Thermoplastic corn starch reinforced with pine wood fibre and calcium carbonate precipitate filler

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Abstract. The shortage of oil and related minerals and also their extreme environmental drawbacks are the main reason for the quick-growing interest in biodegradable polymer composites production. Biodegradable polymer composites are mainly produced from renewable resources which are biologically degradable. In this research, corn starch was plasticized with glycerol. The plasticized thermoplastic corn starch was reinforced with calcium carbonate precipitate powder as a filler and pine wood fibre as reinforcement. Free thermoplastic plasticized corn starch (FTPS), thermoplastic corn starch reinforced with calcium carbonate (CTPS), thermoplastic corn starch reinforced with pine wood (WTPS), thermoplastic corn starch reinforced with pine wood fibre and calcium carbonate precipitate hybrid composite (HTPS) were produced and compared for their mechanical properties like tensile strength and, hardness. DSC and DMA analysis were also done for determining their thermal properties. Moreover, the water absorption test was also carried out to understand their resistance to moisture. WTPS exhibits better results in most of the measured proprieties given that TPS and wood fibre being both hydrophobic resulted in a homogeneous distribution and better interfacial adhesion.

1. Introduction
The use of plastic has been controversial for a long time due to the shortage of facilities or the infrastructures to recycle and its non-sustainable use [1], non-renewability, non-biodegradability, and its venomous additives incorporation. Current trends indicate that steady growth will occur within the use of biodegradable plastics with increasing accessibility of appropriate materials and due to social group and legislative pressure [2]. Some of the current attempts to solve the problem are focusing on mixing plastic materials with natural biodegradable polymers like starch, cellulose, and poly-lactic acid (PLA) which are also cheap [3]. Alternative works opted for chitin to individual form new materials with the specified properties [4] and to scale back environmental pollution. Specifically, biodegradable polymers showed encouraging technical and industrial benefits. Indeed, they can be produced by most plastics processing techniques like injection moulding, extrusion, and compounding. However, some changes are required in line with the conditions and compounding stage and of the shear controlled orientation in injection moulding within the moulding technique [5]. Film extrusion, injection moulding, blow moulding, and thermoforming are the most processing techniques that have used biodegradable polymers and are introduced primarily in three sectors, i.e., packaging [6], agriculture [7], and medicine [8].
Research and improvement in polymeric materials coupled with a suitable filler, matrix-filler interaction and modern techniques to create composites have potential applications in food bundling. Advancement in food bundling/packaging materials is anticipated to develop with the appearance of cheap, renewable and economical materials with improved barrier and mechanical properties [9].

2. Materials and methods

2.1. Natural Materials

Corn starch: Corn starch from HAAS Naturals with 100% corn starch content and moisture content of 12% was used as a matrix to produce the thermoplastic starch.

Plasticizer: Plant glycerine with pharmaceutical quality was obtained from Flora Vita, Kévés Béla Kft (PhEur.9.0, USP Pharmacy quality. Natural vegetable, 99.5% pure, Glycerine E422).

Pine wood fibre: Pine tree wood fibre was crushed and sieved using 250 µm sieve.

Filler: Calcium carbonate precipitate (SOCAL U1S2) was used as a filler for the hybrid composite

2.2. Methodology

2.2.1. Preparation of TPS:

Corn starch produced from Haas Naturals was weighed and mixed with glycerine. 40 gram of glycerin was added to 60 gram of corn starch (2:3 weight %) in a glass beaker. Then, it was mixed manually until it is plasticized. Next, for further homogenization, the mixture in the beaker was put in the furnace at 120 °C for three minutes. Immediately after the solution is released from the furnace it was mixed by a mixer for 5 minutes at 600 rpm. The mixed solution was compressed by compression machines into thin sheets of 1 mm thickness under compression of 20 Mpa and 160 °C for 5 minutes [10].

2.2.2. Preparation of TPS composites:

Table 1, below shows the type and ratio of components used to prepare the composites. For the preparation of WTPS, CTPS and HTPS composite samples; the native starch was first added with powdered calcium carbonate precipitate and crashed pine wood fibre (250 µm particle size) according to the ratio specified and the procedures used to prepare TPS, specified above; are followed. 5 grams of calcium carbonate precipitate was mixed with 55 gram of corn starch. The mixture was mixed manually in a beaker to make it homogeneous [11].

Table1: Type and ratio of raw materials used for sample preparation

| S.No. | Sample Name   | Description                                         | Composition in weight percent | ratio     |
|-------|---------------|-----------------------------------------------------|-------------------------------|-----------|
| 1     | FTPS (free)   | Thermoplastic corn starch                           | 60% corn starch + 40% glycerin | 6:4       |
| 2     | WTPS (wood)   | Thermoplastic corn starch + wood fiber              | 55% corn starch + 5% wood fiber +40% glycerin | 5.5:0.5:4 |
| 3     | CTPS (clay)   | Thermoplastic corn starch + calcium carbonate precipitate (micro, not fully nano) | 55% corn starch + 5% clay + 40% glycerin | 5.5:0.5:4 |
| 4     | HTPS (Hybrid) | Thermoplastic corn starch + wood fiber + calcium carbonate precipitate | 50% corn starch + 5% clay + 5% wood fiber + 40% glycerin | 5:0.5:0.5:4 |
2.2.3. Tensile properties. 
The tensile properties of the starch films were determined on an MTS tensile tester (INSRON 5566) according to ASTM standard D 882-02. Testing was done on four samples each measuring 10 cm × 1 cm randomly cut from the cast films.

2.2.4. Hardness test. The hardness test of the samples was done using a durometer ASTM D2240, Shore D hardness tester. Four measurements in different locations of the sample were carried out and the mean average of all the measurements was taken.

2.3.5. Thermal analysis

2.3.5.1. Differential scanning calorimetry.
The heat flow measurement was made using Perkin Elmer DSC131 Evo at the faculty of materials science and engineering, institute of ceramic and polymer engineering, university of Miskolc. The thermoplastic starch composite specimens of nearly 10 mg mass were heated from 20 to 200°C at a rate of 10°C min−1 and then cooled at the same rate to 20°C and finally reheated to 200°C.

2.3.5.2. Dynamic Mechanical Analysis.
DMA measurements were performed using a PerkinElmer DMA 8000, in BorsodChem, a leading chemical company in Hungary. Measurements were performed under flowing air at a frequency of 0.3Hz, with a maximum dynamic force of 10N, amplitudes up to 16m and heating rate of 3 °C/min. The samples (45×5×2mm3) were cut from the hot-pressed molded plates.

2.2.6. Morphological structure.
The surface features of the TPS composites were observed using a scanning electron microscope (Hitachi Model TM 1000).

2.2.7. Water absorption/ water resistivity test.
Specimens with (10mm*25mm*2mm) were allowed to dry at a temperature of 70 °C for 24 hours. After drying the samples were weighed and their initial weight recorded. The specimens were immersed in a distilled water for intervals of time (minutes) and their weight recorded at each interval as shown in the table below until constant weight is reached. The water uptake of the samples was calculated as follows:

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\text{Percentage of water uptake} = \frac{W_f - W_o}{W_o} \times 100
\]
Where \(W_f\) is the weight of the sample after each immersion and \(W_o\) is the initial weight of the specimen.

3. Result and Discussion
Plasticizing the corn starch, mixing with calcium carbonate and pine wood fibre, heating and pressing were the successive steps followed to produce the required samples. The samples were characterized for their mechanical and physical properties.

3.1. Tensile property of the composites
Figure 1 and 2, below shows the tensile stress test result of the four composites. WTPS reveals greater strength due to the better homogeneity and compatibility (both are hydrophilic), calcium carbonate precipitate filled composite is found less strong due to the hydrophobicity of the filler which also leads to agglomeration. The tensile strain graph shows that free TPS possesses better tensile strain than the other composite samples and decreases with the addition of wood fiber and/or filler. This is due to the fact that intercalation of fillers into starch promotes the formation of a restricted environment against the movement of polymer chains [12].
Figure 1. Tensile strength test of composite samples

Figure 2. Tensile Strain test of composite samples

3.2. Hardness test of the composite samples

The graph in Figure 3 below shows that the hybrid composite (HTPS) has greater hardness followed by wood reinforced TPS. These facts could be attributed to the better interfacial adhesion of the TPS matrix with pine wood fibre reinforcement. The decrease in the hardness of the composite with calcium carbonate precipitate might be due to agglomeration of the filler that leads to inhomogeneity.

3.3 Morphology of the composite samples

The SEM result shown in Figure 4 indicates agglomerations in the composites filled with the calcium carbonate precipitate (CTPS) and the hybrid one (HTPS), but the wood fibre reinforced composite (WTPS) has got better homogeneity. This can be attributed to the hydrophobicity of the calcium carbonate precipitate which hinders the uniform distribution in the composite.

Figure 3. The hardness test result of the composites

Figure 4. SEM test result of the composites

3.4. Water absorption test

As indicated in Figure 5 below, FTPS was found water-sensitive and exhibit higher water absorption rate, followed by CTPS due to agglomeration of the filler. WTPS and HTPS are found less sensitive to water absorption, the latter being the better. All the composite samples started dissolving in the distilled water after 3 hours of the testing period. Similar results are found in related literature [13].
3.5. Thermal analysis

The DSC test result of all the samples is depicted in Figure 6 below as a heat flow versus temperature thermogram. The DSC graph of free TPS and the composite samples indicates that there is a big variation in temperature at which the free TPS and other composite transform to another phase. The melting point of the composites is shifted to a lower temperature for the hybrid composite compared with the other composites. It means the addition of filler and fiber together has brought a major change on the melting temperature of TPS. Figure 6 also shows that the thermogram for TPS is smoother than the other composites but major changes on melting point are not observed when compared with CTPS and WTPS. This was similar to the result obtained by N. R. Savadekar et.al [14].

The curves in the thermogram Figure 7 displays that the glass transition temperature ($T_g$) has increased for both HTPS and WTPS, this might be due to the compatibility of wood fiber to create better interfacial adhesion with TPS. Addition of filler calcium carbonate precipitate doesn’t have a significant effect on the glass transition temperature of the TPS composite. The thermogram below also depicts that the storage modulus decrease with increase in the temperature. The decrease in storage modulus is sharper in free TPS and CTPS than HTPS and WTPS. This is according to the result obtained by [15]. While determining the activation energy of the free TPS sample, Arrhenius equation was used to determine the Arrhenius plot, $\ln(f) = \text{Activation Energy}/(RT)$. The activation energy of the low peak and the high peak were found to be 119KJ/mole and 216KJ/mole respectively for the plasticized starch Figure 8 and Figure 9.
4. Conclusion
TPS composites reinforced by pine wood fibre and calcium carbonate precipitate were prepared by pressure moulding. The samples were characterized for their mechanical, physical and thermal properties. WTPS has shown greater strength due to the better homogeneity and compatibility (both are hydrophilic), CTPS composite exhibit less homogeneity as it is hydrophobic and due to agglomeration effect. According to SEM, DMA, DSC, water absorption and hardness testing, pine wood fibre reinforced TPS sample shows better properties than precipitated calcium carbonate reinforced composites and the hybrid composites, this is due to the compatibility nature of wood fibre with TPS and hydrophobicity of calcium carbonate which leads to coagulation.

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Figure 8. DMA test result of composites at different frequency

Figure 9. Result of the activation energy calculation for low and high peak (Arrhenius plot)
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