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Blends of PLA with modified starch

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Abstract- Poly(lactic acid), PLA, is a biodegradable polymer, but its applications are limited by its high cost and relatively poorer properties when compared to petroleum-based plastics. The addition of starch powder into PLA is one of the most promising efforts because starch is an abundant and cheap biopolymer. However, the challenge is the major problem associated with poor interfacial adhesion between the hydrophilic starch granules and the hydrophobic PLA, leading to poorer mechanical properties. In this paper, cashew nut shell oil(CNSL) maleate was synthesized by grafing CNSL with various weight percents of maleic anhydride (MA) using dicumyl peroxide (DCP) as an initiator. WHEN, CNSL was employed for the surface modifying of corn starch powder, resulting in CNSL-g-STARCH. We obtained CNSL-g-STARCH was mixed with PLA in various weight ratios using twin-screw extruder, resulting in PLA/CNSL-g-STARCH. Finally, the obtained PLA/CNSL-g-STARCH composites were prepared by a compression molding machines. The compatibility, thermal properties, morphology properties, and mechanical properties were characterized and evaluated.

***Keywords** – Polylactic acid, starch, biodegradable polymer, mechanical properties, renewable resources*.

I. INTRODUCTION

The petroleum-derived plastics have been used extensively, causing tons of thousands of plastic waste. The improper disposal of petroleum-derived plastics leads to environmental pollution which has aroused much interest in searching for substitutes [1]. Recently, biodegradable and renewable polymers have been increasingly developed. Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers such as starch, protein, and cellulose; (2) synthetic polymers from natural monomers such as polybutylene succinate (PBS) and polylactide (PLA); and (3) polymers from microbial fermentation such as polyhydroxybutyrate [2]. These polymers are aliphatic polyesters which are biodegradable and compostable thermoplastics derived from renewable resources, such as starch and sugar cane [1]. PLA and PBS are the most promising thermoplastic polymers in this regard. They are compostable which is perfectly suitable for consumer goods and packaging applications. They are derived from renewable resources such as corn, sugar cane and cassava. They are biodegradable polymers which are nontoxical and acceptable mechanical performance but their applications, particularly PLA, are limited by the high cost and relatively poorer properties when compared to petroleum-based plastics. PBS is semicrystalline polymer which exhibits the flexibility when compared to PLA. On the other hand, PLA is brittle polymer due to its high , low crystallinity and low thermal stability. With respect to its chemistry, PLA is synthesized by direct condensation polymerization of the lactic acid monomers or by ring opening polymerization of lactide monomer. There have been several possibilities to modify its property such as the nucleating agent addition, polymer composites, and polymer blend preparation with natural fillers such as starch or cellulose and with natural rubber, respectively [3–6].

The addition of starch into PLA is one of the most promising efforts due its abundant and cheap biopolymer particularly cassava starch since it is the most abundant starch crop produced in the world and the third most important food source for inhabitants of tropical regions. As a result, starch has been used as filler for environmentally friendly plastics [7]. However, the challenge is the major problem associated with poor interfacial adhesion between the hydrophilic starch granules and the hydrophobic PLA, leading to poorer mechanical properties. therefore, several strategies have been adopted to improve the compatibility such as by using compatibilizers or reactive coupling agents [1, 8, 9]. Especially, maleic anhydride- (MA) based compatibilizing agents are the most popular due to their good chemical reactivity, low toxicity, and low potential to polymerize itself under free radical grafting conditions [5]. Wang et al. prepared thermoplastic dry starch (DTPS)/PLA blends by using MA as compatibilizer and dicumyl peroxide (DCP) as initiator to enhance the compatibility between DTPS and PLA [1]. Glycerol was employed as a plasticizer for dry starch to avoid the depolymerization of hydrophobic PLA during melt processing. the plasticization of starch and its compatibility modification with PLA was accomplished in a single-screw extruder by one-step reactive extrusion. The results have been reported that the physical properties and compatibility of DTPS/PLA blends were improved.

II. EXPERIMENTAL

2.1. Materials

PLA pellet (2003D grade) by NatureWorks . It is transparent polymer with a glass transition temperature of 58–60°C and a density of 1.24 g/cm , as reported by the manufacturer. It was vacuum dried at 80 ◦C for at least 8 h before use. Corn starch was purchase from Santosh Food Products Public Company Limited . which was dried in vacuum for 24 h at 100 ^{0}C before use.Cashew nut shell oil was supplied from Shivam cashew industry. Maleic anhydride (≥98% purity) produced by Sigma Aldrich, dicumyl peroxide (98% purity).

2.2 Synthesis of MA-grafted starch

The MA-grafted starches were prepared in a three-neck flask equipped with a Dean-Stark distilling receiver, a condenser and a mechanical agitator. Starch and MA were first charged into the flask,. The reaction temperature was then brought up to 130^{0}C with the agitation. The reaction was kept at this temperature for 1 h and then cooled to room temperature. The final product was dried in vacuo at 80^{0}C for 24 h and then kept in a desiccators. This step is called master batch preparation.

2.3. Master batch formulation:

Table 1 Master Batch Formulation

MATERIAL	**PHR**
STARCH	72.115
CNSL	24.038
MA	2.884
DCP	0.961
TOTAL	100

2.4. Blends

The PLA/starch, PLA/CNSL, PLA/CNSL/starch, and PLA/CNSL/MAgraft- starch (MGST) blends were melt-blended in a SJSZ-10A miniature twin-screw extruder with 40 rpm at 175 ^{0}C for 10 min. The extrudants were then injection molded into the standard testing bars with the barrel temperature of 200 ◦C, mold temperature of 45 ^{0}C, an injection pressure of 5 MPa and a cycle time of 30 min. In the PLA/starch blends, the content of starch was 30 wt.%, 40 wt.% and 50 wt%, respectively. Blends of PLA\starch were prepared in 3 batches, called final batches.

2.5. Formulation of final batches

Table 2 Formulation of Final Batch

MATERIAL	**BATCH 1**	**BATCH 2**	**BATCH 3**	**TOTAL PHR**
PLA (PHR)	70	60	50	100
MASTER BATCH (PHR)	30	40	50	100

III. TESTING

In this paper we have studied on tensile and elongation properties of prepared batches.

3.1. Test specimen preparation

Prepared moulded specimen was in sheet rigid form so from ASTM standard type 1 specimen preparation method was done, which is preferred for material having thickness of 7 mm or less.

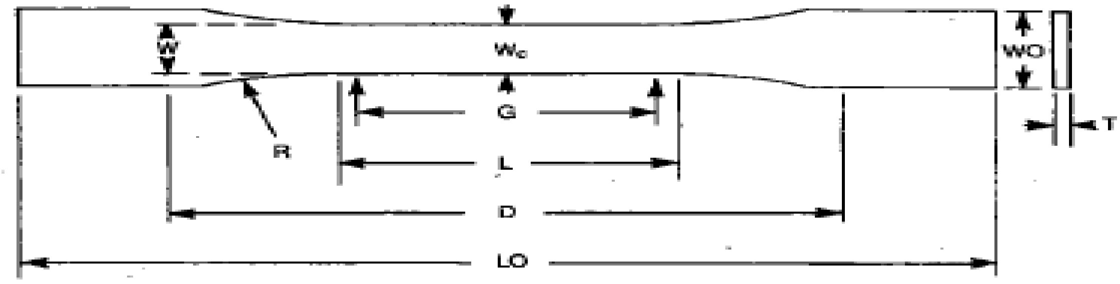


Fig 1 Tensile Specimen

Where W-Width of narrow section
L-Length of narrow section, Wo-Width overall, min., Lo-Length overall min, G-age length,
D-Distance between grips, R-Radius of filet, RO-uter radius

3.2. Procedure

Measure the width and thckness of rigid flat specimens (Fig.1) with a suitable micrometer to the nearest 0.025 mm (0.001 in.) at several points along their narow sections. Measure the thckness of nonrgid specimens in the same maner with the required dial micrometer. Take the width of ths specimen as the distance between the cutting edges of the die in the narrow section. Measure the diameter of rod specimens, d the inside and outside diameters of tube specimens, to the nearest 0.025 mm (0.001 in.) at a minimum of two points 90 apar; make these measurements along the groove for specimens so constrcted.

Place the specimen in the grps of the testing machie, takng care to algn the long axs of the specimen and the grps with an imaginar line joinng the points of attachment of the grps to the machine. The distance between the ends of the gripping suraces, when using flat specimens, shall be as indicated in Fig. 1. Tighten the grps evenly and firmy to the degree necessar to prevent slippage of the specimen during the test, but not to the point where the specimen would be crushed.

Set the speed of testing at the proper rate as required in Section 8, and star the machine.

Record the load-extension curve of the specimen.

Record the load and extension at the yield point (if one exists) and the load and extension at the moment of rupture.

3.3. Calculation

Tensile Strength-Calculate the tensile strength bymdividing the maximum load in newtons (or pounds-force) by the original minimum cross-sectional area of the specimen in square metres (or square inches). Express the result in pascals (or pounds-force per square inch) and report it to three significant figures as tensile strength at yield or tensile strength at break, whichever term is applicable. When a nominal yield or break load less than the maximum is present and applicable, it may be desirable also to calculate, in a similar manner, the corresponding tensile stress at yield or tensile stress at break and report it to three significant figures

Percent Elongation at Break-Calculate the percent elongation at break by reading the extension (change in gage length) at the point of specimen rupture. Divide that extension by the original gage length mid multiply by 100.

IV. RESULT AND DISCUSSION

4.1. Tensile strength

PLA is considered as the brittle polymer derived from low thermal stability occurring during heat processing, leading to its application restriction. PLA tends to reduce thet strength due to incompatibility between starch phase and PLA matrix. In contrast, the loading of CNSL-g-STARCH into PLA results in a significant improvement of strength. The addition of unmodified starch leads to a noticeable reduction in tensile strength due to phase separation between PLA matrix and starch particles, arising from poor interfacial adhesion. The improvement of interfacial adhesion between starch powder and PLA was achieved by surface modification of starch with CNSL oil maleate. As a result, the tensile strength values of PLA/SOMA-g-STARCH composites are higher than those of PLA/starch composites.

Table 3 Tensile test result

MATERIAL	**TENSILE STRENGTH(kg\cc)**
B_1	158
B_2	163
B_3	165

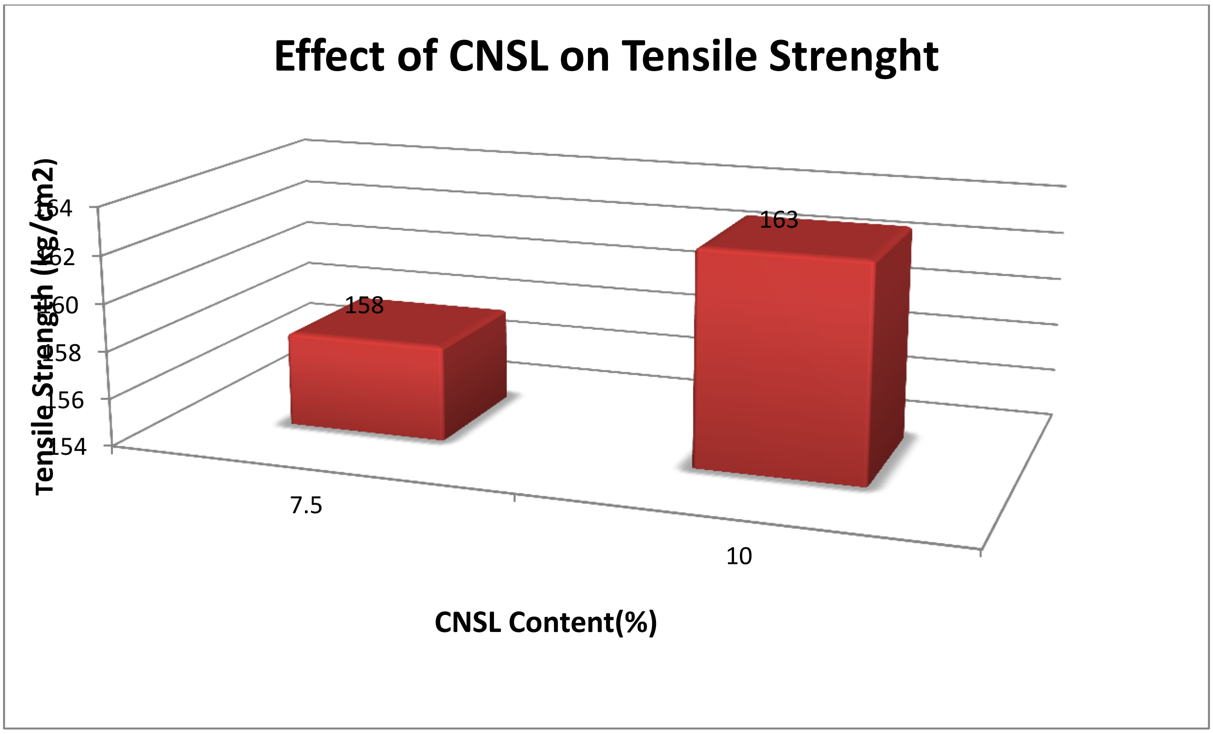
Tensile properties of raw PLA is 210 kg\cc and it is brittle material, it decreases with the addition of native starch alone, because of the incompatibility between native starch and raw PLA, it goes down up to 98kg\cc so there is need to add compatibilizer and plasticizer and here we added CNSL as plasticiser.

The results of above table shows that as we proceeds from B_1 to B_3 tensile strength is increasing that is because of the addition of CNSL, it is because CNSL have tendency to improve tensile properties because of Anacardic acid, Cardol and methyl derivatives of Cardol. The percentage of CNSL in master batch and its effect on tensile properties is shown in table.

Table 4 Effect of CNSL on tensile

BATCH	**CNSL CONTENT (%)**	**TENSILE STRENGTH (kg\cc)**
B_1	7.5	158
B_2	10	163

Fig 2 Effect of CNSL on Tensile Strenght



4.2. ELONGATION AT BREAK:

Table 5 Elongation at break result

MATERIAL	**ELONGATION AT BREAK(%)**
B_1	90
B_2	85
B_3	82

Elongation at break is known as a fructural strength , is ratio between changed length and initial length after the breakage of test specimen. It expresses the capability of a material to resist change of shape without crack formation.

A relative decrease in the percent elongations of PLA/CNSL-g-STARCH composites is observed with an increase in CNSL-g-STARCH content, refrecting that phase separation is likely to occur when a high amount of CNSL-g-STARCH above 10 wt% is employed.

V. CONCLUSION

Maleated CNSL oil was successfully prepared by grafting reaction of CNSL l with maleic anhydride using dicumyl peroxide as an initiator. Then, maleated CNSLB oil was employed for surface modification of cassava starch powder, producing CNSL oil grafted starch powder (CNSL-g-STARCH). The incorporation of SOMA-g-STARCH into polylactic acid by melt extrusion mixing using PLA : CNSL-g-STARCH weight ratios of 70 : 30, 60 : 40, and 50 : 50 was carried out. It was found that the loading of CNSL-g-STARCH into PLA resulted in a significant improvement of impact strength, in case of CNSL-g-STARCH contents which have below 30 wt% due to better interfacial adhesion and good particles distribution. In a similar manner, polymer composites of PLA filled with corn starch-g-soybean oil maleate exhibited higher mechanical properties than polymer composites of PLA filled with unmodified starch powder. It was thought that CNSL oil on the particle surface might play a key role in improving the compatibility as well as performing the plasticity-like behavior.

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