

Analysis of bio-polymeric wet-end paper additives in the context of origami folding applications

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Many of the additives used to strengthen paper during production result in mill effluent that is highly detrimental to aquatic environments, and in an effort to reduce production with toxic chemicals, research has been conducted on the capabilities of bio-polymers to enhance paper strength. Addressing an increase in origami applications in engineering fields, this study characterized the effect of bio-polymeric paper additives on the mechanical properties associated with origami folding applications. Sheets were developed for four bio-polymeric additives, nanofibrillated cellulose (NFC), carboxymethyl cellulose (CMC), guar gum, and chitosan, and were characterized by their thickness, tensile index, and folding endurance. The additions of 10% NFC and 0.8% guar gum solutions showed increases in folding endurance of 13.78% and 11.69%, respectively, with 0.8% guar gum retaining folds marginally better than 10% NFC. The additives showed no significant difference in thickness, grams per square meter (GSM), or cross tensile strength; however, chitosan samples had significantly greater wet tensile strengths. Surprisingly, after the application of 20 double folds, an extreme increase in tensile index was observed, a phenomenon that, if confirmed, could significantly benefit paper applications with repeated folding. The increased folding characteristics in paper with 10% NFC and 0.8% guar could prove effective in origami folding applications.

Keywords: *bio-polymer, bio-polymeric additive, paper additive, origami, folding applications, papermaking, tensile strength*

Paper's versatility has allowed it to be applied in tremendous quantities for practical and artistic uses. In 2022, total paper production weighed in at more than 414 million metric tons, and in order to hold up in its various applications, many chemical additives are utilized to increase paper strength and confer new properties to paper (Statista Research Department, 2024). However, the use of these chemical additives produces mill effluents that are detrimental to the environment, shown to deplete dissolved oxygen levels or induce genetic changes in aquatic organisms. These chemicals can also potentially contaminate drinking water, serving as human carcinogens (Ali & Sreekrishnan, 2001). A possible solution to the toxicity of mill effluents is the use of bio-polymers as paper additives, such as polymers derived from cellulose, hemicellulose, starch, chitin, and gums. Previous research on various bio-polymers by Basu et al. has proven them to be effective strength enhancers and retention agents, especially in dual polymer systems; however, there is much less research on

the effects these additives have on specific strength characteristics (Basu et al., 2021).

Origami, the art of paper folding, is a traditional art form that requires strong paper in order to be folded more easily. The mechanical structure of origami allows movement in one fold to induce movement in other folds across the model, making it particularly effective when applied in engineering solutions that require compact and repeatable movement. This ability, in addition to being a scalable compliant mechanism, has led to its application in engineering fields including nanorobotics, medical robots, and deployable solar arrays. While most origami-inspired engineering uses stronger panel materials and added hinges, strong paper is still essential for a few engineering applications as well as prototyping origami mechanisms.

Origami requires specific strength characteristics that are often not well defined or simply not measured in previous studies. Origami often entails repetitive folding over the same crease

or points of many intersecting folds, leading to tearing along folded lines. Using paper of a higher folding endurance, the number of double folds required to make paper break is one solution to reducing tears in origami paper (admin, 2022). The ideal paper for repetitive folding is also dependent on the characteristics of thickness, folding resistance, and folding elasticity, in addition to folding endurance. Origami applications without scoring or cutting benefit greatly from both a lower force to induce a fold and a lower elastic recovery, especially when many overlapping layers need to be folded (Rao et al., 2013).

This study aimed to quantify the impact of nanofibrillated cellulose, carboxymethyl cellulose, guar gum, and chitosan on origami folding applications by developing handsheets for each additive and determining their effectiveness in folding applications based on the parameters of thickness, folding endurance, and folding elasticity. Handmade abaca paper was developed at the Minnesota Center for Book Arts (MCBA), and each sheet was divided into testing groups for folding endurance and folding elasticity. Thickness and GSM were measured for each sheet. Folding endurance was measured with separate samples from folding elasticity, where folding endurance was measured by testing tensile strength across varying numbers of folds, and folding elasticity was measured by the distance between the ends of a folded strip of paper 1 cm from the fold. The results of this study provided NFC and guar gum as potentially effective for use in origami folding applications and created a basis for future research exploring the effects of dual polymer systems and additional additives.

Methods

Abaca Fiber and Bio-polymeric Additives

Abaca fiber was obtained from Carriage House Paper. Bleached Abaca Fiber sheets were used for papermaking.

Cellulose nanofibers, carboxymethyl cellulose, chitosan, and guar gum were used as bio-polymeric wet-end additives in sheetmaking. CMC was obtained as a white powder from Walmart, guar gum and medium molecular weight chitosan were obtained in the form of white powders from Sigma Aldrich, and cellulose nanofibers were obtained as a

slurry from Cellulose Lab. Cellulose nanofibers were of width 1-80 μm and length 1-50 μm . In percentages based on the dried pulp weight, cellulose nanofibers were added in concentrations of 5% and 10%, CMC was added at 0.2% and 0.8%, guar gum was added at 0.3% and 0.8%, and chitosan was added at 0.5% and 1.5%. Before use in the papermaking process, cellulose nanofibrils were measured by the mass of the cellulose and evenly mixed in water to form a 420 mL solution. CMC and guar gum were dissolved in water to form 420 mL solutions. 1 gram of chitosan was prepared in a 200 mL solution of 1% aqueous acetic acid, and an appropriate amount of the solution was mixed with water to form a 420 mL solution.

Handsheet Development

Pulp beating followed the process outlined in the MCBA European Papermaking class. Pulp combinations are beaten and disintegrated using the Laboratory Beater "Valley." 340.19 g of soaked abaca fiber was ripped into pieces about 25 mm across and beaten in 23 L of water for 10 minutes without weight on the level arm. The mixed fiber was then beaten for 180 minutes under a 5.5 kg weight. 2 L samples of pulp were sampled, and additive solutions were disintegrated in for 15 minutes without weight. Beaten abaca was stored in airtight buckets and refrigerated during storage without draining.

All paper handsheets were made following the papermaking process outlined in the MCBA European Papermaking class. Paper handsheets were developed using a 35 x 21.25 cm wove mould and box deckle, where pulp was placed in the box with a plastic sheet covering the mesh, and the mesh was quickly removed to allow the pulp to drain and form a sheet. The sheets were pressed in a hydraulic press at 6000 psi and then dried using a restraint drying system. Six handsheets were developed for each additive concentration.

Thickness and Grams Per Square Meter

The thickness of individual paper sheets was measured using a caliper with an accuracy of up to 0.01 mm. GSM refers to the grams per square meter of a paper sheet. A 33.5 x 19.5 cm rectangle was first cut out from the handsheets, then the sheet was weighed. The following formula was used to calculate the GSM of the handsheet: $\text{GSM} = \frac{m}{A}$,

where m is the mass of the handsheet in grams, and A is the area of the handsheet in square meters.

Cross Tensile Index and Wet Tensile Index

Tensile index was calculated as the tensile strength of a specimen divided by its GSM. Tensile index was used to account for slight variations in GSM due to the traditional papermaking process. Tensile testing samples were 2.5 x 18 cm rectangular samples that were taken either lengthwise or widthwise from the 33.5 x 19.5 cm sheet, and their tensile strength was measured as the maximum tensile force in newtons divided by the sample width. The Tinius Olsen Model No. H5K-S tensile test machine was used to test for tensile force in accordance with TAPPI 494. The measurements were carried out at a room temperature of approximately 23 °C and relative humidity between 30% and 55%. Cross tensile index is measured as the tensile index of a sample taken lengthwise from the original handsheets. The ratio between the cross tensile index and standard tensile index was calculated as the cross tensile index ratio. Tensile test samples taken widthwise were looped back on themselves, the centers were soaked in deionized water for 5 minutes, and the tensile index was measured while still wet to obtain the wet tensile index. The ratio between the wet tensile index and standard tensile index was calculated as the wet tensile index ratio.

Folding Endurance

Folding endurance is typically defined as the number of times a sample of paper can be double folded before it breaks while under a load (admin, 2022). Due to a lack of equipment to properly measure folding endurance, in this study, it was quantified as the percent decrease in the tensile index of a paper sample after it had been subjected to varying numbers of double folds. Tensile index for quantifying folding endurance was tested using tensile testing samples taken widthwise from the original handsheets and measured with the same procedure and the same conditions as previous tensile index testing. Double folds were carried out by evenly folding a specimen in half perpendicular to the tensile force, creating a gentle and consistent crease using a bone folder, and creasing again along the same line after flipping the fold 360 degrees. A standard tensile index was first tested using an

unfolded specimen, then specimens with 1, 2, 5, 10, 20, and 50 double folds were tested. The tensile index for each group of specimens was plotted against the number of double folds the paper underwent.

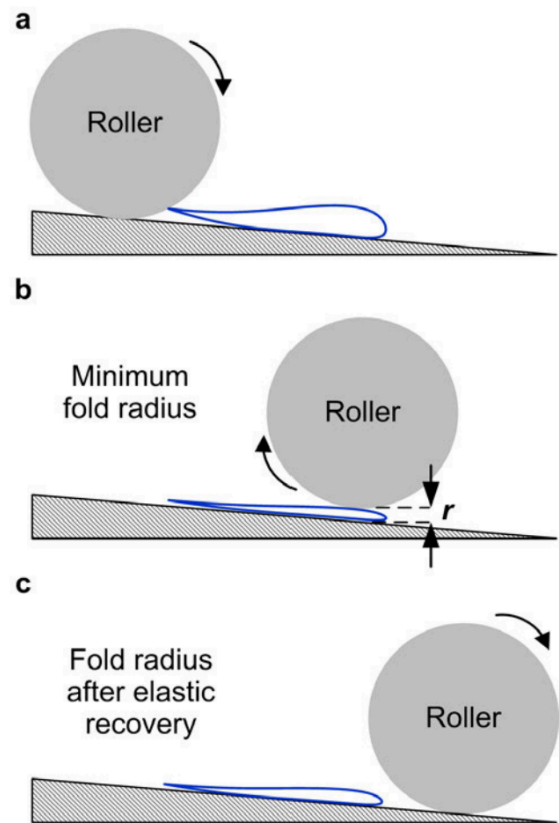


Figure 1. Schematic of the rolling experiment used to determine the relationship between applied force and folding radius. A steel roller of 12.2985 newtons was used to fold strips of width 8, 4, 2, 1, and 0.5 cm. (a) The paper strip is looped over itself and taped to the inclined plane, with the roller placed above it. (b) The roller was allowed to roll over the paper strip in a controlled manner. In this study, the folding radius at the exact folding time was not recorded. (c) The folded strip was allowed to recover. The strip was cut 1 cm from the fold, and the distance between the cut ends was measured. Figure courtesy of Rao et al., 2013.

Folding Elasticity

Folding elasticity is defined as the tendency for paper to rebound following the application of a crease. In this study, folding elasticity was measured using an apparatus similar to the one used in Rao et al., consisting of a weighted roller and an inclined plane. Folding elasticity samples were cut widthwise from the original handsheet with a length of 16 cm and widths of 8, 4, 2, 1, and 0.5 cm. The ends of the paper strips were looped over

themselves and taped to the top of the inclined plane, and the weighted roller was slowly allowed to roll down the plane, folding the paper with a specified force (Figure 1). Each sample width had a related force per unit length exerted by the roller, with 8, 4, 2, 1, and 0.5 cm correlating to 154, 307, 615, 1230, and 2460 N/m, respectively. The folded paper strip was cut 1 cm from the fold, and the distance between the ends of the cut fold was recorded as the elastic radius. The strain (paper thickness divided by the elastic radius) was plotted against the force per unit length exerted on the paper.

Results

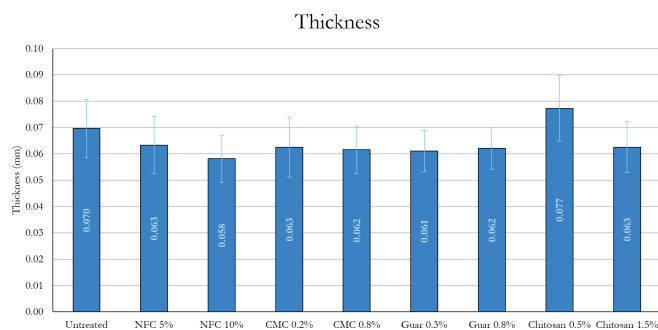


Figure 2. Mean thicknesses of developed paper sheets with concentrations of NFC, CMC, guar gum, and chitosan. Thickness is measured in millimeters using a caliper with an accuracy of up to 0.01 mm. Untreated, n=81; NFC 5%, n=72; NFC 10%, CMC 0.2%, CMC 0.8%, guar 0.8%, guar 0.3%, chitosan 0.5%, n=66; chitosan 1.5%, n=64. All thicknesses fall between 0.5 and 0.9 mm, and there is no statistically significant difference in the thicknesses of the handsheets with additives compared to the untreated samples.

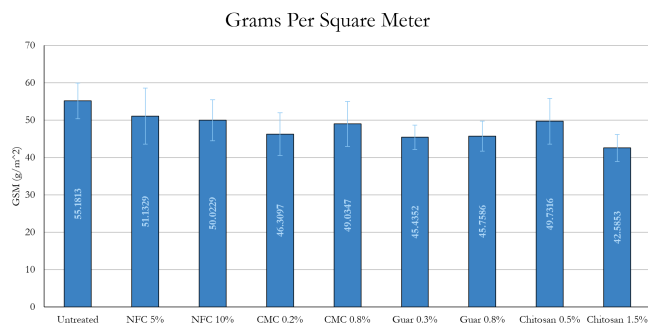


Figure 3. Mean grams per square meter (GSM) of developed paper sheets with concentrations of NFC, CMC, guar gum, and chitosan. GSM is measured in g/m² and is often used as a proxy for thickness. Untreated, n=52; NFC 5%, NFC 10%, n=50; CMC 0.2%, CMC 0.8%, guar 0.8%, guar 0.3%, chitosan 0.5%, chitosan 1.5%, n=26. GSM appears to follow a similar pattern to thickness for each additive.

Thickness and GSM

Across each additive, thickness was consistent, with most thicknesses falling between 0.06 and 0.08 mm (Figure 2). Grams per square meter followed a similar trend to thickness, with higher GSMs for 10% NFC and 0.5% chitosan and lower GSMs for guar gum trials, supporting the correlation between GSM and thickness. Unlike thickness, the GSM of guar gum trials and 1.5% chitosan was significantly lower than 5% NFC (Figure 3). Guar gum and chitosan trials were found to have the roughest surface texture, while CMC trials had the smoothest and most transparent paper.

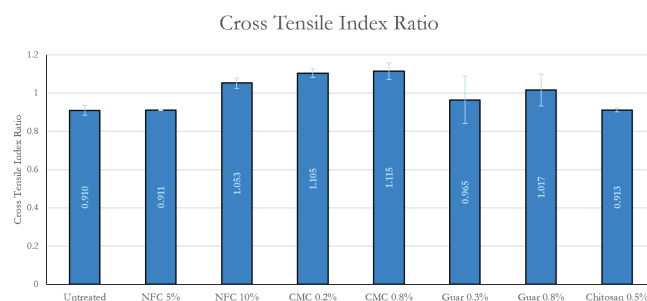


Figure 4. The ratio of cross tensile index against standard tensile index for developed paper sheets with concentrations of NFC, CMC, guar gum, and chitosan. The tensile strength was measured for a strip of paper cut in the direction perpendicular to the standard tensile index tests. Untreated, n=6; all additives, n=4. 10% NFC and CMC trials had significantly greater ratios than the ratio of the untreated trial.

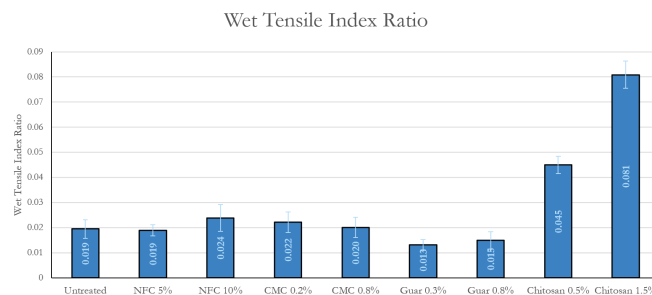


Figure 5. The ratio of wet tensile index against standard tensile index for developed paper sheets with concentrations of NFC, CMC, guar gum, and chitosan. The tensile strength was measured for a strip of paper with the middle soaked in deionized water for 5 minutes. Untreated, n=6; all additives, n=4. Chitosan samples exhibited significantly greater wet tensile indices compared to all other trials.

Cross Tensile Index and Wet Tensile Index

Cross tensile index was expected to be roughly equal to the standard tensile index due to the traditional European papermaking process not significantly favoring a fiber direction. The ratios of cross tensile index and standard tensile index for 10% NFC and CMC trials were significantly greater than a 1:1 ratio, and 0.8% guar gum was also significantly greater than the untreated ratio (Figure 4). The ratio of wet tensile index and standard tensile index was roughly 0.02 for NFC, CMC, and guar, significantly greater for 0.5% chitosan at 0.04, and even greater for 1.5% chitosan at 0.08 (Figure 5).

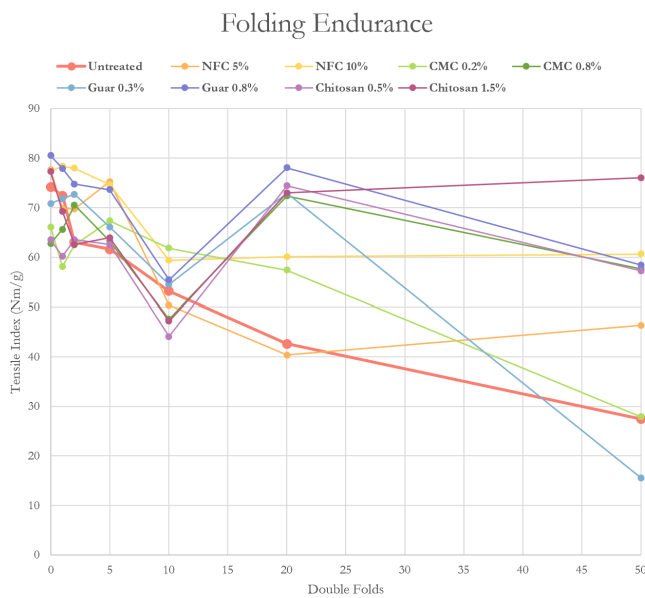


Figure 6. Folding endurance of each additive displayed as the tensile index (Nm/g) vs. the number of double folds applied to a specimen. 0 double folds (DF), 1 DF, 2 DF, n=4; 5 DF, 10 DF, 20 DF, n=2; 50 DF, n=1. Tensile index was compared to the untreated trial and averaged across all double fold counts to calculate a statistic for the increase in folding endurance. 10% NFC and 0.8% guar gum were 13.79% and 11.69% greater than the untreated trial, respectively; however, after 20 and 50 double folds, the tensile index increased in an unexplained phenomenon.

Folding Endurance

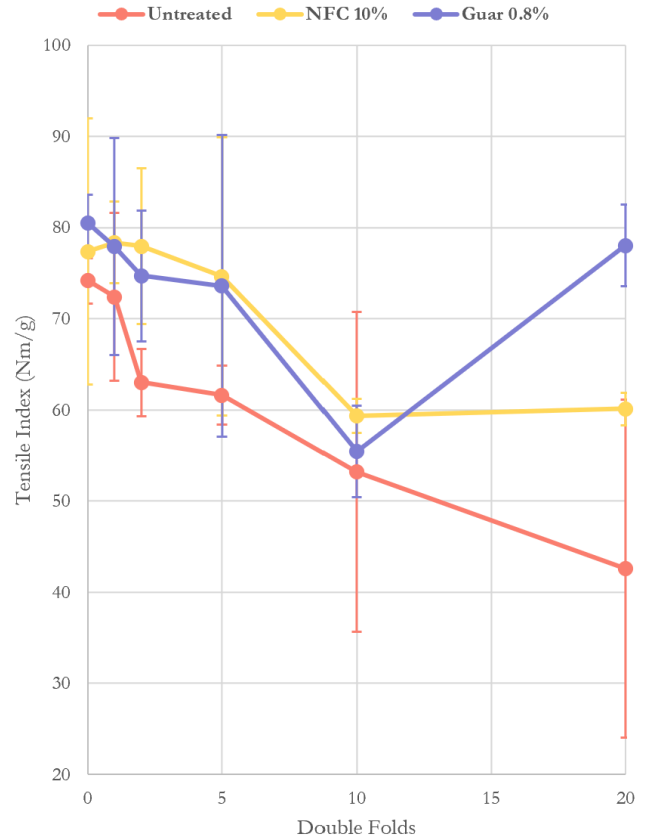


Figure 7. Folding endurance for the untreated, 10% NFC, and 0.8% guar gum trials displayed as the tensile index (Nm/g) vs. the number of double folds applied, including standard error bars. Error bars indicate one standard deviation. Results are presented as mostly not statistically significant, except for trials at 2 double folds.

Folding Endurance

For each additive, the tensile index of 4 specimens was tested for 0, 1, and 2 double folds. 2 specimens were tested for 5, 10, and 20 double folds, and one specimen was tested for 50 double folds. The tensile indices were plotted against the number of double folds, showing that NFC and guar samples outperformed the untreated trial (Figure 6). 10% NFC and 0.8% guar gum were most effective at enhancing folding endurance, with 13.79% and 11.69% increases, respectively (Figure 7). However, the differences were not great enough to conclude a statistically significant result, except for 2 double fold trials. Trials with 20-50 double folds diverged from the downward trend. The tensile index at 20 folds was similar to that of unfolded paper.

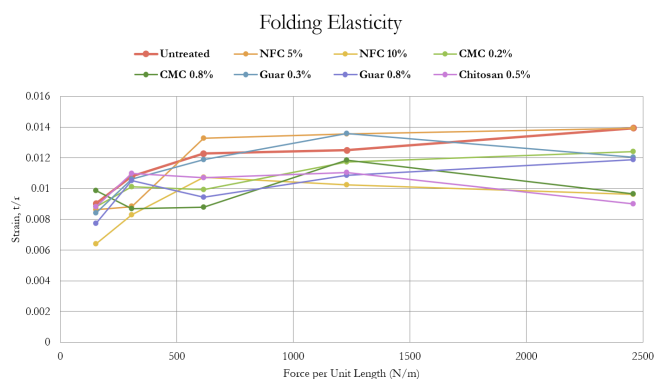


Figure 8. Folding elasticity of each additive displayed as the strain (thickness/elastic radius) vs. the force per unit length (N/m) applied on the paper strip by the roller. The force per unit length was determined by the sample width given a known roller weight. For each trial, $n=4$. There was no significant difference found for the folding elasticity between each additive and the untreated trial.

Folding Elasticity

Strain was plotted against force per unit length for folding elasticity samples to show that 10% NFC, CMC trials, 0.8% guar gum, and 0.5% chitosan retained folds less effectively than in the untreated trials (Figure 8). 0.8% guar performed marginally better than 10% NFC; however, neither result was statistically significant.

Discussion

This study shows the potential of nanofibrillated cellulose, carboxymethyl cellulose, guar gum, and chitosan to effectively serve as an environmentally friendly additive to enhance the folding characteristics of paper for origami applications. While a few additives, particularly 10% NFC and 0.8% guar gum, appeared to have a greater folding endurance and cross tensile strength compared to the untreated trial, the sample size was too small and the difference was not great enough to conclude a statistically significant result.

10% NFC and 0.8% guar did not have significantly greater thicknesses or GSMs, nor did they have a significantly greater folding elasticity, showing that the greater folding endurance provided by the additives is not at the expense of other origami folding characteristics. The statistical difference in the cross tensile index ratio from 1 suggests a stronger grain direction in European traditional papermaking; however, every additive had a greater cross tensile index ratio compared to the untreated trial. The claim that traditionally made

paper is superior to machine made paper is still supported as the traditionally made handsheets had significantly lower differences in the tensile index of each grain direction compared to kami or copy paper. The wet tensile strength of the handsheets, even with the greater wet tensile strength provided by chitosan, was much lower than the 15% wet strength compared to the dry strength standard for wet-strength paper. For applications in the art of origami, the technique of wet-folding may require additional wet-strength agents or sizing agents to prevent tearing.

The most important characteristic for origami folding applications is folding endurance, allowing the paper to function for longer before failure. Folding resistance and folding elasticity are also essential, however they can be decreased through scoring along fold lines. NFC 10% and guar gum 0.8% appeared to have slightly higher folding endurance than the untreated trial; however, only the 2 double fold trials had a statistically significant difference. It is suggested that future research on this subject use greater sample sizes to better determine statistical significance. Surprisingly, folding endurance test trials with 1 or 2 double folds applied rarely broke along the intended fold line, while still having an overall lower tensile index. The process of creasing paper with a bone folder may influence the paper to weaken in locations other than the crease line.

The behavior of the paper after 20 double folds are applied requires significantly more trials to confirm the result and claim statistical significance. The divergence of CMC, guar gum, and chitosan trials from the downward trend back up to a tensile index similar to that of an unfolded sample is extremely unusual, and with the insufficient sample size, its possible that the divergence is a result of random chance. Alternatively, the increase in tensile index could be caused by mechanical changes in the fibers due to the method of folding the paper. A possible mechanical explanation is that the pressure applied by the bone folder increases the contact surface area between the fibers at the fold, thereby disproportionately increasing the hydrogen bonding and strength of the fibers compared to the decrease in strength from the broken fibers. This finding calls for more research to confirm the phenomenon and search for a mechanical explanation, because, if true, the ability to increase tensile strength after

applying folds could be groundbreaking for folding applications.

Overall, the results of this study are insufficient to determine whether any of selected additives nanofibrillated cellulose, carboxymethyl cellulose, guar gum, or chitosan excel in origami folding applications. In part due to limitations on the ability to perform standard tests for folding endurance and wet tensile index, the resulting statistics were not significant. Future research is therefore required to achieve more statistically significant results, as well as discover a mechanical explanation for the increase in tensile index after the application of 20 double folds. However, the results of this study do provide a basis for future research to focus more on the effectiveness of NFC and guar gum additives, additionally addressing a wider range of beating times, additives, and dual polymer combinations.

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