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Synthesis, Characterization and Evaluation of Physical Properties of Biodegradable Composites from Corn Starch

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This research paper deals with the synthesis and characterization of corn starch based composites using resorcinol-formaldehyde as cross linker. Acid, base and moisture resistance studies of the composites were also done. Moreover, biodegradation studies of the composites were also done using composting method and the different stages of the biodegradation were evaluated using scanning electron microscopy.

Keyword: Corn starch, composites, biodegradation, SEM

1. Introduction

Biodegradable polymers play an increasingly significant role in plastic engineering by replacing commodity, non-degradable and nonrenewable petrol-based polymers [1-2]. Biodegradable polymers are designed to degrade upon disposal by the action of microorganisms. Since last decades, many attempts have been focused on grafting or blending of plastic materials with cheap and biodegradable natural biopolymers, such as starch, cellulose, chitin and psyllium to create new materials with desired properties. These biopolymers, especially starch, are abundant, inexpensive, renewable and also degradable [3-5]. The interest in its use in biodegradable plastics are also driven by the inherent biodegradability of starch as a carbon source [6].

Starch is mainly composed of two homopolymers of D-glucose [8]: amylase, a mostly linear α- D (1, 4)-glucan and branched amylopectin, having the same backbone structure as amylose but with many α-1, 6-linked branch points. There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked.

Research on starch plastic composites began in the 1970s [7-8] and several different technologies are currently being studied. The starch can be used in its natural granular form as biodegradable filler or in the gelatinized or destructurized form in starch-based compositions. The biodegradation of PCL-starch compositions starts with the starch consumption and continuously increases with the content in natural filler. Monitoring the sample thickness proved to be useful for the measurement of surface erosion and complementary to scanning electron microscopy [9]. The other possibility is that the amount of the

produced carbon dioxide derived from the biodegradation of the test material can be measured, compared with the theoretical maximal amount and recorded as a biodegradation percentage [10]. The wheat starch/aliphatic polyester blend studied demonstrated excellent biodegradability [11]. Soil burial tests revealed complete biodegradation within eight weeks. Bastioli [12] reported the enhanced biodegradation of PCL in the presence of starch by providing a larger surface area for microbial attack. The compost derived from biodegradable plastics along with other organic products increases the soil organic carbon, water and nutrient retention, while reducing fertilizer inputs and suppressing plant disease. The composting of biodegradable plastics also recycles matter rather than 'locking' it up in resistant materials, particularly when the non-degradable plastics are destined for landfill [13]. Mano [14] examines the use of different types of polymeric matrix composites in hard tissue replacement applications. Roohani [15] reported that nanocomposite materials were prepared from copolymers of polyvinyl alcohol and polyvinyl acetate and a colloidal aqueous suspension of cellulose whiskers prepared from cotton linter. Gojny [16] reported nanocomposites consisting of double-wall carbon nanotubes (DWCNT's) and an epoxy matrix were produced by a standard calendaring technique. Kim [17] reported aromatic polyester nano composites based on poly (ethylene 2, 6-naphthalate) (PEN) and carbon nanotube (CNT) were prepared by melt blending using a twin-screw extruder. Modification of CNT to introduce carboxylic acid groups on the surface was performed to enhance intermolecular interactions between CNT and the PEN matrix through hydrogen bonding formation. Starch based biodegradable polymer and composites have wide application in medicinal [18-21], agriculture [22-23] and food industry [24].

In this research paper biodegradable composites of corn starch using resorcinol-formaldehyde as crosslinker were synthesized. Acid, base and moisture resistance studies of the composites were also done. Moreover, biodegradation studies of the composites were also done using composting method and the different stages of the biodegradation were evaluated using scanning electron microscopy.

2. Materials and Methods

2.1 Materials

Petroleum ether (Merck), methanol (Merck), resorcinol (Merck), formaldehyde (Merck), sodium hydroxide (S. D. Fine), HCl (S. D. Fine) were used as received. Corn-Starch was procured from the local market. Weighing of the sample was done with electronic weighing machine (Afcoset). Drying was carried-out in Hot Air Oven (Jain Scientific Works, Ambala). SEMs of the samples were taken on LEO435VF (Electron microscopy). Hot pressing of the samples was carried-out with Carver Hydraulic Hot Press under 178 KN force.

2.2 Biodegradation Studies

Cross linked matrix was evaluated for its biodegradation behavior by composting method for 60 days. Weights of test samples were taken at a regular interval of 7 days till the samples were completely biodegraded. Further confirmation of the biodegradation was carried-out by SEM studies of different biodegradation stages.

2.3 Acid Resistant Studies

Acid resistance properties of samples were studied by using 5N HCl for 72 hours. Weights of the samples were taken at regular time interval of 6 hours.

2.4 Base resistant studies

Base resistance properties of samples were studied by using 5N NaOH for 72 hours. Weights of the samples were taken at regular time interval of 6 hours.

2.5 Water uptake resistant studies

Water uptake resistance study of the samples was carried out by putting a definite amount of each sample in a definite volume of distilled water and weight of each sample was taken after every 6 hours.

2.6 Synthesis

2.6.1 Preparation of Biodegradable Matrix

Corn-Starch was converted in to a fine powder (400 gm) and the powdered material was kept for cold percolation in petroleum ether (60-70 ^{0}C) for about 72 hours. After removal of the solvent marc left was dried in oven at 40 ^{0}C and again cold percolation was followed with 70% methanol for about 72 hours. Solvent was removed with filtration and the marc left was washed with repeated washings of distilled water till the impurities left were completely removed. The material was dried in oven at 40 ^{0}C and the final weight was taken.

The percentage of the purified powder obtained was calculated as:

$$\% \text{ Matrix powder} = \frac{F_w}{I_w} \times 100$$

Where I_w = initial weight of the material taken; F_w = final weight of the material obtained.

2.6.2 Synthesis of Crosslinker

Resorcinol-Formaldehyde was prepared as per the method described earlier [25].

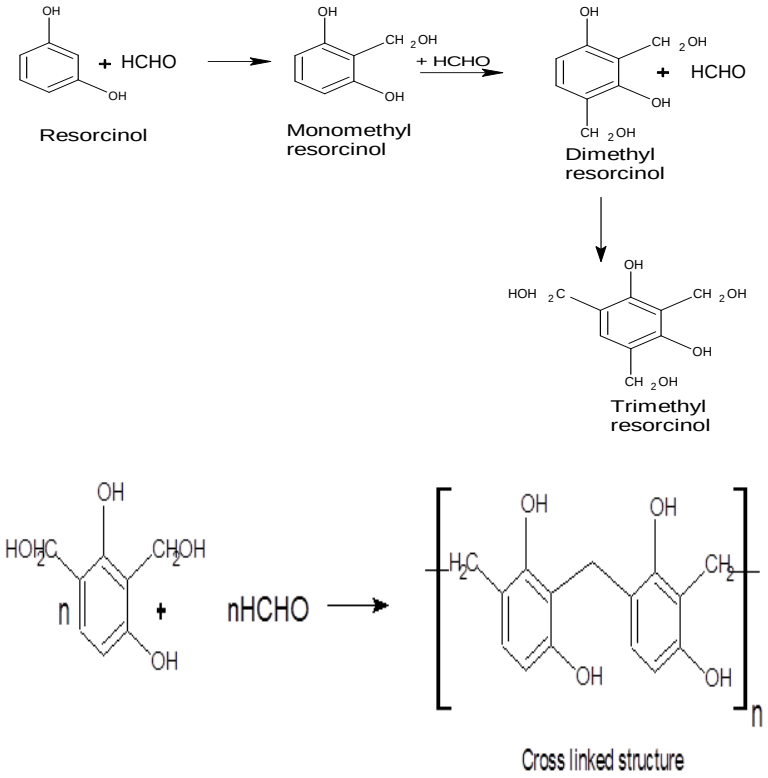
2.6.3 Crosslinking of Biodegradable Matrix

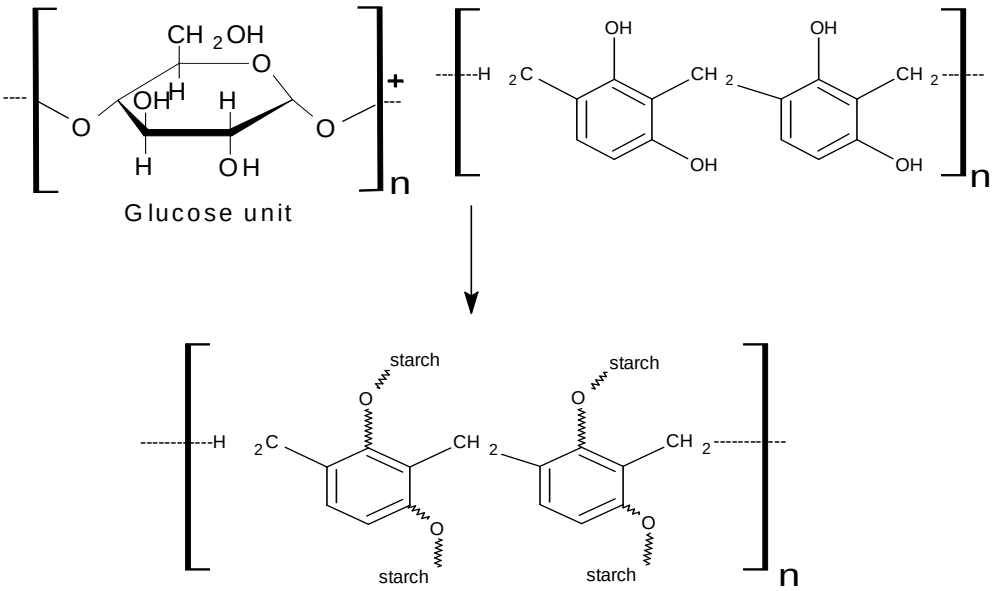
Thick slurry of purified powdered material was prepared with distilled water in a beaker and a definite amount of resorcinol-formaldehyde was added and the mixture was stirred thoroughly so as to obtain a homogenous mixture. The reaction mixture was heated on water bath at 70 ^{0}C for about 30 minutes. The pre-cured mixture was transferred into an iron die and was kept at ambient temperature for about 24 hours. Finally the mixture was cured with hot pressing in a Carver Hydraulic Hot Press at 90 ^{0}C for 60 minutes under 178 KN force.

3. Results and Discussion

3.1 Mechanism

In the natural matrix presence of hydroxyl group provides the active sites where crosslinking with the resorcinol-formaldehyde takes place during precuring and curing process which can be presented through the following mechanism:





4. Characterization

4.1 Scanning Electron Microscopy (SEM)

In order to have the conducting impact, the samples were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over a large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three dimensional appearance with high resolution was obtained in case of cross linked matrix as well as different stages of biodegradation. Intricacies brought about by biodegradation were clearly illustrated by the SEM results of the different samples.

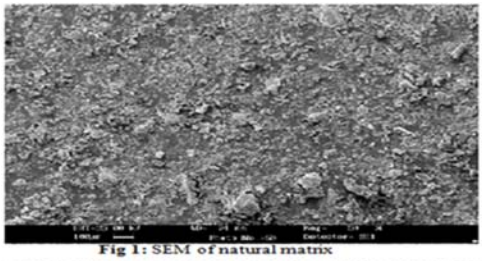


Fig 1: SEM of natural matrix

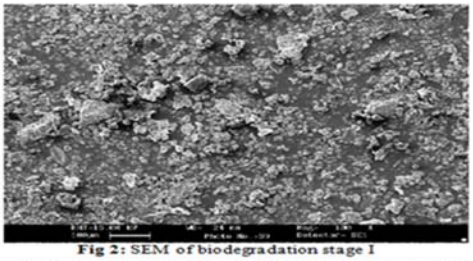


Fig 2: SEM of biodegradation stage I

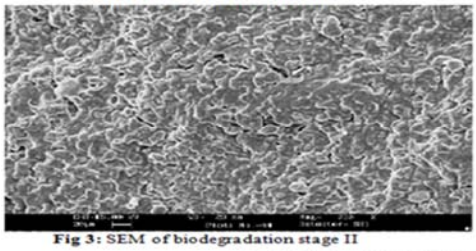


Fig 3: SEM of biodegradation stage II

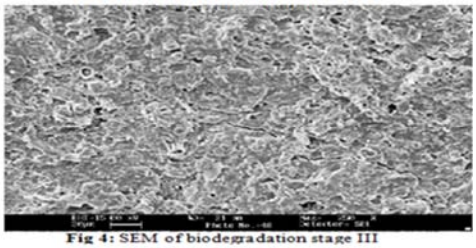


Fig 4: SEM of biodegradation stage III

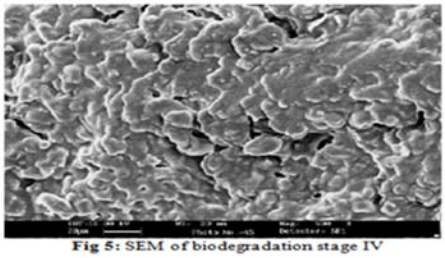


Fig 5: SEM of biodegradation stage IV

The morphological changes in the features of crosslinking matrix after biodegradation at different stages were quite evident from the SEM images. The three dimensional network of the cross linked natural matrix and its breaking down due to biodegradation at Stage-I, Stage-II, Stage-III and Stage IV could be clearly visualized from SEM studies. Moreover, SEM studies clearly exhibited marked differences between the SEMs of cross linked matrix having smooth homogenous surface and that of biodegradation matrices of different stages possessing rough heterogenous surfaces (Fig. 1-5).

4.2 Acid Resistant Studies

From Figure 6 it is evident that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards 5N HCl. The uncross link matrix got disintegrated within 6 hours whereas the cross linked one was found to be stable towards 5N HCl up to 72 hours beyond which the samples got disintegrated. This could be explained on the basis that addition of hydroxyl groups containing resorcinol-formaldehyde to the natural matrix undergoes condensation reaction with the removal of water molecules during precuring and curing process. This resulted in the formation of three dimensional networks containing covalent bonds. Thereby providing resistance against the acid attack.

4.3 Base Resistant Studies

From Figure 7 it is evident that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards 5N NaOH. The uncross link matrix got disintegrated within 6 hours whereas the cross linked one was found to be stable towards 5N NaOH up to 72 hours beyond which the samples got disintegrated. This could be explained on the basis that addition of hydroxyl groups containing resorcinol-formaldehyde to the natural matrix undergo condensation reaction with the removal of water molecules during precuring and curing process, thereby resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the base attack.

4.4 Water uptake resistant studies

From Figure 8 it is evident that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards water uptake, whereas uncross linked matrix was found to be unstable in water. Though there was constant increase in water uptake by the cross linked matrix up to 45 hours (24%) but afterwards rate of water uptake was found to be almost constant and cross linked matrix was found to be stable up to 72 hours. This could be explained on the basis that addition of hydroxyl groups containing resorcinol-formaldehyde to the natural matrix undergo condensation reaction with the removal of water molecules during precuring and curing process, thereby resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the attack of water.

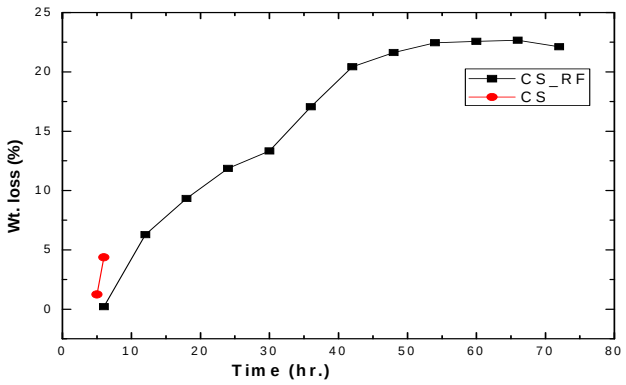


Fig 6: Acid Resistant Studies

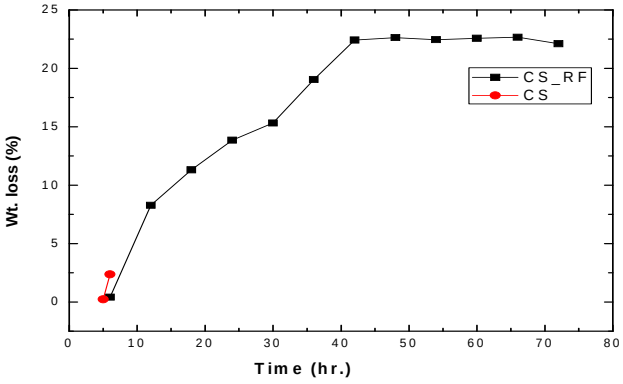


Fig 7: Base Resistant Studies

Wt. of samples at different Time intervals (days)										
S. No.	**Initial weight (gm)**	**7**	**14**	**21**	**28**	**35**	**42**	**49**	**56**	**63**
Natural matrix	1.0	0.55	-	-	-	-	-	-	-	-
Cross-linked matrix	2.93	2.55	1.60	1.10	0.75	0.53	0.40	0.23	0.18	-

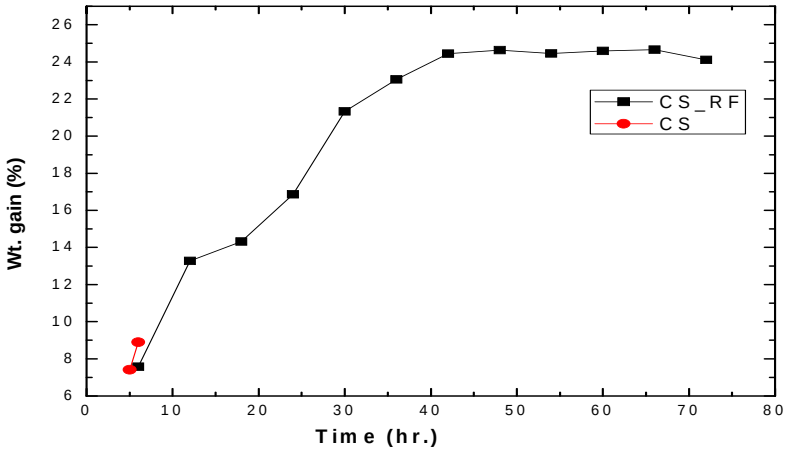


Fig 8: Moisture absorbance studies

4.5 Biodegradation Studies

As is evident from Table 1 that biodegradation of the cross linked matrix takes place under anaerobic conditions. It has been observed that there was a continuous decrease in weight of the sample. Total biodegradation of the sample was found to be achieved after the time interval of 60 days. The mechanism of the biodegradation can be explained through the following anaerobic oxidation:

(Anaerobic Oxidation)

Corn Starch $\longrightarrow$ $CH_4 + CO_2 +$ other lower hydrocarbons

5. Conclusion

Natural matrices have been found to be eco-friendly because they are biodegradable, easily available, cheap and renewable source of raw materials but these natural matrices face a lot of problems like water vulnerability, least resistance towards acids and bases and less mechanical as well as thermal stability. In order to provide chemical resistance, water resistance and mechanical stability to the natural matrices, crosslinker like resorcinol-formaldehyde play an important role. The prepared cross linked matrix was found to be highly biodegradable in nature along with resistance towards acid and base attack. Moreover, this cross linked matrix was found to be stable towards attack by water. Thus, it could be concluded that preparation of biodegradable matrices and their crosslinking with resorcinol-formaldehyde resin as well as reinforcement with CNTs is of great importance from technology point of view.

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