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Synthesis And Characterization of Certain Aliphatic Polyesters Contains Citric Acid Moiety

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ABSTRACT: *Biodegradable aliphatic random copolyesters were synthesized from SeCS, SuCM by using sorbital/ D-mannitol, sebacic acid, succinic acid and citric acid through direct melt polycondensation with titanium tetra isopropoxide as a catalyst. These polyesters were characterized by Viscosity measurements, IR studies, ^{1}H Nuclear Magnetic Resonance Spectroscopy and X-Ray Diffraction analysis. Thermal properties have been analyzed using Differential Scanning Calorimetry Biodegrdability of synthesized polyesters also studied.. This kind of novel biodegradable polyesterr are expected to have potential application in drug delivery.*
Keywords: *Aliphatic Polymers, Biodegradable Polyesters, Enzymatic Degradation.*

I. INTRODUCTION

Polymers find important applications for a variety of commodity products ranging from household articles to nanocomposites. Worldwide production of plastic is more than 110 million tons per year. Almost half of them are discarded within a short time and remained in garbage deposits and landfills for decades. Therefore, synthetic plastics have accumulated in nature at a rate of 25 million tons per year, such a huge production of polymers results in environmental pollution. For this reason, it is necessary to develop more recyclable and/or biodegradable polymers to reduce the amount of plastics in landfills. One way to solve the problems of waste management is to replace bioresistant synthetic polymers, which are in use today, with biodegradable polymers. The development of biodegradable polymers for packaging, sanitary and agricultural uses would partially solve the problem of plastic waste.[1-2] Biodegradation is an efficient and rapid way for eliminating some plastic wastes under composting and land filling conditions.[3-8] There have been a number of biosynthetic and chemosynthetic biodegradable polyesters developed as green polymers and a wide variation in their physical properties and mechanical properties along with biodegradability is favorable for processing these products.[9] Hence, the development of new biodegradable polymer systems has been an area of major research priority. In this study deals with the investigation on the synthesis, characterization and biodegradation properties of certain new polyesters containing aliphatic moieties in the polymer backbone.[10]

Currently, different copolyesters have been synthesized and notable work has been controlled in the preparation, Characterization and use of polymers.[11] Direct melt polycondensation is a very needful method for preparation of polyesters since it is environmentally when compared with other polymeric synthesis technique and consequently it comes under green chemistry.[12] Biodegradable polymers have attracted considerable attention as green material and biomedical engineering application including drug delivery system, artificial implants and functional materials in tissue engineering. Among synthetic polymers, aliphatic polyesters have attracted considerable attention as they combine the features of biodegradability, biocompatibility and physical or chemical properties comparable with many traditional and non biodegradable polymers.[13-21]

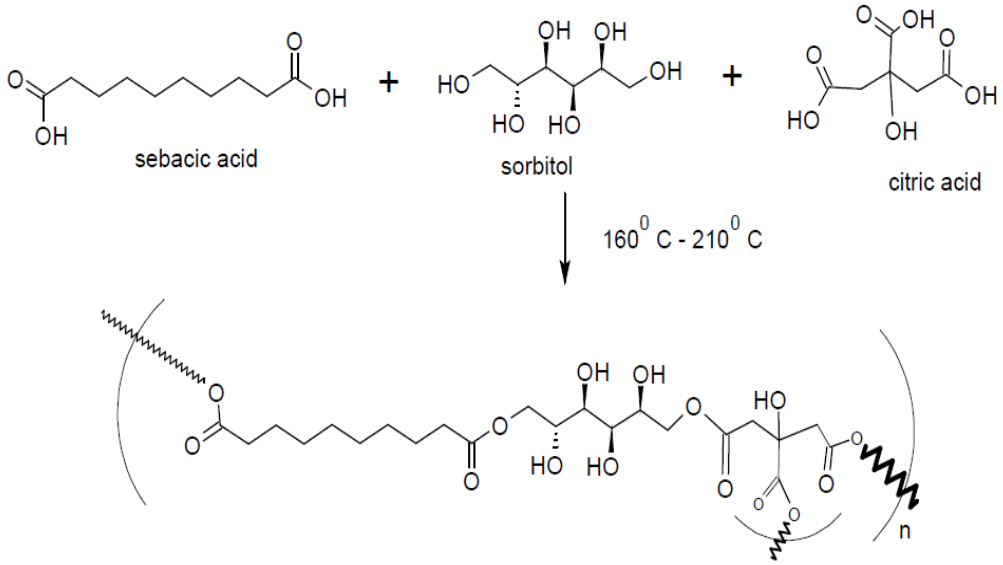
II. MATERIALS

Sebacic acid (SE), Citric acid(C), Sorbital (S) and Succinic acid (Su), Citric acid (C), D-mannitol (M) were purchased from Sigma Aldrich Titanium Tetraisopropoxide (TtiPo), used as a catalyst was purchased from Lancaster. All other chemicals and solvents (AR Grade) were used as such.

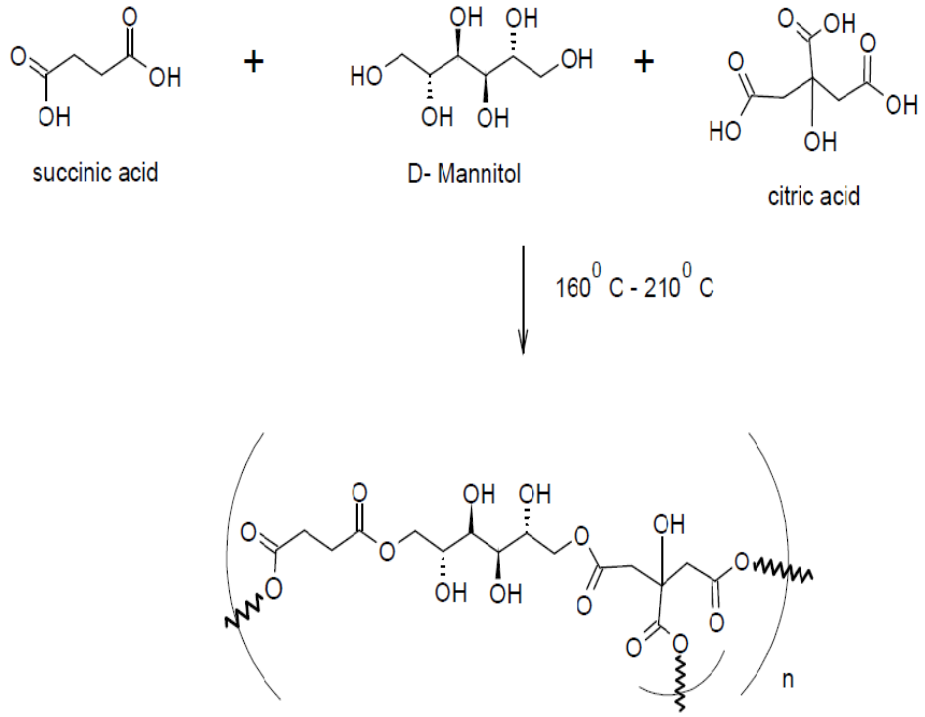
1. Synthesis of copolyesters:

The Aliphatic copolyesters were synthesized from SeCS and SuCM by using a two-step melt polycondensation. A mixture of Sebecic acid (SE) 0.1 mol. Citric acid (C) 0.1 mol and Sorbital (S) 0.2 mol with 0.1 mol of TtiPO as catalyst taken in reaction flask was slowly heated to 160^{o}C for 2 hour to remove water as by product. The prepolymer heated One hour under vaccum condition to increase the molecular weight of the polyester.The synthesized polymer separated using methanol. By using the same method polymer SuCM was

also synthesized. Both polymers were dried under vaccum for charecterisation.The scheme of the polyester synthesis is as follows



Scheme: 1 Synthesis of copolyester SeCS



Scheme: 2 Synthesis of Copolyester SuCM

III. CHARACTERIZATION OF COPOLYESTERS

1.1. Solubility Studies:

The solubility of the polymers was determined in various organic solvents, 10mg of the polyester sample was taken in a small Stoppard test tube and 1ml of the solvent was added. The solubility of polyesters were recorded.

1.2. Viscosity measurements:

Inherent viscosities of the Co polyesters were measured in chloroform at 30 ± 1°C using Ubbelohde viscometer. 25mg of the dry polyester sample was dissolved in 25ml of chloroform. About 20ml of the solution

was taken in the viscometer kept in a thermo state maintained at 30°C and the flow times were determined for the pure solvent first and then for the polymer solution.

From the flow, the relative and inherent viscosity values were calculated using the relationships,

$$\eta_{rel} = \frac{\text{flow time of the polymer solution}}{\text{flow time of the solvent}}$$

$$\eta_{inh} = \frac{2.303 \log \eta_{rel}}{C}$$

Where "C" is the concentration of the polymer solution expressed in g/dL.

3.3 Infrared Spectroscopy:

Infrared spectroscopy has been used extensively in qualitative and quantitative analysis of Copolyesters and in determining the structural units of the polymers.The spectra were recorded using Bruker IFS 66VFT – IR spectrophotometer with KBr pellets in the range of 4000-400cm^{-1} at 25°C.

3.4. Nuclear Magnetic Resonance Spectroscopy:

^{1}H and ^{13}C NMR spectra of copolyesters were recorded using JOEL–GSX–400 spectrometer. DMSO was used as solvent in order to prepare solutions of 5% w/v and TMS was used as internal standard.

3.5. Thermal analysis:

DSC Thermograms were recorded on a PERKIN ELMER PYRIS - 1 differential scanning calorimeter. About 2-4 mg of the polymer sample was heated in an Aluminium pan with pierced lid under nitrogen atmosphere at a scanning rate of 10°C / mts between a temperature range of – 100 °C and 500 °C.

3.6. X-Ray diffraction analysis:

A Siemens D 500 diffractometer with Cu Kα filtered radiations was used for assessing the crystallinity of the polymers. The samples were scanned over the range of 2θangle, from 0º-80º.

3.7. Test for biodegradability of Polyesters:

The biodegradability of the Polyesters Synthesized was assessed by the following test method.

3.7.1 Enzymatic Degradation Test:

Polyester thin films were obtained by hot pressing method. The thin films of area 10 x 10 mm^2 and about 200μm thickness were placed in a Petri dish containing 10ml of phosphate buffer solution (pH 7.00 ± 0.01) with 1mg/mL lipase enzyme originating from Candida Cylindracea. After a specific period of incubation, the films were removed from the dish, washed with distilled water and dried weighed till constant weight.. This procedure was repeated for every chosen time interval: 9,24,48,72 and 90 hours.

The degree of biodegradation was estimated from the weight loss percentage, D.

$$D = \frac{m_0 - m_t}{m_0} \times 100\%$$

Where m_0 is the weight of original films, m_t is the weight of the residual films after degradation at definite time intervals.

IV. RESULTS AND DISCUSSION

4.1. Viscosity Measurement:

Inherent viscosity of the polymers was reported using chloroform at RT at the concentration of 1mg\m1, in presence of Ubbellohde viscometer by studying the values of flow time of pure solvent and polymer. The inherent viscosity of the polymer SeCS and SuCM is 0.73dL/g and 0.65dL/g respectively.

4.2. IR Spectral Studies:

FT-IR of synthesized copolyesters are taken and presented in Fig4.2 (a) & 4.2(b). The synthesized copolyesters showed characteristic absorption band for ester carbonyl stretching. C-O-C stretching and methylene groups as shown in the Table 1.Formation of ester bond during the polycondensation can be confirmed from the specral data.

Table 1 IR Spectral Data of Oligomers SeCS and SuCM

S.no	Absorption frequency cm^1		Assignment
	SeCS	SuCM	
1	1733.9	1730.5	**C=O stretching of ester group**

2	1054,1167	1066,1175	**Co stretching of group**
3	2950.9	2929.0	**Aliphatic C-H stretching**
4	1350	1342	**Aliphatic C-C stretching**
5	965.5	958.2	**C-H bending**

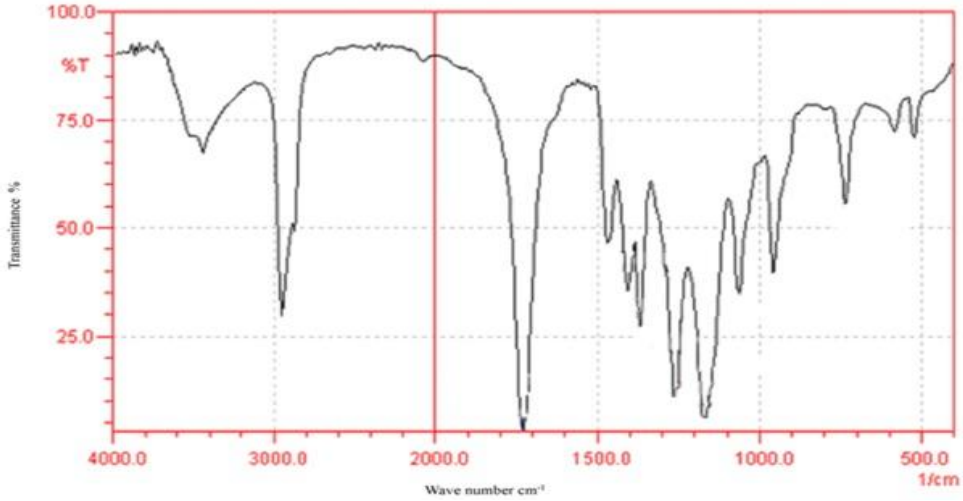


Fig.4.2 (a) IR Spectrum of SeCS

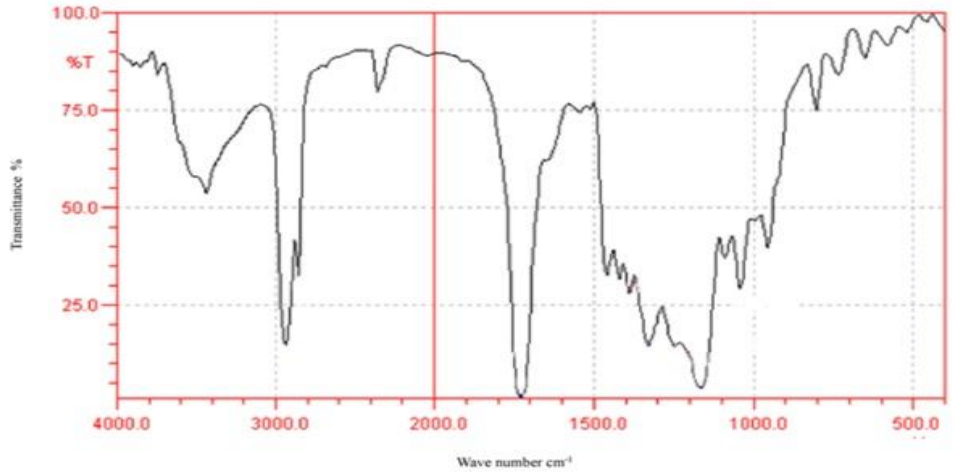


Fig.4.2 (b) IR Spectrum of SuCM

4.3. NMR Spectral Studies:

^{1}H NMR spectra are shown in Fig 4.3(a) &4.3(b). The assignments of the characteristic peaks are given in Table 2.^{13}C NMR Spectra are shown in 4.4(a)& 4.4(b) and the chemical shift value of characteristic peaks along with their assignment are given in Table: 2. All these characteristic peaks in the spectra of polymers show a random distribution of the monomers in it.

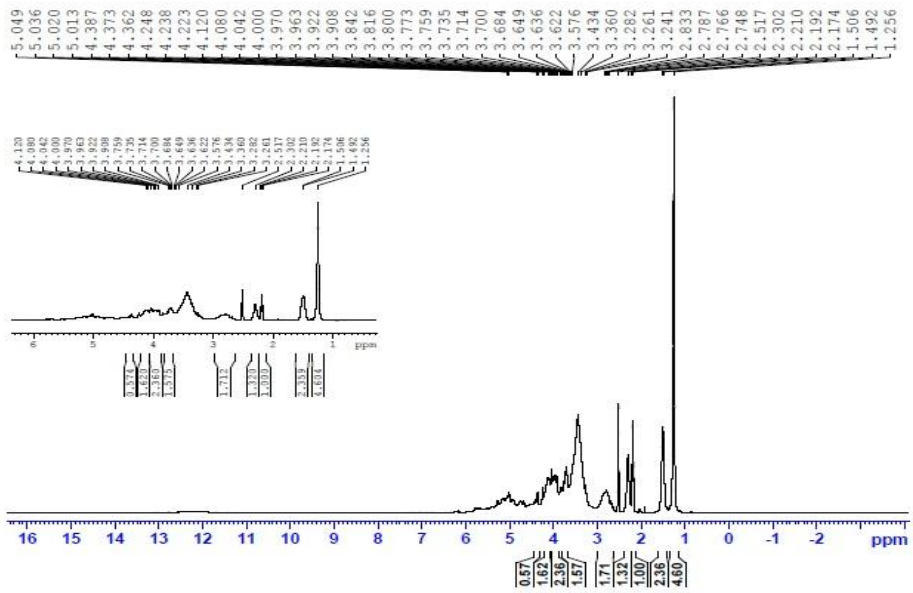


Fig.4.3(a) ^{1}H NMR Spectrum of SeCS

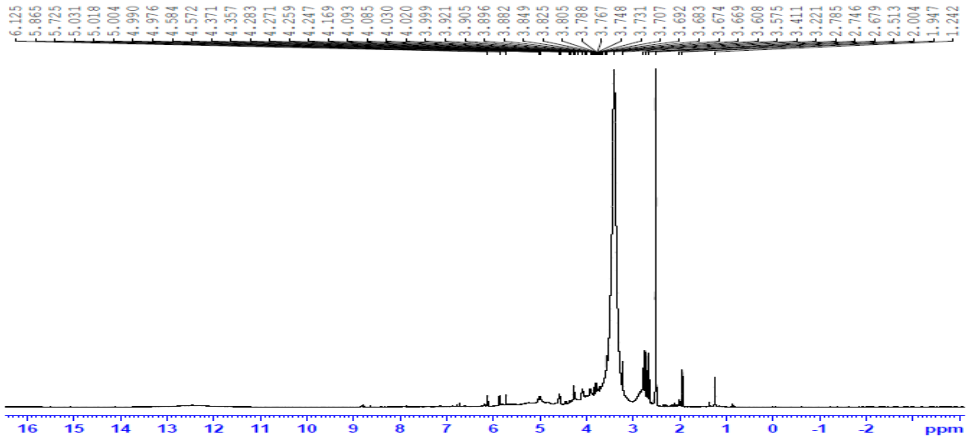


Fig.4.3(b) ^{1}**H** NMR Spectrum of SuCM

Table 2: ^{1}H NMR spectral data of oligomers SeCS and SuCM

S.no	Chemical shift (ppm)		Types of protons
	SeCS	SuCM	
1	4.05	4.10	
2	3.21	3.25	
3	2.2	2.0	Central
4	1.1	1.3	Terminal

3.8. ^{13}C NMR Spectra:

The ^{13}C NMR spectra of oligomers and copolymers were recorded in DMSO solvent. The ^{13}C NMR spectra of the oligomers and the copolyesters are given in Fig. 4.4(a) & 4.4(b) and the assignments for the various peaks observed are given.

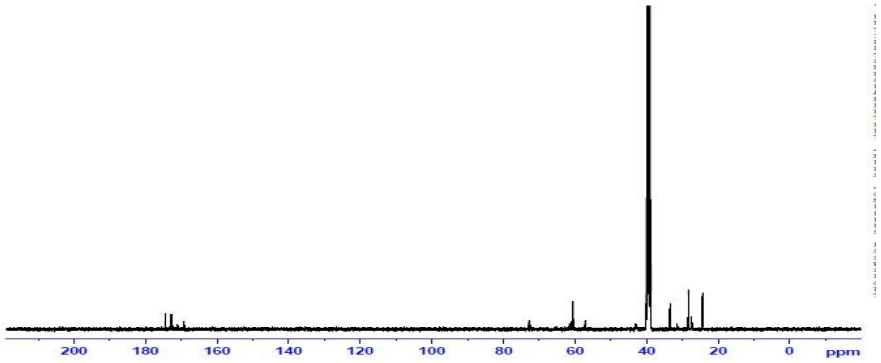


Fig. 4.4(a) ^{13}C NMR Spectrum of SeCS

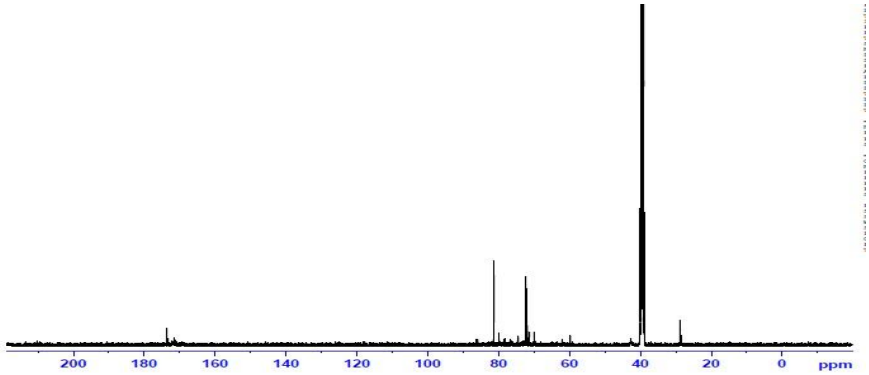


Fig. 4.4(b) ^{13}C NMR Spectrum of SuCM

3.9. Thermal Studies:

The DSC thermograms of the polymers SeCS and SuCM are presented in Fig. 4.5(a) & 4.5(b). These Thermograms show glass transition temperature (Tg) at 42^0c and 31^0C, melting temperature (Tm) at 48^oc and -8.5^oc and decomposition temperature (Td) at 208^oC and 158^oC for the polyesters SeCS and SuCM respectively.

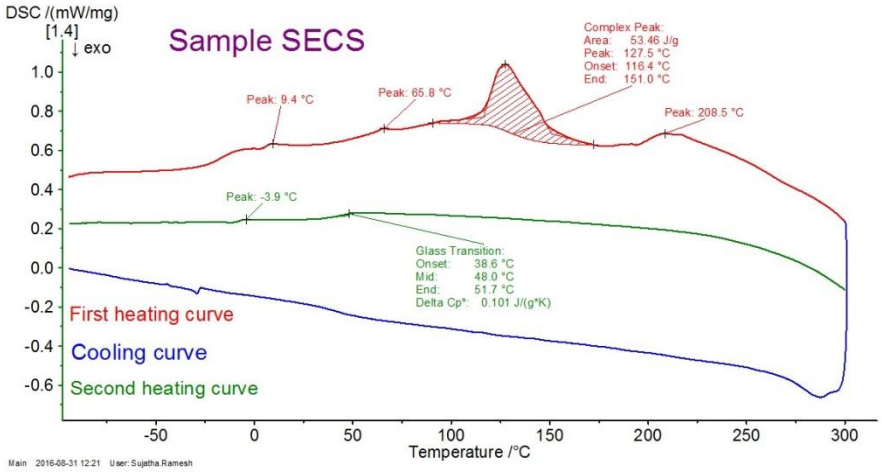


Fig. 4.5(a) DSC Thermograms of polyesters Spectrum of SeCS

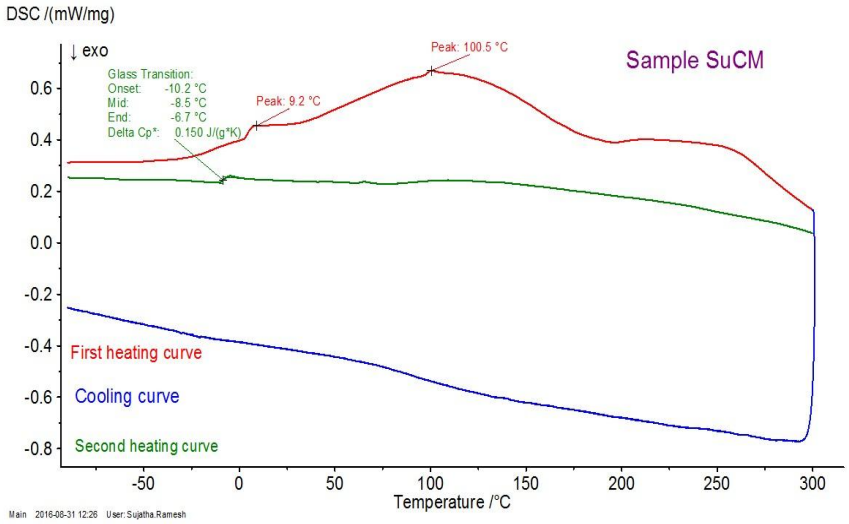
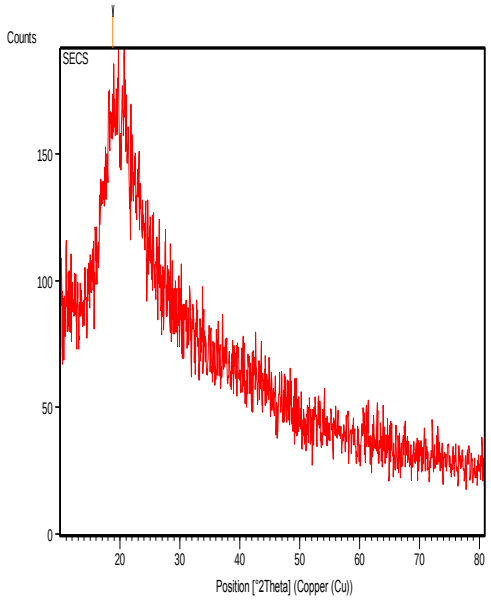


Fig. 4.5(b)DSC Thermograms of polyesters Spectrum of SuCM

Wide Angle X-Ray Diffraction:

Wide Angle X-ray Diffraction Analysis is a primary technique used to determine the degree of crystallinity of the polymers. Features of WAXD analysis is of importance to polymer analysis is the degree of crystallinity. The comparison of the diffractograms of the copolyesters reveals that the copolyesters SeCS and SuCM are found to be more crystalline than the copolyesters. It is worth noting from the diffractograms of the copolyesters that the crystallinity of polyesters. The comparison of the diffractograms of the typical copolyesters indicates that the polyester SeCS exhibits the highest crystallinity whereas its analogue SuCM shows the lowest. X-Ray diffractogram of the synthesized polymers are shown in Fig. 4.6(a) & 4.6(b). The crystalline nature of polyesters was determined from X-ray diffractogram. Gaussian curves are used to describe the amorphous phase and all crystal reflections of a diffractogram. In the X-ray diffractogram, the intensity of diffraction peaks increases with the increase in the length of the flexible spacer group. This is in accordance with the study of Chen et al.. This indicates that the crystallinity of the polymer increases with the length of flexible segments. From the X-ray diffratogram, it is observed that SuCM is highly amorphous in nature than SeCS.



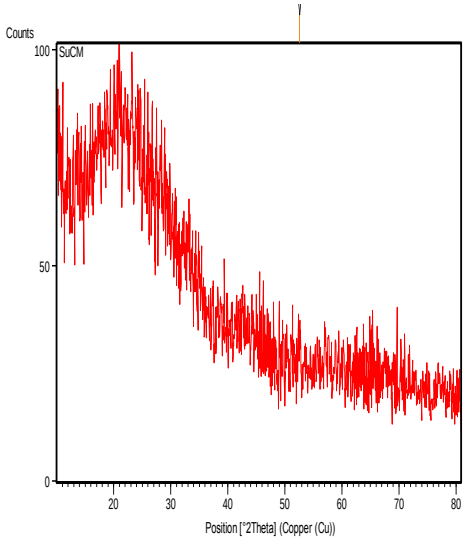


Fig. 4.6(a) WAXD Patterns of Polyesters SeCS **Fig.4.6 (b)** WAXD Patterns of Polyesters SuCM

3.10. Biodegradation Analysis of SeCS and SuCM

The biodegradability of the chemically synthesised polyesters is significantly influenced by the highly ordered chemical structure and physico-chemical properties, such as melting temperature and crystallinity of the polymers The rate of degradation decreases with increase in the melting temperature and orientation of the polymer molecules also reduces the rate of degradation. In the present investigation, the enzymatic degradation was carried out using the enzyme lipase originating from Candida Cylindracea. The weight loss percentage of polyesters, SeCS and SuCM during enzymatic hydrolysis is presented in the following Table 3. Polyester SuCM exhibits higher degradation rate than SeCS. This is supported by the DSC data and XRD patterns of the polyesters.

Table 3 Weight loss Percentage of SeCS and SuCM

Time in Hours	Weight loss (%)	
	SeCS	SuCM
0	0	0
9	2.1	4.1
24	8.9	10.9
48	21.6	23.7
72	32.5	37.2
90	42.8	46.2

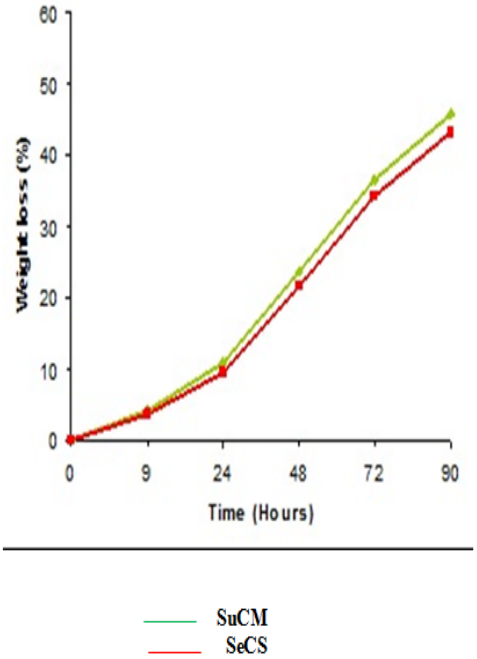


Fig.4.8 Biodegradation Graph of SeCS and SuCM

The rate of enzymatic degradation of SuCM polyesters follows the order, SuCM > SeCS The rate of biodegradation decreases with increase in the number of methylene groups in the repeating unit. This trend is also supported by the thermal data and XRD patterns of the polyesters. SuCM is found to be highly amorphous polymer with low melting temperature, T_m and SeCS is highly crystalline with high melting temperature, T_m.

IV. CONCLUSION

Biodegradable aliphatic random copolyesters were synthesized from SeCS, SuCM by using sorbital/ D-mannitol,sebacic acid,succinic acid and citric acid were obtained by a two step polycondensation reaction in the presence of a highly effective catalyst Titanium tetraisopropoxide at 210 □C. The synthesized copolyesters was characterized and the biodegradation of these polyester were carried out using the enzyme lipase from Candida rugosa. It observed that the copolyester SeCS shows more biodegradable nature than SuCM. In future these polyesters will be used as a drug delivery agents and a ecofriendly polymers.

REFERENCES

[1]. Lenz RN. Prog Polym Sci., 1993; 107:1
[2]. Okada M. Prog Polym Sci., 2002; 27: 87
[3]. Gumargalieva KZ, Zaikov GE. Polym. Degrad. and Stab., 1995; 48: 411-7
[4]. LeinskyD,FritzJ,BraunR.BioresourceTechnol.,2004; 96(2): 197 – 201
[5]. Shimao M. Biodegradation of plastics. Current opinion in Biotechnol., 2001; 12: 242 –7..
[6]. PaggaU,SchaferA,MullerRJ,PantkeM.Chemosphere,2001; 42: 319-31.
[7]. Pagga U. Testing biodegradability with Standardized methods. Chemosphere, 1997; 35(12): 2953 – 72.
[8]. Itavaara M, Karjomaa S, Selin JF. Chemosphere, 2002; 46: 879 – 85.1976,775.
[9]. Fujimaki R, Polym. Degrad. Stab., 1998; 59: 209

[10]. Gordon,S.H.; Imam S.H.; Shogren, R.L.; Govind, N.S.; Greene, R.V. A semi empirical model forpredicting biodegradation profiles of individual polymers in starch-poly-(β-hydroxubutyrateco-βhydroxyvalerate) bioplastic. J. Appl. Polym. Sci. 2000, 76, 1767-1776
[11]. F Migneco;YC Huang; RK Birla; SJ Holliset, Biomaterials, 2009, 30, 6479-6484.
[12]. T Kajiyama; T Taguchi; H Kobayashi; J Tanaka, Polymer Degradation and Stability,2003, 81, 525-530.
[13]. KE Uhrich; A Gupta; TT Thomas; C Laurencin; R Langer, Macromolecules, 1998,31,4120-4125.
[14]. P Sampath; H Brem, Cancer Control,1998,2,130-137..
[15]. DS Muggli; AK Burkoth;SA Keyser; HR Lee; KS Anseth, Macromolecules, 1998,31,4120-4125..
[16].]Pagga U. Testing Biodegradability With Standardized Methods. Chemosphere, 1997; 35(12): 2953 – 72.
[17]. LL Augsburger;RP Shangra;RP Gannini;VP Shah; VK Prasas, D. Bro pham. Sci., 1983,72, 876.
[18]. Mani, R.; Bhattacharya, M. Properties of injection moulded blends of starch and modified biodegradable polyesters. Eur. Polym. J. 2001, 37, 515-526.
[19]. British Pharmacopoeia,1988, vol II, A 141.
[20]. Shinoda, H.; Asou, Y.; Kashima, T.; Kato, T.; Tseng, Y.; Yagi, T. Amphiphilic biodegradable copolymer, poly(aspartic acid-co-lactide) : acceleration of degradation rate and improvement of thermal stability for poly(lactic acid), poly(butylene succinate) and poly(ε-caprolactone). Polym. Degrad. Stab. 2003, 80, 241-250.
[21]. Chen B.K, Tsay S.Y, Chen J. Polymer 2005;46,8624.
[22]. Jaisankar V, Nanthini R, Ravi A and Karunanidhi M. J. Polym. Mater. 2009;26,157