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Solid-state shear pulverization (SSSP) is a unique processing technique for mechanochemical modification of polymers, compatibilization of polymer blends, and exfoliation and dispersion of fillers in polymer nanocomposites. A systematic parametric study of the SSSP technique is conducted to elucidate the detailed mechanism of the process and establish the basis for a range of current and future operation scenarios. Using neat, single component polypropylene (PP) as the model material, we varied machine type, screw design, and feed rate to achieve a range of shear and compression applied to the material, which can be quantified through specific energy input ($E_p$). As a universal processing variable, $E_p$ reflects the level of chain scission occurring in the material, which correlates well to the extent of the physical property changes of the processed PP. Additionally, we compared the operating cost estimates of SSSP and conventional twin screw extrusion to determine the practical viability of SSSP.

INTRODUCTION

Industrial manufacturing of polymeric materials relies on large-scale and continuous processing methods. Twin screw extrusion (TSE) has been established as one of the most prominent commercial techniques to process plastics and other polymer-based materials because of numerous advantages such as excellent flexibility and versatility, high throughput, and low maintenance [1, 2]. Although very successful for processing homopolymer-based products, TSE may have limitations in developing specialty polymer [3, 4], polymer blend [5, 6], and nanocomposite [7, 8] systems due to issues of basic physics, including thermodynamic barriers to achieving desired morphologies and viscosity mismatch. Modified TSE techniques that incorporate processing aids, such as supercritical CO$_2$ [9–13], sonication [14–16], and water [17, 18], have been explored to circumvent these limitations. Recently, a new style of TSE based on a fundamentally different processing state, called solid-state shear pulverization (SSSP) [19–28], has been developed as an alternative polymer processing technique to overcome issues associated with melt processing of polymeric materials.

Inspired by the concept of mechanochemistry [29–31], high shear and compressive forces from the rotating kneading disks in SSSP are applied to the polymeric material in the solid state, well below the melting ($T_m$) or glass transition ($T_g$) temperatures. Depending on the level of mechanical energy absorbed, the material can fracture and fragment at its weakest location [31], sometimes leading to chain scission [19, 24], branching [19], and free radical formation [20, 21]. When SSSP is applied to immiscible polymer blends, eventual in situ block copolymer formation and subsequent compatibilization can occur [20–24]. Additionally, SSSP has been used to fabricate polymer nanocomposites, where the absorbed mechanical energy can translate to exfoliation and/or break up of filler agglomerates while simultaneously dispersing the separated particles extensively in the polymer matrix [25–28]. Unlike other solid-state processes like ball milling [32–34], pan milling [35, 36], and cryogenic milling [37, 38], the continuous production in SSSP is industrially applicable, like traditional TSEs.
Despite the proven success in polymer blend and nanocomposite applications and further potential of SSSP as a robust processing technique for homopolymers, little is known about the detailed mechanism of the process at present [39]. Specifically, processing-structure-property relationship studies of materials undergoing SSSP have been somewhat ad hoc, based on trial and error. Here, we present for the first time a systematic parametric study of the SSSP process, to establish the basis for a range of current and future SSSP operation scenarios. Using neat, single component polypropylene (PP) as the model material, we varied key SSSP processing conditions to determine their effects upon the resulting morphology, structure, and physical properties of the output.

Current state of knowledge in SSSP considers the following adjustable parameters to directly dictate the extent of shear and compression applied to the material: screw design, screw speed, barrel temperature, throughput, feed shape/size, and feed content [19, 24, 27, 28]. Some of these processing parameters are identical to those considered crucial in TSE, whereas parameters like feed shape/size are very unique to SSSP operation. Previous investigations have recognized that the degree of shear and compression arising from these processing parameters can be quantified through two main processing variables, residence time ($\tau$) and specific energy input ($E_p$), and that these variables can be correlated to the physical property changes that occur to the material following SSSP processing [28]. Variable $\tau$ is a measure of the time the materials spend inside the instrument, a familiar concept in TSE operation [40], whereas $E_p$ quantifies the amount the energy input to process a unit mass of the product [41].

The idea of $E_p$ has been previously introduced and discussed in depth for melt and solid-state processes. Different $E_p$ values have been determined for polymer blend processing with batch melt mixing [42] and TSE [43], homopolymer film blowing with single screw extrusion [44], and even food processing using TSE [45]. Furthermore, $E_p$ has been measured for simple pulverization of rubber granules with a single screw solid-state shear extruder [46]. Although the relevant $E_p$ equations vary slightly among these techniques with different processing parameters, the two common key quantities are the power of the motor and the throughput. Masuda and Torkelson [28] have recently applied the $E_p$ concept into SSSP processing:

$$E_p = \frac{(W_T - W_M)}{Q}$$  \hspace{1cm} (1)

In Eq. 1, $W_T$ is the average electric power consumption in the motor drive during SSSP of a product, $W_M$ is the electric power in the motor drive just for rotating the motor without any materials, and $Q$ is the throughput; Eq. 1 essentially determines the energy input for the SSSP motor to process a unit mass of material. When processing PP/carbon nanotube (CNT) nanocomposites, Masuda and Torkelson were able to tune the $E_p$ value by varying the screw design, throughput, and screw speed. The PP/CNT nanocomposite samples processed at $E_p = 6$ and 55 kJ/g showed a 14% and 40% increase in Young’s modulus compared with neat PP material, respectively. The authors attribute this difference in property enhancement to better dispersion of CNTs in PP at higher $E_p$ values. In a similar fashion, we expect $E_p$ to dictate the properties of our model homopolymer system.

As a fundamental processing-structure-property study involving SSSP of polymeric materials, we compare results obtained by using two similar but not identical SSSP instruments available in academia: an older SSSP instrument at Northwestern University and a recently commissioned analog at Bucknell University. This study focuses on machine type, screw design and throughput as the primary parameters to modify, and monitors $E_p$ as the key process variable; changes in each parameter lead to a range of $E_p$ values applied to the polymer, which are correlated with the changes in physical properties observed in the samples.

**EXPERIMENTAL**

**Materials**

Neat PP pellets were supplied from Total Petrochemicals (PP-3276, $\rho = 0.905$ g/cm$^3$; MFI = 2.0 g/10 min at 230°C/2.2 kg) and were used as-received. No solvents, modifiers, compatibilizers, or fillers were used.

**Sample Codes**

The three-character sample code (e.g., B1L) used in this article reflects the combination of three parameters varied in the SSSP processing of PP: equipment type, Bucknell ZE25-UTX (B) or Northwestern ZE25 (N); screw design, mild (1), medium (2), or harsh (3); and material throughput, low (L) or high (H). The codes and the corresponding processing conditions are summarized in Table 1. The differences in the screw designs are displayed in Fig. 1 and discussed in the next section.

**Pulverization Conditions**

PP samples were solid-state-shear-pulverized in two different models of Krauss Maffei Berstorff intermeshing, co-rotating TSEs. Model ZE25-UTX at Bucknell University (B) has a diameter ($D$) of 25 mm throughout its entire length and a length to diameter ratio ($L/D$) of 34. The screws are modular in nature, and designed as a combination of spiral conveying and bilobe kneading/pulverization elements. The barrels are continuously cooled by recirculating ethylene glycol/water (60/40 vol/vol) mixture maintained at $-12^\circ$C by a Budzar Industries BWA-AC-10 chiller. Model ZE25 at Northwestern University (N) has $L/D$ of 26.5, where its first section spanning $L/D = 19$ has $D = 25$ mm and remaining section of $L/D = 7.5$ has...
$D = 23$ mm. The screw elements involved in the 25-mm section are spiral conveying and bilobe kneading elements, whereas those in the 23-mm section are trilobe shearing elements. The barrels are cooled by recirculating ethylene glycol/water at $-7^\circ$C supplied by a Budzar Industries WC-3 chiller. For both pulverization instruments, the barrel section with several kneading elements in the upstream portion of the screws is termed the mixing zone. A conveying zone follows the mixing zone to cool the deformed material before intense pulverization takes place downstream in the pulverization zone. The screw rotation speed was maintained constant at 200 rpm for both instruments. The reported energy input to the motor and material output rates are averages of multiple readings.

Figure 1 is a schematic of the screw designs used in this study. “Harshness” of a screw design relates to the number of kneading and pulverization elements on the screw, as well as the degree of neutral and reverse-driving nature of these elements; the reverse, and to a lesser extent the neutral, kneading/pulverization elements retain the materials in the barrels for longer times, resulting in more energy being applied to the system. For the mild screw design, all forward kneading and pulverization elements were used. The medium screw set has all forward kneading elements in the mixing zone while having two or three neutral and one reverse element in the pulverization zone. The harsh screw design has two forward, three neutral, and two reverse kneading elements in the mixing zone and combination of three forward, two neutral, and two reverse elements in the pulverization zone. The three screw sets of B and N instruments were made to match in both kneading positions and lengths. One major difference between the B and N series, as seen in Fig. 1, is the overall length, with the B series having a higher capacity to cool the materials before pulverization and customize the screw design. Another key distinction is the use of all conventional bilobe elements in the B instrument, as compared with the trilobe pulverization elements that came standard with the N instrument. The physical property results indicate that the downstream pulverization elements can be of either type and result in similar property trends, as discussed in the later section.

Material throughput rate was controlled by a single-screw pellet feeder, Brabender Technologie DS28 for the B series and K-Tron Soder S60 for the N series. The low (L) throughput rate for all screw design and pulverization instrument combinations was set constant at 70 g/h. To determine the high (H) throughput rate for each instrument and screw design, we gradually increased the throughput and operated the instrument until the output material began to agglomerate. The formation of agglomerates indicates that the material is beginning to transition partially into the melt-state, which occurs when the rate of heat generated from fragmentation and fracturing of the pellets greatly exceeds the rate of heat removal by the continuous cooling mechanism. When agglomeration occurs, the barrel temperatures experience a “run-away” effect and rise unsteadily. Figures 2a and b show output material in the solid state and material that has transitioned to the partial melt state, respectively. Note that the high-throughput rate determined at the solid-melt transition is highly dependent on the softening temperature of the material being processed and SSSP parameters used; therefore, this value could be higher or lower for different systems.

### Characterization

The weighted average particle size of the SSSP output was determined with U.S. Standard wire mesh sieves, according to ASTM D1921, Test Method A; each sample was distributed in a series of 16 sieve trays ranging from 2400 $\mu$m to 10 $\mu$m according to the particle/flake size.
Rheological characterization was conducted using a TA Instruments ARES rheometer with 25-mm parallel-plate fixtures at 200°C, for a shear rate range of 0.01 to 100 s⁻¹, with an 8 s delay to allow the systems to equilibrate. The zero-shear rate melt viscosity, ηₒ, was taken as the average value of the Newtonian plateau in a viscosity versus shear rate curve.

Polymer crystallization behavior was characterized using a Mettler-Toledo 882e differential scanning calorimeter (DSC) in a standard isothermal crystallization mode at 132°C, in a nitrogen atmosphere. Specifically, the sample was heated from ambient temperature to 200°C at 10°C/min to erase thermal history and then quickly cooled (50°C/min) to the isothermal temperature. Before testing, the instrument was calibrated with an indium standard.

The heat degradation behavior was monitored using a thermogravimetric analyzer (Mettler Toledo 851e), calibrated with an indium/aluminum standard. The samples were heated from ambient temperature to 600°C at 10°C/min under a nitrogen purge.

Uniaxial tensile testing was conducted according to the ASTM D1708 standard method using a Tinius-Olsen H5K-S universal tester, in conjunction with in-house data acquisition and analysis software. The SSSP output was compression-molded using a PHI (Model 0230C-X1) press, at 200°C for 5 min with 5 ton ram force, and then immediately cooled in a cold press at 10°C under 5 ton ram force. Tensile coupons were cut using a standard dogbone die from Dewes-Gumbs. Samples were first allowed to equilibrate at room temperature for 48 h [25], and then tested at a crosshead speed of 12.7 mm/min (initial strain rate of 0.01/s).

RESULTS AND DISCUSSION

Specific Energy Concept

Table 1 shows the Eₚ values for the different processing conditions used to pulverize PP in either B or N pulverizers, from which two distinct trends can be observed. First, for a given throughput, changing the screw design from mild to harsh leads to an increase in Eₚ; harsh screw design involves the use of neutral and reverse kneading/pulverization elements, which generate backflow and increase the residence time, and in turn the mechanical work applied during processing. Second, for a given screw design, lowering the throughput leads to an increase in Eₚ; this phenomenon follows Eq. 1, which states that lower throughput simply reduces the amount of material inside the barrels at a given time, thus significantly raising the energy applied per gram of material processed. In the end, by controlling the screw design and throughput, we tailored the range of pulverizer Eₚ values from /C24 2k J / g to /C24 33 kJ/g for neat PP. As a comparison, the maximum Eₚ reported for PP/CNT nanocomposites made via SSSP [28] is approximately twice that found for neat PP. The additional specific energy in filled PP is translated from the mechanical work necessary in deagglomerating, scissioning, and dispersing the CNT fillers inside the polymer matrix. Therefore, Eₚ depends considerably on the nature of the material(s) involved as well.

It should be noted that the Eₚ values in Table 1 are based on power contributions in the motor drive of the SSSP instrument with and without material, simply extracted from the instrumentation display. Thus, the Eₚ value is the maximum energy that could be translated to the pulverization of the material. In practice, however, the actual amount of energy consumed by pulverization of the material alone would be less than the actual Eₚ values reported in Table 1, due to various practical energy losses. For example, part of the motor energy translates to excess energy caused by the friction of samples against barrel walls, in the form of heat, which is constantly removed from the system by the circulating coolant. In addition, some power is required to mix and/or move the solid materials forward within the barrels, contrastive to pressure necessary to move molten materials in TSEs. In this study, we neglect these potential energy losses in the Eₚ values for the sake of simplicity. Although such a first-order assumption is sufficient for most of our studies, these energy losses play an important role in differentiating the performance of the two SSSP instruments and explaining some of the observed trends in the next sections. Studies focused on a full energy consumption and modification of Eq. 1 are warranted in the future.
A process variable of great interest in solid-state pulverization of polymeric materials is the powder size of the SSSP output. For this study, a simple ASTM sieve analysis, with the sieve size ranging from 10 to 2400 μm, was conducted. The particle size distribution for the B and N pulverizers are seen in Figs. 3 and 4, respectively. It is evident from these figures that modifying the screw design from the mild to a harsher type, while maintaining other parameters constant, results in a dramatic peak shift to lower particle size and narrowing of the particle size distribution. For example, when comparing B1H to B2H samples, the peak particle size reduces by sixfold, from 1200 to 200 μm, and the width at half maximum by threefold, from 600 to 200 μm. Modifying the screw design to a harsher setting increases the shear of the material, which in turn significantly increases $E_p$. As more time and energy are spent on pulverizing a unit mass of the sample, repeated fragmentation leads to finer and more uniformly sized particles. A comparison of varying throughput within a consistent screw design in B series SSSP, in Fig. 3, shows a small difference in the resulting particle size distribution. Figure 4 exhibits a more prominent shift to lower average particle size with higher throughput, observed in a few of the N series results. In particular, at a mild screw design (N1L and N1H), the peak particle size shifts from 2400 to 1200 μm as the flow rate changes from 70 g/h to 1920 g/h. This trend of decreased particle size with increasing throughput is rather surprising because Eq. 1 indicates that $E_p$ decreases with increasing throughput, and lower $E_p$ contributes to less shearing and compression on the particles, leaving them in large sizes. We address this issue by further scrutinizing $E_p$.

Figure 5 correlates the average particle size of PP samples pulverized to $E_p$ in both the B and N instruments. There are three distinct observations that can be drawn from Fig. 5. First, both pulverizers demonstrate good tunability on the output particle size. The governing trend is that increasing $E_p$ leads to a decrease in weight-average particle size, regardless of the instrument type, screw design, and throughput. As-received PP pellets are nominally ~3 mm in size. When PP is subjected to an $E_p$ of ~2 kJ/g, the particle size decreases to ~1.3 mm for both

![FIG. 3. Particle size distribution for Bucknell ZE25-UTX (B) pulverizer.](image1)

![FIG. 4. Particle size distribution for Northwestern ZE25 (N) pulverizer.](image2)

![FIG. 5. Weight-average particle size of pulverized PP as a function of specific energy input. The black and white symbols represent low and high feed rates, respectively. The dotted curves are guides to the eye.](image3)
pulverizers. At an \( E_p \) input of \( \sim 30 \) kJ/g, the particle size further reduces to 300 \( \mu m \). This simple but significant tunability of the output particle size in SSSP is advantageous in powder applications, such as those in pigment, filler, paint, and additive industries [47, 48].

Second, the unexpected difference in weight-average particle sizes for high and low throughputs for a given screw design in the N pulverizer warrants discussion. Figure 5 shows that the trend curve of weight-average particle size versus \( E_p \) for N instrument’s low throughput (NxL) series does not coincide with the other series being investigated. We hypothesize that the deviation of this series from the universal trend of particle size versus \( E_p \) is due to the difference in energy losses occurring in the SSSP instruments. As discussed in the previous section, the two major energy losses neglected in our \( E_p \) calculation based on Eq. 1 are in the forms of heat removed from the system by the coolant and work to convey the material forward. At low throughputs, these energy losses, especially the latter, are more prevalent. Unlike TSE or high-throughput SSSP operation, the SSSP operates starved at low throughputs; more of the motor energy supplied is used to push the materials down the barrel. Additionally, the N series ZE25 pulverizer contains a transition barrel zone, where the diameter of the barrel constricts from 25 mm to 23 mm, between the mixing and pulverization zones. This constriction is expected to magnify the shaft work necessary to move the materials forward, especially when there is no back pressure built up from large flow of materials. Therefore, higher energy loss in NxL series contributes to higher measured \( E_p \) values than the actual energy applied to the polymer during processing. NxH and B series do not have this discrepancy because the energy losses are less severe and the measured \( E_p \) values mostly reflect the actual energy input to the materials; thus, they follow a universal particle size versus \( E_p \) curve. The B series results do indeed indicate that the energy losses are equivalent for low and high throughputs for a given screw design. Ultimately, if one accounts for the energy loss discrepancy, the particle sizes for both pulverizers would follow a universal relationship, which emphasizes the tunability of the SSSP technique.

The third observation from this correlation is that the weight-average particle size levels off at \( \sim 300 \) \( \mu m \) for both pulverizers at high \( E_p \). This is an important piece of evidence for the particle formation mechanisms in SSSP. During SSSP, the continuous shear and compression significantly fragment the material. At the same time, it is evident that the continuously fragmented polymer chains fuse back together to an average particle size of \( \sim 300 \) \( \mu m \). This threshold average particle size output, independent of processing parameters or \( E_p \) values, is an intriguing and unique phenomenon in the SSSP process. Although we were able to demonstrate the general \( E_p \) universality and the tunable nature of SSSP on the output particle size, sieve analysis is only a semi-quantitative estimate. The SSSP output particles are not necessarily isometric and spherical like those in Fig. 2a, but may often be flakes or short strings, as exemplified by an extreme case in Fig. 2b. In addition, the range of particle sizes presented here only applies to the PP material, and the results would vary depending on the polymer (and filler and additives, if applicable) being processed. Therefore, a comprehensive, systematic and quantitative analysis of SSSP output particles is warranted for various materials. Such a study is currently underway.

Effect of SSSP on the Melt Flow Behavior

High shear and compressive forces applied in the SSSP process is expected to affect the polymer chain morphology to a finite extent [23]. Here, we report the changes in molecular weight, \( M \), for the series of PP in Fig. 6, in the form of zero shear rate melt viscosity, \( \eta_o \). As \( \eta_o \) correlates to \( M \) with \( \eta_o \sim M^{0.4} \) relationship for a monodisperse, entangled polymer [49], the reduced \( \eta_o \) values obtained in the samples indicate that SSSP processing can lead to a range of molecular weight reduction, due to varying degrees of chain scission. In this study, \( M \) reductions (as estimated at zeroth order via \( \eta_o \) by ignoring the polydispersity of the samples) of up to \( \sim 20\% \) achieved in PP are rather modest, considering the extensive \( E_p \) range involved; larger reductions in \( M \) have been observed previously for SSSP-processed polycaprolactone homopolymer [19] and poly styrene/ethylene blends [24]. Therefore, the extent of chain scission in SSSP is also dependent heavily on the physical properties of the materials themselves.

In Fig. 6, a general trend of decreasing \( \eta_o \) with \( E_p \) is observed in each of the B and N series samples, with the B samples showing a consistently lower \( \eta_o \) for a given \( E_p \). This is likely because the B instrument experiences lower...
energy losses and thus more efficient transfer of applied motor energy ($E_p$ as determined in Table 1) to the chain scission of polymers. In contrast, the same input energy $E_p$ to the N pulverizer suffers from higher energy loss to secondary activities (friction, translation, etc.), resulting in lower net energy usable for pulverization; therefore, we expect to see lower levels of chain scission. These results also point to the subtle and slight efficiency difference arising from differences between the B and N pulverizers, as discussed earlier. Recall that the N model had constricted 23-mm diameter barrel pulverization zones and trilobe pulverization screw elements, both of which were necessary to support the large and unsteady torque in the motor. However, the higher torque capacity in the modern B motor allows for simpler SSSP screw and barrel design, and in turn minimal heat generation and energy losses. In the end, the difference in efficiency is minor, and both instruments are indeed capable of providing the same degrees of SSSP outcomes in terms of particle size, melt viscosity, etc.

It is also noteworthy that the curves in Fig. 6 do not have a plateau effect; rather, $\eta_0$ continues to decrease with increasing $E_p$. This is in contrast to the trends of weight-average particle size leveling off above $E_p \approx 30$ kJ/g. Each time the polymer particle fragments in a SSSP process, rupture can occur both inter- and intra-molecularly, the former of which causes the particle-size reduction and the latter molecular weight reduction. However, as these ruptured chains fuse back together to form particles of $\sim 300$ $\mu$m or above in average size, the fusion process is strictly intermolecular in nature, i.e., molecular weight is unaffected by fusion.

**Effect of SSSP on the Thermal Properties**

Isothermal crystallization half-times, $t_{1/2}$, which signify the rate of polymer crystal development, were determined at $132^\circ$C for neat and SSSP-processed PP samples, and recorded in Table 2. In general, PP samples pulverized with either the B or N instrument exhibit a decrease in $t_{1/2}$ with increasing $E_p$; in contrast to the neat unprocessed pellet with $t_{1/2} = 11.9$ min, an $E_p$ value of $\sim 6.5$ kJ/g reduces the $t_{1/2}$ to 8.2–9.3 min, whereas $E_p \sim 30$ kJ/g further reduces it to 5.6–8.2 min. We associate the reduction in $t_{1/2}$ with slight $M$ reduction discussed earlier, which leads to faster chain mobility for crystal growth. The fact that modest reductions in $M$ can lead to a significant enhancement in the crystallization rate has also been previously reported in other polymer systems [51–53]. Table 2 also lists degrees of crystallinity, determined via DSC using the heat of fusion of 100% crystalline PP [50]. Interestingly, there is only a small, several percent variation in polymer crystallinity across the pulverized samples. Therefore, SSSP process does not impact the nature of the crystallizable segments within the PP chains.

Two specific trends from the isothermal crystallization data confirm the previously discussed processing-structure relationship. First, for a given screw design, increasing the throughput (e.g., B1H vs. B1L) leads to an increase in $t_{1/2}$, i.e., slower crystallization. *Equation 1* states that higher throughput causes a decrease in $E_p$, which, according to Fig. 6, leads to lower degree of chain scission. As a result, the chain mobility for crystal growth is slower. Second, for a given throughput, changing the screw design from mild to harsh leads to a decrease in $t_{1/2}$. As discussed earlier, harsher screw designs involve neutral and reverse kneading/pulverization elements, which lead to an increase in the work applied to the polymer during processing. An increase in the value of $E_p$ leads to the reduction of $M$ of the polymer, and in turn greater chain mobility for crystal growth.

Even though the PP crystallization behavior is a strong function of the extent of modest chain scission accompanying SSSP, thermal degradation properties are nearly

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**TABLE 2.** Thermal and mechanical property measurements of neat and SSSP processed PP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific energy (kJ/g)</th>
<th>Isothermal crystallization half-time at $132^\circ$C $t_{1/2}$ (min)</th>
<th>Percent PP crystallinity $X_c$ (%)</th>
<th>Thermal degradation temperature, at 5 wt% loss of total mass $t_{5%}$ (°C)</th>
<th>Young’s modulus $E$ (MPa)</th>
<th>Yield strength $\sigma_y$ (MPa)</th>
<th>Elongation at break $\varepsilon_b$ (%)</th>
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</thead>
<tbody>
<tr>
<td>PP, Pellet</td>
<td>0</td>
<td>11.9</td>
<td>55</td>
<td>399</td>
<td>$1000 \pm 40$</td>
<td>$32 \pm 1$</td>
<td>$640 \pm 80$</td>
</tr>
<tr>
<td>B1L</td>
<td>6.4 ± 2.7</td>
<td>8.2</td>
<td>54</td>
<td>397</td>
<td>$1140 \pm 80$</td>
<td>$32 \pm 3$</td>
<td>$600 \pm 90$</td>
</tr>
<tr>
<td>B1H</td>
<td>2.5 ± 0.1</td>
<td>10.0</td>
<td>51</td>
<td>400</td>
<td>$1040 \pm 30$</td>
<td>$30 \pm 1$</td>
<td>$630 \pm 90$</td>
</tr>
<tr>
<td>B2L</td>
<td>25.0 ± 3.5</td>
<td>6.5</td>
<td>51</td>
<td>399</td>
<td>$1020 \pm 40$</td>
<td>$31 \pm 2$</td>
<td>$610 \pm 40$</td>
</tr>
<tr>
<td>B2H</td>
<td>12.6 ± 1.2</td>
<td>8.0</td>
<td>51</td>
<td>400</td>
<td>$1010 \pm 40$</td>
<td>$31 \pm 2$</td>
<td>$700 \pm 40$</td>
</tr>
<tr>
<td>B3L</td>
<td>30.9 ± 3.6</td>
<td>5.6</td>
<td>52</td>
<td>399</td>
<td>$1080 \pm 50$</td>
<td>$31 \pm 2$</td>
<td>$510 \pm 70$</td>
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<tr>
<td>B3H</td>
<td>21.4 ± 1.6</td>
<td>5.7</td>
<td>51</td>
<td>400</td>
<td>$1040 \pm 50$</td>
<td>$31 \pm 1$</td>
<td>$710 \pm 30$</td>
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<tr>
<td>N1L</td>
<td>8.3 ± 3.0</td>
<td>11.7</td>
<td>53</td>
<td>396</td>
<td>$1040 \pm 60$</td>
<td>$30 \pm 2$</td>
<td>$670 \pm 90$</td>
</tr>
<tr>
<td>N1H</td>
<td>2.2 ± 0.2</td>
<td>12.1</td>
<td>53</td>
<td>398</td>
<td>$1000 \pm 70$</td>
<td>$29 \pm 2$</td>
<td>$650 \pm 110$</td>
</tr>
<tr>
<td>N2L</td>
<td>16.7 ± 3.0</td>
<td>9.0</td>
<td>56</td>
<td>394</td>
<td>$1060 \pm 90$</td>
<td>$32 \pm 2$</td>
<td>$770 \pm 110$</td>
</tr>
<tr>
<td>N2H</td>
<td>6.5 ± 0.5</td>
<td>9.3</td>
<td>56</td>
<td>398</td>
<td>$1080 \pm 80$</td>
<td>$32 \pm 3$</td>
<td>$620 \pm 100$</td>
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<tr>
<td>N3L</td>
<td>32.8 ± 4.6</td>
<td>8.2</td>
<td>52</td>
<td>394</td>
<td>$1100 \pm 50$</td>
<td>$32 \pm 2$</td>
<td>$710 \pm 60$</td>
</tr>
<tr>
<td>N3H</td>
<td>20.3 ± 1.9</td>
<td>9.0</td>
<td>51</td>
<td>395</td>
<td>$1110 \pm 80$</td>
<td>$32 \pm 3$</td>
<td>$620 \pm 90$</td>
</tr>
</tbody>
</table>

* The degree of crystallinity, $X_c$, can be calculated by $X_c = \frac{\Delta H_t}{\Delta H_f} \times 100\%$ where $\Delta H_t$ is the heat of fusion and $\Delta H_f$ denotes heat of fusion for an infinitely large crystal, which is assumed here to be 207.1 kJ/g [50].
unaffected by SSSP. Table 2 shows that differences in the onset thermal degradation temperatures at 5 wt% loss, $T_{\text{deg}}$, among the neat and SSSP-processed PP samples are minimal, 0–6°C. The results show that heat stability of PP is retained after SSSP processing. It is thus important to note that the moderate reduction in $M_e$ arising from SSSP processing of PP does not necessarily correspond to significant property deterioration.

**Effect of SSSP on the Mechanical Properties**

Table 2 shows the mechanical properties of neat PP pellet and processed PP for both Bucknell ZE25-UTX and Northwestern ZE25 pulverizers. It is apparent that the Young’s modulus, $E$, yield strength, $\sigma_y$, and elongation-at-break, $\varepsilon_b$, for all pulverized PP samples are, within experimental error, similar to those of neat PP pellet. This significant finding indicates that the mechanical integrity of the pulverized samples is maintained even though the molecular weight decreases, as much as by 20% at the highest $E_p$ input. Essentially, pulverized PP retains its original room temperature mechanical behavior.

It has been previously established that molecular weight can significantly modify the mechanical properties of a homopolymer [54, 55]. McCormick et al. [54] reported that the elongation at break of a polymer dramatically decreases as its weight average molecular weight ($M_w$) approaches the entanglement molecular weight ($M_e$). Under an applied load, chains with $M_w < M_e$, can pull out from one another and cause localized crazing, ultimately leading to brittle fracture. In contrast, when $M_w > 10M_e$, the elongation at break becomes relatively constant, and exhibits ductile behavior. The results from this study suggest that although $M$ decreased appreciably (20% reduction as discussed earlier), it is still significantly above $10M_e$ ($M_e \approx 3500$ g/mol, based on the rubber elasticity theory [56] and measured plateau modulus), and thus the molecular weight reduction has very little impact on the mechanical properties. In addition, previous polyolefin micromechanical studies [57, 58] have established that fundamental mechanical properties such as elastic modulus and yield strength are mainly dictated by polymer crystallities. Our thermal characterization (Table 2) confirms that the PP crystallinity remains essentially invariant as a function of SSSP processing, and hence, we accordingly expect the mechanical properties to be compromised very little, if at all.

**Operation Cost of SSSP**

One of the main questions that surround the viability of SSSP as a commercial processing technique for polymeric materials is the operating cost. Although SSSP has shown to yield effective dispersion of nanofillers [25–28], compatibilize immiscible polymer blends [20–24], and contribute to the recycling of plastics [19, 22], no previous report has addressed the cost of producing these materials. In light of the $E_p$ values discussed herein, we provide an estimate of the operating cost based on a typical operation of the B unit.

Costing an operation of a continuous SSSP involves consideration of three major factors: energy to run the motor (to convey and pulverize the material), the heat exchange in the chiller compressor (and fan), and the pump work to transport the coolant from and to the chiller. The $W_T$ value for a sample calculation was taken as 1.70 kW from run B1H, which most closely corresponds to a commercial production run equivalent. The coolant chiller compressor and fans, whose power inputs are 9.4 kW and 0.55 kW, respectively, engaged at 16% of full power during a steady-state operation; an approximated average power of 1.66 kW was used for the heat exchange. The chiller recirculating pump, input at 0.92 kW, operates continuously. Thus, the total power usage for all three components was $1.70 + 1.66 + 0.92 = 4.28$ kW. Based on the throughput of the B1H run, the specific energy consumption (SEC) [59] is calculated to be 2.0 kWh/kg; using an electricity cost of $0.10/kWh [60], the overall cost of operation is estimated at $0.43/h, and the energy cost per mass of product at $0.04/kg.

As a comparison of the energy cost between SSSP and conventional TSE, the B instrument in an equivalent extrusion mode is considered. For a PP extrusion at a throughput of 2.2 kg/h, the motor operated at 0.9 kW, and the 1.05 kW cartridge-type barrel heaters engage at an approximated total average of 0.6 kW to maintain the melt temperature during a steady-state operation. The total power usage in the TSE is $0.9 + 0.6 = 1.5$ kW, which corresponds to SEC of 0.68 kWh/kg, the overall operation cost of $\approx0.15$/h, and the energy per product mass cost of $0.07$/kg. As expected, the cost of typical TSE processing is lower than that of typical SSSP processing. However, SSSP is still an economically viable option for polymer processing, especially when one considers its full potential to yield high value-products that cannot be made by conventional TSE, as well as process materials with environmental and safety benefits. It should be recalled that the calculated operating cost is only a first-order estimate for processing PP in a laboratory scale 25 mm diameter SSSP/TSE instrument, without consideration for subsequent molding/shaping of the materials. We expect that the cost would dramatically decrease for SSSP instruments with larger barrels and screws. It is also noteworthy that the SSSP cost is sensitive to the achievable throughput, which is dictated by not only the screw design and speed settings, but the physical properties of the materials, such as $T_m$ and $T_g$, ductility, hardness, and frictional coefficient; studies are underway to elucidate these interrelationships and seek material types for cost-effective processing.

**CONCLUSIONS**

SSSP is an emerging processing technique for various polymer-based materials, and we herein report for the first
time a systematic parametric study of the SSSP process to gain fundamental knowledge of the processing-structure-property relationships. Using neat PP as the model material, comparison of two different models of SSSP instruments as well as that to conventional TSE equipment and evaluation of the effects of key processing parameters were conducted.

The results from this study establish that \( E_p \) is a universal variable that can be used to correlate the morphological changes that occur to the polymer during SSSP processing, including average particle size and molecular weight. Although there are slight differences in some trends between the two instrument models, the concept of specific energy input can be used across different models and screw designs to describe approximately the degree to which shear stresses and compressive forces do work on the material during SSSP processing. The impact of SSSP processing upon various physical properties of the polymer samples can depend on the magnitude of specific energy input. For example, at the highest \( E_p \) value, chain scission of the polymer led to a 60% decrease in \( \eta_o \) and 50% decline in \( t_{1/2} \). Some physical properties can be freely tuned by controlling the \( E_p \) input. On the other hand, \( T_{deg} \) and mechanical properties such as tensile modulus, tensile strength, and ductility remain similar to that of neat PP for all values of \( E_p \) tested with SSSP processing.

Further, processing-structure-property studies of SSSP-processed polymers should not only include a factorial experimental design and analysis with wider range of process parameters like barrel temperature and screw speed, but also focus on the inter-relationships between other SSSP variables like residence time. Universal correlation between processing parameters and key process variables will lead to a better understanding of the SSSP operation and an optimized processing of plastics, polymer blends, and polymer nanocomposites.

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