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Synthesis of biodegradable composite from soy protein using resorcinol-formaldehyde crosslinker

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ABSTRACT

This research paper deals with the synthesis and characterization of composites of soy protein with resorcinol-formaldehyde. Acid, base and water resistance studies of the synthesized composites were also done. Moreover, biodegradation studies of the composites were done using composting method. Characterization of the samples were done using scanning electron microscopy.

Keywords: Soy protein, Composites, Biodegradation, Crosslinker and SEM.

INTRODUCTION

Majority of plastic products are made from petroleum based synthetic polymers that don't degrade in landfill or in compost like environment. Therefore, the disposal of these products possess a serious environmental problem. An environmentally-conscious alternative is to design/synthesize polymers that are biodegradable. Petroleum-based plastics dominate today's plastic market because of their high strength, lightweight, low cost, easy processibility and good water barrier properties. However, most of the synthetic polymers are not biodegradable. Synthetic biodegradable polymers, such as poly(lactic acid), polycaprolactone and poly(hydroxy butyrate) have high production costs. With the increasing concerns of environmental pollution caused by non-biodegradable petroleum-based plastics, increasing efforts have been made to utilize the polymeric materials derived from agricultural products.

The ever-growing environmental threat caused by the widespread consumption of petroleum based polymers and plastics have spurred a thrust into the development of biodegradable or environmentally friendly materials. Eliminating the need for non-renewable fossil fuels, such as coal and oil, reduces the amount of carbon dioxide that enters the atmosphere, which otherwise would contribute to the growing problem of global warming [1-10]. Extensive use of plastics and difficulties in setting up their recycling promote the development of agromaterials. A composite is any material made up of more than one component. Concrete is a composite,

consists of cement and sand and often has steel rods inside to reinforce it. Bio-composite is a material consisting of a natural matrix (resin) and a reinforcement of natural fibers (usually derived from plants or cellulose). Since then, composite materials have gone through significant developments in terms of use of different raw materials, processes and even applications [11-18].

The soybean is a legume, also known as *Glycine max*. Soybeans contain protein, carbohydrates and fats, as well as vitamins and minerals, including calcium, folic acid and iron. They are the only vegetable that have complete protein, with all eight essential amino acids. Linoleic and linolenic acids, two essential fatty acids found in soybeans, aid in the body's absorption of vital nutrients and regulate smooth muscle contraction, blood pressure and the growth of cells. The composite also preferably includes a compatibilizer, a cross-linking agent, and a plasticizer. The composites of this invention offer the advantages of being water resistant and biodegradable. Soy proteins are complex macromolecules containing 20 amino acids [19] with many sites available for interaction with a plasticizer. Therefore, soy protein can be converted to soy protein plastic through extrusion with a plasticizer or cross-linking agent [20-22].

Although the mechanical properties of soy protein plastic can be controlled and optimized by adjusting the molding temperature and pressure or processing parameter and initial moisture content [23-25], the application of soy protein plastic is limited because of its low strength and high moisture absorption. Soybeans contain approximately 42% protein, 20% oil, 33% carbohydrates and 5% ash on a dry basis [25]. Soy proteins are complex macromolecules containing 20 amino acids [26] with many sites available for interaction with crosslinking agent.

MATERIALS AND METHODS

Materials

Petroleum ether (60-80⁰) (Merck), methanol (Merck), resorcinol (Merck), formaldehyde (Merck), sodium hydroxide (S. D. Fine), HCl (S. D. Fine) were used as received. Soy-protein were 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.

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

Acid resistance 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 hour.

Base resistance 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 hour.

Water uptake resistance 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 hour.

Synthesis**Preparation of biodegradable matrix**

Soya bean were converted in to a fine powder (400 gm) and the powdered material was kept for cold percolation in petroleum ether (60-80 °C) for about 72 hours. After removal of the marc left was dried in oven at 40°C and again cold percolation was followed with 70% methanol for about 72 hours. After removal of the solvent the marc left was dried in oven at 40°C and again cold solvent was removed with filtration and the marc left washed with repeated washings of distilled water till the impurities left were completely removed. The material was dried in oven at 40°C and the final 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

Synthesis of crosslinker

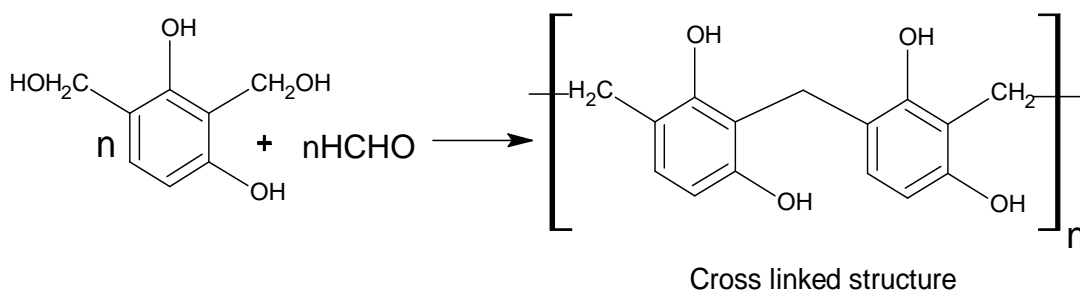
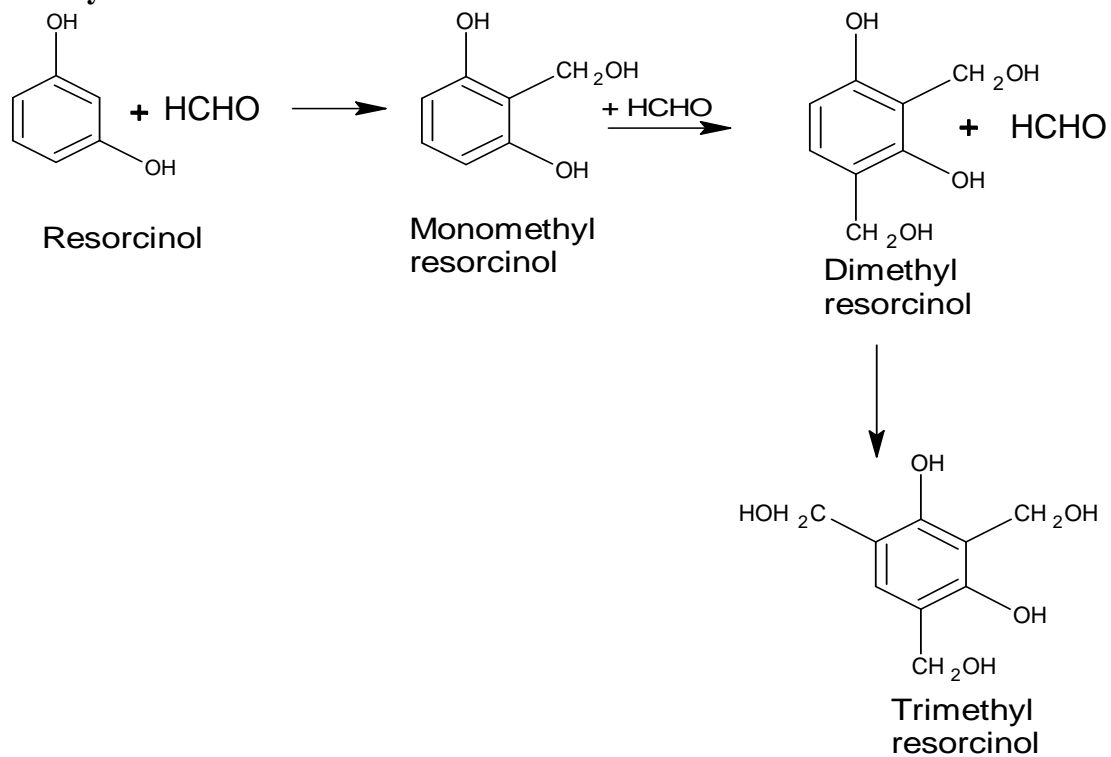
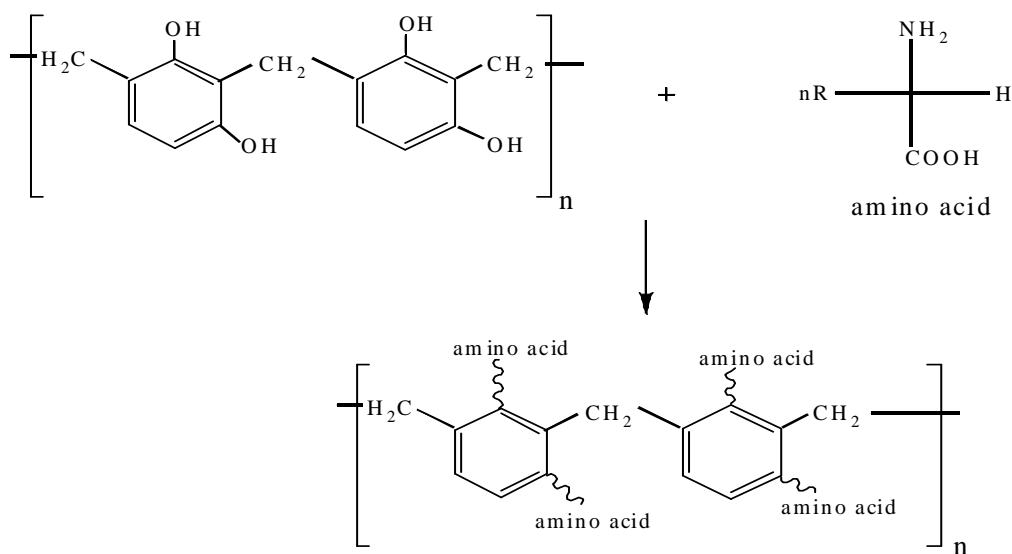
Resorcinol-Formaldehyde resin was prepared as per the method described earlier [27].

Crosslinking of biodegradable matrix

A 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 °C for about 30 minutes. The pre-cured mixture was transferred into a 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 °C for 60 minutes under 178 KN force.

RESULTS AND DISCUSSION**Mechanism**

Hydroxyl group present in the natural matrix are the active sites where crosslinking with the resorcinol-formaldehyde takes place during precuring and curing process which can be presented through the following mechanism:

Formaldehyde-Resorcinol Resin:**Crosslinking with natural matrix**

Characterization**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 crosslinked matrix as well as different stages of biodegradation. Intricacies brought about by biodegradation were clearly illustrated by the SEM results of the different samples. 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 crosslinked natural matrix and its breaking down due to biodegradation at stage I, II and III could be clearly visualized from SEM studies. Moreover SEM studies clearly exhibited marked differences between the SEM of crosslinked matrix having smooth homogenous surface and that of biodegradation matrices of different stages possessing rough heterogenous surfaces. (Figs. 1-4).

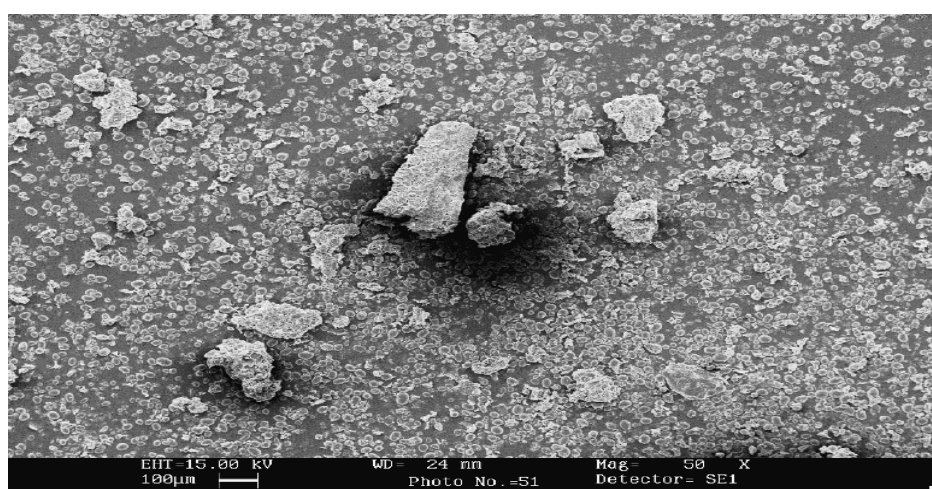


Fig. 1: SEM of natural matrix

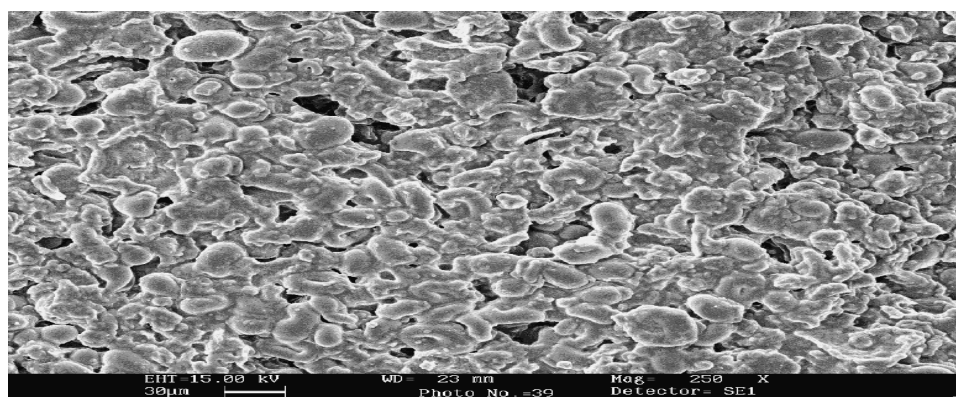


Fig. 2: SEM of biodegradation stage I

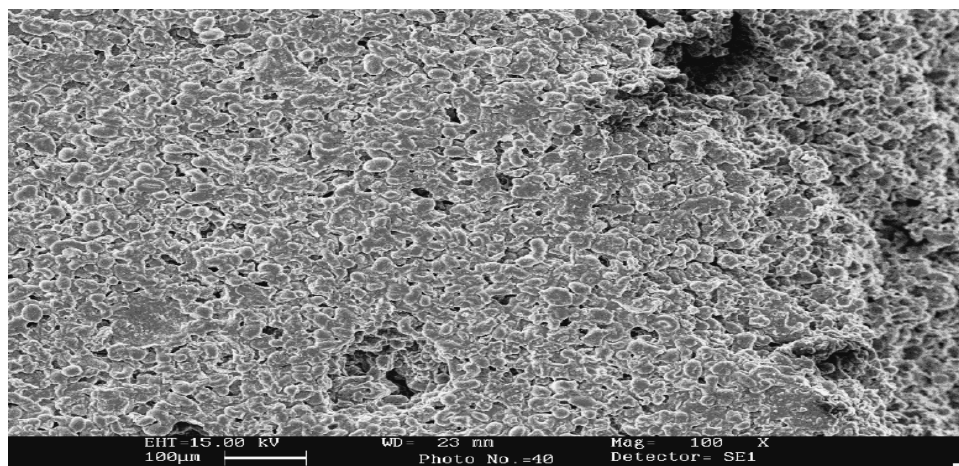


Fig. 3: SEM of biodegradation stage II

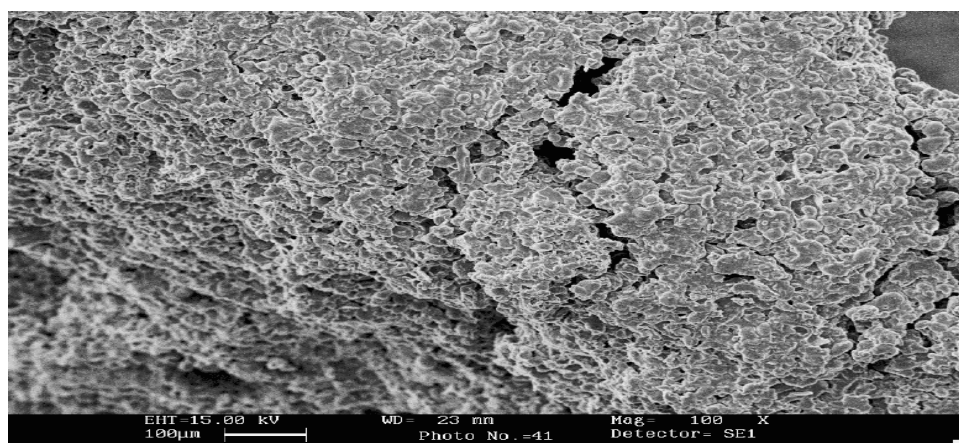


Fig. 4: SEM of biodegradation stage III

Acid resistance studies

As is evident from Fig. 5 that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards 5N HCl. The uncrosslinked matrix got disintegrated within 6 hours where as the crosslinked 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 containing hydroxyl groups undergo condensation reaction with the removal of water molecules during precuring and curing process. There by resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the acid attack.

Base resistance studies

As is evident from Fig. 6 that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards 5N NaOH. The uncrosslink matrix got disintegrated with in 6 hours where as the crosslinked 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 resorcinol-formaldehyde containing hydroxyl groups undergo condensation reaction with the removal of water molecules during precuring and curing process, there by resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the base attack.

Water uptake resistance studies

As is evident from Fig. 7 that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards water uptake, where as uncrosslinked matrix was found to be unstable in water. Though there was constant increase in water uptake by the crosslinked matrix up to 4 hours (25%) but afterwards rate of water uptake was found to be almost constant and crosslinked matrix was found to be stable up to 75 hours. Thus could be explained on the basis that addition of resorcinol-formaldehyde containing hydroxyl groups undergo condensation reaction with the removal of water molecules during precuring and curing process, there by resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the water attack.

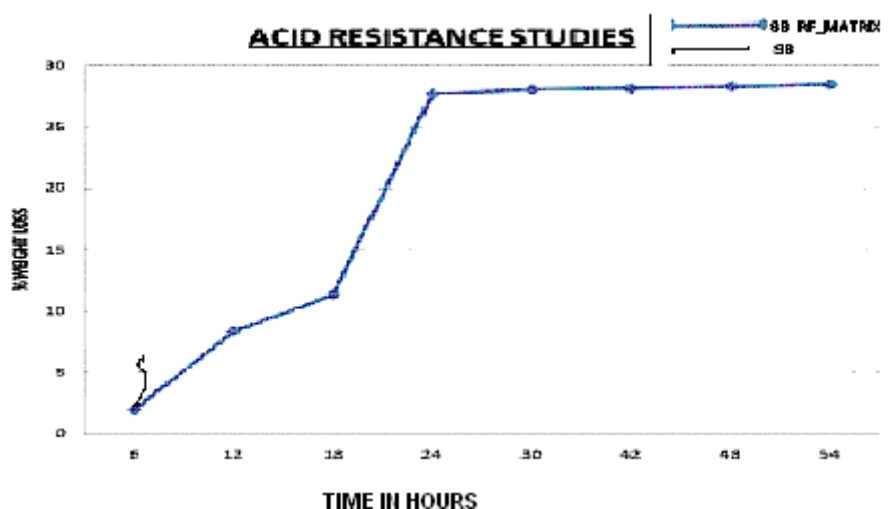


Fig. 5: Acid resistance studies

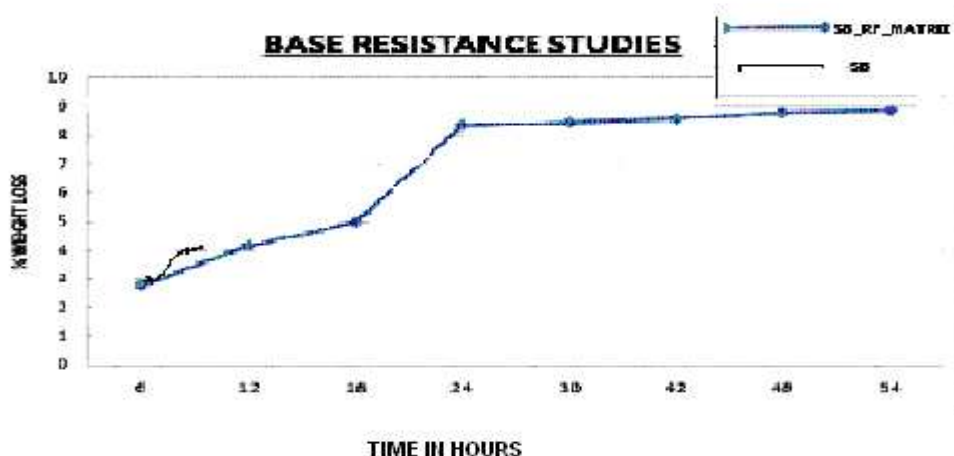


Fig.6: Base resistance studies

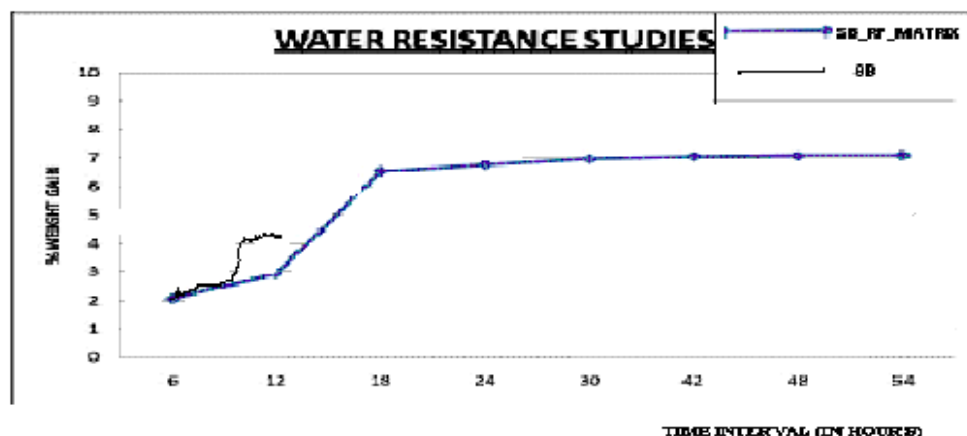


Fig. 7: Water resistance studies

Biodegradation studies

As is evident from table 2.1 that biodegradation of the crosslinked matrix takes place under anaerobic conditions. It has been observed that there was a continuous decrease in weight of the sample and sample was found totally biodegraded after time interval of 60 days. The mechanism of the biodegradation can be explained through the following anaerobic oxidation



Table 2.1 Biodegradation studies of R-F Cross linked soy protein matrix vis-a-vis soy matrix

S. No.	Initial weight	After 7 days	After 14 days	After 21 days	After 28 days	After 35 days	After 42 days	After 49 days	After 56 days
Natural matrix	1.0 gm	.02 gm	----	----	----	----	----	----	----
Cross-linked matrix	1.6 gm	1.3 gm	1.05 gm	0.92 gm	0.64 gm	0.54 gm	0.31 gm	0.13 gm	-----

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