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RESEARCH ARTICLE

Synthesis and Characterization of Cotton Seed Oil based Biodegradable Thermosetting Polymers

J. Shakina* and A. Muthuvinothini
Dept. of Chemistry, Sarah Tucker College (Autonomous), Tirunelveli, Tamil Nadu-627007, India
shakinajudson@gmail.com*; +91 9688022671

Abstract

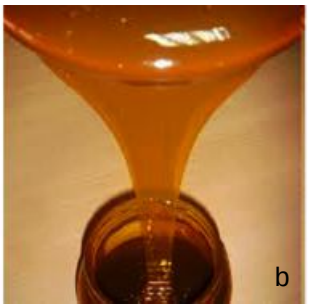
A thermosetting polymer from cottonseed oil has been investigated in this study. The biodegradable oligomeric fumarated resin was prepared by the *in situ* hydroxylation followed by the fumaration of cotton seed oil using controlled reaction conditions. Three new polymeric materials were prepared by varying the concentration of the co-monomers methyl methacrylate (MMA) and butyl methacrylate (BMA). The new polymeric materials exhibited tensile stress-strain behavior ranging from soft rubbers through ductile to relatively brittle plastics. These synthesized polymers were characterized using differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) and its mechanical properties like tensile strength, percentage elongation and hardness were also studied. Hydrolytic test, chemical resistance test and soil burial test were carried out to determine the biodegradability of the synthesized polymer. The synthesized cotton seed oil based polymers expressed greater mechanical properties compared to that of commercially available rubbery materials and conventional plastics. In future, this cotton seed oil based polymers may serve as a replacement in many applications.

Keywords: Biodegradable, soft rubbers, plastics, mechanical properties, thermo gravimetric analysis.

Introduction

Polymers and polymeric materials exhibit excellent mechanical properties, high corrosion resistance, dimensional stability and low assembly costs. Traditionally, polymers and polymeric composites have been derived from petroleum; however, as the application for polymeric materials increase, finding alternative sources of these materials has become critical (Anastas and Zimmerman, 2013). The challenge to replace petroleum-based materials with plant-derived renewable sources implies the application of well-established reactions to the production of compounds that produce materials with competitive performance (Ronda *et al*., 2011). Cellulose, starch, proteins and natural oils have all been examined as possible polymeric feed stocks (Ronda *et al.,* 2013). Vegetable oils are unique among all fats and other oils in that (i) they are the source of fatty acids with more than one double bond, (ii) product uniformity and consistency are relatively high for a naturally occurring materials and (iii) it is non-toxic, biodegradable, renewable resource (Biermann *et al.,* 2000). These materials have economic and environmental advantages that make them attractive alternatives to petroleum based materials (Anastas and Zimmerman, 2013). Cotton seed oil is among the most unsaturated oils, others being safflower, corn, soybean, rapeseed and sunflower seed oils. Cotton seed oil has a ratio of 2: 1 of polyunsaturated to saturated fatty acids and generally consists of 65-70% unsaturated fatty acids including 18-24% monounsaturated (oleic) and 42-52% polyunsaturated (linoleic) and 26-35% saturated (palmitic and stearic) (Jamieson and Baughman, 1920; Hilditch, 1948; Wool and Sun, 2005; Chandramohan and Marimuthu, 2011). Figure 1 shows the images of cotton seed oil and cotton seed resin. Therefore, it was planned to use cotton seed oil for the production of novel addition curable resins by suitably modifying the triglycerides for the production of novel biodegradable bio polyesters.

Fig. 1a. Cotton seed oil and b. cotton seed oil resin.



Materials and methods

Chemicals: Refined cotton seed oil purchased from the market was used as received. Methyl methacrylate (MMA) and butyl methacrylate (BMA), Formic acid (98%, Merck), Hydrogen peroxide (30%, Merck), Benzoyl peroxide (Aldrich), Dimethyl aniline (DMA, Aldrich) and Morpholine (MP, Aldrich), were used without further purification.

Synthesis of oligomeric poly cotton seed oil fumarate resin (O-PCF) resins: Glycerolysis of cotton seed oil was carried out using 30% H_2O_2 and formic acid in ice water bath. The reaction was vigorously stirred overnight. The resulting product was poured into a separator funnel and extracted with ether and the ether extracted product was then reacted with maleic anhydride and the mixture was refluxed for 5 h at 70-80°C and at 160°C for 30 min under vacuum condition to yield a yellow transparent liquid O-PCF resins.

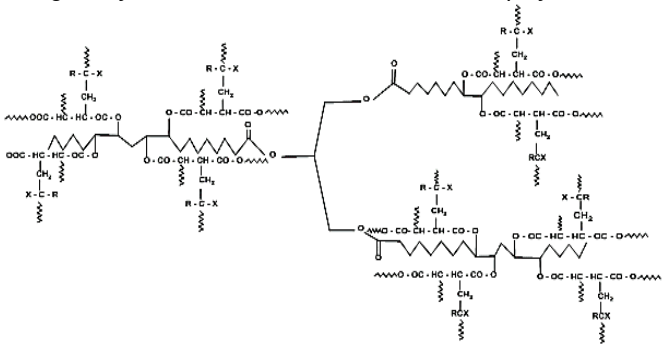
Synthesis of cotton seed oil based biopolyesters: The biopolyesters were prepared by free radical polymerization of O-PCF resin of cotton seed oil with cross linking co-monomer, methyl methacrylate (MMA) and butyl methacrylate (BMA) with a weight ratio [1: 0.7] at room temperature with benzoyl peroxide as free radical initiator and dimethyl aniline as accelerator. Figure 2 shows the synthesis.

Mechanical properties: Tensile strengths of the present biopolyesters were evaluated using dumb-bell-shaped specimens punched out from sheets according to ASTM D 412-87. The gauge length was fixed at 3 cm in each test and the chart and cross head speed was 100 mm/min. H-5KS Houn field Test Equipment S series was used to measure tensile strength. An average value of six test-data was calculated. Shore-A hardness of the specimens were tested by using Durometer type A Shore instrument according to the ASTM, D 2240 standard.

Thermal analysis (TGA-DTA-DSC): Thermal properties of addition-cured biopolyesters were studied by differential thermal analysis and thermogravimetric analysis. In the present work, TGA/DTA studies were carried out using SDT Q 600 V 8.3 Build 101 instrument at the heating rate of 10°C/min from ambient to 700°C in nitrogen atmosphere using 2-5 mg of the sample. Differential scanning calorimetric analysis (DSC) was done as per ASTM E-537-98 using TA Instruments Inc. Samples were heated from room temperature to 600°C, with the heating rate of 10°C/min in nitrogen atmosphere.

Determination of hydrolytic stability: Cross linked biopolyesters (CBP) (3 x 1 x 0.1 cm) were immersed separately in the media (100 mL)-water, alcohol and salt solution (IN sodium chloride) for a period of 60 days under ambient conditions. The loss of weight was determined by vacuum drying the immersed sample.

Fig. 2. Synthesis of cotton seed oil based biopolyesters.



Stability in boiling water was also determined by immersing the samples in boiling water for 5 days. After 5 days, the samples were cooled to room temperature and removed, dried by vacuum-drying and the dimensions and weight were measured. The loss of weight (%) in each sample was calculated.

Determination of stability in hostile chemical environment: The degradation of the newly prepared cross linked biopolyesters in hostile acidic, basic and oxidation media was studied by immersing the specimen (3 x 1 x 0.1 cm) separately in 100 mL of the selected solution for a period of 60 days. Dilute hydrochloric acid (1N); sodium hydroxide (1N), hydrogen peroxide (30%) and alc. potassium hydroxide were used.

Determination of stability in organic solvents: The stability of the newly prepared cross linked biopolyesters in common organic solvents-ethanol, n-butyl alcohol, glycerol, carbon tetrachloride, petroleum ether etc. and compatible solvents like benzene, toluene, N, N-dimethyl acetamide (DMA) and N, N-dimethyl formamide (DMF) was studied by immersing the specimens in the chosen solvents in air-tight-containers at 28 ± 1°C for 60 days.

Soil burial test: The replicate pieces of the sample (5 cm x 3 cm) were buried in the garden soil at the depth of 30 cm from the ground surface for 3 months, inoculated with the sewage sludge having ability to adhere and degrade the polymer film. The test specimen was periodically removed from the soil and the specimen was then gently washed to remove attached soil and dust after being dried in vacuum oven. The extent of degradation was examined by weight loss and surface observation. Scanning Electron Microscope (SEM) was used for assessing surface damages of polymeric sheet subjected to soil burial test.

Antimicrobial studies: Antimicrobial activity was evaluated by agar diffusion method. Both test samples were sterilized by autoclaving before performing the test and finished by agar diffusion method. The test was done in triplicates. Gentamycin (10 µ/disc) of positive control was used for antimicrobial activity testing.

Table 1. FT-IR probable assignment of cotton seed oil, hydroxylated cotton seed oil and oligomeric poly cotton seed oil resin.

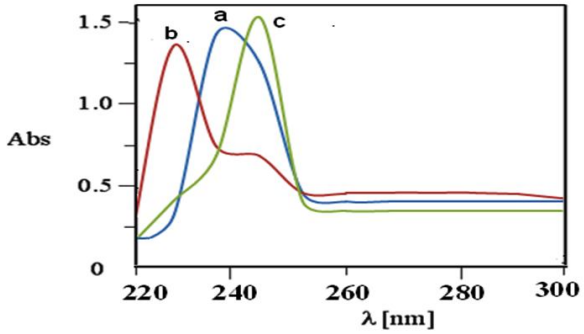
Probable assignment	Cotton seed oil (cm^{-1})	Hydroxylated cotton seed oil (cm^{-1})	O-PCF resin (cm^{-1})
-CH_2 Group	2924(S)	2924(S)	2924(S)
-C-O- Group in GM	2553(S)	2535(S)	2553(S)
C=O in esters	1720.5(S)	1710.5(S)	1720.5(S)
Terminal–CH_3-Groups	1454.3(M)	1354.3(M)	1454.3(M)
Carboxyl Group of acids	1367.7(S)	1267.7(S)	1367.7(S)
-CH-CH-Stretching	1016.6(S)	1019.6(S)	1016.6(S)
CH_2-sequences of the aliphatic chains	799.1(S)	799.1(S)	799.1(S)
-OH Group	-	3404(B)	3440(W)

The microbial strains used for bacterial adhesion study were *Escherichia coli* and *Candida albicans* obtained from MTCC.

Results and discussion

UV-VIS spectra: The UV spectra of all the oils and hydroxylated triglyceride oil resins and for the O-PTF biopolyester resins have been investigated (180-520 nm). The oil sample showed an electronic absorption band around 262 nm. The hydroxylated resin exhibited a blue shift when compared with the corresponding parent oil which is attributed to the substitution of hydroxyl group at the unsaturated moiety. There is also decrease in the absorbance in comparison with that of parent oil is due to the substitution of the hydroxyl group at the olefinic double bond and also distortion of geometry. The substantial red shift in electronic absorption exhibited in (O-PTF) biopolyester resin due to the substitution of the fumarate group and also due to the distortion in geometry of the molecule by the introduction of fumarate group. Figure 3 shows the UV-Vis spectrum of cotton seed oil, hydroxylated cotton seed oil and O-PCF resins.

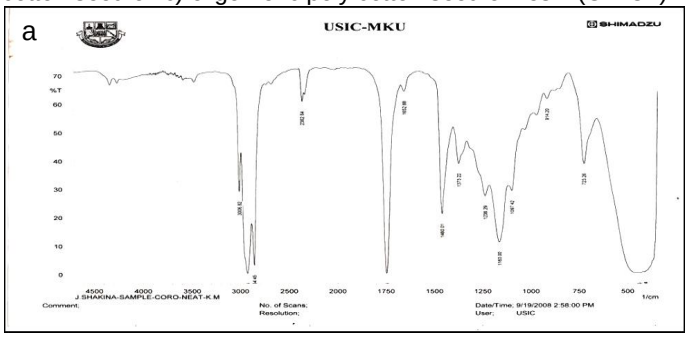
Fig. 3. UV Spectra of a) Cotton seed oil, b) hydroxylated cotton seed oil, c) O-PCF resins.

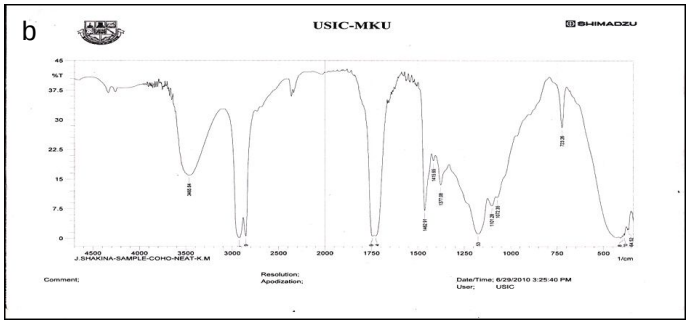


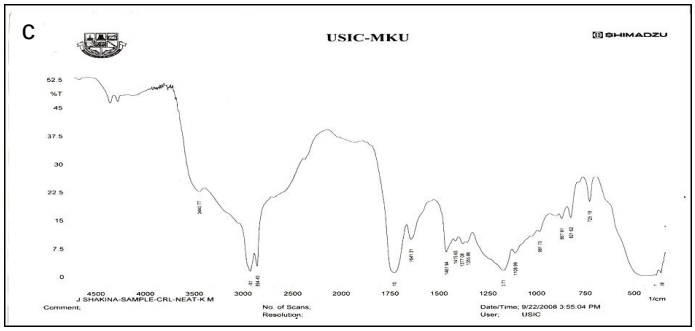
FT-IR spectral analysis: The FTIR spectra of cotton seed oil, HT resins, O-PCF resins are recorded between 500-4000 cm^{-1}. In hydroxylated triglyceride resins, the FT-IR spectra showed a strong absorption band at 3477 cm^{-1}, due to the present of free -OH group in the molecule. The corresponding peak is completely reduced in the O-PCF resins indicates the entire -OH group get substituted. A strong absorbance band in 2925 cm^{-1} is due to the presence of C=O of the glyceryl ester moiety.

A strong band in 2850 cm^{-1} is due to the symmetrical –C–H bond in –CH_2 group of the side chain. Figure 4 shows the FT-IR spectrum of cotton seed oil, hydroxylated cotton seed oil and oligomeric poly cotton seed oil resin (O-PCF). The FT-IR probable assignment of cotton seed oil, hydroxylated cotton seed oil and oligomeric poly cotton seed oil resin was tabulated (Table 1).

Fig. 4. FT-IR spectrum of a) cotton seed oil b) hydroxylated cotton seed oil c) oligomeric poly cotton seed oil resin (O-PCF).

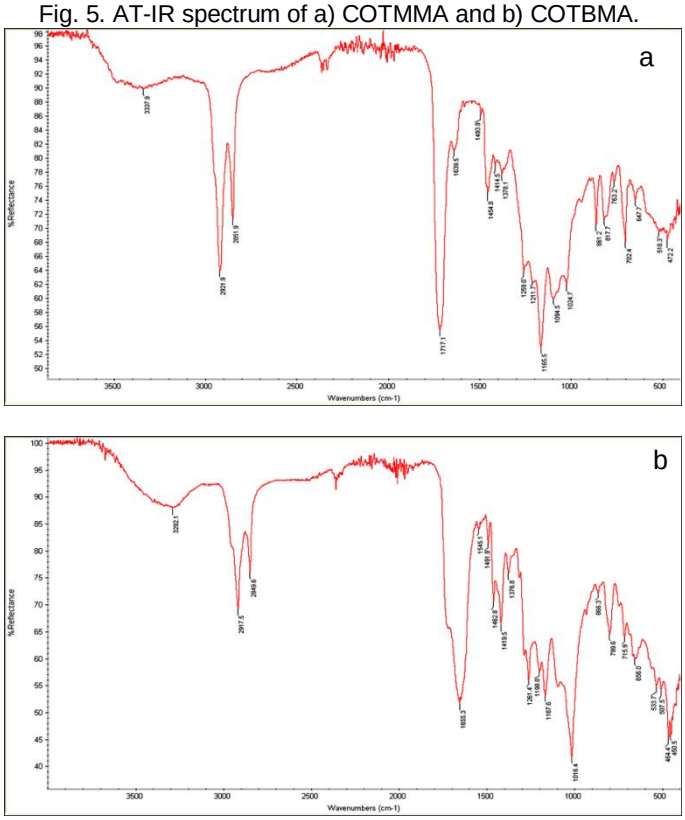






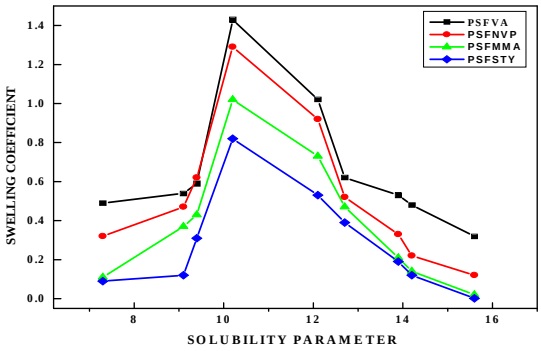
AT-IR studies: The completion of cross linking was studied by AT-IR spectral studies. The AT-IR spectrums of different triglyceride polyesters are shown in Fig. 5.

Fig. 5. AT-IR spectrum of a) COTMMA and b) COTBMA.



The AT-IR spectrum of cross linked biopolyesters (CBP) based on poly (cottonseed oilfumarate) biopolyester resin and vinyl monomers: The AT-IR spectrum of Poly (cotton seed oil fumarate) biopolyester resin cured with vinyl monomers MMA and BMA (Fig. 5) shows responses in the region 1723 cm^{-1}, 1736 cm^{-1} due to C=O stretch in esters. The peaks of cured samples are almost the same and the absence of peak around 1637 cm^{-1} indicates the absence of double bonds. The peak appeared in the region at 980 cm^{-1} is the resin to the C-H bending of trans-fumarate linkage. The disappearance of the peak appeared in the same region in biopolyesters are due to the extensive cross linking of CH=CH fumarate linkages with vinyl monomers. The values are tabulated in Table 2.

Fig. 6. The variation of swelling coefficient with solubility parameter for the cross-linked bio polyesters of poly (cotton seed oil fumarate).



Swelling properties: The swelling studies of the newly prepared polyesters have been carried out in solvents having different solubility parameters, methanol (13.5), ethanol (12.3), dimethyl acetamide (10.8), tetra hydro furan (9.3) and dimethyl formamide (12.1). All these polyesters undergo slight swelling in solvents MeOH, EtOH, THF, dimethyl formamide and benzene reveal that present polyesters are also cross linked. Due to the higher degree of swelling (Swelling coefficient) only in N, N-dimethyl acetamide, it is understood that the solubility parameter of the new poly ester is 10.8. The degree of swelling in a non-reactive solvent determines the degree of cross linking and the molecular weight between the cross links. The variation of swelling co-efficient with solubility parameter is given in the Fig. 6. The molecular weights between cross links and the cross link density and the present materials confirm the cross linked character. The cross link density of the biopolyesters based on Poly (cotton seed oil fumarate) is comparatively higher than the other oil based polyesters. The cross link density of the cross linked biopolyesters based on styrene is comparatively higher than the corresponding vinyl based materials.

Thermal properties

Thermo gravimetric analysis and differential thermal analysis (TGA-DTA): Thermal properties of cross linked biopolyesters are influenced mainly by molecular weight between cross links and the degree to which segments form stiff sequences and elastically active branch points. The segments constituting stiff sequences are due to the vinyl monomers cross linked with fumarate groups.

Table 2. AT-IR probable assignment of cross linked biopolyesters (CBP).

Probable assignment	COTMMA (cm^{-1})	COTMMA (cm^{-1})
-CH_2 Group	2955(S)	2923(S)
-C-O-Group in GM	2952(S)	2954(S)
C=O in esters	1723(S)	1736.9(S)
Terminal –CH_3- Groups	1454(M)	1452(M)
-C-O-C Stretching in vinyl ester	1167(S)	1164(s)
-CH-CH-Stretching	1021(S)	1020(s)
CH=CH fumarate linkages	982(S)	986(s)

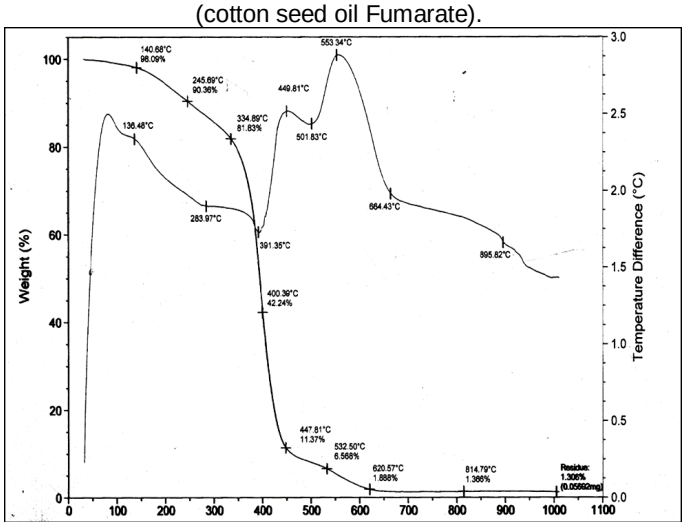
Table 3. TGA data of crosslinked biopolyesters of poly (cotton seed oil fumarate).

Polyesters	Temperature (^{0}C) at the end of each stage of degradation (Weight loss, %)				50% weight loss	Residue (mg)
	Tstart	I stage	II stage	III stage		
COTMMA	140.48	245.09 (9.13)	334.05 (18.13)	620.57 (99.74)	391.55	0.05692

Table 4. The DTA data of cross-linked Biopolyesters of Poly (cotton seed oil Fumarate).

Material	Endothermic response (^{0}C)			Exothermic response (^{0}C)		
	$Endo_1$	$Endo_2$	$Endo_3$	Exo_1	Exo_2	Exo_3
COTMMA	283.97	391.35	601.63	136.48	440.81	663.84

Fig. 7. TGA data of cross-linked Biopolyesters of Poly (cotton seed oil Fumarate).



Free aliphatic long chains can impart flexibility to the cross linked mass. The appearance of peaks for the softening, decomposition and cross linking was observed for the cross linked biopolyesters (CBP). Figure 7 shows the TGA and DTA data of cross-linked biopolyesters of poly (cotton seed oil Fumarate) (Table 3 and 4). DTA curves do not exhibit any remarkable endothermic softening. DTA curves show multistage endothermic peaks characterizing thermal decomposition also the curves indicate mild softening at less than 100°C which is due the disruption of the physical cross links. The DTA curves also indicate more than three endotherm above 200°C for chain scission, degradation and more than two exotherms for cross linking of the degraded fragments. The stage of degradation and weight loss is due to the initial degradation of vinyl monomer present in the fumarate ester linkage chain at low temperature which is due to the flexibility of the vinyl group even in the cross linked state of bio poly esters.

Differential scanning calorimetry: Figure 8 shows the DSC curve of cross linked biopolyesters of Poly (cotton seed oil Fumarate). DSC provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer.

Table 5. The DSC data of crosslinked biopolyesters of poly (cotton seed oil fumarate).

O-PCF Resins	T_g◦C	ΔHm (◦C)
COTMMA	66.36	476.55,683.51
COTBMA	77.68	184.91, 328.0, 471.22

Polymer crystallinity can be determined with DSC by quantifying the heat associated with melting (fusion) of the polymer. The DSC studies revealed the glass transition temperature and the TG values clearly indicate the polymer is semi crystalline in nature. Table 5 shows the DSC data of cross linked Bio polyesters of Poly (cotton seed oil Fumarate).

Mechanical properties: One of the most extensively used mechanical tests for polymers is the tensile or stress-strain test. The data on the mechanical properties of thermosetting polymers such as tensile strength, tear strength, elongation at break (%), and shore hardness are collected in Table 6. The shore-A hardness is defined as the resistance offered by the rubber and similar materials to the penetration of truncated cone (Shore-A). The results indicate that the products are typical thermosetting polymers with densely cross linked structures. The cross link density differs significantly from one another which are a direct result of different degrees of unsaturation of the different macro monomers employed. Among the cross linked biopolyesters, styrene based polyesters and methyl methacrylate based biopolyesters have higher tensile strength which may be attributed to the higher cross link density and vinyl acetate based polyesters have the lowest cross link density. Cross linking increases the tightness of the polymer network and reduces the molecular mobility of the chains between the junctions. The magnitude of the rubbery modulus indicates cotton seed oil based polyesters have more cross link densities than those of other polyester thermosets. As cross linking increases, the number of conformation that the polymer chain can adopt decreases and thus increasing the stiffness of the polymers. As a result, a crack is initiated during the tensile process; more energy is required for the crack to propagate in a material with a higher degree of cross linking until failure occurs. Thus, cross linking also increases the ultimate tensile strength of the polymers.

Table 6. The mechanical properties of crosslinked biopolyesters of poly (cotton seed oil fumarate).

Polyesters	Tensile strength (MPa)	Tear strength (KN/m)	% elongation at break	Hardness shore (A)	Crosslink density (Mol/m^3)	Tensile modulus (MPa)
PCSFBMA	20.156	15.30	52.0 ± 1.6	72	3.073	31.27 ± 1.02
PCSFMMA	26.345	32.12	71.31 ±1.6	73	6.276	200.61 ± 0.82

Table 7. Evaluation of stability in chemical environment.

Polyesters	Weight loss (%)		
	Acid (1N HCl)	Base (1N NaOH)	Oxidant (30% H_2O_2)
COTMMA	2.34	23.55	1.20
COTBMA	1.90	10.23	0.43

Table 8. Evaluation of stability in organic solvents.

Polyesters	Diethyl ether	Acetone	Toluene	Benzene	CCl_4
COTMMA	0.05	0.20	0.05	0.10	0
COTBMA	0.05	0.05	0.05	0.10	0.05

The high strength and high modulus reflect the strong and hard character of these poly esters. The MMA based polyesters are soft and weak due to the lower cross link density. Increase in elongation in ductile polymers is also due to the flexibility of the chain introduced by the co-monomers.

Evaluation of stability in chemical environment: The performances of a polymeric material for intended application for intended duration largely determine the service life of the product. The comprehensive account of physical and mechanical properties combined with durability of any polymeric material can enable to decide the duration of its functioning satisfactorily before it needs repair or replacement. Another important parameter to be taken into account is the effect of physical aging in the structural organization of polymer. The changes that can occur in a material with aging can affect its application, performance and life time. Aging under outdoor exposure and end-use continuous exposure leads to loss of properties due to degradation of polymer. The more dominating routes of degradation are hydrolysis and oxidation induced by various chemical environments. Polymers can also undergo degradation by exposure to high temperature (thermal degradation), oxygen, ultraviolet light, moisture, radiation and various chemical agents. The hostile reactive chemical environment acid, base and oxidizing agent also induce degradation of polyesters. Dilute acids and bases induce hydrolytic attack on polyesters. Oxidizing agents induces oxidation of residual double bonds present in the cross-linked polyester materials. Acid and base-induced hydrolysis is similar to water-induced hydrolysis though the magnitude of hydrolytic degradation is larger in the case of former. The weight losses of polyesters are presented in Table 7.

Stability in organic solvents: The non-reactive chemical environment influences the stability of polyesters by solvation and dissolution of polymers. Diethylether which is compatible for dissolution of vegetable oil resins and aliphatic organic solvent, dimethyl acetamide which is compatible for the dissolution of polyesters are selected for the present studies on the effect of organic solvents. In addition to these two organic solvents, the commonly used aromatic solvent viz. toluene and benzene are also used in the present study. The polyesters showed lowest degradation rate, this is due to the hydrophobic nature of this polymer network that rises from long aliphatic hydrocarbon chain of fatty acid part of the oil chemical structure. Table 8 shows the evaluation of stability in organic solvents.

Biodegradation: Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degradation. Different end products are formed depending upon the degradation pathway. Polyesters are polymers in which component monomers are bonded via ester linkages**.** Fig. shows the photograph of polyesters before the soil burial degradation test and Fig. 8 shows the photograph of polyesters after soil burial degradation test for 28 days. The original polymer film exhibits a relatively smooth surface. However after 28 days in the soil, large number of holes, cavities, and pin hole were observed in polymer film, Fig. 8 and 9 indicated that the polymer surface was attacked by the microorganism under soil environment.

Antimicrobial studies: The ability to decontaminate surfaces of the cross-linked polyester (CBP) was investigated using gram positive *E. coli* and fungi *Candida albicans*. The studies with the cross-linked poly (Fumarate) biopolyester reveal some antimicrobial activity against *E. coli* and *Candida albicans*.

Fig. 8. Biodegradation test (soil burial test).

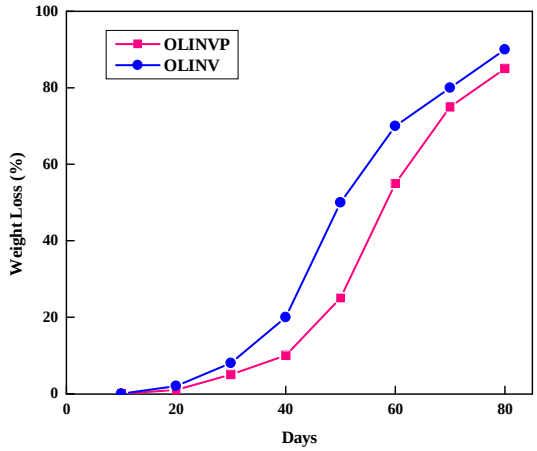


Fig. 9. Biodegradation test (soil burial test) (degradation 30, 60 and 70 days).

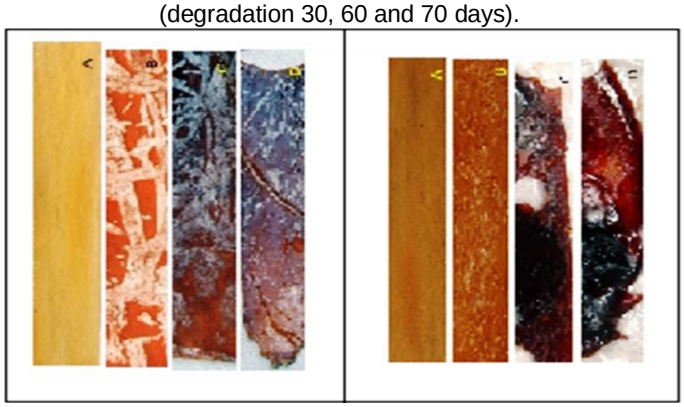


Table 9. Antimicrobial studies with zone of inhibition.

Sample code	*E. coli*	*C. albicans*
COTMMA	7 mm	3 mm
COTBMA	6 mm	4 mm
Gentamycin-10 mg	24 mm	19 mm

The zone of inhibition varies with variation in vinyl monomer and polyester resin composition. Antimicrobial activity of n-vinyl pyrollidone based biopolyesters is comparatively higher than the other prepared biopolyesters. With the present investigation, novel biodegradable and self-disinfecting biopolyester materials could be developed without voids and internal cracks and tackiness. Table 9 shows the antimicrobial activity of polyester using *E. coli* and *C. albicans* indicating the zone of inhibition.

Conclusion

The outcome of these studies has revealed that the newly prepared cross linked bio polyesters are potential biodegradable material for various consumer application like package materials and agricultural applications. The cured polyester films are used for medical purposes as absorbable sutures and agricultural films. In bio-application, their bio-compatibility and bio-degradability play an important role. Unsaturated polyesters resins are used for a variety of applications, achievement of moldable materials free from voids and internal cracks and a tack free cross linked surface with appreciable mar resistance, solvent resistance and resistance, solvent resistance and resistance to bacterial attack during the use is also a major problem in the polyester resin field. While many efforts to overcome this problem have been made, none of these have been fully successful. The present research findings open a new route and scope for the development of low cost addition-curable smart bio polyesters, moulded materials and coatings using the naturally available edible oil raw materials for consumer and engineering applications.

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