Importance of superior dispersion versus filler surface modification in producing robust polymer nanocomposites: The example of polypropylene/nanosilica hybrids

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ABSTRACT

With polymer nanocomposites, achieving highly effective dispersion of agglomerated nanofiller and major or optimal property enhancements remain challenges. A commonly posited solution is to improve the polymer-filler surface thermodynamic compatibility; this approach has led to significant improvements in some cases, but it has not provided a general solution. We address the question of whether achieving a metastable, well-dispersed state is better than compatibilization in attaining the goal of major property enhancements. We use solid-state shear pulverization to produce well-dispersed polypropylene (PP) nanocomposites with up to 8 or 9 wt% pristine nanosilica (p-NS) or organically modified nanosilica (m-NS). Microscopy shows that as-received, tens-of-micron-sized p-NS and m-NS agglomerates undergo very good dispersion, with ~10–100 nm size-range nanofiller in hybrids. Rheology is consistent with very good dispersion, with only 92/8 wt% PP/p-NS indicating incipient nanofiller network formation. The PP/p-NS hybrids have superior Young’s modulus and tensile strength. Relative to PP, modulus increases by 22% and 12% and tensile strength by 19% and 14% for 99/1 wt% PP/p-NS and 99/1 wt% PP/m-NS, respectively. The PP/p-NS hybrids have the largest increases in modulus (46% at 8 wt% p-NS) and tensile strength (22% at 6 wt% p-NS). Upon melting and crystallization, both PP/p-NS and PP/m-NS result in PP β-crystal formation at 1 wt% nanosilica, with p-NS having a greater effect. The PP/p-NS hybrid shows larger increases in thermal stability and nucleating efficiency for PP crystallization. Thus, with very good dispersion, unmodified nanofiller in a metastable dispersed state can result in more robust nanocomposites than when modified nanofiller is used to compatibilize the polymer–nanofiller interface.

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1. Introduction

The pioneering work on Nylon 6/layered silicate nanocomposites by Toyota researchers [1] more than twenty years ago has inspired extensive research aimed at achieving major property enhancements in polymer nanocomposites. With regard to polyolefin nanocomposites, research with various nanofillers [2–39] has often led to property improvements but, in many cases, to disappointing outcomes relative to expectations. As noted in numerous review articles, fabrication of robust nanocomposites with relatively homogeneous (or very good) nanofiller dispersion remains a key challenge [40–50]. In 2009 a summary article on a polymer science and engineering workshop stated, “The property advantages offered by (organic/inorganic) hybrid materials has stimulated huge activity in this area, but processing, for example, even to produce something as conceptually simple as a homogeneous dispersion of nanoparticles has proven remarkably difficult.” [51] With some exceptions, progress has been slow on this issue.

The challenge of nanofiller dispersion has several origins. The enormous surface-to-volume ratio and attractive interparticle interactions ranging from relatively strong, e.g., hydrogen bonding, to relatively weak, e.g., van der Waals interactions, lead to nanofiller being heavily agglomerated before mixing with polymer. Conventional melt processing imparts limited stresses that are usually insufficient to achieve excellent nanofiller dispersion in polymer. Other research strategies used to achieve relatively homogeneous
dispersion such as solvent processing and in situ polymerization are not industrially scalable or are commercially unattractive and have exhibited severe limits to nanofiller levels that can be effectively dispersed [13.52–59].

Some researchers have hypothesized that very good dispersion and optimal property enhancements can be achieved in a general way by chemically modifying the nanoparticle surface (and/or the polymer chemical structure) in order to make the filler more compatible with polymer [40–50.60]. It is interesting that the posited solution to the problems of dispersion and property enhancements is based on thermodynamics as complex polymer materials “are frequently used, through advanced processing, in non-equilibrium structures, the vast majority of which are in metastable states.” [51] The thermodynamic approach to overcome limited dispersion and nanocomposite property enhancement has led to success in some cases [4–8], partial improvement in other cases [19–22], and null results or failure in yet other cases [23–27].

Some of the disappointing outcomes result from property degradation associated with modification used to improve thermodynamic compatibility. For example, a number of studies of polyolefin nanocomposites have employed maleic anhydride grafted polyolefin as a compatibilizer, chemical modification of nanosilica or both organo-modifying groups, e.g., amine, silane, and polymer grafting, of a combination of the two approaches [25,40,41]. In order to overcome poor dispersion in polypropylene (PP)/clay hybrids prepared by melt mixing, Hasegawa et al. [9] used maleic anhydride-modified polypropylene (PP-g-MAH) and octadecylamine-functionalized clay. While they observed significantly better clay exfoliation and dispersion, even at −5 wt% clay loading, they obtained the same value of Young’s modulus for the relatively well-dispersed PP-g-MAH/clay nanocomposite as in neat, unmodified PP. Young’s modulus, which is measured within the elastic regime (<1% strain), is expected to depend strongly on the extent of filler agglomerate size reduction and dispersion (but not on interfacial adhesion) [61]. While modification improved dispersion, it led to a major reduction in PP-g-MAH molecular weight relative to unmodified PP and thus a reduction in polymer modulus.

In yet other cases, unmodified nanoparticles resulted in better nanocomposite properties than modified nanoparticles. For example, Wu et al. [19] compared the effect of polymer grafting to nanosilica on PP/nanosilica hybrids. Upon addition of −7 wt% nanosilica to PP, they observed a 30% enhancement in modulus relative to neat PP with unmodified nanosilica but only a 10% increase with polymer-grafted nanosilica. Notably, the quality of dispersion in the two nanocomposite systems was not directly addressed. (In addition, in some cases polymer grafting to nanoparticles can result in complex morphologies in polymer/nanoparticle hybrids [19,50], which can add further complication to the issue of dispersion.) Related poor outcomes have been observed with tensile strength of nanocomposites made with modified nanofiller and/or modified polymer [9,19–27], where favorable interfacial interactions are expected to play a role in property enhancements [19–27]. The use of compatibilizer or modification of filler and/or polymer can also pose other challenges in melt processing of hybrids. For example, modification often comes at the cost of thermal stability, as exemplified by alkyl amine functionalization of clay which leads to major reductions in the onset degradation temperature of many polymer/clay nanocomposites [62,63] and thus degradation during melt processing of the nanocomposites.

Here, we have undertaken a study in which we achieve very good nanofiller dispersion in polymer independent of chemical modification. With similar, high levels of dispersion in both unmodified and modified hybrids, we are able to specifically address the issue of whether improving the thermodynamic compatibility of polymer/nanofiller interfaces is key to enhancing properties of polymer nanocomposites in the presence of very good dispersion. It is possible to achieve very good nanofiller dispersion which is superior to that obtained with conventional melt processing by a number of solid-state processing methods, including ball milling [64–70], pan milling [71–73], cryo-grinding [74–77], and solid-state shear pulverization (SSSP) [69,78–94]. By processing polymers hybrids in the solid state rather than the melt state, the materials can be exposed to higher levels of stresses and forces leading to greater agglomerate fragmentation and break up and very good nanofiller dispersion. As with many polymeric materials, well-dispersed polymer nanocomposites produced in this manner will in many cases be in non-equilibrium, metastable states which will remain largely unperturbed over long times under use conditions.

In the current study, we disperse nanofiller with SSSP, a continuous, industrially scalable process that uses a twin-screw melt extruder that is modified to cool rather than heat the polymer so that it is processed in the solid state near ambient conditions. In past work, SSSP has been used to produce polymeric materials that are difficult or impossible to produce via conventional melt processing. For example, SSSP has been used to produce in situ compatibilized and quasi-nanostructured immiscible polymer blends [78–80] and to achieve intimate mixing of polyethylene and ultrahigh molecular weight polyethylenes [81] that, due to extraordinary viscosity mismatch, cannot be mixed by conventional melt processing. It has also been used to produce ester and maleic anhydride functionalized PP [82,83] and long-chain branched PP [84] with dramatically suppressed molecular weight reduction relative to that accompanying functionalization by melt processing. Finally, it has been used to obtain very good to excellent dispersion in polylefinns, superior to that by conventional melt processing, of many unmodified fillers and nanofillers [69,85–93], including carbon nanotubes [85], graphite [86,87], rice husk ash [88], and cellulose nanocrystals [89] that have no favorable interactions with PP beyond van der Waals interactions. In particular, we compare tensile, rheological, crystallization, and thermal degradation properties of PP/nanosilica nanocomposites made by SSSP with 1–9 wt% of pristine, unmodified nanosilica (p-NS) or modified silica (m-NS). The p-NS is fumed silica composed of finely divided amorphous silicon dioxide, which has been described as having three main size scales: primary particles of 10–30 nm that are fused into aggregates of 100–250 nm, which build up to clusters hundreds of microns in size [13,95,96]. The p-NS has a 200–300 m²/g surface area with a large number of surface hydroxyl groups [95]. The m-NS is produced by organically modifying the hydroxyl groups on p-NS with hexamethyldisiloxane (HMDS) [96].

2. Experimental section

2.1. Materials

Polypropylene (Total Petrochemicals, density = 0.905 g/cm³, MFI = 2 g/10 min) was used as received. Two types of fumed silica (SiO₂) nanoparticles were used, each with an average nanoparticle diameter of 12 nm as reported by the supplier, Degussa AG. One type was hydrophilic silica (Aerosil 300, p-NS, 300 m²/g surface area). A second type was hydrophobic silica (Aerosil R812, m-NS, 230–250 m²/g surface area), which was produced by surface modification of hydrophilic nanoparticles (Aerosil 300) with HMDS [96].

2.2. Preparation of PP/nanosilica nanocomposites

Polypropylene pellets were fed to a Berstorff ZE-25 pulverizer with a K-tron S-60 feeder at a feed rate of ~100 g/h. (Although the
ZE-25 pulverizer is a pilot-plant/research-scale instrument, a commercial scale apparatus has processed polyolefins at rates exceeding 150 kg/h [88]. Nanosilica was added to the pulverizer using a powder feeder (Brabender Technologies Inc. DSSR 12-1 volumetric feeder) at different feed rates to obtain desired filler content (~1–9 wt%) in the composite. The PP pellets and silica nanoparticles were pulverized using a 200 rpm screw speed and a screw design able to impart high specific energy to the material (see ref. [94] for a detailed description of screw design and energy inputs). The pulverizer barrels were cooled by a recirculating ethylene glycol/water mix (−7 °C, Budzar Industries WC-3 chiller). Details of the apparatus and processing conditions are available in refs. [88–92].

2.3. Characterization of PP/nanosilica nanocomposites

Field-emission scanning electron microscopy (FE-SEM) samples were prepared by melting and extruding the material obtained from the SSSP apparatus with an Atlas Electronic Devices MiniMax molder (cup-and-rotor mixer). Morphologies of cryo-fractured sections were obtained via a SU8030 instrument after sputtering with gold/palladium (Denton DeskIII). The FE-SEM images of as-received nanosilica were acquired after casting from water onto Si wafers. Transmission electron microscopy (TEM) images were acquired using a JEOL 1230 TEM on 70-nm thick sections which were obtained using a Leica Ultracut S microtome at room temperature. Uniaxial tensile test samples were prepared by compression molding with a PHI (Model 0230C-X1) press at 200 °C. Field-emission scanning electron microscopy (FE-SEM) samples were prepared using a Leica Ultracut S microtome at room temperature. The FE-SEM images of as-received PP/nanosilica samples were obtained using a JEOL 1230 TEM on 70-nm thick sections which were obtained using a Leica Ultracut S microtome at room temperature.

Small amplitude oscillatory shear measurements (TA Instruments ARES rheometer) were done at 200 °C with a 25 mm parallel plate fixture and frequencies of 0.01−100 rad/s.

3. Results and discussion

3.1. Dispersion and morphology of PP/nanosilica nanocomposites

Fig. 1 shows electron micrographs of as-received nanosilica and PP/nanosilica nanocomposites made by SSSP. Fig. 1a and b compare FE-SEM images of as-received p-NS and m-NS, which reveal the presence of agglomerates with a size range of ~1 μm to tens of microns. The p-NS nanoparticles exhibit interparticle attraction due to the high concentration of surface silanol groups [13,95,96]. Despite surface modification of m-NS, van der Waals forces are sufficient for particle agglomeration [95]. Thus, process methods that can achieve good filler dispersion within the polymer matrix are needed regardless of the nature of the filler surface.

In contrast, poor filler dispersion and little or no agglomerate size reduction have been reported when hybrids are made by melt processing; examples of fillers yielding poor outcomes with melt mixing include not only pristine and surface modified nanosilica particles but also modified silicates, bundled CNT, and cellulose nanocrystals [1−39,99−104]. The agglomerates are visible to the naked eye [103,104]. In contrast, Fig. 2 compares photographs of compression-molded samples of 94/6 wt% PP/p-NS and PP/m-NS nanocomposites made by SSSP. There is no distortion of the underlying image or scattering of light caused by the silica nanofiller; this result is expected based on the nanoscale sizes of the filler shown in Fig. 1g–h.

3.2. Mechanical properties of PP/nanosilica nanocomposites

Fig. 3 and Table 1 compare tensile properties of PP/p-NS and PP/m-NS hybrids as a function of nanosilica content. Relative to neat PP, addition of rigid nanosilica to PP leads to increases in Young’s modulus and tensile strength. In general, greater enhancements are obtained with p-NS. With 1 wt% filler, the PP/p-NS nanocomposite exhibits a 21% increase in Young’s modulus and a 15% increase in tensile strength relative to neat PP while the PP/m-NS nanocomposite exhibits a 12% increase in Young’s modulus and a 14% increase in tensile strength. Greater differentiation is observed with 2 wt% filler, where the PP/p-NS nanocomposite shows 32% and 17% increases relative to neat PP in Young’s modulus and tensile strength, respectively, and the PP/m-NS nanocomposite shows 17% and 10% increases in Young’s modulus and tensile strength.
strength, respectively. Over the range of 1—9 wt% nanosilica, the PP/p-NS nanocomposites exhibit the maximum increase in Young’s modulus (46% at 8 wt% p-NS) and tensile strength (22% at 6 wt% p-NS) relative to neat PP.

How well do the observed enhancements in modulus agree with expectations based on simple models for polymer/filler hybrids? We address this question in an approximate manner via the Voigt model, which was originally designed for a parallel arrangement of
well-dispersed particulate fillers aligned in the direction of load; however, the upper bound Young’s modulus predicted by the Voigt model has been described as being applicable to most particulate composites/nanocomposites [61].

\[
E^{\text{upper bound}} = E_p V_p + E_m (1 - V_p) \tag{2}
\]

where \(E_c\), \(E_p\), and \(E_m\) are the Young’s moduli of the composite, particulate filler, and polymer matrix, respectively, and \(V_p\) is the volume fraction of filler in the composite. Using values of 73 GPa and 2.64 g/cm\(^3\) for the modulus and density of silica [105,106], the Voigt model predicts an upper bound of 1500 MPa for the modulus of the 99/1 wt% PP/p-NS nanocomposite, which is in good agreement with the measured modulus of 1450 \(\pm\) 50 MPa for the nanocomposite made by SSSP. At 8 wt% nanosilica, the Voigt model predicts an upper bound of 3500 MPa for Young’s modulus, well above the measured value of 1750 \(\pm\) 50 MPa. A part of this difference in the level of agreement between the predicted upper bound and measured value can be ascribed to the effectiveness of dispersion achieved by SSSP. At very low filler levels, e.g., 1 wt%,
SSSP is very effective at filler dispersion. While SSSP retains superior dispersion capability relative to conventional melt processes with increasing filler content, there is a reduction in dispersion effectiveness at higher loadings, as observed in other polymer hybrids made by SSSP [86].

Adding rigid filler to PP is expected to reduce elongation at break [85–89]. Notably, the strains at break for p-NS and m-NS nanocomposites are similar up to 6 wt% nanosilica, although with 1 wt% silica the p-NS nanocomposite exhibits no reduction within error relative to neat PP. Only at 8 to 9 wt% nanosilica loadings do the m-NS nanocomposites exhibit a higher strain at break. Even at 8 to 9 wt% nanosilica loadings with vastly reduced elongation at break, both p-NS and m-NS nanocomposites remain ductile. Similar decreases in elongation at break have been reported with well-dispersed and exfoliated PP/graphite nanocomposites made by SSSP [86,87].

3.3. Comparison with mechanical properties of PP/nanosilica nanocomposites from the literature

We limit comparison to reports in which individual nanosilica particles were 10–50 nm in diameter [19–27]. Young’s modulus depends on agglomerate break up and dispersion. Using melt mixing, Liu et al. [25] employed 5 wt% p-NS and 5 wt% maleic anhydride modified PP as compatibilizer to produce PP/p-NS composites and reported no change in modulus relative to neat PP. They also observed no change with 5 wt% m-NS. Also using melt mixing, Wu et al. [19] reported no increase in modulus by adding 1 wt% p-NS to PP and only a 21% increase by adding ~6 wt% p-NS. In contrast, using SSSP we obtain 21 and 39% increases in modulus upon adding 1 and 6 wt% p-NS, respectively, to PP. The enhancements in Young’s modulus for PP/p-NS composites obtained in the current study (by SSSP) exceed those in the literature [107].

Studies have indicated that surface treatment of fillers is needed to improve composite tensile strength [60,61]. However, studies of PP/nanosilica composites made by melt mixing have not supported this claim. Ruan et al. [20] reported no change in tensile strength upon adding 1 wt% p-NS to PP and a 7% decrease upon adding 5 wt% p-NS. Modification of p-NS by grafting polystyrene or poly(ethyl acrylate), ostensibly to improve compatibility with PP, resulted in a maximum 4% increase or no change in tensile strength relative to neat PP, respectively. Liu et al. [25] reported no improvement in yield stress upon adding p-NS or m-NS to PP and that using PP-g-MAH as compatibilizer also failed to improve tensile strength. Bikiaris et al. [24] incorporated up to 7.5 wt% nanosilica, with p-NS showing no improvement in tensile strength and m-NS addition resulting in a maximum 9% increase in tensile strength relative to neat PP. In contrast, with nanocomposites made by SSSP, we obtain 19% and 14% increases in tensile strength upon adding 1 wt% p-NS and 1 wt% m-NS to PP, respectively. The maximum enhancements in tensile strength with p-NS and m-NS addition to PP by SSSP are 22% and 17%, respectively.

Regardless of modification or compatibilization, these results show that greater enhancements in modulus and tensile strength are obtained in composites in which nanosilica agglomerates have undergone major size reduction and dispersion by SSSP as compared to hybrids made by melt mixing where size reduction and dispersion are less effective. Even with very good size reduction and dispersion, slightly better properties are obtained with pristine nanosilica instead of nanosilica that has been modified to improve thermodynamic compatibility. When filler is truly nanoscale, van der Waals forces between polymer and filler may be sufficient to result in interfacial characteristics consistent with improved mechanical properties [85–93].

Previous SSSP studies provide many examples of (nano)composites prepared with unmodified filler that exhibit major property enhancements relative to neat polymer (and better than those obtained with melt-mixed hybrids). When made by SSSP, 97.5/2.5 wt% PP/graphite nanocomposites result in 100% and 60% increases in Young’s modulus and yield strength, respectively, relative to neat PP [86]. When made by SSSP followed by melt mixing, 99.1/0.9 wt% PP/carbon nanotube nanocomposites result in a 57% increase in modulus [85]. When made by SSSP, low density polyethylene (LDPE) nanocomposites with 10 wt% cellulose nanocrystals exhibit a 69% increase in Young’s modulus, a 30% increase in yield strength, and an unchanged elongation at break relative to neat LDPE [89]. In a study related to silica, SSSP-processed 81/19 wt% PP/rice husk ash composites exhibit a 50% increase in modulus relative to neat PP [88]. (Rice husk ash is agricultural waste material that is ~90 wt% silica [88].) The results from the current and previous SSSP studies and literature studies comparing the performance of composites of PP with p-NS and m-NS made by melt mixing indicate that size reduction or break up and good dispersion of fillers are key to achieving major property enhancements in polymer (nano)composites regardless of modifications to improve interfacial interactions.

3.4. Rheological characterization of PP/nanosilica nanocomposite

Fig. 4 compares shear storage modulus as a function of frequency ($G’(o)$) and nanosilica content for PP/p-NS and PP/m-NS nanocomposites. For both nanocomposite types, a very small reduction in $G’$ occurs relative to neat PP upon adding 1 wt% nanosilica, which is likely due to a very small reduction in PP molecular weight (a maximum of ~3% reduction in $M_w$ is observed when neat PP is subjected to SSSP processing of similar harshness [82]) with SSSP processing. (We note that reductions in $G’$ could also arise from chain disentanglements near the nanoparticles surfaces.) Accounting for that, only very small differences in $G’$ are observed relative to neat PP over the frequency range of 0.1–100 rad/s with addition of up to 6 wt% nanosilica, and the $G’(o)$ data are in accord with liquid response. Increasing the nanosilica content above 6 wt% results in little change in $G’$ at the high frequency limit (100 rad/s); however, at the low frequency limit (0.1 rad/s), $G’$ increases from 300 Pa for neat PP to 1800 Pa for 92/8 wt% PP/p-NS (and to 850 Pa for 91/9 wt% PP/m-NS). A small reduction in the $G’$-dependence of $G’$ at low $\omega$ is characteristic of small levels of or incipient network formation of filler in the composite [95,108].

The perturbation to the low-$\omega$ response of the 92/8 wt% PP/p-NS nanocomposite is small in comparison to responses reported in the literature for composites with percolated network formation [108–111]. Bartholome et al. [108] incorporated 5 vol% (~10 wt%) p-NS into polystyrene by solvent processing and, with plots of the type in Fig. 5, observed a prominent low-$\omega$ plateau in $G’$ at a value of ~30,000 Pa; in contrast, $G’ < 100$ Pa at $\omega = 0.1$ rad/s for neat PS. This greater than factor of 300 difference in $G’$ values and the plateau were attributed to a percolated network formed by hydrogen bonding between particles/agglomerates which contain surface hydroxyl groups. In comparison, when they made PS-grafted nanosilica particles and added them to PS, they observed major reductions in $G’$; with the three types of PS-grafted nanoparticles made in their study, the values of $G’(0.1 \text{ rad/s})$ for the nanocomposites were more than factors of 10–100 higher than the value for neat PS [108]. They concluded, “The steric hindrance generated by the grafted PS chains enables partial destruction of the agglomerates that compose the original silica particles when the latter are dispersed … in a polymer matrix.” Based on a comparison of rheology, the 92/8 wt% PP/p-NS nanocomposite produced in the current study by SSSP, which exhibits only a factor
of 6 increase in \( G'(0.1 \, \text{rad/s}) \) relative to neat PP, is less agglomerated and better dispersed than the ~10 wt% nanosilica nanoparticles that had been compatibilized by PS grafting and co-dissolved with PS in benzene prior to lyophilization.

Fig. 5 reinforces the point regarding incipient network formation in the 92/8 wt% PP/p-NS nanocomposite. This figure shows logarithmic plots of \( G' \) as a function of shear loss modulus \( (G'') \); such plots are analogous to Cole–Cole plots used in dielectric spectroscopy or Han plots used in characterizing temperature-induced microstructural changes in block copolymers and blends or the presence of long-chain branches in homopolymers [112–115]. With a single-phase melt, different curves of \( G' \) as a function of \( G'' \) are expected to coincide. Hence, this type of plot is highly sensitive to percolated network formation in a hybrid [109].

For example, relative to neat polycarbonate, Potschke et al. [109] observed more than a factor of 90 increase in \( G' \) at a fixed \( G'' \) for a 95/5 wt% polycarbonate/carbon nanotube (CNT) nanocomposite with a percolated CNT network. In contrast, when plotted in this format, only the 92/8 wt% PP/p-NS nanocomposite indicates outside experimental error the presence of incipient network formation; this is evident from the fact that at \( G'' = 2000 \, \text{Pa} \), \( G' \) is a factor of 2 higher for 92/8 wt% PP/p-NS than for neat PP and the other nanocomposites.

The incipient network formation in the 92/8 wt% PP/p-NS nanocomposite may lead to limited property degradation. For example, the incipient network formation is consistent with the fact that strain at break is lower in the 92/8 wt% PP/p-NS nanocomposite than in the 91/9 wt% PP/m-NS nanocomposite. (See Table 1.) Thus, when agglomerates undergo major size reduction and excellent dispersion, the use of nanoparticles with surface modification that reduces the likelihood of agglomerate re-formation (e.g., by eliminating the possibility of interparticle hydrogen bonding) may provide advantages in some instances, e.g., with regard to strain at break in nanocomposites with sufficiently high nanofiller levels to accommodate network formation.

### 3.5. Nucleating efficiency of nanosilica particles for PP crystallization

Fig. 6a and Table 2 show the effects of well-dispersed p-NS on PP crystallization. Nanofillers are often good nucleating agents for PP crystallization due to their large surface-to-volume ratio [22, 85–87, 89]. Relative to neat PP, incorporating 1 wt% p-NS in PP by SSSP leads to a ~3 °C increase in \( T_c \) while incorporating 6 wt% p-NS results in a ~5 °C increase. The PP/p-NS hybrids exhibit a significant increase in PP crystallinity from 51.5% for neat PP to 56.6% for 99/1 wt% PP/p-NS. The addition of p-NS to PP also leads to increased crystallization rate as observed by isothermal crystallization half-time, \( \tau_{1/2} \), measured at 140 °C; \( \tau_{1/2} \) decreases from

![Figure 4](image.png)  
**Fig. 4.** Shear storage modulus, \( G' \), at 200 °C as a function of angular frequency for a) PP and PP/p-NS composites, and b) PP and PP/m-NS composites prepared by SSSP.

![Figure 5](image.png)  
**Fig. 5.** Cole–Cole plots showing shear storage modulus (\( G' \)) as a function of loss modulus (\( G'' \)) for a) PP pellet and PP/p-NS composites, and b) PP pellet and PP/m-NS composites prepared by SSSP. (Data obtained at 200 °C.)
44 min for neat PP to 19 min for 97/3 wt% PP/p-NS and 16 min for 94/6 wt% PP/p-NS.

Calculating the nucleating efficiency [98] allows for quantitative comparison of the effectiveness of well-dispersed p-NS and m-NS as nucleating agents. Using eq. (1) and a value of $T_{c,max} = 140.2 \degree C$ (see calculations in supporting information), 1 wt% p-NS has NE = 18% while 6 wt% p-NS has NE = 29% in the SSSP-processed PP nanocomposites. In contrast, Qian et al. [116] incorporated p-NS (with ~16 nm diameter) in PP by melt processing and observed no change in crystallinity relative to PP crystallinity after 10,800 s at 140 \degree C.

Results by Qian et al. indicated a 0% NE for up to 3 wt% p-NS loadings as high as 3 wt% and a 4 \degree C increase for a filler loading of 5 wt%. As described by Jain et al. [22], the results by Qian et al. indicated a 0% NE for up to 3 wt% p-NS and an 8.5% NE for 5 wt% p-NS. Jain et al. [22] also studied in situ prepared nanosilica in PP and obtained a maximum 20% NE for 0.2−1.0 wt% loadings and reported small decreases in NE for loadings above 1.5 wt%. In the current study, SSSP enables excellent p-NS agglomerate size reduction and dispersion that lead to the highest reported NE (29%) for nanosilica in PP. As shown in Fig. 6b and Table 2, effects of agglomerate size reduction and dispersion by SSSP are evident in the crystallization behavior of PP/m-NS nanocomposites. However, surface modification with hydrophobic groups results in slight degradation of the nucleation ability of m-NS relative to p-NS. The PP/m-NS nanocomposites exhibit a maximum NE of 22%. While this value exceeds literature values for PP/nanosilica hybrids, it is below the maximum NE of 29% obtained here with PP/p-NS composites. Thus, well-dispersed p-NS nanoparticles outperform well-dispersed m-NS nanoparticles in enhancing PP crystallization.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature for crystallization $T_c$ (°C)</th>
<th>Percent polymer crystallinity $X_c$ (%)</th>
<th>Isothermal crystallization half-time measured at 140 °C $t_{1/2}$ (min)</th>
<th>Nucleating efficiency NE (%)</th>
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<td>51.5</td>
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<td>-</td>
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<td>51.7</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>97/3 wt% PP/m-NS</td>
<td>126.4</td>
<td>54.2</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>94/6 wt% PP/m-NS</td>
<td>126.3</td>
<td>52.7</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>91/9 wt% PP/m-NS</td>
<td>125.8</td>
<td>51.4</td>
<td>18</td>
</tr>
</tbody>
</table>

* $T_c$ reported here have a maximum one standard deviation error of ±0.5 °C.

* $X_c$ measurements reported here have a maximum one standard deviation error of ±0.5%.

### 3.6. Melt transition and β-crystals in PP/nanosilica nanocomposites

Melting behavior of PP provides information on the perfection and size distribution of crystalline lamellae and the presence of metastable crystalline structures such as β-crystals [22,117–123], which increase PP impact strength and toughness [121,122] but reduce yield strength, modulus, and ductility following yield [117,121,122]. Relative to neat PP, well-dispersed PP/p-NS hybrids exhibit a slightly narrower melting peak (Fig. 7a), which indicates the formation of lamellae with a narrower size distribution. Neat PP crystallizes predominantly into a stable α-crystalline structure (α-PP) with a −165 °C peak melt temperature [22,121]. Incorporating p-NS into PP by SSSP does not affect the α-PP peak melt temperature, but an additional, small melting peak at 145 °C is observed for all p-NS loadings which is due to β-crystals of PP [22]. (α- and β-phase crystals have similar crystallization onset temperature, which disallows its use to discern the presence of β-phase crystals.) The PP/m-NS composites (Fig. 7b) also have a small melting peak at 145 °C which is less prominent than in p-NS nanocomposites. Thus, there is some loss in β-crystal nucleating ability of m-NS relative to p-NS.

Fig. 6. Isothermal crystallization curves (140 °C) for neat PP and PP/nanosilica composites made by SSSP with a) pristine nanosilica, and b) modified nanosilica. (Note: Normalized crystallinity is relative to PP crystallinity after 10,800 s at 140 °C.)
Fig. 7. Nonisothermal melting curves for neat PP and PP/nanosilica composites made by SSSP with a) pristine nanosilica, and b) modified nanosilica. (Note: Curves are shifted vertically to improve clarity.)

Fig. 8 compares TGA data of neat PP with PP/p-NS and PP/m-NS nanocomposites. (Samples of p-NS and m-NS were also evaluated by TGA; within error, they exhibit no mass loss up to 500 °C.) We define thermal degradation temperatures corresponding to 5% and 10% mass loss as $T_{5\%}$ and $T_{10\%}$, respectively. Neat PP exhibits $T_{5\%} = 410$ °C and $T_{10\%} = 425$ °C. Adding p-NS to PP by SSSP leads to greater enhancement in thermal stability compared to m-NS. For example, relative to neat PP, 99/1 wt% PP/p-NS exhibits 15 °C and 12 °C increases in $T_{5\%}$ and $T_{10\%}$, respectively, while 99/1 wt% PP/m-NS exhibits only 5 °C increases in $T_{5\%}$ and $T_{10\%}$.

The presence of well-dispersed nanofiller with large surface area provides a barrier to the diffusion of degradation products, thus improving the hybrid thermal stability [40,41,63,90]. However, modification of nanosilica with a hydrophobic organic compound as in m-NS reduces the thermal stability of PP/m-NS relative to that of PP/p-NS. Relative to unmodified fillers, literature reports have indicated lower stabilities for organically and silane functionalized clay and CNTs and their composites [62,63,100]. Thus, with well-dispersed PP/nanosilica hybrids, thermal stability considerations indicate a distinct advantage for the use of pristine silica.

3.7. Thermal degradation of PP/nanosilica nanocomposites

The nanocomposites made by SSSP exhibit the highest nucleating efficiency for PP/nanosilica hybrids ever reported in the literature, 29% for 94/6 wt% PP/p-NS. In addition, this study reports the first PP/nanosilica nanocomposites made by mixing pre-existing nanosilica with PP to exhibit a non-zero nucleating efficiency at only 1 wt% nanosilica content (NE = 29% for 99/1 wt % PP/p-NS) and β-crystal formation after melting and recrystallization by enhancements in polymer nanocomposites is to improve the polymer-filler surface thermodynamic compatibility. Research over the past two decades has indicated that this approach does not provide a general solution. We address the issue of whether achieving a metastable, well-dispersed state with unmodified filler can be better than polymer-filler surface compatibilization in attaining major enhancements for a broad range of properties in polymer nanocomposites. We produce well-dispersed PP/nanosilica nanocomposites by SSSP which achieves agglomerate size reduction and dispersion without regard to interfacial compatibility between polymer and nanofiller. Nanocomposites are made with up to 8 or 9 wt% pristine nanosilica, with hydroxyl groups on the surface, or organically modified nanosilica. Microscopy reveals very good dispersion of p-NS and m-NS, with nanofiller in the −10–100 nm size range in hybrids. Rheology is also consistent with very good dispersion. Thus, both nanocomposite types have very similar, well-dispersed states, eliminating differences in dispersion as a factor in property enhancements. The PP/p-NS nanocomposites exhibit a broad range of properties that are superior to those of PP/m-NS, including Young’s modulus, tensile strength, thermal stability, PP crystallization onset temperature, isothermal PP crystallization half-time, PP crystallinity, and nucleating efficiency for PP crystallization. For well-dispersed nanocomposites and the properties tested here, these results indicate that unmodified nanofiller in a metastable well-dispersed state can lead to more robust nanocomposites than organically modified nanofiller. Implications of these results are that van der Waals interactions between polymer and truly nanoscopic filler are sufficient to achieve optimal improvements for many properties and that “compatibilization” of the nanofiller with the polymer by low molecular weight organic modifications can limit the property improvements.

A commonly posited solution to the long-standing problems of achieving highly effective dispersion and optimal property enhancements in polymer nanocomposites is to improve the polymer-filler surface thermodynamic compatibility. Research over the past two decades has indicated that this approach does not provide a general solution. We address the issue of whether achieving a metastable, well-dispersed state with unmodified filler can be better than polymer-filler surface compatibilization in attaining major enhancements for a broad range of properties in polymer nanocomposites. We produce well-dispersed PP/nanosilica nanocomposites by SSSP which achieves agglomerate size reduction and dispersion without regard to interfacial compatibility between polymer and nanofiller. Nanocomposites are made with up to 8 or 9 wt% pristine nanosilica, with hydroxyl groups on the surface, or organically modified nanosilica. Microscopy reveals very good dispersion of p-NS and m-NS, with nanofiller in the −10–100 nm size range in hybrids. Rheology is also consistent with very good dispersion. Thus, both nanocomposite types have very similar, well-dispersed states, eliminating differences in dispersion as a factor in property enhancements. The PP/p-NS nanocomposites exhibit a broad range of properties that are superior to those of PP/m-NS, including Young’s modulus, tensile strength, thermal stability, PP crystallization onset temperature, isothermal PP crystallization half-time, PP crystallinity, and nucleating efficiency for PP crystallization. For well-dispersed nanocomposites and the properties tested here, these results indicate that unmodified nanofiller in a metastable well-dispersed state can lead to more robust nanocomposites than organically modified nanofiller. Implications of these results are that van der Waals interactions between polymer and truly nanoscopic filler are sufficient to achieve optimal improvements for many properties and that “compatibilization” of the nanofiller with the polymer by low molecular weight organic modifications can limit the property improvements.

4. Conclusions

A commonly posited solution to the long-standing problems of achieving highly effective dispersion and optimal property enhancements in polymer nanocomposites is to improve the polymer-filler surface thermodynamic compatibility. Research over the past two decades has indicated that this approach does not provide a general solution. We address the issue of whether achieving a metastable, well-dispersed state with unmodified filler can be better than polymer-filler surface compatibilization in attaining major enhancements for a broad range of properties in polymer nanocomposites. We produce well-dispersed PP/nanosilica nanocomposites by SSSP which achieves agglomerate size reduction and dispersion without regard to interfacial compatibility between polymer and nanofiller. Nanocomposites are made with up to 8 or 9 wt% pristine nanosilica, with hydroxyl groups on the surface, or organically modified nanosilica. Microscopy reveals very good dispersion of p-NS and m-NS, with nanofiller in the −10–100 nm size range in hybrids. Rheology is also consistent with very good dispersion. Thus, both nanocomposite types have very similar, well-dispersed states, eliminating differences in dispersion as a factor in property enhancements. The PP/p-NS nanocomposites exhibit a broad range of properties that are superior to those of PP/m-NS, including Young’s modulus, tensile strength, thermal stability, PP crystallization onset temperature, isothermal PP crystallization half-time, PP crystallinity, and nucleating efficiency for PP crystallization. For well-dispersed nanocomposites and the properties tested here, these results indicate that unmodified nanofiller in a metastable well-dispersed state can lead to more robust nanocomposites than organically modified nanofiller. Implications of these results are that van der Waals interactions between polymer and truly nanoscopic filler are sufficient to achieve optimal improvements for many properties and that “compatibilization” of the nanofiller with the polymer by low molecular weight organic modifications can limit the property improvements.

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cooling. The observation of β-crystal formation in the SSSP-made hybrids occurs at even lower silica content than that reported (>2 wt% nanosilica) when nanosilica was prepared in situ in PP [22].

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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.2015.05.015.

References
