigue strength of the composite increased with increasing carbonized or uncarbonized eggshell filler loading up to 12.5%. However, the toughness and ductility decreased with increasing carbonized and uncarbonized eggshell filler loading up to 15%. The composite with 12.5% carbonized eggshell filler had the best mechanical properties, good interfacial interaction and minimum corrosion [126]. This AA2014 metal composite with 12.5% carbonized eggshell filler had very similar mechanical properties as AA2014 metal composite with 10% SiC, and a much cheaper cost than the latter [127]. The corrosion rate decreased by addition of SiC particles up to 7.5% and with eggshell particles up to 12.5%, and increased after heat treatment for all reinforced metal matrix composites [127]. Precipitation hardening parameters were optimized for the AA2014 aluminium alloy composite with 5% carbonized eggshell filler [128]. An investigation of AA2014 metal matrix composites containing different proportions of both SiC and carbonized eggshell particles showed that the tensile strength and fatigue strength for the composites with 2.5% SiC and 7.5% carbonized eggshell particles were higher than for composites with other proportions of mixed filler. The toughness of the composites decreases with increasing SiC/carbonized eggshell weight ratio. The lowest corrosion rate was measured for the composite with 2.5% SiC and 12.5% carbonized eggshell filler [129]. Tribological tests have shown that minimum wear rate was achieved for AA2014 composite with 6.5% carbonized eggshell and 11% SiC [79].

Other research on eggshell filler in metal composites also focused mainly on aluminium matrix with one or more reinforcement filler materials. Bose et al. [91] reported that the incorporation of waste carbonized eggshells, cow dung ash, snail shell ash and B_4C in aluminium alloy composite with SiC led to increased hardness, tensile strength and fatigue strength, and decreased ductility, fracture toughness and corrosion rate. They also showed that carbonized eggshell particles as reinforcement in Al matrix resulted in composites with better tribomechanical properties than uncarbonized eggshell and SiC +

snail shell ash reinforcements. Composite of Al6061 alloy with eggshell particles were made by Dwiwedi et al. [92]. The results showed that the composite with 4% eggshell filler loading had the best properties, and that higher loading resulted in a higher porosity and particle agglomeration causing poor mechanical properties [92]. Similarly, Hayajneh et al. [101] found that 3% eggshell particle loading in Al composite improved the hardness, compressive strength and wear resistance of the composite, whereas higher loading of 6 and 9% led to poorer composite properties. Hybrid composites with aluminium matrix were prepared with graphite and eggshell reinforcement particles [78]. Incorporation of 1.5% graphite and 3% eggshell particles led to an increase in compressive strength and hardness of the composites, but higher loadings lead to a decrease in these properties. Another study also prepared graphite-aluminium composites with different fillers of Si, SiC and eggshell particles in order to improve microhardness and thermal expansion [130]. The paper shows that the graphite-Al composite with 20% Si and 20% eggshell particles has enhanced microhardness and lowered thermal expansion. Besides aluminium composites, also zinc-eggshell powder composites were prepared [88]. In this case, the composite was produced as coating on mild steel. The study reported that the addition of eggshell particles enhanced the surface finish and coating thickness of the zinc deposition, and that it improved corrosion resistance and thermal stability of the zinc coating of mild steel [88].

4.5. Hydroxyapatite composites, geopolymers and other ceramic composites

Eggshell has been used in several studies as a source of calcium for the synthesis of hydroxyapatite. Kumar et al. [131] developed a protein delivery agent by eggshell derived calcium deficient hydroxyapatite nanoparticles with alginate coating. Thereby, nanoparticles with Ca/P molar ratios of 1.67, 1.61 and 1.51 covering the range from stable hydroxyapatite to degradable tricalcium phosphate phases were produced by microwave-accelerated wet chemical synthesis. Another study synthesized hydroxyapatite from chicken eggshells by wet chemical synthesis and modified this with silicon and polylactic-*co*-glycolic acid by the freezing/lyophilization method [100]. The study showed that the synthesized composite was bioactive and biocompatible with osteoblastic cells. A hydrothermal method was used to synthesize hydroxyapatite from chicken eggshell for the development of a high density polyethene (HDPE) composite with hydroxyapatite particles (up to 40%) [84]. The composites showed enhanced mechanical properties except for impact energy. The composite with 40% hydroxyapatite had the highest flexural strength and modulus, yield strength and Young's modulus and wear resistance properties, whereas the composite with 20% hydroxyapatite had the highest fracture toughness value. A composite of polylactic acid/polybutene adipate-co-terephthalate (PLA/PBAT) with hydroxyapatite made from eggshells was also produced for biomedical applications [104]. The composite showed an increase in tensile properties with up to 15% hydroxyapatite, which were well dispersed in the matrix. Polycaprolactone composites were made with up to 30% hydroxyapatite particles made from eggshell [85]. The particles increased the thermal stabilities of the composite up to 300 °C. The composite also had better swelling behaviour and lower degradation percentages. In another study, hydroxyapatite particles were incorporated in a chitosan-based composite, which also led to a higher thermal stability [86]. The roughness increased with the addition of hydroxyapatite particles, and the swelling decreased.

Rahman et al. [132] synthesized nanoscale calcium deficient hydroxyapatite (with Ca/P ratio of about 1.53) from chicken eggshells and combined this in a composite with protein-based polymer extracted from defatted soybean residues. In these nanocomposites, uniform dispersion was achieved by surface modification of the hydroxyapatite particles with sodium polyacrylate in the soy protein isolate, enabling significantly enhanced tensile modulus and strength. Glycerol was added as a natural plasticizer. Hartatiek et al. [97] made β-tricalcium phosphate (β-TCP) from eggshells and used this in a composite with zirconia (ZrO_2) via a solid-state reaction method. Vickers hardness test results showed that the β-TCP/ ZrO_2 composite with 60% ZrO_2 had the highest hardness, and the one with 70% ZrO_2 had the highest electrical conductivity and lowest porosity. Jirimali et al. [82] used eggshells to make calcium oxide and hydroxyapatite, which they then incorporated as filler in a linear low density polyethene (LLDPE) by melt compounding (Fig. 9; [82]). The produced composites showed enhanced hardness, impact strength and tensile strength. The filler also improved the flame retardant ability and thermal stability of the composites. Chaudhari et al. [83] made also hydroxyapatite from waste eggshells. Then, they functionalized carbon nanotubes and graphene nanosheets with this hydroxyapatite to use those as fillers (up to 5%) in LLDPE composites. The fillers improved the mechanical properties (tensile strength and impact strength) of the composites in comparison with neat LLDPE, and decreased flammability. The carbon nanotubes/hydroxyapatite/LLDPE composites had higher hardness but lower tensile strength than the graphene oxide/hydroxyapatite/LLDPE composites.

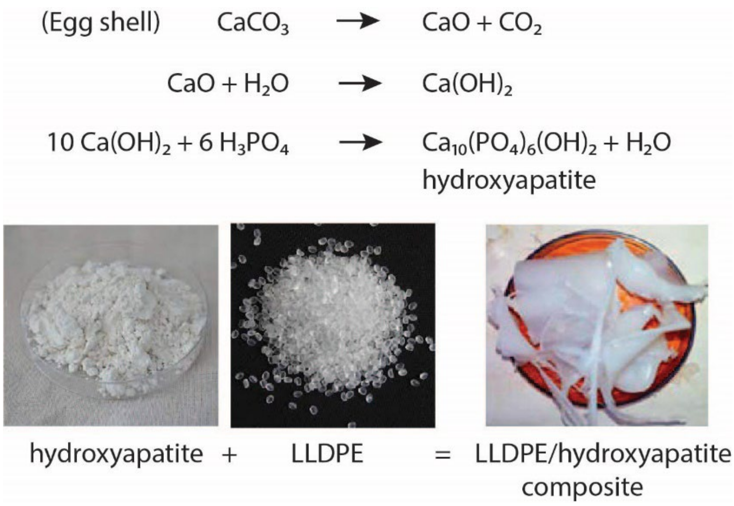

Fig. 9. Overview of the main chemical reactions and some pictures of the materials in the production of LLDPE/hydroxyapatite composite. Figure modified from Jirimali et al. [82].

Eggshell powder was combined with TiO_2 in a composite intended as a potential ingredient in toothpaste formulation, and its buffering effect and acid-resistant properties were evaluated [62]. The results from tests with citric acid show that modification of eggshell particles with TiO_2 do not change their carbonate buffering properties. Tests with dentine discus showed that nanoeggshell-TiO_2 composite effectively occluded dentine tubules [133]. Eggshell was also used in a few studies on geopolymers. A 50/50 ratio of eggshell powder to fly ash was used as raw material with activator solution of sodium silicate and sodium hydroxide to produce geopolymers with optimum unconfined compressive strength and split tensile strength [134]. A Na_2SiO_3/NaOH ratio of 2 led to geopolymers with optimal mechanical properties [74]. Raw material of calcined chicken eggshell, nano-silica and rice husk ash was also used in the production of geopolymer with metakaolin [107].

5. Application of food waste eggshells in composite material adsorbents, catalysts, additives and functional materials

5.1. Adsorbents

Eggshell waste has been used for the production of new composite adsorbents. Lunge et al. [35] synthesized an alumina supported carbon composite, which was evaluated for selective fluoride removal from synthetic water, groundwater and wastewater. The removal capacity is significantly influenced by the composite synthesis parameters. Composites were made with pyrolyzed eggshell powder and palm leaf biomass to generate efficient sorbents for the removal of nitrate from aqueous solutions [52]. Eggshells were pyrolyzed along with rice straw agricultural waste for the generation of CaO-biochar composites, that were applied for the removal of phosphate from aqueous solution in a pH range of 5 to 11. The composite with an eggshell / rice straw ratio of 1:1 showed a maximum phosphate adsorption capacity of 231 mg/g [87]. Epichlorohydrin crosslinked chitosan/eggshell composites were developed for cadmium adsorption, and had an adsorption capacity of 11.8 mg/g [135]. Anthill-eggshell composite was developed by thermal treatment for the removal of hexavalent chromium from aqueous solution. An adsorption capacity of 82.2% was achieved under optimum adsorption conditions [89].

Eggshell particles were utilized to stabilize Pickering emulsion structures for the synthesis of erythromycin-based molecularly imprinted polymers, which have excellent adsorption capacities [39]. Sodium methacrylate solution polymerisation was carried out for the synthesis of hydrogel with incorporation of eggshell particles of different sizes. The results showed that the hydrogel with 60 wt% eggshell particles is a good adsorbent for crystal violet, whereas the fillers cause a slight decrease in the adsorption capacity for methylene blue [40]. A superabsorbent nanocomposite was made with guar gum and eggshell powder using free radical graft copolymerization, and this composite has a 1000% water absorption [136]. Incorporation of some eggshell waste powder in poly(acrylamide-co-potassium acrylate) can improve the absorption of water in the hydrogel, as well as its mechanical properties [48]. Also another composite adsorbent was developed for the removal of methylene blue, and was made from anthill and eggshell mixture [90]. Eggshell household waste was also used in the synthesis of membranes as adsorbents for the removal of RBV-5R from aqueous solutions [73]. Eggshell has also been used in adsorbents for CO_2 capture. Hosseini et al. [95] prepared and functionalized biodegradable calcined eggshell/sodium alginate beads with ammonia and obtained a CO_2 adsorption capacity of 0.2380 mmol/g with 45% CO_2 concentration at a pressure of 1 bar and a temperature of 30 °C (Fig. 10; [95]).

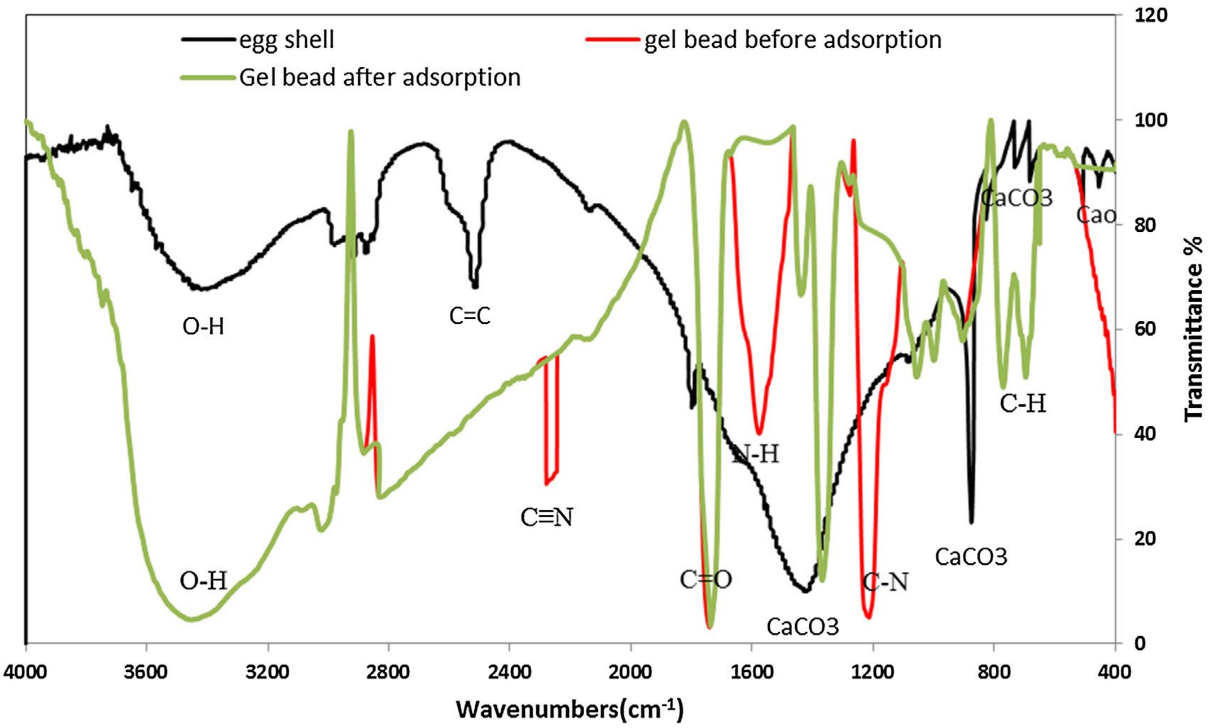

Fig. 10. FTIR spectra of the eggshell material and the prepared gel beads both before and after CO_2 adsorption. Figure from Hosseini et al. [95], reprinted with permission from Elsevier.

5.2. Catalysts

Photocatalytic activity was achieved in sol-gel composites with eggshell powder and TiO_2, with tests performed through the degradation of Acid Red B under solar light irradiation, showing enhanced photocatalytic activity with increased TiO_2 loading [137]. Eggshell derived CaO surfaces were loaded with Pd nanoparticles to form a new nanocomposite used for photocatalytic wastewater treatment; this was tested for crystal violet photocatalytic degradation [105]. In a different application, a reusable heterogeneous catalyst for the Hantzsch condensation reaction was produced using eggshell waste material as source of $CaCO_3$ to modify magnetic Fe_3O_4 particles [60]. Calcined eggshell powders with 4% Au nanoparticle loading were used as a nanocomposite material for catalytic reduction of 4-nitrophenol, removing this pollutant from water [106] (Fig. 11; [106]).

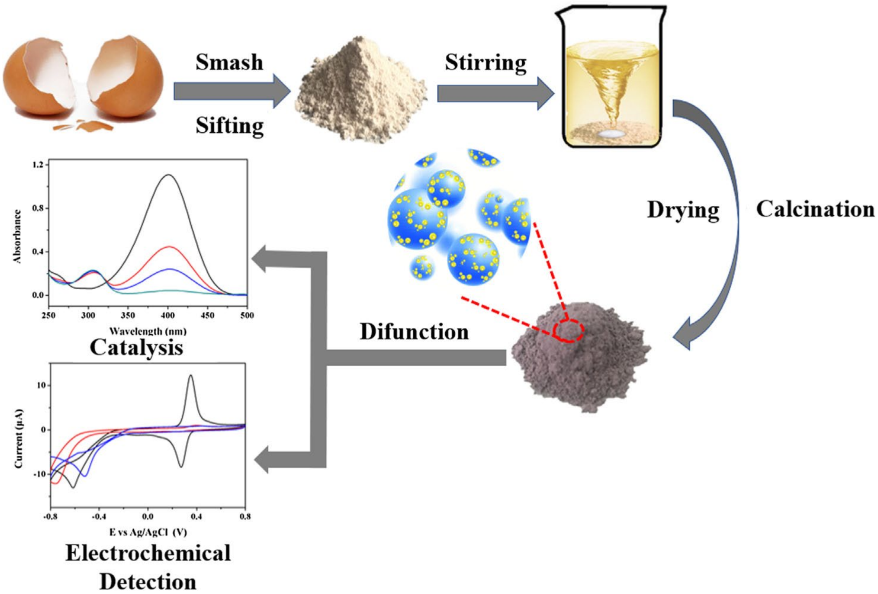

Fig. 11. Sketch of the synthesis procedure for nanocomposites of Au and calcined carbonate from eggshell waste and $HAuCl_4$ precursor, for electrochemical detection and catalytic reduction. Figure from Ding et al. [106], reprinted with permission from Elsevier.

Composites were also made with K_2CO_3 and eggshell derived CaO as catalysts for gasification of sub-bituminous coal at atmospheric pressure, and showed that the addition of eggshell derived CaO increased yields of hydrogen by 123% [81]. In another application, eggshell was used in a magnetically recyclable catalyst for the conversion of waste oil to biodiesel [98]. Similarly, a composite anthill-eggshell catalyst was synthesized and used to convert low-grade oil into biodiesel via a single-step transesterification process [99]. For this purpose as catalyst, anthill-eggshell-Ni-Co mixed oxides composites were prepared using a co-precipitation method, and the results showed a maximum biodiesel yield of 90% at a reaction temperature of 70 °C for a catalyst loading of 3 wt% [67]. Catalytic and fuel additive applications of calcined eggshell powder were investigated, showing that $Ca(OH)_2$ particles, obtained after calcination at 900 °C for five hours, showed better properties in comparison with $CaCO_3$ particles [102].

5.3. Additives and functional materials

Eggshell waste has been used as an alternative to conventional foaming agents in the production of glass foams, for example foaming of recycled cathode ray tube glasses [138]. The incorporation of eggshell derived calcium hydroxide nano- and microparticles have a flame retardant effect on ethylene vinyl acetate composites, and thus increased the polymer degradation temperature [103]. Eggshell particles can also be used in asphalt, and improve its physical and thermal properties and water absorption ability [71]. Concerning the use of eggshell waste for functional materials, antibacterial fillers have been synthesized by modifying eggshell powder with copper to form nanoparticles for use in polymer nanocomposites [72]. Coatings with superhydrophobic functionality have been made by modification of eggshell microparticles with stearic acid, and then dispersion in polystyrene [64] (Fig. 12; [64]).

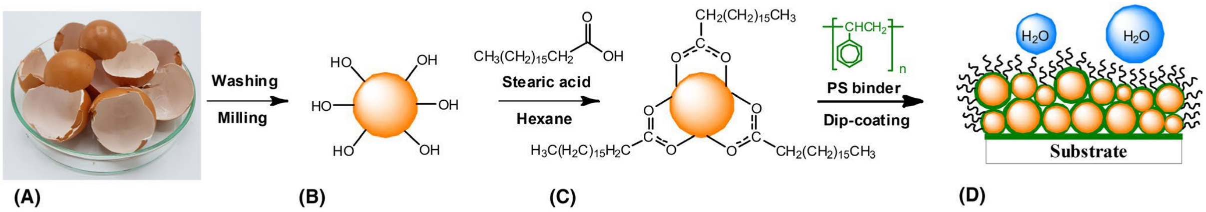

Fig. 12. FTIR spectra of the eggshell material and the prepared gel beads both before and after CO_2 adsorption. Figure from Seeharaj et al. [64], reprinted with permission from Blackwell Publishing - John Wiley and Sons.

6. Valorization, commercialization and industrial upscaling

Eggshell waste generally ends up in landfills and causes pollution. This eggshell disposal comes at a cost of about 100,000 dollars annually for egg processing plants in the United States [139]. Turning this waste into products adds value with economic and environmental benefits. Only few studies have been conducted on the commercialization and industrial upscaling aspects of eggshell waste valorization. The waste can be used as an alternative to limestone ($CaCO_3$) or lime (CaO) depending on the extent of heat treatment. Commercial ground limestone and lime cost about 100 dollars per ton. Moreover, the extent of heat treatment also leads to material of different color (Fig. 5), which can play a role in the applications in which the waste material is used [139]. Previous studies have presented the valorization of eggshell ash as a replacement for lime to treat soil [140]. However, a life cycle analysis showed that there is a significant energy cost due to the heat treatment process at 800 °C to produce the lime from eggshells through calcination [8]. Nevertheless, this heat treatment and related energy costs are also part of the conventional processing and production process of lime from limestone. Valorization of eggshell waste has also been demonstrated on laboratory scale for use in the production of fumaric acid, where eggshell $CaCO_3$ served as neutralizing agent [141]. Similarly, eggshell waste has been valorized on laboratory scale as adsorbent for the application in water and wastewater pollutant removal [6]. The economic benefit of turning eggshell waste into added-value products, such as eggshell-based hydroxyapatite, can lead to an economic benefit that is at least five times higher than the cost of conventional disposal of eggshell waste, besides the high environmental benefit [9]. Pilot scale applications with valorization of eggshell waste have been reported in the field of cosmetics, and at industrial scale for co-composting [7]. Given the quick decay of organic material on the eggshells, the most suitable locations for eggshell recovery are close to the processors. An egg processing plant in the UK also started treatment and processing of eggshell waste, both reusing the $CaCO_3$ shell and the eggshell membrane. The cost of processing is covered by the avoided cost of landfill disposal. The company provides the eggshell $CaCO_3$ powder as a low-cost filler for plastics. Conventional limestone $CaCO_3$ powder is about 10 times cheaper than the cost of the polymer (about 2,000 pound per ton), and the cost of eggshell $CaCO_3$ filler will need to match this in order to play a bigger role on the market. Still, eggshell $CaCO_3$ powder is lighter than conventional limestone powder and presents thus an additional advantage. The processing costs can be kept low through optimizing the procedures, such as use, type and extent of heat treatment, chemical treatment, and physical treatment. Besides the cost, the uptake of this eggshell $CaCO_3$ powder by the industry will further depend on the availability, continuous supply and performance, and the processing procedures need to be standardized upon optimization.

7. Analysis and discussion

Based on the synthesis of the literature, the major findings can be analysed and discussed. This is presented here in two parts, first the structural composites including polymer, matrix and ceramic composites, and second, composite material adsorbents and catalysts.

7.1. Structural composite materials

The addition of eggshell filler can lead to improvement of the mechanical properties of the composite material. The filler loading and the filler/matrix interfacial interaction are the most important factors that determine the mechanical properties of the composite. Homogeneous dispersion of the filler particles in the matrix and a good compatibility and adhesion between the matrix and the filler lead to better mechanical properties. Modification of the eggshell filler by e.g. pimelic acid or stearic acid can help improve particle dispersion and particle/matrix bonding. Also a smaller filler particle size generally correlates with better mechanical properties of the composite. In thermoplastic polymer composites, filler loadings of 5 to 10 wt% generally resulted in composites with good flexural strength and impact toughness. The impact strength of composites with eggshell filler is better for modified filler. Tensile strength and strain at break decrease and Young's modulus and flexural modulus increase at higher filler loading. Composites with eggshell filler have a higher Young's modulus than composites with conventional $CaCO_3$ due to a better bonding between eggshell filler and the polymer matrix. Moreover, eggshell particle composites with maleic anhydride compatibilizer or silane coupling agent have higher Young's modulus and flexural modulus and smaller elongation at break than such composites without compatibilizer. Similarly, in thermoset composites a filler loading at up to about 5 wt% results in good tensile and flexural strength, and impact toughness. Eggshell filler has a higher surface area than conventional $CaCO_3$ filler of similar particle size; this can improve the bonding between filler and matrix. The Young's modulus and flexural modulus are good in thermoset polymer composites with 15 wt% eggshell filler loading. High filler loadings of 20 wt% or more can lead to agglomeration of the eggshell particles, which deteriorates the mechanical properties. Some studies have indicated that incorporation of the eggshell membrane in the filler could enhance the filler/matrix bonding due to the presence of functional groups in the membrane. Moreover, eggshell membrane can accelerate the curing rate in epoxy resin due to amide and hydroxyl functional groups, but it is not as efficient as synthetic catalyzer. The eggshell membrane has also a catalysing effect on the curing rate of rubber composite (thus the vulcanization process). Uniform dispersion of eggshell filler (slightly enhanced by surface modification) and good interfacial adhesion between eggshell filler and elastomer matrix result in improved tensile strength, tear strength, hardness and swelling resistance properties of the eggshell particle elastomer composite similar or better than composite with commercial $CaCO_3$ particles.

In metal matrix composites, uncarbonized or carbonized eggshell powder can be used as reinforcement, for example in aluminium alloy composites to improve the mechanical properties, such as tensile strength and hardness, as well as corrosion resistance. However, toughness and ductility decrease with filler loading up to 15%. Optimal filler loading varies between studies, and range between 3-4% and 12.5%. The higher loading only leads to better mechanical properties if particle agglomeration and porosity increase can be avoided. Generally, the eggshell powder is added alongside other reinforcement material in the metal composite.

Eggshell waste is used as a source for Ca to make hydroxyapatite in composite materials. The applications of these hydroxyapatite composites are mainly in the biomedical sector, for example as drug delivery agents. Composites of thermoplast polymers with 15 to 40% eggshell derived hydroxyapatite particles were made with good flexural strength and modulus, yield strength, Young's modulus, wear resistance and fracture toughness, and improved thermal stability and better swelling behaviour. The material properties and the effect of the preparation method are very important for the efficiency of the material in its application. For example, the polymorphism, crystal shape, size and defects can significantly impact the effectiveness of the material, and mechanical treatment can cause conversion of the material, leading to different physicochemical and biological properties of the composite. In geopolymers and concrete, the use of eggshell powder lowers the workability due to the high water absorption of the eggshell material. The setting time is decreased as the material provides higher nucleation sites which accelerate the chemical reactions. An improved compressive strength can be achieved with addition of 10 to 15 wt% eggshell powder.

7.2. Composite material adsorbents and catalysts

Eggshell derived composite adsorbents and catalysts are generally produced with calcined eggshell powder. Calcination of eggshell $CaCO_3$ leads to the formation of CaO, and hence, it causes a change in the composition and the structure of the material. The thermal treatment of the eggshell powder leads to a more homogeneous nature of the texture of the composites and an increase of the surface area. Hence, the calcination conditions (between 600 and 1000 °C) strongly affect the adsorbent or catalyst performance. It is important that the material has a good system of pores and channels with access to the well distributed active catalytic species. Such eggshell derived adsorbents have been successfully applied for the removal of e.g. nitrate, phosphate, cadmium, chromium, crystal violet, methylene blue from aqueous solutions. Composites with calcined eggshell powder were also produced to act as photocatalysts or heterogeneous catalyst for condensation, reduction or gasification reactions, and biodiesel production. Eggshell derived catalyst generally results in similar or higher yields than catalysts produced from other sources.

8. Conclusions

The importance of food waste eggshells as a source raw material for composites has dramatically increased in the last five years. The range of types of composites, polymer, metal and ceramic matrix composites, and applications, adsorbents, catalysts, additives and functional materials, is very broad, and has been discussed in this review. An overview of the different eggshell treatment methods and parameters has been presented, as well as the main properties of composite structural materials. The eggshell material can be used as $CaCO_3$ particles after washing, drying and grinding, or in carbonized or calcined form after heat treatment at high temperature. The review shows that the parameters in different studies are very variable, and hence, it is challenging to compare results and draw consistent trends. However, the studies indicate that the mechanical properties of polymer composites are generally improved for a smaller eggshell particle filler size, and with surface modification of the filler. It has also been interpreted that the eggshell membrane can enhance the adhesion between the eggshell particles and the matrix polymer, and it can accelerate the curing of thermoset resins. Carbonized eggshell powder has been used as a reinforcement in metal composites, and calcined eggshell powder serves the production of hydroxyapatite, and composite catalyst materials and adsorbents.

9. Future perspectives

Further research will be of interest in the following aspects:

Many works focus on the preparation method of the produced material and on testing results. However, little remains known about the fundamental underlying mechanisms. More systematic studies may be needed that document structure-property-function relationships. This will require multidisciplinary team work involving material engineers, chemists, and experts in the various application fields.

An economic assessment and life cycle analysis will be required to evaluate whether food waste eggshells are an economically viable alternative to limestone as a source of $CaCO_3$ particles. The main factors playing a role in this assessment will involve: (i) the more widespread source sites of eggshell waste in comparison to limestone mines, and thus the transport factor between collection and production, (ii) the lower energy requirements for the grinding process of eggshells in comparison to limestone but higher requirements for the washing process, (iii) comparison between several types of uses of eggshell waste, e.g. as Ca source in animal food, soil treatment, or niche composite applications.

Standard procedures will need to be established for the treatment of eggshell material (washing, drying and surface treatment) for specific applications (e.g. as filler in specific polymer materials), and these processes will need to be industrially upscaled. The sustainable supply of this waste material in sufficient quantity will also need to be guaranteed. Processing standard operating procedures will also need to be established to work industrially with the material for the production of specific composite materials with consistent high performance.

Wider applications of composite materials using eggshell waste may be investigated. In particular, added-value products are of interest. More focus may be needed on the aspects that make eggshells different from conventional $CaCO_3$ fillers, such as the more porous structure and the organic components.

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