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ACRYLIC ACID/CITRIC ACID BASED POLYMERICHYDROGEL: SYNTHESIS, CHARACTERISATION AND APPLICATIONS

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ABSTRACT

Citric acid based polyester hydrogel network cross-linked with acrylic acid was synthesized by the melt polycondensation method without adding a catalyst. The structure of the polymeric hydrogel was characterized by Fourier transform infrared spectroscopy (FT-IR) and 1H NMR spectral studies. The surface morphology of the synthesized hydrogel was studied. The influence of the swelling behavior of polymer hydrogel in water was studied and the antibacterial activity of the synthesised hydrogel was evaluated against Staphylococcus aureus and Escherichia coli microorganisms. Degradation studies were evaluated by soil burial test.

KEYWORDS*: Citric acid, Acrylic acid, Hydrogel, Antimicrobial activity and Soil Burial.*

INTRODUCTION

Hydrogels have the notable property of a three dimensional network with crosslinked polymers as it is hydrophilic in nature which can absorb large amounts of water but are insoluble in any solvent. The high swelling nature of hydrogels is due to the presence of hydrophilic groups, chain flexibility and large surface area among the polymer chains. pHsensitive hydrogels can have ability to change absorption behavior and volume due to ionization of functional groups [1, 2, 3]. Recently Hydrogels found an application in designing biodegradable food packaging materials [4].
Acrylic acid (AA) based hydrogels have distinct applications in the biomedical field, since the AA can be formulated at different concentrations. It can be fabricated into different sizes. It has wide application in controlled drug delivery systems [5].

Citric acid (CA) is one of the non-toxic multifunctional monomers thatare involved in the Krebs cycle and it has been used for the preparation of polyester as it possesses active carboxyl groups. CA derivatives have distinct properties in balancing hydrophilicity, enhancing biocompatibility and actively participate in cross linking reactions.

Based on this view, we aimed to report on the preparation of hydrogel using Citric acid based polyesters and

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Acrylic acid. The swelling studies, soil degradation and antibacterial activity of the synthesized hydrogel were evaluated.

MATERIALS

Acrylic acid (AA), Citric acid (CA), Sebacic acid (SA), Diethylene glycol (DEG) of reagent grade were consumed from Sigma Aldrichand were used without further purification.

EXPERIMENTAL METHODS:

SYNTHESIS OF PRE-POLYMER (PCSD):

The pre-polyester was first synthesized by the melt polycondensation method without adding any catalyst**.** The reaction was carried out by taking equimolar amount of reactants such asCitric acid (99% purity), Diethylene glycol (99% purity) and Sebacic acid. Calculated molar amounts of citric acid (0.025 mol-4.8g) , Diethylene glycol (0.025-2.65g) and Sebacic acid (0.025 mol-5.05g) were weighed and melted in a three neck round bottomed flask fitted with a mechanical stirrer [6] . The mixture was stirred for almost one hour at 140 ° C. The Completion of the reaction was observed by the formation of a white-colored sticky gel-like compound of PCSD.

SYNTHESIS OF POLYMERIC HYDROGEL (PACSD):

Acrylic acid (0.025 mol-1.7mL) was added to pre-polymer PACSD at 140° C with constant stirring for 2 hour. The formation of glassy gel implies the completion of the reaction. The un reacted monomers are eliminated by soaking the obtained gel product in distilled water for 24 hours. The polymer hydrogel PACSD was dried in an oven at 200 ° C for 24 hours.

CHARACTERISATION

FOURIER TRANSFORM INFRA-RED SPECTRA (FT-IR)

The functional groups present in PACSD hydrogel can be identified with KBr using a Perkin Elmer IR Spectrometer at the scan range of 400-4000cm^{-1}

^{1}H NMR SPECTROSCOPY(^{1}H-NMR)

The^{1}H NMR spectra of the synthesized Pre-polyester (PCSD) was determined on AV 500 MHz Bruker D8 Advance III Spectrometer by using d6-DMSO solvent.

SCANNING ELECTRON MICROSCOPY (SEM)

The structure and morphology of polymeric hydrogel was studied using a HITACHI S-3000 scanning electron microscope (SEM).

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SWELLING STUDIES

The Swelling studies of the polymeric hydrogel were measured using distilled water. The percentage swelling of the hydrogel was measured in distilled water. The dried gel was pre-weighted to know the initial mass (W_0) suspended in the water. The hydrogel was removed from the water at different time intervals. Blotted dried with filter paper and weighed (Ws). The dried polymeric hydrogel was weighed for dry mass (W_d). The Swelling (%) can be calculated by the formula: (W_d-Ws/Ws) x 100

ANTIBACTERIAL STUDIES

The antibacterial activity of the synthesized polymeric Hydrogel was carried by agar disc diffusion method on Muller Hinton agar (MHA) method. The MHA medium is poured into the petri plate. After the medium was solidified, the inoculums were spread on the solid plates with sterile swabs moistened with the bacterial suspension. The disc was placed in MHA plates and 20 µl of hydrogel (Concentration: 1000µg, 750µg and 500 µg) were placed in the disc. The plates were incubated at 37 ºC for 24 hours. Then the antimicrobial activity of the prepared hydrogel was determined by evaluating the zone of inhibition [7].

SOIL BURIAL TEST

The Solid polymeric hydrogel was placed for soil burial test in a pot containing enriched soil inoculum. Solid hydrogel was removed from the soil for selected time periods and the percentage degradation of the polymeric hydrogel was calculated [8]. The percentage degradation of the polyester can be calculated by the formula = [Mt- Mo/Mo] X 100, Where, Mo = Initial mass of the sample Mt = Final mass of the sample (after removing from the soil).

RESULTS AND DISCUSSION

FOURIER-TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

The Infrared spectrum of synthesized polymeric Hydrogel (PACSD) is shown in the fig.1. The peak at 1714 cm^{-1} confirms the presence of carbonyl group (-C=O) due to ester formation. The C-O-C stretching vibrations of ester groups can be identified by the appearance of a peak at 1179 cm^{-1}. A broad peak at 3431cm^{-1} confirms the presence of a hydrogen-bonded hydroxyl group. A shoulder peak at 2951 cm^{-1} and peak at 1399 cm^{-1} which correspond to the aliphatic –CH2– stretching and bending bands, respectively.

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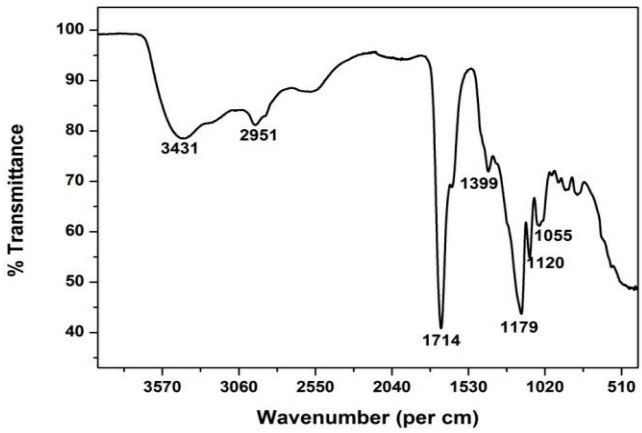

FIGURE 1- FT-IR SPECTRA OF POLYMERIC HYDROGEL (PACSD)

^{1}H NMR SPECTRAL ANALYSIS

^{1}H NMR spectra of synthesized pre-polymer (PCSD) is shown in the fig.2. The multiplet that appeared at 2.762-2.756 ppm were attributed to the methylene protons of citric acid. The multiplet that located at 3.356 ppm were due to protons in $–OCH_2CH_2$- group from DEG [1]. the multiplet at 1.58 - 1.264 ppm were due to the central $–CH_2$ group of sebacic acid. The multiplet located at 2.508-2.504 ppm were attributed to the protons of $–CH_2CO$ group.

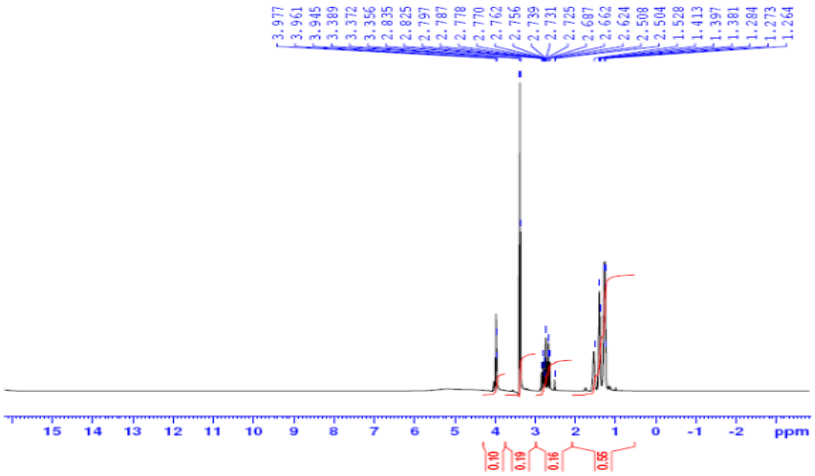

FIGURE 2- ^{1}H NMR SPECTRUM OF PRE-POLYMER (PCSD)

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SCANNING ELECTRON MICROSCOPY (SEM)

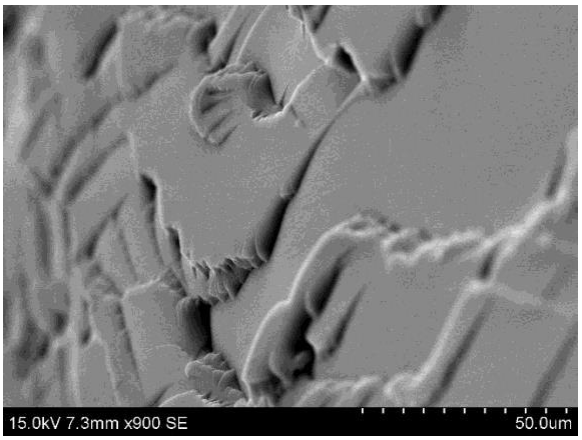

FIGURE 3-. SEM image of PACSD

The surface morphology of the synthesized polymeric hydrogel was studied using a Scanning electron microscope. The appearance of the surface was irregular smooth, which seems to exhibit a high adsorption rate of solvent. It is worth investigating the swelling behavior of hydrogel with respect to environmental stimuli, which are important factors for their applications [9]. It is noticeable that irregular pores accommodate the absorption fluid easily on the surface which is suitable for potential application in bio-medical field. It is also notable that Acrylic acid based polyester hydrogel exhibits strong interaction within the polymer matrix.

ANTIBACTERIAL ACTIVITY

The antibacterial activity of different ratios of PACSD was examined against Staphylococcus aureus and Escherichia coli microorganisms. The clear inhibition zone around the polymeric hydrogel indicates better antibacterial activity. The results indicate that the PACSD hydrogel exhibited a greater decrease in bacterial growth. With this mind, the outcome of the study is a major step towards sustainable management of bacterial contamination utilizing active packaging. The antibacterial activity of the hydrogel is presented in the table 1.

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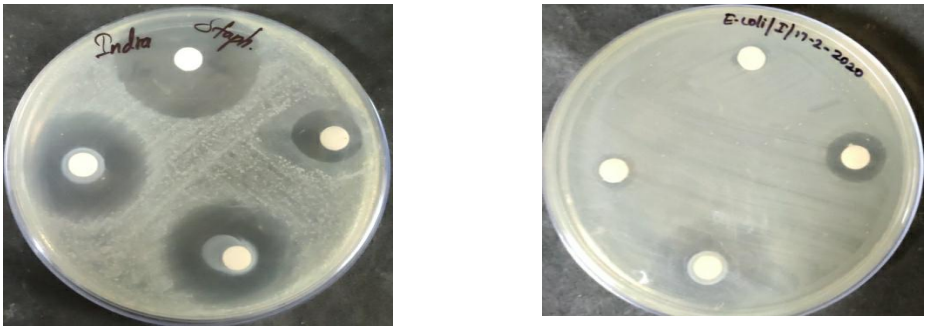
TABLE-1 ANTIBACTERIAL ACTIVITY OF HYDROGEL (PACSD)

Organisms	Zone of Inhibition (mm)			Antibiotic (1mg/ml)
	Sample (1mg/ml)			
	1000	750	500	
Staphylococcus aureus	29	27	26	23
E.coli	10	8	8	15



Staphylococcus aureus ***E.coli***

FIGURE 4- IMAGES OF ZONE OF INHIBITION

SOIL BURIAL TEST

The soil degradability of the hydrogel was evaluated by gravimetric method by inserting the small pieces of dried hydrogel into the soil with frequent watering the soil. The samples were removed from the soil at a regular interval of time period. In the beginning, degradation took place at a slower rate and increased gradually after 5 days and is shown in the fig.5. In soil degradation, the degradation takes place predominantly on the surface of the polymer which is expected to enhance the amorphous nature of the polymer matrix as it acts as a soft segment.

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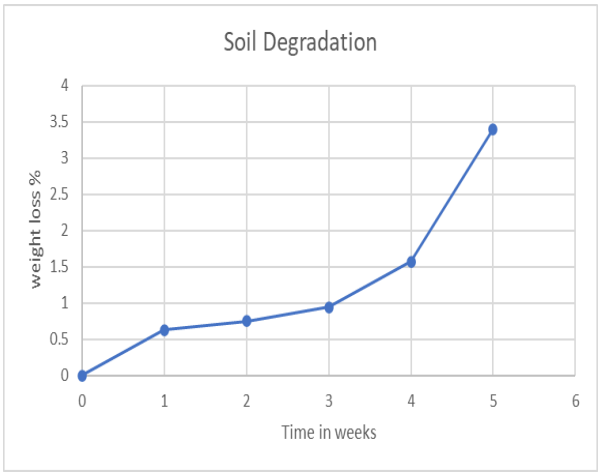

FIGURE 5- SOIL DEGRADABILITY OF POLYMERIC HYDROGEL

SWELLING STUDIES

The polymer solvent compatibility and degree of cross linking plays an important role for the study of swelling behavior of any polymer network. The presence of hydrophilic groups and increase in cross linking density between citric acid based polyester and acrylic acid in the synthesized polymeric hydrogel creates a better swelling behavior in water. The Fig. 6. depicted that there is gradual increase in swelling frequently with a period of time.

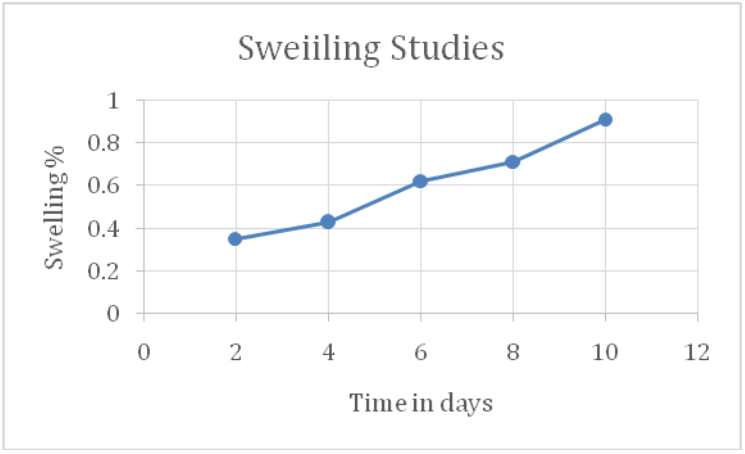

FIGURE 6- SWELLING STUDIES OF THE PREPARED HYDROGEL

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CONCLUSION

Acrylic acid/citric acid-based polymeric hydrogel with acrylic acid was synthesized by melt polycondensation method without adding catalyst. Spectral techniques such as FT-IR, ^{1}H NMR and SEM analysis were studied. The presence of citric acid monomer provides a greater swelling behavior in hydrogel. The surface morphologies of hydrogel exhibit a perfect homogeneity. The swelling studies show that the synthesized hydrogel exhibited higher swelling behavior.The anti-bacterial study is towards providing a sustainable management of bacterial contamination utilizing active packaging. Since it exhibits better degrading property, it can be used in mulching films in Agriculture. Hence, synthesized hydrogel will be a great benefit in food packaging industry, agriculture, controlled release of drugs to pH-sensitive human bodies.

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