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Research Article

Ageing Characteristics Of Novel Polyesters Based On Rice Bran Oil

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Abstract

Polyesters are synthesised from acrylated epoxidised rice bran oil resin with monomers such as vinyl acetate, n-vinyl 2-pyrrolidone, methyl acrylate and benzoyl peroxide as the initiator. The ageing characteristics of the newly prepared polyesters have been studied. These studies revealed that ageing characteristics of vinyl acetate and vinyl pyrrolidone based polyesters shows very good hydrolytic stability and thermally more stable than methyl acrylate based polyesters. The antimicrobial activity of polyester based on methyl acrylate is comparatively maximum zone of inhibition than the other polyesters.

Keywords

Rice bran oil, acrylated epoxidised rice bran oil resin, vinyl acetate, n-vinyl 2-pyrrolidone, methyl acrylate, ageing, biomedical applications.

1.INTRODUCTION

Traditionally, polymers have been derived from petroleum, polymers are widely used for technical purposes. Depending in their usage area, it should be expected that they exhibit some specific properties such as thermal stability, flexibility, resistance to chemicals, biocompatibility and biodegradability, adhesion to metallic substances, gas permeability, electrical conductivity and non-flammability [1].

Vegetable oils are most important renewable resources and easily occurring in nature [2]. Vegetable oils are triglycerides which contain different fatty acids such as oleic acid, linolenic acid, linoleic acid, stearic acid and palmitic acid [3]. Some example of these renewable resources are polysaccharides such as cellulose, starch and glycerol esters of fats and oils [4]. Rice bran oil is the oil extracted from hard outer layer of rice that has unique content and rich in bioactive components. Main components of rice bran oil is γ-oryzanol [5], which is a mixture of the ferulic acid esters and alcohols triterphene [6]. Gamma oryzanol is a fat soluble compound having sterols and fatty acid held by ester bond, and this bond breakage requires esterase or lipase enzymes [7].

The most important aspect of synthesizing biodegradable polymers relates into their ability to undergo degradation within the biosphere on coming into contact with micro-organisms, enzymes or under natural environmental conditions. The main problem associated with designing biodegradable polymers is the optimization of their chemical, physical and other mechanical properties as well as their biodegradability [4, 8].

Ageing is most important effect that limits the lifetime of plastics. It is slow and irreversibly changes in properties of polymers under the action of light, heat or chemicals such as acids, alkalis and some salts [9]. Biodegradation takes place through the action of enzymes and or chemical deterioration associated with living organisms. This event occurs in two steps. The first one is the fragmentation of the polymers into lower molecular mass species by means of either abiotic reactions, i.e. oxidation, photo degradation or hydrolysis, or biotic reactions, i.e. degradation by microorganisms. This is followed by bioassimilation of the polymer fragments by microorganisms and their mineralization.

Biodegradability depends not only on the origin of the polymer but also on its chemical structures and the environmental degrading conditions. Enzymes and microorganisms can degrade the low molecular weight oligomers. Biodegradable polymers are used in the medicine, packaging and agriculture. Bio-polyesters are widely used in tissue engineering because they have good strength and an adjustable degradation speed [10].

Bio-polyesters can be interpreted as polyesters of strictly biological origin. Bio-polyesters have been synthesized by biological means, for instance by enzyme-catalyzed polymerization reactions. Moreover, there are hybrids between these two strict definitions of polyesters. For example, monomer synthesis of poly (lactic acid) by a biological process in which lactic acid is produced microbially by the fermentation of a renewable, polysaccharide-based resource. Lactic acid is subsequently polymerized chemically into PLA by a condensation reaction.

Poly (lactic acid) PLA and poly (glycolic acid) PGA are aliphatic polyesters that readily degrade by chemically-induced hydrolysis under physiological conditions. Therefore, PLA and PGA and their respective copolymers have found broad applications as bioresorbable sutures, implants and drug delivery systems [11].

2. MATERIALS AND METHODS

2.1 Materials

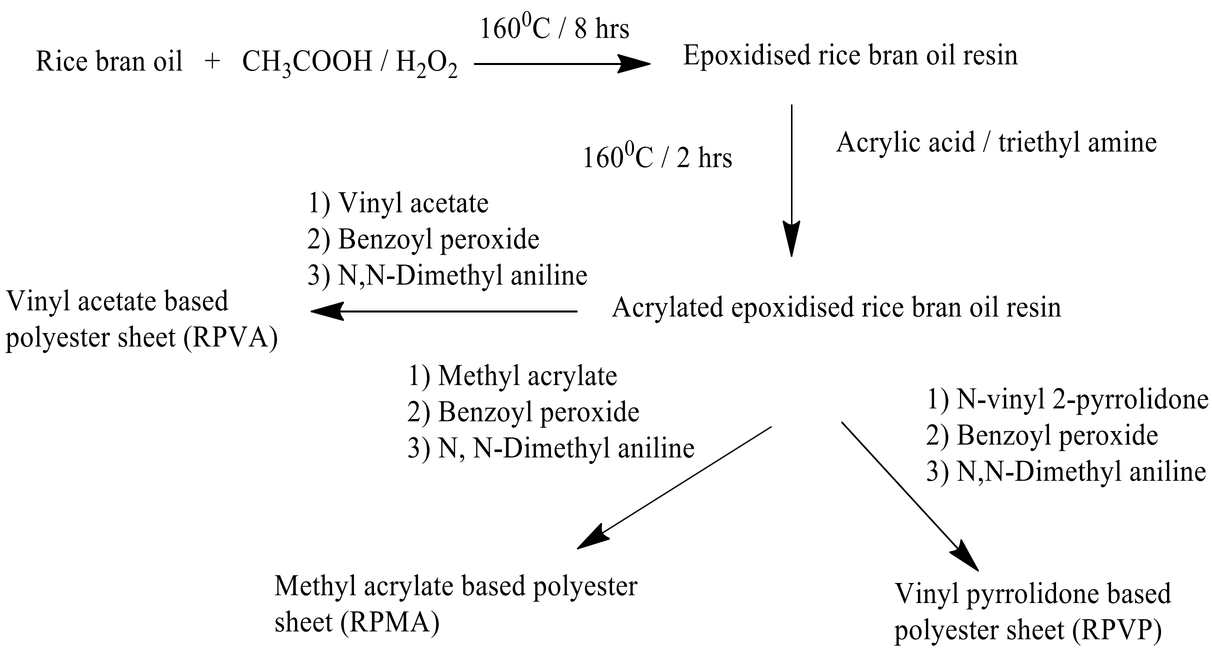
Table 1 Chemicals used for the synthesis of crosslinked bio-polyesters

Chemicals	Received
Rice bran oil	Local market
Acrylic acid	Sigma-Aldrich
Triethylamine	Sigma-Aldrich
N,N-dimethylaniline	E. Merck

Benzoyl peroxide	E. Merck
Methyl acrylate	Sigma-Aldrich
Vinyl acetate	Sigma-Aldrich
n-vinyl 2-pyrrolidone	Sigma-Aldrich

2.2 Preparation of crosslinked bio-polyesters

Crosslinked polyester sheets (RP30VA, RP30MA, RP30VP) were synthesized by the acrylated epoxidised rice bran oil resin in the presence of benzoyl peroxide was used as the initiator, N,N-dimethylaniline as the accelerator and 30% vinyl acetate as the monomer. The above mixture was stirred well and poured into an clean silicon oil spreaded glass plate. The mixture poured glass plate was cured in vacuum oven at 160^0C for 8 h. The same procedure was followed for 30% methyl acrylate and 30% vinyl pyrrolidone monomers.



Scheme 1. Synthesis of crosslinked polyesters

2.3 Ageing characteristics of polyesters

The studies on the stability of polyesters under various ageing conditions were carried out using the general guidelines of ASTM standards. The conditioning as well as specimen preparation was followed using appropriate procedure discussed in the following sections. The determination of stability was mainly carried out by weight loss estimation. Neat polyester sheets were used for the sample preparation.

2.3.1 Determination of weight loss in hydrolytic conditions

The weight loss of crosslinked polyester sheets (3 × 1 × 0.1 cm) were immersed separately in the media (100 ml) water, alcohol and salt solution (1N sodium chloride) for a period of 2 months under ambient conditions. The medium was changed and fresh medium was added at an interval of one week. The sheets were removed at the end of the exposure, allowed to dried in vacuum oven and then weighed.

2.3.2 Determination of weight loss in organic solvents

The solubility of polyesters was determined in organic solvents such as chloroform, toluene, acetone, benzene, dimethyl acetamide (DMA). The prepared polyester sheets were conditioned and weighed before exposing to solvent. The sample was immersed in solvent in an air-tight container at 23 ± 1^0C for 2 months. The solvent was changed and fresh solvent was added at the interval of one week. The polyester sheets were removed after 2 months dried in vacuum oven and weighed.

2.3.3 Determination of weight loss in hostile chemical environment

The degradation of polyesters in hostile acidic (1N HCl), basic (1N NaOH) and oxidation medium (H_2O_2) was studied. The medium was changed and the fresh medium was added at the interval of one week. The polyester sheets were removed at the end of exposure, dried in vacuum oven and then weighed.

2.3.4. Determination of stability under thermal ageing

The stability of polyesters under prolonged exposure in thermal environment (thermal ageing) was evaluated. The newly prepared polyester sheets were kept in an oven at 60 ± 2^0C. Then the sheets were removed from the oven, cooled to ambient temperature and weighed.

2.3.5 Soil burial test

Biodegradation of the polyesters prepared from rice bran oil and canola oil were studied by soil burial test. For soil burial test, the replicate pieces of the prepared polyester sheets (5×3 cm) were buried in the garden soil at the depth of 30 cm from the ground surface for 2 months, inoculated with the sewage sludge having ability to adhere and degrade the polymer film. After 2 months, the sheets were removed and gently washed with distilled water to remove attached soil and dust after being dried vacuum oven[12]. The extent of degradation was examined by measuring the weight loss and surface observation.

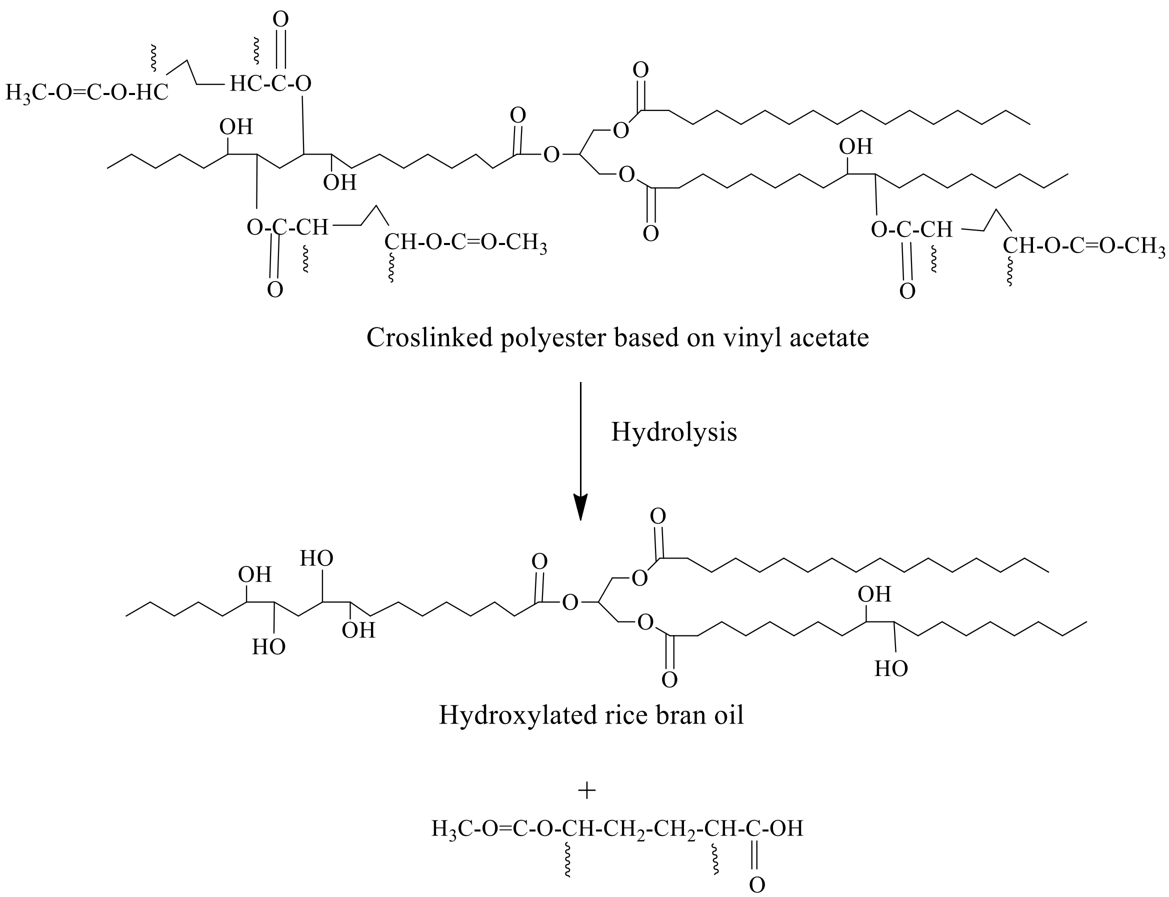
2.3.6 Evaluation of performance under antimicrobial activity

Antimicrobial activity was evaluated by agar diffusion method. The test was done in triplicates. Amikacin of positive control was used for antimicrobial activity testing. The microbial strains used for bacterial adhesion study were gram negative bacteria such as *Serratia marcens* and gram positive bacteria such as *Bacillus subtilis*. The diameters of zones are measured to the nearest millimeter with vernier calipers or a thin transparent millimeter scale.

3. RESULTS AND DISCUSSIONS

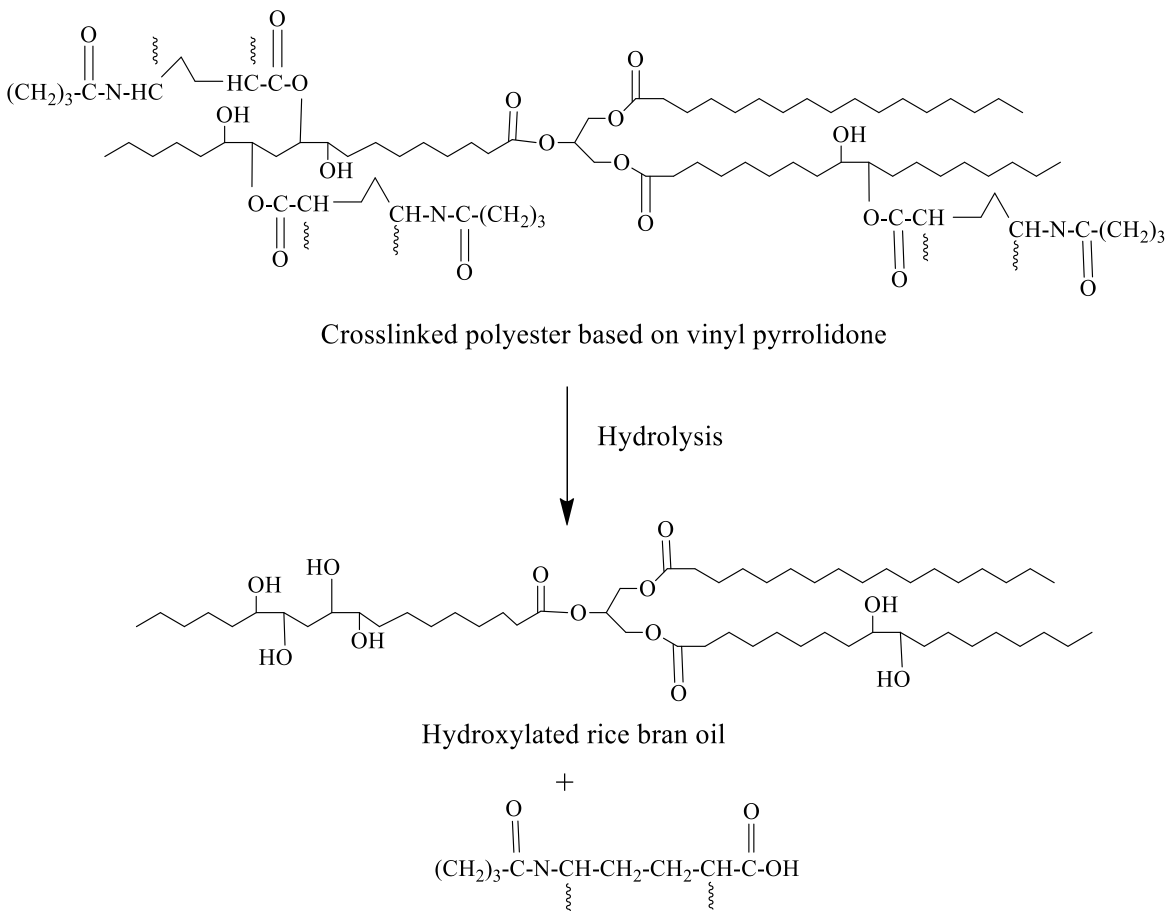
3.1 Hydrolytic degradation of polyesters

There is small weight loss in newly synthesised high crosslink density of the polyesters such as vinyl acetate, n-vinyl 2-pyrrolidone. However, a maximum weight loss is observed in the low crosslink density of the polyester such as methyl acrylate in water, ethanol and salt solution. The hydrolytic attack on the ester linkage in the triglyceride unit with the liberation of carboxyl terminated polyester fragment.



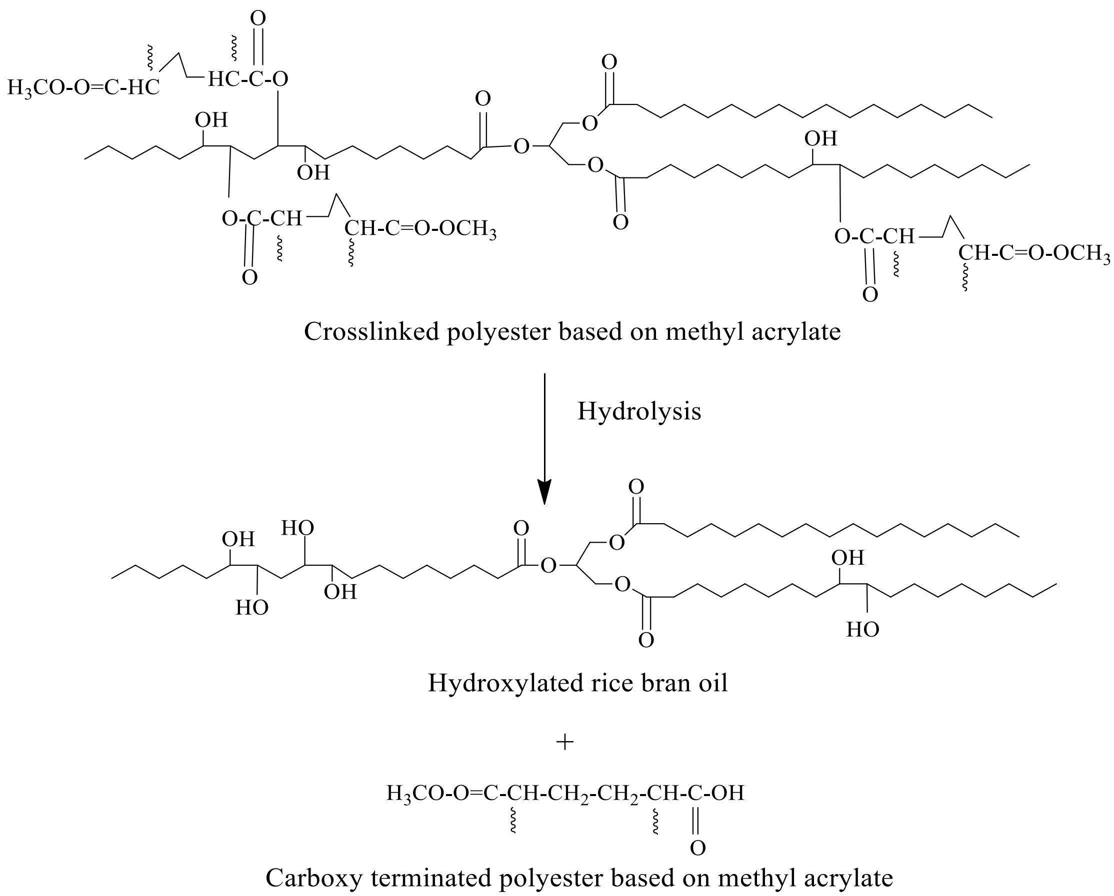
Carboxy terminated polyester based on vinyl acetate

Scheme 2. Hydrolytic degradation of polyester based on vinyl acetate



Carboxy terminated polyester based on vinyl pyrolidone

Scheme 3. Hydrolytic degradation of polyester based on vinyl pyrrolidone



Scheme 4. Hydrolytic degradation of polyester based on methyl acrylate

NaCl solution influences the hydrolytic condition of the crosslinked polyesters. Since the ionic permeation in the biodegradable crosslinked polyesters matrix is considerable, the effect of Na^+, Cl^- ions on the degradation is also significant[13]. The weight loss of the present polyesters are presented in Table 2.

Table 2. Weight loss (%) of polyesters under hydrolytic conditions

Polyesters	Weight loss (%)

	Ethanol	**Sodium chloride solution (1N)**	**Water**
RP30MA	0.15	0.19	1.14
RP30VP	0.11	0.14	0.55
RP30VA	0.05	0.05	0.24

3.2 Stability of polyesters in organic solvents

The solvents such as dimethyl acetamide, toluene, benzene, acetone and chloroform are selected for the present work. All the polyesters are found to swell in DMA, which is penetrate into the polyester matrix and causes increases in weight. High crosslink density of the rigid polyesters such as vinyl acetate, vinyl pyrrolidone shows small weight losses and low crosslink density of the methyl acrylate based polyester and the weight loss in DMA as shown in Table 3.

Table 3. Weight loss (%) of polyesters under organic solvents

Polyesters	**Weight loss (%)**				
	Chloroform	**Toluene**	**Acetone**	**Benzene**	**DMA**
RP30MA	0.28	0.27	0.23	0.13	0.13
RP30VP	0.32	0.16	0.20	0.10	0.11
RP30VA	0.19	0.03	0.14	0.06	0.08

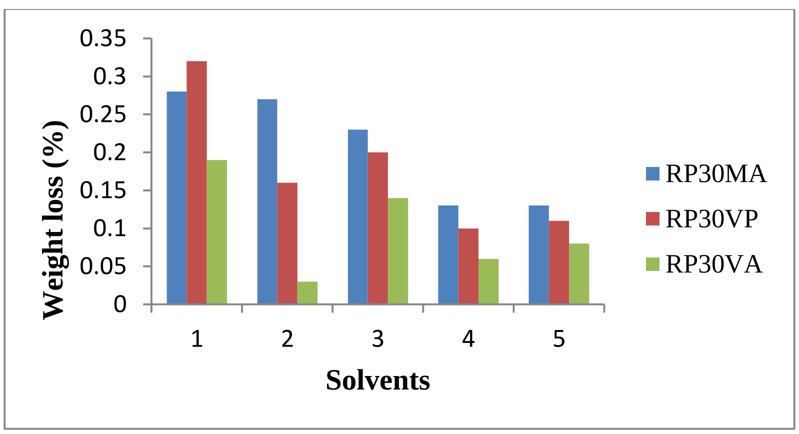


Figure 1. Stability of polyesters in various solvents

3.3 Oxidative degradation of the polyesters in hostile chemical environment

It has been found that vinyl acetate, vinyl pyrrolidone based polyesters are stable towards acid, base and oxidant medium. The degradation of polyesters are very high in NaOH. Since, the polyesters with ester linkages can be easily hydrolyzed in the presence of alkalis. But there is a slight percentage of degradation in methyl acrylate based polyester sheet as presented in Table 4.

Table 4. Weight loss (%) under hostile chemical environment

Polyesters	Weight loss (%)		
	Acid (1 N HCl)	Base (1 N NaOH)	Oxidant (30% H_2O_2)
RP30MA	2.07	20.24	5.03
RP30VP	1.78	14.25	3.23
RP30VA	1.45	10.61	1.28

3.4 Stability of polyesters under thermal ageing

The oxidative degradation in thermal ageing is mediated by the formation of radical by auto oxidation and absorption of oxygen to produce hydroperoxide radicals. The hydroperoxide radicals abstract hydrogen present in the labile group and create macro radical. Therefore, production of polyester macro radicals and recombination of macro radicals are the possible changes in the thermal ageing. There is small weight loss for vinyl acetate and vinyl pyrrolidone based polyesters under thermal ageing have been presented in Table 5.

Table 5. Weight loss (%) of polyesters under thermal ageing

Polyesters	Weight loss (%)
RP30MA	1.69
RP30VP	1.32
RP30VA	0.98

3.5 Soil burial degradation test

Weight loss (%) of crosslinked polyesters are given in Table 6. After period of two months of soil burial the prepared polyesters weights are losses due to microorganism attack, thus confirmed that the present polyesters are biodegradable. The polyester based on methyl acrylate shows maximum weight loss while polyester based on vinyl pyrrolidone and vinyl acetate shows the lowest weight loss in soil burial degradation due to its low crosslink density.

Table 6. Weight loss (%) of polyesters under soil burial degradation

Polyesters	Weight loss (%)

RP30MA	1.326
RP30VP	1.288
RP30VA	1.222

3.6 Antimicrobial studies

The antimicrobial activities of polyesters are investigated using gram negative bacteria *Serratia marcens* and gram positive bacteria *Bacillus subtilis*. The microbial activity images of crosslinked polyesters are shown in Figure 2 and the results are given in Table 6. Among prepared polyesters, methyl acrylate polyester shows maximum zone of inhibition against gram positive bacteria such as *Bacillus subtilis* and minimum zone of inhibition adhered in gram negative bacteria such as *Serratia Marcens*.

Table 7. Inhibition zone (mm) of crosslinked bio-polyesters

Polyesters	**Microorganisms**	
	Serratia Marcens	***Bascillus subtilis***
RP30MA	10	16
RP30VP	13	14
RP30VA	12	12

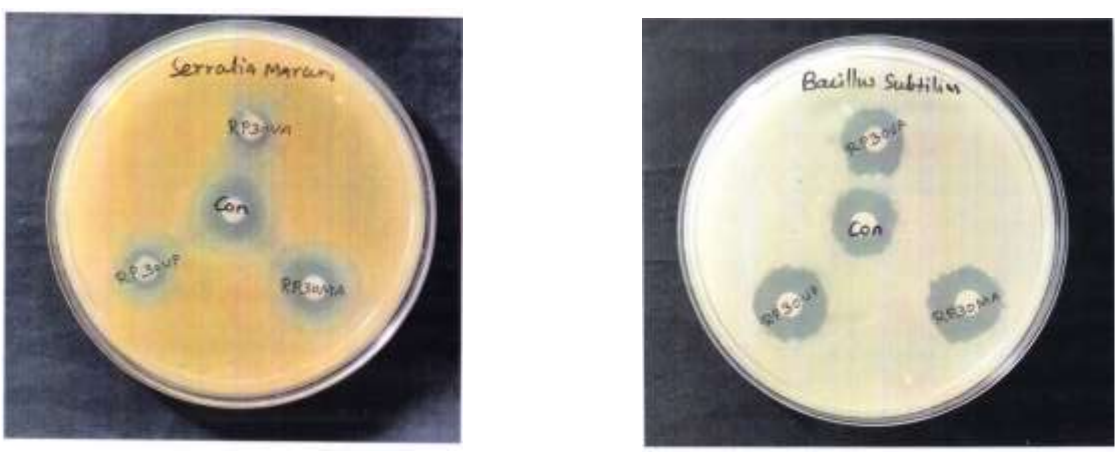


Figure 2. Culture plates of crosslinked bio-polyesters using *Serratia marcens* and *Bacillus subtilis*

4 CONCLUSIONS

The ageing characteristic shows that vinyl acetate and vinyl pyrrolidone based polyesters are stable when compared to methyl acrylate based polyesters. Also, it possesses very good hydrolytic stability than methyl acrylate based polyesters. Vinyl acetate and vinyl pyrrolidone based polyesters are thermally more stable. But the methyl acrylate based polyesters are found to undergo mild degradation due to lower crosslink density. The vinyl acetate and vinyl pyrrolidone based crosslinked bio-polyesters undergo retarded degradation when compared to the methyl acrylate based polyesters due to the higher crosslink density. The antimicrobial activity of polyester based on methyl acrylate is comparatively maximum zone of inhibition than the other polyesters. The prepared polyesters are used for biomedical applications.

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