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Biodegradable composites from black gram and resorcinol-formaldehyde-Synthesis, characterization and evaluation of physical properties

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ABSTRACT

This research paper deals with the synthesis of biodegradable composites of black gram with resorcinol-formaldehyde as crosslinker. Acid, base and water resistance properties of the composites were also done. Biodegradation studies of the samples were done using soil composting method. Different stages of biodegradation were characterized using scanning electron microscopic studies.

Keywords: Composite, biodegradation, SEM, acid-base resistance studies.

INTRODUCTION

Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. As a result of growing awareness of the interconnectivity of global environmental factors, principles of sustainability, industrial ecology, eco-efficiency, green chemistry and engineering are being integrated into the development of the next generation of materials, products and processes [1–5]. The depletion of petroleum resources coupled with increasing environmental regulations are acting synergistically to provide the impetus for new materials and products that are compatible with the environment and independent of fossil fuels. The combination of bio-based polymer and natural fibres are expected to solve this problem [7-13]. Hence, many studies on natural fiber reinforced plastics have been reported. Composite materials, especially “green composites,” fit well into this new paradigm shift.

Biodegradable polymers are designed to degrade upon disposal by the action of micro organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, and lactic acid. The need to create alternative biodegradable water-soluble polymers for down-the-drain products such as detergents and cosmetics has taken on increasing importance. Consumers have, however, so far attached little or no added value to the property of biodegradability, forcing industry to compete head-to-head on a cost performance basis with existing familiar products. In addition, no suitable infrastructure for the disposal of biodegradable materials exists as yet. Most of the commodity polymers, which constitute 80% of the polymer market, are based on nonrenewable petroleum, whose price is unstable and are non-biodegradable. While producing fossil based materials such as petroleum from biomass takes 106 years, only about to 1-10 years are required for the conversion of CO_2 into biomass, through plants. In order to produce fully renewable and biodegradable nano-composites, both the polymeric matrix and the reinforcement must be derived from renewable resources. Accordingly, attempts have been made to produce “new polymers”, including sustainable polymers, using renewable natural resources, where the rate of CO_2 fixation equals its consumption rate [14].

Bismarck *et al*., [15] found that biodegradability of a composite depends mainly on the chemical structure of the polymer matrix, i.e. the degree of cross linking. Petricca *et al.*, [16] have synthesized the Hydroxyapatite-biodegradable polymer composites were synthesized by a colloidal non-aqueous chemical precipitation technique at room temperature. Mehta *et al*., [17] reported the biocomposites made with various natural fibers including, big blue stem grass, jute, and industrial hemp. By combining different natural fibers in varying mass fractions, hybrid biocomposites were made using this process. Sam *et al*., [18] observed that the tensile strength and elongation at break of ferrite filled natural rubber composites were found to decrease with the increase of both types carbon black loading. Liu *et al*., [19] reported the effects of fibre content, diameter, surface modification and arrangement forms on the biodegradability of Poly(butylene succinate) (PBS)/jutecomposites by compost-soil burial test. Nakagaito and Yano [20] found out a new method to obtain composites of phenolic resin reinforced with microfibrillated cellulose with a wide fiber content was established and the mechanical properties were evaluated by tensile test. Lee *et al*., [21] have investigated that the natural polymers and their derivatives are attracting increasing interest as promising biodegradable materials that can meet the environmental and recycling demands from society.

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

MATERIALS AND METHODS

Materials

Petroleum ether (60-80^0) (Merck), methanol (Merck), resorcinol (Merck), formaldehyde (Merck), sodium hydroxide (S. D. Fine), HCl (S. D. Fine) were used as received. Black grams 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.

Synthesis

Preparation of biodegradable matrix

Black grams were converted in to a fine powder (400 gm) and the powdered material was kept for cold percolation in petroleum ether (60-70^0) 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 40^0C 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

Synthesis of crosslinker

Resorcinol-Formaldehyde was prepared as per the method described earlier [22].

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 70^0 for about 30 minutes. The pre-cured mixture was transferred into a metallic 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 90^0C for 60 minutes under 178 KN force.

Preparation of biodegradable composite

Pre-cured biodegradable matrix crosslinked with resorcinol-formaldehyde was transferred to the metallic die and was kept as such at ambient temperature for about 24 hours followed by hot pressing at 90^{θ} for 60 minutes in 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 hours.

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 hours.

Water up-take resistance studies

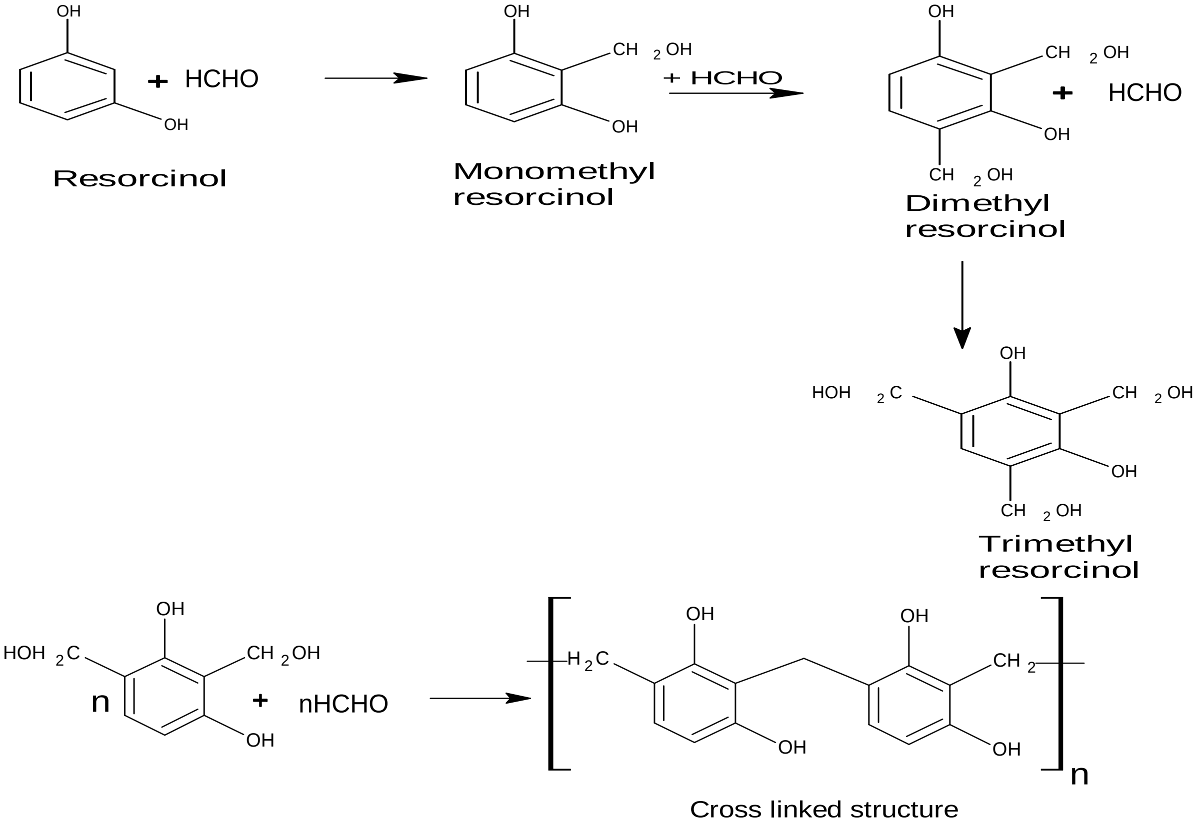
Water uptake resistance study of the samples was carried out by putting a definite amount of each sample in a definite volume of distilled water and weight of each sample was taken after every 6 hours.

RESULTS AND DISCUSSION

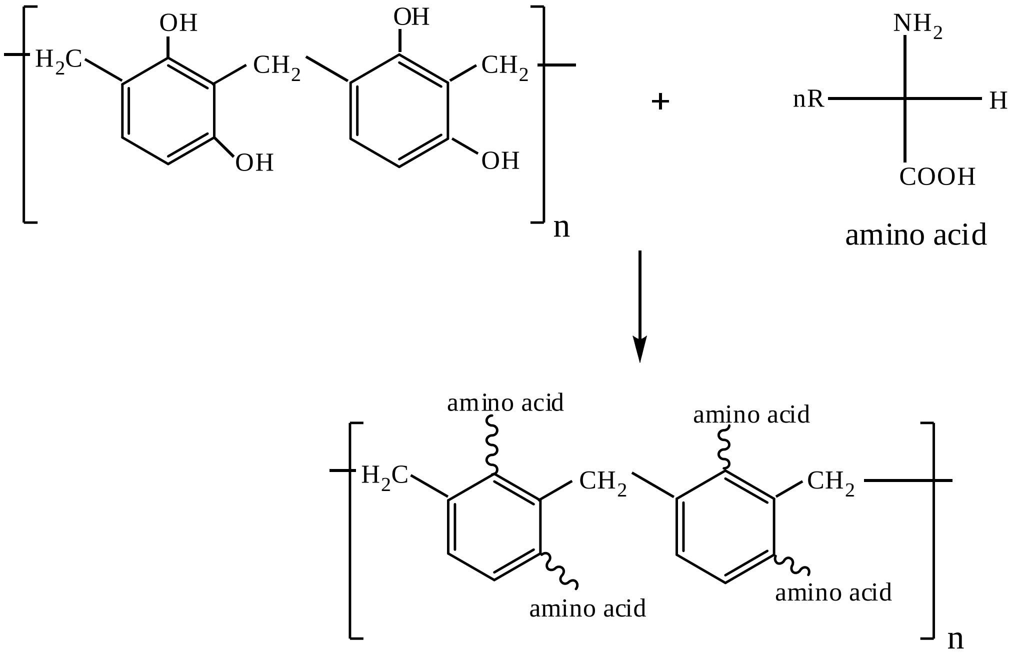
Amount of the purified matrix powder obtained after extraction with different solvents was found to be 55.6%.

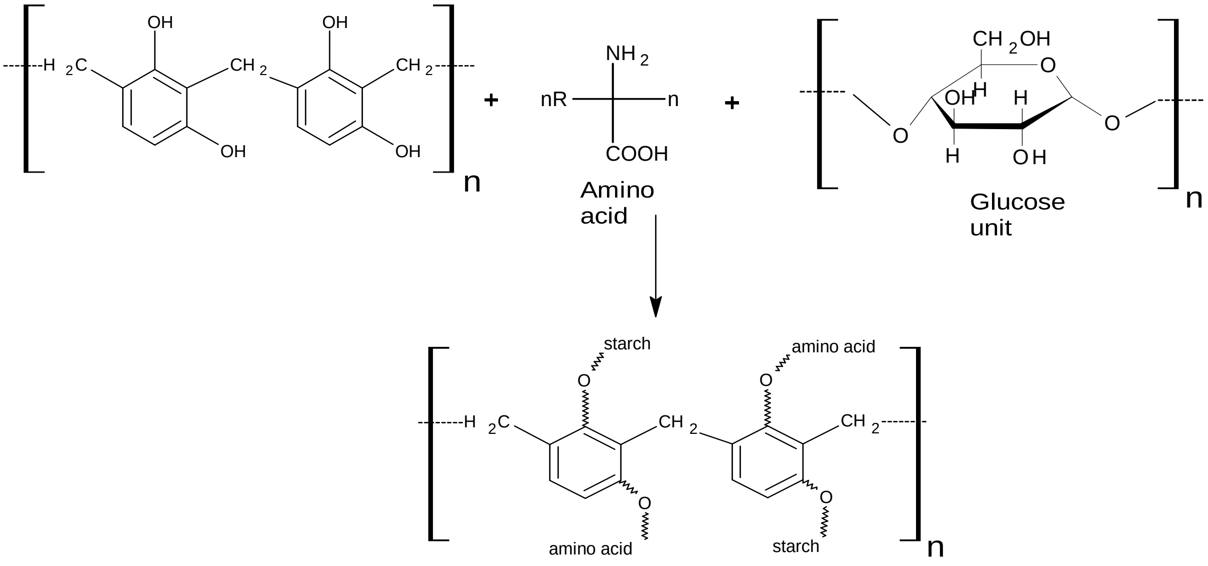
Amino groups and hydroxyl groups present in the natural matrix are the active sites where crosslinking with the resorcinol-formaldehyde takes place during precuring and curing process which can be presented through the following mechanism:

Formaldehyde-Resorcinol Resin:



Cross-linking with Natural Matrix:





Characterization

SEM studies

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 it's breaking down due to biodegradation at Stage-I, Stage-II and Stage-III could be clearly visualized from SEM studies. Moreover, SEM studies clearly exhibited marked differences between the SEMs of crosslinked matrix having smooth homogenous surface and that of biodegradation matrices of different stages possessing rough heterogeneous surfaces (Figures 1 - 4).

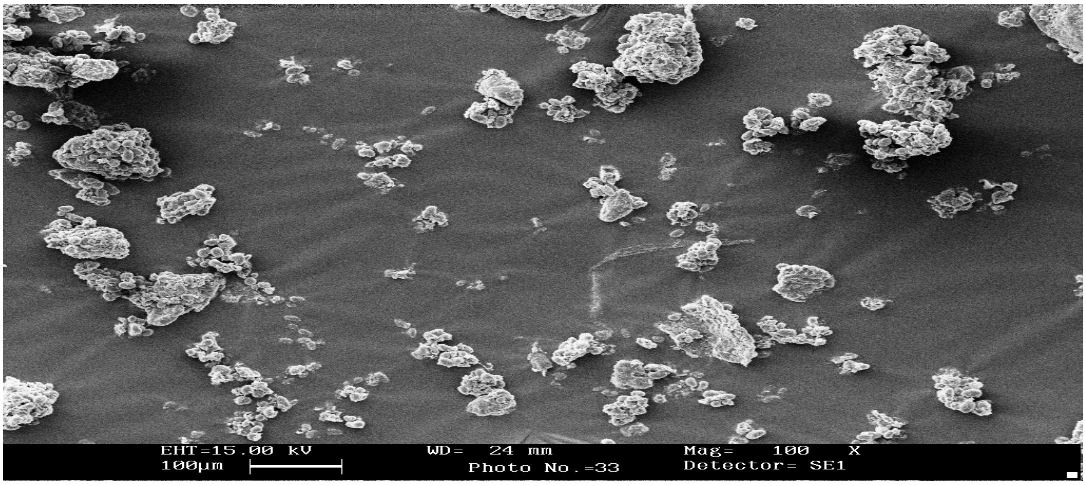


Fig. 1: SEM of black gram matrix

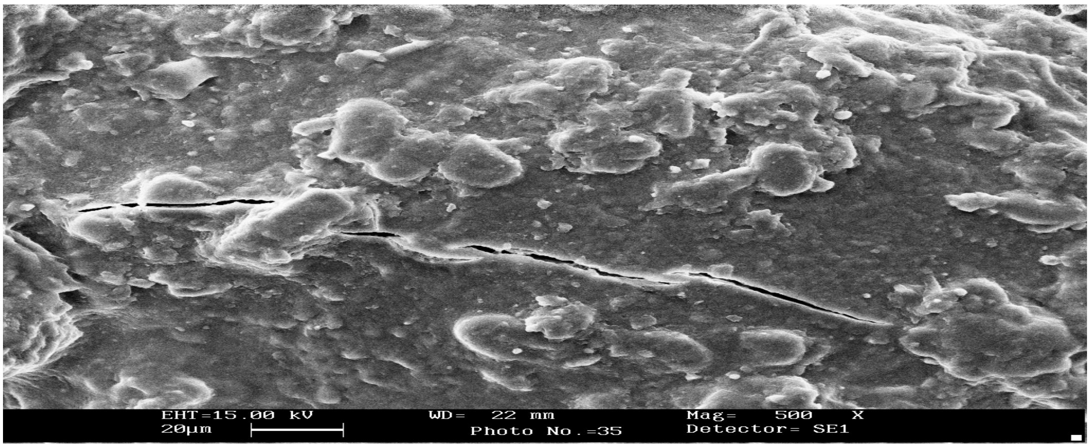


Fig.2: SEM of Biodegradation stage-I

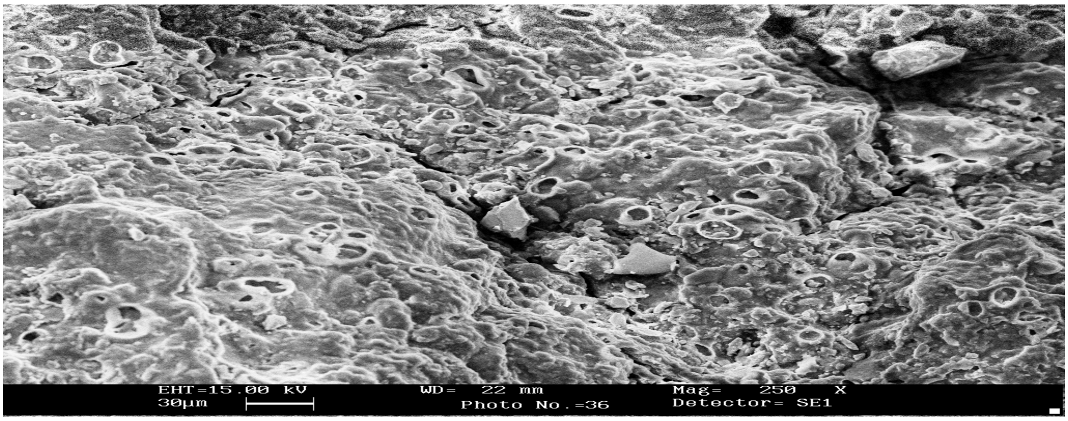


Fig. 3: SEM of Biodegradation stage-II

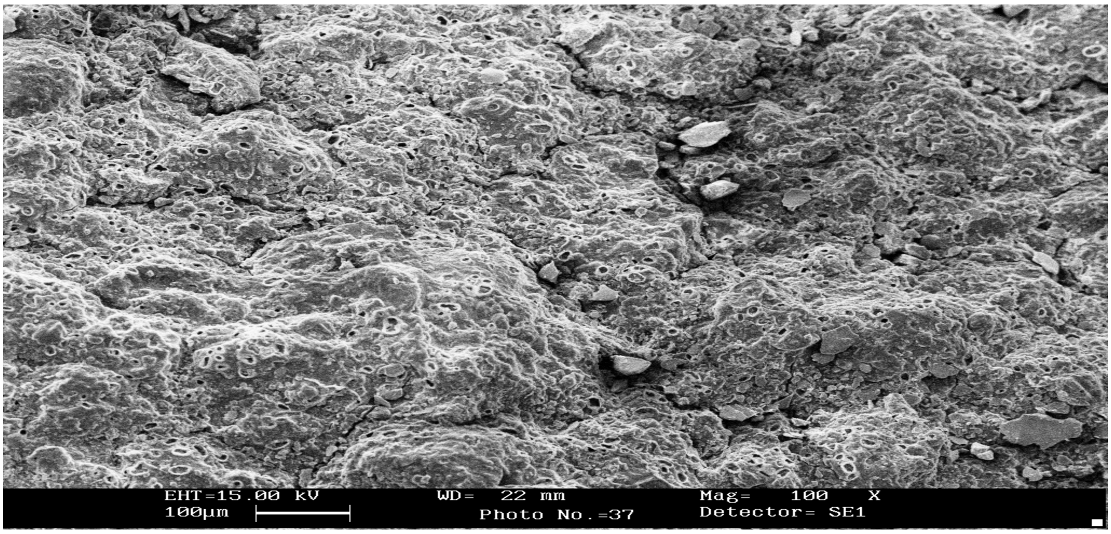


Fig. 4: SEM of Biodegradation stage-III

Acid base 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 with in 6 hours whereas 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 R-F to the natural matrix containing hydroxyl groups and amino groups undergo condensation reaction with the removal of water molecules during precuring and curing processes. Thereby resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the acid attack.

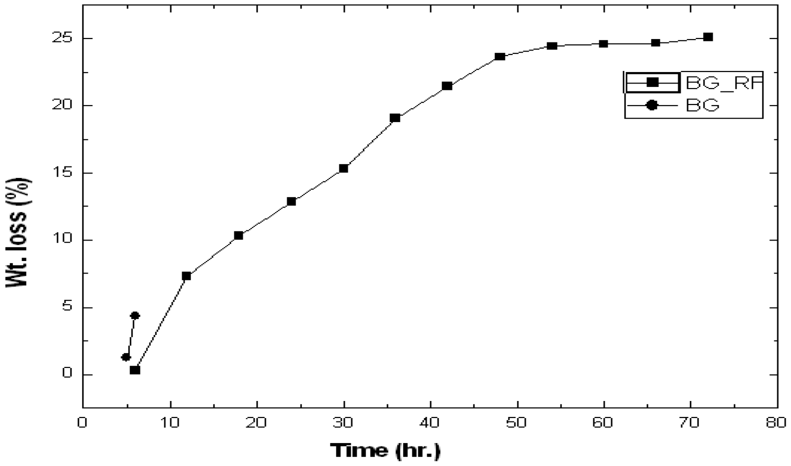


Fig. 5: Acid resistance studies

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 uncrosslinked matrix got dis-integrated with in 6 hours whereas 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 to the natural matrix containing hydroxyl groups and amino groups undergo condensation reaction with the removal of water molecules during precuring and curing processes, thereby resulting in the formation of three dimensional network containing covalent bonds. Thus providing resistance towards the base attack.

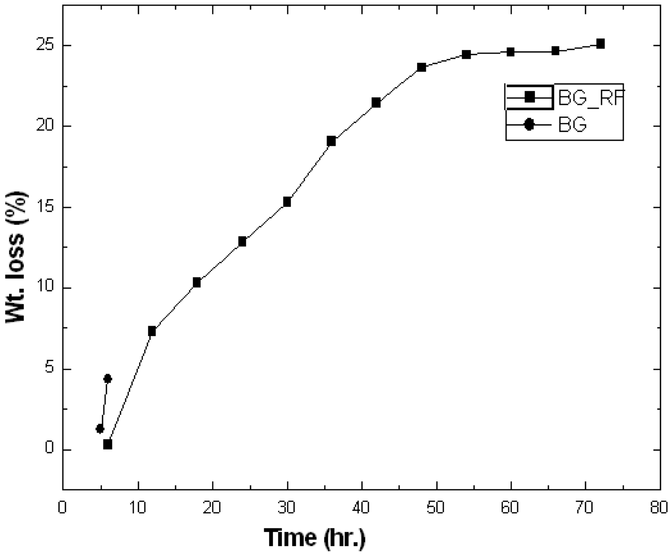


Fig. 6: Base resistance studies

Water resistance studies

As is evident from Fig. 7 that natural matrix after crosslinking with resorcinol-formaldehyde got a lot of resistance towards water uptake, whereas uncrosslinked matrix was found to be unstable in water. Though there was a constant increase in water uptake by the crosslinked matrix up to 40 hours (24%) but afterwards rate of water uptake was found to be almost constant and crosslinked matrix was found to be stable up to 72 hours. This could be explained on the basis that addition of resorcinol-formaldehyde to the natural matrix containing hydroxyl groups and amino group undergo condensation reaction with the removal of water molecules during precuring and curing processes, thereby resulting in the formation of three dimensional network containing covalent bonds. Thus, providing resistance towards the water attack.

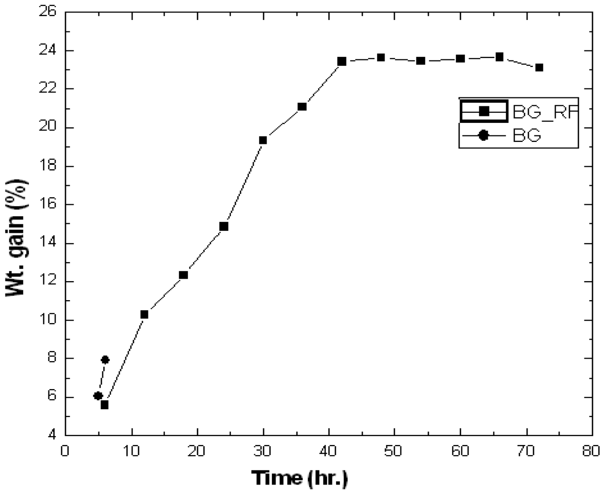


Fig. 7: Water resistance studies

Biodegradation studies

As is evident from Table 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.

$$\text{Protein} \xrightarrow{\text{Anaerobic Oxidation}} CH_4 + CO_2 + \text{Other lower hydrocarbons} + \text{Oxides of nitrogen } NO_x$$

Table 1: Biodegradation studies of R-F Cross linked Black Gram matrix

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	0.6	-	-	-	-	-	-	-	-
Cross-linked matrix	1.22	1.10	0.95	0.89	0.73	0.54	0.38	0.34	0.26	-

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 crosslinked matrix was found to be highly biodegradable in nature along with resistance towards acid and base attack. Moreover, this crosslinked 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 is of great importance from technology point of view.

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