



## Evaluation of performance of cross linked biopolyesters of Cardanol and Castor oil and their IPNs under bacteriological attack

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### ABSTRACT

Biodegradable crosslinked biopolyesters based on the fumarate ester of castor oil and methylolated cardanol were prepared using naturally available byproducts of cashew nut shell liquid (cardanol) and castor oil by the condensation of the crosslinking agent's vinyl acetate (VA), n-vinyl pyrrolidone (VP), acrylonitrile (AN), methylacrylate (MA) and methyl methacrylate (MMA) respectively. These biodegradable polyester resin blends were subjected to antimicrobial activity under bacterial attack.

**Keywords:** Vinyl acetate (VA), n-Vinyl pyrrolidone (VP), Acrylonitrile (AN), Methylacrylate (MA) and Methyl methacrylate (MMA), Poly (cardanol fumarate) resin, Poly (castor oil fumarate) resin.

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### INTRODUCTION

There is an increasing trend in the chemical industry to introduce new processes that should meet requirements such as generation of nearly zero waste chemicals, reduced energy input and use of raw materials derived from non fossil primary sources. The impact of raw material resources used in the manufacture of a polymeric product and the ultimate disposal, biodegradability or recyclability of the product has to be considered while designing the product. Polymers with hydrolysable backbones are susceptible to biodegradation under particular conditions. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions [1].

The current interest in cheap, ready available biodegradable polymeric materials has encouraged the development of such materials from readily available, renewable inexpensive natural sources [2-7]. To improve the mechanical properties of such polymers or to modify their degradation rate, natural polymers are often chemically modified.

Plant oils containing hydroxyl fatty acids are important raw materials for the polymer production. They can be polymerized to form elastomeric networks and are used as alternative material resources to petro-chemical derived resins. The polymers obtained from plant oils are biopolymers; they are often biodegradable as well as non-toxic. Among the myriad of plant oils, castor oil presents singular chemical and physical properties. It is a triglyceride of fatty acids which occurs in the seed of the castor plant, *Ricinus Communis*. In comparison with other oils; it presents high viscosity, high polarity, very low vapour pressure and optical activity. The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives. Castor oil is not

only compatible with, but also plasticizes a wide variety of natural and synthetic resins. Castor oil has become an important raw material for the production of polyurethanes, IPNs, biodegradable polyesters etc. Castor oil can generate high polymer with limited crosslink density and offers toughening characteristics to brittle and highly crosslinked composite materials.

Cardanol, a major constituent of CNSL (Cashew nut shell liquid) is a meta substituted phenolic compound. The unique feature that makes cardanol as an interesting monomer is the presence of a meta substituent of a C<sub>15</sub> unsaturated hydrocarbon chain with 1-3 double bonds and the phenolic character of the cardanol. Compared with conventional polymeric materials, cardanol based polymers can have improved functional characteristics (such as toughness, processability and hydrophobicity) due to the long meta substituent alkyl chain and rigid phenyl group.

Biodegradable polyesters are widely employed as porous structure in tissue engineering because they typically have good strength and an adjustable degradation speed [8]. Besides their biodegradability, biopolymers have other characteristics as air permeability, low temperature seal ability and so on [9]. Biodegradable polymers used in packaging require different physical characteristics, depending on the product to be packaged and the store conditions. In the chemistry of condensation polymers, the maleation of natural oils, etherification of hydroxyl groups of ricinolic and eleostearic acids and cis and trans isomerization generally occurs during the polycondensation process. In polyester chain, maleic anhydride is incorporated mostly as fumarate groups. This is desirable phenomenon, as fumarate forms are more reactive in copolymerization process with vinyl monomer. It has a favorable effect on thermal and mechanical properties of obtained materials [10, 11]. In the unsaturated polyester chemistry the number and position of double bonds is an important factor responsible for their properties.

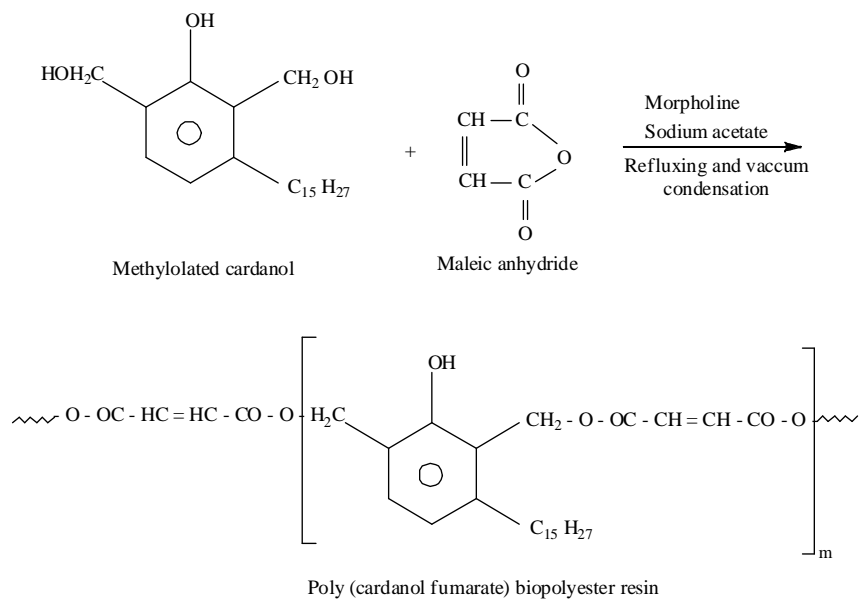
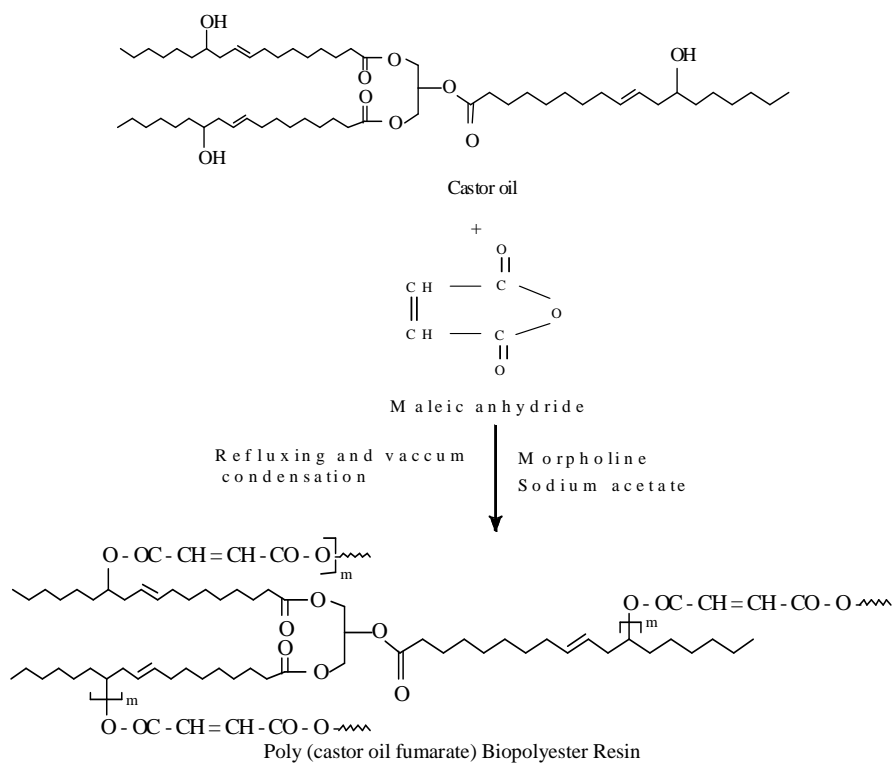
With the emergence of novel polymer systems and technologies, which enhance performance characteristics of the end products and replace conventional polymer processing methods, the science on addition-curable resins have occupied major importance in recent years. Therefore, it is relevant and important to investigate plant oil-based addition-curable polyester resin, bio polyesters and IPNs through environmentally safe processing methods towards the development of value-added products. So the present cross linked biopolyesters and IPNs were studied with the antimicrobial activities.

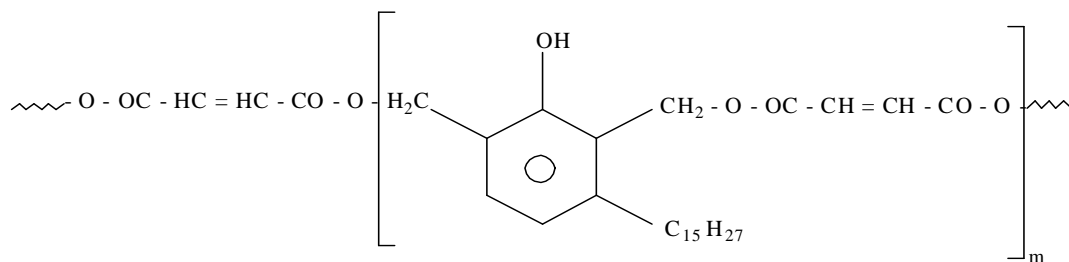
## EXPERIMENTAL SECTION

### 2.1 Preparation of crosslinked bio polyesters of poly cardanol and poly castor oil fumarate biopolyesters

The poly cardanol fumarate resin (MCFR) was prepared by heating 1 mole of methylolated cardanol with 2 mole of maleic anhydride using morpholine and sodium acetate catalyst given in reaction scheme 1. The poly castor oil fumarate resin (CFR) was prepared by heating 3 moles of castor oil with 1 mole of maleic anhydride using morpholine and sodium acetate as catalysts represented in reaction scheme 2. [12]

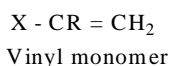
The polyesters of poly (cardanol fumarate) resin, (MCFR) / poly (castor oil fumarate) resin, CFR were prepared by reacting MCFR/CFR with vinyl monomers in the weight ratio of 1:0.5 in presence of benzoyl peroxide and dimethyl aniline, then casted on a clean silicone oil-coated glass plate and cured in hot air oven at 80<sup>o</sup>C for 6h.[12] The polymer sheets of poly cardanol fumarate prepared with vinyl acetate, vinyl pyrrolidone, acrylo nitrile, methyl acryllate and methyl methacryllate were coded as MCFR-VA, MCFR-VP, MCFR-AN, MCFR-MA and MCFR-MMA and with poly castor oil fumarate were coded as CFR-VA, CFR-VP, CFR-AN, CFR-MA and CFR-MMA respectively. The preparation of crosslinked biopolyesters are given in reaction scheme 3 and reaction scheme 4.

**Reaction Scheme 1: Synthesis of Poly (Cardanol Fumarate) Biopolyester Resin****Reaction scheme 2: Synthesis of Poly (Castor Oil Fumarate) Biopolyester Resin**

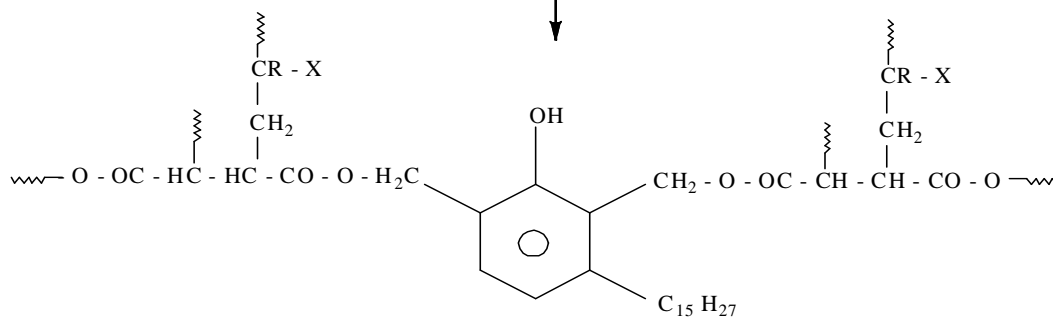


Poly (cardanol fumarate) biopolyester resin

+



Dibenzoyl peroxide      Dimethyl aniline



Cross linked poly (cardanol fumarate) biopolyester

Where

**Vinyl monomer**

Vinyl acetate  
Methyl acrylate  
Methylmethacrylate  
Acrylonitrile

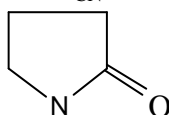
**X**

OCOCH<sub>3</sub>  
COOCH<sub>3</sub>  
COOCH<sub>3</sub>  
CN

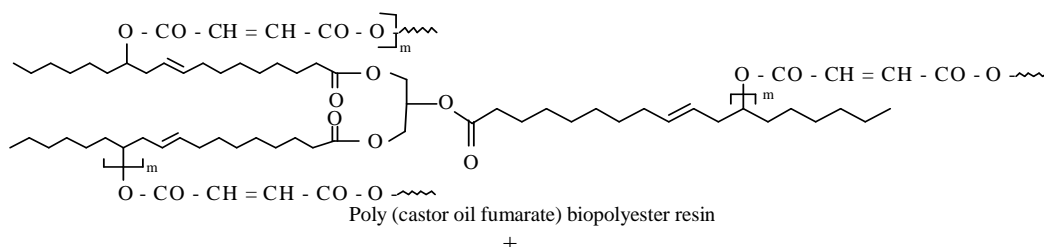
**R**

H  
H  
CH<sub>3</sub>  
H

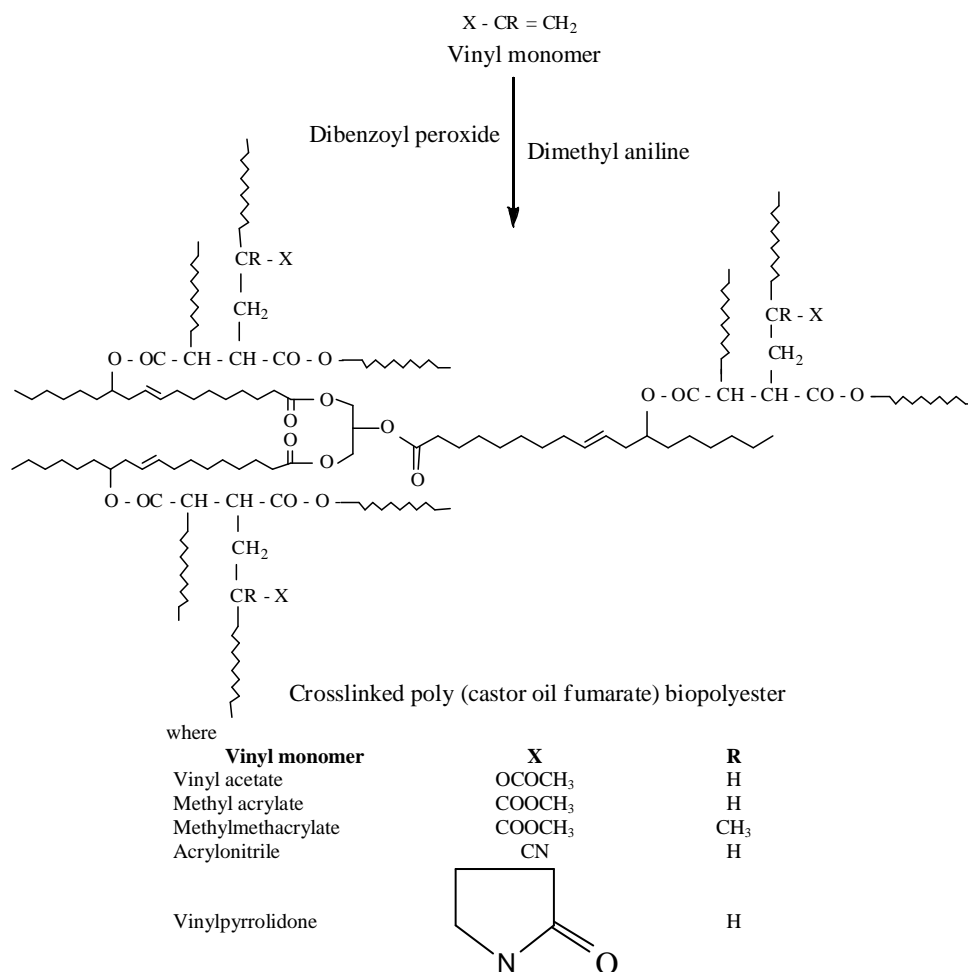
Vinylpyrrolidone



Reaction scheme 3: Crosslinking of Poly (Cardanol Fumarate) Polyester Resin with Vinyl Monomers



+



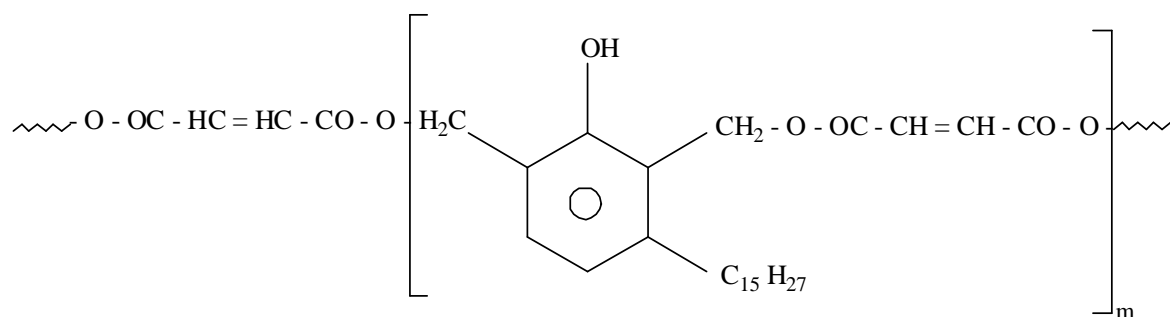
Reaction scheme 4: Crosslinking of poly (castor oil fumarate) polyester resin with vinyl monomers

## 2.2 Preparation of Interpenetrating Polymer Networks of Poly cardanol and Poly castor oil Fumarate Polyester Resin with Vinyl Monomers

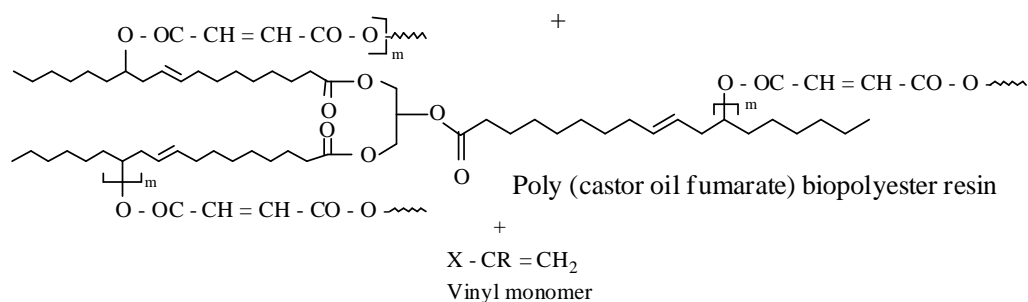
Biodegradable and cross linked interpenetrating polymer networks were prepared by co-crosslinking of poly(cardanol fumarate) polyester resin (MCFR) and poly(castor oil fumarate) polyester resin (CFR) in 1:1 weight ratio to get a blend [12]. This blend was mixed with the cross linking agent, vinyl monomers in 1:0.5 weight ratio in presence of benzoyl peroxide (initiator) and dimethyl aniline (accelerator) and then casted on a clean silicone oil spreaded glass plate, cured in hot air oven at 80°C for 6 hours. The IPNs prepared with the cross linking agent, vinyl acetate (VA), vinyl pyrrolidone (VP), acrylo nitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA) were coded as CFMCF-VA, CFMCF-VP, CFMCF-AN, CFMCF-MA and CFMCF-MMA respectively. The preparation of IPNs is given in reaction scheme 5.

## 2.3 Studies of biopolyesters and IPNs under Bacteriological condition

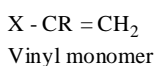
The performance of the present cross linked biopolyesters and IPNs under bacterial attack conditions were evaluated by investigating antimicrobial activity. Spherical discs of 10 mm diameter were used. All the test samples were sterilized by autoclaving. Agar diffusion method was followed. The test was done in triplicates. Netromycin (10µg/disc) of positive control (coded as NT) was used. The cross linked biopolyesters and IPNs (coded as P) and extract of the cross linked biopolyesters and IPNs (prepared with chloroform) (coded as PS) were used as tests. The bacterial strains used for the study were *Klebsiella pneumonia* (gram negative) and *Bacillus cereus* (gram positive).



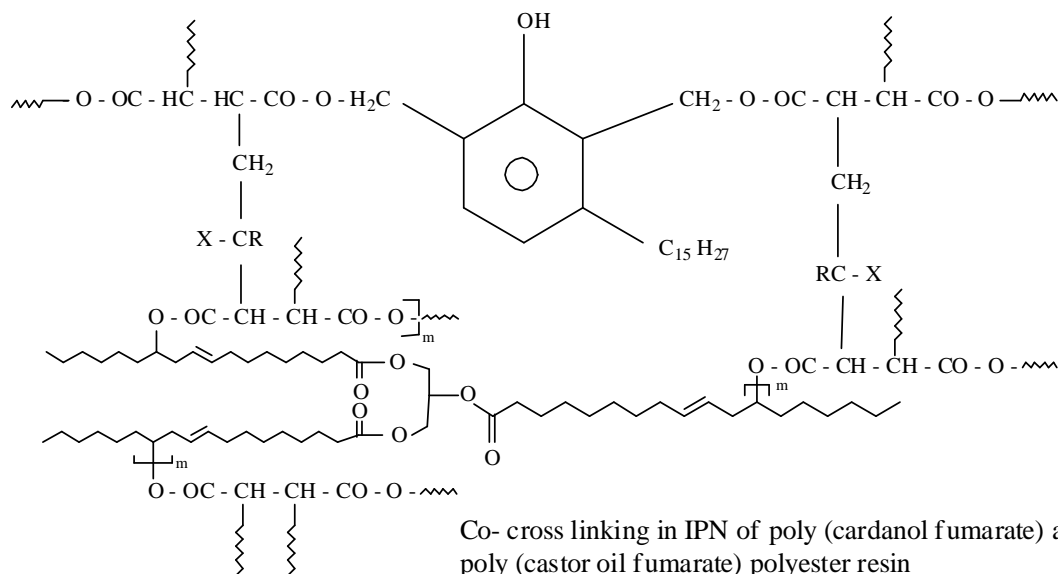
Poly (cardanol fumarate) biopolyester resin



Poly (castor oil fumarate) biopolyester resin



Dibenzoyl peroxide      Dimethyl aniline



Co-cross linking in IPN of poly (cardanol fumarate) and poly (castor oil fumarate) polyester resin

Reaction scheme 5: Co-Crosslinking of Poly (Cardanol Fumarate) and Poly (Castor Oil Fumarate) Through the Vinyl Monomer

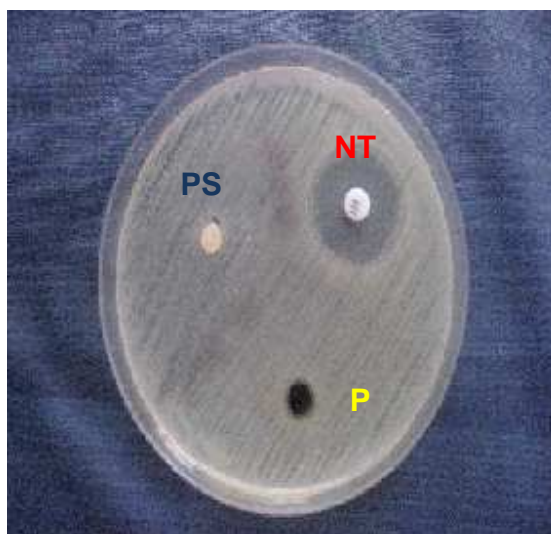
## RESULTS AND DISCUSSION

Achievement of tack-free crosslinked biopolyester surface with appreciable mar resistance, solvent resistance and capable of killing bacteria on contact during the use is a major challenge. Most of the conventional polyesters exhibit tackiness due to retardation of crosslinking in the surface by the presence of air. Such surfaces are prone to bacterial attack during the use. The present crosslinked biopolyesters (CBP) and IPNs have tack resistance due to completion of crosslinking in the surface. Decontamination and neutralization of surfaces from bacteria and spores

is an essential process for the successful use of the product. The ability to decontaminate the surfaces inoculated with bacterial spores is extremely important. Therefore self-decontaminating surfaces may be able to perform in such situations. The ability to decontaminating surfaces of the crosslinked biopolyesters (CBP) and IPNs was investigated using gram positive *Bacillus cereus* and gram negative *Klebsiella pneumoniae*.

**Table 1: Zone of Inhibition on Biopolyesters and IPNs**

Cross linked Biopolyesters/IPNs	Zone of inhibition with polymer (mm)	
	<i>Klebsiella pneumoniae</i>	<i>Bacillus cereus</i>
Crosslinked biopolyesters (CBP) of poly(castor oil fumarate)-vinyl monomer		
CFRVA	5	7
CFRVP	8	8
CFR-MA	7	7
CFR-MMA	8	6
CFR-AN	10	8
Crosslinked biopolyesters (CBP) of poly(cardanol fumarate)-vinyl monomer		
MCFRVA	25	24
MCFRVP	17	16
MCFR-MA	23	21
MCFR-MMA	19	15
MCFR-AN	21	17
Poly (cardanol fumarate) and poly(castor oil fumarate)-vinyl monomer IPNs		
CFMCFVA	27	15
CFMCFVP	21	18
CFRMCFR-MA	37	15
CFRMCFR-MMA	21	13
CFMCFR-AN	24	16



**Figure 1: Culture Plates of Bacteria With Crosslinked Biopolyester Of Poly (Cardanol Fumarate) Polyester And Vinyl Acetate with *Bacillus Ceres*, NT: Netromycin, P: Polymer, PS : Polymer Extract**

The studies with the crosslinked poly (cardanol fumarate) biopolyester and IPNs reveal some antimicrobial activity against *Bacillus cereus* and *Klebsiella pneumoniae*. The zone of inhibition varies with variation in vinyl monomer and polyester resin composition. Relatively the antimicrobial activity of crosslinked poly (castor oil fumarate) biopolyester is comparatively lower than in poly (cardanol fumarate) biopolyester and IPNs. The data on zone of inhibition is given in Table 1. Representative optical photographs of culture plates of *Bacillus cereus* and *Klebsiella pneumoniae* with crosslinked poly (cardanol fumarate) biopolyester and IPNs are given in Figure 1 to Figure 4. The zone of inhibition with test material and chloroform solution is demonstrated in relation to netromycin (NT). Comparing with netromycin, the studies reveal that present crosslinked biopolyesters and IPNs are marginally inhibiting bacterial attack.

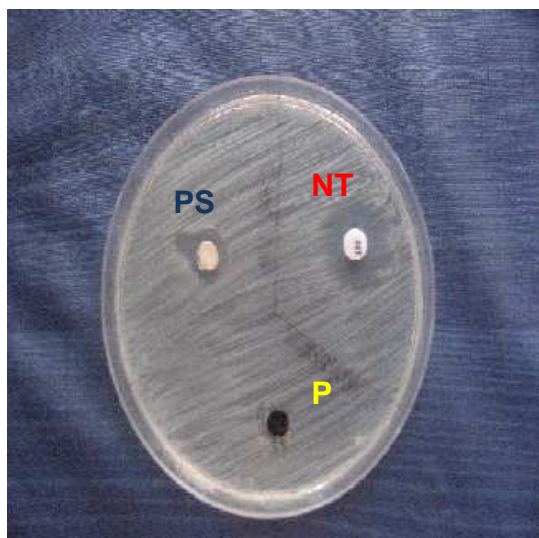


Figure 2: Culture Plates of Bacteria With Crosslinked Biopolyester Of Poly (Cardanol Fumarate) Polyester And Vinyl Acetate with Klebsiella Pneumonia. NT: Netromycin, P: Polymer, PS : Polymer Extract

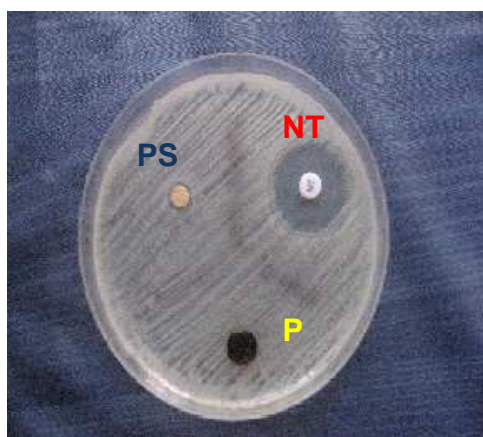


Figure 3: Culture Plates of Bacteria with IPN of Poly (Cardanol Fumarate) and Poly (Castor Oil Fumarate-Methyl Acrylate. with Bacillus Ceres NT: Netromycin, P: Polymer, PS : Polymer Extract

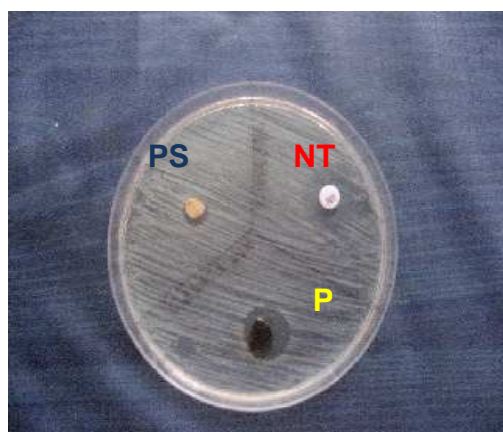


Figure 4: Culture Plates of Bacteria with IPN of Poly (Cardanol Fumarate) and Poly (Castor Oil Fumarate-Methyl Acrylate. with Klebsiella Pneumonia. NT: Netromycin, P: Polymer, PS : Polymer Extract



It has been reported that the bactericide mechanism starts with the adsorption of bactericide onto a bacterial cell carboxylate surface followed by diffusion through the outer layers of the cell. The bonding to the cytoplasmic membrane and disruption of this membrane to result in the release of  $K^+$  ions through leakage occurs, which results in degradation of the cell structure and release of cell contents, thus resulting in the death of the cell [13]. Bactericidal functional groups are designed to target the cell membrane.

Bactericides have received much attention for decontaminating the surfaces. The conventional liquid sporicidal agents are based on halide releasing compounds (e.g., hypochlorites and iodophores), reactive oxygen releasing agents (e.g., peroxides and peracetic acid), and aldehydes (e.g., formalin and glutaraldehyde) [14]. Biocidal functional groups Quaternary ammonium, pyridinium, and phenolic compounds are known to possess biocidal activity and have been used in a variety of applications and numerous commercially available products. These compounds have not only found utility as biocides but also as phase transfer catalysts and mobility systems designed to aid in the drug delivery processes. They have also been reported to possess antiseptic properties. The antimicrobial activity observed with the present crosslinked poly (cardanol fumarate) biopolyesters and IPNs is attributed to presence of cardanol unit.

### CONCLUSION

The present poly (cardanol fumarate) and poly (castor oil fumarate) biopolyester resins are mutually soluble. Therefore molecular interpenetration occurs in the case interpenetration of polymer networks. Moreover the present biopolyester resins are mutually soluble co-crosslinking of poly (cardanol fumarate) and poly(castor oil fumarate) through the vinyl monomer takes place in addition to the individual crosslinking of polyester resin with vinyl monomer. The antimicrobial activity of crosslinked poly (cardanol fumarate) biopolyester and IPNs is comparatively higher with the poly (castor oil fumarate) biopolyester. The presence of cardanol unit accounts for the higher antimicrobial activity.

### Acknowledgement

The authors like to thank the management of Dr.Sivanthi Aditanar College of Engineering, Tiruchendur, Tamilnadu, India for providing facilities and support.

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