STABILIZED & OPTICALLY TAILORED PLASMONIC NANOCOMPOSITE PREPARATION USING LABORATORY SCALE EXTRUSION

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Abstract

One of the chief impediments to the wider adoption of nanocomposites is the challenge of maintaining nanoscale features while employing bulk preparative techniques. Nanoparticle fillers may tend to aggregate or become destabilized during processing at temperatures required to process engineering thermoplastics. We report a study where nanoparticles of varying aspect ratios were stabilized with robust shells and then compounded using a laboratory scale extruder. Optical plaques were produced via injection molding, and the resultant nanocomposites were assessed for their optical and morphological properties.

Introduction

Plasmonic nanoparticles, which exhibit resonances based on the localized oscillation of electrons (plasmons) and can couple with incident light to yield tunable absorption characteristics, have enjoyed increasing interest in the scientific literature over the past decade. Tunable electronic and optical properties make them attractive for exploration in several application areas including photovoltaics,[1,2] integrated photonics,[3,4] and biochemical engineering.[5,6,7] Gold nanorods (GNRs) have risen to prominence, resulting from their good stability,[8], synthetic accessibility[9,10,11] and optical versatility[10,11,12]. The production of polymer nanocomposites (PNCs) that incorporate GNR additives has been the focus of multiple groups[13,14,15,16,17].

The successful fabrication of GNR-PNCs often entails the modification or functionalization of the GNR additive [13] and/or implementation of a grafting mechanism [14]. Modification of the surface functionality enables favorable dispersion of the GNR throughout the polymer matrix, reducing the propensity for significant aggregation [13,14]. The most widespread deposition routes are generally solvent-based (i.e. solvent-cast), which makes the resulting PNCs susceptible to drying defects. These arise due to the slow evaporation process and manifest as non-uniform dispersion, edge effects, poor reproducibility, and film imperfections [18]. The former two defects result in a loss of desired optical properties and the latter two are problematic for microelectronic and industrial processing.

Industrially, extrusion and injection molding are widely accepted methods to prepare high quality polymer products. Extrusion is used to mix polymers, and can generate a form with a constant cross section or diameter governed by process conditions and die shape i.e. rods, sheets, pipes, insulation coatings [19]. During extrusion, the polymer is simultaneously melted and sheared, allowing for efficient compounding /mixing of the melt [20]. Injection molding can then be employed to produce complex parts with high reproducibility and quality. Melt processing is therefore ideal for the exploration of optically functional PNCs. Of chief concern is the survivability of the additives, as the temperatures required for melt processing are dependent on the desired host polymer, and can easily require processing above 200 °C for most engineering thermoplastics.

In the context of GNR additives, limited thermal stability can lead to particle breakdown (coalescence) and loss of the desired additive properties (optical, plasmonic, mechanical strength, conductivity etc.). In particular, GNRs may degrade at relatively low temperatures (below 200 °C) or when exposed to high laser fluence [21,22,23]. The mechanism is the melting of the surface layer of the gold particle [24] at a temperature well below the bulk melting temperature; the minimization of the liquid surface tension causes the particles to revert to a spherical shape [22]. Composto and coworkers [25] have explored the thermal annealing properties of polyethylene glycol thiol functionalized GNRs in polymethylmethacrylate (PMMA) composites. This work 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. The surface melting can be mitigated by appropriate functionalization strategies, and many groups have applied a passivation layer to enhance thermal stability. There have been reports employing carbon [26], titanium oxide [27], zirconia [28] and mesoporous silica shells. The synthetic accessibility and matrix compatibility of silica suggests it may be the best candidate for stabilizing GNRs. A silica shell improves the survivability of the modified GNRs, although the surface treatment does not completely prevent shape deformation [29]. Moreover, 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 report, 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.

**Materials**

**Gold Nano-rod Fabrication**

GNRs were fabricated by a seed-mediated growth method in accordance with previous reports\[10,11\] [10,11]. Unless specified, all reagents were purchased from Sigma Aldrich, St. Louis MO and prepared in water. Seeds were used within 5 hours of preparation.

Growth solutions were prepared for 3 batches of different sized GNRs (volume=300 mL); the batches were termed B1, B2 and B3. The morphological characterization of the rods can be found in Table 1.

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

**GNR functionalization**

B1 GNRs were functionalized with polyethylene glycol thiol (6000 MW, PEG-SH) by methods previously described in literature [30].

B2 and B3 GNRs were functionalized with porous silica shells (Si) and an outer silane layer for modified hydrophobicity. The growth of silica (Si) shells was accomplished by applying a modified Stober method reported by Murphy et al [31]. Further functionalization of the silica shell was achieved using a method modified from a previous literature report [32]. Hydrophobicity of the silica shell was modified by functionalization with a silane coupling agent (HTCS, n-Hexyltrichlorosilane).

**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. Initially, polymeric resin pellets [poly(methylmethacrylate) (PMMA), Acrylite M30, AMCO Plastics) were dissolved in chloroform (200-300 mg/mL). Based on a rough estimation of solution concentration, 10-15 mL of the concentrated 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.

**Preparation of final composite (PNC)**

To produce the final PNCs, extrusion and injection molding was performed. Briefly, the master-batch was fed along with pelletized PMMA feed stock (CYRO Industries, Acrylite M30, Mn = 56 kDa, Mw = 85 kDa, PDI = 1.52) into a 15 cc Micro-Compounder (DSM Xplore). After a 10 minute compounding interval 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.

**Instrumental characterization**

The optical properties of the GNRs in composite or solution form 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). Finally, the glass transition temperature was measured using differential scanning calorimetry (DSC, TA Instruments Discovery Series).

**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.

The initial characteristics of the GNRs are highlighted in Table 1, which shows the aspect ratios and measured length/width of the nanorod cores. Table 2 provides information on the surface stabilization layer, as well as the measured thickness of the coating, and the optical properties of the as-prepared GNRs in solution (indicated by the λ H2O values).
Table 1: Gold Nanorod Morphology Before/After Melt Processing

<table>
<thead>
<tr>
<th>GNR</th>
<th>AR</th>
<th>Length (nm)</th>
<th>Width (nm)</th>
</tr>
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<tbody>
<tr>
<td>B1</td>
<td>2.5 +/- 0.6</td>
<td>41.8 +/- 8.8</td>
<td>16.8 +/- 1.6</td>
</tr>
<tr>
<td>B2</td>
<td>3.4 +/- 0.7</td>
<td>38.7 +/- 6.5</td>
<td>11.7 +/- 1.6</td>
</tr>
<tr>
<td>B3</td>
<td>5.3 +/- 1.1</td>
<td>75.3 +/- 10</td>
<td>14.2 +/- 1.0</td>
</tr>
<tr>
<td>Post B1</td>
<td>1.8 +/- 0.3</td>
<td>33.8 +/- 5.2</td>
<td>18.5 +/- 3.1</td>
</tr>
<tr>
<td>Post B2</td>
<td>2.8 +/- 0.5</td>
<td>32.5 +/- 5.7</td>
<td>11.8 +/- 1.3</td>
</tr>
<tr>
<td>Post B3</td>
<td>4.2 +/- 0.8</td>
<td>67.5 +/- 6.9</td>
<td>16.4 +/- 3.2</td>
</tr>
</tbody>
</table>

Table 2: Surface treatment and optical properties of GNRs & composites

<table>
<thead>
<tr>
<th>GNR</th>
<th>Coat.</th>
<th>Thick. (nm)</th>
<th>( \lambda ) H2O (nm)</th>
<th>( \lambda ) cast (nm)</th>
<th>( \lambda ) PNC (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>PEG</td>
<td>~5 nm</td>
<td>701</td>
<td>731</td>
<td>623</td>
</tr>
<tr>
<td>B2</td>
<td>Silica</td>
<td>32.5 +/- 1.1</td>
<td>771</td>
<td>786</td>
<td>712</td>
</tr>
<tr>
<td>B3</td>
<td>Silica</td>
<td>18.5 +/- 1.1</td>
<td>995</td>
<td>1003</td>
<td>917</td>
</tr>
</tbody>
</table>

The process to produce the desired PNCs employed an intermediate cast film with a high loading of GNR (e.g. a master-batch), which was diluted with additional polymer in a lab-scale conical twin-screw extruder with a recirculation channel. The master-batch approach was primarily employed as a safety precaution, which obviated the need to handle dried nano-particulates and entailed no risk of aerosolization during mixing. The cast master-batch also prevented significant agglomeration of the nanoparticles as the film dried. This provided a buffer between the individual GNRs and in turn prevented their collapse into larger particles that would resist re-dispersion into a true nano-scale phase.

The twin-screw compounding employs a feed-throat with a manually actuated plunger, this facilitated the feeding of the master-batch feedstock. Briefly, the films were sectioned into smaller strips, fed into the feed-throat with the piston removed, and the re-installation of the piston forced the sections into the conical screws. Pellets of virgin polymer were combined with the master-batch feedstock, to yield a desired quantity of polymer with a desired loading level.

Representative plots of the processing runs are shown in Figures 1 & 2; respectively B1 and B2 compounded in PMMA. The plateau region of each force plot represents the interval of recirculation in the extruder barrel. The melt temperature and screw speed are plotted on the secondary axis. Inclusion of the GNRs did not substantially alter the processing conditions of the PMMA. After the initial run (first plateau), some of the melt was extruded and molded via injection molding. Additional PMMA was added to the remainder of the melt and a second processing cycle was executed (second plateau). This resulted in dilution of the filler in the next batch of extruded/molded components. The ultimate loading for each PNC is given in Table 3.

Figure 1: Processing conditions for PNCs containing B1 in PMMA.

Figure 2: Processing conditions for PNCs containing B2 in PMMA.
Table 3: Compositions of PNCs after extrusion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass %</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1.58</td>
<td>0.78</td>
</tr>
<tr>
<td>B1 dilute</td>
<td>0.85</td>
<td>0.42</td>
</tr>
<tr>
<td>B2</td>
<td>1.48</td>
<td>0.73</td>
</tr>
<tr>
<td>B2 dilute</td>
<td>0.63</td>
<td>0.31</td>
</tr>
<tr>
<td>B3</td>
<td>1.18</td>
<td>0.59</td>
</tr>
<tr>
<td>B3 dilute</td>
<td>0.49</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The optical properties of the GNRs was assessed using UV-Vis spectroscopy after each stage of the process. Each GNR exhibits a plasmon resonance (manifested as an optical absorption) arising from both geometric axes, longitudinal and transverse. The resonance arising from the longitudinal axis is chiefly sensitive to aspect ratio and the refractive index (RI) of the host matrix. The transverse axis resonance is less influenced by the geometric and environmental parameters, and occurred at ~510-550 nm. The λ_max observed for the longitudinal resonance is provided in Table 2. Initial spectra were obtained in an aqueous solution, and then were compared to the cast master-batch film and of the extruded PNC.

The optical properties of the cast master-batch films exhibited a slight red-shift in λ_max, which can be attributed to the change in refractive index in the host matrix compared to the aqueous solution reference. In contrast, for the PNC all of the samples exhibited a blue-shift in λ_max. This shift can be attributed to a morphological change of the GNRs during the melt-processing. However, the shape of the optical spectrum in all cases suggests the preservation of the basic rod morphology. The measured change in AR and dimensions, determined by measuring the GNRs after compounding, is provided in Table 1.

Figure 3: GNRs prior to integration into polymer

Transmission electron microscope images of the isolated GNRs (prior to functionalization and integration) are shown in Figure 3 and images of the isolated GNRs after melt processing are depicted in Figure 4 (respectively B1 (A), B2 (B), B3 (C)). A direct comparison of Figures 3 &4 reveals a slight change in AR, although it should be noted that Fig 4-B3 is taken at twice the magnification of the others (scale bar = 50nm instead of 100nm as in other images).

Figure 4: GNRs isolated from PNCs show slight reduction in AR.

While the reduction in AR was measurable, the PNCs largely maintained the desired optical properties. The stabilizing shells were effective at preventing the GNR reversion to spherical particles (see refs 23, 24), and the ultimate optical properties could be tuned by correlating surface treatment and process conditions to yield a specific GNR AR in the final part.

The PNCs were formed into transparent plaques for optical testing using injection molding. The high shear forces experienced during the fill process resulted in a significant degree of ordering of the GNRs in the flow direction. This is most readily observed for panel C (B3) in Figure 5, which should be the most susceptible to shear alignment due to its higher AR.

Figure 3: GNRs hosted in PNC, demonstrating shear alignment from injection molded plaques.

Conclusions

A two-step process was employed in which the GNRs were first solution-cast into a polymer matrix to generate a 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. Polymethylmethacrylate (PMMA) (processed at ~235 °C) was used to demonstrate the ability to use melt-processing to prepare optically tuned PNCs. 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 TEM 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.

References