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Thermoplastic Starch (TPS) Based Bio-disintegrable Polymers - Combination of Modified Potato Starch with Polyolefins

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Abstract: ***Research is striving for achieving a target of fully biodegradable polymer product and in that direction an effort has been made and presented in this paper. The combination of thermoplastic starch based natural polymers and typical in use synthetic polymers has been done to develop biodegradable polymeric materials. The first and foremost use of these materials could be in industry for packaging applications. The materials developed during study are Biodegradable plastics with varying characteristics. Different types of biodegradable polymer compositions were prepared using modified potato starch with different poly olefins through melt processing technique on laboratory scale. Efforts have been made to utilize various modifiers available as on date like Glycerol, Sorbitol and Urea introduce thermoplastic properties in starch then these processed thermoplastic starches were melt processed in Haake Rheocord with polyolefin's like LDPE, LLDPE, HDPE and PP. The system thus prepared has been characterized through methods available as on date. Water Absorption studies were also conducted on samples thus prepared and biodegradation through soil burial method was performed on laboratory scale. Observations were that modification of starch leads to an increase in the thermoplastic character in sample blends thus prepared along-with increased thermal stability in starch. During comparison study of different modifiers it was observed that GTPS blend gives better mechanical, thermal and chemical properties than STPS and UTPS blends. During Biodegradation study the observations were that biodegradability got enhanced with the increased % of TPS in blends. Since, starch concentration associates with the degradation through microorganism, higher concentration of TPS causes considerable compatibility between bacterial phase and chemical strength of plastic. Whereas, starch being less crystalline and hydrophilic in nature compared to LDPE, is more prone to microbial attack.***

Keywords: GTPS: Glycerol Thermoplastic Starch; STPS: Sorbitol Thermoplastic Starch; UTPS:Urea Thermoplastic Starch, iodegradable polymer; LDPE: Low Density Polyethylene; LLDPE: Linear Low Density Polyethylene; HDPE: High Density Polyethylene; PP: Poly propylene

1. Introduction

Demand is the fuel for development of innovative biopolymers materials all over the world. Researchers are striving for achieving the desired target of biodegradable polymer product. The advantages of synthetic polymers are obvious, including predictable properties, batch-to-batch uniformity and can be tailored easily [1]. But due their non degradation capability focus is shifted on to natural polymers, which are inherently biodegradable [2] and can provide the capabilities like synthetic polymers to meet different requirements. Starch is regenerated from carbon dioxide and water by photosynthesis in plants [3]. Owing to its complete biodegradability [4], low cost and renewability [5], starch is considered as a promising candidate for developing sustainable materials[6, 7]. Many efforts have been exerted to develop starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more applications [8–10]. In the present study different types of biodegradable polymer compositions were prepared using modified potato starch with different poly olefins through melt processing technique on laboratory scale using various modifiers like Glycerol, Sorbitol and Urea and conducted mechanical, thermal, chemical, water absorption and biodegradation studies on laboratory scale.

2. Experimental

Materials: The Native potato starch with 10.0% moisture (in powder form) Glycerol (in liquid form), Sorbitol (in powder form) and Urea (in powder form) was procured from M/s S. D. Fine Chemical Ltd. Pune, India. Low Density Polyethylene (LDPE), Linear Low Density Poly Ethylene (LLDPE), High Density Poly Ethylene (HDPE) and Polypropylene (PP) polyolefin's were procured from M/s Reliance Industries, India. MA-g LDPE, MA-g HDPE, MA-g-LLDPE and MA-g-PP were procured from M/s Pluss Polymer Pvt. Ltd. Faridabad, Haryana.

2.1 Sample Preparation

Modification of starch to prepare TPS using different plasticizers: Native potato starch and one of the plasticizers (glycerol, sorbitol and urea) were mixed in the ratio of 70:30 through grinding & shearing in a high speed mixer at 2500-3000rpm at room temperature for 3-5min., thereafter the starch was left for 24 hours in an airtight plastic bag at room temperature. Structural changes in starch have taken place with the contact of modifier.

Preparation of TPS & Polyolefin's blends: Different formulations of blends are prepared using Polyolefin's and different type of TPS (GTPS, STPS & UTPS). Samples contained 10% MA-g-PP as compatibilizer with

compositions of TPS (GTPS, UTPS, STPS) as shown in table 1.

Table 1: Sample Compositions

Sample Compositions: A									Sample Compositions: B								
LDPE -GTPS			LDPE-STPS			LPDE-UTPS			LLDPE -GTPS			LLDPE-STPS			LLPDE-UTPS		
Sample No.	LDPE %	GTPS %	Sample No.	LDPE %	STPS %	Sample No.	LDPE %	UTPS %	Sample No.	LLPDE %	GTPS %	Sample No.	LLDPE %	STPS %	Sample No.	LLPDE %	UTPS %
A-1	85	5	A-6	85	5	A-11	85	5	B-1	85	5	B-6	85	5	B-11	85	5
A-2	80	10	A-7	80	10	A-12	80	10	B-2	80	10	B-7	80	10	B-12	80	10
A-3	75	15	A-8	75	15	A-13	75	15	B-3	75	15	B-8	75	15	B-13	75	15
A-4	70	20	A-9	70	20	A-14	70	20	B-4	70	20	B-9	70	20	B-14	70	20
A-5	65	25	A-10	65	25	A-15	65	25	B-5	65	25	B-10	65	25	B-15	65	25
Sample Compositions: C									Sample Compositions: D								
HDPE -GTPS			HDPE-STPS			HPDE-UTPS			PP -GTPS			PP-STPS			PP-UTPS		
Sample No.	HDPE %	GTPS %	Sample No.	HDPE %	STPS %	Sample No.	HDPE %	UTPS %	Sample No.	PP%	GTPS %	Sample No.	PP %	STPS %	Sample No.	PP%	UTPS %
C-1	85	5	C-6	85	5	C-11	85	5	D-1	85	5	D-6	85	5	D-11	85	5
C-2	80	10	C-7	80	10	C-12	80	10	D-2	80	10	D-7	80	10	D-12	80	10
C-3	75	15	C-8	75	15	C-13	75	15	D-3	75	15	D-8	75	15	D-13	75	15
C-4	70	20	C-9	70	20	C-14	70	20	D-4	70	20	D-9	70	20	D-14	70	20
C-5	65	25	C-10	65	25	C-15	65	25	D-5	65	25	D-10	65	25	D-15	65	25

Where: Native Potato Starch (70%) + Glycerol (30%) – GTPS, Native Potato Starch (70%) + Sorbitol (30%) – STPS, Native Potato Starch (70%) + Urea (30%) – UTPS

2.2 Mechanical Properties (ASTM D 638)

Preparation was done through die-punch of the compression molded sheet. Dumble shaped specimen were prepared. Test conditions were: 30°C temperature and 38%RH.

2.3 Water Absorption Test (ASTM D 570)

The sample size was 50 mm x 50 mm in square shape. Before dipping in distilled water, sample was cleaned, pre-dried and weighed. Sample left for 24 hours in water at normal room temperature and humidity. Thereafter sample was brought to room temperature and weighed after drying.

2.4 Chemical properties: Chemical Resistance Test (ASTM D 543)

Samples of size 50mm x 50mm were prepared from extruded sheets. The thickness of samples was 3.0mm. Various percentage and normality of chemical solution were taken. The test being applied to 24 hr. for observation, after and before keeping the sample in chemical up to 24 hr.

2.5 Thermal Analysis

Thermal properties of batches of GTPS/LDPE, LLDPE, HDPE & PP samples were evaluated using a Differential Scanning Calorimeter (DSC) model Pyrix-6, Perkin Elmer Corporation, UK, Diamond DSC & Thermo Gravimetric Analyser of M/s Perkin Elmer.

2.5 Biodegradation Study (ASTM D 5338- 93)

It is a laboratory respirometeric method that uses compost pile as a biotic function. It is convenient to use especially designed flask. **Biotic Medium**: The test was carried out through incubation in soil & activated compost was used for the purpose.

3. Results and Discussion

3.1 Mechanical Properties

In the figure depiction of effects of plasticizer GTPS on the tensile properties of samples have been shown. Here observation is that tensile strength was hardly affected in the GTPS compositions varied from 0 to 30%. Initially, tensile strength and tensile modulus have slightly changed from 5 to 15% in various TPS batches but as the percentage of TPS increased tensile strength and tensile modulus decreased significantly ~20-30%. The PP show linear decrement in mechanical properties.

Tensile properties of composition (A) blends with GTPS	
% of GTPS	Tensile strength (MPa)
0	12.37
5	10.79
10	10.49
15	10.48
20	09.42
30	08.82

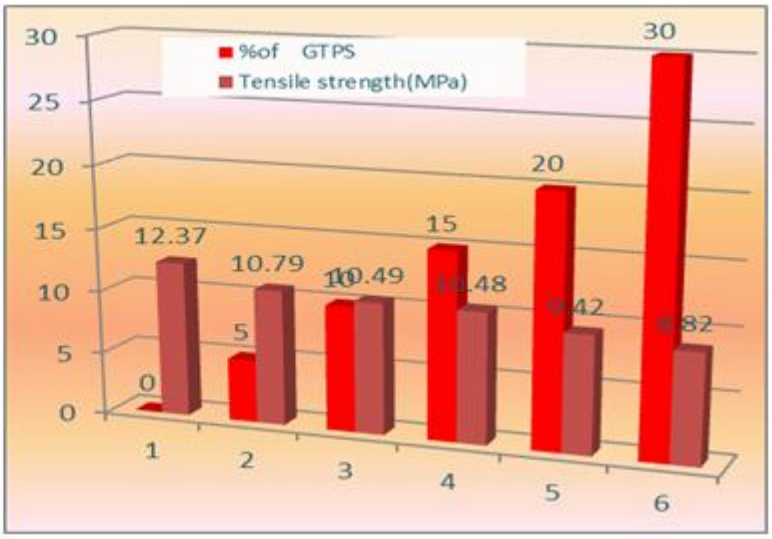
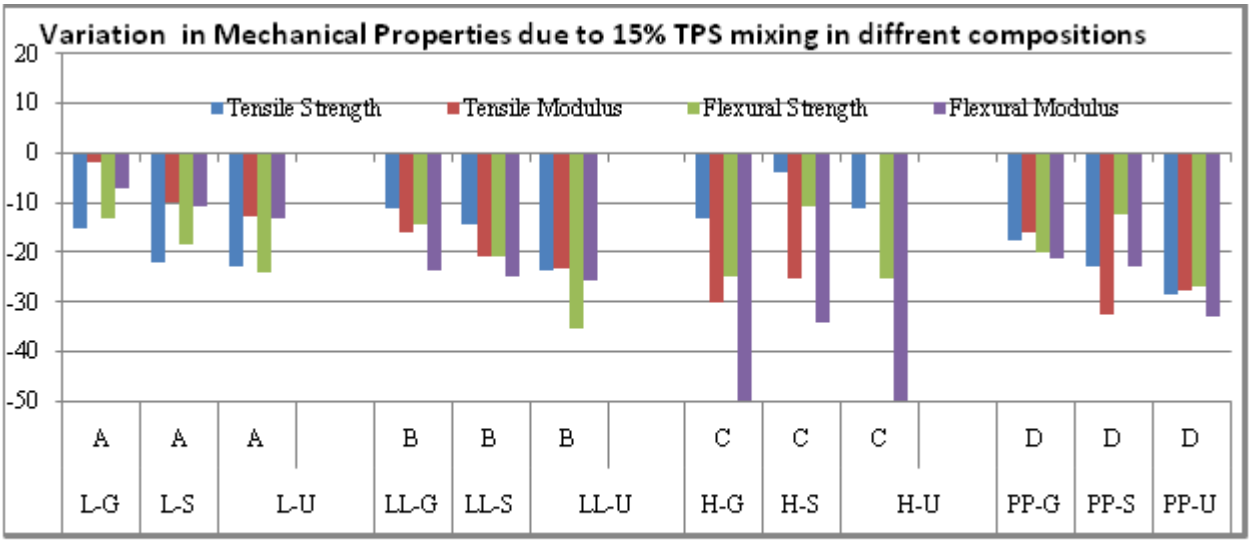


Figure 1: Tensile properties of composition (A) blends with GTPS

L-G: LDPE with GTPS, LL-G: LLDPE with GTPS, H-G: HDPE with GTPS, PP-G: PP with GTPS
L-S: LDPE with STPS, LL-S: LLDPE with STPS, H-S: HDPE with STPS, PP-S: PP with STPS
L-U: LDPE with UTPS, LL-U: LLDPE with UTPS, H-U: HDPE with UTPS, PP-U: PP with UTPS



L-G: LDPE with GTPS, LL-G: LLDPE with GTPS, H-G: HDPE with GTPS, PP-G: PP with GTPS
L-S: LDPE with STPS, LL-S: LLDPE with STPS, H-S: HDPE with STPS, PP-S: PP with STPS
L-U: LDPE with UTPS, LL-U: LLDPE with UTPS, H-U: HDPE with UTPS, PP-U: PP with UTPS

Figure 2: Variation of Mech. Prop. due to 15% TPS mixing in different compositions

On subsequent loading, comparatively glycerol TPS/Polyolefin's blends shown better tensile strength and modulus than sorbitol TPS and urea TPS/polyolefin's blends. The decrements of all mechanical properties monitored in TPS/polyolefin's Blends have shown a pattern as shown in figure 2. TPS/PP showed better flexural properties & decrease in percentage variation in various mechanical properties was lower in TPS/polyolefin's blends. Trends were because urea has higher Tg with little internal flexibility hence, urea TPS blends have inferior mechanical properties than glycerol.

3.2 Water Absorption Study

The water absorption observed for all samples after 24 hours of immersion in water. As expected the water absorption has increased with the increase of percentage of starch in the compositions. Increasing the percentage of TPS in PE and PP have enhanced samples solubility in water, because modified starch make the hydrogen bonding with water molecule. Since the TPS has ranged upto 30% most of TPS molecule migrated into the water. Therefore water absorption is increased with the increase % of TPS.

Glycerol TPS > Sorbitol TPS > Urea TPS

3.3 Chemical Properties

Initially batches of TPS/Polyolefin's blends showed negligible change in weight after keeping the sample for 24 hrs in various chemicals. As the percentage of TPS increased, little decrement in weight was observed. However in initial batches, little increment in weight also noted. But this increment was not considerable. So as a consequence, GTPS/LDPE, LLDPE, HDPE and PP blends showed the better chemical resistance in comparison of STPS & UTPS and show poor chemical resistance in HCL N/2 solution.

3.4 Thermal Analysis

Optimized batches on mechanical study basis (with 5% starch) were analyzed wherein Tm shows little change as expected due to %TPS increase in polymer blends. The melting point of blends has increased slightly due to modifiers (Glycerol, Sorbitol and Urea). The value of ΔH and peak area was found increasing with increase of starch contents. Exothermic graph indicated that initially there is no change in Tm, but it increases as the starch contents increase. In GTPS blends slight decrease in decomposition temperature is observed up to 5-15% TPS loading but after that decrease is more as TPS loading increases from 20-30%.

Table 2 & 3: Effect on Tm, ΔH, & decomposition temperature of different TPS/ Polyolefin's blends

Table 2:

% age of	Composition A		Composition B		Composition C		Composition D	
TPS	Tm in °C	Δ J/gm	Tm in °C	Δ J/gm	Tm in °C	Δ J/gm	Tm in °C	Δ J/gm
0	113.10	77.59	123.1	74.46	117.0	95.13	168.4	76.15
5	113.40	71.28	124.0	85.73	118.0	103.6	169.0	79.62
10	114.50	87.31	125.5	97.98	118.76	113.5	169.4	70.00
15	114.20	88.57	126.0	97.91	117.44	126.4	169.6	57.09

Table 3:

Batches	Max. decomposition temp. (°C) for composition A	Max. decomposition temp. (°C) for composition B	Max. decomposition temp. (°C) for composition C	Max. decomposition temp. (°C) for composition D
0%TPS	409.15	427.54	438.24	443.13
5%	401.66	421.32	426.43	416.85
10%	399.81	410.39	418.76	409.06
15%	391.33	404.54	409.12	403.83

3.5 Biodegradation study (ASTM D 5338- 93)

Soil burial testing has been conducted on UTPS compositions shown in figure 3, for a month. The degradation rates show that Urea TPS/olefins were most susceptible to micro-organisms & have very high rate of biodegradation of more than 18% within 30 days time in polyolefins like PP and HDPE. This shows the potential of the blends from biodegradability point of view.

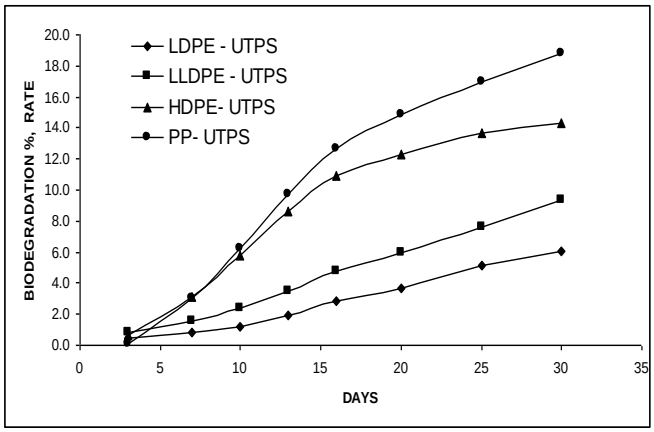


Figure 3: Biodegradation of the Polyolefin's with UTPS blends after soil burial

4. Conclusion

Modification of starch leads to an increase in the thermoplastic character along-with increased thermal stability. GTPS blend provided better mechanical, thermal and chemical properties in comparison with STPS and UTPS blends. During Biodegradation study enhancement of biodegradability with increased %TPS in blends was observed. Since, starch concentration associates with the degradation through microorganism, higher concentration of TPS caused considerable compatibility between bacterial phase and chemical strength of plastic. Whereas, starch being less crystalline and hydrophilic in nature compared to LDPE, is more prone to microbial attack. Water absorption behavior of TPS/ polyolefin blends increases with increase the TPS percentage due to degradation, deterioration of starch molecule through moisture and starch hydrophilic nature. Biodegradability of TPS blend increased with the % of TPS in blend, since starch concentration associates the degradation through microorganism.

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