Effects of ultrasonication process on crystallinity and tear strength of thermoplastic starch/cellulose biocomposites

Ismail Ibrahim1,*, Azlin Fazlina Osman1, and Tan Leong Ping1

1Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis, Arau, Perlis 02600, Malaysia.

Abstract. The thermoplastic starch (TPS)/cellulose biocomposites were manufactured as green biocomposite films. TPS was produced through plasticization process in which the mixture of starch granule and plasticizers (water and glycerine) went through the stirring and heating process. Cellulose was used as filler and prepared in suspension form through ultrasonication process involving isolation of cellulose in water medium. The ultrasonicated cellulose suspension was added into the TPS matrix to produce TPS/cellulose biocomposites by film casting. The effects of ultrasonication duration (1, 2, 3, 4 and 5 hours) on the crystallinity and tear strength of the TPS/cellulose biocomposite films were investigated. Based on the XRD results, crystallinity of the cellulose and biocomposite were altered by the cellulose ultrasonication process. The tear strength of the TPS biocomposites were greatly enhanced when 5-hours ultrasonicated cellulose was employed as filler. The biocomposites demonstrated 241% higher tear strength than the pure TPS film. This could be related to the transformation of the cellulose into more isolated fiber, with enhanced crystallinity for better reinforcing effect to the TPS matrix.

1 Introduction

Nowadays, synthetic plastics are regular daily basis used materials. It is undeniable, although petroleum derived synthetic plastics possess good mechanical properties, they are apparently non-biodegradable and non-renewable [1]. In fact, many analysts emphasized that plastic waste prompts to environmental issues. Therefore, the development of environmental friendly yet sustainable packaging plastic has become major research of today’s scientists and researchers. [2, 3]. Thermoplastic starch (TPS) is a renewable, biodegradable bioplastic, used to replace the synthetic plastics, especially in film products like packaging. Nonetheless, the fundamental inconveniences of TPS plastics include their low tensile and tear properties, which can restrict their long term application, especially when exposed to water/humidity and weathering. The naturally hydrophilic characteristic of TPS is the main cause of its high tendency in absorbing water. Degradation of the hydrated TPS may result in deterioration of its mechanical performance and durability [4, 5].

* Corresponding author: ismailibrahim@unimap.edu.my
Therefore, the properties of TPS need to be improved to be more comparable to commodity plastics for use in packaging application. In conjunction with this, the TPS has been reinforced with several types of cellulose fibers. Previous research indicated that good dispersion of cellulose fiber leads to the improvement in the mechanical properties of the TPS composite, such as tensile and tear strength [6, 7]. This shows that homogeneous dispersion of cellulose fiber in the TPS matrix can significantly influence the mechanical properties of the TPS/cellulose biocomposites. In previous work, the ultrasonicated cellulose was added into the TPS matrix in dry form. This caused low dispersion efficiency of cellulose in the TPS matrix, due to re-agglomeration of the ultrasonicated cellulose after the drying process [5]. We believed that the use of cellulose in suspension form which is added directly into the TPS suspension upon the ultrasonication process can result in improved dispersion of cellulose in the matrix.

In this project, TPS biocomposites films were produced by reinforcing the matrix with the ultrasonicated cellulose fiber. Several ultrasonication duration were used to isolate the fiber which were; 1, 2, 3, 4 and 5 hours. The effect of the ultrasonication duration on crystallinity of the cellulose and the TPS/cellulose biocomposites was analysed. Furthermore, the most optimum ultrasonication duration to produce the highest value of TPS/cellulose biocomposite tear strength was determined.

2 Materials and methods

2.1 Materials

The starch (corn-based) was supplied by Sigma-Aldrich, code number S4126 in 2 kilogram poly bottle packing. This corn starch contains approx. 73% amylopectin and 27% amylose. The microcrystalline cellulose powder was obtained from Sigma-Aldrich, with product code number of C6288. It was produced from cotton liners with particle size of ~20μm. The cellulose acts as filler in the TPS biocomposite. The glycerol or also known as glycerine was used as plasticizer and supplied by the HmbG Chemicals with the code, C0347-91552409. Sodium bicarbonate from HmbG Chemicals (C0735-2134330) was used as expanding agent for the production of the TPS film.

2.2 Methods

2.2.1 Plasticization of starch

The plasticization of starch was done to form the thermoplastic starch (TPS). The process starts with mixing the corn starch with distilled water in the ratio of 1:20. After that, the plasticizer, glycerol was added to the starch solution by the ratio of 1:50. The mixture was continuously stirred at 75-85°C until gelling. The starch plasticization process completed after 45 minutes.

2.2.2 Ultrasonication of cellulose

The cellulose suspension was prepared by mixing the powder form of cellulose with the TPS solution in a ratio of 1:100. The cellulose was isolated through the ultrasonication process by using Branson Digital Ultrasonic Disruptor/Homogenizer, Model 450D with 20% amplitude, 20 seconds pulse on and 10 seconds pulse off for 1.0 hour, 2.0 hours, 3.0 hours, 4.0 hours and 5.0 hours respectively. The process was done to isolate and disperse the cellulose prior being added into the TPS solution. Long period of ultrasonication could
result in overheating and degradation of cellulose, therefore the ultrasonication of cellulose was done in the ice bath.

### 2.2.3 Preparation of thermoplastic starch/cellulose composite

The prepared cellulose suspension was added into the TPS solution. The mixture was stirred continuously at 75-85°C until it is became thick and almost transparent. After that, 0.5 grams of sodium bicarbonate powder was dissolved with 30mL of distilled water and added into the mixture. The mixture was continuous stirred to about 5 minutes. Following, the casting process took place; mixture (biocomposite suspension) was then poured into a non-stick sheet mold and place into the oven at 45°C for 24 hours drying process. The dried film was removed from the mold and cut accordingly for testing. The formulations of the TPS biocomposites are shown in Table 1.

### Table 1. The formulation of thermoplastic starch/cellulose biocomposites

| Ultrasonication of Filler | Isolation Period (hour) | Thermoplastic Starch (Matrix) (wt%) | Cellulose (Filler) (wt%) |
|---------------------------|-------------------------|-------------------------------------|--------------------------|
|                           |                         | 100                                 | -                        |
|                           | 0                       | 95                                  | 5                        |
|                           | 1.0                     | 95                                  | 5                        |
|                           | 2.0                     | 95                                  | 5                        |
|                           | 3.0                     | 95                                  | 5                        |
|                           | 4.0                     | 95                                  | 5                        |
|                           | 5.0                     | 95                                  | 5                        |

### 2.2.4 X-ray diffraction (XRD)

The X-ray diffractometer (Bruker D2 Phaser, USA) was used to identify the cellulose and composite phase formation. The crystalline formation of the thermoplastic starch and the cellulose which are isolated using different ultrasonication time was investigated. Each specimen of samples was placed in the sample holder and scanned by a range of $2\theta = 10^\circ$ - $60^\circ$ with the scan speed of 2°/min. The crystallinity of samples was characterized through the test.

### 2.2.5 Tear test

The tear strength was measured by using the Instron Machine, according to ISO 34 -1:1994 Method B(a). The test was run using the angle test specimen (type B) without a nick. Crosshead speed of 500 mm/min was applied. The average tear strength values were determined for each of the samples.

### 2.2.6 Scanning electron microscopy (SEM)

Scanning Electron Microscope (JEOL JSM-6460LA) was used to analyse the topography and morphology of the non-ultrasonicated and ultrasonicated cellulose (4 and 5 hours). The specimens were coated with platinum by using JFC-1600 Auto Fine Coater (JEOL Ltd., Japan) prior to SEM observation. The specimens were observed under magnification of 1,000X to see changes in the cellulose fibres’ shape and size.
3 Results and discussion

The X-ray diffraction (XRD) was used to investigate the crystallinity of the corn starch, TPS and its biocomposites. Figure 1 shows the XRD patterns of the cellulose, corn starch, TPS and the TPS/cellulose biocomposites incorporating the non-ultrasonicated cellulose and 5-hour ultrasonicated cellulose. Table 2 summarizes the crystallinity index values (%) of all the materials which were obtained through the XRD analysis.

![X-ray diffraction patterns for cellulose, corn starch, TPS and its biocomposites.](image)

Fig. 1. X-ray diffraction patterns for cellulose, corn starch, TPS and its biocomposites.
Table 2. Crystallinity of the cellulose, corn starch, TPS and TPS/cellulose composites based on XRD analysis.

| Sample                        | 2θ (°)                | Crystallinity (%) | Amorphous (%) |
|-------------------------------|-----------------------|-------------------|---------------|
| Cellulose 0 (Without         | 15.38, 22.55,         | 42.30             | 57.70         |
| ultrasonication)             | 37.46                 |                   |               |
| Cellulose 5 (With 5 hours     | 15.43, 22.70,         | 43.10             | 56.90         |
| ultrasonication)             | 34.54                 |                   |               |
| Corn Starch                  | 3.24, 5.08, 15.08,    | 54.70             | 45.30         |
|                              | 17.52, 23.06          |                   |               |
| TPS Film                     | 22.73, 34.40, 47.96,  | 29.80             | 70.20         |
|                              | 53.82                 |                   |               |
| TPS/Cellulose 0 Film         | 22.14, 33.76, 39.30,  | 49.50             | 50.50         |
|                              | 47.50, 53.22          |                   |               |
| TPS/Cellulose 5 Film         | 21.43, 33.07, 38.88,  | 46.30             | 53.70         |
|                              | 46.82, 52.62          |                   |               |

Based on Figure 1, the XRD pattern of cellulose fiber reveals diffraction peaks around 2θ=15.4° and 22.6° which typically represent cellulose type I. Furthermore, there are slight difference between the cellulose without ultrasonication and cellulose undergoes 5 hours of ultrasonication with respect to their peaks (2θ shifted from 15.38° to 15.43°) and its crystallinity index (increased from 42.30% to 43.10%). The obtained results indicated that the ultrasonication process has increased the crystallinity of the cellulose. This was due to the acoustic cavitation produced during ultrasonication treatment. Ultrasound was proved to efficiently formulate fibrillation of cellulose as the coupling of high-power ultrasound into liquids creates extreme shear forces [8]. In other words, the cellulose structure has been reorganized and become more orderly (crystalline) in the portion from longer and thicker fiber into shorter and thinner fiber when the cellulose was ultrasonicated in water medium. The corn starch shows a C-type crystallinity pattern with peaks at 2θ=3.24° (characteristic of B-type polymorphs), 15.08° and 17.52°, (characteristic of both A and B-type polymorphs) and 23.06° (characteristic of B-type polymorphs). After it is converted into a TPS film, there was a typical B-type crystallinity pattern which was clearly observed through 2θ peak = 22.73° (characteristic of B-type polymorphs) [9]. It corresponded to VH-type, and it is mainly characterized by the intense peak at 2θ=22.73°. The VH-type consists of amylose recrystallization induced by lysophospholipids and complex forming agents such as isopropanol and glycerol [10]. Upon the addition of cellulose to the starch matrix, the peaks at 2θ=22.14° and 33.76° (for cellulose without ultrasonication) and 2θ=21.43° and 33.07° (for cellulose with 5 hours ultrasonication), which correspond to the XRD pattern of cellulose I are observed. The results also show that the addition of cellulose significantly increased the crystallinity of the film. Although the starch peak’s locations did not change obviously in XRD pattern, the intensities were increased significantly by the
addition of cellulose within the TPS matrix. The addition of well-dispersed cellulose fiber can enhance nucleation for TPS matrix crystallization, thus resulting in the increased crystallinity of the biocomposite film [11]. Based on the results in Table 2, 5 hours-ultrasonicated cellulose which reinforced into the TPS matrix has a little drop on its crystallinity (46.30%) as compared to the TPS with the cellulose without ultrasonication (49.50%). The crystalline region of the cellulose fibers has little damaging due to the ultrasonication treatment, meanwhile, it was affected by the high processing temperature (85°C) when the cellulose reinforcing into the TPS, resulting in the inclination of crystallinity. The high crystalline fibers could be more effective in providing better reinforcement for composite materials because of high young’s modulus of the crystal region along the longitudinal direction [11].

Based on Figure 2, the tear strength of the biocomposite film sample was significantly increased when the non-ultrasonicated cellulose fiber was added into the TPS. However, the tear strength decreased as the TPS matrix was added with cellulose that being ultrasonicated for 1, 2, 3 and 4 hours. This shows that the application of 1 to 4 hours of ultrasonication did not allow adequate fibrillation of the cellulose for its transformation into reinforcing fiber. As proved through SEM analysis, the 4 hours-ultrasonicated cellulose did not show much difference when compared with the non-ultrasonicated cellulose. However, when the ultrasonication duration was further proceeded for 5 hours, much more fibrillation process could occur for better isolation of the cellulose fiber (see Figure 3a, b and c). The isolated cellulose could provide greater reinforcing effect to the TPS matrix due to its higher aspect ratio fiber (smaller fiber diameter). When the TPS was reinforced with the 5 hours-ultrasonicated cellulose, the tear strength increased from 0.521 MPa to 1.256 MPa. It demonstrated 241% increment in tear strength when benchmarked with the pure TPS film. The research indicated that homogenously distributed filler can penetrate within polymeric chains and restrict the slippage of the macromolecules, thereby enhance the tear resistance of the host polymer [12, 13]. The XRD results also indicate that the crystallinity of TPS was increased when it is incorporated with 5-hours-ultrasonicated cellulose. This could also be the reason why the tear strength of the TPS was successfully increased.

![Figure 4.9](image-url)

**Figure 4.9:** Comparison of tear strength between TPS and TPS biocomposite with different ultrasonication period cellulose.

---

**Fig. 2.** Comparison on tear strength between the neat TPS and TPS biocomposites.
The TPS/cellulose biocomposite films were prepared by using 5wt% of cellulose as filler. Prior to the biocomposite production, the cellulose was subjected to ultrasonication process for 0, 1, 2, 3, 4 and 5 hours. The effects of the ultrasonication process on the crystallinity and tear strength of the biocomposite were studied. XRD analysis indicates that there are slight difference between the cellulose without ultrasonication and cellulose undergoes 5 hours of ultrasonication with respect to their peaks (2θ shifted from 15.38° to 15.43°) and its crystallinity index (increased from 42.30% to 43.10%). The obtained results proved that the ultrasonication process has increased the crystallinity of the cellulose. Isolation of the cellulose fibers and enhancement of the cellulose’s crystallinity led to the improvement of the TPS biocomposite’s tear strength. The highest tear strength of TPS/cellulose biocomposite film was obtained when the 5hours-ultrasonicated cellulose was employed as filler. It demonstrated 241% increment in tear strength when benchmarked with the pure TPS film.

The authors would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant no: FRGS/1/2019/TK10/UNIMAP/03/2 from the Ministry of Education Malaysia.

References

1. B. Luijsterburg and H. Goossens, H. Conservation and Recycling, E 85, (2014)
2. R. A. Gross, B. Kalra, Science. E 297, 5582 (2002)
3. M. Kolybaba, L.G. Tabil, S. Panigrahi, W.J. Crerar, T. Powell, B. Wang, Biodegradable Polymers: Past, Present, And Future. In ASABE/CSBE North Central Intersectional Meeting (American Society of Agricultural and Biological Engineers, 2006)
4. S.N.S. Syed Adam, A.F Osman & R. Shamsudin, Sains Malaysiana. E 47, 6 (2018)
5. A.M.T.L. Ashafee, *Effect of Hybrid Cellulose/Bentonite Filler and Dispersing Parameters to Crystallinity, Low Temperature Tear and Tensile Properties of Thermoplastic Starch Composites for Refrigerated Food packaging Application*, (Master Thesis, Universiti Malaysia Perlis, 2017)

6. B. Ruxanda, T. Carmen-Alice, S. Iuliana. BioRes. E 9, 1 (2014)

7. N.L.I. Zailuddin, A.F. Osman, S. Husseinsyah, Z. Ariffin, F.H. Badrun, Mechanical Properties and X-Ray Diffraction of Oil Palm Empty Fruit Bunch All-Nanocellulose Composite Films, *Proceedings of the Second International Conference on the Future of Asean (ICOFA).* E 2 (2017)

8. W.S. Ratnayake, R. Hoover, T. Warkentin, Starch-Stärke. E 54, 6 (2002)

9. E.D.M. Teixeira, C. Lotti, A.C. Corrêa, K.B. Teodoro, J.M. Marconcini, L.H. Mattoso, J. App. Poly. Sci. E 120, 4 (2011)

10. Y. Chen, C. Liu, P.R. Chang, X. Cao, D.P. Anderson, Carbohydrate Polymers. E 76, 4 (2009)

11. W. Chen, H. Yu, Y. Liu, Y. Hai, M. Zhang, P. Chen, Cellulose. E 18, 2 (2011)

12. Z. Peng, L. Kong, S. Li, Y. Chen, M. Huang, Composites Science and Technology, E 67, 15-16 (2007)

13. A.F. Osman, G.A. Edwards, T.L. Schiller, Y. Andriani, K.S. Jack, I.C. Morrow, P.J. Halley, D.J. Martin, Macromolecules. E 45, 1 (2011)