Well-mixed blends of HDPE and ultrahigh molecular weight polyethylene with major improvements in impact strength achieved via solid-state shear pulverization

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A B S T R A C T
Compared with conventional polyolefins, ultrahigh molecular weight polyethylene (UHMWPE) possesses outstanding impact strength and crack resistance that make it desirable for a wide variety of applications. Unfortunately, UHMWPE has an ultrahigh viscosity that renders common, continuous melt-state processes ineffective for making UHMWPE products. Attempts to overcome this problem by blending UHMWPE with lower molecular weight high-density polyethylene (HDPE) by melt processing have typically led to poorly dispersed blends due to the vast viscosity mismatch between blend components. Here, we present solid-state shear pulverization (SSSP) as a mild, continuous, and simple approach for achieving effective and intimate mixing in UHMWPE/HDPE blends. These SSSP blends are easily processed by post-SSSP melt extrusion; for an SSSP blend with 50 wt% UHMWPE, we observe more than a factor of 1000 increase in viscosity at a shear rate of 0.01 s⁻¹ but less than a factor of 5 increase at 100 s⁻¹, the latter being more typical of melt-processing operations. Using extensional rheology, we confirm the strain hardening behavior of SSSP blends. Shear rheology and crystallization data show that the mixing between UHMWPE and HDPE can be improved with subsequent passes of SSSP and single-screw extrusion. Finally, we show that blending via SSSP leads to dramatic improvements in impact strength: as compared to literature results, injection-molded sample bars made from SSSP blends with 30–50 wt% UHMWPE exhibit very high values of notched Izod impact strength, 660–770 J/m (the impact strength of neat HDPE was 170 J/m).

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1. Introduction

Compared to conventional polyolefins, ultrahigh molecular weight polyethylene (UHMWPE) possesses several advantageous mechanical properties, including very high impact strength and crack resistance [1–3], which make it highly desirable for medical (e.g., joint prosthesis), industrial (e.g., lead acid battery separators), and defense (e.g., ballistic cloth for bullet-proof vests) applications [2–5]. Unfortunately, as a result of its ultrahigh molecular weight (MW), high degree of chain entanglements, and ultrahigh melt viscosity [6–9], UHMWPE cannot be processed via conventional melt extrusion or injection molding. Instead, UHMWPE is processed by less broadly used batch methods such as ram extrusion [4,5], compression molding [10,11], or sintering [12,13]. In addition to resulting in extraordinarily high pressure requirements during conventional melt processing, the high degree of entanglements also leads to prevalence of grain boundaries or fusion defects during sintering and compression molding [1,4]. These defects occur because the long relaxation times associated with melt-state UHMWPE hinder diffusion of chains from one melt-state UHMWPE particle to another [1,4,14]. Improvements in UHMWPE processability have been achieved by decreasing the degree of chain entanglements via dissolution in a suitable solvent [15,16] or employing atypical polymerization techniques or conditions that result in formation of single chain crystals (e.g., polymerization with decreased number of active sites or single-site catalysts [17–20] and/or by using decreased polymerization temperature [21–23]). Reduction of entanglements leads to enhanced chain mobility, toughness, drawability, and fatigue resistance as well as decreased oxygen permeability and reduced pressure requirement for conventional melt processing.
leads to the formation of poor blend morphologies (e.g., large
enormous viscosity mismatch between blend components that
have also been used to decrease die pressure associated
with UHMWPE; because sintering and compression molding are well-established
approaches for successfully processing much higher melt viscosity
materials than is typically achievable with melt extrusion or
ingection molding, improvements in these processes do not
necessarily imply that improvements will be observed with con-
tventional melt processes as well. Finally, these solvent-based and
polymerization methods also do not provide irreversible solutions
to the problems posed by entanglements because disentangled
chains can re-entangle during melt-state heating [8,24–26].

Attempts have also been made to improve UHMWPE process-
ability by blending with lower MW polyethylene (PE) [27–35] and
died low polypropylene (PP) [36–39]. Process aids such as poly(ethylene
glycol) have also been used to decrease die pressure associated
with extrusion of UHMWPE blends [29]. Efforts to improve
UHMWPE processability by blending with lower MW PE by con-
tventional melt processing have been grossly hampered by the
everous viscosity mismatch between blend components that
leads to the formation of poor blend morphologies (e.g., large
UHMWPE agglomerates in the lower MW PE matrix) [31,32]. To
achieve good dispersion in UHMWPE/high-density polyethylene
(HDPE) blends, harsh and/or complex processing conditions have
been used [10,31–35]. Ruff et al. [35] demonstrated that by
employing multi-stage polymerizations, well-mixed blends of
UHMWPE and lower MW PE could be prepared; this approach to
blending utilizes a complex system of polymerization and requires
significant changes to polymerization conditions from one stage to
the next [35]. Batch blending by solution processing has also been
shown to lead to better mixing in UHMWPE blends as compared to
melt processing [39]. Although resulting in well-mixed blends,
solution blending typically requires large quantities of organic
solvents such as decalin [33,34].

Boscoletto et al. [31] compared UHMWPE/HDPE blends that
were prepared via melt processing by batch mixing for 10–30 min,
single-screw extrusion alone, or single-screw extrusion followed by
batch mixing for 30 min. They showed that the best mixing be-
tween UHMWPE and HDPE components was achieved by single-screw
extrusion followed by batch melt mixing for 30 min; poor
dispersion (which led to mediocre blend properties) was observed for
blends that were prepared by single-screw extrusion only [31]. Lim et al. [32] prepared UHMWPE/HDPE blends in the melt state
using a batch mixer at 30 rpm rotor speed (20 min) followed by a
two-roll mill (5 min) and subsequent compression molding
(25 min). Although necessary for good mixing, such long processing
times can lead to thermal degradation (e.g., the onset of degra-
dration for processing at a 30 rpm rotor speed was ~23 min [32]). The
complex multi-step processes, long process times (which may
cause undesirable effects such as MW reduction, branching, or
crosslinking), and low throughput (due to the batch nature) render
blending via such harsh melt processing methods unattractive as
an approach to produce commercial-scale quantities of well-mixed
UHMWPE/HDPE blends. Thus, there remains major interest in
finding a simple, mild, continuous approach for preparing well-
mixed UHMWPE/HDPE blends.

Interest in UHMWPE/PE blends is often associated with the
potential to enhance the impact properties of the lower MW PE
[29–32,35]. Expected improvements in material properties are
closely linked to blend morphology: ineffectively mixed blends have poorer mechanical properties as compared to their effectively
mixed counterparts [31,32,35]. Boscoletto et al. [31] demonstrated
that improving the mixing between components by increasing
shear stresses associated with melt processing enhances impact
and crystallization properties of UHMWPE blends. They studied
two 20/80 wt% UHMWPE/HDPE blends that were prepared with
the same blend components but different levels of harsh melt
processing that resulted in different levels of shear stresses and,
consequently, different degrees of mixing. The blend that was
prepared using higher shear stresses resulted in superior mixing
and a notched Izod impact strength of ~250 J/m while the blend
prepared with lower shear stress had a notched Izod impact strength of ~220 J/m (the parent HDPE had a notched Izod impact strength of ~110 J/m [31]).

Besides improvements in processability and properties, the
crystallization behavior of blends containing ultrahigh MW poly-
mers (UHMWPE/HDPE blends [40–43], ultrahigh molecular weight
PP (UHMWPP)/PP blends [44–46], and UHMWPE/PP blends [39,40,47]) is also of major interest. Such blends have been studied for
their ability to undergo flow-induced crystallization and the
impact of this crystallization on properties [40,48]. Research
[40,41,46] has shown that oriented precursors to crystallization (believed to contain the higher MW component, which has much
longer relaxation times) are induced by flow to form the ‘shish-
kebab’ morphologies while the lower MW components form the majority of the ‘kebabs’. For these studies, blends are typically prepared by solution blending because the
large viscosity mismatch between blend components disallows the
use of melt processing to achieve the excellent dispersion that
is required for these studies.

Although solution blends represent the ideal case for highly
effective dispersion of the ultrahigh MW blend component, the
requirement for copious amounts of solvent makes solution
blending broadly inapplicable for large-scale commercial applica-
tion (an exception is solution spinning of fibers). On the other hand,
simple, continuous conventional melt processing methods used in
large-scale commercial production of typical polymer blends are
not suitable for achieving effective dispersion in blends containing
an ultrahigh MW component. This is because of the vast viscosity
mismatch between blend components and the high-pressure re-
quirements for melt processing (due to the presence of an ultrahigh
MW component). To suppress the pressure requirements and
improve processing feasibility, some studies have used neat parent
HDPE with very high melt flow indices and/or have melt processed
their blends at unconventionally low screw speeds [30,49].
Regardless, continuous conventional melt processes (e.g., single
screw extrusion) have mostly led to modest improvements in
material properties when used as the sole method for blending
UHMWPE and HDPE [30,49,50]. In the present study, we employ a
novel, mild, continuous process method called solid-state shear
pulverization (SSSP) for effectively blending up to 50 wt% UHMWPE
with HDPE. By coupling SSSP with single-screw extrusion, we also
extend our ability to tune the effective mixing between
UHMWPE and HDPE.

Solid-state shear pulverization uses a twin-screw melt extruder
modified with a cooling system to maintain the polymer in the solid
state [51–62]. This process is accompanied by high shear stresses and
compression forces that cause repeated fragmentation and
fusion of material; conditions are tuned by feed rate, screw speed,
screw design, and temperature [51]. In addition to being solvent-
less, SSSP is industrially scalable; polyolefins have been processed by
SSSP with a commercial-scale apparatus at rates exceeding 150 kg/hr.Compatibilization and intimate mixing of immiscible
blends [52–54] and effective dispersion and exfoliation of fillers in
composites and nanocomposites can result from SSSP [57–60,63].
Recently, we showed that SSSP can be used to synthesize maleic
anhydride grafted PP with strongly suppressed MW reduction [61]
and ester functionalized PP with moderate MW reduction using a symmetric organic peroxide alone [62]. Past studies also demonstrated the utility of SSSP in achieving effectively mixed blends where blend components have significantly mismatched viscosities, which hampers mixing via conventional melt extrusion [55,56]. Here, by taking advantage of the near-ambient temperature conditions associated with SSSP, we circumvent the challenge presented by melt processing UHMWPE and HDPE blend components which have a vast viscosity mismatch. Processing by SSSP, which is done in a simple manner, leads to effective dispersion even though it is sufficiently mild that it leads to negligible chain scission (which could otherwise lead to degradation via MW reduction) of neat HDPE. The UHMWPE/HDPE blends obtained from SSSP, which are easily processed by conventional melt extrusion and injection molding, exhibit very high values of notched Izod impact strength as compared to those reported in the literature.

2. Experimental

2.1. Materials

Ultrahigh molecular weight polyethylene (SigmaAldrich) with weight average MW between 3,000,000 and 6,000,000 g/mol (average powder particle size ~ 5–50 µm; reported by supplier) was used as received. High-density polyethylene (Equistar: MFI = 6.0 g/10 min; ASTM D-1238, tested at 190 °C and using a 2.16 kg weight; reported by supplier) was used as received. Xylene (SigmaAldrich) was used as received. A phenolic antioxidant, Songnox 6260 (Songwon), was used as received. Antioxidants (2.2. Preparation of UHMWPE/HDPE blends

The HDPE pellets and UHMWPE powder were pulverized at 200 rpm screw speed and 100 g/hr feed rate for HDPE pellets. The UHMWPE was added via a side hopper using a powder feeder (Brabender Technologie Inc. DDSR12-1 volumetric feeder) at varied feed rates depending on the desired weight fraction of UHMWPE in the blend. The pulverizer was a pilot-plant/research-scale Berstoff twin-screw extruder modified with a cooling system (Budzar Industries WC-3 chiller operating at −6 °C); the same apparatus was used in previous SSSP studies [51–62]. The SSSP apparatus consisted of two sections. The first section, with \( L/D = 26.5 \), had a 25 mm diameter barrel with the screw consisting of spiral conveying elements and bi-lobe kneading elements (2 forward, 1 reverse, and 1 neutral element). The second section, with \( L/D = 7.5 \), had a 23 mm diameter barrel containing tri-lobe shearing elements (3 forward, 2 reverse, and 2 neutral elements) which facilitated good mixing and dispersion of the powdery UHMWPE in the HDPE.

Between the two sections, there was a small transition zone going from 25 to 23 mm diameter. (Depending on the motor used, SSSP can be done with all bi-lobe elements and a 25 mm diameter barrel throughout the apparatus.) For comparison, a 5/95 wt% UHMWPE/HDPE blend, Soln-5%, was prepared by co-dissolution in xylene at 130 °C and with 1 wt% Songnox 6260; the blend was crystallized out of solution by decreasing the solution temperature to room temperature, precipitated with methanol, and then dried overnight in a vacuum oven at 70 °C. An additional 5/95 wt% UHMWPE/HDPE blend, MM-5%, was prepared by melt mixing for 10 min at 160 °C with an Atlas Electronic Devices MiniMAX molder (cup-and-rotor mixer) at maximum rotor speed and with three steel balls in the cup to provide chaotic mixing. (Maric and Macosko previously demonstrated that the use of such a cup-and-rotor mixer with three steel balls yielding chaotic mixing can approximate the mixing achieved by twin-screw melt extrusion [64]). Table 1 shows details of sample composition and processing methods.

2.3. Single-screw extrusion of UHMWPE/HDPE blends

Post-SSSP melt extrusion was done in a Randcastle RCP-0625 microextruder (screw diameter = 0.625 in, length/diameter = 24). Blends were processed at a 50 rpm screw speed. For SSSP-5%, SSSP-10%, and SSSP-20%, the extruder barrel was maintained at 175–180 °C while the die temperature was 170 °C. For SSSP-30% and SSSP-40%, the extruder barrel was held at 185–190 °C and the die temperature was 175 °C. For SSSP-50%, the barrel temperature was 195–205 °C and the die temperature was 190 °C. Temperatures were increased with increasing UHMWPE content in order to reduce die pressure during processing [65,66].

2.4. Rheological measurements

Neat HDPE and UHMWPE/HDPE blends were tested with 1 wt% Songnox 6260 added to each sample to prevent thermal degradation. For small amplitude oscillatory shear experiments, samples were compression molded into discs using PHI presses; data were collected at 150 °C, with 2% strain over a frequency range of 0.01–100 rad/s (measuring from high to low frequency), using a strain-controlled Rheometrics Scientific ARES rheometer equipped with 25 mm parallel plates. For extensional flow, samples were compression molded into ~0.8 mm thick films that were cut into strips with ~9.5 mm widths and ~22 mm lengths; data were collected at 150 °C using a Sentamanat Extensional Rheometer [67] fixture mounted in the ARES rheometer. Extensional flow data were

<table>
<thead>
<tr>
<th>Sample</th>
<th>Processing method</th>
<th>UHMWPE content (wt%)</th>
<th>Crystallization onset temperature (°C)</th>
<th>Crystallinity (%)</th>
<th>Young's modulus (MPa)</th>
<th>Yield stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat HDPE (as received)</td>
<td>–</td>
<td>–</td>
<td>118</td>
<td>69</td>
<td>980 ± 50</td>
<td>27</td>
</tr>
<tr>
<td>Neat HDPE (after SSSP)</td>
<td>SSSP</td>
<td>–</td>
<td>118</td>
<td>68</td>
<td>990 ± 60</td>
<td>27</td>
</tr>
<tr>
<td>Neat UHMWPE</td>
<td>–</td>
<td>Solution blending</td>
<td>100</td>
<td>124</td>
<td>500 ± 40</td>
<td>34</td>
</tr>
<tr>
<td>Soln-5%</td>
<td>–</td>
<td>Melt mixing</td>
<td>5</td>
<td>121</td>
<td>990 ± 60</td>
<td>26</td>
</tr>
<tr>
<td>SSSP-5%</td>
<td>SSSP</td>
<td>5</td>
<td>121</td>
<td>69</td>
<td>950 ± 50</td>
<td>26</td>
</tr>
<tr>
<td>SSSP-10%</td>
<td>SSSP</td>
<td>10</td>
<td>121</td>
<td>68</td>
<td>950 ± 50</td>
<td>26</td>
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<tr>
<td>SSSP-20%</td>
<td>SSSP</td>
<td>20</td>
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<tr>
<td>SSSP-30%</td>
<td>SSSP</td>
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<td>930 ± 50</td>
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<tr>
<td>SSSP-40%</td>
<td>SSSP</td>
<td>40</td>
<td>121</td>
<td>56</td>
<td>850 ± 20</td>
<td>22</td>
</tr>
<tr>
<td>SSSP-50%</td>
<td>SSSP</td>
<td>50</td>
<td>122</td>
<td>57</td>
<td>800 ± 80</td>
<td>21</td>
</tr>
</tbody>
</table>
collected at strain rates of 0.01–0.10 s⁻¹; extensional viscosities were corrected for thermal expansion by accounting for the effect of melt- and solid-state densities on cross-sectional area [67,68]. Data for the linear viscoelastic envelope were obtained by fitting a multimode linear Maxwell model to oscillatory shear data.

2.5. Thermal and mechanical properties

A Mettler-Toledo differential scanning calorimeter (DSC 822e) was used for thermal analysis. Non-isothermal crystallization data were obtained from a 10 °C/min cooling ramp.

Films with ~0.7 mm thickness were prepared for tensile testing using PHI presses. Samples were prepared according to ASTM D1708; dumbbell-shaped specimens were cut from films using a Dewes-Gumbs die. An MTS Sintech 20/G (100 kN load cell; crosshead speed = 5 cm/min) was used to obtain Young’s modulus and yield stress at room temperature.

Notched Izod impact tests were prepared by injection molding according to ASTM D256 using a Morgan Press (Morgan Industries Inc.) and pellets of extruded blends (SSSP of the blend was followed by single-screw extrusion and pelletizing). Barrel zone and nozzle zone temperatures were 205 and 220 °C, respectively, for neat parent HDPE, SSSP-5%, SSSP-10%, and SSSP-20%; barrel and nozzle zone temperatures were 220 and 230 °C, respectively, for SSSP-30%, SSSP-40%, and SSSP-50%. Average impact bar dimensions were 3.2 × 12.7 × 63.5 mm; ten bars were tested for each sample. Notched Izod impact strength measurements were obtained at room temperature using an IT504 Tinuis Olsen impact tester.

3. Results and discussion

3.1. Dispersion of UHMWPE in UHMWPE/HDPE blends

Fig. 1 compares photographs of thin films (~0.3 mm thick) of Soln-5%, SSSP-5%, and MM-5%. Of the three films, only MM-5% shows clearly visible agglomerates of UHMWPE that are very poorly dispersed in the HDPE matrix, with some agglomerates being ~4 mm wide. Unlike MM-5%, neither Soln-5% nor SSSP-5% shows any discernible indication of UHMWPE agglomerates when viewed at this scale. Although there is no visible indication of agglomerates in SSSP-5%, this does not mean that blending via SSSP results in the same degree of mixing (i.e., mixing on the molecular glomerates in SSSP-5%, this does not mean that blending via SSSP viewed at this scale. Although there is no visible indication of agglomerates when ~4 mm wide. Unlike MM-5%, neither Soln-5% nor SSSP-5% shows any discernible indication of UHMWPE agglomerates when viewed at this scale. Although there is no visible indication of agglomerates in SSSP-5%, this does not mean that blending via SSSP results in the same degree of mixing (i.e., mixing on the molecular level but rather of effective dispersion of UHMWPE powder in the HDPE matrix. We provide further discussion on the implications of UHMWPE mixing via SSSP in later sections.

3.2. Shear and extensional viscosity of UHMWPE/HDPE blends: rheology characterization

A major concern for UHMWPE/HDPE blends is the effect of UHMWPE on blend viscosity and, consequently, melt processability of the blend. Fig. 3a compares magnitudes of complex viscosity (|η’|) of neat parent HDPE (as received), neat HDPE (after SSSP), SSSP-5% and Soln-5%. The neat parent HDPE and neat HDPE (after SSSP) samples exhibit nearly identical |η’| values at all frequencies, with the low frequency region (< 0.1 rad/s) at an approximate plateau indicative of zero-shear-rate viscosity response. From these results, it is evident that under the processing conditions used in this study, SSSP alone has negligible effects on the MW of HDPE, i.e., the SSSP processing of HDPE leads to no or negligible chain scission.

Fig. 3a also shows very strong effects of UHMWPE on Soln-5% blend dynamics, resulting in an extraordinarily pronounced shear thinning region at low frequency. Substantial deviations of |η’| values from those of neat HDPE occur because blend components of Soln-5% are mixed on a molecular level, allowing for the long relaxation times associated with UHMWPE to have very strong effects on blend dynamics. The effect of UHMWPE on SSSP-5% blend dynamics, though distinctly present, is markedly less than that observed for Soln-5%. The difference in the extent of the effect of UHMWPE on blend dynamics is easily explained by the degree of mixing between blend components: whereas solution blending results in dispersion on a molecular level, blending via SSSP results in good dispersion of UHMWPE but not in mixing on a molecular level. Therefore, despite the fact that no visible agglomerates of UHMWPE are observed in thin films of both Soln-5% and SSSP-5% (Fig. 1), oscillatory shear rheology data demonstrate that the degree of mixing achieved via a single pass of SSSP, though greatly improved over conventional melt mixing, is not identical to that achieved with solution blending. Attempts to obtain reproducible rheology data for MM-5% proved futile because of the substantial inhomogeneities associated with poor UHMWPE dispersion.

Fig. 3b shows |η’| values for neat HDPE (parent and after SSSP) and all SSSP blends. As the amount of UHMWPE in the blend increases, the effect of UHMWPE on blend dynamics increases as

![Fig. 1. Dispersion of UHMWPE in 5/95 wt% UHMWPE/HDPE blends prepared via solution blending (Soln-5%), SSSP (SSSP-5%), and melt mixing (MM-5%). Size bar = 2 mm in each image.](image)
well. Of particular importance is the effect of UHMWPE on viscosity in the high frequency region. Relatively small increases in $|\eta'|$ are observed for SSSP blends in this region; for example, SSSP-50% displays only a factor of 5 increase in $|\eta'|$ over that of neat HDPE at a frequency of 100 rad/s in comparison with more than a factor of 1000 increase in $|\eta'|$ at a frequency of 0.01 rad/s. According to the Cox-Merz rule [69], the shear rate ($\dot{\gamma}$) dependence of steady-state shear viscosity ($\eta$) is equal to the frequency ($\omega$) dependence of $|\eta'|$ (i.e., $|\eta'|(\omega) = \eta(\dot{\gamma})$; with $\omega = \dot{\gamma}$). Thus, with such moderate increases in $|\eta'|$ (or steady-state shear viscosity) at high frequencies (or shear rates), SSSP blends have the potential to be easily processed via post-SSSP melt extrusion where typical shear rates are generally exceed 100 s$^{-1}$ [70].

Another important feature observed in Fig. 3b for SSSP blends containing 10–50 wt% UHMWPE is the enhancement in viscosity with decreasing frequency at low frequency ($<0.1$ rad/s). This behavior is in contrast to the apparent zero-shear-rate viscosity regime observed for neat HDPE (as received and after SSSP). These increases in $|\eta'|$ at low frequency indicate the presence of relaxation processes occurring on very long time scales in the SSSP
blends. This slow relaxation behavior was also apparent during sample loading, where normal forces produced by squeezing the samples between rheometer plates caused the samples to not relax fully even after 30 min of annealing in the melt. The presence of these slow relaxation processes provides evidence that there is some degree of mixing of blend components on a molecular level. In other words, although UHMWPE has an ultrahigh viscosity, its presence in the blend is not as a simple solid-like filler, because solid fillers tend to cause increases in $\eta$ across the entire frequency range without resulting in shear thinning at low frequency. The type of low frequency behavior present in the SSSP blends has also been observed in systems with broad molecular weight distributions (particularly bimodal blends [71, 72]) and long-chain branching [73, 74]. Such increases in $\eta$ with decreasing frequency in the low-frequency region often provide an indication that a particular polymer system has the capacity to undergo strain hardening.

Strain hardening, which is generally probed by extensional rheology [67, 68], is an important characteristic for polymer systems that require high melt strength during processes such as blow molding, film molding, or thermoforming. Strain hardening is characterized as an increase in extensional viscosity ($\eta^e$) over the linear viscoelastic curve [75–78] and is associated with the capacity for a polymer to undergo homogeneous deformation during melt processes that require material extension or stretching [79, 80]. Strain hardening has been observed in bimodal blends [75, 76, 81]; the characteristic increase in $\eta^e$ with increasing time is attributed to the presence of components with distinctly different relaxation times [82], with higher MW components contributing to longer relaxation times [6, 83]. With respect to UHMWPE/HDPE blends, the vast viscosity mismatch between components accounts for very different relaxation times, with UHMWPE contributing extremely long relaxation times [6, 83]. Thus, it is not surprising that we observe strong strain hardening effects in SSSP-20% as shown in Fig. 4. Extensional viscosity data were unable to be collected for neat HDPE because of its low viscosity; neat parent HDPE and HDPE after SSSP had zero shear viscosities of ~3 kPa s, far below the 10 kPa s minimum requirement for testing with a Sentamanat Extensional Rheometer. However, previous research has shown that HDPE undergoes negligible strain hardening [84].

The linear viscoelastic envelope (LVE) shown in Fig. 4 was determined using a multimode Maxwell fit to oscillatory shear data and following Trouton’s relation for uniaxial extension ($\eta^e(t) = 3\eta^p(t)$, where $\eta^p$ is the linear viscoelastic transient shear viscosity upon flow inception). As seen in Fig. 4, there is a systemic difference between the LVE and $\eta^e$ at short times. This difference could be attributed to several factors. The first is the possibility that the SSSP-20% sample was not undergoing perfectly homogeneous uniaxial deformation during testing. Indeed, when sample dimensions were measured before and after testing, changes in width and thickness showed that the deformation did not follow expectations for homogeneous uniaxial elongation [85, 86]. Instead, sample deformation was intermediate between uniaxial and planar extension. Since the Trouton ratio in planar extensional flow is 4 rather than 3, this effect would lead to positive deviations in extensional viscosity data relative to linear viscoelastic predictions, as seen in Fig. 4, although the magnitude of deviation observed here cannot be fully explained in this way. Another possible explanation for the discrepancy between the LVE and $\eta^e$ is related to the interplay between sample preparation and the extremely long relaxation times of UHMWPE. Different sample preparation and loading protocols in oscillatory shear and extensional flow testing and the fact that none of these tests was likely performed on fully relaxed samples could contribute to this discrepancy [68, 83]. Regardless of these complexities, the strong strain hardening seen in Fig. 4 is consistent with the presence of a population of slowly relaxing molecules indicated by $\eta^e$ behavior at low frequencies.

### 3.3. Crystallization behavior of UHMWPE/HDPE blends: DSC characterization

Table 1 shows percent crystallinity ($x_{crys}$) for neat HDPE and UHMWPE/HDPE blends which was determined using Eq (1):

$$x_{crys} = \left( \frac{\Delta H_f}{\Delta H_{f0}} \right) \times 100\%$$

(1)

where $\Delta H_f$ is the sample enthalpy of fusion and $\Delta H_{f0}$ is enthalpy of fusion for 100% crystalline PE ($\Delta H_f = 293$ J/g [87]). From Table 1, a comparison between $x_{crys}$ and crystallization onset temperature ($T_{crys}$) values of neat parent HDPE and those of neat HDPE (after SSSP) shows that, under the conditions used in this study, SSSP alone has negligible effects on $x_{crys}$ and $T_{crys}$ of HDPE. Neat UHMWPE (as received) shows distinctly lower $x_{crys}$ and higher $T_{crys}$ values than neat HDPE. (See Table 1.) The difference in $x_{crys}$ is because of the extraordinarily entangled nature of UHMWPE chains [88, 89].

The effect of UHMWPE on $x_{crys}$ and $T_{crys}$ in blends provides some insight into the effectiveness of mixing. For blends with 5 wt% UHMWPE (i.e., MM-5%, SSSP-5%, and Soln-5%), the addition of UHMWPE results in negligible change in $x_{crys}$ for all three blends but notable increases in $T_{crys}$ only for SSSP-5% and Soln-5% (within error, no change was observed in $T_{crys}$ for MM-5%). Fig. 5a shows heat flow curves for non-isothermal crystallization of MM-5%, SSSP-5%, Soln-5%, and neat parent HDPE. The strong similarity between heat flow curves for MM-5% and neat parent HDPE implies that addition of UHMWPE has negligible effect on HDPE crystallization when the blend is prepared via melt processing. In contrast, heat flow curves for both SSSP-5% and Soln-5% show distinct effects of UHMWPE on HDPE crystallization and suggest co-crystallization of blend components [31, 90]. A magnification of the crystallization onset region shows a clear presence of

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![Fig. 4. Extensional viscosity at Hencky strain rates — 0.01, 0.03, and 0.10 s⁻¹ for SSSP-20%. The LVE was obtained using a multimode Maxwell model fit to oscillatory shear data (see Fig 3b). All data were collected at 150 °C.](image-url)
two crystallization peaks for MM-5%; the secondary peak is present as a small ‘hump’ and results from UHMWPE crystallizing separately from HDPE. The absence of this peak for both SSSP-5% and Soln-5%, coupled with the high $T_c$ values, provides compelling arguments for co-crystallization, which occurs as a result of the effective mixing achieved during SSSP. This observation also supports the presence of some degree of molecular level mixing between blend components in SSSP-5%.

Fig. 5b shows heat flow curves for all SSSP blends. As UHMWPE content increases, the width of the crystallization peak increases; this is associated with an increase in heterogeneity in dispersion [27]. For SSSP-30%, the heat flow curve shows a presence of more than one peak, representative of even greater heterogeneity in dispersion leading to regions that are richer in UHMWPE vs. regions that are leaner in UHMWPE. These heat flow curves demonstrate that as UHMWPE content increases in SSSP blends, the effectiveness of dispersion decreases. Data from Table 1 show that $T_c$ values remain invariant (within error) with increasing UHMWPE content for all SSSP blends. In contrast, $\chi_{crys}$ decreases with UHMWPE content of 20 wt% and higher. The decrease in $\chi_{crys}$ is explained by the effect of replacing large amounts of HDPE with UHMWPE, which crystallizes in the neat state to a much smaller extent than neat HDPE. Despite indications from non-isothermal crystallization data of decreasing effectiveness of dispersion with increasing UHMWPE content, the strongly increasing $|\gamma|$ values in the low frequency region suggest that blending via SSSP results in some degree of molecular level mixing even for blends with higher UHMWPE content.

3.4. Tensile and impact properties of UHMWPE/HDPE blends

A comparison between Young’s modulus ($E$) and yield stress ($\sigma_y$) for neat HDPE before and after SSSP demonstrates that under the processing conditions used in this study, SSSP has negligible effect on HDPE tensile properties (i.e., $E$ and $\sigma_y$ before and after SSSP are identical within error). For neat UHMWPE, $E$ is less than that of neat HDPE while $\sigma_y$ is greater than that of neat HDPE. The decrease in $E$ is closely related to the decrease in $\chi_{crys}$ while the increase in $\sigma_y$ is a consequence of the increase in chain entanglements and the presence of tie chains, which improve the drawability of the samples [90,91]. In Table 1 we show that $E$ is invariant for blends up to 30 wt% UHMWPE; the $\sigma_y$ values also undergo no change within error for blends up to 20 wt% UHMWPE. Beyond these compositions, additional UHMWPE results in decreases in $E$ and $\sigma_y$. Although the decreasing trend in $E$ could be explained by decreasing $\chi_{crys}$, the decreasing trend in $\sigma_y$ is more complicated and could be related to the decreased effectiveness of dispersion and poor wetting and/or little co-crystallization between blend components [90]. Further investigations are warranted to better understand the relationship between $\chi_{crys}$, MW, MW distribution, and mechanical properties in these UHMWPE/HDPE blends.

The effect of UHMWPE on the notched Izod impact strength values of UHMWPE/HDPE blends is of particularly great interest; the general expectation is that the addition of UHMWPE to a lower MW polymer will lead to increases in impact strength [29–32]. In Fig. 6, we show the effect of UHMWPE on the notched Izod impact strength of each SSSP blend. Each SSSP blend was first extruded using single-screw extrusion and then pelletized before being injection molded into impact bars, which were then notched according to ASTM standards (ASTM D256). The HDPE used in making our SSSP blends exhibited a notched Izod impact strength of 170 J/m in the neat state. This value lies near the high end of a range of 30–200 J/m typically reported for notched Izod impact strength of HDPE samples [92,93]. In addition to the effect of processing conditions, several other factors can affect the impact strength of UHMWPE/HDPE blends: the impact strength of the neat parent

![Fig. 5. Non-isothermal crystallization curves for (A) neat HDPE pellets (bold curve), MM-5% (dotted curve), Soln-5% (short-dashed curve), and SSSP-5% (long-dashed curve) and (B) all SSSP blends (SSSP-5%, SSSP-10%, and SSSP-20% are denoted with arrows while SSSP-30%, SSSP-40%, and SSSP-50% are shown as the dotted curve, short-dashed curve, and long-dashed curve, respectively).](image-url)
chain scission (leading to MW reduction), crosslinking, and/or unconventional processes that had low throughput and/or deleterious effects such as the formation of a blend with higher impact strength, this addi-
tional processing could lead to deleterious side effects during processing. In some cases, the processing that was used was harsh: in order to achieve good welding between UHMWPE and HDPE domains, Ahmad et al. [29] annealed samples under high temperature and pressure conditions for very long times. Such conditions may lead to MW reduction, branching, and crosslinking of HDPE [95,96]; the presence of significant levels of branched chains could also be responsible for the higher impact strength [92]. Although leading to high impact strengths, such harsh processing is unlikely to be used for large-scale production of UHMWPE/HDPE blends.

Unlike previous attempts to prepare well-mixed blends of UHMWPE and HDPE [29–32,42,49,50,97,98], SSSP presents a continuous, mild, and scalable approach for preparing well-mixed UHMWPE/HDPE blends that show major improvements in impact strength. While Boscoletto et al. [31], Lim et al. [32], and Ahmad et al. [29] demonstrated improvements in impact strength with UHMWPE addition to HDPE, all three studies were based on harsh and/or unconventional processes that had low throughput and could lead to deleterious side effects during processing. In some other studies [30,42,49,98], unusually low screw speeds (e.g., 20 rpm) and deliberately chosen neat parent HDPE with extremely low viscosity or high MFI (e.g., 20 g/10 min, ASTM D1238) were used in order to reduce pressure requirements for melt processing via twin screw extrusion. By taking advantage of the low processing temperature associated with SSSP, we are able to prepare well-mixed blends of UHMWPE and HDPE in a simple, mild, and continuous manner and without limitations related to the choice of MW for the neat parent HDPE. Additionally, because these SSSP blends are well-mixed, they can be easily processed by post-SSSP melt extrusion (as demonstrated in this study using a single-screw extruder).

3.5. Effect of processing on UHMWPE dispersion: DSC and rheology characterization

In order to study the effect of post-SSSP processing on blend properties, blends prepared via SSSP were melt extruded using a single-screw extruder. A comparison between non-isothermal crystallization heat flow curves before and after extrusion generally showed an improvement in UHMWPE dispersion after single-screw extrusion. Negligible effect of post-SSSP extrusion is observed for SSSP-5% (see Supporting Information). For SSSP-30% we observe that the heat flow curve smoothens into one uniform broad peak after single-screw extrusion as opposed to the several peaks that are present for the sample before extrusion (see Fig. 7). As previously explained, the presence of several peaks is a consequence of poor dispersion and the existence of regions that are either richer or leaner in UHMWPE. However, after single-screw
extrusion, the presence of one uniform, broad peak attests to the fact that the dispersion of UHMWPE is improved by post-SSSP melt extrusion.

Although no change (within error) is observed after single-screw extrusion of the SSSP-5% sample in non-isothermal DSC crystallization curves, oscillatory shear rheology data show significant improvement in mixing as demonstrated by increases in $\eta^*$ after post-SSSP single-screw extrusion (see Fig. 8a, SSSP-5%, P1, E1). To study how the dispersion of UHMWPE can be tuned, samples were subjected to a second pass of SSSP and extrusion: blends were first prepared via SSSP, extruded using a single-screw extruder, pelletized, processed a second time via SSSP, and then finally extruded again using a single-screw extruder. After the second pass of SSSP and extrusion, $\eta^*$ values of SSSP-5% increased and tended towards those of Soln-5% (see Fig. 8a, SSSP-5%, P2, E2). This effect indicates that by combining SSSP and single-screw extrusion we are able to tune the degree of dispersion towards the type of ideal dispersion demonstrated for Soln-5%, prepared by solution blending. Fig. 8b shows the effect of processing conditions on SSSP-30%: the degree of dispersion of UHMWPE is improved when SSSP-30% is single-screw extruded after the first pass of SSSP and improved further with the second pass of SSSP followed by single-screw extrusion. However, the increases in $\eta^*$ with additional processing for SSSP-30% are less dramatic than those for SSSP-5% because of the difficulty associated with dispersing such large quantities of UHMWPE in the blend.

Boscoletto et al. [31] demonstrated that improvements in UHMWPE dispersion resulted in improvements in impact strength for UHMWPE/HDPE blends. However, for SSSP blends, a second pass of SSSP (which results in further UHMWPE dispersion as demonstrated by rheology and non-isothermal crystallization) leads to no change in impact strength within error (see Supporting Information). This result may suggest that the degree of dispersion achieved by the first pass of SSSP alone is sufficient to achieve maximum impact strength for a given blend composition. As mentioned in the previous section, the effect of processing on impact strength could relate to observations made by Krishnaswamy and Yang [90] with respect to the possible need for both dispersion and some degree of segregation between UHMWPE and HDPE to achieve improvements in impact strength. Further studies are underway to help elucidate how the extent of UHMWPE dispersion can affect a range of mechanical properties.

4. Conclusion

We demonstrated that effective blending of UHMWPE/HDPE blends containing up to 50 wt% UHMWPE can be achieved using SSSP. Solid-state shear pulverization presents a continuous, mild, and scalable approach for preparing well-mixed UHMWPE/HDPE blends.
blends that can be easily processed by post-SSSP melt extrusion and demonstrate major improvements in impact strength. By preparing UHMWPE/HDPE blends via SSSP, we were able to circumvent processing constraints associated with viscosity mismatch, the major drawback to preparing effectively mixed UHMWPE/HDPE blends via conventional melt extrusion alone. For a blend prepared with 5 wt% UHMWPE via SSSP, we observed no visibly discernible agglomerates of UHMWPE in thin films of the blends (as was the case with a blend of similar composition prepared via solution blending). Additionally, as a result of the effective mixing achieved for both SSSP and solution-blended samples (each containing 5 wt% UHMWPE), non-isothermal crystallization data showed that blend components participated in co-crystallization. On the contrary, for a blend prepared by melt mixing and containing 5 wt% UHMWPE, easily visible UHMWPE agglomerates and no indication of co-crystallization were observed as a result of the poor dispersion of UHMWPE in the HDPE matrix.

In addition to demonstrating the absence of visibly discernible agglomerates of UHMWPE for all SSSP blends (up to 50 wt% UHMWPE), we showed that only modest increases in viscosity were observed at high shear rates (or frequencies), an indication that SSSP blends can be easily processed via post-melt extrusion. Using non-isothermal crystallization and oscillatory shear rheology, we showed the tunability of the degree of mixing, by coupling SSSP with single-screw extrusion: after a second pass of SSSP and single-screw extrusion, we observe improvements in the degree of mixing. Using extensional rheology, we also showed that SSSP blends have the capacity to undergo strain hardening; this observation was in good agreement with the pronounced shear thinning behavior at low shear rates (or frequencies) observed for all SSSP blends. Finally, we observed vast improvements in notched IZOD impact strength; for blends with 30–50 wt% UHMWPE, impact strengths of 660–770 J/m were achieved, a dramatic increase from the 170 J/m impact strength of the neat parent HDPE and very high relative to those reported in the literature.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.07.050.

References

As compared to injection molding, compression molding leads to better consolidation of UHMWPE and higher impact strength values for UHMWPE/HDPE blends. Additionally, as the molding time and pressure increases impact strength increases for bars molded by compression molding. The extremely long compression molding times used by Ahmad et al. (see Ref. [29]) can be correctly expected to lead to dramatic increases in impact strength. Unlike the study carried out by Ahmad et al. (see Ref. [29]), the impact bars for SSSP blends presented herein were prepared using a simple laboratory-scale injection molder, which provides no opportunity for UHMWPE consolidation during molding. Thus, we anticipate even higher values of impact strength for the SSSP blends (than those presented in this study) if the impact bars had been prepared using compression molding.

Using twin-screw extrusion, Li and coworkers [30,42] prepared UHMWPE/HDPE blends with up to 40 wt% UHMWPE using a low MW neat HDPE (MFI = 20 g/10 min at 190 °C) and an 80 rpm screw speed in order to improve processing feasibility. They demonstrated that by inducing the formation of shish-kebabs using oscillatory shear injection molding (OSIM) (a specialized approach to injection molding), they are able to prepare UHMWPE/HDPE blends with notched Izod impact strength ~43 kJ/m² for a 40/60 wt% UHMWPE/HDPE blend [42]. The neat parent HDPE had a notched Izod impact strength of ~6 kJ/m² when it was molded by conventional injection molding and ~16 kJ/m² when impact bars were molded by OSIM. [30] Li and coworkers [30,42] also show that, as compared to conventional injection molding, molding via OSIM results in blends with higher impact strength values. Nonetheless, the notched Izod impact strength values reported in our study are consistently greater than those reported for OSIM blends with UHMWPE content of 20 wt% or more [30,42].