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Green composites of polypropylene and eggshell: Effective biofiller size reduction and dispersion by single-step processing with solid-state shear pulverization

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ABSTRACT

Eggshell (ES), a waste byproduct from food processing and hatcheries, contains ~95% calcium carbonate (CC), making it a potentially attractive, less expensive substitute for commercial CC. Past work used complex grinding–sieving and/or chemical modification steps to aid in dispersing ES in polymers such as polypropylene (PP). Both steps add to the cost and reduce the green aspect of the composite. Here, green composite materials of PP with 5–40 wt% unmodified ES shards of several centimeters in size are directly processed using continuous, single-step solid-state shear pulverization (SSSP). Electron microscopy and particle size analysis show very good dispersion with some ES particles near the nanoscale in the composite. Well-dispersed ES particles dramatically increase PP crystallization rates with a 5–7% increase in PP crystallinity. The very good dispersion leads to a major increase in Young's modulus (87% increase relative to neat PP for 40 wt% ES) and a modest increase in hardness; composites exhibit reductions in yield strength, elongation at break, and impact properties. Mechanical and crystallization properties are equal to or better than the best literature data for PP/ES composites without chemical modification made by multi-step approaches involving melt processing. In addition, the composites exhibit high thermal degradation temperatures compared to neat PP, indicating the potential for ES to improve processing stability. Composites with 20–40 wt% ES exhibit solid-like rheological response with no crossover of shear storage and loss moduli. Nevertheless, PP/ES composites retain viscosities close to that of neat PP at shear rates experienced in melt processing. Overall, property enhancements resulting from superior dispersion of ES in PP achieved by SSSP reveal ES to be a promising green filler for thermoplastics.

1. Introduction

Polymer composites with inorganic fillers such as glass fibers, silica nanoparticles, graphene, carbon nanotubes and nanofibers have been studied extensively over the past two decades [1–12]. Inorganic mineral fillers like calcium carbonate (CC), silica, and talc have gained interest as low cost fillers for thermoplastics [13–21]. These fillers offer significant enhancement in stiffness, crystallization rate and thermal stability [8,22–27]. There has been growing demand for green and renewable substitutes for inorganic fillers [28–33]. Such fillers offer major advantages such as low density as well as reduced cost and mechanical wear during processing. Widely investigated green fillers include natural fibers, rice husk, and wood flour [29–33].

As reported by CNN in 2012, there is an interest among food processing companies to find uses for chicken eggshells (ESs) [34]. Approximately 250,000 tons of ES are produced world-wide by food processing industries annually [35]. Most ES waste is disposed in landfills or turned into low value protein supplements for animal feed. Eggshells typically contain about ~95% CC with the remainder being organic material [36–38]. This makes waste ES an excellent source of bio-mineral CC; moreover, the abundant supply makes ES an attractive candidate for replacing CC in thermoplastic composites.

Despite its potential as a green alternative to CC, fewer than twenty studies have investigated the possibility of exploiting ES as a composite filler [39–54], about one-half of which focused on polyolefins as the matrix [39–46]. A patent for the preparation of PP/ES composites by melt extrusion was registered by Universidad

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de Chile in 2006 [40]. That patent and subsequent papers by Toro et al. [41,42] describe a detailed grinding procedure using a flat-metal-blade crusher to produce particles which are sieved using an ASTM 100 mesh. The resulting ES powder was dried at 100 °C for 8 h and then ground further in a concentric-metal-ring mill to obtain particles that pass through an ASTM 400 mesh. The resulting ES powder contained particles of variable size, 50 vol% of which was less than 8.4 μm and 90 vol% of which was less than 27.5 μm. This material was melt mixed with PP to obtain composites with 40 wt% ES. The end product resulting after these multiple steps exhibited an 85% increase in Young's modulus, a 12% decrease in yield strength, and a 47% decrease in impact strength.

Ghabeer et al. [42] investigated the effect of chemical modifications on ground ES powder with an average particle size of 90 μm. The ES powder was treated with stearic acid in an attempt to improve its adhesion with PP matrix. Composites containing 40 wt% untreated ES powder exhibited no change within error in Young's modulus or PP crystallinity. Treatment of ES with stearic acid increased the Young's modulus of the composite (relative to neat PP) by 200% due in part to increased crystallinity of the sample. Kumar et al. [45] used isophthalic acid to chemically treat ES and observed 3–18% increases in tensile modulus in PP composites using the modified ES relative to those using unmodified ES or CC. In order to increase the composite impact strength, Lin et al. [44] examined the use of pimelic acid to convert CC in ES into a β-nucleating agent for PP crystallization and observed a 228% increase in impact strength. Supri et al. [43] showed a 130% enhancement in Young's modulus for polyethylene (PE)/ES composites using PE grafted maleic anhydride as compatibilizer while Sutapun et al. [46] observed improvements in composite impact strength when using PE grafted maleic anhydride relative to unmodified PE. In spite of these property enhancements, ES has failed to become a major commercial filler due in part to the complex steps required to achieve good dispersion of ES. Batch grinding–sieving steps add to cost and chemical modifications used in attempts to improve ES dispersion impair the "green" aspect of ES composites (Fig. 1a).

Here, we investigate the potential of using a single-step, continuous, and industrially scalable process called solid-state shear pulverization (SSSP) [11,12,55–69] to produce well-dispersed, green composite materials of PP/ES with significant property enhancements (Fig. 1b). Although the current study employs a lab-scale/pilot-plant apparatus, polyolefins have been processed at throughputs exceeding 150 kg/h using a commercial-scale SSSP apparatus at Northwestern University [66]. The SSSP apparatus is a modified twin-screw extruder in which materials are cooled rather than heated, so that the polymer is processed below its glass transition temperature if amorphous or below its melting temperature if semicrystalline. The use of near-ambient temperature aids in exposing polymers to higher forces and stresses in the solid state than normally encountered in conventional twin-screw melt extrusion. The absorption of mechanical energy during SSSP results in material fracture followed by random fusion of the materials, which is repeated many times during the average residence time of the material in the pulverizer. SSSP eliminates the common limitations of thermodynamics, viscosity, and degradation encountered in melt processing of polymers. Previously, SSSP has been used to produce well-dispersed polymer nanocomposites with fillers such as clay, graphite and carbon nanotubes [11,12,57–59]. In addition, SSSP has been used to produce compatibilized blends systems in which the dispersed-phase size approaches 100 nm [60,61]. The formation of trace levels of block copolymers at the polymer blend interface resulting from recombination of polymer radicals has been cited as the reason for immiscible blend compatibilization observed in SSSP [62–64]. Green composites of PP with starch and rice husk ash have been produced with SSSP [65,66]. Recently, SSSP was used to functionalize PP with maleic anhydride and ester moieties without significant reduction in PP molecular weight, which accompanies industrial melt-state processes employed to achieve such grafting [67,68].

This work explores the potential of using the single-step SSSP process in the novel production of green PP/ES composite materials. As shown in Fig. 1b, the current study utilizes ES shards that are several centimeters in size without any chemical modification.

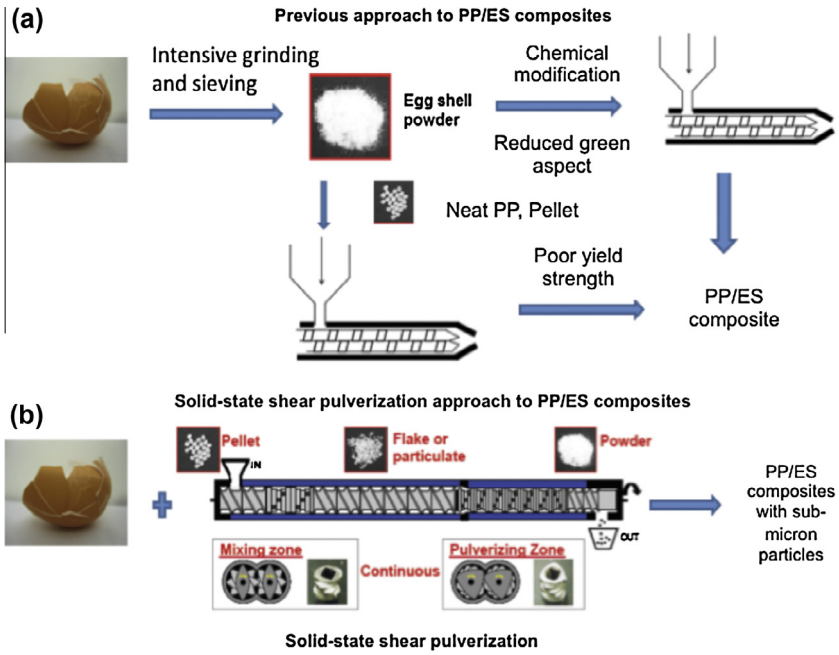

Fig. 1. (a) Previous approach to produce PP/ES composites involves multiple grinding/sieving and chemical modification steps to produce ES particles which are further melt processed with PP to yield the final composite; (b) single-step solid-state SSSP with input of unmodified, several-centimeter ES shards produces sub-micron ES particles in the final PP/ES composite material.