Process induced alignment of gold nano-rods (GNRs) in thermoplastic polymer composites with tailored optical properties

*Devon A. Boyne, Alice M. Savage, Mark H. Griep, Frederick L. Beyer and Joshua A. Orlicki**

ABSTRACT: Manipulation of the electronic and optical properties of plasmonic nanomaterials offers unique and exciting opportunities for several fields including opto-electronics, bio-medical engineering and photovoltaics. In particular, gold nanorods (GNR) represent a class of plasmonic nanomaterials that provide tunable optical properties from the visible to the near infrared regime. Herein, we have developed a highly effective method to prepare polymer nanocomposites (PNCs) doped with GNR additives utilizing extrusion and injection molding. A key outcome is that the process is amenable to scalable manufacturing and can produce highly reproducible PNCs with excellent optical properties. The resultant PNCs display good particle dispersion, minimal aggregation and a high retention of the optical properties as confirmed by UV-Vis spectroscopy and transmission electron microscopy. The nano-additives are incorporated into different thermoplastics to demonstrate the versatility of this method for different matrices and to

demonstrate stability over the extrusion processing temperature range (235-335°C). Furthermore, the tractability of this method is demonstrated by incorporating GNRs with different morphologies (aspect ratio, stabilizing layer, etc.). Finally, partial flow-induced alignment is demonstrated, the degree of which is modulated by the length and monodispersity of the GNR nano-additive. Ultimately, we report an optimized methodology to produce high quality GNR-PNCs with tailorable optical properties that can be adapted for scalable manufacturing.

1. INTRODUCTION:

Interest in plasmonic based nanotechnology has risen over the past decade. Versatile characteristics, including tunable optical and electrical properties, make plasmonic nanomaterials attractive to several industries including biochemical engineering [1-3], photovoltaics [4,5] and integrated photonics [6,7]. Plasmonic nanoparticles exhibit resonances based on the localized oscillation of electrons (plasmons), which can couple with incident light and lead to tunable optical absorptions over the visible (Vis) to the near infrared (NIR) regime. In recent years, gold nanorods (GNRs) have been elevated to the forefront of plasmonic nanoparticle technology, resulting from their high stability [8], synthetic accessibility [9-11] and optical tunability [10-12]. For certain applications, such as signal enhancement (e.g. surface enhanced Raman, antennas, light concentrators) [13-15], optical lens (e.g. polarizers) [13,16] and sensing [17], incorporation of plasmonic nanoparticles into bulk polymeric material while retaining the plasmonic properties is essential. Furthermore, an elastomeric host matrix can lead to the development of mechanically responsive plasmonic materials [20]. Several groups have focused their efforts on the fabrication of polymer nanocomposites (PNCs) that incorporate GNR additives [13,16,18-20]. Strategies have been developed to obtain spatial control over the nanoparticle

assembly/dispersion including mechanically blended composites, nanoparticle block copolymer composites (arranged by phase miscibility) and electrospinning [20]. The polymer-based composites are the most amenable to scalability but can be limited in their control over the particle dispersion.

The successful fabrication of GNR-PNCs often entails the pre-functionalization of the GNR additive [13] and/or implementation of a grafting mechanism [16]. This pre-treatment allows for dispersion of the GNR throughout the polymer matrix without significant aggregation [13,16]. However, the deposition routes are generally solvent-based (i.e. drop-cast or spin cast), which makes the GNRs susceptible to defects resulting from the slow evaporation process such as non-uniform dispersion, edge effects, poor reproducibility, and film imperfections [21]. The former two defects result in a loss of desired optical properties and the latter two are problematic for microelectronic and industrial processing. Consequently, to adapt GNR-PNCs to real world applications and retain their structural-optical properties, scalable processing methods must be developed to retain sufficient dispersity of the additive, throughout the PNC and maintain high reproducibility.

Extrusion and injection molding are well established methods to prepare high quality polymer products. Extrusion is used to produce polymer forms with a constant cross section or diameter governed by process conditions and die shape i.e. rods, sheets, pipes, insulation coatings [22]. During extrusion, the polymer is simultaneously melted and sheared, allowing for efficient compounding /mixing of the melt [23]. The targeted melt temperature depends on the polymer crystallinity, melting point, and desired viscosity during mixing [23]. Following the extrusion/compounding phase, the polymer is forced out through a die leaving an elongated molten polymer [23]. The extrusion product is collected and loaded into an injection molding

apparatus which uses high pressure to force the molten polymer through an opening and into a mold cavity [23]. Melt processing requires high temperatures dependent on the polymer being processed which can easily rise above 200 °C for most engineering thermoplastics.

For thermal processing of PNCs, poor thermal stability of the additives can lead to particle breakdown (coalescence) and loss of the desired additive properties (optical, plasmonic, mechanical strength, conductivity etc.). In particular, GNRs degrade at relatively low temperatures (below 200 °C) and at high laser fluence [24-26]. This degradation occurs well below the melting point of bulk gold due to surface melting [27] and results in shape deformation of GNRs into spheres [25]. Investigations into the thermal annealing of polyethylene glycol thiol functionalized GNR polymethylmethacrylate (PMMA) composites by Composto et al [28] revealed the highest rate of degradation occurred within the first 30 minutes followed by the slow conversion of GNRs to spheres over a period of 8 days. To circumvent this issue, many groups have applied a passivation layer to enhance thermal stability, employing carbon [29], titanium oxide [30], zirconia [31] and mesoporous silica shells. From the standpoint of synthetic accessibility and matrix compatibility, silica is the best candidate. While the incorporation of a silica shell improves the survivability of the modified GNRs, the surface treatment does not completely prevent shape deformation [32]. Several studies report this behavior for GNRs below 200 °C, but only a limited number of studies report the systematic effects of applied heat during polymer processing for the temperature range of 200-300 °C, a range which is necessary to facilitate extrusion and injection molding of most engineering polymers.

In this contribution, a master-batch extrusion and injection molding process was developed to safely produce high quality GNR-PNCs with good particle dispersion and minimal additive degradation. The ultimate goal was the retention of the optical and structural integrity of the

dispersed GNRs in bulk polymers to demonstrate their potential for the integration into scalable manufacturing processes. A two-step process was employed in which the GNRs were first solution-cast into a polymer matrix to generate the master-batch at high additive loading; the intended loading for the final PNC was then achieved by simultaneous feeding of the master-batch polymer film and virgin polymer resin during polymer extrusion. The final PNCs were prepared by injection of the extrudate into a pre-formed mold. Two different polymers were used to demonstrate successful integration of GNRs into a PNC; polymethylmethacrylate (PMMA) (processed at ~ 235 °C) and polycarbonate (PC) (processed at ~ 285 °C and injection molded at 335 °C). Three different aspect ratios (AR) were investigated to illustrate the effect of morphology and ability to tailor the plasmonic absorptions of the composites over a wide wavelength range (600-1000 nm). Finally, the shear induced alignment of GNRs was demonstrated by small-angle X-ray scattering (SAXS) for the GNRs with the longest longitudinal axis. This is exciting, as successful alignment of GNRs could lead to modulated optical materials resulting from the strong polarization dependent absorption properties of anisotropic plasmonic nanoparticles. Furthermore, a scalable and facile methodology for alignment could prove essential in optical component manufacturing.

2. EXPERIMENTAL

2.1. Gold Nano-rod Fabrication

GNRs were fabricated by a seed-mediated growth method in accordance with previous literature [10,11]. Unless specified, all reagents were purchased from Sigma Aldrich, St. Louis MO and prepared in water. For a typical procedure, a gold seed solution was prepared by mixing 9.9 mL cetyltrimethylammonium bromide (100 mM, CTAB) and 100 μ L of chloroauric acid (50 mM, HAuCl_4). Seed growth was initiated by rapidly adding 0.46 mL of ice cold sodium

110 borohydride (10 mM, NaBH_4) under continuous mixing. This facilitated the reduction of
111 HAuCl_4 and formation of gold seeds. Mixing was stopped after ~ 1 minute and the solution was
112 incubated at 29°C for ~ 1 hour. Seeds were used within 5 hours of preparation.

113 Growth solutions were prepared for 3 batches of different sized GNRs (volume=300 mL); the
114 batches were termed B1, B2 and B3. The growth solutions of B1 and B2 GNRs (respectively;
115 $\text{AR}=2.5 \pm 0.56$ & 3.4 ± 0.71) were prepared as follows. Initially, two 150 mL solutions of
116 sodium salicylate (0.02 M, Na-Sal) were prepared in CTAB (100 mM). Following the complete
117 dissolution of the Na-Sal (facilitated by ultrasonication while heating), 3 mL of silver nitrate (4
118 mM AgNO_3) was added to each solution and gently mixed by inversion. The solutions were
119 incubated for 15-30 minutes in a 29°C water bath. In the meantime, two 150 mL solutions of 1
120 mM and 0.56 mM HAuCl_4 were prepared. For this particular procedure, the magnitude of the
121 GNR AR is inversely related to the concentration of HAuCl_4 in the growth solutions. Following
122 the incubation period, the dilute HAuCl_4 solutions were added to the Na-Sal solutions and mixed
123 on a shaker for 15 minutes. A color change from pale yellow to clear was observed, signaling the
124 partial reduction of the HAuCl_4 . Next, 7.5 mL of hydroquinone (0.1 M, HQ) was added and
125 mixed for ~ 1 min to complete the reduction of the HAuCl_4 . Finally, 480 μL of seed solution was
126 injected into each solution. The final solutions were mixed by inversion for ~ 15 seconds and
127 incubated overnight in a 29°C water bath. To induce the growth of larger aspect rods (B3,
128 $\text{AR}=5.3 \pm 1.1$ nm), growth solutions were prepared in the absence of Na-Sal and with a
129 different ratio of reactants. Briefly, a 300 mL solution containing AgNO_3 (0.15 mM) , HAuCl_4
130 (0.5 mM) was prepared in CTAB (100 mM). To this solution, 7.5 mL of HQ (0.1 M) was added
131 and mixed for ~ 1 -2 minutes (until the solution was clear) to reduce the HAuCl_4 . In the final step,

4.80 mL of seed solution was injected, mixed by inversion for ~ 15 seconds and incubated overnight at 29°C.

For all batches, resultant GNRs were purified by centrifugation to remove excess reactants (2X, 7500 RPM) and dispersed in water or dilute concentrations of CTAB depending on the desired post-functionalization.

2.2. PEG functionalization (organic stabilization)

B1 GNRs were functionalized with polyethylene glycol thiol (6000 MW, PEG-SH) by methods previously described in literature [40]. Briefly, 30 mL of PEG-SH (0.2 mM) was added to 270 mL of purified GNRs in water. This solution was vortexed (~ 30 seconds) and mixed on a **mechanical** shaker at room temperature for 1.5 hours. Excess PEG was removed by centrifugation (3X @ 7500 RPM): following the 1st purification GNRs were re-dispersed in acetone and after the 2nd and 3rd purification the GNRs were dispersed in 20-30 mL of chloroform.

2.3. Silica functionalization and organic stabilization

B2 and B3 GNRs were functionalized with porous silica shells (Si) and an outer silane layer (HTCS, n-Hexyltrichlorosilane) for hydrophobicity. The growth of silica (Si) shells was accomplished by applying a modified Stober method reported by Murphy et al [41]. Prior to Si shell growth, purified GNRs were re-dispersed in 0.7 mM CTAB. The concentration of CTAB dictates the approximate thickness of the Si shell. The pH was adjusted to ~10.6 and mixed for 30 min [for a total volume 300 mL, 1.2 mL of sodium hydroxide (100 mM, NaOH) was added]. At the conclusion of the incubation period, 2.7 mL of tetraethyl orthosilicate (TEOS, 20% in methanol) was added to promote the condensation of Si around the GNRs. The solutions were

mixed overnight on a shaker at room temperature. The Si capped GNRs were purified (3X, 7500 RPM) and re-dispersed in 300 mL of ethanol (ETOH).

Utilizing a method modified from previous literature [42], hydrophobicity was obtained by functionalization with a silane coupling agent (HTCS, n-Hexyltrichlorosilane). Briefly, 4 mL of ammonium hydroxide (~30% in water, NH_4OH) was added directly to the solutions of Si-GNRs in ETOH and sonicated for 10 minutes. Under continuous sonication, 30 mL of a dilute HTCS solution (2.4% in chloroform) was injected. Sonication continued for ~30 minutes, and subsequently mixed on a shaker ~ 2-3 hours. As a consequence of the hydrophobicity induced by the silane layer, during the mixing the GNRs fell out of solution and had to be re-dispersed by sonication several times. Finally, the GNRs were purified by centrifugation (3X, 7500 RPM) and dispersed in 20-30 mL of chloroform.

2.4. Preparation of intermediate composite (master-batch)

Following the stabilization of GNRs in chloroform, an intermediate cast film master-batch (~10-15% GNRs in PMMA) was prepared for all three GNR-matrix combinations investigated. Initially, polymeric resin pellets [either polymethylmethacrylate (PMMA, Acrylite M30, AMCO Plastics) or polycarbonate (PC, Specialty Polymer Products (SP2))] were dissolved in chloroform (200-300 mg/mL). Based on a rough estimation of solution concentration, 10-15 mL of the respective GNR solution was added to the dissolved polymer with the intention of reaching a final loading between (10-15 wt/wt %). The solution was sonicated for 5 minutes and cast into a circular glass crystallization dish (diameter, 9.65 cm). The crystallization dish was covered with another dish and allowed to dry for 24 hours. Following the drying period, the resultant film was divided into smaller pieces to prepare for further processing. The final wt/wt % was determined

by subtracting the total weight of the intermediate composite after drying from the initial weight of the polymer resin (before dissolution) then dividing by the final mass of the polymer.

2.5. Preparation of final composite (PNC)

To produce the final PNCs, extrusion and injection molding was performed. A full description of the process and processing conditions and description of a representative sample is available in the SI. Briefly, the master-batch was fed along with pelletized PMMA feed stock (CYRO Industries, Acrylite M30, $M_n = 56$ kDa, $M_w = 85$ kDa, $pdi = 1.52$) into a 15 cc Micro-Compounder (DSM Xplore). After a specific compounding interval (S.I.) the extrudate was collected and transferred to a 12 mL Injection Moulding Machine (DSM Xplore). The final PNC plaques were prepared in 1 inch squares with a thickness of 1.27 mm (DSM part # 1200005501). In a similar fashion, diluted batches were prepared of the remaining extrudate after 3 replicates were injection molded.

2.6. Instrumental characterization

The optical properties of the GNRs in water and GNR-PNCs were assessed by UV-vis spectroscopy (Perkin Elmer UV/Vis/NIR Spectrometer Lambda 1050, 3B WB detector module, Waltham, MA). Liquid samples employed a quartz cuvette with a pathlength of 1 cm, and for final composites the pathlength was determined by the thickness of the mold. The physical attributes of the GNRs and GNR-composites (AR, size, dispersity) were determined by transmission electron microscopy (TEM, JEOL 2100F, Peabody, MA) at an operating voltage of 200 kV and small-angle X-ray scattering (Rigaku S-MAXS, 3000 SAXS camera). A full list of relevant operating conditions and sample preparation is available in the SI. Finally, the glass transition temperature was measured using differential scanning calorimetry (DSC, Perkin Elmer Discoveries Series).

3. RESULTS AND DISCUSSION

The successful integration of GNRs into polymer matrices was accomplished by a three step process: (1) fabrication and stabilization of GNRs in an organic solvent, (2) preparation of a cast intermediate film with a high loading of the GNRs (10-15 wt/wt%) and (3) incorporation into a polymer matrix via an extrusion/injection molding process to achieve a final loading of 0.5-2 wt/wt%. Low loadings were chosen to prevent inter-particle coupling and interaction in the final composites. For well disperse particles, changes to the maximum absorption values are linear. To demonstrate this an additional set of loadings is provided in the supplemental section. Three sizes of GNRs were selected to represent a wide absorption and morphological range; B1 (AR=2.5 $\pm$ 0.56), B2 (AR=3.4 $\pm$ 0.71), and B3 (AR=5.3 $\pm$ 1.1). The individual dimensional parameters (i.e. length and width) along with the optical shifts ($\Delta\lambda_{\text{LSPR}}$) induced as a result of processing are located in Table 1 and used as a reference throughout the discussion. In addition to the PMMA preparation, B3 GNRs were prepared in a PC matrix to demonstrate the temperature stability and versatility of this method as it applies to different polymers. The ability to successfully integrate GNRs into polymer composites with high dispersity allows for adaptation into scalable manufacturing processes, representing an essential step to the real world application and large-scale processing of GNR composite material.

Table 1: Optical shifts induced by processing conditions and geometrical parameters for B1, B2, & B3.

Optical Absorptions				
Aspect Ratio	Coating	λ_{LSPR} (nm)	λ_{LSPR} (nm)	λ_{LSPR} (nm)
	Thickness (<i>d</i> , nm)		(Cast PNC)	(Final PNC)

		(H ₂ O)		
(B1) 2.5 ± 0.56	PEG-SH	701	731	623
	($d \sim 1\text{-}5\text{ nm}$)			
(B2) 3.4 ± 0.71	SiO ₂	771	786	712
	($d = 32.5 \pm 1.1\text{ nm}$)			
(B3) 5.3 ± 1.1	SiO ₂	995	1003	917
	($d = 18.5 \pm 1.05\text{ nm}$)			
(B3-PC) $5.3 \pm 1.1^*$	SiO ₂	995	982	973
	($d = 18.5 \pm 1.05\text{ nm}$)			

219 *B1-B3 was processed in PMMA, B3-PC was processed in polycarbonate

Figure 1. TEM micrographs of GNRs prior to integration into polymer composites (A) B1 GNRs ($AR=2.5 \pm 0.56$), (B) B2 GNRs (3.4 ± 0.71) and (C) B3 GNRs (5.3 ± 1.1).

220 3.1. Gold nano-rod characteristics (prior to integration)

221 The morphologies of the three GNR batches prior to integration into polymers (B1, B2 and
 222 B3) are depicted in Figure 1; respectively A, B & C. Aspect ratios were determined from self-
 223 assemblies of each core size functionalized with PEG to avoid measuring overlapping particles,

224 micrographs are available in the supplementary information (Figure S2). In addition to
 225 differences in the size of the GNRs, the TEM micrographs reveal distinct differences in the outer

226 layers for each batch (Figure 1). These differences derive from the selected functionalization
 227 layer of the GNR. For B1 (Figure 1A), a PEG layer with typical thiol bond is employed for
 228 hydrophobicity whereas for B2 & B3 (Figure 1 B & C; respectively) a porous silica shell with a
 229 HTCS overcoat was applied (dimensions in Table 1). The PEG passivation layer for the B1
 230 GNRs is indistinguishable from the carbon support film on the TEM grid. Spherical and non-rod
 231 shapes are observed in all three TEM images which represents impurities as a result of the
 232 fabrication process. A larger number of spherical impurities were observed for the B2 GNRs.
 233 The variation in the type of functionalization (PEG vs. porous SiO₂) is presented mainly to
 234 demonstrate the versatility of the developed method to accommodate the processing of GNRs
 235 with different outer layers structures.

The optical absorption spectrum for each GNR with final functionalization is shown in Figure 2. GNRs exhibit two plasmonic resonances (manifested as optical absorptions) that represent the collective electron oscillations that occur about both geometrical axes (length and width). The lower energy resonance is associated with the longitudinal axis and the higher energy resonance is associated with the transverse axis. The position of the longitudinal peak (λ_L) was sensitive to the AR of the GNR and the refractive index (RI) of the bulk matrix, whereas the transverse peak for all ARs occurred at ~510-550 nm. Assuming the dielectric of the GNR is the same, as a general rule of thumb, a larger AR and higher RI values will lead to lower energy resonances. The purity of the GNRs in solution can be qualitatively assessed by observing the ratio (R) of the peak intensities between the longitudinal peak and the transverse peak. A low ratio would imply greater spherical impurities as the high energy absorption overlaps the absorption of residual

Figure 2: Optical spectra of all three GNR batches in water (blue) represents the B1, (purple) represents the B2 and pink represents the B3 GNRs.

nano-spheres. The peak ratios (R) for the B1, B2 and B3 GNRs are above 1.5 (respectively 1.7, 1.7 and 3.7), which suggests the GNR yield is greater than 63% for B1 & B2 and 79% for B3 [this number was determined by adding the intensity of both peaks and finding the percentage attributed to the longitudinal peak].

Figure 3: Pictorial representation of the transition of GNRs from solution to intermediate cast film and final extruded/injection molded PNC.

3.2. Preparation and characterization of PNCs

A pictorial representation for the processing of the GNRs into PNCs is shown in Figure 3. Visual inspection of the intermediate master-batch (Figure 3) reveals a colorimetric gradient throughout the film and a noticeably darker color at the film edges. Similar variations were present in all master-batches and implies non-uniform dispersion of the GNR additive. Non-uniform dispersion is a common difficulty when solvent casting composite films that do not kinetically trap the particles during formation (e.g. spin-coating) and can be the result of several factors including additive/bulk matrix incompatibility, agglomerations, laboratory conditions (temperature, % humidity) and the particle movement towards the film edges (edge effects). In contrast to the solvent-cast master-batch, a uniform color absent of noticeable edge effects is obtained for the extruded/molded PNC (Figure 3). This suggests that the combination of mechanically sheared mixing and controlled part dimensions promotes uniform dispersion and corrects for the variations observed in the intermediate step. The color change (purple to blue) between the intermediate composite and final composite can be attributed to processing conditions and is discussed in the later sections.

267

268

3.3. Optical Characterization

269 The influence of processing techniques on the morphology and optical properties of the GNRs
 270 was assessed by monitoring changes in the optical spectra and visual inspection of the films.
 271 Figure 4D depicts the final PNCs for all batches, the white text is the average position of the
 272 longitudinal plasmonic band (λ_L) for three replicates. Figure 4 (A, B and C) represents the optical
 273 transition between solution-based GNRs (solid black lines, in H₂O), a drop-cast PNC film (solid
 274 red lines, solvent based, Δ = 25-29 °C) and the final extruded/injection molded composite (solid
 275 green lines, solvent free, Δ < 200 °C) for all three batches; respectively B1 (Figure 4A), B2
 276 (Figure 4B) and B3 (Figure 4C). Remarkably, in reference to the final PNCs (solid green lines),
 277 even though all three batches were continuously compounded for 10 minutes at 235 °C, distinct
 278 absorptions characteristic of intact GNRs may still be discerned. This is in contrast to Composto

279 et al who found that (for unsupported GNR films, not in a bulk matrix) the complete thermally
280 induced conversion of GNRs to spheres occurs at 180°C [28]. Spectrally, this would result in one
281 plasmonic resonance at ~550 nm and the disappearance of the longitudinal resonance. A survey
282 of literature reveals that for GNRs dispersed in a bulk polymer matrix, the temperature at which
283 complete conversion occurs can be increased to 250 °C [33]. Thus, the incorporation of surface-
284 modified GNRs into a bulk film offers complimentary mechanisms (e.g. GNR surface
285 stabilization, reduced exposure to O₂) to reduce the kinetics of GNR degradation allowing for a
286 wider thermal processing window.

287 Comparison of the spectral position of the λ_L before and after processing can give insight into

288 the physical changes that occur to the GNRs. For all batches, the λ_L of the drop-cast polymer

289 (solid red lines) is red-shifted from the λ_L of the aqueous phase GNRs (Figure 4 A-C, dotted

290 black lines). This is expected, and occurs due to differences in the bulk RI between water and
 291 PMMA; respectively 1.33 refractive index units (RIU) [34] and 1.49 RIU [35]. In contrast, the
 292 λ_L for the final PNCs (solid green lines) is blue shifted from the aqueous phase GNRs;
 293 respectively 78 nm (B1, Figure 4A), 59 nm (B2, Figure 4B) and 78 nm (B3, Figure 4C). Since
 294 the spectral position of the absorption is a function of both the RI of the surrounding matrix and
 295 the size or AR of the GNR, the blue-shift implies a reduced AR. This can likely be attributed to
 296 thermal reshaping and partial loss of the structural integrity. Moreover, although shifted, the
 297 retention of the spectral shape suggests that the basic morphology (rod-shaped) has been retained
 298 for all three sizes of GNRs and therefore, represents an accessible optical range of ~ 600 -1000

Figure 5: (A) Optical spectra of all three stages of processing, (dashed black line) aqueous phase GNRs, (dotted gray line) solution cast PNC and (solid black line) final extruded/injection molded PNC in PC, (B) corresponding picture of final PNC composite.

nm.

To expand the utility of this process to a wider range of thermoplastics B3 GNRs were dispersed in PC which required both a higher melt processing temperature (285 °C vs. 235 °C) and injection molding temperature (325°C vs. 235°C) when compared to PMMA. The optical spectra of the resultant PC-PNC (B3-PC) is depicted in Figure 4 for all three stages of the process; aqueous phase (solid black line), intermediate master-batch (solid red line) and the final composite (solid green line). Comparable to the PMMA-PNC, the PC-PNC revealed a 64 +/- 5.4 nm blue-shift from the aqueous GNRs and retained the characteristic spectral features of GNRs. The differences in the spectral shift of the plasmonic peak for PC and PMMA is likely related to dielectric effects as PC has a higher RI than PMMA (1.58 RIU [36] vs. 1.49 RIU). The ability of GNRs to retain their morphological and optical properties at 285/325°C expands the range of melt processing temperatures and consequently the types of viable matrices to include a wide range of engineering thermoplastics such Trogamid, Ultem, etc.

Aggregation was spectrally assessed by variations in the spectral shape between the drop-cast and final PNCs (full width half max, FWHM) and visually identified in intermediate PNCs by regular islanding throughout the films, non-uniform contrast and dark film edges (distinct visual variations were not observed in final PNCs). It is important to mention that the differences in B1 PNCs could not be determined due to overlap between the longitudinal and transverse peak, possibly due to increased agglomeration for the less stable PEG (polymer) shell. The B2 GNRs displayed a 6.7% increase in spectral broadness when compared to the aqueous phase GNRs, a significant improvement from its drop-casted counterpart (25%). The B3 GNRs (large-AR batch) displayed reduced spectral broadening in the spectra of the final PNC for both PMMA and PC, respectively 3.4% and 3.6%. In contrast, drop-cast PNCs for the B3 AR batches displayed

enhanced broadening for both polymers, 11% (PC) and 5.6% (PMMA). The differences in the spectral broadening between the intermediate and final composites (for both batches) may be attributed to partial aggregation of the GNRs in the solvent-cast films. The reduced broadening for the longer aspect ratio GNRs in PNCs when compared to water is less obvious and may result from differences in the orientation of the GNRs in the polymer matrix, known to cause differences in the spectral profiles [37].

Figure 6. TEM micrographs of PNCs for (A) B1, (B) B2 and (C) B3 GNRs. TEM micrographs of recovered GNRs for each batch (D) B1 (E) B2 and (F) B3. To recover GNRs, portions of the final PNCs were dissolved and the GNRs were purified out.

329 3.4 Physical characteristics of final PNC

330 The physical distribution of GNRs in the final polymer matrix was determined by
331 transmission electron microscopy (TEM). TEM micrographs of all three of the final PNCs is
332 depicted in Figure 6. Good dispersion, with the interparticle spacing generally exceeding $\sim 1\text{-}2$
333 μm , was observed for all three samples, indicating that both the Si-HTCS and PEG coatings
334 promote excellent miscibility. Although clusters of several GNRs were sometimes observed,
335 there was no evidence of large aggregates in the interrogated regions. Ultimately, TEM
336 micrographs of the GNR batches confirms the results from the optical analysis that imply the
337 GNRs retained their rod-shape and were highly dispersed throughout the polymer films.

Figure 7. High angular dark field images of large batch GNRs, gamma adjusted to highlight differences in silica shell thickness.

338 Given the high dispersion of GNRs in the polymer matrices, the GNRs were concentrated by
339 dissolving portions of the final PNC in chloroform and recovering by centrifugation so that the
340 final AR of the GNRs could be determined. The AR was calculated by measuring 60 only non-
341 overlapping particles. Representative micrographs are depicted under their respective batch in

Figure 6 (D, E &F). For the PEG-capped GNRs (B1 GNRs, Figure 6D), large deformed shapes suggest possible the formation of agglomerates. This agglomeration effect is not apparent in the micrographs of B2 and B3 which have a protecting silica layer. Although, there are some non-rod structures in Figure 6 (E, F), these structures are silica-capped which implies that they were present in the solution phase (prior to processing). It is important to mention that only rod-like particles are measured, therefore the AR measurement does not account for the higher incidence of agglomerates formed for the PEG capped GNRs (B1). Corresponding to optical analysis, the AR of the GNRs for the batches were reduced (Table S1), 15%, 10%, and 11% for B1, B2, and B3 respectively. The largest deviation in the AR was observed for the PEG-capped small batch and suggests the PEG-GNRs are more unstable than the Si-GNRs which is similar to implications from optical analysis. Interestingly for all batches, a decreased length (9%, 9%, and 5% respectively) and an increased width (5%, 1%, and 7% respectively) was observed. The decrease in the core length is particularly evident when looking at high-angle annular dark-field scanning TEM (HAADF STEM) images of the B3 recovered GNRs (Figure 7). A difference in the thickness of the silica shell can be discerned at the tips of the GNRs (identified by a square box, Figure 7) suggesting a loss of core material leaving a void in the outer shell and has been observed in previous thermal studies of GNRs [25]. As discussed in the introduction and optical analysis section, material loss due to thermal degradation preferentially occurs at the GNR tips leading to a reduction of length. The slight increase in width is less apparent and could possibly imply the transformation from a rod to a more ellipsoidal shape. Furthermore, based on the Two-Sample t-test the thickness of the SiO_2 is the same for all samples before and after processing.

Figure 8. SAXS 2D profiles for B1, B2, B3, and B3-extrudate.

364 Small-angle X-ray scattering (SAXS) is a convenient method to determine the average particle
365 size and gain insight on the orientation and periodicity of particles within a composite system
366 [38]. Figure 8 depicts the 2D SAXS patterns associated with the final PNCs. The degree of
367 anisotropy can be deduced by the symmetry of the scattering pattern. B1 (Figure 8A) and B2
368 (Figure 8B) display symmetric patterns, indicating that the morphology is isotropic. B3 (Figure
369 8C) displays an elongated pattern arising from an anisotropic morphology. This observed

370 anisotropy in B3 is due to the parallel orientation of the GNRs to the flow during processing and
371 has been observed previously for highly ordered GNRs within a nematic crystal [39]. The long
372 range alignment of GNRs is likely a result of the shear forces applied during extrusion and
373 injection molding, as Dunstan et al [37] demonstrated shear induced alignment of GNRs parallel
374 to the direction of flow in Newtonian Fluids. To determine if the alignment occurred during the
375 extrusion or injection molding process a small piece of the extrudate (collected prior to injection
376 molding) was tested for B3 and is depicted in Figure 8D. In contrast to the injection molded
377 PNC, the 2D pattern for the extrudate displays isotropic scattering and implies that a majority of
378 the alignment occurs during the injection molding processes. Moreover, the degree of alignment
379 for the GNRs must be related to the net geometry of the fully formed core shell particle. Sample
380 B3 is more elongated ($AR = 4.2 \pm 0.84$) and therefore is more likely to align by shear forces
381 whereas B1 ($AR = 1.8 \pm 0.27$) and B2 ($AR = 2.8 \pm 0.49$) are more spherical which reduces the
382 influence of shear alignment along the longitudinal axis. Thus, for future studies the degree of
383 alignment in the PNCs could be enhanced by particle AR, particle loading, and modifications to
384 the molding parameters (viscosity of melt, geometry of mold, temperature).

Figure 9. SAXS 1D profiles for B1, B2, and B3 including the calculated size distribution models.

385

386 To measure the length of the GNRs in the bulk PNCs, the one-dimensional SAXS data for the

387 extruded samples were fit using a model for scattering from core-shell cylinders. The SAXS data

388 and model fits are shown in Figure 9. The absence of a primary correlation peak or down-turn in

389 the low- q intensity indicates that the nanoparticles are generally dilute (dispersed). The best fit to

390 the data was seen for sample B3, which showed the clearest form factor scattering features, and

391 gives a mean cylinder length of 86.8 ± 0.9 nm. The SAXS data for B1 and B2 show fewer

392 pronounced features, resulting in a broader size distribution from the model which (in the

393 absence of isotropy) suggests broader nanoparticle size distributions. This can partially be

394 attributed the higher incidence of **spherical impurities** for the as-fabricated GNRs in B1 and B2

395 when compared to B3. Furthermore, the increased intensity at low- q in the SAXS data for all

batches suggests the presence of some large-scale (micron) fluctuations in GNR distribution in the final PNCs.

The variations in the prediction of the geometrical parameters of the GNRS between SAXS and TEM are summarized in Table S4. Although the widths of the GNRs are predicted within 8% for all batches, the predictions of length have a higher variation (25% for B1, 2.4% for B2, and 32% for B3). This level of discrepancy between SAXS and TEM is not unusual as SAXS is a bulk measurement, whereas TEM is limited by the volume of material sampled. Furthermore, in addition to differences in the sensitivity of the instrumentation, the prediction of the length via SAXS could be affected by inhomogeneities in the sample (i.e. voids at NP tips, impurities etc) and the use of a cylindrical model with flat ends where the actual GNRs have rounded ends with shells that extend well past the flat end of the model cylinder.

4. CONCLUSION

To conclude, we have introduced a master batch extrusion and injection molding process to obtain bulk composites of highly dispersed, partially aligned GNRs within a polymer matrix. Through integration of multiple GNR morphologies ($AR=2.6-5.3$) into the polymers we are able to obtain selected optical properties over a wide wavelength range (600-1000 nm). Furthermore, we demonstrate the successful integration into two polymer matrices (PMMA and PC) which represents a melt processing range of 235-335 °C and suggests utility in a variety of engineering thermoplastics such as Trogamid, Ultem, etc. Optical and physical analysis reveal high dispersity and retention of the cylindrical rod structure is obtained through the use of this method. Partial process induced thermal degradation was observed resulting in a blue-shift in the optical spectra and reduction of the AR after extrusion/molding processing, however, this can be accounted for by selecting a GNR of higher AR prior to processing to obtain the desired optical wavelength and/or GNR size. Furthermore, SAXS results suggest the partial alignment and long range order

of GNRs within the bulk polymer likely the result of shear during extrusion processing, the degree of which is directly related to the size and size dispersity of the GNR additive. In summation, the development of this procedure enables the scalable production of GNR PNCs with excellent dispersion and high reproducibility. This process can be expanded to different morphologies of GNRs and various thermoplastic matrixes. Finally, the flow induced alignment of the GNRs can be improved by modifying processing conditions and selection of a longer GNR allowing for the ability not only to produced highly dispersed but also highly oriented films.

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