Rice husk ash (RHA) is an agrowaste byproduct resulting from the incineration of rice husks for power production; white RHA is \( \sim 90 \) wt\% or more silica, which makes it a potentially sustainable and inexpensive substitute for commercial (less “green”) silica filler. Past research on polypropylene (PP)-RHA hybrids made by melt processing has yielded modest increments in Young’s modulus, reduced yield strength, and drastic reductions in elongation at break relative to neat PP. Using the industrially scalable solid-state shear pulverization (SSSP) process, PP-RHA hybrids are made with 4–38 wt\% RHA. As determined by microscopy and other methods, composites made by SSSP have much better RHA dispersion than composites reported in the literature made by twin-screw extrusion. The superior dispersion leads to major enhancements in tensile modulus (up to 100% increases relative to neat PP) while maintaining the yield strength of neat PP and remarkably high values of elongation at break (e.g., 520% at 19 wt\% RHA), far higher than composites made by melt processing. The properties of hybrids made by SSSP are competitive with and in some cases superior to those of PP hybrids made with commercial silica. The PP-RHA hybrids also exhibit major increases in hardness, approaching that of polycarbonate in the case of a 36 wt\% RHA hybrid. The 36 wt\% RHA hybrid exhibits solid-like rheology at low frequency. Nevertheless, all PP-RHA hybrids made by SSSP exhibit viscosities at moderate to high shear rates that are little changed from that of neat PP.

**INTRODUCTION**

Filler addition is a widely accepted method of enhancing polymer properties. Synthetic fillers, such as glass fibers, silica nanoparticles, graphene, and carbon nanotubes and nanofibers, have been studied extensively in the production of composites and nanocomposites [1–18]. Fillers derived from nature, in some cases with chemical modification, but non-biobased have also received much attention in the production of polymer hybrids; such fillers include graphite, thermally expanded graphite, organically modified clay, and fumed silica [9, 11, 18–23].

The thrust toward sustainable development and growing environmental concerns have prompted researchers to investigate approaches for replacing expensive synthetic fillers or chemically modified fillers from natural resources with less expensive fillers that are biobased, derived from natural resources, and without major chemical modification. Recent studies have focused on cellulose and lignocellulosic materials including wood flour, natural biobased fibers, and rice husks [24–35]. In addition to enhanced material properties, polymer composites containing cellulosic fillers may offer added benefits such as recycling of waste materials, low density, low cost, and reduced mechanical wear during processing [31, 36]. Rice husks, a major byproduct of the rice milling industry, contain cellulose, hemi-cellulose, lignin, and roughly 20 wt\% amorphous silica. Because of their high energy content, rice husks are often used as fuel in electric plants and boilers. The burning of rice husks leaves behind large quantities of agrowaste called rice husk ash (RHA), the disposal of which is considered a major environmental issue [37, 38]. Depending on combustion conditions, RHA contains 55–97 wt\% silica, primarily in amorphous form (opaline), with the remainder consisting of carbon that cannot be easily eliminated because it is trapped within the silica structure. Based on the amount of silica present, the ash is classified as either white RHA (WRHA), which is relatively high in silica content, or black RHA (BRHA), which is relatively low in silica content. The detailed characterization of RHA has been previously reported [36, 39–42].
Because of its very low cost (~US $0.04–0.10/kg [43, 44]) and high silica content, RHA has been studied as a filler in synthetic and natural elastomers [36, 42, 45–48] and thermoplastics [49–56]. Regarding elastomers, there is major interest in using RHA in place of more expensive and “less green” silica as filler in tires. Although silica is derived from sand, it requires additional processing to be useful for incorporation in tires, where the presence of appropriately dispersed silica reduces rolling resistance and improves wet grip. As reported in January 2013 in The Economist, an Italian tiremaker is setting up a Brazilian factory that will extract both power and RHA from rice husks; it is estimated that by 2015 the factory will provide almost one-third of the silica-based filler the tiremaker needs for the 400,000 tons of tires it makes annually in Brazil [57]. Regarding thermoplastics such as polypropylene (PP), studies have reported mixed results for RHA composites made by melt processing [39, 54, 56]. For example, Siriwardena et al. [54] observed a 77% increase in tensile modulus relative to neat PP in PP composites with 29 wt% RHA; however, the PP composites exhibited major reductions in elongation at break, from 766% for neat PP to 194% in composites with 9 wt% RHA and 29% in composites with 17 wt% RHA. Reviews of previous polymer-RHA composite studies are found in Refs. [36] and [40].

The apparently poor adhesion between the hydrophilic RHA filler and the hydrophobic PP matrix has been cited as a major contributor to the poor performance of RHA as a filler and the major reduction in elongation at break relative to neat PP [39, 50, 54, 56]. Surface modifiers and coupling agents have been used in an attempt to improve RHA dispersion and adhesion in PP, in some cases enhancing mechanical properties compared to unmodified RHA [50]. Such coupling agents involve additional chemistry, increasing the cost and reducing the “green” nature of RHA, and can result in deterioration of properties like Young’s modulus [50], thus defeating the purpose of cost-effective, synergistic, and environmentally friendly composites.

Here, we have used a continuous, industrially scalable process called solid-state shear pulverization (SSSP) [12, 20, 21, 58–66] to overcome difficulties encountered with producing well-dispersed, synergistic PP-RHA composites. Although the current study has used a pilot-plant/research-scale apparatus, polyolefins have been processed by SSSP at Northwestern University with a commercial-scale apparatus at rates exceeding 150 kg/h. This process uses a modified twin-screw extruder in which the materials are cooled rather than heated so that the polymers are processed at temperatures below their glass transition temperature, if amorphous, or melt transition temperature, if semicrystalline. Because the materials are processed in the solid state during SSSP, they can be exposed to much higher levels of shear stresses and compressive forces than experienced in a conventional twin-screw melt extruder. When sufficient mechanical energy is absorbed by the material during SSSP, the material fragments is fused together randomly again in the process. This fragmentation and fusion process is repeated many times during the several-minute average residence time within the pulverizer. As a result, SSSP can be used to fabricate well-exfoliated and/or well-dispersed, synergistic nanocomposites [12, 20, 21, 59, 67], with fillers ranging from layered sheet structures such as clays [59] and as-received graphite [20, 21] to entangled agglomerates such as carbon nanotubes [12]. In addition, SSSP yields improved dispersion over melt mixing in the production of PP-starch composites [60] and can produce nanostructured polymer blends in which the dispersed phase approaches 100 nm in diameter [61]. In some cases, SSSP yields in situ blend compatibilization [62, 63] by producing small levels of block copolymer; small levels of chain scission during SSSP result in polymeric radicals that can recombine at blend interfaces leading to block copolymer formation [64]. Recently, PP has been functionalized with maleic anhydride by SSSP without the severe molecular weight reduction that accompanies functionalization by reactive melt extrusion, which is the process used commercially for functionalizing PP [66].

In particular, we have used SSSP to effectively disperse 4–38 wt% RHA in PP. For comparison, composites with 5 and 10 wt% RHA were made by melt mixing. The morphological, mechanical, crystallization, thermal degradation, and rheological properties of the hybrids made by SSSP and by melt mixing are compared, demonstrating the good dispersion of RHA achieved by SSSP and the importance of that dispersion in enhancing properties. Comparisons are made with properties reported in the literature for PP-RHA composites made by melt processing, which show the superior outcomes by SSSP. Comparisons are also made with properties reported in the literature for composites made by melt processing with commercial silica. These comparisons suggest that composites made by SSSP with nearly zero-cost RHA may be highly competitive with those made by melt processing with more expensive, less green silica.

**EXPERIMENTAL**

**Materials**

PP (Total Petrochemicals, 0.905 g/cm³ density, MFI = 2.0 g/10 min at 230°C/2.2 kg, as reported by the supplier) and polycarbonate (Bayer, 1.2 g/cm³, MFI = 4.5 g/10 min at 300°C/1.2 kg, as reported by the supplier) were used as received. Unmodified WRHA (N.K. Enterprises, India; 2.3 specific gravity, 25 μm average particle size, and 91 wt% silica, as reported by the supplier) was used as received.

**Preparation of PP-RHA Composites**

PP pellets and varying amounts of RHA (nominally 5, 10, 20, 30, and 40 wt%) were manually dry blended and...
fed to a Berstorff ZE-25P SSSP apparatus using a K-tron Sodron S-60 feeder. The pulverizer has a section with a 25 mm diameter barrel followed by a second section with a 23 mm diameter barrel. Between these two sections is a small transition zone in which the barrel diameter decreases from 25 to 23 mm. The 25 mm section contained spiral conveying and bilobe kneading elements (mixing zone), resulting in mixing between the PP and RHA. The 23 mm section contained trilobe shearing elements, which is where the bulk of the pulverization was done on the PP/RHA hybrids. It should be noted that, depending on the motor running the screw, SSSP can be done using strictly bilobe elements [65]. Additionally, regardless of the use of bilobe or a mix of bilobe and trilobe non-conveying screw elements, SSSP can also be done with all sections of the instrument using a 25 mm diameter barrel.

The barrels of the SSSP instrument were cooled by a recirculating ethylene glycol/water mix at \(-7^\circ\text{C}\) supplied by a Budzar Industries WC-3 chiller. A screw design imparting relatively high levels of specific energy input [65] to the polymer hybrid was used, with the mixing zone containing one reverse, two neutral, and three forward kneading elements and the pulverization zone containing three forward, two neutral, and two reverse shearing elements. Samples were processed at a screw speed of 200 rpm, yielding a fine powder output [65].

Melt-mixed composite samples were prepared at 200°C for 15 min in a cup-and-bob rotor mixer (Atlas Electronic Devices MiniMax molder) at maximum rotor speed of 160 rpm with three steel balls in the cup to provide chaotic mixing [68]. Samples with RHA loadings exceeding 10 wt% were unable to be prepared by melt mixing with this small-scale mixing apparatus.

Characterization

Field-emission scanning electron microscopy (FE-SEM) samples were prepared by melt extrusion at 200°C via the MiniMax molder. The morphologies of RHA and cryofractured sections of PP-RHA composites made by SSSP and by melt mixing were obtained via a Hitachi cryofractured sections of PP-RHA composites made by SSSP, samples processed with nominally 5, 10, 20, 30 and 40 wt% RHA were characterized by thermogravimetric analysis and found to contain 4, 10, 19, 29 and 20, 30 and 40 wt% RHA, respectively. A minimum of three samples per composition were analyzed, showing excellent reproducibility. Neat PP left behind no measurable residue at 700°C.

Rheological behavior was characterized using a TA Instruments ARES rheometer with a 25 mm parallel plate fixture at 200°C. Test samples were prepared using compression molding and the procedure described above for tensile and hardness test samples. Small-amplitude oscillatory shear measurements were done as a function of frequency from 0.01 to 100 rad/s.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows a typical FE-SEM image of as-received RHA after light sonication for 30 min in an attempt to reduce agglomerates to individual particles. The micrograph shows particles and agglomerates in the size range of 1–100 μm. RHA exhibits strong interparticle attraction because of silanol groups on the surface that
render RHA particles hydrophilic. The hydrophilic nature of the RHA surface has been given as a reason for the major difficulty in dispersing agglomerates by conventional melt processing, e.g., twin-screw extrusion [50].

Figure 2a and b shows pictures of a PP5RHA composite prepared by melt mixing and a PP4RHA composite prepared by SSSP, respectively. (The naming convention for the composite PP5RHA means that the composite contains 5 wt% RHA based on thermogravimetric analysis of RHA content in the composite.) Melt mixing results in PP5RHA hybrids that contain WRHA agglomerates, some approaching 1 mm in size and visible to the naked eye, that are poorly dispersed in the PP matrix. In contrast, PP4RHA composites prepared by SSSP exhibit a uniformly black color consistent with very good RHA dispersion. These conclusions are supported by FE-SEM micrographs that show the presence of ~30–50 μm size RHA particles/agglomerates in samples made by melt mixing (Fig. 3a) and RHA particles of 1–10 μm size in the hybrid made by SSSP (Fig. 3b). Both simple visual inspection and electron microscopy of the composites demonstrate the effectiveness of SSSP in dispersing RHA in polymer, thereby overcoming the issue of poor RHA dispersion that accompanies melt processing.

**Mechanical Properties—Tensile**

Table 1 summarizes the effect of RHA content on the mechanical properties of PP-RHA composites produced by SSSP. The Young’s modulus increases with RHA content, exhibiting a 50% increase over neat PP for PP19RHA and a 100% increase for PP38RHA. The yield strength of composites produced by SSSP is nearly invariant with RHA content. Relative to neat PP, PP10RHA exhibits a 4% increase in yield strength and PP38RHA exhibits an 8–9% decrease. Within error, the composites retain the neat PP elongation at break of 740% up to 10 wt% RHA content. The PP19RHA composite exhibits 520% elongation at break, and the PP29RHA composite remains ductile with 70% elongation at break.

Figure 4 compares the Young’s modulus of the composites made by SSSP and by melt mixing in this study. With melt-mixed samples, only two RHA loadings are shown; the small-scale melt-mixing apparatus used in this study did not yield consolidated samples at RHA content above 10 wt%. The melt-mixed composites with up to 10 wt% RHA filler exhibited a Young’s modulus that was unchanged or increased by less than 10% relative to neat PP. In contrast, PP10RHA made by SSSP exhibited a 28% increase in Young’s modulus, which is indicative of the important role of RHA dispersion in improving properties.

In a similar vein, comparison with literature data for PP-RHA composites made by melt processing shows that SSSP results in better properties. Turmanova et al. [56]...
reported that PP-RHA hybrids with 20 wt% RHA resulted in a 22% increase in Young’s modulus and a 14% decrease in yield strength, values that are far worse than those for the PP19RHA hybrid made by SSSP (50% increase in Young’s modulus and 2% decrease in yield strength, as shown in Table 1). Siriwardena et al. [54] reported that PP-RHA hybrids with 29 wt% RHA exhibited a 56% increase in Young’s modulus and a 27% reduction in yield strength, values that are not as good as those for the PP29RHA hybrid made by SSSP (64% increase in Young’s modulus and 5% decrease in yield strength as shown in Table 1). Finally, Fuad et al. [49] reported 20–37% reductions in yield strength for PP-RHA composites with 18–39 wt% RHA, which compare unfavorably with the 2–8% reductions in yield strength for PP-RHA composites made by SSSP with 19 to 38 wt% RHA.

As shown in Fig. 5, the most dramatic deterioration in the properties of PP-RHA composites made by melt processing is in elongation at break. For the melt-mixed composites made in the current study, the elongation at break decreased from 740% in neat PP to ~250% (with a high degree of sample-to-sample variability associated with variable RHA dispersion) and 7% for PP5RHA and PP10RHA, respectively. In contrast, over this range of RHA content, the composites made by SSSP exhibited essentially the same elongation at break as neat PP. Poor outcomes were also reported for elongation at break in literature studies for PP-RHA hybrids made by conventional twin-screw melt extrusion or melt mixing. At 17–20 wt% RHA, elongation at break was reported as 127% [49], 29% [54], and 20% [56], factors of 4–26 smaller than the 520% elongation at break obtained in the PP19RHA sample made by SSSP. At ~10 wt% RHA, literature reports of elongation at break in samples made by melt processing were 40% (a factor 13 to 14 reduction from the neat PP value of 598%) [56] and 194% (a factor of nearly 4 reduction from the neat PP value of 766%) [54]. In contrast, PP10RHA made by SSSP had an elongation at break unchanged from that of neat PP. We believe that the superior dispersion and particle size reduction of

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus $E$ (MPa)</th>
<th>Yield strength $\sigma_p$ (MPa)</th>
<th>Elongation at break $\varepsilon_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP, pellet</td>
<td>900 ± 50</td>
<td>28.0 ± 0.2</td>
<td>740 ± 40</td>
</tr>
<tr>
<td>PP4RHA</td>
<td>980 ± 20</td>
<td>28.6 ± 0.6</td>
<td>750 ± 50</td>
</tr>
<tr>
<td>PP10RHA</td>
<td>1,150 ± 40</td>
<td>29.1 ± 0.2</td>
<td>700 ± 40</td>
</tr>
<tr>
<td>PP19RHA</td>
<td>1,350 ± 40</td>
<td>27.4 ± 0.5</td>
<td>520 ± 70</td>
</tr>
<tr>
<td>PP29RHA</td>
<td>1,480 ± 60</td>
<td>26.6 ± 0.4</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>PP38RHA</td>
<td>1,810 ± 70</td>
<td>25.6 ± 0.3</td>
<td>10 ± 1</td>
</tr>
</tbody>
</table>

Note: Reported errors are one standard deviation.

FIG. 3. Field-emission scanning electron micrographs of (a) PP5RHA prepared by melt mixing and (b) PP4RHA prepared by SSSP. [size bar = 20 μm in (a) and (b).]
RHA achieved via SSSP may explain the major improvement in elongation at break compared to composites prepared by melt processing techniques. Similar behavior has also been observed with PP-graphite nanocomposites made by SSSP [20, 21].

We note that at the two highest loadings, 29 and 38 wt% RHA (15 and 20 vol% RHA), in this study, there is a transition from highly ductile behavior, with elongation at break of 70%, to barely ductile behavior, with elongation at break of 10% just after the yield point. The loss of ductility is likely due to the 38 wt% RHA hybrid forming a percolated network even with the excellent dispersion of RHA that accompanies SSSP processing. Support for the percolated network formation is provided in discussion of rheological behavior below.

In any case, the superior agglomerate breakup and dispersion achieved by SSSP results in a 50% enhancement in modulus and significant retention of yield strength and elongation at break of PP-RHA composites up to ~19 wt% RHA content. In contrast, at the same RHA content, melt processing leads to hybrids with limited enhancement of modulus and significantly degraded yield strength and elongation at break. Furthermore, SSSP allows for the production of PP-RHA composites at 29 wt% filler with yet greater improvement in modulus, almost no loss of yield strength, and retention of ductility with a 70% elongation at break. These properties can be achieved in SSSP-processed hybrids without any chemical modification of the RHA surface. We note that chemical modification has been previously suggested [50] as being important for good adhesion between the hydrophobic PP and hydrophilic RHA. Our results indicate that optimal dispersion may be more important than optimal interfacial interactions in the preparation of synergistic PP-RHA composites.

Given the superior performance of PP-RHA composites made by SSSP, it is also important to consider how the composites perform in comparison with those made with commercial silica. Given that WRHA is very low cost and contains more than 90% silica and given the environmental benefit of reusing a waste product like RHA for value-added products, there is commercial interest in substituting RHA for more costly silica fillers in polymer composites [57]. Previous studies [54, 56] comparing unmodified RHA fillers with commercial-grade silica fillers in thermoplastics have shown that RHA dramatically underperformed. Table 2 compares literature results for PP-silica composites made by melt processing with those obtained here for PP-RHA composites made by SSSP. Both silica and RHA filler improve tensile modulus significantly, although greater improvements are observed with silica. For example, at 17 wt% silica, modulus increases by 62% [54], slightly above the 50% increase obtained with 19 wt% RHA. A greater difference is observed at 29 wt% filler, where silica and RHA result in increases in modulus of 119% [54] and 64%, respectively. However, the RHA composites made by SSSP exhibit vastly superior elongation at break, with the silica-filled systems exhibiting brittle behavior at all compositions [54]; at the same filler compositions, the RHA composites remain highly ductile. The PP-RHA composites made by SSSP also exhibit superior elongation at break in comparison with PP-silica nanocomposites made by dispersing nanosilica via melt processing. Liu and Kontopoulou [70] reported a 29% decrease in elongation at break at 5 wt% loading of Aerosil 200 nanosilica while PP10RHA made by SSSP exhibited only a 5% reduction in elongation at break. Finally, the PP-RHA composites exhibit slightly less degradation of yield strength than the silica composites. Given the fact that RHA is far less expensive than fumed silica or nanosilica and is viewed as a more green filler, this comparison indicates that thermoplastic-RHA composites made by SSSP may have

![FIG. 5. Elongation at break of PP-RHA composites: (△) made by SSSP in this study, (X) made by melt mixing in this study, (○) from Ref. [49], (○) from Ref. [54], and (○) from Ref. [56]. (Note: The data from Refs. [49] and [54] were obtained at much slower crosshead speeds than in this study.)](image-url)

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Increase in Young’s modulus</th>
<th>% Change in yield strength</th>
<th>% Decrease in elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica filled PP [54]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-9 wt% silica</td>
<td>46</td>
<td>-2</td>
<td>99.3</td>
</tr>
<tr>
<td>PP-17 wt% silica</td>
<td>62</td>
<td>-6</td>
<td>99.6</td>
</tr>
<tr>
<td>PP-23 wt% silica</td>
<td>83</td>
<td>-10</td>
<td>99.7</td>
</tr>
<tr>
<td>PP-29 wt% silica</td>
<td>119</td>
<td>-12</td>
<td>99.8</td>
</tr>
<tr>
<td>RHA filled PP (SSSP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP10RHA</td>
<td>28</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>PP19RHA</td>
<td>50</td>
<td>-2</td>
<td>29</td>
</tr>
<tr>
<td>PP29RHA</td>
<td>64</td>
<td>-5</td>
<td>90</td>
</tr>
<tr>
<td>PP38RHA</td>
<td>101</td>
<td>-8</td>
<td>98</td>
</tr>
</tbody>
</table>

Changes are reported relative to neat PP.
advantages in selected applications over thermoplastic-silica composites made by conventional processing.

**Mechanical Properties—Hardness**

A major increase in hardness accompanies the increase in modulus with the SSSP-based incorporation of RHA into the PP matrix. Figure 6 compares Vickers hardness values for various PP-RHA composites made by SSSP with polycarbonate, a thermoplastic renowned for its hardness. The incorporation of RHA into PP increases the hardness, even at only 4 wt% loading. The PP29RHA composite has a Vickers hardness that is 28 MPa higher than that of neat PP. The PP38RHA composite has a Vickers hardness that is 48 MPa higher than that of neat PP and only 13 MPa below that of polycarbonate. These results indicate that well-dispersed PP-RHA composites made by SSSP can be very effective in not only greatly enhancing modulus while maintaining ductility, but also tunably increasing hardness toward that of polycarbonate, an engineering thermoplastic of much higher cost than PP.

**Crystallization Behavior**

Further proof of the synergy provided by the good filler dispersion in the SSSP-based PP-RHA composites is provided by crystallization behavior. Figure 7 shows non-isothermal crystallization curves obtained at 10°C/min cooling rates for neat PP and the PP19RHA composite made by SSSP and demonstrates a shift in crystallization onset and peak temperatures to higher temperature in the composite. Table 3 summarizes the effect of RHA content on the PP crystallization kinetics, including the non-isothermal crystallization onset temperature, $T_{c, onset}$. The $T_{c, onset}$ value increases by 4–10°C as RHA content increases from 4 to 38 wt%. This behavior is qualitatively consistent with what has been reported in other PP composites and nanocomposites made with a variety of well-dispersed fillers or nanofillers and arises from the fact that the PP-filler interface serves as a site for heterogeneous nucleation of crystals [12, 17, 20]. No change in $T_{c, onset}$ was observed in the 10 wt% PP-RHA hybrid made here by melt mixing, which is consistent with the poor filler dispersion accompanying melt processing. That result is also consistent with literature data on PP-RHA hybrids made by twin-screw melt extrusion which exhibited no significant enhancement in $T_{c, onset}$ [51].

Isothermal crystallization curves measured by DSC at 140°C are shown in Fig. 8. Isothermal crystallization half-times derived from these curves are listed in Table 3 and show a monotonic reduction in half-time with increasing RHA content. Consistent with the high PP crystallizability, Table 3 also shows that the PP crystallinity level, as determined from the non-isothermal crystallization peak area, is nearly invariant with RHA content.

**Thermal Degradation**

Figure 9a compares thermal degradation behavior of neat PP and PP in the composites made by SSSP. In the

![FIG. 6. Vickers hardness values for (a) polycarbonate, (b) neat PP, (c) PP4RHA, (d) PP10RHA, (e) PP19RHA, (f) PP29RHA, and (g) PP38RHA. (Note: The maximum one standard deviation error bar is ±2 MPa. Error bars are too small to include in the figure.)](image1)

![FIG. 7. Non-isothermal (10°C/min) crystallization curves for neat PP and PP19RHA composite made by SSSP.](image2)
case of the composites, the % mass loss is based only on the PP in the composite, not the total composite mass. (As shown in Fig. 9b, RHA is thermally stable with no mass loss up to 700°C.) Neat PP shows almost no mass loss up to 350°C and about 5% mass loss at 395°C. The temperature at 5% PP mass loss is taken here as the onset degradation temperature, \( T_{\text{deg}} \). The presence of well-dispersed RHA in the PP-RHA composites made by SSSP dramatically increases the thermal stability of PP. The PP4RHA composite exhibited a 28°C increase in \( T_{\text{deg}} \) relative to neat PP. The maximum \( T_{\text{deg}} \) was obtained in the PP10RHA composite, with a 43°C increase in \( T_{\text{deg}} \) relative to neat PP. In contrast, in the 5 and 10 wt% RHA composites made by melt mixing (data not shown), \( T_{\text{deg}} \) increased by only 5 and 10°C, respectively. Similarly, relative to neat PP, Fuad et al. [51] reported only a 2–3°C increase in the thermal stability of PP-RHA composites made by twin-screw melt extrusion. These results indicate that the very good RHA dispersion achieved by SSSP is strongly correlated to the enhancement of composite thermal stability.

Figure 9b and Table 4 report the final RHA residue and \( T_{\text{deg}} \) in each PP-RHA composite made by SSSP. With composites made by SSSP, the small decreases in \( T_{\text{deg}} \) with increasing RHA content above 10 wt% may have occurred because slightly less dispersion was achieved at higher filler contents. Related conclusions have been reached about decreasing levels of dispersion with higher nanofiller content in PP-graphite nanocomposites made by SSSP [21]. The vastly enhanced thermal stability of PP-RHA composites made by SSSP is likely due to the well-dispersed ash acting as a thermal insulating barrier that protects the PP from degradation.

**Rheology**

Figure 10 shows the magnitude of complex viscosity and shear storage modulus at 200°C as a function of frequency for neat PP before SSSP and neat PP, PP19RHA, PP29RHA and PP38RHA after SSSP processing. Based on the Cox-Merz rule related to the equivalency of frequency in oscillatory shear measurements and shear rate in simple shear flow experiments [71], Fig. 10a is equivalent to a plot of shear viscosity as a function of shear rate. Neat PP shows a decrease in viscosity after SSSP processing which can be explained by very small levels of flow.

**TABLE 4.** Thermal degradation behavior of neat PP and PP-RHA composites prepared by SSSP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature for polymer degradation( T_{\text{deg}} ) (°C)</th>
<th>RHA content in composite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP, pellet</td>
<td>395</td>
<td>0</td>
</tr>
<tr>
<td>PP4RHA</td>
<td>423</td>
<td>4</td>
</tr>
<tr>
<td>PP10RHA</td>
<td>438</td>
<td>10</td>
</tr>
<tr>
<td>PP19RHA</td>
<td>434</td>
<td>19</td>
</tr>
<tr>
<td>PP29RHA</td>
<td>433</td>
<td>29</td>
</tr>
<tr>
<td>PP38RHA</td>
<td>427</td>
<td>38</td>
</tr>
</tbody>
</table>

\*Reported as temperature corresponding to 5% loss in PP mass.
of chain scission and molecular weight reduction that occur during SSSP. The small effects of SSSP on PP viscosity and molecular weight have been described in detail in Refs. [62] and [65].

It is noteworthy that the PP19RHA and PP29RHA composites exhibit viscosities and storage moduli that are only slightly higher than those of neat PP (before SSSP) for all frequencies or shear rates greater than 1 s\(^{-1}\). In contrast, the PP38RHA hybrid exhibits much higher viscosity and shear storage modulus at all frequencies (or shear rates) tested, especially at low frequency. In particular in the low frequency region PP38RHA shows a much weaker frequency dependence of shear storage modulus which is consistent with a change in the nature of rheological response from liquid-like for PP, PP19RHA and PP29RHA to more solid-like for PP38RHA. Furthermore, both the viscosity and storage modulus responses of PP38RHA are characteristic of a composite with fillers that form a percolated network [21, 72, 73] within the polymer matrix. Even with the superior ability of SSSP to disperse fillers within a polymer matrix, the dispersion achieved by SSSP may invariably lead to a percolated network when the filler constitutes a large volume fraction of the composite. In the case of PP38RHA, the composite is 20 vol% RHA.

Because of the very good dispersion of RHA filler in the PP composites made by SSSP, the shear flow behavior is modified relatively little by incorporation of as much as 29 wt% RHA. Even with the 38 wt% RHA composite, the viscosity is only about a factor of 3 higher than that of neat PP at shear rates of 100 s\(^{-1}\) commonly found in conventional melt processing techniques like twin-screw extrusion and injection molding. These results indicate that PP-RHA composites made by SSSP with RHA contents ranging as high as 38 wt% can be melt processed relatively easily into final products.

**SUMMARY**

The SSSP process was used for the first time to produce synergistic PP-RHA hybrids with 4 to 38 wt% RHA. As shown by electron microscopy, thermal degradation (with a maximum 43°C increase in \(T_{\text{deg}}\) in a PP-RHA hybrid relative to neat PP) and crystallization studies and by comparison with the research literature, SSSP can achieve RHA dispersion levels that have not been attained by conventional melt processing. Relative to neat PP, the well-dispersed PP-RHA composites made by SSSP exhibit major enhancements in tensile modulus (increasing by 50% at 19 wt% RHA and 100% at 38 wt% RHA) while maintaining almost the same yield strength as neat PP and exhibiting remarkable ductility (with elongation at break of 520% at 19 wt% RHA and 70% at 29 wt% RHA, far beyond the values reported for melt-mixed composites). These properties are dramatically better than those reported in previous studies that produced PP-RHA hybrids by melt processing [49, 54, 56]. The hybrids made by SSSP also undergo major increases in hardness with increasing RHA content; the hybrid with 38 wt% RHA exhibits a 48 MPa increase in Vickers hardness above that of neat PP and is within 13 MPa of the Vickers hardness of polycarbonate. Because RHA was used without surface modification, these results indicate that optimal dispersion may be more important than optimal interfacial interactions in preparing synergistic PP-RHA hybrids.

The PP-RHA hybrids produced by SSSP also exhibit performance rivaling or better than that of PP hybrids made by melt processing with more expensive, less green commercial silica. The PP-RHA hybrids show modulus enhancements less than but approaching those of the PP-silica composites (50 to 101% increases in modulus for 19 to 38 wt% RHA as compared with 62 to 119% increases for 17 to 29 wt% silica [54]). More impressively, the PP-RHA hybrids show a slight advantage in yield strength (2 to 8% reductions relative to neat PP for 19 to 38 wt% RHA compared with 6 to 12% reductions for 17 to 29 wt% silica [54]) and dramatically better ductility and elongation at break (the PP-silica hybrids fractured at 1 to 5% strain [54]).
At low frequencies, the 38 wt% RHA hybrid exhibits solid-like rheological behavior that is consistent with the presence of a percolated RHA network. However, at shear rates that are commonly present in twin-screw extrusion and injection molding, each hybrid exhibits little change in viscosity relative to neat PP, which indicates that the hybrids can be easily melt processed into final products. The combination of major property enhancements derived from SSSP-based filler dispersion, performance that is competitive with more expensive and less green hybrids, easy processing of hybrids into final products, and industrial scalability of the process used to produce the hybrids make SSSP a strong candidate for potential commercial production of RHA composites with PP and other polymers. Studies are underway with this goal in mind.

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