EFFECT OF TEMPERATURE ON MECHANICAL PROPERTIES OF THE EGGSHELL

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ABSTRACT

In this study, chicken eggshells consisting of 96-97 % calcium carbonate ($CaCO_3$) or limestone and 3-4 % organic membrane have been studied as fillers in polymer composite materials, which represents an innovative solution to add value to this bio-waste. Large quantities of waste eggshells are available at egg-breaking plants. The membrane may present an obstacle in the properties of a composite material. One potential treatment method for membrane removal is the use of heat at elevated temperature. However, a high temperature may affect the eggshells' mechanical properties, which may affect the composites' mechanical properties when "heat treated" eggshells are used as fillers. Studies have shown that high temperatures cause thermal damage to mineral limestone, resulting in reduced mechanical properties. This study aims to determine how temperature affects the eggshell elastic modulus and hardness. The nano-indentation method will be used to measure these parameters at different temperatures. The results will determine if the organic membrane can be removed by heat treatment and how much heat can be applied to eggshells before their mechanical properties deteriorate.

1 INTRODUCTION

Environmental awareness, high cost of petroleum, rising prices due to global instability, and independence of the industries from petroleum derivatives are vital reasons why industries are tending expansion of their products from petroleum to bio-based composites. Eggshells (ES) can be used as a bio-based/bio-waste filler in composite materials for various applications [1]. The most important source of large quantities of eggshells worldwide is egg-breaking plants [2], where a critical challenge these industrial plants face, is the waste they incur from eggshells. This challenge is accentuated by the annual increase in the number of available eggshells due to the expanding demands of the egg market [2, 3]. Developing novel applications for waste eggshells can be a win-win strategy for both egg-breaking plants and industry owners. For example, the egg-breaking plants eliminate their eggshell waste, while industries who manufacture composite materials can potentially replace the use of expensive polymers with bio-based/ bio-waste filler materials such as eggshells [1, 4].

Eggshells are a rich source of calcium carbonate that have the potential to be used as a bio-waste filler in various polymers as replacements for mineral calcium carbonate. Several authors have applied eggshells instead of conventional mineral calcium carbonate in the polymer composites [1, 5]. In a recent article, the effect of different particle sizes and concentrations of the eggshells on the mechanical properties of the poly lactic acid (PLA) composites was evaluated. According to this study, increasing the concentration of eggshells improved the mechanical properties of PLA composites, such as tensile strength and elastic modulus. Furthermore, composites containing smaller ES fillers had improved tensile strengths compared to composites with larger fillers [5]. On the other hand, a related study assessed the effect of eggshells as a filler on the mechanical properties of bio-based polyethylene (PE) as a green polyethylene polymer. The results showed that ES particles strongly improved the mechanical properties of bio PE, such as stiffness, hardness, flexural, and tensile modulus [1].

Determination of mechanical properties of the ES by itself is vital since the property of the eggshell will have an effect on the overall properties of the final product [1, 6]. Several studies have been conducted to determine the elastic modulus and hardness of eggshells at room temperature [6, 7]. In general, the ES elastic modulus and hardness have been measured by a Berkovich nano-indentation device [6, 7].

The studies showed that the mechanical properties of mineral rocks, such as limestone, change significantly by increasing the temperature [8, 9]. According to these investigations, the mechanical properties of limestone, such as elastic modulus and hardness tended to decrease at high temperatures [8, 9]. One study evaluated the effect of high temperature on the physical-mechanical properties of mineral limestone, such as density, porosity, water absorption, tensile strength, and hardness of the limestone. The results showed that the hardness values decreased for all types of limestone such as, Sivrihisar Beige (sparitic limestone) and Daisy Beige (biosparitic limestone). It was observed that the hardness values changed at approximately 200 °C [8]. In another study, the effect of temperature on the elastic modulus of limestone was investigated. According to these results, the maximum elastic modulus was observed for the sample at room temperature, and the elastic modulus reduced beginning at 100 °C [9].

Since ES consist of 96-97 % calcium carbonate ($CaCO_3$), it was anticipated that a significant change in mechanical properties of this natural bio-filler would be observed at high temperatures. The elastic modulus and hardness are two critical mechanical properties sensitive to temperature. The aim of this study was to investigate the effect of heating from room temperature (23 °C) to 750 °C on the elastic modulus and hardness of the eggshell.

2 MATERIALS AND METHODS

2.1 Preparation of Materials

White chicken eggshells were obtained from a local producer in Saskatchewan, Harman Eggs (a Star Egg Company Limited product). The eggshells were initially dried at 105 °C for 24 hours. To investigate the effect of temperature on the mechanical properties of eggshells, specimens were heat treated at 100 °C, 150 °C, 300 °C, 450 °C, 600 °C, and 750 °C using a heating rate of 10°C/min in an air atmosphere using a Lindberg/Blue M box furnace for 1 hour (Figure 1). One dried sample was not heat treated and used as the control.

2.2 Mechanical tests: Measurement of eggshell elastic modulus (E) and hardness

The elastic modulus and hardness were evaluated with a nano-indentation tester fabricated by the Centre of Tribology Inc., Campbell, CA, USA. The equipment was configured to follow the Oliver-Pharr method [10]. A constant load of 5 mN was applied with a Berkovich type indenter. A creep time of 30 sec (hold time) was kept to allow deformation to completely occur. The loading and unloading speed was kept at 0.2 mN/sec, resulting in 25 sec loading and unloading time. Since the curvature of the eggshell surface was anticipated to influence the readings, the sample sizes were kept as small as possible with an approximate sample size of 10 mm x 10 mm to reduce the curvature and its effect from the measurements.

2.3 Scanning electron microscopy (SEM)

Eggshell sample morphology and surfaces were observed by scanning electron microscopy (SEM) using a JEOL JSM-6010 LV (Tokyo, Japan) with an operating voltage of 10 kV. Prior to the analysis, the samples were coated with a thin layer of gold to improve electrical conductivity.

3 Results and discussion

3.1 Digital images

Digital images of the eggshells before and after the heat treatment from room temperature (RT) to 750 °C are shown in Figure 1. As expected, the eggshells' color is white at room temperature (23 °C). By increasing the temperature to 100 °C and 150 °C, the ES color began to change to a pale yellow. The color of the samples was dark brown at 300 °C where the organic membrane began to decompose. At 450 °C, the eggshell changes to light brown and appears to have become very fragile. After this temperature, the sample color changed to dark gray at 600 °C, although some parts of the samples remained light brown. At 600 °C, decomposition of $CaCO_3$ begins, and the structure of the eggshell breaks down/collapses completely at 750 °C as evidenced for the final samples, which were in powdered form and were too fragile to manipulate. Thermal decomposition of calcium carbonate to calcium oxide (CaO) has been reported to occur in a range between 600 °C to 700 °C [3, 9].

3.2 Elastic modulus

Figure 2 shows the experimental data collected for the eggshell elastic modulus values at 23 °C, 100 °C, and 150 °C, and these findings have been compared with the literature results achieved for the elastic modulus of mineral limestone submitted to high temperatures. The maximum elastic modulus observed for the eggshells and the mineral limestone was at room temperature. By increasing the temperature, the structure of both eggshells and limestone samples changes, which caused a reduction in their stiffness. The maximum elastic modulus of the eggshells reached 43.4 ± 3.9 GPa at 23 °C, but decreased by 9.67% and 22.58% at 100 °C and 150 °C, respectively. In other words, the results showed that the samples' elastic moduli values decreased by increasing the temperature. Measurement of the elastic modulus was possible for the samples heat-treated up to 150 °C. However, the elastic modulus could not be measured by the instrument/Berkovich method above 150 °C since the samples were too weak as they contained fragile structures[1].

According to Figure 2, from 23 °C to 150 °C, the elastic modulus values for the limestone samples are slightly higher than the eggshell samples. For example, at room temperature and 100 °C, the elastic modulus of the eggshell is lower by 40.66% and 45.02%, respectively, compared to the mineral limestone. After 300 °C, the limestone elastic modulus drops sharply, according to its steep slope, whereas the eggshell elastic modulus will also reduce abruptly

[1] Elastic modulus and hardness results for the eggshell samples heat-treated at 100°C are currently being repeated in the laboratory. The final results for 100°C will be presented at the conference.

after 150 °C due to its fragility. The differences may be explained by the crystal structure and chemical bonding of the eggshell material [9].

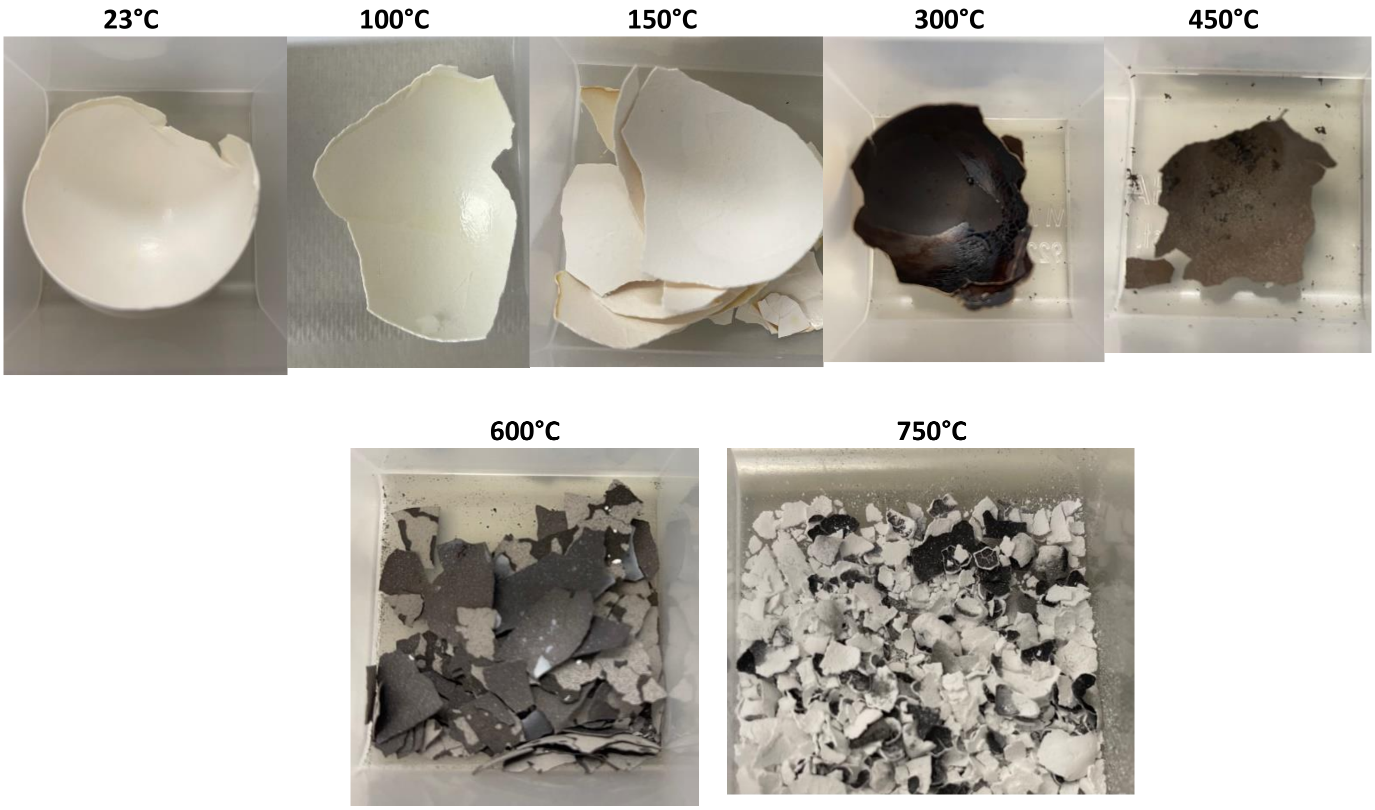

Figure 1. Behavior change of eggshell samples after heating from 23°C to 750°C.

3.3 Hardness

Figure 3 shows the change in hardness values of the eggshell with temperature. The eggshell hardness reached a maximum of 1.16 ± 0.12 GPa at room temperature, and decreased as the temperature increased. At 150 °C, the hardness of the eggshell decreased by 75.86% compared to the unheated sample. Similar to the elastic modulus results, the hardness value could not be measured using the equipment/Berkovich method due to the eggshell fragility and weakened structure above 150 °C.

According to Figure 3, the reduction of the eggshell hardness becomes significant above 100 °C, which is similar to the reduction of the eggshell elastic modulus in Figure 2. In a related study, Ozguven et al. [8] studied the effect of temperature on the hardness of mineral limestone. However, the authors applied a different method to measure the limestone hardness, but the reported results were similar to those obtained herein. For instance, at 200 °C, there was a considerable reduction in hardness which is approximately similar (by visual inspection in Figure 1) to what occurred for the eggshell samples.

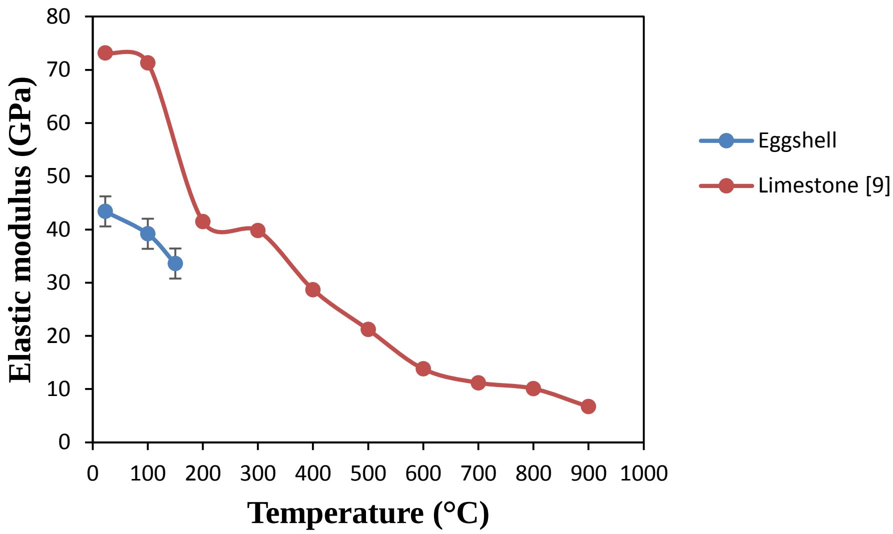

Figure 2. Variation in the elastic modulus of eggshell and limestone samples with temperature.

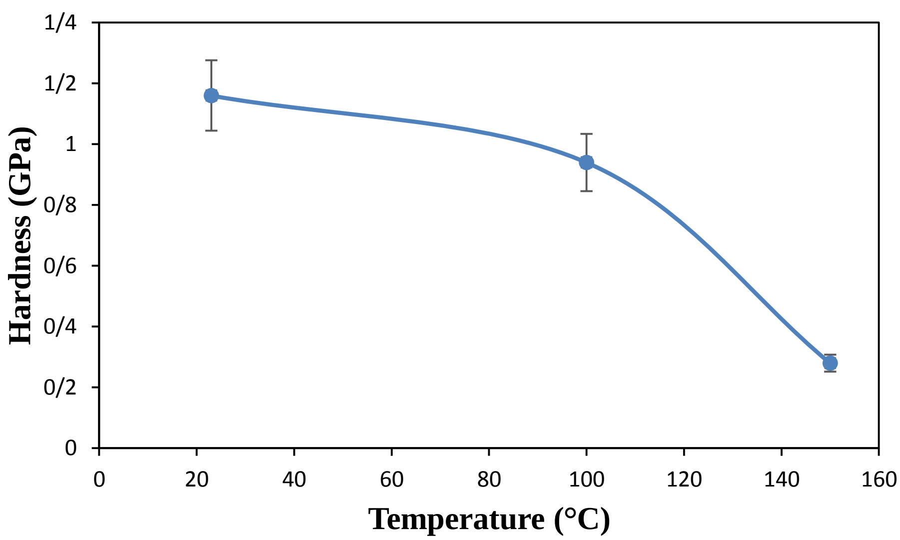

Figure 3. Variation in the hardness of eggshell samples with variable temperature.

3.4 SEM micrographs

SEM images of the eggshell exterior and interior heated at 23 °C, 150 °C, 300 °C and 450 °C are shown in Figures 4 and 5, respectively. According to Figure 4, the eggshell exterior structure changed from strong and brittle at 23 °C to being more fragile and weak at higher temperatures as shown by the cracked surface (cf. Fig. 4 c and d). In Fig. 5 a , at 23 °C the interior surface appears intact, while at 150 °C (cf. Fig. 5 b) there are some holes that appear at the surface which helps to confirm the changes in fragility and weakness of the structure. The eggshell is composed of four layers as viewed from outside to inside: the cuticle is the outermost layer surrounding the eggshell, the shell structure (Testa layer), a mammillary layer which contains two membranes (the outer membrane and the inner membrane) and finally the yolk [2, 11]. According to Figure 5 b, upon increasing the temperature to 150 °C, the first inner membrane layer of the eggshell begins to breakdown as depicted by the larger holes. Increasing the temperature to 300 °C, the inner membrane is totally removed and the outer membrane is visible (cf. Fig. 5 c) in the form of a fibrous network. The outer membrane is entirely removed at 450 °C (cf. Fig. 5 d.), and the knob structures related to the Testa layer are observed. As a strong protective layer, it appears the mammillary layer holds the knob structures together. By increasing the temperature and removing the outer and inner membranes at 450°C, the perceived protective layers no longer form a solid structure. This phenomenon may justify the weak structure of eggshells at high temperatures. The fragility and weakened structure affected the mechanical properties of the eggshells, such as elastic modulus and hardness, as explained in sections 3.2 and 3.3.

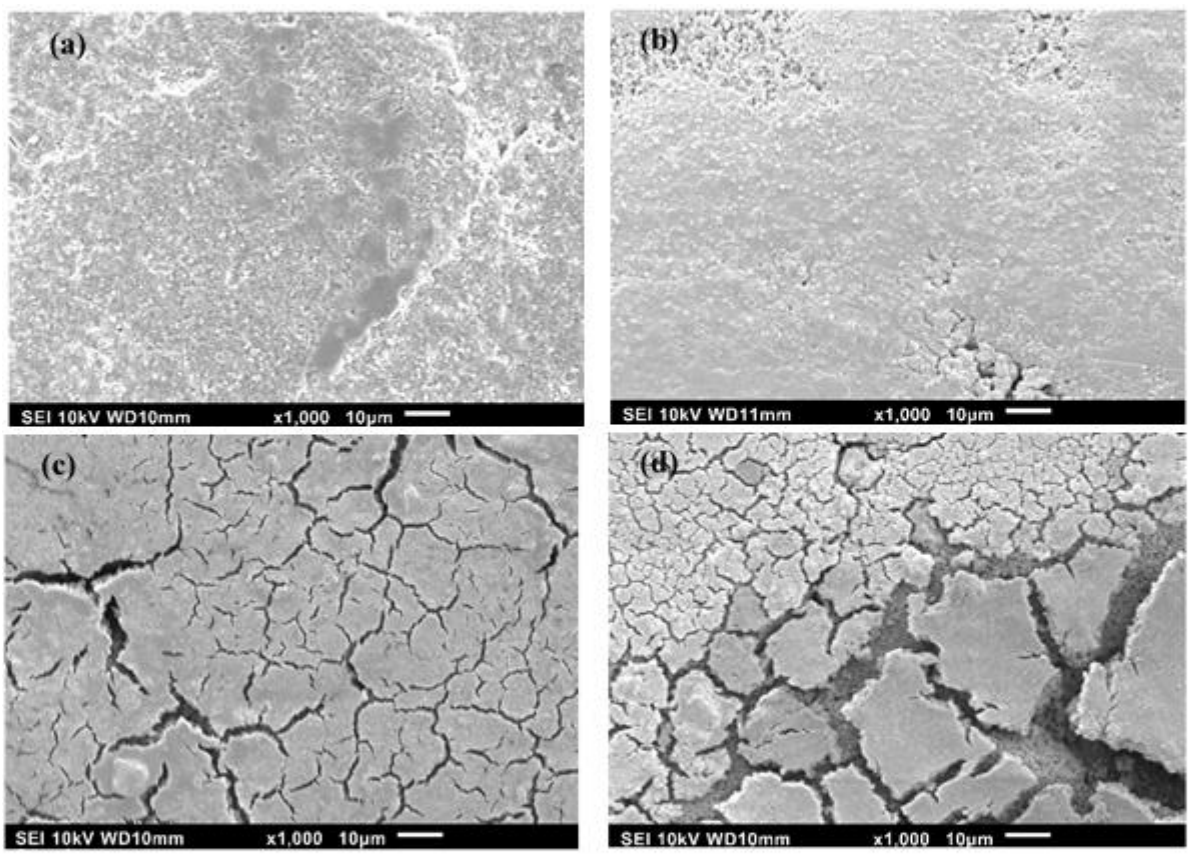

Figure 4. Scanning electron microscopy images of the exterior of the eggshell samples that were treated at variable temperatures: a) 23°C, b) 150°C, C) 300°C and d) 450°C.

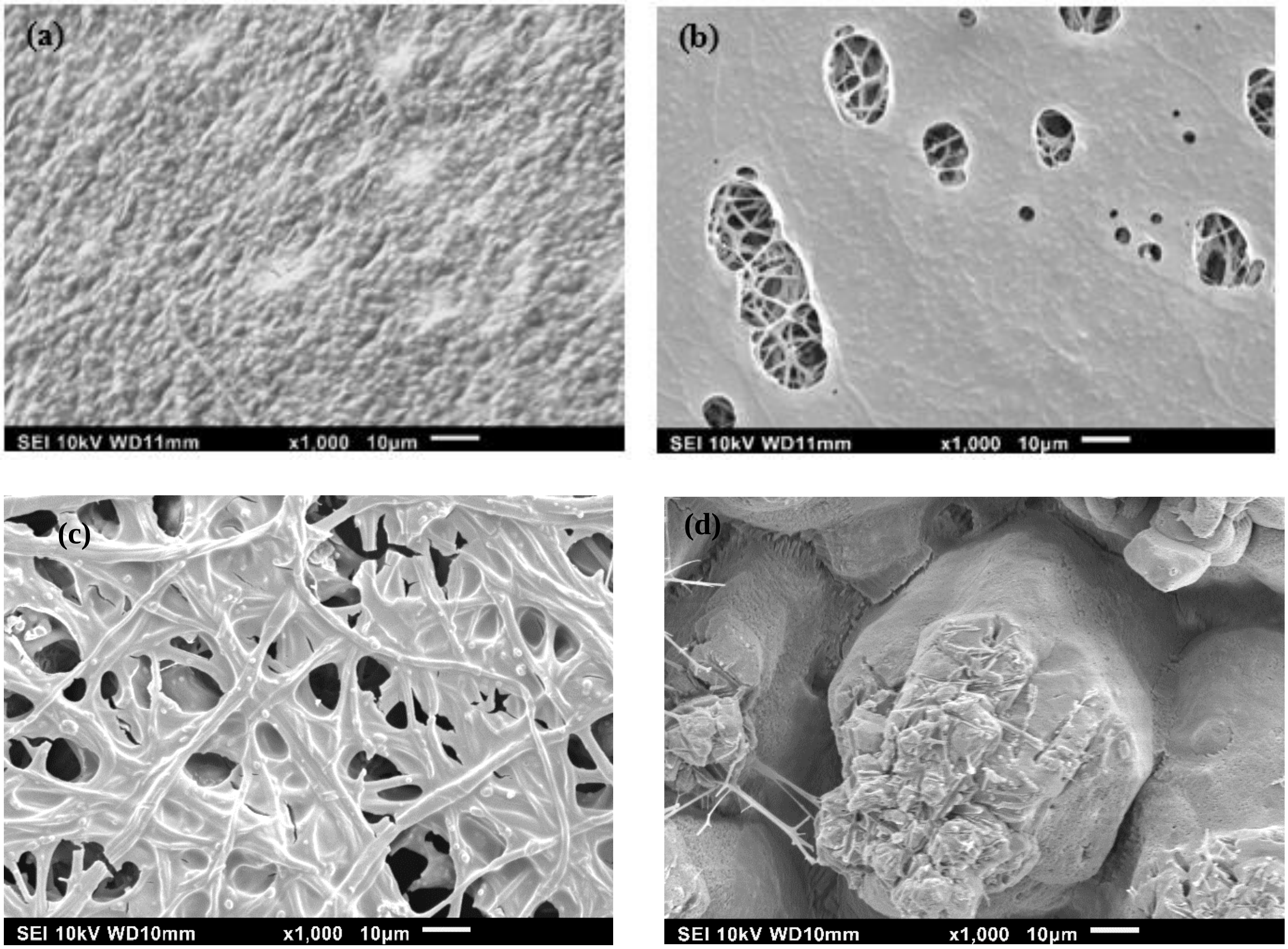

Figure 5. Scanning electron microscopy images of the interior of the eggshell samples treated at variable temperatures: a) 23°C, b) 150°C, C) 300°C and d) 450°C.

4 Conclusion

This study aimed to investigate the effect of temperature on the mechanical properties of the eggshell, such as elastic modulus and hardness. The results showed that the eggshell elastic modulus and hardness values became reduced incrementally by increasing the temperature. The maximum elastic modulus and hardness values were observed to be 43.4 ± 3.9 GPa and 1.16 ± 0.12 GPa, respectively at room temperature. A significant drop in elastic modulus and hardness of the eggshells began after 100 °C and were considerable at 150 °C. In other words, the reduction of the elastic modulus and hardness values for the eggshell samples were sensitive, with a steep descending slope for temperatures above 100 °C. Elastic moduli results of the eggshell samples were compared with mineral limestone from previously reported literature studies. Similar to the eggshell elastic modulus and hardness properties, the limestone also reduced in value as the temperature increased and this reduction was significant above 100 °C for both calcium carbonate materials. The SEM images of the exterior and interior of the eggshells' revealed that the structure was deteriorated upon increased temperature. Removing the mammillary layer appears to weaken the eggshell structure since it is predicted that these membrane layers strongly hold the knob structures together. According to this study, heating the eggshells to remove the membrane may not be a suitable method as the reduction in mechanical properties are affected by elevated temperatures.

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