

**ANTAL KERPELY DOCTORAL SCHOOL OF
MATERIALS SCIENCE AND TECHNOLOGY**



**Development and Characterization of Modified Starch Polymer and
Polymer Composites**

PhD Thesis Booklet

By

Gerezgiher Alula Gebresas

Supervisor: Tamas Szabo (Associate Professor)

Head of the Doctoral School

Prof. Dr. Valéria Mertinger

**Institute of Ceramic and Polymer Engineering
Faculty of Materials and Chemical Engineering
University of Miskolc**

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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, non-renewability, non-biodegradability, and its toxic additives incorporation. Current trends indicate that steady growth will occur within the use of biodegradable plastics with increasing accessibility of appropriate materials due to social group and legislative pressure. Biodegradable polymers are materials whose chemical and physical properties deteriorate and totally degrade when exposed to microbes, aerobic, and anaerobic processes. Some of the current attempts to solve the problem are focusing on mixing plastic materials with natural biodegradable polymers like starch, cellulose, and polylactic acid (PLA) which are also cheap [1]–[3]

Starch is a readily available biopolymer derived primarily from grains and tubers that is completely biodegradable [4]–[6]. Being renewable and biodegradable, starch has been seeking the attention of many researchers worldwide to replace the environmentally unfriendly conventional plastics [7]–[12]. A number of physical, and chemical modification techniques has been utilized to modify starch [13]. Variety of chemical agents are used to chemically modify starch film. Cross-linking, Grafting polymerization, Oxidation, Etherification, Esterification are among the chemical modification methods of starch [13].

Crosslinking or cross-ligation is interconnection of linear or branched chains in a polymer. Ether or ester bonds are formed when the reagents react with the hydroxyl groups in starch molecules crosslinking process [14]. Some examples of polysaccharide materials which have been crosslinked with polycarboxylic acids are starch granules [15], starch nanoparticles [16], starch films [17], starch gels [18].

Significant number of researches are done on modification of starch using crosslinking agents, fillers and reinforcements, but there is still a huge gap in replacing the conventional plastics by bioplastics. This study basically concentrates on the limitation of researches involving the many easily available and non-toxic carboxylic acids which can potentially replace the toxic plastics.

With a purpose of improving mainly the water resistivity and related physical and mechanical property of starch biopolymer, plasticizers (glycerol), cross linking agents (carboxylic acids), fillers (clays), and natural fibers (Enset) was used to modify the physical and chemical nature of starch using crosslinking, pressure moulding and solution casting techniques.

2 Literature Summary and knowledge gap

Due to its renewability, biodegradability, low cost, and abundance of -OH chemistry, which opens it up to endless modification possibilities and melt processability in the presence of plasticizers, starch, a renewable polysaccharide polymer, has received extensive research and commercial interest as a feedstock. However, due to limitations in its hydrophilicity, thermal, and mechanical properties, rapid degradability, and strong intra- and intermolecular hydrogen bonding of the polymer chains, it cannot be widely used in industry as a renewable biopolymer. Therefore, modification is required to alleviate these limitations and create desirable properties. Granules of starch in an aqueous suspension can react to create cross-linked starch. The hydrogen bonds in the granule are reinforced by cross-linking, which forms chemical bonds that act as molecular bridges. Since the cross-linking process involves treating the starch while it is still in its granular form, the amount of chemical cross-links added to the starch is often quite small when compared to the starch's weight and the total number of anhydroglucose units in the granule. The majority of cross-linked starches will have 1 cross-link every 100–3000 anhydroglucose units.

The reaction conditions for starch might be extremely variable depending on the temperature and the specific reagent used for the cross-linking. Alkali sodium hydroxide is frequently used to accelerate the process. Commonly, neutral to mildly alkaline conditions are used to conduct the reactions. Sometimes the reactions also take place in an acidic environment.

The majority of researches reviewed revealed most of the studies undertaken are on regularly used acids and their derivatives, including acetic anhydride, succinic anhydride, and citric acid. Nevertheless, this analysis of the literature has revealed that various carboxylic acids and their derivatives have a significant potential for producing modified starches.

The complexity of modifying starch is reported to be very high, and by altering just one reaction parameter, a new product with totally distinct characteristics might be produced.

Positive outcomes have been observed as a result of the work done on TPS modification using natural fillers and fibers. Cotton, sugar palm, and cassava are some examples of natural fiber reinforcements that enhance mechanical properties but have a negative impact on water resistance.

Clay is another filler that has increased water resistance but has the drawback of lowering mechanical property, according to some studies. This suggests that TPS composites, if further investigated, may soon replace petroleum-based polymer composites.

2.1 Knowledge gap

Many studies are being conducted to physically and chemically modify corn starch. One of the chemical modification techniques, crosslinking, enhances the properties of starch-based polymers, but the majority of cross-linkers either have negative effects on the functionality of biopolymers or are toxic. As a result; Cross-linking of starch with green cross-linking agents have been studied; however, there is still a limitation in expanding the research on more easily available and non-toxic carboxylic acids.

The studies reviewed on crosslinking of starch using carboxylic acids focus on optimizing the reaction conditions like molar ratio of the reagent/cross-linker, reaction temperature and pH, and some also tried to include factors like type and amount of catalyst, reaction duration and stirring speed. They lack to examine which property/feature is primarily responsible for cross-linking.

They use very diverse ways of sample preparation and different reaction conditions; and came up with varying findings on the process parameters, reaction conditions and the property of the modified starch. This shows that a lot is left to be studied on crosslinking of starch so that standard and optimized production method and product quality is met.

The other modification approach is the making of starch polymer composites. Adding fillers and reinforcement fibers have been utilized to modify its properties. But, still the improved starch based polymers composites are unable to replace the conventional polymers, indicating that much research is needed to improve the properties and reach the desirables. Consequently, investigating new polymer composites by modifying corn starch with fillers (calcium carbonate precipitate and clay) and Enset fibers which are not previously well studied was found necessary.

2.1.1 Specific Objectives of the study.

- Validate and optimize process parameters for crosslinking starch polymers and polymer composites
- Investigate the effects of the intrinsic nature (Molecular structure, acidity, solubility, carbon chain length) of carboxylic acids on starch crosslinking
- Investigate the effect of the natural fibers and fillers on the physical and thermal properties of corn starch. .
- Improve the physical and chemical property of corn starch polymer film

3 Experimental

3.1 Materials

100% corn starch with a moisture content of 11.4% and ash content of 0.14% was obtained from HAAS Naturals. Tartaric acid (food grade) was obtained from Tarjan es Tarsa Kft. Hungary. The citric acid (food grade) was purchased from Herman Ker Bt. Hungary. Oxalic acid (99%) was purchased from Sigma Aldrich. Terephthalic acid, 99+% was purchased from thermos scientific and pyromellitic acid anhydride was obtained from Apollo Scientific. Succinic acid (99.6%) was obtained from VWR international Leuven Belgium. Malonic acid was obtained from Apollo Scientific ltd United Kingdom. Malic acid (DL-Malic acid 98%) was purchased from Alfa Aesar, Thermo Fisher (Kandel) GmbH, Germany. Pharmaceutical quality grade glycerol was purchased from Flora Vita, Kévés Béla Kft, PhEur.9.0, USP Pharmacy quality, Natural vegetable, and 99.5% pure Glycerin E422. HCl and NaOH were purchased from Sigma-Aldrich and were used as catalysts and pH adjustments during the chemical reaction. The property of the carboxylic acids used is shown in table 3.1.

Sodium Montmorillonite (SOCAL U1S2) and Iron rich kaolinite clay were dried and milled in a rotary miller and micro clay with 63 μ m particle size was used for this experiment as fillers for the hybrid starch composite film preparation. Ensete fiber, a plant fiber brought from Ethiopia and Pinewood fibre found in Hungary was used as reinforcements in this study.

Table 3. 1 Property of the carboxylic acids

| Acid | Molecular Weight (g/mol) | pKa | | | Melting Point | Solubility in water (at 20 °C) |
|--------------|--------------------------|------------------|------------------|------------------|---------------|--------------------------------|
| | | pKa ₁ | pKa ₂ | pKa ₃ | | |
| Citric | 192 | 3.13 | 4.76 | 6.39 | 153°C | 1330 g/L |
| Tartaric | 150 | 2.89 | 4.40 | | 275°C | 1330 g/L |
| Oxalic | 90 | 1.27 | 4.28 | | 365°C | 95.5 g/L |
| Malic | 134 | 3.4 | | | 130 °C | 558 g/L |
| Malonic | 104 | 2.83 | | | 135°C | 763 g/L |
| Succinic | 118 | 4.2 | | | 184°C | 58 g/L |
| Terephthalic | 166 | 3.51 | 4.82 | | 300°C | 0.015 g/L |
| Pyromellitic | 254 | 1.92 | 2.87 | 4.49 | 285°C | 15 g/L |

3.2 Fabrication of Modified Starch Samples

3.2.1 Crosslinking of Starch

Corn starch plasticization and crosslinking and film formation are processed as depicted in fig. 3.1.

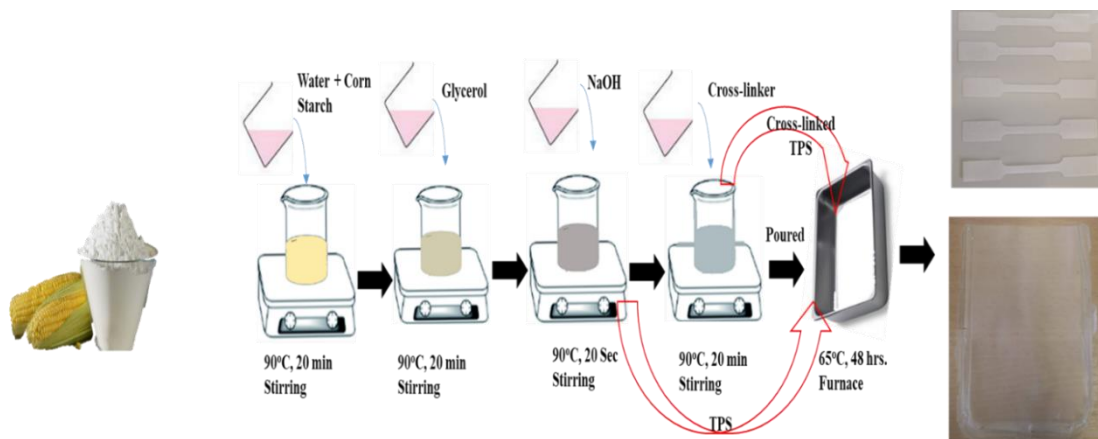


Figure 3. 1 Crosslinking process flow chart

3.2.2 Preparation of TPS Composites using Compression Moulding

For the preparation of TPS; 40 gram of glycerol was added to 60 gram of corn starch. The mixture was then was put in the furnace at 120 °C for three minutes. Then after, the solution was mixed for 5 minutes at 600 rpm with a mixer. The mixed solution was compressed by compression moulding machine into thin sheets of 1 mm thickness under a compression pressure of 20 MPa and a temperature of 160°C for 5 minutes. For composite samples; 60 gram native starch was first added with 5 grams of powdered calcium carbonate precipitate and crashed pinewood fibre (250 µm particle size) to prepare CTPS, WTPS respectively and 5 g each of the fiber and the precipitate for HTPS, and then 40 g glycerol was added; and the procedures used to prepare TPS were followed.

3.3 Characterization and Testing Methodology

Water Absorption, Fourier Transformed Infrared Spectroscopy, Dynamic Mechanical Analysis, Thermogravimetric Analysis, Differential Scanning Calorimetry, X-ray Diffraction, Scanning Electron Microscope, Tensile properties and Hardness Test were used to test, characterize, and analyze the physical and chemical properties of the prepared samples.

4 Result and Discussion

4.1 Crosslinking of Starch Using Citric Acid

Starch film samples prepared using different techniques and reagents were characterized for their water absorption, surface morphology, thermal and mechanical property, and structural change. Samples 3CTPS, NCTPS and HCTPS are prepared at 3, 6, and 12 pH respectively, to assess the effect of pH on crosslinking potential. Crosslinking was found better on NCTPS and 3CTPS, but lower on HCTPS. This shows that crosslinking/esterification reaction in citric acid, glycerin and starch is better achieved at about 6 pH. Samples NCTPS and CCTPS were prepared to evaluate the effect of curing on crosslinking potential. CCTPS is sample NCTPS cured at 165^oC for 10 minutes. Result has indicated that NCTPS is better crosslinked than CCTPS. ACTPS was prepared in a new and innovative method to crosslink the surface of the TPS film immersing it into a solution of citric acid and alcohol at about 70^oC; no significant change in properties compared to the controlled TPS sample are observed. CTPS, and CS are prepared to assess the effect of glycerin on the degree of crosslinking. Results showed that the availability of glycerin is a critical factor for the crosslinking and plasticity property of the film. CS samples were brittle and easily disintegrated in water as crystals. Generally, citric acid has increased the water resistance (fig.4.1) of starch crosslinking the chains of starch molecules reducing the amount of hydroxyl group.

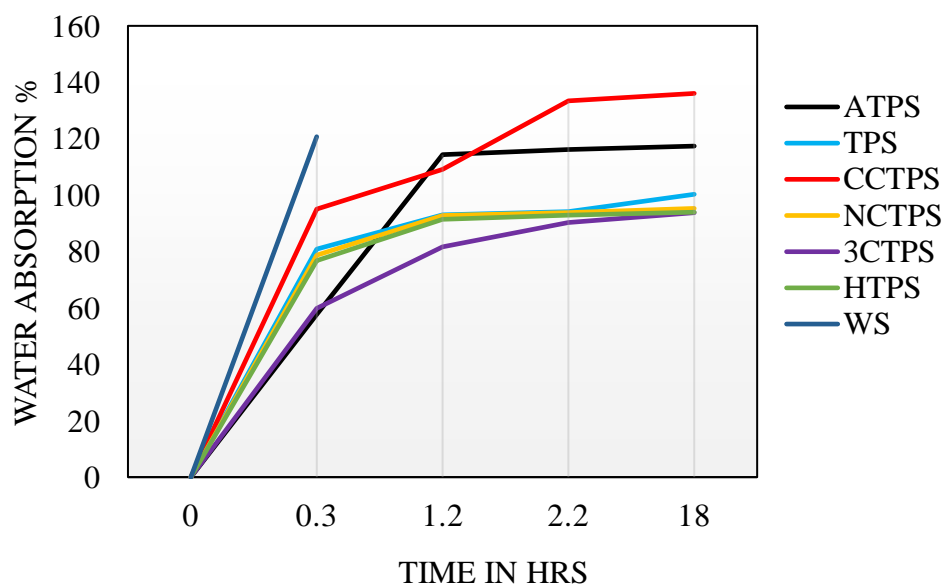


Figure 4. 1 Water Absorption Test Result

4.2 A Comparative Study of Carboxylic Acids on the Cross-Linking Potential of Corn Starch Films

This experimental work is intended to produce starch film samples cross-linked with tartaric, oxalic, and citric acid and correlate the structure and property of carboxylic acids to the cross-linking potential and property of starch polymer films used for non-food applications. In this experiment, 8 g of native corn starch was added to 200 g distilled water. 2.88 g glycerol was then added to the slurry to prepare TPS, consequently, 1.6 g tartaric, citric and oxalic acids were added as crosslinking agents to prepare samples TaTPS, CTPS and OTPS respectively.

The new peaks on the FTIR spectrum fig. 4.2 at 1728 cm^{-1} , 1725 cm^{-1} , and 1738 cm^{-1} for samples prepared with citric, oxalic, and tartaric acids, respectively, indicates that a reaction has occurred between the acids and starch. The X-ray analysis fig. 4.3 exhibited a decrease in the number and intensity of diffraction peaks in the modified starch due to the esterification reaction that destroys the crystalline nature of starch and forms an entangled chain of amorphous structure. The relative degree of crystallinity determined from the XRD diffractograms table 4.1 also proves that citric acid has reduced the crystallinity of native corn starch from 36.62% to 27.44%. Citric acid cross-linked starch has significantly improved the strain (112.66 %) and tensile strength (3.95 MPa) of starch compared to TPS, TaTPS, and OTPS (see table 4.2). Comparing the water absorption rate of TPS, which is about 140%, with that of CTPS and TaTPS, which is about 60%, as shown in fig. 4.4, determines that there is a significant improvement in the water resistance of starch by cross-linking using citric acid and tartaric acid.

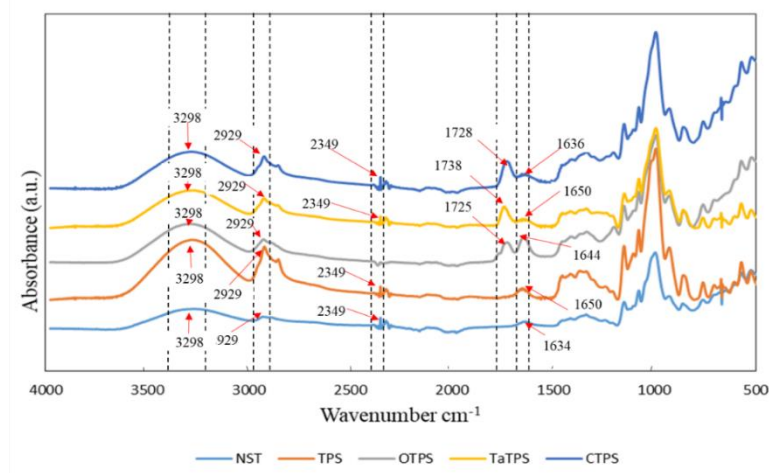


Figure 4. 2 FTIR Spectrum of Samples

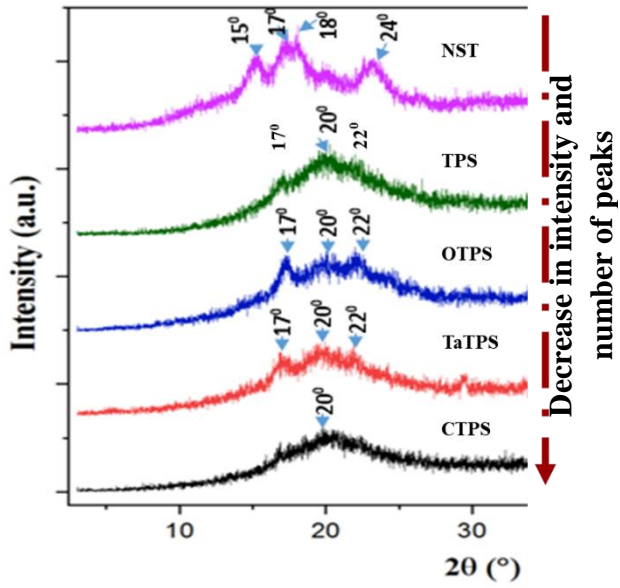


Table 4. 1 Degree of crystallinity of samples

| Samples | NST | TPS | CTPS | TaTPS | OTPS |
|-----------------------------|------|------|------|-------|------|
| Degree of Crystallinity (%) | 36.6 | 31.4 | 27.4 | 29.6 | 30.9 |

Figure 4. 3 X-Ray Diffractograms of Modified Starches

Table 4. 2 Tensile Test Result of Samples

| Samples | Maximum Tensile Stress (MPa) | Maximum Tensile Strain (%) |
|---------|------------------------------|----------------------------|
| TPS | 2.39 ± 1.3 | 108.6 ± 7.6 |
| OTPS | 3.05 ± 0.9 | 58.5 ± 6.5 |
| TaTPS | 3.36 ± 1.2 | 89.3 ± 9.3 |
| CTPS | 3.95 ± 0.9 | 112.6 ± 11.1 |

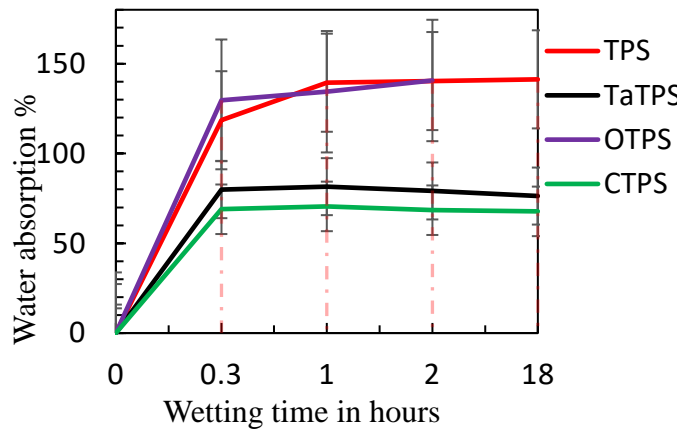


Figure 4. 4 Water Absorption Test Results

4.3 Effects of Acidity, Number of Hydroxyl Group, and Carbon Chain Length of Carboxylic Acids on Starch Cross-Linking

This experimental work is envisioned evaluate the effects of acidity, number of hydroxyl group, and carbon chain length modifying agents on starch cross-linking.

In this experiment, 8 g of native corn starch was added to 200 g distilled water. And then 2.88 g glycerol was added to the slurry to prepare TPS; consequently, 1.6 g succinic, malonic and malic acids were added as crosslinking agents to prepare samples STPS, MoTPS and MaTPS respectively. Starch film samples prepared using carboxylic acids, namely malonic acid, malic acid, and succinic acid as cross-linker, and glycerol and water as plasticizers were characterized and tested.

Test results revealed formation of ester as a result of cross-linking. Crosslinked samples were found to be less viscous. There is a high degree of cross-linking with malic acid as a cross-linking agent, followed by succinic and malonic acid. Peaks 1717 cm^{-1} , 1712 cm^{-1} , and 1718 cm^{-1} in fig. 4.5 show C=O stretching vibration [19, 20] caused by ester formation as a result of cross-linking. The absence of such peaks in the TPS sample indicates that the cross-linking is primarily caused by the reaction between starch and the crosslinking acids [21]. Because of an increase in the number of ester bonds in malic and malonic acid cross-linked starch, the normalized intensity of the spectral peaks is seen to be higher than in succinic acid cross-linked starch and non-crosslinked TPS. When reacted with succinic acid, the less water solubility of succinic acid may have played a significant role in the reduction of ester bonds in the starch structure. Table 4.8 shows that the maximum tensile stress and maximum tensile strain of TPS are 2.4% and 108.6%, respectively, and that it has a relatively low tensile strain and tensile stress compared to the other samples. It could be because thermoplastic starch contains a higher concentration of hydrogen bonds and more crystalline structure. The maximum tensile strain, also known as elongation at break, of succinic, malonic, and malic acid cross-linked starch was measured to be 119.9%, 140.9%, and 175.7%, respectively see table 4.8, which is a significant improvement over TPS. This result is consistent with the findings of other similar studies [22, 23]. The increase in tensile strain is due to the change of starch from semi-crystalline structure to amorphous structure due to cross-linking (ester linkage formation). The maximum water absorption capacity of TPS, MoTPS, and STPS is found to be around 140%, and the water absorption capacity of MaTPS is 80% as shown in figure; this shows a considerable improvement in the water resistance of starch when cross-linked using malic acid. The cross-linked samples' tensile strength has increased compared to TPS, which is directly related to the

transition of starch granules from semi-crystalline to an entangled amorphous structure with increased number of crosslinking bridges.

Even though malonic acid is 16 percent more acidic and 36 percent more soluble than malic acid, the presence of one more hydroxyl functional group in malic acid has a greater influence on cross-linking. Increased carbon chain length on succinic acid has a negative effect on cross-linking reaction, which could be attributed to its effect on acidity and solubility reduction. An increase in the number of hydroxyl groups and acidity promoted cross-linking starch on the respective orders, whereas an increase in the carbon chain length has affected cross-linking negatively.

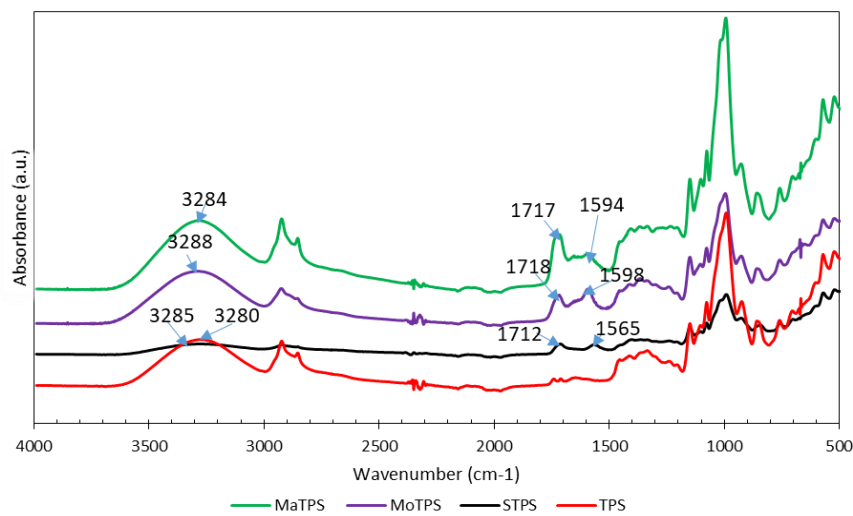


Figure 4. 5 FTIR Spectrum of samples

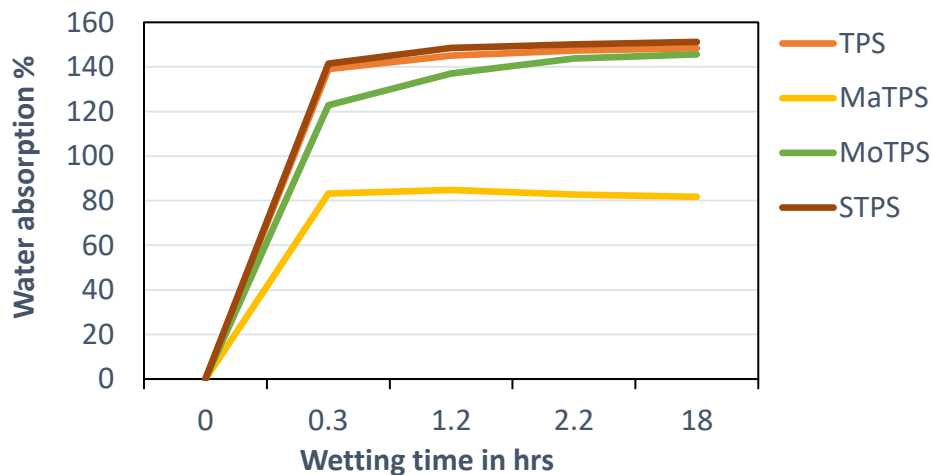


Figure 4. 6 Water absorption test results

Table 4. 3 Tensile Test Result of Samples

| Samples | Maximum Tensile Stress (MPa) | Maximum Tensile Strain (%) |
|--------------|------------------------------|----------------------------|
| TPS | 2.4 ± 1.3 | 108.6 ± 7.7 |
| MoTPS | 7.4 ± 1.4 | 140.9 ± 8.8 |
| MaTPS | 4.8 ± 0.5 | 175.7 ± 9.5 |
| STPS | 2.5 ± 0.2 | 119.9 ± 5.2 |

4.4 Cross-linking of Starch Using Terephthalic acid and Pyromellitic dianhydride

Corn starch was modified using terephthalic and Pyromellitic acids. The reaction was performed under 3, 5, 7, and 11 pH. The ratio of the modifying acids was varied from 5%, 10% and 20% (W/W) of corn starch.

Strong FTIR peaks were observed at 1728 cm^{-1} , 1725 cm^{-1} , and 1738 cm^{-1} in the PTPS samples unlike for the TeTPS samples which indicates the formation of ester bonds with pyromellitic dianhydride modified starch.

Thermogravimetric plots fig. 4.7 indicates that unlike TPS and TeTPS, the thermograms obtained from PTPS samples show similarities up to a temperature of 250°C . TPS and TeTPS films exhibited four degradation steps, but the PTPS modified samples are degraded at three distinct steps. The first degradation step for TPS is $50\text{-}100^{\circ}\text{C}$, which is the evaporation water. This step is also happening in TeTPS with a very slight difference. The second degradation step for PTPS (third for TPS and TeTPS) occurs from $280\text{-}340^{\circ}\text{C}$ representing the decomposition of starch. Beyond this temperature the PTPS samples show a very slow (inclined curve) decrease in weight which is a sign of stability. The TeTPS samples show almost similar (vertical curve) pattern with TPS till about 340°C . Fig. 4.7 C show that PTPS11 a sample prepared at pH of 11, has less stability than PTPS 3 and PTPS 5. This indicates that the crosslinking reaction can produce stable crosslinked polymers at higher pH.

The maximum water absorption rate (fig. 4.8) of the TeTPS samples exceeds 150% whereas for PTPS samples is still below 150%. Unlike TeTPS, the tensile strength of property of PTPS shown in table 4.4 is improved to 5.4 MPa which is huge improvement compared 2.39 MPa of TPS .

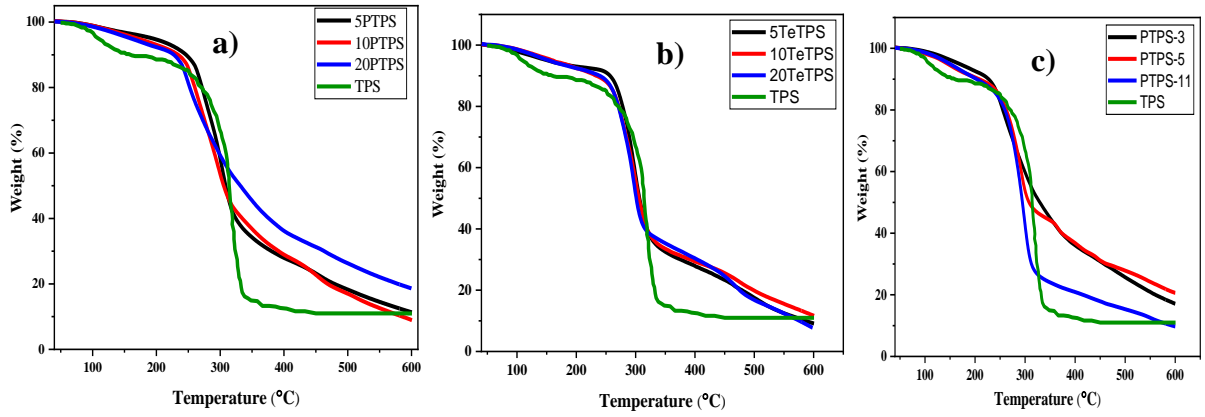


Figure 4. 7 TGA Thermographs of the Samples

Table 4. 4 Tensile Test Result of Samples

| Samples | Maximum Tensile Stress | Maximum Tensile Strain |
|---------|------------------------|------------------------|
| | (MPa) | (%) |
| TPS | 2.4 ± 1.3 | 108.6 ± 7.6 |
| 5PTPS | 5.4 ± 0.2 | 80.2 ± 9.8 |
| 5TeTPS | 2.0 ± 0.1 | 71.5 ± 3.8 |
| 10PTPS | 3.5 ± 0.4 | 97.8 ± 6.6 |
| 10TeTPS | 2.3 ± 0.5 | 87.7 ± 9.5 |
| 20PTPS | 3.1 ± 0.3 | 66.4 ± 4.5 |
| 20TeTPS | 1.9 ± 0.3 | 67.3 ± 3.9 |

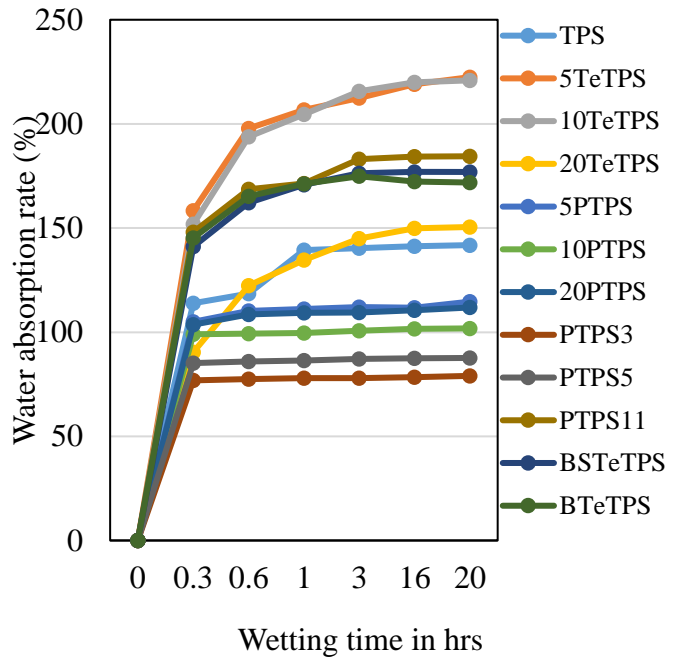


Figure 4. 8 Water Absorption Rate of Samples

4.4 Thermoplastic Corn Starch Reinforced with Pinewood Fibre and Calcium Carbonate Precipitate Filler

TPS composites reinforced by pinewood fibre (WTPS) and calcium carbonate precipitate (CTPS) and hybrid (HTPS) were prepared by compression moulding.

The DSC test result of all the samples is depicted in fig. 4.9 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 relaxation 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 relaxation of TPS. Fig. 4.9 also shows that the thermogram for TPS is smoother than the other composites that major changes on melting point are not observed when compared with CTPS and WTPS.

WTPS reveals greater strength of 1.02 MPa which is a huge improvement compared to TPS, HTPS and CTPS (see fig. 4.10). Free TPS possesses a tensile strain of 70.8% which is better compared to the other composite samples and decreases with the addition of wood fibre and/or filler. The hybrid composite HTPS has greater hardness of 41 kg/mm² (fig. 11) followed by wood reinforced TPS. This could be attributed to the better interfacial adhesion of the TPS matrix with pinewood fibre. HTPS exhibits a maximum water absorption rate of less 90% followed by WTPS as shown in fig. 4.12 which is comparably better than TPS. This indicates that reinforcing TPS with calcium carbonate filler improves the water absorption resistance of thermoplastic starch.

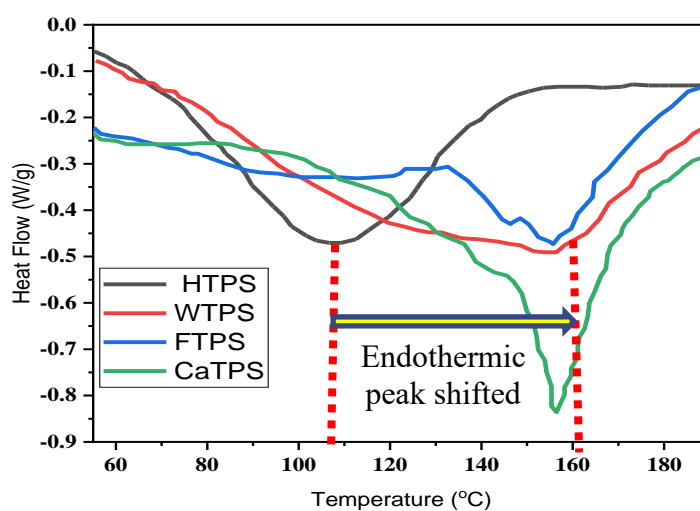


Figure 4. 9 DSC Thermogram of Composite Samples

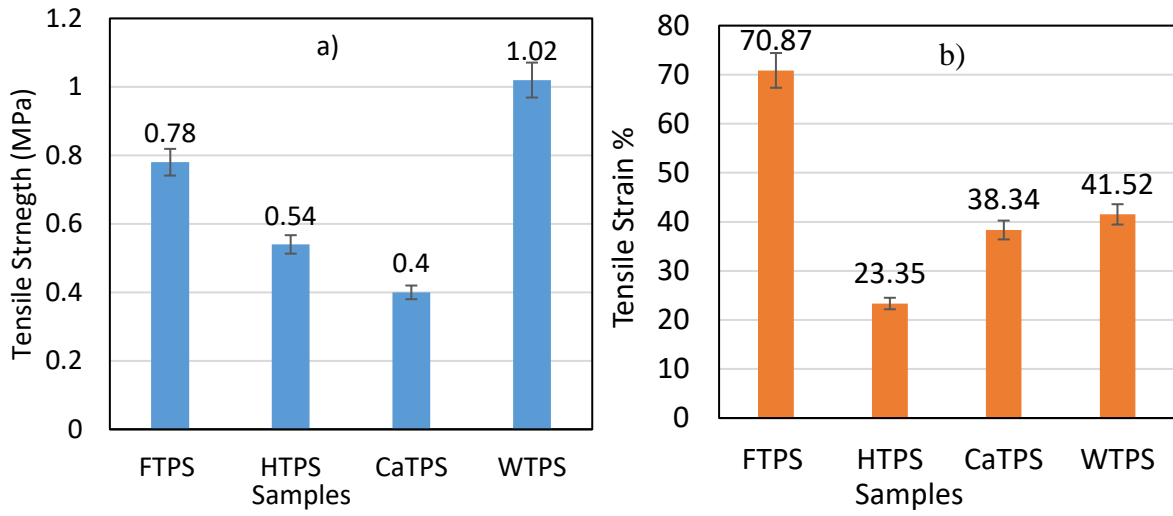


Figure 4. 10 a) Tensile Strength Test b) Tensile Strain Test Result of Composite Samples

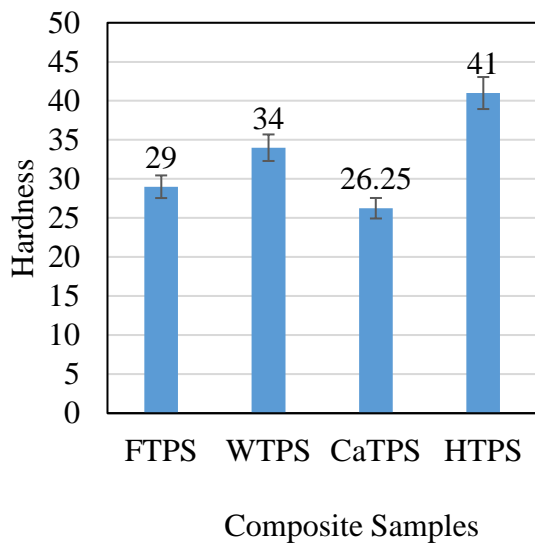


Figure 4. 11 Shore Hardness Test Result

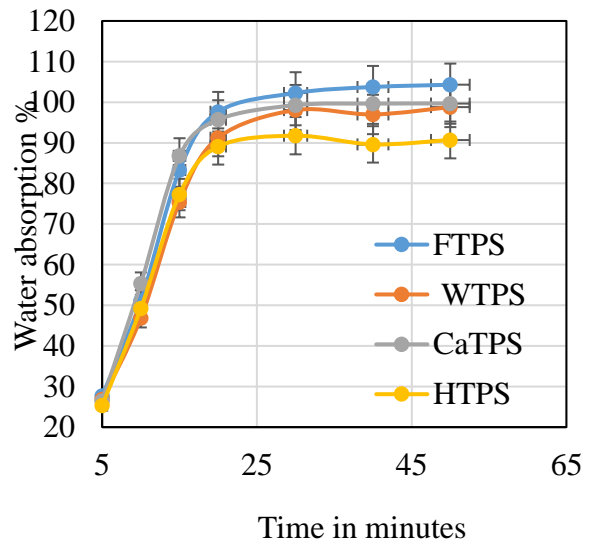


Figure 4. 12 Water Absorption Result

4.4 Tartaric Acid Crosslinked Hybrid Starch Composites

Starch film samples prepared using tartaric acid as cross-linker (TaS), sodium montmorillonite clay (TaMcS), termite clay (iron rich kaolinite) (TaTcS) as fillers, cellulosic natural fiber (enset fiber) (TaFS) as reinforcement; and glycerol and water as plasticizers were characterized and tested. Formation of new peak at 1742 cm^{-1} on the FTIR spectrum for the samples prepared under the addition of tartaric acid indicated that crosslinking reaction has occurred between tartaric acid and starch.

The maximum tensile stress and elongation at break table 4.5 of tartaric acid crosslinked starch and TPS samples were found to be 4.4 MPa and 73.51%; and 2.29 MPa and 118% respectively. The elongation at break of TaS has reduced by half compared to TPS while the tensile strength is almost doubled. TaS and TaMcS have maximum water absorption rate of about 85% and 100% respectively (fig. 13) which a huge improvement compared to TPS and TaTcS which is 140% and 160% respectively.

Thus, the tartaric acid crosslinked starch has got better water resistance, and tensile strength than TPS, which is considered good property for packaging materials. Addition of clay fillers didn't significantly improve the water resistivity due to coagulation. Reinforcing of starch with cellulosic natural fibers has also negatively influenced the water resistivity even if it has significantly improved the strength.

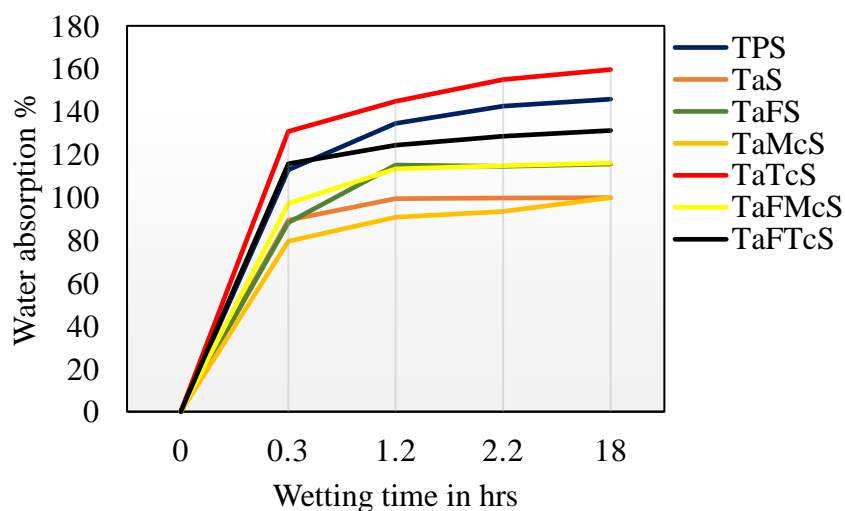


Figure 4. 13 Water Absorption Test Result

Table 4. 5 Tensile Test Result of Samples

| Samples | Maximum | Maximum |
|---------|----------------|------------------|
| | Tensile stress | Tensile strain |
| | (MPa) | (%) |
| TaMcS | 3.9 ± 0.5 | 50.5 ± 5.2 |
| TaFS | 2.6 ± 0.3 | 45.6 ± 3.9 |
| TaFMcS | 2.3 ± 0.2 | 36.6 ± 4.2 |
| TaS | 3.4 ± 0.3 | 73.5 ± 5.6 |
| TaFTcS | 3.2 ± 0.4 | 37.1 ± 5.8 |
| TaTcS | 3.1 ± 0.2 | 64.5 ± 9.3 |
| TPS | 2.3 ± 0.5 | 117.8 ± 10.2 |

5 The Most Important Observations of the Work

Thesis 1

We have effectively produced cross-linked corn starch polymer thin film using carboxylic acids as a cross-linker optimizing the process parameters. We investigated that availability of plasticizer is a critical factor for the cross-linking reaction and the plasticity property of the thin polymer film. We examined that the addition of sodium hydroxide before the addition of acids helped the swelling of the starch. The swelling happens due to breakdown of the intermolecular hydrogen bonds and the formation of new hydrogen bonds with water to form a larger, open structure. Alkali helps the de-bonding process by chain scissoring and helps the formation of new bonds within adjacent chains at the same time. This type of bond formation could help to improve the tensile properties of the materials

The appearance of new absorbance peaks on the FTIR spectrum for ester functional group; the decrease in number and intensity of the diffraction peaks on the X-Ray diffractograms and degree of crystallinity, including water absorption have proved that crosslinking has occurred.

Thesis 2

Number of OH group per molecule, Acidity and carbon chain length (CH₂) of carboxylic acids were investigated for their effects on crosslinking potential of thermoplastic starch. We investigated that the presence of an additional OH group in the carboxylic acids has helped form more hydrogen bonding between starch molecules. Acidity of the carboxylic acids is found to be a factor for better cross-linking potential. The increase in carbon chain length (CH₂); has negatively affected its cross-linking potential. Thus, among the three variables studied, we investigated that increase in the number of hydroxyl groups and acidity promoted cross-linking of starch on the respective orders, whereas increase in the carbon chain length has affected cross-linking negatively.

Thesis 3

Effects of number of carboxyl and hydroxyl functional groups; and solubility and other properties of carboxylic acids for crosslinking corn starch were examined. We investigated that the number of carboxyl functional groups in the carboxylic acids was found to have a more significant cross-linking impact. This could be because carboxyl groups can form stronger ester bonds with the hydroxyl groups of starch; than the hydrogen bonds that the hydroxyl groups can. Consequently, CTPS outperforms TaTPS, OTPS, and TPS in properties such as water resistance, tensile strength, and dimensional stability. The improved property of TaTPS over OTPS is also due to the increased number of hydroxyl groups in tartaric acid than oxalic acid.

Thesis 4

Corn Starch film samples prepared using tartaric acid as cross-linker, sodium montmorillonite clay, termite clay (iron rich kaolinite) as fillers, cellulosic natural fiber (inset fiber) as reinforcement; and glycerol and water as plasticizers were characterized and tested. Both chemical and physical modification (crosslinking and reinforcing) techniques were used simultaneously. We explored that the inclusion of fillers don't hinder the crosslinking reaction. Tartaric acid can effectively crosslink corn starch even in the presence of fillers and improve the mechanical and water resistance property. Reinforcing of starch with cellulosic natural fibers and clay has significantly improved the strength and water absorption resistance

Thesis 5

We prepared thin sheets of composite corn starch samples reinforced with pinewood fibre and calcium carbonate precipitate under a compression pressure and heating using a compression moulding machine. We investigated that the reinforcing starch using pinewood fibre provides better strength than reinforcing it with calcium carbonate precipitate and the hybrid composite. We also demonstrated that the hybrid composite has greater hardness and water absorption resistance followed by WTPS. This could be attributed to the better interfacial adhesion of the TPS matrix with pinewood fibre reinforcement. Moreover, we verified that WTPS exhibits better results in most of the measured properties given that TPS and wood fibre being both hydrophilic resulting in a homogeneous distribution and better interfacial adhesion.

Thesis 6

Corn starch was modified using terephthalic acid and Pyromellitic acid dianhydride under varying pH and ratio. We observed that unlike terephthalic acid; the Pyromellitic acid dianhydride has crosslinked corn starch. This could be due to the less number of carboxylic group per molecule and the very limited solubility of terephthalic acids compared to Pyromellitic acid dianhydride. As a result, the mechanical, water resistance and thermal property of the Pyromellitic acid crosslinked corn starch (PTPS) is significantly improved compared to TPS and TeTPS.

6 List of Publications

Journal Papers

1. Gerezgiher Alula Gebresas, Tamás Szabó, Kálmán Marossy, A comparative study of carboxylic acids on the cross-linking potential of corn starch films, *Journal of Molecular Structure*, Volume 1277, 2023, 134886, ISSN 0022-2860, <https://doi.org/10.1016/j.molstruc.2022.134886>.
2. Gerezgiher Alula Gebresas, Tamás Szabó, Kálmán Marossy, Effects of acidity, number of hydroxyl group, and carbon chain length of carboxylic acids on starch cross-linking, *Current Research in Green and Sustainable Chemistry*, Volume 6, 2023, 100354, ISSN 2666-0865, <https://doi.org/10.1016/j.crgsc.2022.100354>.
3. Gerezgiher Alula Gebresas, Tamas Szabó, Crosslinking of Starch Using Citric Acid. *IOP Conference Series: Materials Science and Engineering*, (2022, July). In *Journal of Physics: Conference Series* (Vol. 2315, No. 1, p. 012036). IOP Publishing <https://doi.org/10.1088/17426596/2315/1/012036>
4. Gerezgiher, A. G., Tamási, K., Ibrahim, J. F. M., Kónya, C., & Szabó, T. (2020, April). Thermoplastic corn starch reinforced with pine wood fibre and calcium carbonate precipitate filler. In *Journal of Physics: Conference Series* (Vol. 1527, No. 1, p. 012042). IOP Publishing. <https://doi.org/10.1088/1742-6596/1527/1/012042>
5. T.B. Yallem, E. Kassegn, S. Aregawi, A. Gebresas (2020, February). Study on effect of process parameters on tensile properties of compression molded natural fiber reinforced polymer composites. *SN Applied Sciences* (Vol. 2, No. 3, pages 1-8). Springer Nature Switzerland AG. <https://doi.org/10.1007/s42452-020-2101-0>
6. AG Gerezgiher, HA Bsrat, A Simon, T Szabó, (2019 March). Development and characterization of sisal fiber reinforced polypropylene composite materials. *International Journal of Engineering and Management Sciences* (Vo.4, No.1, p.348-358). University of Debrecen Publishing Platform. <https://doi.org/10.21791/IJEMS.2019.1.43>.

Oral and Poster Presentation

1. Gerezgiher Alula Gebresas, Bsrat Halefom Aregay, Simon Andrea, Szabó Tamás, Development and characterization of sisal fiber reinforced polypropylene composite material for car door interior trim panel application, International Scientific Conference on Advances in Mechanical Engineering (ISCAME 2018), Debrecen, Hungary, 10/12/2018
2. Gerezgiher, Alula Gebresas, Flammability and chemical resistance of sisal fiber reinforced waste polypropylene composites, Antal Kerpely Doctoral School of Materials Science & Technology PhD forum, Miskolc, Hungary, 11/22/2018
3. Gerezgiher Alula Gebresas and Tamas Szabo, Property of Thermoplastic Corn Starch Reinforced With Natural Fiber and Filled With Calcium Carbonate Precipitate, International Scientific Conference on Advances in Mechanical Engineering, Debrecen, Hungary 7-9 Nov.2019
4. Gerezgiher Alula Gebresas and Tamas Szabo, Development and Characterization of Hybrid Biodegradable Polymer Composites, (ic-rmm4) 4th International Conference on Rheology and Modeling of Materials, Miskolc, Hungary, 7-10 Oct. 2019
5. AG Gerezgiher, K Tamási, JFM Ibrahim, C Kónya, T Szabó, Thermoplastic corn starch reinforced with pine wood fibre and calcium carbonate precipitate filler, Journal of Physics: IOP Conference Series (Vol. 1527, No. 1.), 1/20/2020, p. 012042
6. Gerezgiher Alula Gebresas and Tamas Szabo, Improving the Water Resistivity of Starch by Using Plasticization and Crosslinking as Modification Techniques, 9th Interdisciplinary Doctoral Conference (IDK2020), University of Pécs, Hungary, 27-28th of November 2020
7. Gerezgiher Alula Gebresas and Tamas Szabo, Modification of corn starch for improving the physical and mechanical properties for packaging purpose, Materials science day of PhD students, University of Panonia. 16, November, 2020
8. Gerezgiher Alula Gebresas, Tamas Szabo, Cross-Linking of Thermoplastic Starch For Improving Its Water Resistance And Physical Properties, MAS 14th International European Conference On Mathematics, Engineering, Natural and Medical Sciences, Széchenyi István University, Hungary, 3/26/2021
9. Gerezgiher Alula Gebresas, Tamas Tsabo, Modification of biodegradable Thermoplastic Corn starch for use in packaging, ic-cmtp6 the 6th International Conference on Competitive Materials and Technology Processes, Miskolc, Hungary, Oct/04/2021
10. Gerezgiher Alula Gebresas, TAMAS Szabo, Crosslinking of starch using citric acid, IOP conference series, Materials Science and Engineering, 3/3/2022

11. Gerezgiher Alula Gebresas, TAMAS Szabo, Crosslinking of starch using citric acid, International Scientific Research Conference, Van University, Turkey, 3/27/2022
12. Gerezgiher Alula Gebresas, TAMAS Szabo, Fabrication and Characterization of Corn Starch Films Modified by Acid Crosslinking, International Istanbul Congress, Istanbul, Turkey, 3/17/2022

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