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Preliminary Study of Potential Bioimplant from Glycerol Plasticized Starch-Microcrystalline Cellulose Composite

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Abstract
Biodegradable and bio-based substitutes for conventional plastics are on the rise in these past decades. One of the applications of bioplastic is for biomedical implants or bioimplant. Starch was plasticized using glycerol at varying amounts (40% and 60% of dry starch mass) to produce thermoplastic starch (TPS). A reinforcement filler of microcrystalline cellulose (MCC) was used to improve the mechanical properties. The MCC content in this study was also varied (0%, 2%, 4%, and 8% w/w). This paper studies the mechanical properties of starch-MCC composites for their potential as bioimplant. The optimum glycerol and MCC contents from the results are 40% glycerol and 8% MCC with 2.97 MPa tensile strength and 7.20% strain at break. Thus, the sample has the potential application in bioimplant material for trabecular bone replacement, which has an average tensile strength of 2 MPa and strains at a break of 2.5%.

Keywords:
Bioimplant;
MCC;
Starch-MCC composite;
Strain at break;
Tensile strength;
Thermoplastic starch;

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INTRODUCTION

Researchers have studied various biomasses to open up alternatives in plastic pollution reduction, including those from oil palm empty fruit bunches [1], sugarbeet [2], microalgae [3][4], silk [5] and starch [6]. One of the emerging applications of bioplastics is for a biomedical implant. Bioimplants are prostheses designed to help bring back physiological functions [7]. This definition implies that bioimplants should have decent levels of biocompatibility as well as decent mechanical properties. The biocompatibility with human bodies includes non-toxicity, biodegradability, and bioactivity/bio-inertness. Biodegradable polymers, especially polyesters, have been shown to serve this purpose relatively well and many types of research have been done on biopolyesters-based materials intended for bioimplant [8][9]. However, pure polyesters are hydrophobic and tend to have poor cell-adhesion [9][10]. In an attempt to solve this issue, this study investigated starch-based polymer, which is naturally hydrophilic, biocompatible, and biodegradable, to examine its potential to be used as a bioimplant.

Considering starch as a brittle material, the addition of plasticizer, heat, and shear are required to help starch lose its crystallinity and become thermoplastic. The chosen plasticizer should be polar and hydrophilic with a small molecular size [11]. These allow plasticizer

molecules to move around the granular starch, interrupting inter/intra-molecular hydrogen bonds of starch and replacing them by starch-plasticizer interaction, which quickly softens the structure [11, 12, 13]. The problem is that thermoplastic starch possesses poor mechanical properties such as tensile strength and Young's modulus. Moreover, pristine TPS absorbs water. It should be hindered because an increase in water content during storage or application could change glass transition temperature (T_g) and crystallinity of the TPS (B-type crystallinity) [14]. The amount of water absorbed depends on the relative humidity at which the TPS is placed, the type of plasticizer, and temperature [14][15].

Studies show that MCC filler's presence helps various TPS improve its mechanical properties and reduce water uptake [15, 16, 17]. This study examines the bioimplant potential of starch-based polymer, which is naturally hydrophilic, biocompatible, and biodegradable. Experiments were carried out to observe the effect of concentration of microcrystalline cellulose (MCC) as a reinforcement filler and glycerol as a plasticizer on the mechanical properties of TPS.

MATERIALS AND METHODS

Materials

In this paper, the starch was obtained from Smart-Lab. Other materials include glycerol as a plasticizing agent of the starch to give the starch thermoplastic properties, distilled water as a solvent for mixing, and microcrystalline cellulose (MCC) as the reinforcement filler the thermoplastic starch-based composite. Glycerol and MCC were obtained from Merck.

Synthesis of Thermoplastic Starch

Starch was weighed, then plasticizing agent (glycerol) was added at varying mass (as an independent variable, 40% and 60% of dry starch mass). Water was also added as a solvent at ten times the mass of the starch. The mixture was stirred at 350 rpm under a temperature of 90^0C and atmospheric pressure using a magnetic stirrer set equipped with a hot plate. The stirring was carried out until the starch solution becomes gelatinized (thermoplastic starch).

Addition of MCC

The MCC - which depends on the desired MCC concentration – was made into a suspension in water (10-20 times the MCC mass) and added into the thermoplastic starch solution. The solution was then stirred again at 350 rpm and 90^0C for approximately half the time as the first stirring (thermoplastic starch making). The solution was poured into an evaporation dish and dried in an oven for 18 hours under 55^0C temperature. The dried samples were then conditioned for 48 hours under room temperature and humidity (25^0C, 60%) before undergoing the next step, the mechanical testing.

Mechanical Testing

The samples were cut into regular rectangular pieces. The baseline sample was pure thermoplastic starch with no added reinforcement filler (0% MCC). The mechanical properties of the samples with added reinforcement filler (2%, 4%, and 8% MCC) were compared to the mechanical properties of the base sample (with no added reinforcement filler).

Each sample was cut into three pieces since there are three separate tests for each sample. Since the tensile strength - by definition - is the maximum stress that can be applied to the sample before it starts to break, the tensile strength (in MPa) is also equal to the maximum load (force) applied (in Newtons) before the sample starts to break divided by the cross-sectional area of the sample (in mm^2).

The first mechanical parameter, the tensile strength, was calculated according to the following equation (by inputting the maximum load):

$$\sigma = \frac{F}{A} \quad (1)$$

σ= stress (MPa)
F = load (force, N)
A = cross-sectional area (mm^2)

Another mechanical parameter to be tested is the elongation (strain) at the break, calculated according to the following equation:

$$\varepsilon = \frac{\Delta L}{L_0} (* 100\%) \quad (2)$$

ϵ= strain
ΔL= elongation (mm)
L_0 = initial sample length (mm)

The mechanical tests – both for tensile strength and strain at break – were carried out using Force Tester MCT-2150 (A&D, Japan) mechanical testing device.

RESULTS AND DISCUSSION

Tensile Strength

The data for the tensile strength values for the samples with 40% and 60% added glycerol are shown in Figure 1 and Figure 2, respectively.

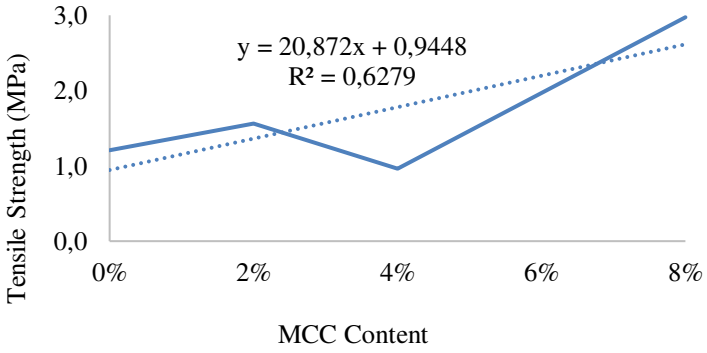

Figure 1. Tensile Strength Profile for 40% Glycerol Samples

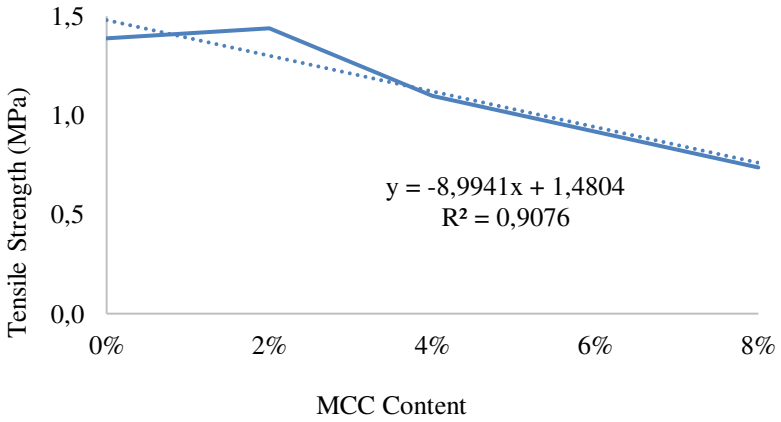

Figure 2. Tensile Strength Profile for 60% Glycerol Samples

Figure 1 shows that the control sample (0% MCC content) with 40% glycerol has an average tensile strength of around 1.21 MPa. The trend is upwards. The addition of 8% MCC increases the tensile strength significantly, by nearly 150% (2.5-fold), than the sample without MCC, from 1.21 to 2.97 MPa.

As seen from Figure 2, the sample with no added MCC in the 60% glycerol samples has an average tensile strength of 1.39 MPa. Contrary to the results from the samples with 40% glycerol, the samples with 60% glycerol see a downward trend in tensile strength values as the MCC content increases. The sample with the most MCC content (8% added MCC) has roughly half (0.74 MPa), the tensile strength of the sample with no added MCC.

Strain at Break

The value of strain or elongation at break is another mechanical property of the samples that are tested. The value of the strain at break can be traced in the strain profile by finding the value of strain when the stress (load) reaches the maximum point (i.e., when the stress begins to decrease). The device used for the strain at break calculation is the same as the one used for calculating the stress (tensile strength).

Data for strain at break values for the samples with 40% glycerol are shown in Figure 3. As seen from this figure, the strain at break values for the samples with 40% glycerol has a downward trend. It can be inferred from the strain at break data that by increasing the amount of MCC added to the sample, the value of the strain (elongation) at break decreases. Combined with the increasing value of the tensile strength, adding more MCC to the sample increases the Young modulus since the value of Young modulus is equal to stress divided by strain.

The data for strain at break values for samples with 60% added glycerol are shown in Figure 4. As seen from this figure, for the samples with 60% added glycerol, there are no noticeable trends (except for the slight increase in strain at break values from 2% to 8% MCC samples, but the 0% MCC sample has noticeably higher strain at break value compared to 2%) in the strain at break profile. The common feature of the samples with 60% glycerol is the relatively high values of strain (elongation) at break (ranging from 12.8% to 18.6%). In other words, the samples with 60% glycerol content are relatively flexible and extensible compared to the samples with 40% glycerol.

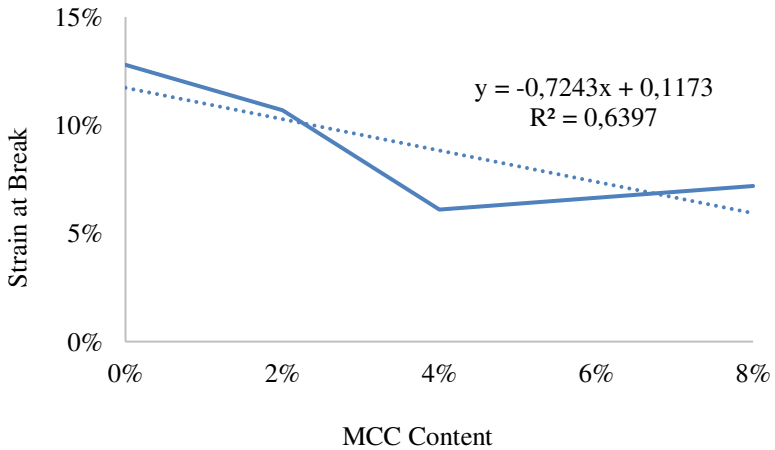

Figure 3. Strain at Break Profile for 40% Glycerol Samples

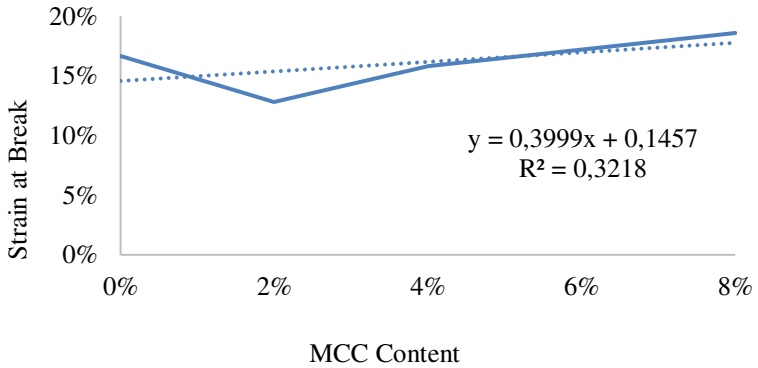

Figure 4. Strain at Break Profile for 60% Glycerol Samples

Tensile Strength

One of the factors affecting the tensile strength of TPS is the ratio between amylose and amylopectin of the native starch. High amylose content leads to higher tensile strength, whereas a high level of amylopectin lowers it [11]. The magnitude of the measured tensile strength in this study is more or less to the same degree as that observed by Ren *et al*. [18], who performed a study on potato-based TPS with varying plasticizer and halloysite nanotubes content.

As previously mentioned, the tensile strength for the samples with 40% glycerol increases as the amount of MCC increases. This increasing trend agrees with other studies on different TPS composites conducted by Wittaya [16]; Maulida et al. [17]; Ren et al. [18]; Jumaidin et al. [19]; and González et al. [20]. Tensile strength is largely determined by the intermolecular interaction between starch, glycerol, and MCC. The increasing tensile strength is most likely caused by the formation of a hydrogen bond network between MCC and the starch [16, 17, 18]. Cellulose and starch also have a similar chemical structure that might facilitate MCC integration in the starch matrix. This allows proper stress transfer between the starch matrix and the MCC, which is reflected in the improved tensile strength of the composites [19][20]. The errors (i.e., the low R-squared value) may stem from the fact that the drying is uneven - the moisture content throughout the sample could be uneven due to the shape of the container (evaporating dish) which resembles a bowl. Thus, the moisture-rich part accumulates in the center of the sample (the evaporating dish). As the moisture content also has a significant effect on the tensile strength of the samples, the errors thus occur.

For the samples with 60% glycerol content, the tensile strength slightly decreases as the amount of MCC increases. This downward trend is less pronounced (-8.99 gradient) than the upward trend of the samples with 40% glycerol content (+20.87 gradient), albeit with significantly higher accuracy (R-squared of 0.908 vs. 0.628). This might be due to the filler not being well distributed among the TPS containing 60% glycerol. Thus, aggregates of MCC might be formed, which leads to phase discontinuation. The formation of aggregate seems more salient as MCC content increases in the composite, shown from the tensile strength that is further decreased. Such a trend was also observed by Fahrngruber et al. [21], using corn-based TPS reinforced with 1 – 5 wt% potato fiber. Wittaya [17] observed an opposite trend in rice-starch based TPS at MCC content of 0 – 35 wt%, yet at MCC > 35%, the tensile strength is also decreasing.

In general, the values of tensile strength for the samples with 60% glycerol are lower than that of 40% glycerol samples, especially the one with 8% MCC content (0.74 MPa vs. 2.97 MPa; four times lower tensile strength). This is likely because plasticizers or glycerol in this case, despite giving flexibility to starch-based bioplastics, actually decrease the hardness

[16][22] and weaken the intermolecular hydrogen bond between the matrix (starch) and the reinforcement filler (MCC) [23].

Strain at Break

The data given in Figure 3 showed that for samples with 40% glycerol content, the strain at break values see a downward trend as the MCC content increases. Fahrngruber et al. [19], Jumaidin et al. [20], and Gonzalez et al. [21] observed similar results. However, Ren et al. [18] had a contrary result, in which the strain increases with increasing filler content. All, except Fahrngruber et al. [21], obtained composites with good intermolecular force, as proven by increasing tensile strength with increasing filler content. Thus, the different observable trend might be due to the different filler size used. Comparing the result obtained in this study versus those mentioned beforehand, the composites whose filler's particle size is at least micrometric tend to have lower strain at break versus the neat TPS (without filler). On the other hand, composites with nanometric fillers tend to have higher elongation compare to the pristine TPS.

The factor contributing to the decrease in the strain at break is likely similar to that contributing to the increasing trend of tensile strength, i.e., the hydrogen bond between MCC and starch strengthens the starch-MCC composite and reduces the elasticity (the strain/elongation at break values). When the filler size is on the nanometric scale, the effect of hydrogen bond competes with the effect of plasticizer, in which the later tend to increase the strain at break.

For samples with 60% glycerol content, the strain values at break are higher than that of 40% glycerol content samples. A large amount of plasticizer added contributes a lot to the elasticity (elongation/strain at break values) since it increases the spacing between the molecules [23]. The lack of trend in the strain at break for samples with 60% glycerol might result from the contending effect between the higher glycerol content and the presence of aggregates in the composites at varying MCC concentration.

Feasible Application as Bioimplant Material

Overall, the sample with the highest tensile strength value is the sample with 40% glycerol and 8% MCC, with 2.97 MPa – almost twice higher than the sample with the second-highest tensile strength value (40% glycerol, 2% MCC content, 1.56 MPa). According to a review [9], trabecular bone and cardiovascular tissues are examples of bodily tissues with an average tensile strength of less than 2.97 MPa [24][25]. Therefore, the sample with 40% glycerol and 8% MCC meets the tensile strength standard requirement for trabecular bone and cardiovascular tissues. However, the sample with 40% glycerol and 8% MCC also has relatively low strain at break (7.20%). Since the bioimplant for cardiovascular tissues requires high elasticity standards [25], the sample has the potential as a scaffold to replace trabecular bone, which has an average strain at break of 2.5% [24]. The group of Reis has done extensive studies on the use of commercially available corn starch-based polymeric blend as a scaffold for bioimplants [26, 27, 28, 29, 30, 31]. Thus, further study needs to be performed on the obtained composite to fulfill the intended purpose properly. Biocompatibility, scaffold processing method, the effect of body fluid on its properties, ability to guide cell proliferation, and degradation rates are the necessary properties that need to be further studied.

CONCLUSIONS

The presence of MCC in this study increases tensile strength. It decreases strain at break for samples with 40% glycerol due to hydrogen bonds forming between the starch matrix and MCC. For samples with 60% glycerol, there seems to be the formation of aggregates that

compete with the effect of hydrogen bonds and plasticizer. This leads to a decrease in tensile strength with no specific trend for strain at break. The optimum sample obtained was 40% glycerol content and 8% MCC content, as the tensile strength is fairly high compared to other samples (2.97 MPa) (2.97 MPa tensile strength, 7.20% strain at break). This sample meets the mechanical criteria for the bioimplant material intended to replace the trabecular bone (2 MPa tensile strength, 2.5% strain at break).

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