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THERMOPLASTIC STARCH BASED POLYMER BLENDS: SYNTHESIS, CHARACTERISATION AND ANALYSIS OF STABILITY

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ABSTRACT

In the present work, thermoplastic starch from cassava starch was grafted with epoxy derived from castor oil polyol. Fresh starch, prepared from cassava root tuber was polymerised and blended with epoxy in different compositions leading to variations in properties. The synthesized polymer blends could be filled or reinforced with nano-silica for effective functionality by eco-friendly means. The synthesized blends were characterized using FT-IR, Scanning Electron Microscope, EDAX and the water uptake percentage and soil bio-degradability were studied. Further, mechanical and thermal stability of the blends were characterised. With further developments, these starch-based nanocomposites can be expected to replace conventional polymers for variety of applications.

Keywords: Polymer Blends, Soil Bio-Degradbility, Cassava Starch, Water Uptake Percentage

1. INTRODUCTION

In today's world, the utilization of nonbiodegradable and petrochemical-based plastic packaging materials has been a major environmental concern due to their poor biodegradability1. According to the literature, 200 million tons of non-biodegradable plastics (approximate) per year are produced all over the world2. Therefore, the interest toward the utilization of biodegradable materials has been more intense during the last few decades. Biodegradable polymers can be classified into two categories: artificially produced biodegradable polymers and natural biopolymers. Synthetic biodegradable polymers such as aliphatic polyesters, polyhydroxy alkenoates (PHAs), and polyglycolic acid are derived from petroleum-based resources. However, natural polymers such as starch, cellulose, and proteins are produced from natural resources such as plants and animals3. Natural biopolymers have several advantages over synthetic biodegradable polymers such as sustainability, renewability, abundancy, and low price as they are natural products.

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Starch has been preferred over other biopolymers as it is easily available, cheap, and biodegradable4. Starch based nanocomposites have gained significant attention due to their biodegradable nature and potential applications in various fields and biomedical devices6. But the films composed entirely of starch lack in terms of mechanical properties5. Starch can be blended with other biopolymers or other synthetic polymers to produce fully biodegradable or partially degradable films with improved packaging properties. The incorporation of Nanoparticles like nano-silica enhances the mechanical and barrier properties of starch films6.For the preparation of completely/partially biodegradable film, starch can be blended with other biopolymers for effective functionality. Nano-silica enhanced the mechanical properties of starch based films and has increased the tensile strength by 54%7. Silica nano particles have low toxicity8. Also, they are biocompatible, optically transparent, stable, and, at the same time, exhibit high specific surface area and can be used in food packaging films to improve their heat sensitivity and mechanical strength9. Food packaging is the largest revenue share globally of plastic packaging materials and accounts for 30% of global plastic production10. Environment-friendly packaging materials are gaining interest in the food industry to reduce plastic pollution and ensure environmental protection from plastic pollution11, 12. The shifting of consumers' desires for healthier, safer, and more convenient food items has prompted advancements in the development of natural food packaging materials13, 14.

2. MATERIALS AND METHODS

Cassava starch, Glacial acetic acid, epoxy (previously derived from castor oil polyol), Glycerol, Maleic anhydride, Double deionized water of analytical grade were used.

2.1. GRAFTING OF STARCH

Graft copolymerization of starch was done by taking water as solvent. Starch was soaked overnight at 30 °C in the solvent to swell and to activate reactive sites on the surface. Further, acetic acid was added drop wise into the reaction media and the concentration of acid was maintained. The reaction mixture was heated at 50 °C for 150 min with continuous stirring. Grafted copolymers of starch were extracted with ethanol using a vacuum distillatory set to remove any soluble impurities or unreacted chemicals. The sample was dried in a hot air oven at 50 °C for 24 h and stored at room temperature in an airtight container.

2.2. PREPARATION OF EPOXY-TPS BLENDS

Previously synthesized epoxy and TPS are heated to their respective melting points and the molten state polymers are mixed with constant stirring with compatibilizer maleic anhydride. The reaction begins when the hydroxyl group (-OH) from the starch backbone of TPS, which is nucleophilic in nature, attacks one of the carbonyl carbons in the cyclic anhydride ring of maleic anhydride. This attack opens the anhydride ring, creating a carboxylic acid group and an ester bond. It then reacts with the epoxy to form a polymer blend.

$$\mathbf{TPS\text{-}OH + C_2H_2\,(CO)_2\,O \longrightarrow TPS{-}OCO{-}CH{=}CH{-}COOH}$$

$$\mathbf{TPS{-}OCO{-}CH{=}CH{-}COOH + Epoxy \longrightarrow Epoxy\text{-}TPS\ blend}$$

2.3. SHEET PREPARATION

Melt mixed polymers were mould casted in a clean mould free of moisture, dust and other impurities. The cast was rested for a day and then subjected to slow heating in a drying oven until complete cure. The cured blends were subjected to characterisation studies.

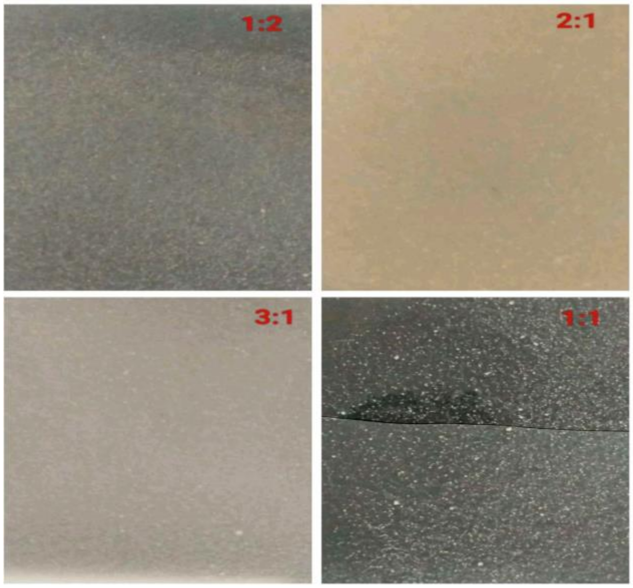

Figure 1 Epoxy-TPS bends

Epoxy-TPS blends (Epoxy: TPS)	Composition
1:2	1 part of epoxy with 2 parts of TPS
2:1	2 parts of epoxy with 1 part of TPS
3:1	3 parts of epoxy with 1 part of TPS
1:1	Equal parts of epoxy and TPS

Table 1 Compositions of Epoxy-TPS blends

3. RESULTS AND DISCUSSION

3.1. FT-IR SPECTRAL ANALYSIS

Starch and TPS was characterized using PerkinElmer Fourier transform infrared (FT- IR) spectrophotometer in the range from 4000 cm-1 to 400 cm-1. The similar peaks show the ideal nature of starch in both the graphs. The new prominent peaks indicate the formation of plasticized moieties effectively.

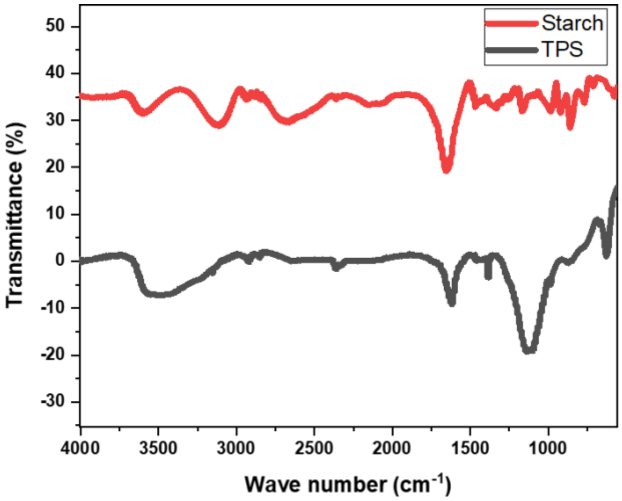

Figure 2 FT-IR analysis of Starch & TPS

In the above spectrum, the broad peak around 3500 cm^{-1} is due to O–H stretching within the molecules of starch and TPS. The peaks at around 2800 cm^{-1} correspond to C–H stretching vibrations. Peak at 1650 cm^{-1} is due to H–O–H bending vibrations in the molecule. Peak at around 1400 cm^{-1} corresponds to the C–H Bending vibrations. Overall, the FT-IR spectrum of starch shows higher intensities for peaks associated with the ordered structure (C–O stretching and O–H bonds). TPS shows reduced intensities for these peaks, indicating the conversion of ordered regions into a plasticized phase. These modifications improve the flexibility and processability of TPS.

3.2. SCANNING ELECTRON MICROSCOPY

Starch and TPS were characterized using SEM. Tungsten filament coated with zirconium dioxide layer was used as an electron source.

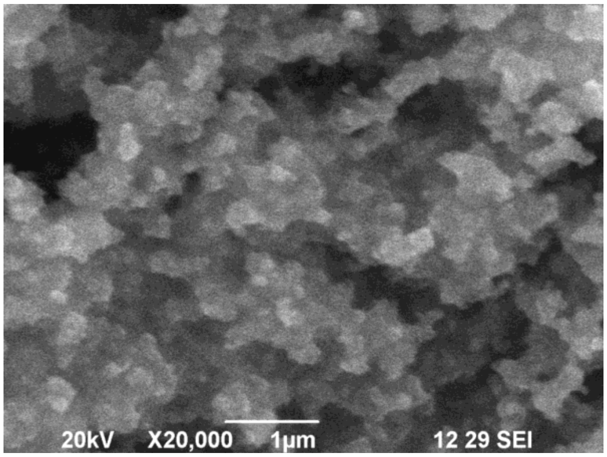

Figure 3 SEM image of Starch

Figure 4 SEM image of TPS

This SEM image illustrates the successful transformation of native starch into TPS, with a homogeneous, non-porous, and smooth microstructure. Such a structure is indicative of good plasticization, which is critical for developing biodegradable materials with enhanced flexibility and durability.

3.3. EDAX STUDIES

EDAX of TPS showed the elemental composition of it. It merely comprised of C&O.

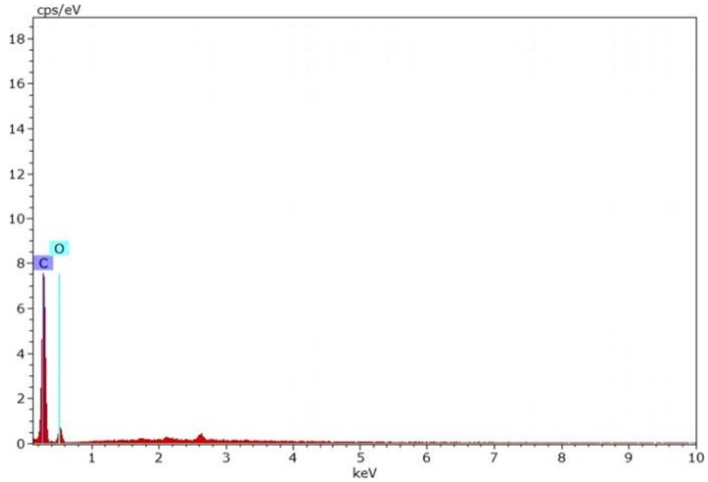

Figure 5 EDAX of TPS

Element	Atomic Percentage (%)	Atomic Weight Percentage (%)
C	81.71	77.03
O	18.29	22.97

Table 2 Elemental composition of TPS

3.4. WATER UPTAKE (%)

Sample Type	Water Uptake Percentage (%)
Pure Starch	45
Starch + 1% Nano Silica	35
Starch + 5% Nano Silica	30
Starch + 10% Nano Silica	25
Starch + 15% Nano Silica	20

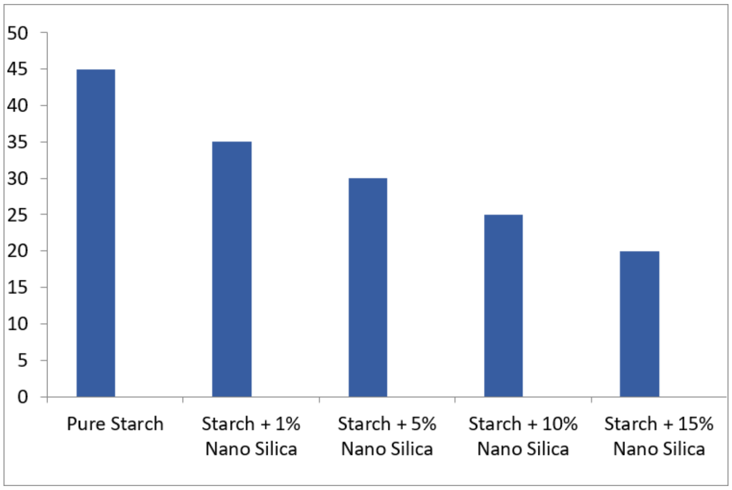

Figure 6 Water Uptake % graph

As the concentration of nano-silica increases in the composite, the water uptake percentage decreases. Pure starch shows the highest water uptake, indicating that the addition of nano silica reduces the material's hydrophilicity. Starch has a high affinity for water due to its hydroxyl groups, which leads to significant water absorption. The incorporation of nano silica creates a more complex network, reducing the overall hydrophilicity. This can lead to reduced water uptake as the silica particles may fill voids and create a barrier to water penetration.

3.5. SOIL BIODEGRADABILITY

Soil biodegradability refers to the breakdown of materials in soil through the action of microorganisms, fungi, and other soil organisms. Starch-based materials are known for their biodegradability, but the presence of nano-silica can influence the degradation rate. The presence and activity level of microorganisms in the soil affect degradation rates. Temperature, moisture, and pH can significantly impact the biodegradation process. The ratio of starch to nano silica also determines how quickly the material breaks down.

Sample Type	**Weight Loss %**		
	Day 0	**Day 15**	**Day 30**
Pure Starch	100	78	55
Starch + 1% Nano Silica	100	70	50
Starch + 5% Nano Silica	100	65	40
Starch + 10% Nano Silica	100	60	30
Starch + 15% Nano Silica	100	55	25

3.6. MECHANICAL PROPERTIES

Composition (epoxy-TPS)	**Tensile strength (MPa)**	**Elastic Modulus (GPa)**	**Brinell Hardness Number (kg/mm²)**	**Compressive strength (MPa)**
1:2	35	1.5	40.54	80
2:1	54	1.75	51.64	96.4
1:1	47	1.69	46.75	90.35
3:1	63	2.1	55.79	100.25

Table 5 Mechanical Properties of epoxy-TPS blends

High TPS content leads to lower tensile strength, stiffness, hardness, and compressive strength. The weaker properties stem from the low rigidity of TPS and poor interfacial bonding with epoxy. High epoxy content provides the best mechanical properties. The dominance of epoxy ensures excellent load-bearing and surface resistance, although flexibility might be reduced.

3.7. TG-DTA

The curve of (3:1) shows higher residual weight at high temperatures, indicating greater thermal stability compared to other ratios. The curve of (1:2) has lower thermal stability, with faster degradation at lower temperatures. Multiple degradation stages may be evident, likely associated with the breakdown of TPS and the epoxy polymer. Higher Epoxy Content (3:1) shows improved thermal stability due to the stronger cross-linked structure of the epoxy network. Higher TPS Content (1:2) leads to lower thermal stability, as TPS degrades more readily due to its organic nature.

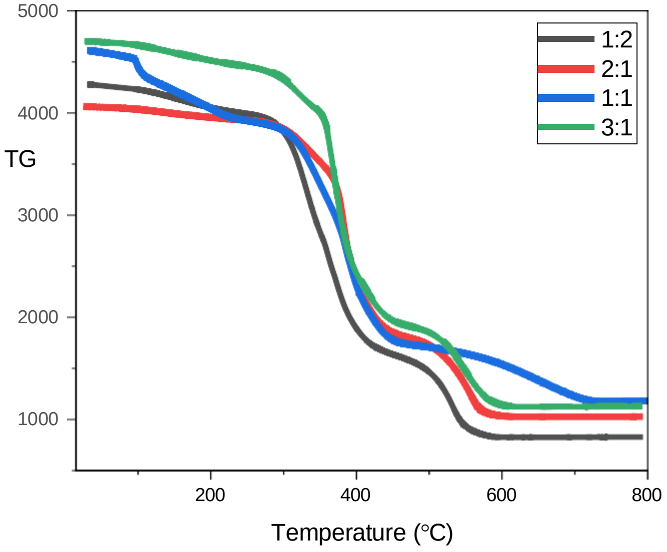

Figure 7 TGA of epoxy-TPS blends

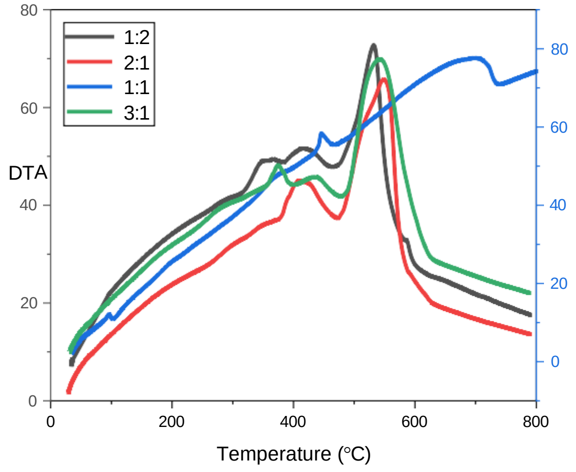

Figure 8 DTA of epoxy-TPS blends

4. CONCLUSION

The spectral studies have proved the formation of plasticized starch i.e., TPS effectively from starch. The SEM images have also confirmed the same by showing the clear surface morphologies of the former and latter. The elemental analysis shows the weight and atomic percentage of C&O in the lattices. The thermal stability can be observed to be comparatively high for blends with high epoxy content. The mechanical stability also depends on the epoxy in the matrix. Thus, it is clear that thermoplastic starch is a versatile polymer with good soil-biodegradability and water uptake percentage but in terms of mechanical and thermal stability it requires reinforcement which could be offered by blending with other polymers or by filling it with a nanoparticle.

CONFLICT OF INTERESTS

None.

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