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Research Article

STUDIES ON BIO BASED POLYESTERS - THERMAL AND MECHANICAL PROPERTIES

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ABSTRACT

Bio based polyesters from sunflower oil have been investigated. The oligomeric fumarated sunflower oil resin was prepared from *insitu* condensation of maleic anhydride with hydroxylated sunflower oil under controlled reaction conditions. Four new polymeric materials were prepared by varying types of the comonomers Vinyl acetate (VA), N-vinylpyrrolidone (NVP), methylmethacrylate (MMA) and styrene (STY). The new polymeric materials exhibited tensile stress – strain behavior of high cross link density with elastomeric nature to relatively brittle plastics. These sunflower oil-based thermosets show glass transition temperatures ranging from 60 to 82ºC, show high thermal stability, and relatively good damping property despite their high aliphatic (fatty acid) content. They were characterized with respect to their resistance to chemical agents and mechanical properties such as tensile strength, tear strength percentage elongation and hardness. Thermal characterizations such as thermo gravimetric analysis (TGA), Differential thermal analysis (DTA) were carried out. These sunflower oil polymers possessed mechanical properties comparable to those of commercially available elastomeric materials and conventional plastics and this may serve as a replacement in many materials.

Key Words: *Sunflower Oil, Polyester, Tensile Strength, Tear Strength*

INTRODUCTION

The use of bio-based renewable resources for the production of useful chemicals and new materials has grown rapidly during the past few years. This is motivated by the potential advantages offered by the bio-based resources, in environment compatibility and economical feasibility, as compared to the traditional petrochemical derivatives (Biermann *et al.*, 2000, Shogren *et al.*, 2004, Baumann *et al.*, 1988). Polyol, a polyhydroxy compound, is an important building block of polyurethanes and polyesters that are useful in wide range of applications such as construction, coatings agents, adhesives, sealants, elastomers, resins etc. Polyols are traditionally produced from petroleum. However, the production of polyols from petrochemicals is costly, requires a great deal of energy and also has adverse effects on the environment. Research in recent years has thus focused on alternative, non-petroleum based sources of polyesters that are renewable, less costly and more ecofriendly. The biopolyesters synthesized from vegetable oils are an attractive alternative for this purpose and has therefore drawn considerable current attention (Sherringham *et al.*, 2000). Vegetable oils such as sunflower, canola, corn, olive, palm and soy oils are being explored for the synthesis of polyesters. The vegetable oil molecules must however, be chemically transformed to introduce hydroxyl groups for formation of polyols. Among the different vegetable oils, the soy oils have been the more widely explored for polyol synthesis. In addition to being an abundant and inexpensive vegetable oil, there are few other compelling reasons to use soy-oil as the major 'green' feedstock for bio-polyol synthesis and subsequent preparation of polyesters. Sun -oil is highly unsaturated oil (high iodine value ~ 120 - 140) and its number of unsaturations is higher than other vegetable oils (for example, iodine values of palm oil, corn oil, rapeseed oil, are ~ 64, 71, and 84, respectively (Juan Carlos Ronda *et al.*, 2011). It is mainly composed of Triglyceride (TG) molecules) derived from unsaturated Fatty Acids (FA) such as linoleic acid (75 %), oleic acid (22 %), (Sabin *et al.*, 1997). The average number of double bonds per molecule is 4.8. The excellent number of unsaturation present in it makes it a good candidate for polyester synthesis. For the formation of polyesters, the sun-oil molecules need to be chemically transformed so that the double bonds are converted into hydroxyls then followed by the addition of maleic anhydride to form a oligomeric fumarated resin and this acts as a macro homomonomer which upon free radical addition cured with vinyl comonomers to form high crosslinked polyesters.

MATERIALS AND METHODS

Refined sunflower oil purchased from the market was used as received. Sunflower oil is semidrying oil contains mainly oleic and linoleic acid bearing one and two double bonds on their chain respectively. The average molecular weight of the sunflower oil based on ester value was found to be 890 g / mol. Formic acid (98% ,Merck), hydrogen peroxide (30%, Merck), Benzoyl peroxide (Aldrich) Dimethyl aniline (DMA, Aldrich), Morpholine (MP, Aldrich) were used without further purification. The Cross linking agent and co monomers Vinyl acetate (VA), methyl methacrylate (MMA), N- vinyl pyrrolidone (NVP) and styrene (STY) were purchased from Aldrich and purified by conventional drying and distillation procedure.

Infrared qualitative analysis of all the addition-cured biopolyesters were carried out using Nicolet 5700 FTIR spectrometer based on ASTME 1252-98 (Re-approved 2002) and E 573-01. The IR spectra were recorded on thin sheets using an Attenuated Total Reflection (ATR) accessory (Smart Miracle) Zn Se crystal with clean and dry samples. Specific gravity, iodine value, hydroxyl value and intrinsic viscosity of the resin were determined according to the IS Standard 840-1964.Molecular weight of the resin was determined by gel permeation chromatography using μ-styragel columns, $100A^0$ and $500A^0$ UV detector and 280 nm filter. The Polyesters were subjected to thermo gravimetric analysis (TGA) studies at a rate of 100C/min in air using Perkin Elmer, Diamond TG/DTA instruments. Acid, alkali and solvent resistance were estimated according to ASTM Standard D 3137, C 267. The tensile properties of the poly esters are measured on an Instron (Norwood, MA, USA) 4202 according to the ASTM D882-97 standard. Dumbbell shaped specimens were cut out from the polyester using an ASTM D 638 Type V cutter. At least five identical specimens prepared by cutting the material from a polymer sheet were tested and the results averaged. The tear strength of the polymer was determined using a Zwick universal testing machine as per ASTM Standard D624.Indentation hardness (ShoreA) was determined as per ASTM Standard D2240.Hardness tester Durometer was used.

Synthesis of Macro Monomer Oligomeric Poly (Sunflower Oil) Fumarate Resins (o-PSuF)

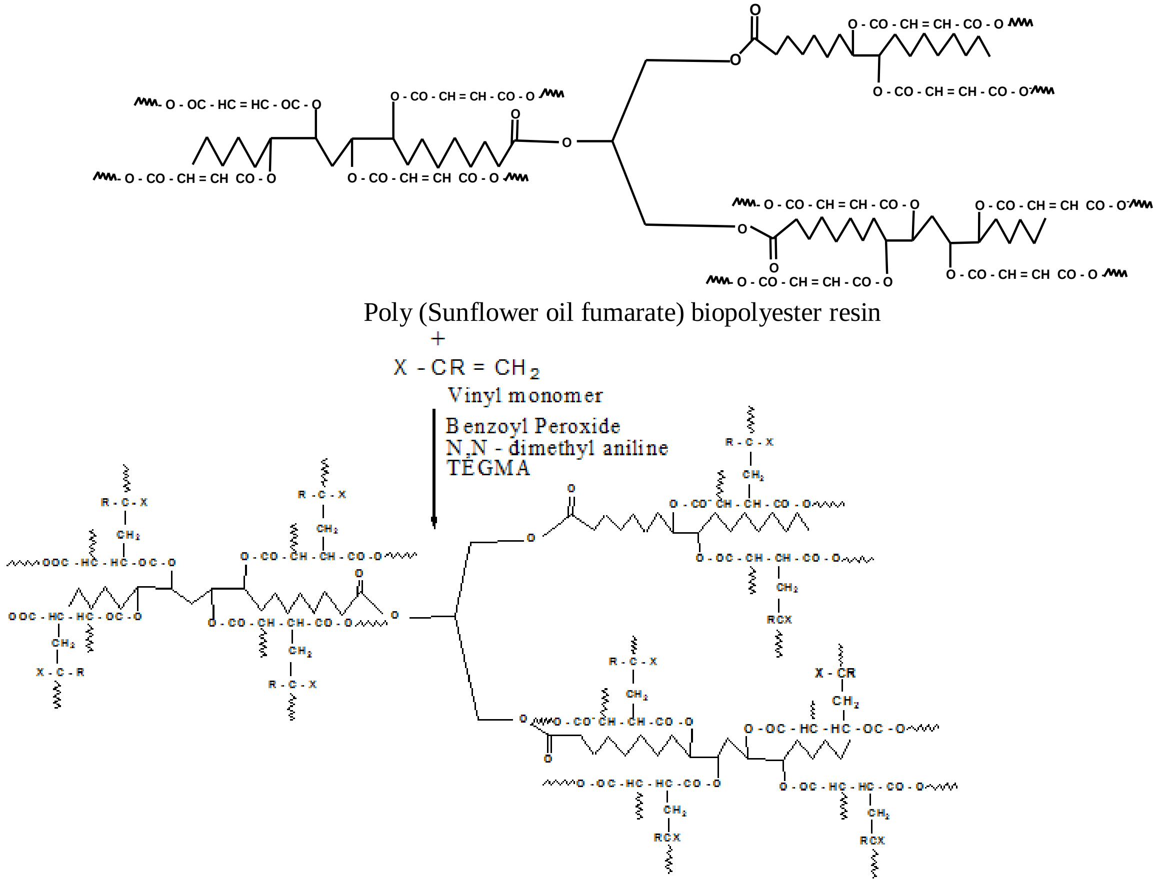
Hydroxylation of sunflower oil was carried out using 30% hydrogen peroxide and formic acid 1000 ml of triglyceride oil was mixed with 1000 ml of 97% formic acid and 550 ml 30% (H_2O_2). Ice water was used externally to keep the temperature below 40^oC. The reaction was vigorously stirred over night. The resulting emulsion was poured into a separatory funnel and extracted with ether. The aqueous layer was washed with water, then with dilute solution of Na_2CO_3 and finally with saturated sodium chloride solution. The resulting ether layer was dried over anhydrous sodium sulphate and the ether was removed by a rotatory evaporator. The resulting product was hydroxylated triglyceride sunflower oil resin (HTSuO) with an average 8.9 hydroxyl groups per glyceride from the ^{1}HNMR analysis. The hydroxylated triglyceride resin was then reacted with maleic anhydride to get oligomeric poly (sunflower oil) fumarate resins (o-PSuF). 400g of hydroxylated sunflower oil and 144.4 g of MA was added when the mixture was warmed to 60^oC under string. Morpholine was used as catalyst. The reaction mixtures was refluxed for 5 hours at 70 - 80oC and then at 160oC ± 2oC for 30 minutes under stirring condition yield a brown transparent liquid resin oligomeric poly (sunflower oil) fumarate with an 8:1 molar ratio of MA to hydroxylated triglyceride of sunflower oil. The hydroxylated triglyceride sunflower oil resin (HTSO) and oligomeric poly (sunflower oil) fumarate resins (o-PSuF) obtained were analyzed by physicochemical methods like iodine value, saponification value, specific gravity and viscosity and spectral analysis by UV, IR and NMR analysis.

Preparation of Biodegradable and Cross Linkable Poly (Sunflower Oil) Fumarate co-Vinyl Monomer Based Polyesters

The unsaturated addition curable poly (sun oil fumarate) bio polyester resins were prepared by using hydroxylated sunflower oil and maleic anhydride. The final oligomeric resin contain fumarate ester linkages in all the three fatty acid units contains the hydroxyl groups. The analysis of molecular weight indicates the oligomeric nature of the resin. This unsaturated resin undergo addition curing with vinyl comonomers vinyl acetate, methylmethacrylate, N-vinyl pyrrolidone and styrene by free radical mechanism with free radical initiator benzoyl peroxideand accelerator dimethyl aniline and cross linking agent TEGMA. Four biodegradable and crosslinked polyester materials were prepared using the above formulation and coded as PSuFVA, PSuFMMA, PSuFNVP and PSuFSTY. The curing of polyesters was completed for about 6 hours at room temperature and kept at desiccators. Then the materials were evaluated.

RESULTS AND DISCUSSION

Sun flower oil contains 75% unsaturated oleic and linoleic acid high degree of unsaturation makes it possible to polymerize it into useful materials.



Vinyl Monomer	X	R
Vinyl Acetate	$OCOCH_3$	H
Methylmethacrylate	$COOCH_3$	CH_3
n-Vinylpyrrolidone	C_6H_9NO	H
Styrene	C_8H_8	H

Figure1: Scheme for the synthesis of cross linked biopolyesters (CBP) based on Poly (sunflower oil) fumarate and vinyl monomers

The reaction of the hydroxyl functional triglyceride with maleic acid at 160^{o}C incorporates fumarates into the triglycerides of sunflower oil. The unsaturated monomer can then be blended with reactive comonomers vinyl acetate, methylmethacrylate, N-vinyl pyrrolidone and styrene by cured by free radical polymerization. Figure 1 scheme reports the conversion of sunflower oil into useful sold polymers .the advantages of these polymeric materials are low cost, availability from the renewable natural resources and their possible degradability.

Spectral Studies

The synthesized resins were characterized by FTIR and ^{1}HNMR techniques. The FTIR spectra of all sun flower, hydroxylated sun flower and o-PTFSU resins are recorded between 500 cm^{-1} to 4000 cm^{-1}(Figure 2-4). FT-IR spectra of sunflower oil samples show that there exist notable difference in the band around 3006 cm^{-1} assigned to the C-H stretching vibration of the cis-double bond =CH. The oil composition affects the exact position of the band and yields shifts when the proportion of the fatty acid changes. Sun flower oil showed a maximum absorbance at 3008.82 cm^{-1}. This is due to the higher proportion of linoleic acyl groups (Sabin *et al.*, 1997). The 2925.81 cm^{-1} band is attributed to the symmetric stretching vibration of the aliphatic CH_2 groups. The peak appeared at 3008.82 cm^{-1} of sunflower oil due to the presence of C-H stretching of the *cis*-double bonds (=CH) become weak or disappeared in hydroxylated oil, which may due to the substitution of the hydroxyl group at the olefinic double bond. Also the peak around 1656.01 cm^{-1} in sunflower oil indicated the C=C stretching vibration of *cis* olefins also disappeared in the all hydroxylated resins supported the substitution happened only at the olefinic bonds. In hydroxylated triglyceride resins, the FT-*IR spectra showed a strong absorption band at 3434.02 cm^{-1}, due to the present of free -OH group in the molecule. The peak appeared at ~3434.02 cm^{-1} for hydroxyl group substitution in unsaturated acid units of oleic, linoleic and, linolenic of the vegetable oils. The corresponding peak is drastically reduced in the O-PTFSU resins drastically indicated the - OH group get substituted. A strong absorbance band in 2925 cm^{-1} is due to the presence of C=0 of the glyceryl ester moiety. A strong band in 2855.42 cm^{-1} is due to the symmetrical -C-H bond in -CH_2-group of the side chain. The HTO resins show the carbonyl band of triglyceride ester group at 1725.21 cm^{-1} and the maleated hydroxylated shows the carbonyl band of triglyceride combined with maleate group at 1641.31 cm^{-1}. The O-PTF resins displays the absorption characteristic of Trans double bond at 982.66 cm^{-1}, proving that the rearrangement of the maleate group to the fumarate group. The possible peaks in H^{1}NMR for quantitating unsaturated fatty acids are those of olefinic protons *(*5.3 - 5.4 ppm), protons attached to the bis-allyllic carbons (2.78 - 2.75 ppm), protons attached to allilylic carbon (2.0 - 2.3 ppm), methylene -CH_2- (1.3 - 1.6 ppm) and the terminal methyl protons (0.8 - 0.9 ppm). The peaks at 4.1 - 4.3 ppm originate from the protons in the methylene groups of the triglyceride. The peak at 5.3p pm indicates the presence of olefinic protons in the oil. This peak disappeared in the hydroxylated resin showing that the olefinic double bond is replaced by the hydroxyl group and reappeared in the fumarated resins due to the presence of unsaturated group (Figure 4). The protons in the -CH_2 - group between the C=C double bonds appear at 2.7 - 2.8 ppm. This peak is shifted to 3 - 3.2 ppm in the hydroxylated resin due to the deshielding caused by the oxygen atom of the hydroxyl group. This peak is shifted to 3.1 - 3.2 ppm in the fumarated resins due to the deshielding effect of hydroxyl and carboxylate ester linkages are shown in the figure -6.The strong peak at 1.3 ppm is attributed to the long chain having more than five -CH_2 - groups. The peak at 0.95 to 2.3 ppm is due to the long aliphatic side chain (Thomas *et al.,* 2009).

The completion of cross linking of the crosslinked biopolyesters was studied by AT-IR spectral studies. The AT-IR spectra of crosslinked biopolyesters (CBP) based on poly (sunflower oil fumarate) biopolyester resin and vinyl monomers are given in figures. The carbonyl band of 1754cm-^{1} in the poly (sunflower oil fumarate) biopolyester resin is shifted to 1707.9in PSuFVA, 1707.1 in PSuFMMA, 1711.8 in PSuFNVP, 1721.5 in PSuFSTY. The maximum shift is observed in hard polymers and minimum shift in ductile polymers. This is due to the tightness of the polymer network and reduced molecular mobility in brittle polymers. The AT-IR spectrum of crosslinked biopolyesters (CBP) based on Poly (sunflower oil fumarate) biopolyester resin and vinyl monomers are given in Figures 7-10.

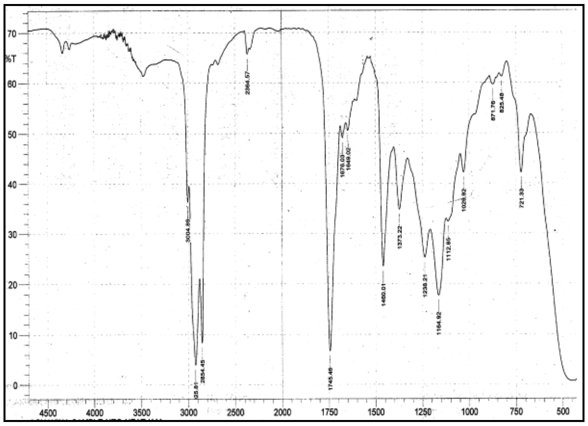


Figure 2: FT-IR Spectra of sunflower oil

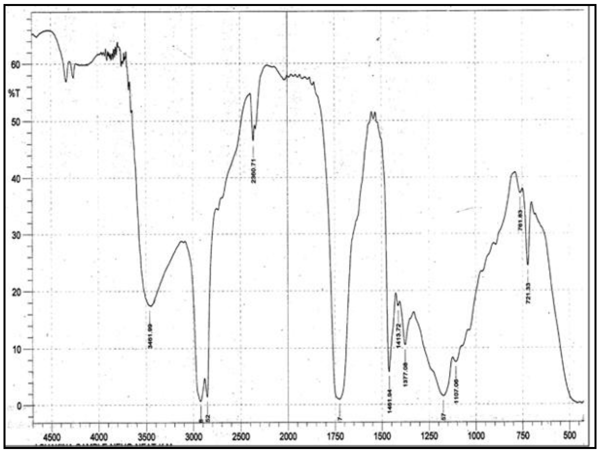


Figure 3: FT-IR Spectra of hydroxylated sunflower oil

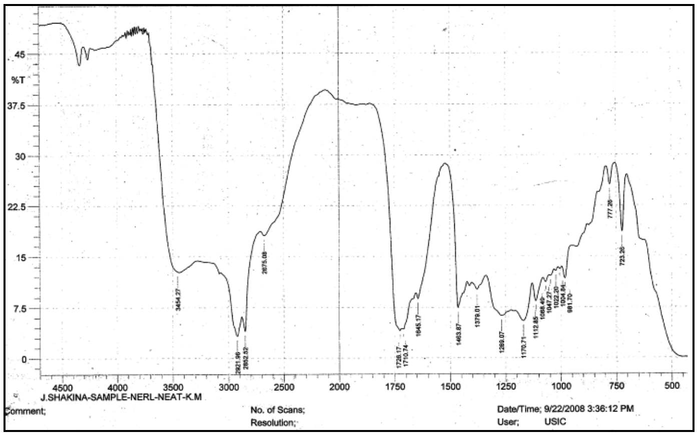


Figure 4: FT-IR Spectra of addition curable poly (sunflower oil fumarate) biopolyester resin

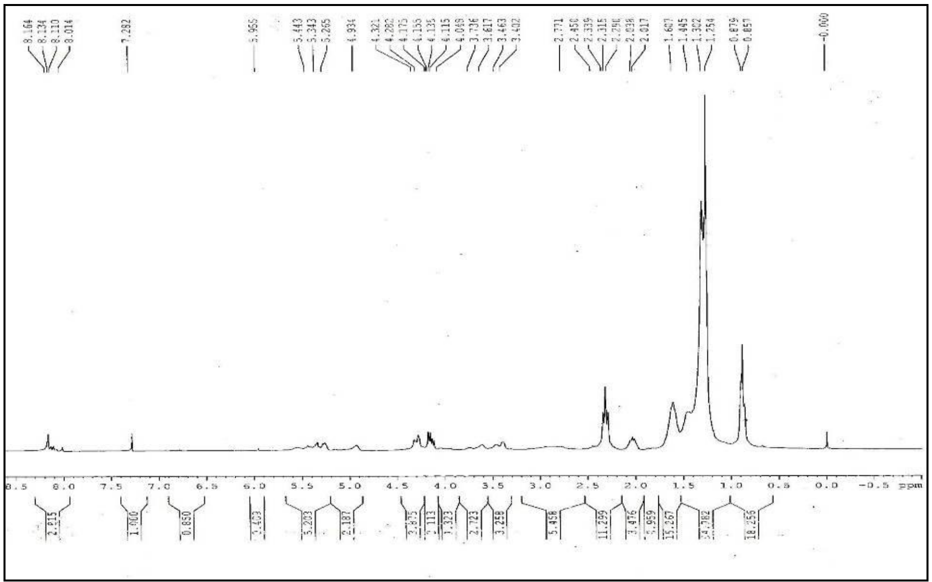


Figure 5: H^1 NMR spectra of hydroxylated sun flower oil

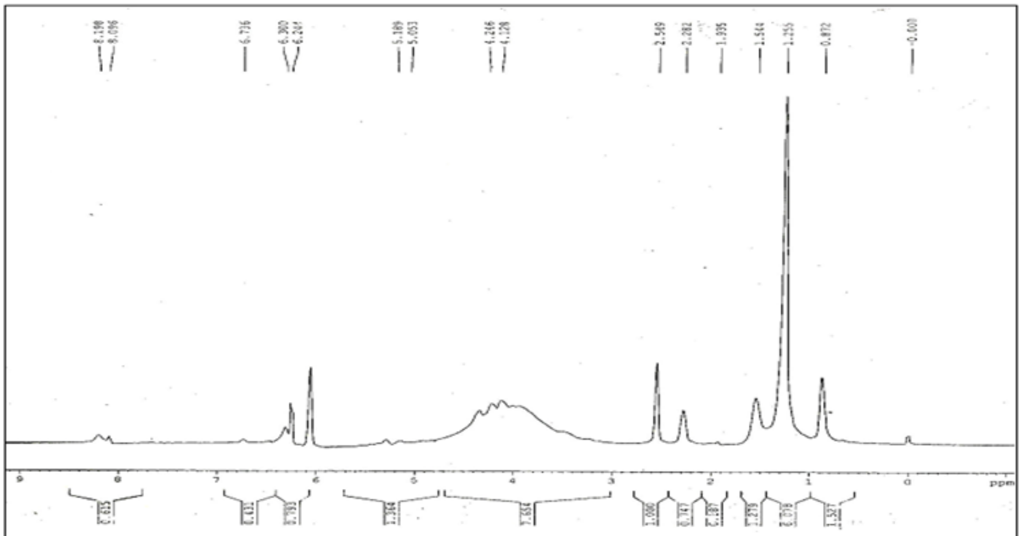


Figure 6: H¹NMR Spectra of *addition curable poly (sun oil fumarate) biopolyester resin*

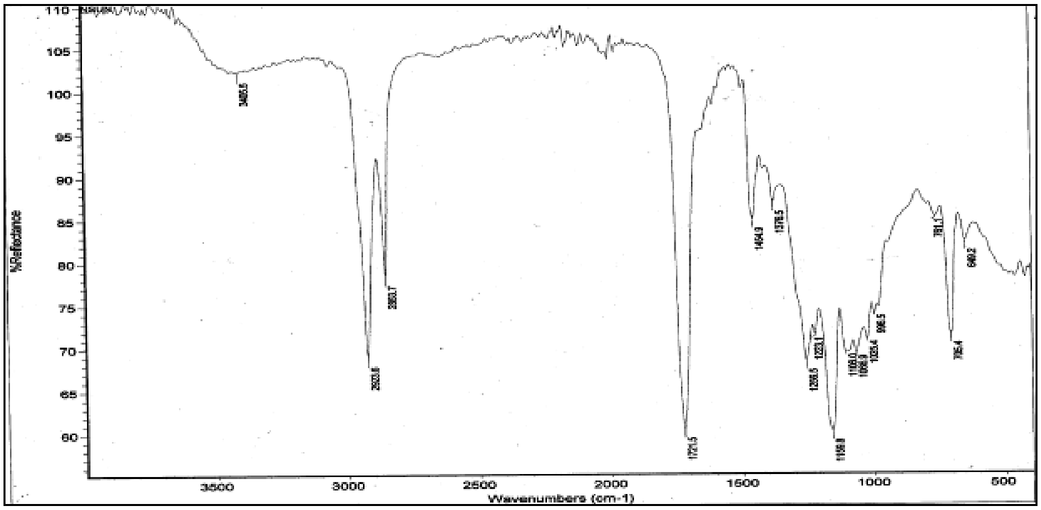


Figure 7: AT-IR spectrum of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin and vinyl acetate

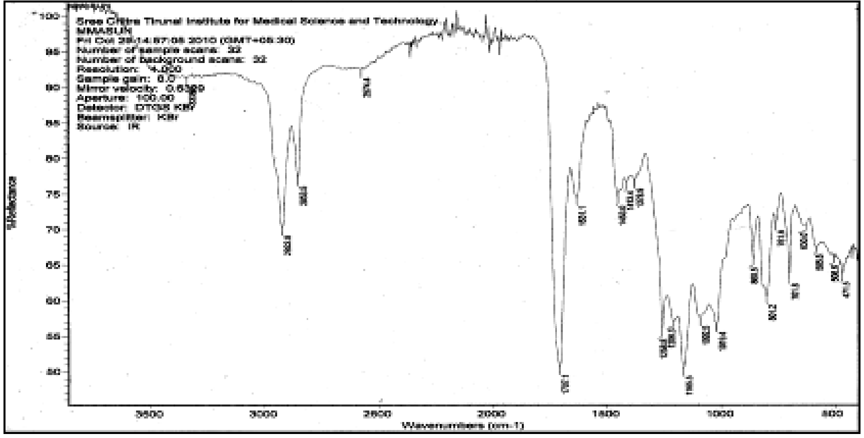


Figure 8: AT-IR spectrum of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin ad methyl methacrylate

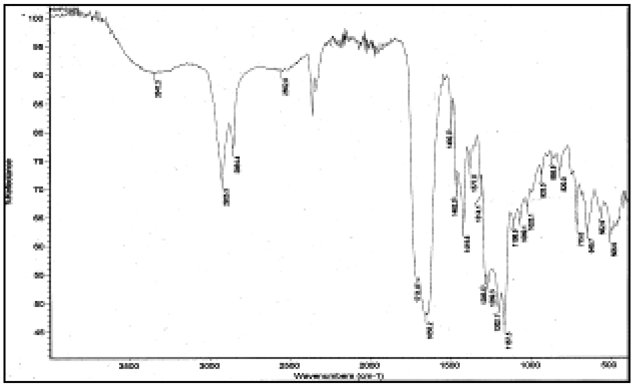
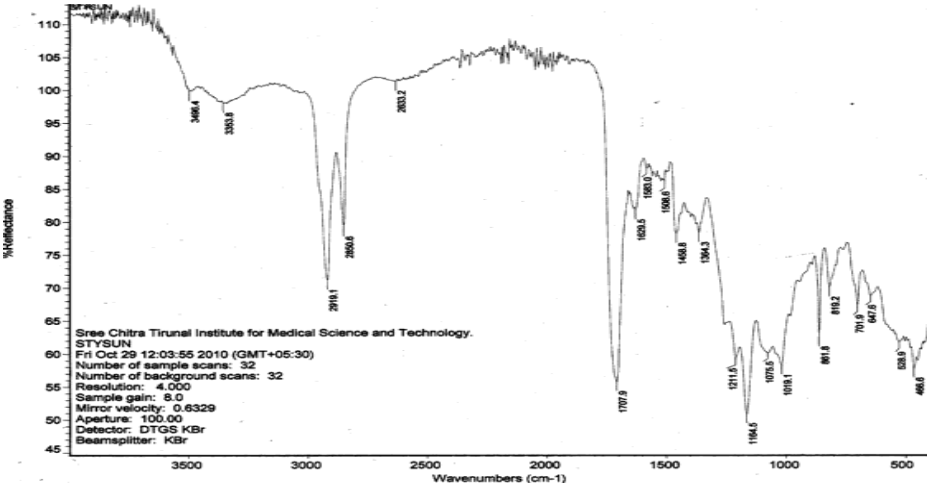


Figure 9: AT-IR spectrum of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin ad n-vinyl pyrrolidone



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Sample gain:  8.0
Mirror velocity:  0.6329
Aperture:  100.00
Detector:  DTGS KBr
Beamsplitter:  KBr
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Figure 10: AT-IR spectrum of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin and styrene

Thermal Properties

The TGA curves for decomposition of crosslinked show more than three stages of decomposition. The thermo gravimetric data of biopolyesters show that they are invariably stable under moderate temperature conditions, 10% weight loss occurs only at reasonably high temperatures. The thermo gravimetric data of sun based biopolyesters shows the initial degradation temperature interestingly the T_{start} of vinyl acetate based biopolyesters is appreciably lower than that of other sun based biopolyesters. During degradation, the reactions of chain scission and further cross linking occurred simultaneously with an increase in the number of chemical bonds in the net work that led to the char structure formation at the end of the process. (Umare *et al.,* 2007)

The DTA curves do no exhibit any remarkable endothermic peak for softening .DTA curves show multi stage endothermic peaks characterizing thermal decomposition. The DTA curves of the biopolyesters indicate mild softening at less than 140^{o}C which is due to the disruption of physical crosslinks. The DTA curves also indicate three endotherms, above 200^{o}C for chain scission and degradation, more than two exotherms for crosslinking of the degraded fragments of the biopolyesters. The thermal degradation of the present sun based biopolyesters can follow two major pathways viz side group elimination and random scission. With the present sun based biopolyesters the initial degradation with the cleavage of long alkyl side chains takes place with the first endotherm. This is due to the flexibility of the long alkyl side chain and subsequent degradation occurred in the main chain of the polyesters. From the figures 11-13 the DTA analysis exhibits endothermic and exothermic response alternatively starting from 200 to 700^{o}Cwhich is attributed to the alternate events of thermal degradation and subsequent cross linking of chain fragments with higher crosslink density (Sathiyalekshmi *et al.*, 2004).The data are presented in the Table 1. The thermal stability of biopolyesters rated in terms of temperature at which the initial degradation with chain scission and weight loss starts. The thermal stability of sun based biopolyesters is in the order PSuFSTY> PSuFMMA> PSuFNVP> PSuFVA.

Table 1: TGA-DTA data of poly (sun oil fumarate) Resin with vinyl monomers

Polyesters	**Temperature (^{o}C) at the End of Each Stage of Degradation (Weight Loss,%)**				**50% Weight Loss**	**Residue (mg)**	**DTA**					
	T Start	**I Stage**	**II Stage**	**III Stage**			**Exo_1**	**Exo_2**	**Exo_3**	**Endo1**	**Endo2**	**Endo3**
PSuFVA	138.35 (3.2)	249.76 (24.80)	497.55 (92.32)	-	367.83	0.07035	173.69	418.65	-	225.23	312	
PSuFNVP	139.55 (4.50)	259.24 (30.76)	402.64 (67.35)	712.03 (97.130)	330.20	0.01704	139.95	436.07	614.42	301.22	537.54	-
PSuFMMA	130.52 (2.80)	231.01 (14.25)	305.54 (21.13)	688.32 (96.14)	380.52	0.1192	353.55	427.84	609.47	285.27	390.82	526.38
PSuFSTY	155.36 (2.64)	299.89 (14.47)	355.22 (22.51)	653.32 (98.682)	420.22	0.00997	447.16	586.81	-	180.48	391.65	525.93

Differential scanning calorimetry (DSC) provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer.The percentage crystallinity can be calculated from the DSC curve using the relation

% Crystallinity = (ΔHm – ΔHc) / ΔHm°· 100%

In this equation, the heats of melting and cold crystallization are in terms of J/g. The term ΔHm° is a reference value and represents the heat of melting if the polymer were 100% crystalline. This reference heat of melting has been established for each of the commonly used polymers and some of these are listed as Polymer ΔHm°(J/g) Nylon 6-230.1, Nylon 6,6-255.8, PET-140.1, Polypropylene-207.1, Polyethylene-293.6. The PerkinElmer Temperature Dependent Crystallinity software directly provides these values to make the assessment of the percent crystallinity more convenient and easier .From the DSC studies the glass transition temperature (Tg^{o}C) and the melting temperatures (TmoC) were calculated. The Tg values clearly indicated that the polymers are semi crystalline in nature the values are displayed in Table 2. During degradation, the reactions of chain scission and further cross linking occurred simultaneously with an increase in the number of chemical bonds in the net work that led to the char structure formation at the end of the process.

Table 2: DSC properties

Polyester	**Sample Melt Onset Temperature (^{o}C)**	**Melt Peak Temperature (^{o}C)**	**Enthalpy (J/g)**	**Crystallinity (%)**	**Tg(^{o}C)**
PsuFVA	139.36	539.25	713.1	35	63.74
PsuFNVP	139.15	713.72	636.7	24	71.67
PsuFMMA	145.09	614.46	325.1	12	75.71
PsuFSTY	357.16	593.53	505.3	18	92.69

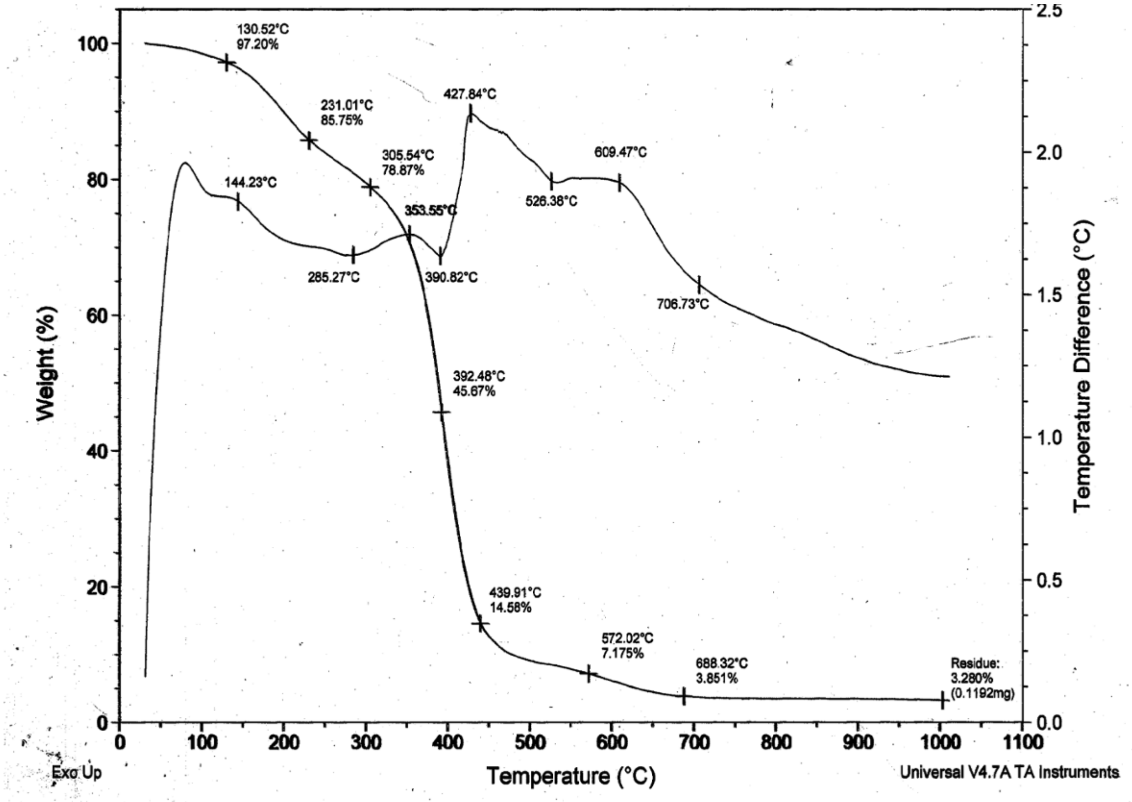

Figure 11: TGA/DTA curve of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin and methyl methacrylate

In the present work the calculation of kinetic parameters was performed by an approach with the application of the Freeman-Anderson method. (Suwanprasop *et al.*, 2004) The equation used for the Freeman-Anderson method is as follows:

$$\Delta \log\left(-\frac{dw}{dt}\right) = n\Delta \log \overline{w} - \frac{E_a}{2.303\ R}\Delta\left(\frac{1}{T}\right)$$

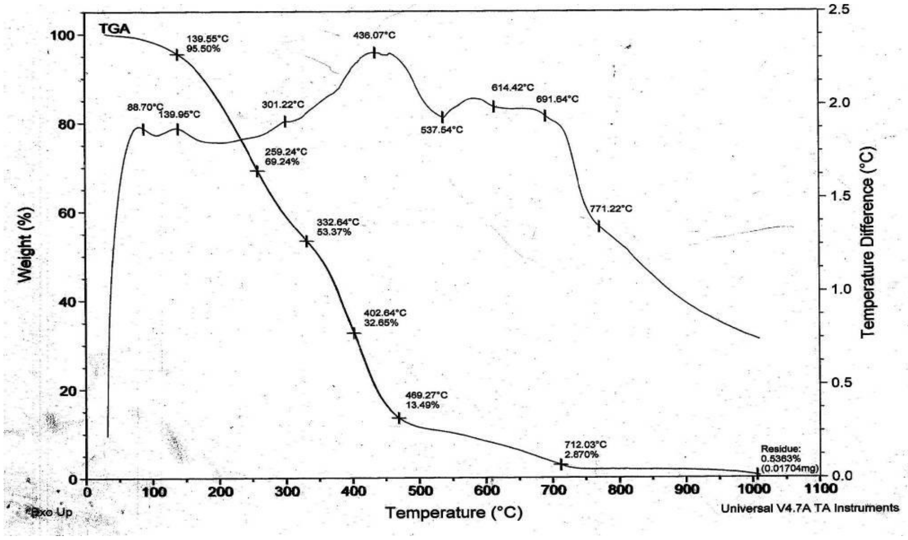

Figure 12: TGA/DTA curve of crosslinked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin and NVP

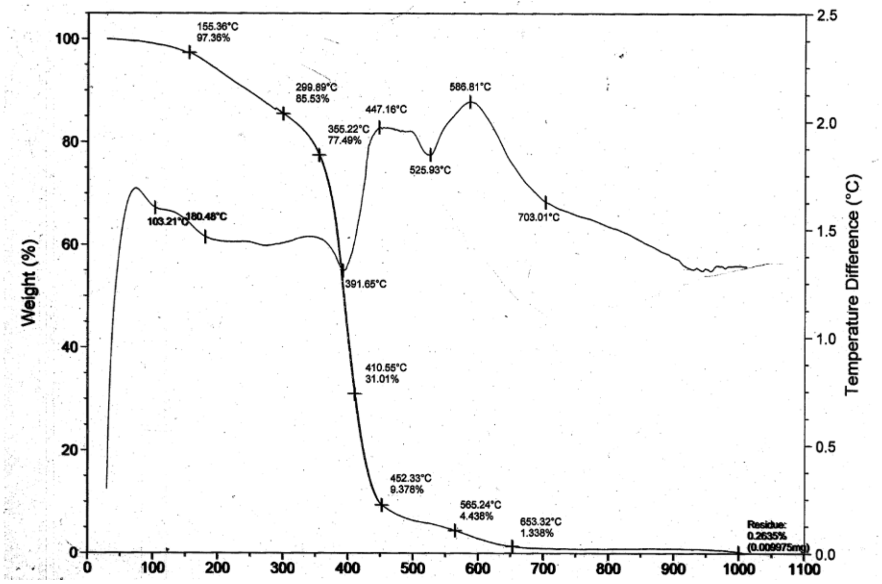

Figure 13: TGA/DTA curve of cross linked biopolyesters (CBP) based on Poly (sun oil fumarate) biopolyester resin and styrene

Kinetics of Thermal Degradation (Freeman-Anderson Method)

Where -dw/dt is the rate of decomposition (calculated from DTG measurements), w is the residual mass (calculated from TG measurements) at constant difference in 1/T (0.1x 10^{-3}), ‘n’ is the order of reaction and E is the energy of activation.(Ganga Raju Achary et al 2012) Freeman-Anderson plots for kinetic parameters in the temperature ranges of 200^0C to 300 ^{0}C and 315^0C to 440^0C respectively were obtained by plotting Δ log(-dw/dt) against Δlog*w* corresponding to a constant difference in 1/T. According to Equation, the plot of Δlog (-dw/dt) against Δlog (w) for equal interval of Δ(1/T) would be a straight line with slope equal to n and the intercept equal to –E/R Δ(1/T).

Kinetic Parameters for the Thermal Degradation

The thermal degradation of polymers is a complex process. So it becomes very difficult to obtain the exact kinetic parameters of each reaction involved in the decomposition process of the polymer blends because of the complexities in identifying the temperature intervals of the individual reactions due to superposition of different stages of reaction and the shift in temperatures of thermal effects on DTA curve (Mishra et al ,1996).But such kinetic parameter calculations help to a greater extent in understanding the complexities involved in the thermal degradation of polymers. Thermo gravimetric analysis (TGA) is widely used for the determination of the kinetic parameters of polymer degradation. Table - 3 shows the kinetic parameter data such as activation energy and order of reaction for the various decomposition reactions taking place in the thermal degradation of the polymer blends at various temperature ranges using the Freeman-Anderson’s approach.

The Freeman-Anderson plots, for kinetic parameters were obtained by plotting Δlog(-dw/dt) against Δlog*w* corresponding to a constant difference in 1/T in the temperature range of 200°C to 300 °C and 315°C to 450 °C. Table shows the activation energies (Ea) and order of the reactions (n) of the thermal degradation of the polymer blends at various temperature ranges. The kinetic parameters also agree with the thermal analysis data that the PSFSTY is more stable than the other polymer.The average activation energy between 200^0C and 450^0C was found to be 25.83, 48.95, 55.74 ,73.79 for the polymer blends PSuFVA, PSuFNVP, PSuFMMA, PSuFSTY having 2.6, 4.17, 1.845 and 2.135 as average order of the reactions respectively. From the data it may be inferred that PSuFSTY is thermally more stable than the other three biopolyesters. The Freeman –Anderson method also predicts that the PSuFSTY is more cross-linked than the other biopolyesters. The nonlinearity of the plots between 300-450 ^{0}C in Figure predicts the complex reactions involved in the thermal degradations of the blends. Overall, the Freeman-Anderson approach is found to be in good agreement with the experimental thermal data with little deviations.

Table 3: Kinetic Parameters of Thermal decomposition of biopolyesters by Freeman-Anderson Method

Biopolyesters	**Temperature Range(^{o}C)**	**Ea(KJmol-1)**	**n**	**r^2**
PSuFVA	200-300	22.32	3.12	0.998
	315-450	29.34	2.10	0.845
PSuFNVP	200-300	42.56	2.05	0.993
	315-450	55.34	2.12	0.972
PSuFMMA	200-300	49.57	2.19	0.985
	315-450	61.91	1.50	0.986
PSuFSTY	200-300	69.23	2.13	0.999
	315-450	78.34	2.43	0.971

Mechanical Properties

The tensile strength of the polyesters are largely influenced by the presence of aromatic groups, ether groups, long alkyl chain, dangling chains, branching and cross linking and also degree of hydrogen bonding. (Sathiyalekshmi *et al.*, 2004) 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. 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 Shore-A hardness of the PSuFSTY oil biopolyesters shows the higher hardness among all the biopolyesters prepared from sunflower oil copolymerized with the vinyl monomers. The biopolyesters are thermosets due to the cross linking through the multiple carbon-carbon double bonds present in the oligomeric poly triglyceride vegetable oil biopolyester resin of sunflower oil and the comonomers VA, MMA, NVP, STY. Generally, free radical initiator, benzoyl peroxide accelerates the copolymerization reaction with vinyl monomer through the conjugated double bonds as reported elsewhere (Li and Larock, 2001). The samples of biopolyesters obtained using different comonomers have characteristics that vary from rubber to hard plastics..They appear to be plastics with crosslink densities ranging from 7.940-3.212x10^{3}. 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 is a direct result of different degrees of unsaturation of the different macro monomers employed. Among the cross linked biopolyesters, styrene based polyesters and methyl meta acrylate 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 (Nielson and Landel, 1994).The magnitude of the rubbery modulus indicates styrene 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 crosslinking until failure occurs. Thus, cross linking also increases the ultimate tensile strength of the polymers. (La Scala and Wool, 2005) It is obvious that with more fumarate unit modification both flexure and tensile properties increases. The modification with fumarate unit increases the chemical functionality of the polyester resins resulting in a increase in crosslink density. Thus, from these results, the modulus and strength of triglyceride based polymers can be increased by simply increasing the chemical functionalities of the triglycerides. The mechanical properties of the crosslinked addition cured biopolyesters such as tensile strength, tear strength, elongation to break shore hardness are given in the Table 4.

Table 4: Mechanical properties of polyesters

Polyesters	Tensile strength (Mpa)	Tear Strength (KN/m)	% elongation at break	Hardness Shore (A)	Crosslink density Mol/m^3	Mol. wt. between crosslinks (mol^{-1})	Tensile Modulus (MPa)
PSuFVA	14.39 ±1.34	26.12	47.0 ± 1.6	75	3.123	320	83.25 ± 0.12
PSuFMMA	30.20 ±0.45	23.11	32.31 ± 1.5	77	5.255	190	268.61 ± 0.83
PSuFNVP	23.54 ±0.32	34.62	67.42 ± 0.3	86	4.203	237	344.13 ± 0.56
PSuFSTY	39.47 ±0.67	47.63	44.01± 0.4	92	6.549	152	72 ± 0.54

Reactivity of Polyesters towards Chemical Reagents

The chemical reactivity of polyesters is studied using 1N hydrochloric acid, 1N sulphuric acid, 1N acetic acid, 1N sodium hydroxide, 30% hydrogen peroxide, 1N sodium chloride, diethyl ether, toluene, ethanol and water and the percentage weight loss of the polyesters are furnished in Table 5.From the results, it has been found that polyesters from vinyl acetate based monomers have shown a slight percentage of degradation is within 2% towards acids, and oxidizing agent and toluene. There was a considerable weight % change in alkali medium. There was 2% change in weight when these polyesters are treated with 1N sodium chloride, diethyl ether, ethanol and water.

Table 5: Chemical reactivity of polyesters: Percentage of weight loss polyesters

Polyesters	1N HCl	1N H_2SO_4	1N CH_3COOH	1N NaOH	30% H_2o_2	1N NaCl	Toluene	Diethyl Ether	Ethanol	Water
PSUFVA	1.78	2.73	0.03	28.34	0.87	0.05	0	0	0.03	2.23
PSUFMMA	1.87	2.02	0.02	11.45	0.84	0.03	0	0	0	0.04
PSUFNVP	1.95	2.15	0.01	15.22	0.95	0.04	0	0	0	1.28
PSUFSTY	1.12	2.04	0	10.42	0.03	0	0	0	0	0.02

CONCLUSION

The development of novel polyesters from sunflower oil is reported. The TGA analysis shows that there are three decomposition region of the unreacted oil present in the bulk polymer, degradation and char formation of the cross linked biopolyesters and finally due to the oxidation of the char residues in air. PSYSTY polyester was observed to thermally more stable than other polymer samples due to high crosslink density. The styrene based polyesters possess better mechanical properties than the other vinyl monomer based polyesters. All the polyesters are stable towards the chemical reagents. With the present investigation novel biodegradable and self disinfecting biopolyester materials could be developed without voids and internal cracks and tackiness.

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