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SYNTHESIS AND CHARACTERIZATION OF NOVEL BIODEGRADABLE ALIPHATIC AND AROMATICCOPOLYESTERSPOLY ETHYLENE SUCCINATE-CO-ETHYLENESEBACATE), POLY (BUTYLENE ADIPATE-CO-BUTYLENE TEREPHTHALATE)

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Abstract:

In this paper, we report on the synthesis of certain novel aliphatic biodegradable copolyesters namelypoly(ethylene succinate-co- ethylene sebacate), poly(butylene adipate-co- butylene terephthalate)were carried out using Poly(ethylene succinate), Poly(ethylene sebacate)polybutyleneadipateand Poly(butylene terephthalate) in presence of Poly Phosphoric acid. The polyesters were characterised by solubility, viscosity measurements, IR, ^{1}H NMR and ^{13}C NMR spectral methods. The thermal properties were studied using differential scanning calorimetry. The X ray patterns were collected on Xraydiffractometer, The percentage of biodegradation of the synthesized copolyesters was investigated by enzymatic hydrolysis using the enzyme *Candida rugosa*lipase. The morphological analysis was carried out using Scanning Electron Microscope

Key Words: Biodegradable Polyesters, Random Copolyesters & Aliphatic Polyester

1. Introduction:

In the world today, increasing volumes of polymers are manufactured and used for various applications because of their versatility and ability to be mass-produced. However, they usually do not naturally decompose, and they are considered to cause some environmental problems. The biodegradable polymers have attracted considerable attention as green materials and biomaterials in pharmaceutical, medical and biomedical engineering applications including drug delivery systems, artificial implants and functional materials in tissue engineering. The production and consumption of synthetic polymeric materials have grown progressively due to their low cost, as well as their resistance to physical aging and biological attacks. Aliphatic polyesters have been recognized as one of the most promising biodegradable materials because they are readily susceptible to biological attack and their degradation products, water-soluble oligomers and the starting diols and acid or hydroxyl acid, are non-toxic and can enter the metabolic cycles of bio-organisms. The biodegradability of a polymer is based on the presence of hydrolyzable or oxidizable linkages in the backbone. The rate of biodegradation of polyesters depend on the chemical composition, sequence length, molecular weight, hydrophilic/hydrophobic balance, as well as on the morphology of the sample, e.g. degree of crystallinity, size of spherulites, surface area of the samples, additives, etc.

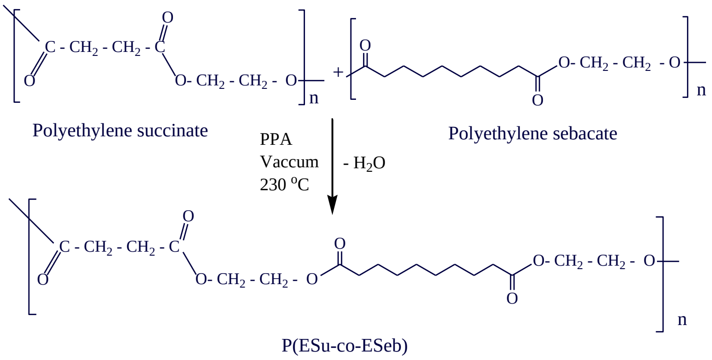
2. Experimental Section:

2.1 Materials: Succinic acid (99%), Adipic acid (99%) Sebacic acid (99%) and Terephthalicacid(99%)were purchased from Aldrich used as such. Ethylene glycol and 1,4-Butanediol were supplied by Merck used as such.

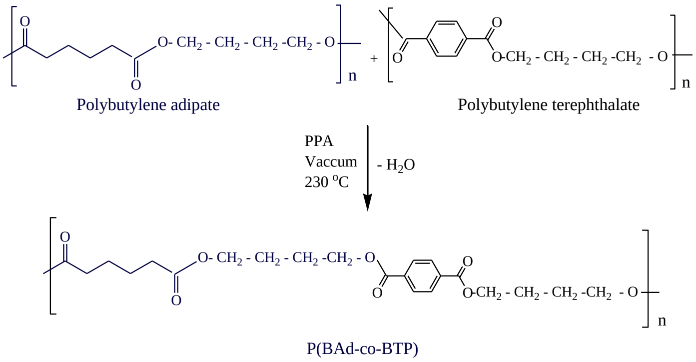
2.2 Synthesis of Polyesters: Synthesis of aliphatic copolyesters was carried out by two stage melt polycondensation method in a three necked round bottom flask. At the first stage, the oligomers were prepared using dicarboxylic acid (succinic acid, sebacic acid, adipic acid and terephthalic acid) and 1,4-butanediol or ethanediol in a molar ratio 1:1 was charged into the reaction flask of the polycondensation apparatus. The reaction mixture was purged with nitrogen gas and heated in an oil bath. The temperature of the reaction mixture was raised to 150^{0}C for 20 minutes and then the temperature was gradually raised by 10^{0}C every minute to the final temperature 210^{0}C.

This condition was maintained for 2 hours to remove the water being the esterification by-product when water ceased to be generated, 0.2 mole of titanium tetra butoxide(TBT) catalyst was placed into the reaction mixture and the polycondensation was carried out under gradually reducing pressure with final vacuum less than 0.5 mm Hg. The reaction mixture was maintained under these conditions for 20 hours. Generally the reaction is stopped when the viscosity of the reaction mixture is so high that rotation is not possible.

The viscous slurry was cooled in the reactor under nitrogen; the oligomer was dissolved in chloroform and precipitated in 10 fold amount of vigorously stirred ice cold methanol. The precipitated oligomers were filtered and dried in vacuum to constant weight. The reaction mixture was heated at 210 °C under nitrogen atmosphere and stirred at a constant speed, 500 rpm. The first step, esterification is considered to be complete after the collection of theoretical amount of water, which was removed from the reaction mixture.



Scheme-1



Scheme-2

2.3 Characterization of Copolyesters: The synthesized co-polyesters were characterized by solubility determination, viscosity measurements, spectral studies and biodegradation analysis.

2.4 Solubility Studies: Solubilities of co-polyesters were determined in various organic solvents. 10 mg of the copolyester was taken in a small stoppered test tube and 1ml of the solvent was added. The solubility was noted in different solvents.

2.5 Viscosity Measurements: Inherent viscosities of the co-polyesters were measured in chloroform at 30°C ± 1°C using Ubbelhode viscometer. For this flow times were determined for the pure solvent and 1% polymer solution by weight at room temperature.

2.6 Fourier-Transform Infrared Spectroscopic Analysis: The IR spectra of co-polyesters were recorded using Bruker IFS 66 V–IR spectrophotometer with KBr pellets in the range of 4000-400cm^{-1} at 25°C.

2.7 Nuclear Magnetic Resonance Spectroscopic Analysis: ^{1}H and ^{13}C NMR spectra of co-polyesters were recorded using JOEL-GSX-400 spectrometer. $CDCl_3$ was used as solvent and TMS was used as an internal standard.

2.8 Thermal Analysis: DSC thermograms were recorded on a PERKIN ELMER PYRIS-1 differential scanning calorimeter. About 2-4 mg of the copolyester sample was heated in an aluminium pan with pierced lid under nitrogen atmosphere at a scanning rate of 10°C/minutes between temperature ranges of -100°C to 450°C.

2.9 Powder X-Ray Diffraction Analysis (PXRD): The XRD patterns were collected on a Shimadzu XRD-600 diffractometer, with Cu-Ka radiation (l = 1.54 Å), 30 kV potential and 20 mA current. The samples were analysed as powders.

2.10 Biodegradation Analysis: The co-polyester thin films were prepared by hot pressing method. The thin film (10x10 mm^2 and 200m thickness) were placed in a petri dish containing 10 ml of phosphate buffer solution and 0.1 mg of *Candida rugosa*lipase. After a specific period of incubation, the films were removed from the petri dish, washed with distilled water, dried and weighed till a constant weight was obtained. This procedure was repeated for every time interval (0, 24, 48, 72, 96, 120 hours).The percentage of buffer degradation of the synthesized copolyesters were also investigated by phosphate buffer solution.

2.11 Morphological Observation: The morphological analysis was carried out using a SS 550 Scanning Electron Microscope (Shimadzu). The acceleration voltage was 7 kV and the samples were sputtered with gold prior to the analysis. The samples were analyzed as thin film.

3. Results and Discussion:

3.1 Solubility: The co-polyesters are freely soluble in chloroform and carbon tetrachloride, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in N,N'-DMS and acetone. The prepared copolyesters are insoluble in water, hexane, diethyl ether and methanol.

3.2 Viscosity of the Polyesters: The inherent viscosity of the random co-polyesters were calculated from the relative viscosity which were obtained from the flow time of the pure solvent and polyester solution using Ubbelohde viscometer in chloroformat 30°Cand at the concentration of 0.10g/dL. The viscosity value of P(ESu-co-ESeb)is higher than the P(BAd-co-BTP) polymer. Among polymers of comparable molecular weight, rigid polymers possess a higher viscosity value than flexible one.

3.3 Spectral Studies:

3.3.1 IR Spectra: The IR spectra of the synthesized pre-polymers show a strong absorption bond at around 1730cm^{-1}, which is characteristic absorptions of carbonyl stretching vibration of ester groups and thus confirmed the formation of polyesters. The bonds centered at around 2947 and 2932cm^{-1} were assigned to methylene (-CH_2-) groups for the diacids/diols and observed in all the spectra of the polyesters.The broad stretch at 3430 cm^{-1} was attributed to the stretching vibration of the hydrogen bonded carboxyl and hydroxyl groups..

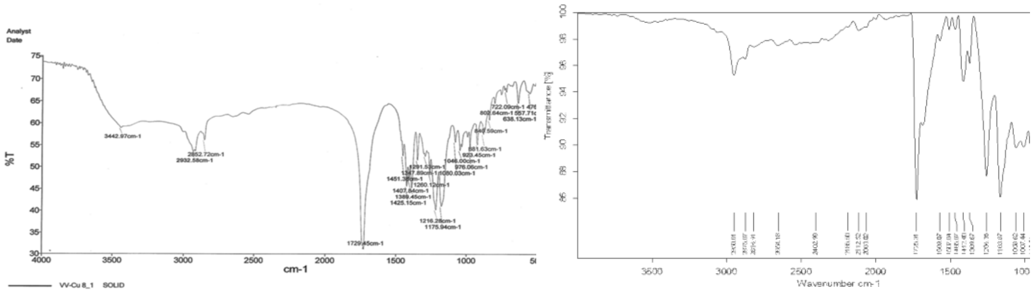


Figure 1: IR SPECTRUM OFP(ESu-co-ESeb) and P(BAd-co-BTP)

3.3.2 ^{1}H NMR Spectra: The ^{1}HNMRspectra of the polyesters are presented in Fig 3-4.

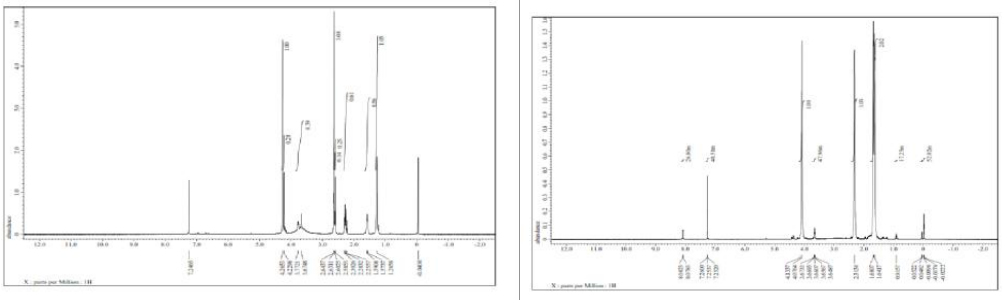


Figure 3: ^{1}H -NMR SPECTRUM OF P(ESu-co-ESeb) and P(BAd-co-BTP)

The ^{1}H NMR spectrum of PESu spectra exhibited the characteristic peaks at 4.27-4.28 and 2.64-2.66 ppm for –O-CH_2- of ethanediol, -CO-CH_2- of succinic acid respectively, while the PESeb showed the characteristic peaks at 4.24-4.25, 2.28-2.32 and 1.28-1.59 ppm corresponding to protons of –O-CH_2- of ethanediol, -CO-CH_2- of sebacic acid and –CH_2- of sebacic acid respectively. All these characteristic peaks are found in the spectrum of the copolyesterP(ESu-co- ESeb) given in Figure (3). The ^{1}H NMR spectrum of PBAd exhibited the characteristic peaks at 3.64-4.10, 2.31 and 1.60–1.72 ppm for –O-CH_{2-} of butanediol, -CO-CH_2- of adipic acid and –CH_2- of butanediol and adipic acid respectively, while the PBTP spectra showed the characteristic peaks at 7.38-7.96, 4.23-4.31 and 1.48-1.91 ppm for Ar-CH of terephthalic acid, –O-CH_2- of butanediol and -CH_2- of butanediol respectively. All these characteristic peaks are found in the spectrum of the copolyesterP(BAd-co- BTP) given in Figure (3).

3.3.3 ^{13}C NMR Spectra of Oligomers:

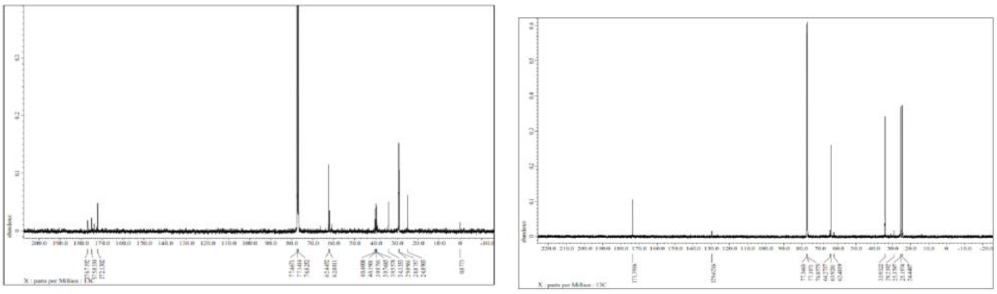


Figure 4: ^{13}C -NMR SPECTRUM of P(ESu-co-ESeb) and P(BAd-co-BTP)

The ^{13}C NMR spectra of PESu exhibited the peaks at 28.87-29.40,61.04-62.45 and 172.12 ppm for -CH_2- of succinic acid , -OCH_2- of ethanediol and -CO of succinic acid respectively, while the PESeb spectra showed the peaks at 24.89-29.17, 34.15, 62.09 and 173.63 ppm for -CH_2- of sebacic acid , –COCH_2- of sebacic acid, -OCH_2- of ethanediol and –CO of sebacic acid respectively. All the characteristic peaks of PBSu and PESeb were also found in the copolyesterP(ESu-co-ESeb) given in Figure (4). The ^{13}CNMR spectra of PBAd exhibited the signals at 24.44-25.37, 29.22, 33.93, 62.41-64.28 and 173.40 ppm for -CH_2- of adipic acid , -CH_2-of butanediol, -COCH_2 of adipic acid, -OCH_2- of butanediol and -CO of adipic acid respectively, while the PBTP spectra showed the peaks at 29.86, 62.01 and 129.46 ppm for CH_2- of butanediol, -OCH_2 - of butanediol and –Ar-CH of terephthalic acid respectively. All the characteristic peaks of PBAd and PBTP were also found in the copolyesterP(BAd-co-BTP) given in Figure (4).

3.3.4 Thermal Analysis: The polyesters were further characterised by thermal analysis and the DSC thermograms. The melting temperature T_m, the glass transition temperature T_g and decomposition temperature T_d were found to be 39.9°C, -59.4°C and 388.4°C and 53.4°C, -7.4°C and 356.0°C for the co-polyesters P(ESu-co-ESeb) and P(BAd-co-BTP)respectively. It was found that the melting temperatures and the glass transition temperature decreased with increasing number of methylene units.

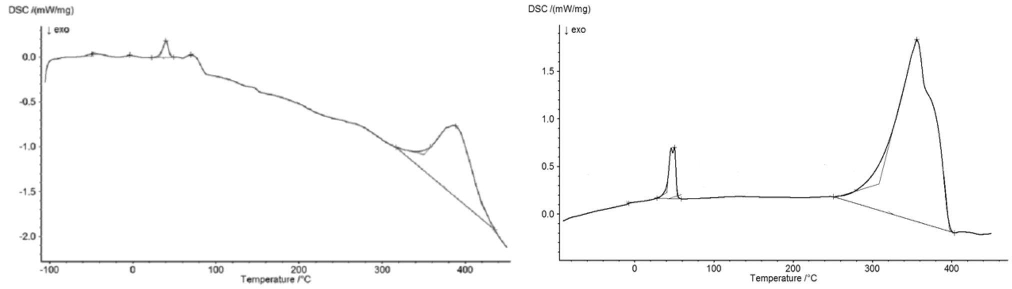


Figure 5: DSC Thermogram of P(ESu-co-ESeb) and P(BAd-co-BTP)

3.3.5 Powder XRD Analysis: The X ray patterns were collected on a Shimadzu XRD-600 diffractometer, with Cu-Ka radiation (l = 1.54 Å), 30 kV potential and 20 mA current. The samples were analysed as powders. The 2T values were found to be 20.54 (753), 21.82 (380), 23.80 (366), 26.36 (681), 31.70 (297), 38.74 (244) for the co-polyester P(ESu-co-ESeb)and 17.66 (1769), 22.02 (899), 22.74 (512), 25.50 (402), 28.18 (842)for the co-polyester P(BAd-co-BTP) respectively. The less crystalline co-polyesterhas high rate of biodegradation. More crystalline co-polyester has low rate of biodegradation.

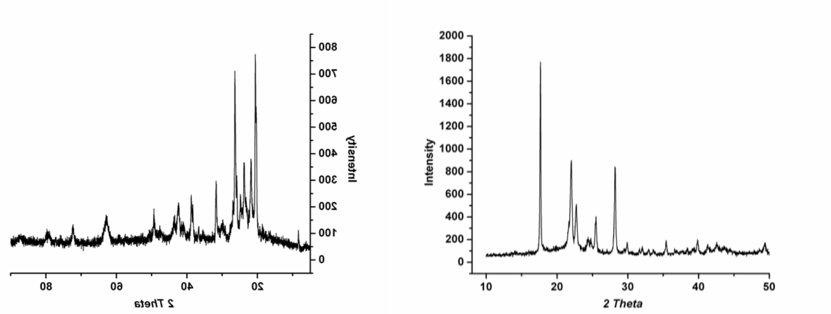


Figure 6: PXRD of P(ESu-co-ESeb) and P(BAd-co-BTP)

3.3.6 Biodegradation: The percentage of biodegradation of the synthesized copolyesters was investigated by enzymatic hydrolysis using the enzyme *Candida rugosa*lipase and phosphate buffer solution. It appears that the key factor affecting the degradation was its crystallinity. The percentage of Biodegradation of the synthesized copolyesterPBSu-co-PESu is higher than PBSu-co-PBAd.

Table 1

Hrs	% of Biodegradation	
	P(ESu-co-ESeb)	P(BAd-coBTP)
24	12.04	2.78
48	23.91	5.64
72	36.04	8.43
96	48.09	11.29
120	59.96	14.08

Table 2

Hrs	% of Buffer degradation	
	P(ESu-coESeb)	P(BAd-coBTP)
24	7.51	1.12
48	15.13	2.33
72	22.65	3.61
96	30.16	4.74
120	37.59	5.94

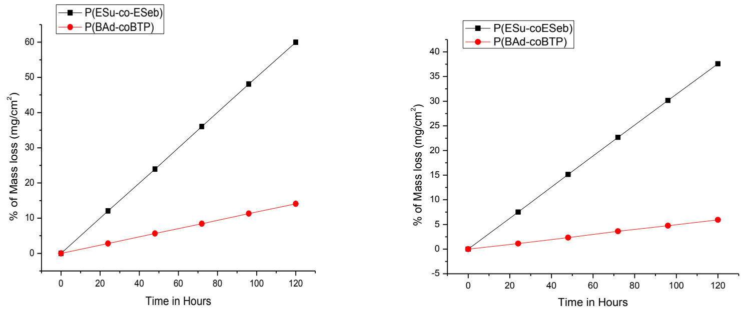


Figure 7: Biodegradation & Buffer Degradation

3.3.7 Scanning Electron Microscope (SEM): The morphological analysis was carried out using a SS 550 Scanning Electron Microscope (Shimadzu). The acceleration voltage was 7 kV and the samples were sputtered with gold prior to the analysis. The samples were analyzed as thin film.

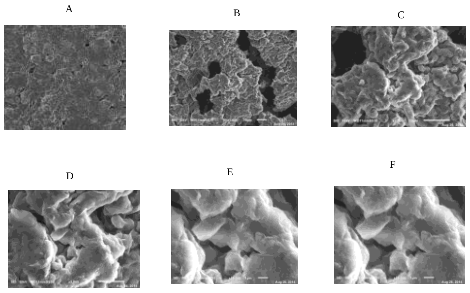


FIGURE: 75 SEM micrographs of P(ESu -co-ESeb) surface: (A) before degradation (B,C,D,E,and F) after degradation

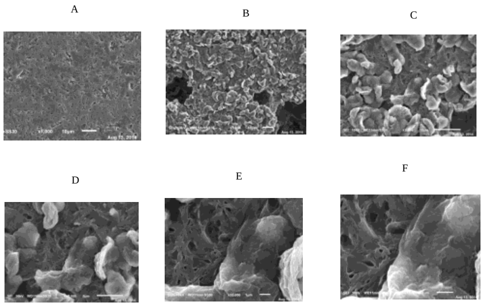


FIGURE: 78 SEM micrographs of P(BAd-co-BTP) surface: (A) before degradation (B,C,D,E,and F) after degradation

Figure 8: SEM microgram of P(ESu-co-ESeb) and P(BAd-co-BTP)

4. Conclusion:

This work deals with the synthesis and characterization of aliphatic bio-degradable co-polyesters. In all polyesters have been synthesized by direct melt poly-condensation of diols and diacids using high T and high vacuum. Aliphatic co-polyesters combine the biodegradability and biocompatibility of aliphatic polyesters with the physical properties and thermal properties of aromatic polyesters. They will be playing an important role in maintaining an ecologically friendly environment. These co-polyesters were synthesised with a view of increasing their solubility and improving their mechanical properties. The two co-polyesters were found to be freely soluble in chloroform and carbon tetrachloride. The inherent viscosities of these polyesters showed that the polyester containing succinate units had higher viscosity than the polyester containing adipate unit. The probable structure of the repeating units present in these polyesters were assigned on the basis of NMR spectral data. From the DSC thermograms it was shown that the introduction of methylene units in the di-acid decreased the Tm and Tg.

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