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Nanoindentation Investigation on Chitosan Thin Films with Different Types of Nano Fillers

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Abstract

Chitosan nanocomposite thin films were fabricated using two types of chitosan natural polymer (cross-linked chitosan (CLCS) and non-cross-linked chitosan (NCLCS)), with three different weight percentages nano-fillers (Graphene (G) and fullerene (F)). Nanoindentation tests were performed to investigate the local mechanical properties of the produced nanocomposite in comparison to the unreinforced chitosan thin films. Nano hardness values (H) and indentation modulus (E) were measured using 5 and 10 μm spherical indenters. The addition of nano fillers enhanced the hardness of both types of films with the amount of hardening being directly proportional to the fraction of nano filler added($p<0.001$). Crosslinking has also significantly increased the hardness ($p< 0.001$). The larger indentation returned a lower hardness. The use of different radii nano indenters underlined the indenter size effect due to the differing strain fields. The promising mechanical properties resulting from this research will allow using the fabricated nanocomposites for tissue engineering, biomedicine, drug delivery, electronics, energy, surface coatings and packaging applications.

Keywords: nanoindentaion, hardness, nanofillers

1. Introduction

Chitosan is a potential source of natural polymer since it is a biocompatible, biodegradable, and nontoxic material. It has several uses in the industry, including but not limited to being a drug delivery carrier, biomedical material for scaffolds in the medical industry (Ottenbrite, Dasha, & Chiellini, 2011), and an edible coating in the food packaging industry (Sorrentino, Gorrasi, &Vittoria, 2007). Chitosan has the ability to be easily formed into film shaving mechanical properties similar to other commercial natural polymers such as cellulose (which has a medium strength (Kamil & Shahidi, 2002). The mechanical properties of chitosan depend on its chemical structure and molecular size. The addition of fillers within a chitosan enhances the mechanical properties of the thin films (Koros, 2002). Graphene nano-filler has exceptional structure and outstanding mechanical properties. Therefore, a graphene-chitosan nanocomposite is expected to combine the flexibility and processability of chitosan together with the mechanical strength of graphene (Morooka & Kusakabe, 1999). Another nano-filler that has good potential in this field is fullerene due to bridging the chains between the nanoparticles and the matrix (Fahim, Marei, Salem, & Mamdouh, 2015). In this study, nano-composites were fabricated from chitosan as a matrix and fullerene and graphene as reinforcing materials, separately. Nanoindentation was used for the mechanical characterization of the chitosan thin films. The choice of nanoindentation is driven by it being a valuable tool in extracting the local mechanical properties of significantly small specimens that will experience difficulties if the use of macro or micro-hardness testing techniques is attempted (Díez-Pascual, Gómez-Fatou, Fernando, & Araceli, 2015).

2. Experimental section

2.1Materials

Chitosan: (ChitoClear® cg1600), 76% degree of acetylation, was purchased from Primex. Sodium tripolyphosphate (TPP) purchased from Sigma Aldrich, was used to synthesize chitosan nanoparticles. Chemicals used for dissolving chitosan were purchased from Sigma Aldrich including NaOH, HCl, and acetic acid (Ac-OH, 99% purity). Graphene, (Sky Spring Nanomaterials, Inc. USA), and Fullerene (Carbon 60, 99.5+%, SES Research, USA), were used to produce the chitosan nanocomposite thin films (Fahim et al., 2015).

2.2 Film Processing

The non crosslinked and cross linked chitosan solutions were mixed with the two nanofillers at different wt.% (0.1, 0.5, 1) wt. % by solvent mixing. Mixing was performed with constant stirring for an hour to produce a clear homogeneous solution. The solutions were used to produce non-cross-linked CS nanocomposites (NCLCS/G and NCLCS/F), and cross-linked CS nanocomposite (CLCS/G and CLCS/F) thin films. The solutions were poured in flattened containers and dried at room temperature (Fahim et al., 2015).

2.3 Experimental Procedures

The nanoindentation experiments on the thin films were performed on a NanoTest platform (Micromaterials, UK) at room temperature. Cone indenters with spherical diamond tips, of 5µm and 10 µm diameters were used in this study to investigate the effect of indenter size on the results. The average thickness of each film was 0.2 µm and the film was glued with epoxy on a glass slide for stability during testing. The load was held at maximum value (3 mN) for 60s in order to avoid the creep and account for material relaxation. Three indentations were performed on each sample. The indentations were spaced 100 µm away from each other to avoid the interaction between the plastic strain fields created by each indentation. The depth of penetration is recorded as the load is applied to the indenter. In this work a spherical tip was used to analyze the nano hardness of the film. The spherical tip provides an even transition from elastic to elastic–plastic contact. It is appropriate for measuring soft materials (Fischer-Cripps, 2011). The depth profile data was less than10% of the film's thickness. Reduced modulus (E) and hardness values (H) were obtained using the Nanotest software which is based on the Oliver and Pharr analysis (Oliver & Pharr, 2004).

2.4 Statistical Analysis

IBM® SPSS Statistics® was used in this paper to carry out a comparative multi-variate analysis showing the effect of nano-filler addition and crosslinking on the hardness, reduced modulus, elastic and plastic work of the thin films.

3. Results and Discussion

Nanoindentation experiments were conducted since they are less destructive than tensile testing. The direct results from a nanoindentation experiment are load versus displacement. The hardness is the calculated mean stress using the highest load value and the residual indentation area of the tip. For as spherical indenter, it changes as a function of penetration depth. Furthermore, the reduced modulus is calculated at the beginning of the unloading process. The results in this work will highlight the effect of adding fullerene (F) and Graphene (G) to both Non cross linked chitosan (NCLCS) and cross linked chitosan (CLCS) nanocomposite films on hardness, reduced modulus, plastic and elastic work.

3.1 Effect of the Addition of Fullerene and Graphene on the Hardness of Chitosan Films

The results in Figure 1 show that the addition of nano-fillers significantly increased the hardness of the chitosan films with an amount of hardening sequentially proportional to the amount of filler added. The addition of 1% F showed an increase of 93% in hardness with the NCLCS membranes and 30% increase with the CLCS membranes using the 5 µm spherical nanoindenter. The addition of 1% G showed an increase of 90% nano hardness with the NCLCS membranes and 29% increase with the CLCS membranes using the 5 µm spherical nanoindenter. The increase in hardness with the addition of G and F suggested that both nano-fillers were mechanically dispersed into the NCLCS and CLCS matrices during the wet mixing process forming a carbon network within the polymer. The structural arrangement of the nanoparticles within the nanocomposite films offers superior interfacial adhesion due to the layered structure of graphene that ease the sliding of chitosan chains next. Moreover the miniature clusters of fullerene were easily dispersed within the polymeric chains as shown in Figure 2. Moreover, the nano-fillers restrict the mobility and deformation of the matrix by introducing a mechanical restraint. However the higher value of nanohardness upon addition of the F-nanofiller was due to the small size clusters of F-nanofiller that were distributed within the CS polymer chains (Siracusa, Romani, & Rosa, 2008).

The whole range of hardness values is higher in the CLCS membranes than it is in the NCLCS as shown in Figure (1b). This could be attributed to the effect of crosslinking of the CS membranes with the TPP (Fahim et al., 2015).Cross-linking significantly raises the hardness of the films ($p<0.001$) as demonstrated in Figure 3 due to the decrease in flexibility within the polymer chains. Once the chains are formed due to crosslinking, they are mechanically and thermally stable, making them hard to break (Díez-Pascual et al., 2015). This agrees with previously published studies on thin films, which demonstrated that crosslinking agents decrease the extensibility and enlarge the stress at break for thin films (Jennifer, Vondran, & Schauer, 2008).

a b

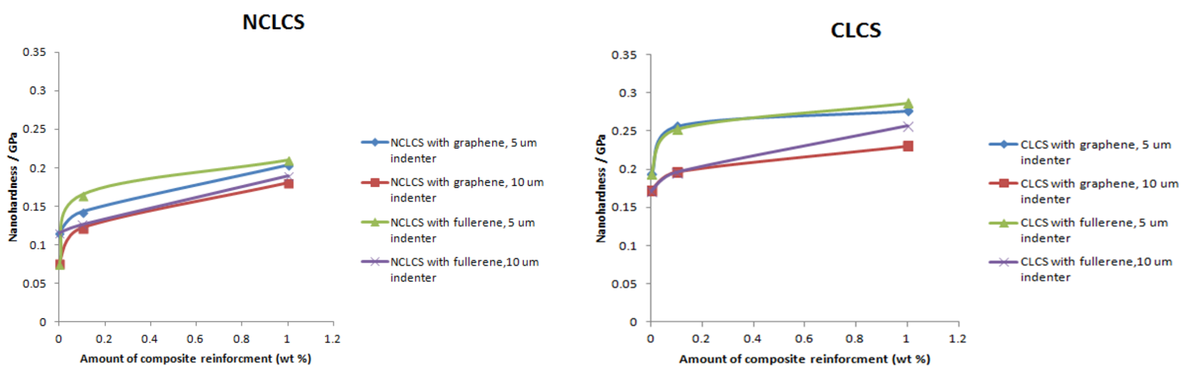


Figure 1. Effect of the addition of fullerene and Graphene on hardness of NCLCS and CLCS membranes

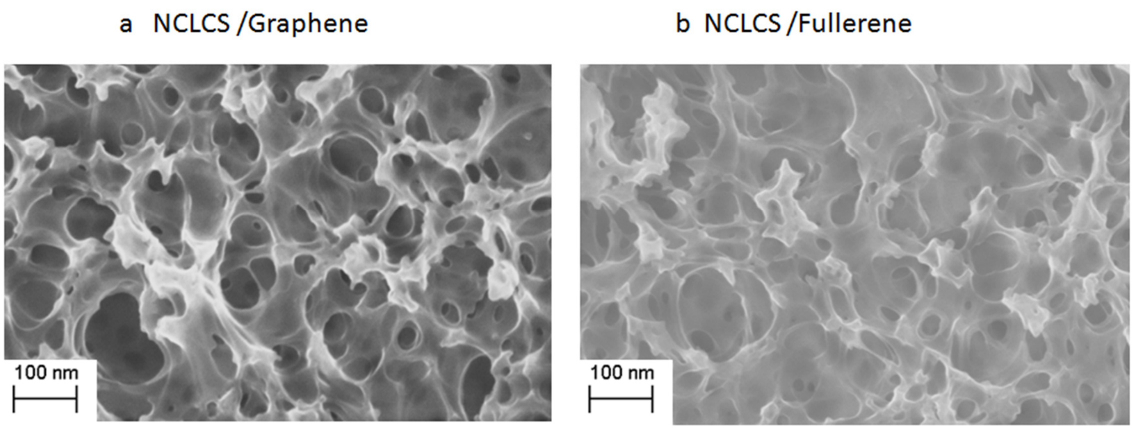


Figure 2. Interfacial adhesion of a) graphene and b) fullerene within NCLCS membranes

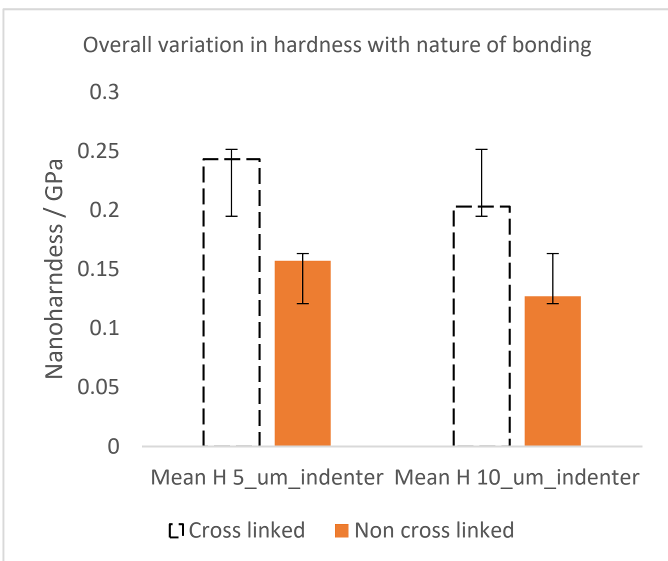


Figure 3. Comparison of hardness in NCLCS and CLCS membranes with 5 and 10 µm indenter

Multi variate analysis was able to identify the part of the overall hardness variation due to the different shape strain fields under the two radii indenters, and concluded that the measured hardness was significantly lower ($p< 0.001$) when measured with the larger radii. This is an expected indenter size effect. It is illustrated in Figure 3 that the hardness values measured using the larger diameter indenter (10 µm) was significantly lower than the those measured with the smaller diameter spherical tip (5µm) ($p<0.001$). The strains induced by the indenter with the larger radius are lower than the strains induced by the smaller indenter (Oommen & Van Vliet, 2006). As the indenter geometry is enlarged the stress distribution is transformed to a flatter and irregularly-scattered distribution with respect to the loading axis thus decreasing the nanohardness values with an average of 50% as shown in Figure (1a&b). The mean nanohardness for each indenter for cross-linked and non cross linked films varied by similar amounts (Figure 3), in line with the effect that cross-linking effects the yield stress of the material. Furthermore, it is shown in Figure 4 that the indentation with the 5 µm diameter indenter indicated that fullerene was a more effective hardener than Graphene ($p< 0.01$). The indentation size effect on hardness was less noticeable when comparing fillers, than when comparing the effect of cross-linking, at least in the concentrations used in this study.

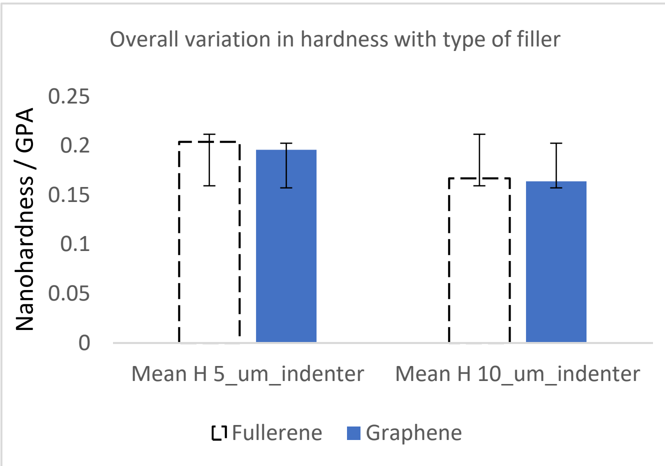


Figure 4. Overall variation in hardness with the type of nanofiller

3.2 Effect of the Addition of Fullerene and Graphene on the Reduced Modulus of the CLCS and NCLCS Membranes

The mean values of reduced modulus using the spherical tip suggested that the cross-linked films are stiffer as would be expected. However, the reduced modulus measurements using 10 µm diameter indenter indicated higher values rather than 5 µm diameter indenter as shown in Figure 5. There is no statistical significance between the two materials using the larger indenter, In Figure 6, we notice that the reduced modulus of the graphene reinforced films is higher due to the nature of Graphene flakes. One would expect a crossover in layers which dominate the stiffness of the films. Graphene reinforcement shows significant filler stiffening due to its larger size and sheet like structure as was previously mentioned by Díez-Pascual (Díez-Pascual et al., 2015). This might be attributed to the load transfer between the polymer (matrix) and the nanofiller (reinforcement). The load transfer along the Graphene flakes is governed by the interfacial shear stresses and the strength of adhesion between the flake and polymer (Fan et al., 2010; Lahiri et al., 2012). While the spherical shape of fullerenes, isotropy implies the same nominal response along all directions leading to a lower strength of adhesion in fullerene reduced modulus values (Chang & Asanka, 2016).

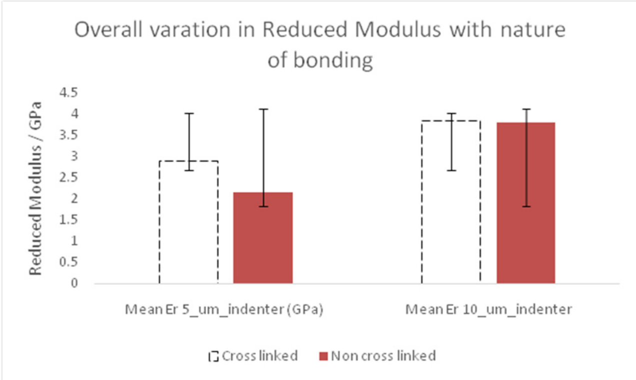


Figure 5. Comparison of the reduced modulus in NCLCS and CLCS membranes with 5 and 10 µm indenter

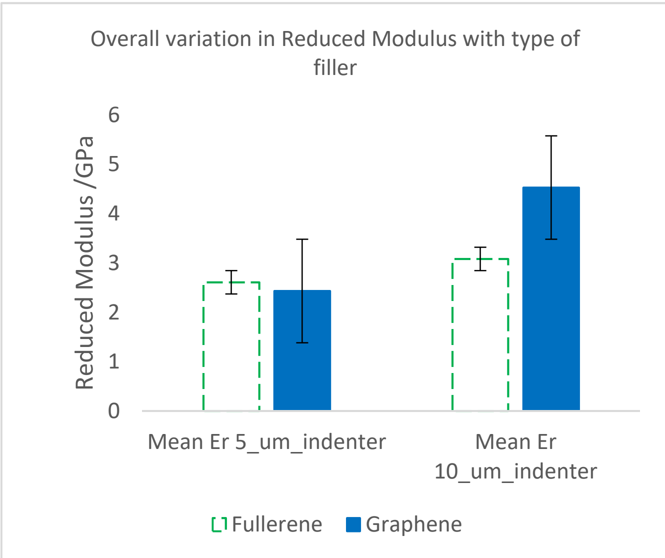
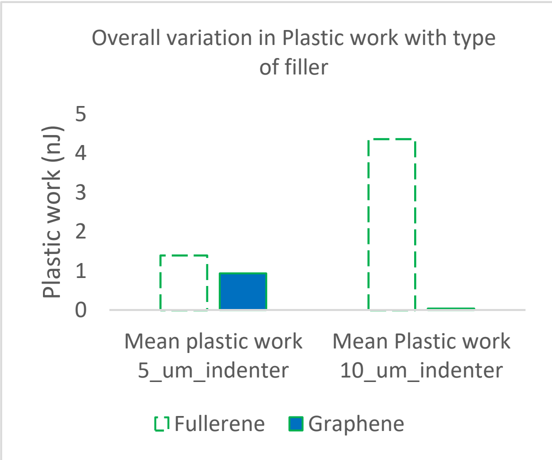


Figure 6. Overall variation in reduced modulus with type of filler

3.3 Effect of Addition of Fullerene and Graphene on Plastic and Elastic Work of NCLCS and CLCS Membranes

The general linear model analysis comparing 0, 0.1 % and wt.1% additions found that the amount of plastic work was significantly different as filler was added for both sizes of tip ($p<0.001$), and elastic work differs significantly for the 10um indenter as shown in Figure 7. Statistically the only one which is significant ($P<0.003$) is elastic work done by 10um indentation which shows that the fullerene reinforced films had a higher value of elastic work and extraordinary shock absorbing performance owing to their hollow, close caged, onion-like structures (Zhu et al., 2003). The addition of fullerene hampers the molecular motion and affect the mobility in the matrix introducing new energy dissipating mechanisms leading to enhanced toughness in the nanocomposite (Zhu, Sekine, Li, 2005). The higher plastic or elastic work at the 10 µm diameter is attributed to the larger diameter of the indenter. Contact force calculations reveal that reversible incipient plasticity occurs under the small indenter, i.e. the plastically deformed surface can be restored upon withdrawal of the indenter, while the plasticity under the large diameter indenter seems is irreversible (Shao, Tang, Li, & Zhao, 2013).



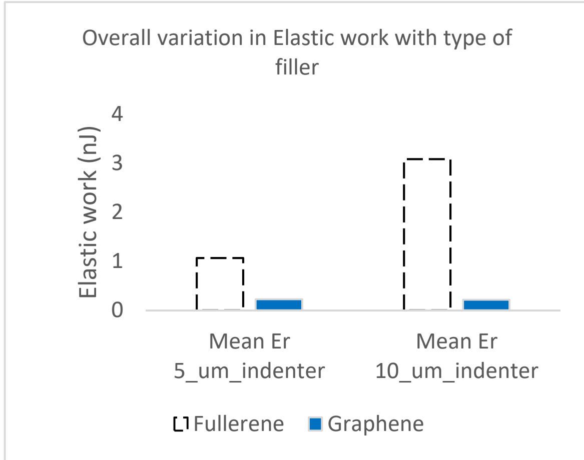


Figure 7. Comparison of plastic and elastic work with type of nanofiller

4. Conclusion

Spherical indenter are useful for characterizing soft materials. However the data clearly showed the indenter size effect on measured hardness and modulus. The values of the nanohardness and reduced modulus differed depending on the radii of the indenter used. Both the crosslinking and the addition of nanofillers had a combined effect on increasing the nanohardness and the reduced modulus. Moreover, the addition of fullerene enhanced the nanohardness values significantly while the addition of Graphene improved the stiffness of the nanocomposite. The macro hardness of cross linked and non cross linked chitosan films were measured using Vicker's indenter geometry and the results were ranging between 0.2-0.5 GPa. There is a slight difference in these results and the ones measured through nanoindentation due to the micro dislocations affecting the macro hardness test and softening the samples. However the same result was confirmed that creating cross-links in the chitosan films improves the macro hardness (Ashkan, Jayatissaa, & Jayasuriya, 2012).

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