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Green polypropylene/waste paper composites with superior modulus and crystallization behavior: Optimizing specific energy in solid-state shear pulverization for filler size reduction and dispersion

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ABSTRACT

Solid-state shear pulverization (SSSP) is a continuous process that overcomes challenges in producing well-dispersed polymer composites that cannot be made by twin-screw melt extrusion. We use SSSP to produce 85/15 wt% polypropylene/waste paper biocomposites with polypropylene pellets and 2-cm-square waste paper pieces as starting material. Single-pass SSSP achieves effective filler size reduction and dispersion within the polypropylene matrix. We determine how waste paper size reduction and composite properties are functions of specific energy input and tune specific energy input by SSSP screw design and throughput. Composites made at moderate to high specific energy input (14–35 kJ/g) have 25 to nearly 50% of filler particles at sub-micron size; relative to neat polypropylene, composites exhibit a 70% increase in Young's modulus, retention of neat polypropylene yield strength, and a ~50% reduction in crystallization half-time. Estimates indicate that the cost of such biocomposite materials made by SSSP is less than that of virgin polypropylene.

1. Introduction

Filler addition is a conceptually simple and often cost-effective strategy for preparing new polymeric materials with synergistic properties [1–5]. Recently, there has been much focus on the production of greener polymer composites [1–10], including novel routes for recycling cellulose-rich waste materials such as waste cardboard [6]. Importantly, the use of greener feedstocks for the preparation of composites reduces reliance on fossil-fuel-based polymers [1–5,7]. Besides contributing to sustainability, such composites offer benefits such as low cost, improved stiffness, thermal and acoustic insulation, and low abrasion to processing equipment [8–10]. However, producing relatively homogenous filler dispersion has proven to be exceedingly difficult. Melt processing techniques such as twin-screw melt extrusion (TSE) have been the preferred commercial techniques to process plastics and polymer hybrids due to advantages like processing versatility and flexibility, high throughputs, and cost effectiveness [11,12]. Although TSE has demonstrated great success in processing a variety of polymer-based products, the same cannot always be said for the preparation of composites and nanocomposites [1–5,13–18]. In particular, preparing biocomposites by conventional melt processing is fraught with challenges such as the inability of TSE to provide sufficiently large stresses to break up filler agglomerates, massive viscosity mismatches, and filler degradation at temperatures typically employed for melt processing (cellulosic fillers degrade quickly at temperatures near or exceeding 200 °C) [1–7,10,14–21].

Research in composites manufacturing to address these challenges has often been based on optimizing thermodynamics, including surface modifications of the filler and addition of low molecular weight compatibilizer to improve polymer–filler interactions [15–17]. Such chemistries have led to successes in a few cases but have not provided a general solution [14–17]. Relatively few studies have employed modifications of conventional, industrially scalable melt processing techniques in an aim to achieve superior filler dispersion and synergistic properties. Some of the modifications to TSE include use of supercritical CO_2 as a process aid [22–24], ultrasonication [25,26], and liquid feeding [27,28]. Solid-state processing has been remarkably successful in achieving excellent dispersion and size reduction of fillers in polymer matrices without the need for additional chemistries, which add to the cost of processing [6,8–10,18,19,29–53].

In contrast to conventional melt processing, solid-state processing can impart extraordinarily large forces and stresses to the

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materials [6,8–10,18,19,29–53]. Batch solid-state processes such as pan milling, ball milling, and cryogenic milling have been adapted to expose blends and hybrids to large stresses, leading to superior filler dispersion and consequently excellent material properties [29–38]. A processing technique called solid-state shear pulverization (SSSP) [6,8–10,18,19,21,33,39–53] combines the advantages of solid-state processing with the versatility and continuous nature of TSE and is able to overcome challenges associated with melt processing of polymer hybrids. As typically practiced, SSSP employs a twin-screw extruder modified to cool rather than heat the material. Kneading and pulverizing screw elements in SSSP apply large shear stresses and compressive forces to the materials in the solid state. Depending on the energy input, fracture and fragmentation occur at weak points, resulting in limited chain scission and free radical formation [39,40]. Recent studies have taken advantage of conditions afforded by SSSP to achieve maleic anhydride or ester functionalization of polypropylene (PP) and to produce long-chain branched PP and well-dispersed blends compatibilized by in situ production or addition of block or gradient copolymers [39–45]. Success has also been achieved in producing composites and nanocomposites, where the absorbed mechanical energy can lead to simultaneous particle-size reduction and dispersion/debundling of highly agglomerated fillers in the polymer [6,8–10,18,19,21,33,46–52]. There is a need for developing an improved understanding of the processing–structure–property relationships associated with SSSP in order to optimize the preparation of such hybrids.

Specific energy input (E_p) is a parameter that is sometimes used with processing operations such as batch melt mixing and TSE, among others, to correlate process conditions with observed property enhancements [54–58]. Masuda and Torkelson [52] extended this concept to SSSP in order to understand the correlation between processing conditions such as screw design, throughput rates and screw speed and the property enhancements obtained in PP/carbon nanotube (CNT) nanocomposites. Specific energy input (E_p) can be estimated as follows [52]:

$$E_p = (W_T - W_M)/Q \quad (1)$$

where W_T is the average electric power consumption in the motor drive during SSSP of hybrids, W_M is the electric power in the motor drive for rotation in the absence of any material, and Q is the throughput. As such, E_p determines the energy input for the SSSP motor to process a unit mass of material. Masuda and Torkelson took advantage of the modular nature of the SSSP apparatus to tune E_p by varying screw design, throughput and screw speeds [52]. Relative to neat PP, 14% and 60% increases in Young's modulus were obtained for 99/1 wt% PP/CNT nanocomposites made by SSSP with E_p values of 6 and 55 kJ/g, respectively [52]; the greater enhancement in modulus at higher E_p was attributed to superior nanotube dispersion.

Recently, a parametric study of SSSP processing on PP homopolymer was performed to gain fundamental understanding of processing–structure–property relationships [53]. The E_p value was correlated with changes in PP powder particle size, very limited changes in PP molecular weight, and changes in some physical properties including isothermal crystallization half-time. There is a need for a similar studies focused on preparing green polymer composites by SSSP.

Here, we adopt the concept of E_p to optimize processing conditions of green composites via SSSP. Using the example of PP biocomposites incorporating 15 wt% waste paper (WP) with pre-SSSP dimensions of ~2 cm × ~2 cm × 0.1 mm as filler, we demonstrate that good size reduction and mechanical property enhancements can be achieved at intermediate E_p values. More importantly, WP was incorporated in PP without de-inking. Waste paper accounts for a significant fraction of the total municipal solid waste generated in the US [59]. Kraft pulping of wood employed in paper production results in partial elimination of hemicellulose and lignin [60–62]. Waste paper is chemically composed of cellulosics (~90%), lignin (<10%), with the rest being binders/adhesives such as starch and acrylamides [61,62]. Due to difficulties associated with melt processing PP/WP composites, Yuan et al. noted, "Because of the poor compatibility of PP and paper flour, it is nearly impossible to prepare. . .PP/paper flour blends with good mechanical properties." [63]. A recent literature report has demonstrated the ability of SSSP to produce well-dispersed PP composites with corrugated cardboard without the use of compatibilizers [6]. In addition to cellulose, WP contains lignin, which has been shown to be an effective thermal stabilizer for polymers [6,10].

In this study, a correlation between E_p and property enhancements is developed to optimize the production of novel, synergistic green composites of PP with WP via SSSP. Composites were prepared with different E_p values to tune the extent of filler size reduction and dispersion. Analysis of WP particle size distribution within the PP matrix reveals that very good dispersion and filler size reduction can be achieved at moderate E_p. In addition, increasing E_p results in a major reduction in the small number and size of macroscopic particles that are not incorporated well into the PP matrix after a single SSSP pass. Relative to neat PP, the 85/15 wt% PP/WP composites made by SSSP at moderate to high E_p show major property enhancements including a ~70% increase in modulus and a significant increase in crystallization rate.

2. Experimental section

2.1. Materials

Polypropylene pellet with density of 0.905 g/cm^3 and MFI of 9 g/10 min (ASTM D1238, 230 °C and 2.2 kg) was from Total Petrochemicals. Waste paper (mixture of office paper, wrapping sheets and other workplace paper discards, which are typically ~90% cellulose, <10% lignin, with the rest being binders/adhesives such as starch and acrylamides [61,62]) was obtained locally and cut into ~2 cm × ~2 cm pieces without de-inking or additional treatment. No surface modification, solvent or compatibilizer was used in this study.

2.2. Pulverization conditions for the preparation of PP/WP biocomposites

The PP pellets and 15 wt% WP pieces were dry blended and fed to a Berstorff ZE-25 intermeshing, co-rotating TSE using a K-tron S-60 feeder. The pulverizer has two sections. The first section with a L/D = 19 has a diameter of 25 mm and contains conveying and bilobe kneading elements, allowing for intimate mixing between PP and WP. Following this is a smaller section with L/D = 7.5 where the barrel diameter changes from 25 to 23 mm. (SSSP can be performed with all sections having a 25-mm-diameter barrel.) The 23-mm-section contains trilobe shearing elements, in which the bulk of the pulverization and particle size reduction take place. Depending on the motor running the apparatus, the pulverizer can be run with all bilobe elements. The SSSP barrels are cooled by a recirculating ethylene glycol/water mix at −7 °C (Budzar Industries WC3 chiller). Conveying elements feed the PP/WP mix to the barrel section with several kneading elements referred to as the mixing zone. A conveying zone follows where the well-mixed, deformed materials are cooled before intense pulverization takes place downstream. The materials then pass through a region with trilobe shearing elements where the bulk of the pulverization occurs. The screw speed was maintained at 200 rpm, yielding a fine powder or flakes depending on the screw design employed.

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