Fabrication of Chitosan Bioplastic Diffraction Gratings from Crab Shell Waste Blended with Cornstarch via Soft Lithography

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Abstract

The rising demand in the seafood industry leads to significant waste, which, if not properly disposed of, causes environmental issues. There is a need to bridge the gap between seafood production and waste management by transforming waste into a valuable resource. This study uses various laser sources to produce bioplastic diffraction gratings from seafood waste and evaluate their diffraction performance. It reports the diffraction efficiency at two laser wavelengths for chitosan bioplastic diffraction gratings made from crab shell waste blended with starch. Chitosan was extracted from crab shell waste through four main steps: demineralization, deproteinization, depigmentation, and deacetylation. A chitosan-starch mixture was prepared and then poured into a master mold for elastomer gratings, replicated from a commercial grating. Gratings with groove densities of 600 lines/mm and 1200 lines/mm were successfully produced. Using a He-Ne laser (633 nm) with 0.8 mW power and an Ar+ ion laser (514.5 nm) with 25 mW output power, the diffraction efficiencies of the fabricated bioplastic gratings were measured. Results showed that the measured diffraction angles closely matched theoretical predictions. The diffraction power efficiencies of the bioplastic gratings were comparable to those of polydimethylsiloxane (PDMS) grating replicas. These findings demonstrate the compatibility of a chitosan-starch blend with soft lithography for fabricating diffraction gratings.

Keywords*:* bioplastic, chitosan, diffraction angle, diffraction grating, and starch

1. Introduction

Due to the rapid growth of the fishing and seafood industries, a growing population and rising demand for seafood products, solid waste disposal has become a persistent problem in coastal communities. Exoskeleton and shell waste are disposed of in large quantities on land and water. These materials account for nearly 35% and 40% of the waste generated from seafood production, and if improperly discarded, will pollute the environment (Veugopal, 2022; Tan *et al*., 2022). It is crucial to find alternative uses and develop disposal and treatment processes for seafood waste (Monteiro *et al*., 2016). Crab shells containing 10% to 72% chitin are wasted even when chitin can be extracted and prepared for chitosan conversion (do Vale *et al*., 2021).

Chitin is the second-most abundant polymer from crustacean shell waste from shrimp and crabs (Chen and Yan, 2020). It is a polymer with repeating units of N-acetyl-D-glucosamine linked by 1,4-β-glycosidic bonds, containing a small amount of deacetylated monomer units, which enables practical applications in medicine, biotechnology, and biomimetics (Tsurkan *et al*., 2021). Chitosan is abundantly found in crustaceans, such as shellfish, including crab, lobster, and shrimp, and can be derived from chitin through a process of deacetylation. A natural polymer with a wide range of applications from nanotechnology to medicine and agriculture (Dimzon and Knepper, 2014), chitosan is a material used in thin films for laser processing, contact lenses, and waveguides (Aesa and Walton, 2020). Limitations of chitosan in bioplastic packaging applications have been noted, including low mechanical and thermal flexibility, as well as poor water and gas barrier permeability (Gao *et al.,* 2021).

Starch, a carbohydrate composed of linear amylose and intensely branched amylopectin, is a highly abundant polymer in nature and is easily processed (Lee *et al*., 2021). It is a low-cost material used in agriculture, medicine, and packaging (Jiménez-Regalado *et al*., 2021; Li *et al*, 2013). As a bioplastic, starch has several drawbacks, including its hydrophilic nature and weak mechanical properties, which necessitate the addition of cellulose fillers such as chitosan (Ginting *et al*., 2018; Karua and Sahoo, 2020). The addition of chitosan in tapioca starch film exhibited high tensile strength and improved glossiness with negligible effect on its transparency, lightness, and luminosity (Shapi'i and Othman, 2016).

Natural polymers have been used in medical and biological applications in optical devices due to their high permeability and biocompatibility properties (Huszank *et al*., 2010). For example, polymeric gratings fabricated using a SiO_2/Si-based mold were employed as biosensors (Barrios *et al*., 2011). Diffraction gratings are optical materials that separate light at different wavelengths into spectra, which can then be used to examine the structure and composition of materials. Diffraction efficiency is an important technical parameter in assessing the performance of diffraction gratings. Optimizing grating groove type and manufacturing technique are among the parameters to improve the efficiency of a diffraction grating (Wang *et al*., 2022). It is widely used in many fields such as spectroscopy, laser beam splitters and combiners, scanners, and liquid crystal displays (Yin *et al*., 2022). The widespread use of diffraction gratings in optical multiplexes, signal processors (Cao *et al*., 2020), integrated optics, holography, and optical switching has led to advancements in fabrication techniques involving polymer materials, including soft lithography (Li *et al*., 2021). Soft lithography offers design flexibility, low cost, and highly faithful replication of gratings at the nanoscale (Pada and Guerrero, 2017; Guerrero *et al*., 2007). Grating grooves are replicated by casting a prepolymer liquid onto a master mold (Liu *et al*., 2006).

In this paper, the researchers discuss the fabrication of a bioplastic diffraction grating through soft lithography of chitosan, extracted from crab shell waste, blended with corn starch as a base material. Successful replication and gratings performance are confirmed through diffraction experiments. Results may confirm the viability of the fabricated bioplastic grating, demonstrating comparable performance across different laser sources. Most gratings are made of metals and glass; these materials can be replaced by a bioplastic grating, enabling the development of a low-cost and lightweight optical instrument, such as a spectrophotometer. To the best of the researchers' knowledge, this is the first report on the performance of diffraction gratings fabricated from chitosan derived from crab shell waste blended with corn starch at different laser wavelengths.

2. Methodology

2.1 Extraction of Chitosan

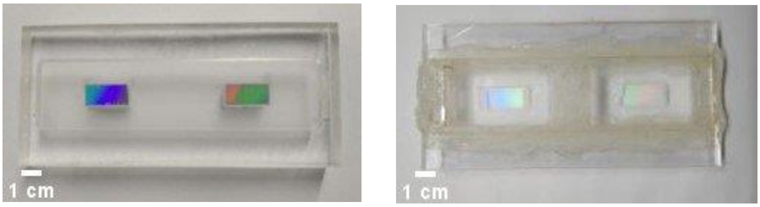
Corn starch was obtained from a local supermarket. Chitosan was prepared based on four major steps: demineralization, deproteinization, depigmentation, and deacetylation (Hassan *et al.*, 2022). Collected crab shell wastes were washed with running water and oven-dried at 60°C for 24 hrs. Turned into powder using a kitchen blender and kept in a hermetic container. In the demineralization step, the crab shell powder was treated with 4% HCl acid at a solid-to-solvent ratio of 1:20 for 1 hour with constant stirring at 120 rpm using a magnetic stirrer at room temperature (25°C). In deproteinization, the demineralized crab shell powder was treated with 15% NaOH at a solid-to-solvent ratio of 1:10 for 2 hours, stirred constantly at 120 rpm at 60°C in a magnetic stirrer. For depigmentation, the deproteinized crab shell powder was treated with 0.5% NaClO at a solid-solvent ratio of 1:25 for 30 min, constantly stirred at 120 rpm at 40°C in a magnetic stirrer. For the deacetylation step, the depigmented crab shell powder was treated with 50% NaOH for 6 hours at a solid-solvent ratio of 1:40, with constant stirring at 120 rpm and a temperature of 80°C in a magnetic stirrer. The chitosan derived from crab shell waste has a degree of deacetylation (%DD) of 82% (Gumayan *et al.*, 2022).

2.2 Soft Lithography Grating Fabrication

Two stages of soft lithography were employed to fabricate the bioplastic gratings. First, an elastomeric replica of a master grating was created. An original mold was prepared using two commercially available diffraction gratings (Edmund Scientific), each measuring 25.4 mm x 12.5 mm, with distinct groove densities of 600 and 1200 lines/mm. The masters were fixed in slots within a recessed area on a plexiglass block (80 mm x 40 mm x 4 mm), with the grating surface elevated 2 mm from the recess floor. Soft lithographic replication of the commercial gratings, as seen in Figure 1a, was performed using Sylgard 184, a polydimethylsiloxane (PDMS) elastomer that is transparent and mechanically stable over a temperature range of -50°C to 200°C (Pada and Guerrero, 2017).

Liquid PDMS was prepared by mixing a prepolymer with the curing agent in a 10:1 ratio, then poured into the mold until the recess was filled and the gratings were fully covered. The elastomer in the mold was degassed for three hours and allowed to solidify for five to seven days at room temperature (25°C). Upon curing, the PDMS layer was carefully lifted from the mold. The replicated grating surfaces are complementary copies of the originals with their groove densities.

The elastomer layer imprinted was fastened with the replicated grating surfaces between two plexiglass sheets, as shown in Figure 1b. The top plexiglass sheet features an opening that accommodates an elastomer area of 80 mm x 40 mm, introducing a 4 mm depression into which the chitosan-starch solution can be poured.



(a) (b)

Figure 1. Photographs of grating molds with commercial gratings (a) and PDMS grating replicas (b)

The liquid solution of chitosan-starch was prepared by dissolving 0.3 g of extracted chitosan in 100 mL of a 3% acid solution and constantly stirring at 300 rpm with a magnetic stirrer at 100°C. In preparing the liquid solution of starch, 0.3 g of starch was dissolved completely in 20 mL of distilled water and constantly stirred at 120 rpm with a magnetic stirrer at 80°C.

To fabricate the bioplastic grating, 10 mL of starch solution was slowly added to 90 mL of chitosan solution, followed by constant stirring at 120 rpm with a magnetic stirrer at room temperature (25°C) until complete homogeneity was achieved. The homogenized solution was poured into the elastomeric grating mold. The recorded curing time for the bioplastic gratings was seven days at 25°C.

A bioplastic grating with 600 lines/mm was successfully replicated as seen in Figure 2a. The film around the grating was removed. Dispersion on the grating surface confirms the faithful replication of groove structures. Similar results were observed in a replica with a groove density of 1200 lines/mm, as evidenced by visible colors on the grating surface in Figure 2b.

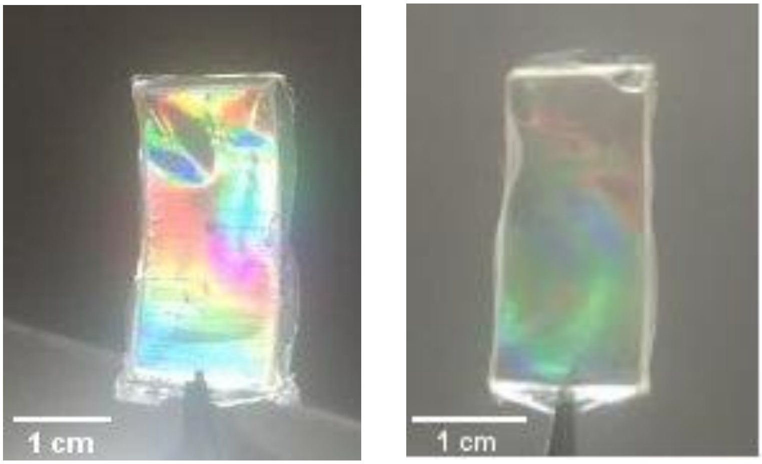


Figure 2. Gratings fabricated via soft lithography from chitosan blended with starch, having groove densities of 600 lines/mm (a) and 1200 lines/mm (b)

2.3 Diffraction Experiments

The diffraction performance of the bioplastic gratings was evaluated using the setup shown schematically in Figure 3. Measurement was performed inside the dark room of Optics and Photonics Laboratory of the Ateneo de Manila University. Two laser sources were used: a 25 mW Ar^+ laser (Modu-Laser) with wavelength λ = 514.5 nm and a 0.8 mW He-Ne (Uniphase) with wavelength λ = 633 nm, with the beams aligned to be at normal incidence to the grating. The target grating was mounted on a custom holder and the output diffraction pattern was observed on a viewing screen. The distances from the grating to the viewing screen and between the center spot and the 1st-order diffraction spot were measured to obtain the experimental diffraction angle.

The theoretical value (18°) was computed from the grating equation for normal incidence, $m\lambda = d\sin\theta$ with order m = 1. Where λ refers to the wavelength of the laser source, d denotes the grating period, and θ is the diffraction angle.

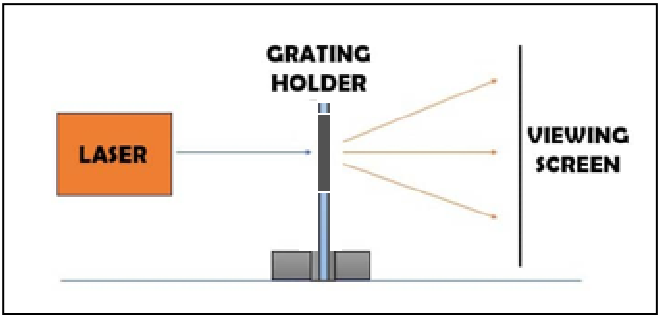


Figure 3. Schematic diagram of the experimental setup (top view)

3. Results and Discussion

3.1 Grating Response at 514.5 nm Laser wavelength

Visible first- and second-order diffraction spots were generated with a bioplastic grating replica having 600 lines/mm (Figure 4a). With the spacing from the 0^{th}-order spot to the 1^{st}-order spot and the distance between the grating and viewing screen, the first-order diffraction angle $\theta = 18.05 \pm 3°$ was obtained with only a 0.4% deviation from the theoretical value of 18.00°.

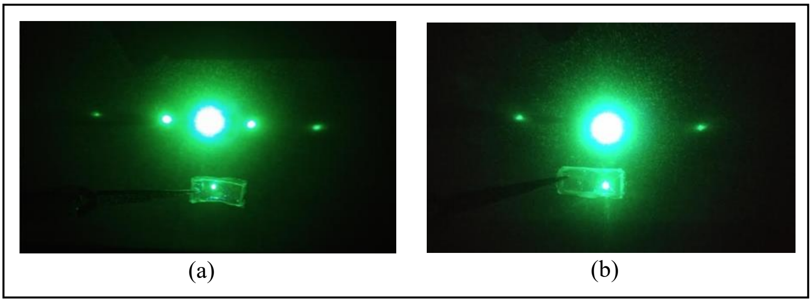


Figure 4. Diffraction patterns generated with a 514.5 nm laser source by gratings with 600 lines/mm (a) and 1200 lines/mm (b)

The output of a bioplastic grating replica with 1200 lines/mm is a single diffraction order, seen in Figure 4b. Both diffraction spots were distinct with a measured diffraction angle θ of $38.62 \pm 7°$, with a difference of only 1.4% from the value given by the grating equation (38.10°). Excellent agreement of experimental and theoretical values for the two bioplastic grating replicas indicates high fidelity of the soft lithographic copying process. Small percentage errors in the angle of diffraction can be attributed to imperfections on the surface of the bioplastic material. A slightly curved surface was observed, caused by the internal strain during the curing process.

3.2 Grating Response at 633 nm Laser wavelength

A clear first-order diffraction pattern was generated with a bioplastic grating replica having 600 lines/mm (Figure 5a) using a 633 nm wavelength laser source. The second diffraction order was also visible. The measured first-order diffraction angle θ of 22.17 ± 4° deviates by 0.6% from the theoretical value (22.31°).

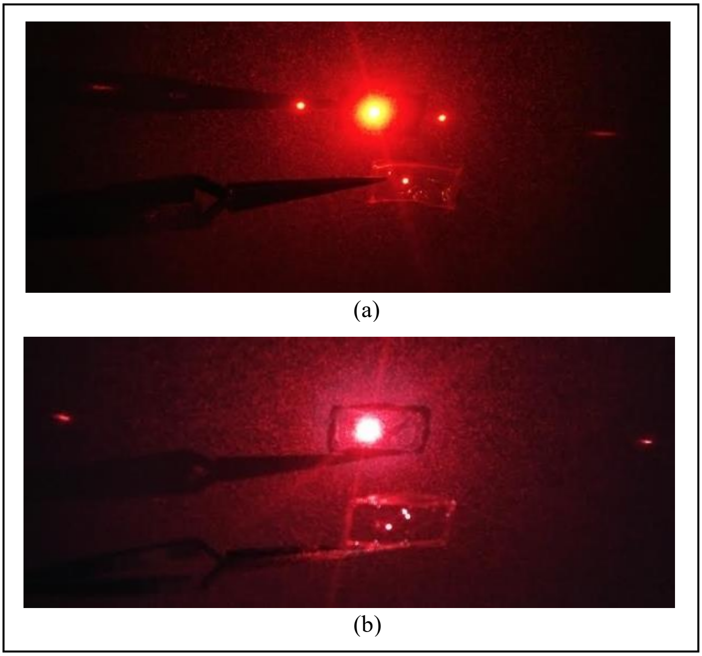


Figure 5. Diffraction patterns generated with a 633 nm laser source by gratings with 600 lines/mm (a) and 1200 lines/mm (b)

For the bioplastic grating replica having 1200 lines/mm, a single diffraction order was generated, as in Figure 5b. Both diffraction spots were distinct with a measured diffraction angle θ of 51.00 ± 9°, with an error of 2.6% from the value given by the grating equation (49.40°). Minimal deviation between experimental and theoretical values for the two bioplastic grating replicas with a 633 nm wavelength laser source indicates the compatibility of the bioplastic material with the soft lithographic copying process.

3.3 Grating Power Efficiency

The diffraction efficiency of the bioplastic grating using a 514.5 nm wavelength laser source at m = 1 is measured with a power meter (Edmund Optics). For a bioplastic grating replica with 600 lines/mm, the efficiency was found to be 0.5%, comparable with that of the PDMS master grating, which had an efficiency of 1%. An efficiency of 0.2% was found for a replica with a groove density of 1200 lines/mm, comparable with the 0.7% efficiency of the corresponding PDMS master grating.

With a 633 nm laser source at m = 1, the measured efficiency of the bioplastic grating replica with 600 lines/mm was found to be 0.3%, comparable with that of the PDMS master grating, which had an efficiency of 1%. An efficiency of 0.3% was found for a replica with a groove density of 1200 lines/mm, comparable to the 0.7% efficiency of the corresponding PDMS master grating.

4. Conclusions and Recommendation

The researchers report the diffraction performance at 514.5 nm and 633 nm of bioplastic gratings fabricated from chitosan from crab shell waste blended with starch, with groove densities of 600 and 1200 lines/mm. Diffraction patterns generated by the bioplastic replicas agree with theoretical values from the grating equation at normal incidence. The result implied the viability of chitosan-starch as a material in fabricating bioplastic gratings via soft lithography. Measured power efficiencies for the bioplastic gratings are comparable to those of PDMS grating replicas.

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