# Studies on Poly (Sunflower Oil Fumarate) Bio polyester Composites Based on Sunflower Oil and Sisal Fibre

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***Abstract*- Biopolyesters were synthesised from naturally available sunflower oil. Sunflower oil has been used for the preparation of biopolyesters for its several applications. Hydroxylated sunflower oil (HSO) has been carried out by formic acid and hydrogen peroxide. Further poly (sunflower oil fumarate) biopolyester resin (SFPR) were synthesised from hydroxylated sunflower oil and it characterised by FT-IR and $^1$H NMR. Poly (sunflower oil fumarate) biopolyester composites were synthesised from poly (sunflower oil fumarate) biopolyester resin with acrylo nitrile, benzoyl peroxide, dimethyl aniline. Natural fibres such as sisal, banana, coir fibre etc. were locally available in abundance. Biopolyester composites have been prepared from natural fibre with different ratios. The biopolyester composites were characterised by FT-IR, swelling analysis, solvent absorptivity percentage, soil burial test and SEM analysis.**

***Key words*: Sunflower oil, Biopolyesters, Natural fibre, Swelling analysis, SEM analysis.**

## I. INTRODUCTION

Polymers are giant molecules of high molecular weight, call macromolecules, which are build up by linking together of a large number of small molecules called monomers. Polymers are having different chemical structure, physical properties, thermal characteristics, mechanical behavior etc[1].

Natural oils are one of the most important classes of bio-resources for producing polymeric materials. The main components of oils are triglycerides-esters of glycerol with three fatty acids. The oil-based polyurethane, polyester, polyether and polyolefin are the four most important classes of polymer[2]. Natural oils and fatty acids are used for polymer applications such as polymer additives, building blocks for thermoplastic polymers, adhesives and composites[3].

Sunflower oil is basically triglycerides commonly derived from the fatty acids linoleic acid and oleic acid. Different constituents of sunflower oil are lecithin, tochopherols, carotenoids and waxes. This oil is light in taste and colour and has high vitamin E content. It is a mixture of monosaturated and polysaturated fats with little saturated fat levels[4].

Unsatuated polyesters are generally prepared from a saturated and unsaturated acid which are condensed with dihydric alcohols. A three dimensional structure is formed by cross linking polyester back ground with a vinyl monomer. It is used for the production of serving trays, flat sheets, lampshade and corrugated sheets for building industry, ammonium boxes, disposable glass tanks and various containers[5].

Natural fibres such as coir, cotton, sisal, hemp fibres. These fibres contain lingo cellulose in nature. The fibres are eco-friendly, light weight, strong, renewable, cheap and biodegrable. The fibres can be used to reinforce both thermosetting and thermoplastic matrices. The fibre composites are very cost-effective material especially in building and construction, packaging, automobile and railway coach interiors and storage devices[6]. Polymer composites are used for manufacturing aerospace, marine, automotive, electrical and sports good[7].

## II. EXPERIMENTAL

### *C. Materials*

Sunflower oil purchased from local market. Fomic acid, hydrogen peroxide, maleic anhydride, morpholine, acrylo nitrile were purchased from

Sigma-Aldrich. Sisal fibre was procured from local sources.

*B. Synthesis of poly (sunflower oil fumarate) biopolyester resin*

Sunflower oil was carried out using 30% hydrogen peroxide and formic acid, in ice water bath. The reaction was vigorously stirred at 8 hours. Then it was poured into a separator funnel and extracted with ether. The resulting product obtained as hydroxylated sunflower oil. The resulting product was reacted with maleic anhydride, sodium acetate, morpholine and the mixture was refluxed for 2 hours at 70-80ºC and 160ºC for 20 minutes under vacuum condition using rota mandle to yield a yellow transparent liquid poly (sunflower oil fumarate) biopolyester resin.

*C. Synthesis of poly (sunflower oil fumarate) biopolyester and their composites*

The poly (sunflower oil fumarate) biopolyester neat sheet and their composites were umarate ed by treating poly (sunflower oil umarate) biopolyester resin with triethylene glycol dimethacrylate, benzoyl peroxide, dimethyl aniline and acrylo nitrile. The neat sheet was coded as SFB. The treated sisal fibre with varying compositions (5%, 10%, 15%) added to the above mixture. The mixture was poured into the clean silicon oil spreaded glass mould. The mixture was dried in vacuum air oven at 80ºC for 6hours. The 5%, 10% and 15% sisal fibre reinforced composites were coded as SFBSL5, SFBSL10 and SFBSL15.

## III. CHARACTERISATION

*A. Spectral studies*

FT-IR spectral analysis of synthesised resin and composites were analysed by KBr pellet method via Shimadzu FT-IR 8400S spectrometer. $^1$H NMR spectra of synthesised resin was reported by $CDCl_3$ with tetramethyl silane though internal method.

*B. Determination of swelling coefficient*

The biopolyester neat sheet and their composites were subjected to swelling experiments. The density of biopolyester neat sheet and their composites were analysed using ASTM D792 method.

The swelling coefficient 'Q' was evaluated using the formula,

$$\text{Swelling coefficient (Q)} = \frac{\text{Weight of the solvent in swelled polymer}}{\text{Weight of the swelled polymer}} \times \frac{d_r}{d_s}$$

Where,

$d_r$ = Density of polymer

$d_s$ = Density of solvent

*C. Determination of solvent absorptivity percentage (%)*

Swelling behaviour of biopolyester and their composites were also studied. Each biopolyester sheet was put in 3ml of different solvents for 24 hrs. After 24 hrs, the excess solvent on the biopolyester sheet was detached by using filter paper. Then it was weighed and the solvent absorptivity percentage was evaluated using the following equation,

$$\text{Solvent absorptivity percentage} = \frac{W_2 - W_1}{W_1} \text{ X } 100$$

Where,

$W_1$ = Weight of the dry sample

$W_2$ = Weight of the sample after absorption of the solvent

*D. Soil burial test*

The biopolyester neat sheet and their sisal fibre reinforced composites (5 x 3 cm) were buried in the soil at a depth of 30 cm from the ground surface for 60 days, inoculated with compost having the capacity to hold and degrade the polymer. At fixed time, the samples were detached, washed with distilled water in order to ensure the stop of the degradation, dried out at room temperature to a constant weight and stored in dusk.

Degree of biodegradation,

$$D = \frac{W_O - W_t}{W_O} X\ 100$$

Where,

$W_o$ = Weight of the original film

$W_t$ = Weight of residual film after degradation for different time

*E. Scanning electron microscope analysis*

Scanning electron microscope analysis was conducted (ESEM-Quanta 200, Fei) to study the degradation of biopolyester sheet and their composites before and after soil burial degradation test.

## IV. RESULTS AND DISCUSSION

*A. Characterisation of poly (sunflower oil fumarate) biopolyester resin*

*FT-IR analysis*

The FT-IR spectra of hydroxylated sunflower oil resin and poly (sunflower oil fumarate) biopolyester resin as shown in Figure 4.1 and Figure 4.2. The hydroxylated sunflower oil resin was showed the peaks at 3472.77 $cm^{-1}$ due to the formation of free -OH groups. The poly (sunflower oil fumarate) biopolyester resin was showed the carbonyl band of sunflower oil combined with fumarate group at 1731.94 $cm^{-1}$.

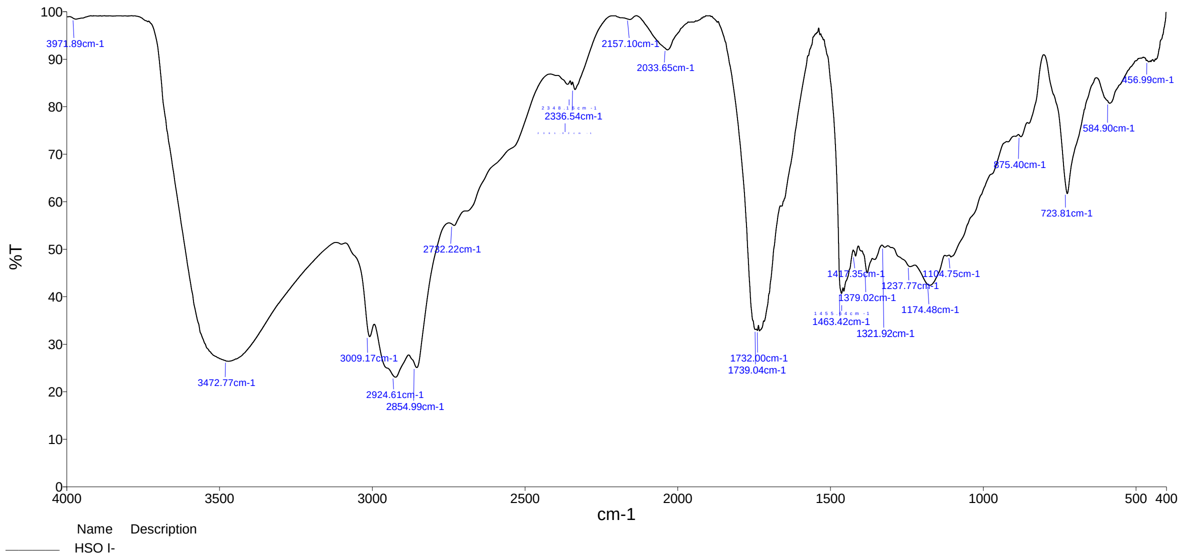



Figure 4.1 FT-IR spectrum of hydroxylated sunflower oil resin

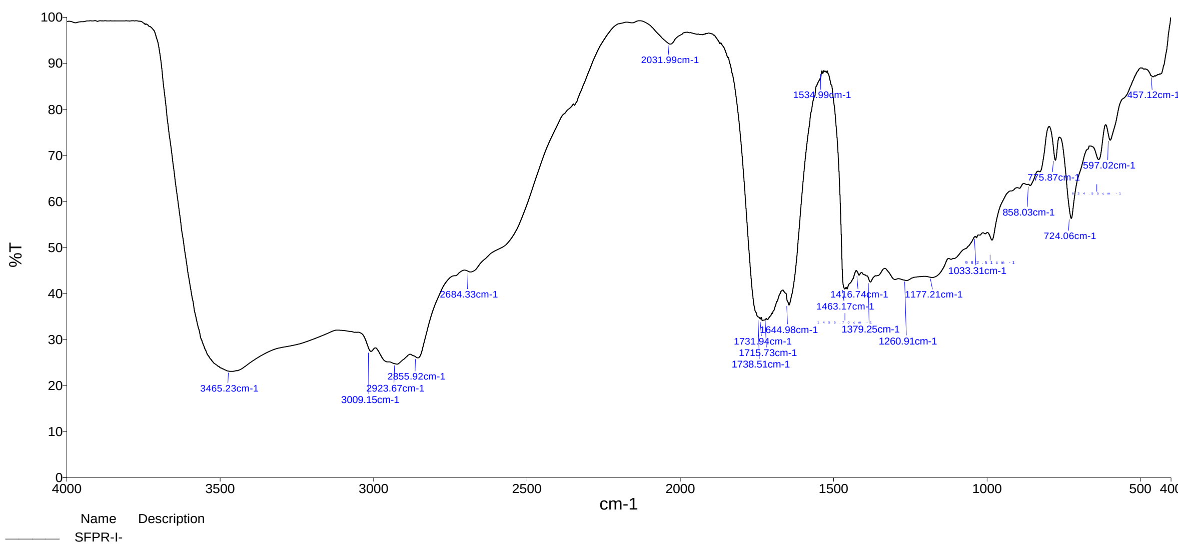



Figure 4.2 FT-IR spectrum of poly (sunflower oil fumarate) biopolyester resin

*$^{1}$H NMR analysis*

The $^{1}$H-NMR spectra of hydroxylated sunflower oil resin and poly (sunflower oil fumarate) biopolyester resin as shown in Figure 4.3 and Figure 4.4. The hydroxylated sunflower oil resin showed the peak was confirmed at 5.316-5.376 ppm was disappeared in the hydroxylated oil resin showed that the olefinic double bond was replaced by the hydroxyl group. The poly (sunflower oil fumarate) biopolyester resin showed that the peak at 3.440-3.465 ppm in the fumarated resins was due to the deshielding effect of hydroxyl and carboxylate ester linkages.

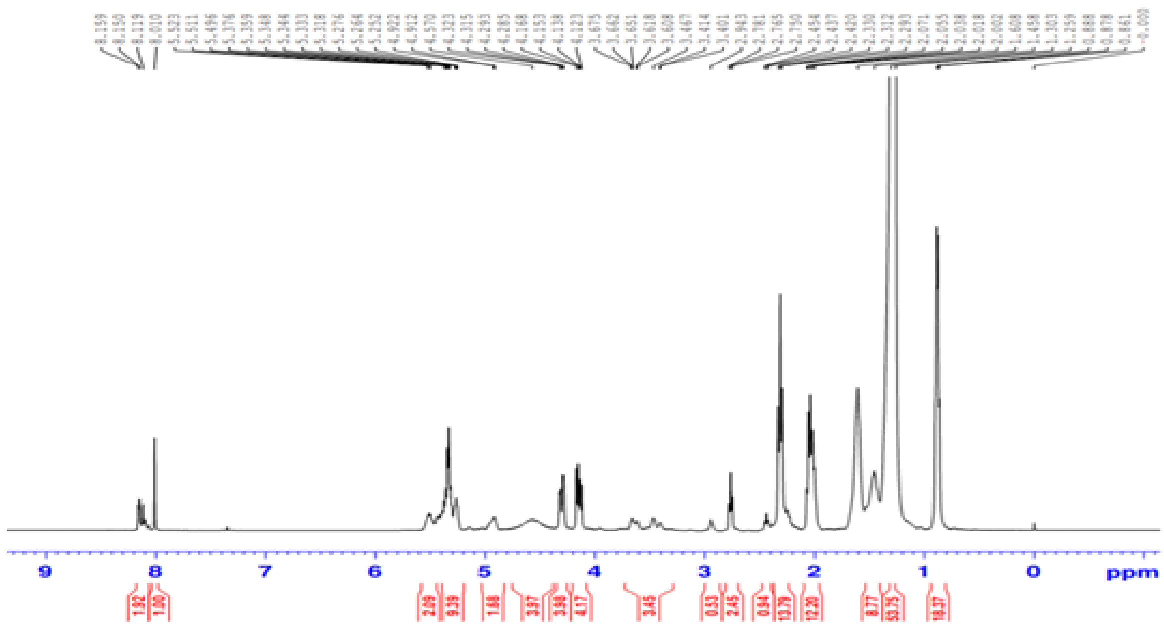


Figure 4.3 $^{1}$H-NMR spectrum of hydroxylated sunflower oil resin

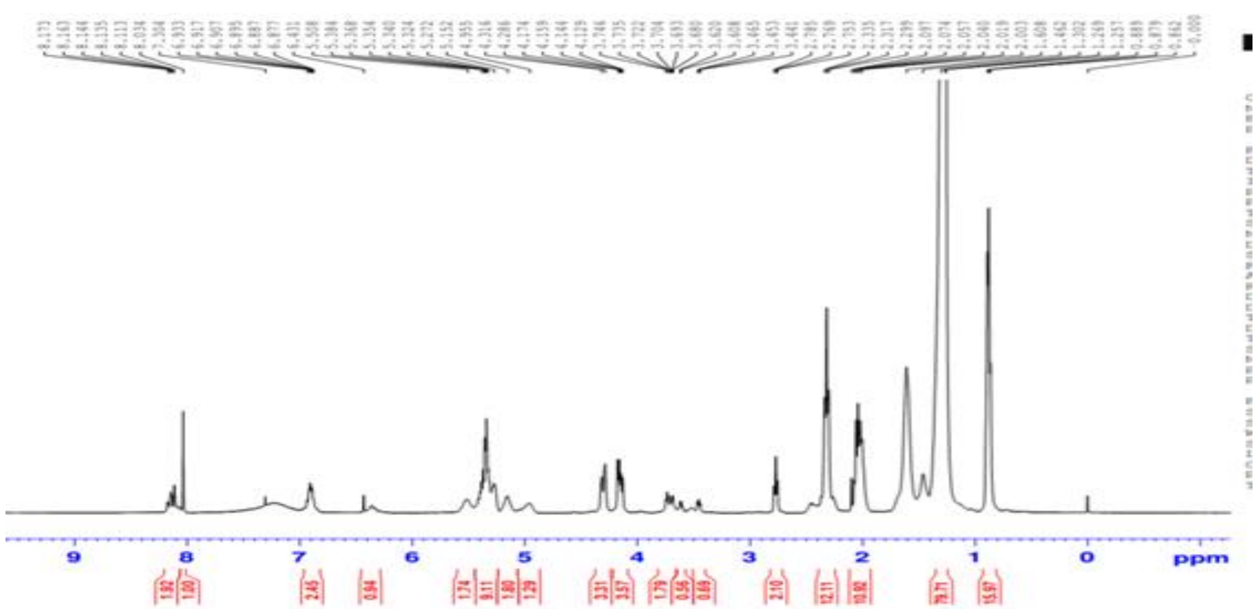


Figure 4.4 $^{1}$H-NMR spectrum of poly (sunflower oil fumarate) biopolyester resin

*B. Characterisation of poly (sunflower oil fumarate) biopolyester and their composites*

*FT-IR analysis*

FT-IR spectra of poly (sunflower oil fumarate) biopolyester and their composites were given in Figure 4.5-4.7. The FT-IR spectra of poly (sunflower oil fumarate) biopolyester sheet (SFB) almost same as that of poly (sunflower oil fumarate) biopolyester resin (SFPR) but the absence of peak at 1644.98 cm$^{-1}$ was indicated the absence of double bonds. A FT-IR spectrum of sisal fibre reinforced poly (sunflower oil fumarate) biopolyester composite was showed that the irregular bands present in the spectra.

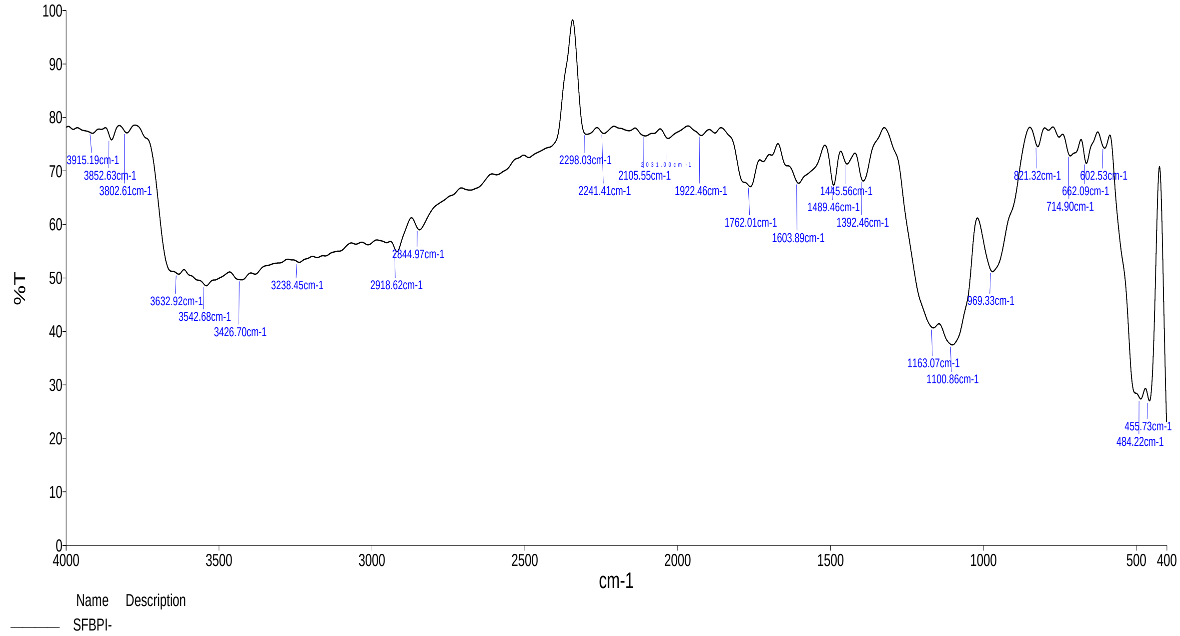



Figure 4.5 FT-IR spectrum of SFB

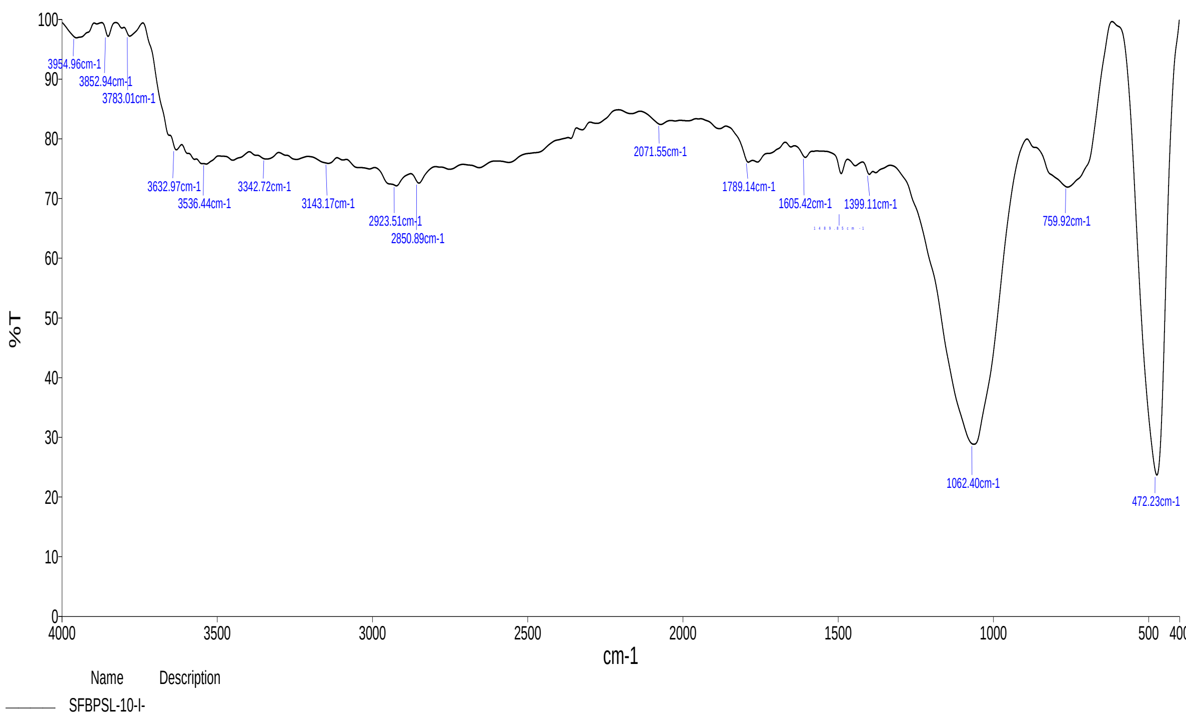



Figure 4.6 FT-IR spectrum of SFBSL10I

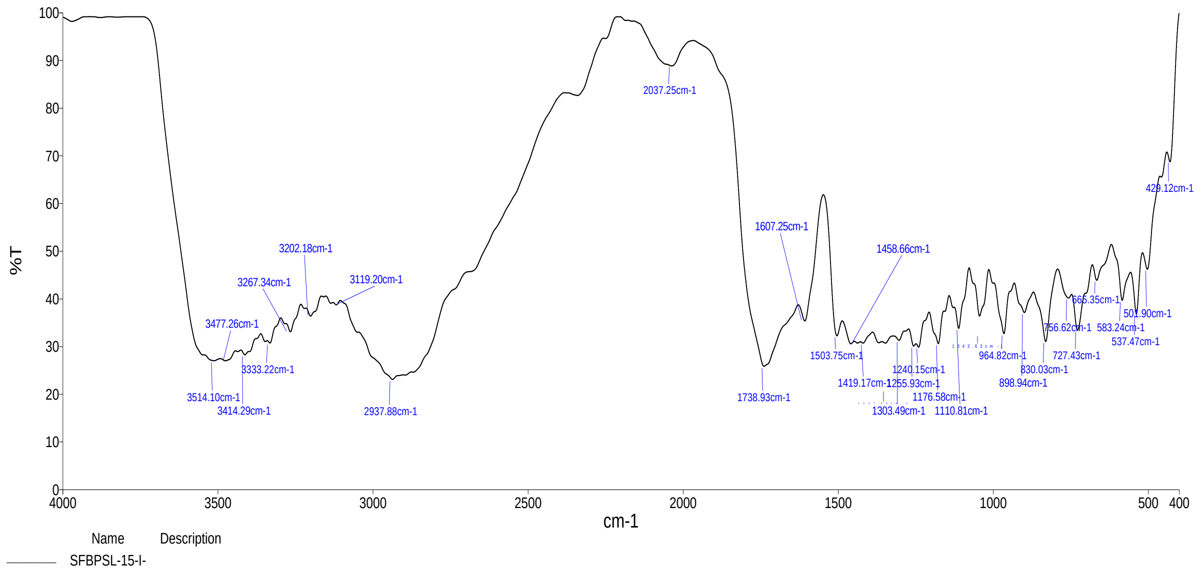



Figure 4.7 FT-IR spectrum of SFBSL15I

*Swelling coefficient*

The swelling coefficient of the biopolyester neat sheat and their composites were high in dimethyl acetamide. These revealed that the biopolyester neat sheet and their composites have been crosslinked. The crosslinked biopolyesters will only swell and not dissolve in a non-reactive solvent. The degree of swelling in a non-reactive solvent was used to determine the degree of crosslinking and the molecular weight (Mc) between crosslinks. The swelling coefficient of biopolyester and their composites were given in Table 1.

Table 1 Swelling coefficient of biopolyester neat sheet and sisal fibre reinforced composites

| Biopolyesters and their composites | EMK | DMA | Toluene | Chloroform |
|---|---|---|---|---|
| SFB | 0.25 | 1.14 | 0.27 | 0.30 |
| SFBSL5 | 0.25 | 1.12 | 0.27 | 0.31 |
| SFBSL10 | 0.24 | 1.12 | 0.23 | 0.33 |
| SFBSL15 | 0.29 | 1.11 | 0.29 | 0.34 |

*Solvent absorptivity percentage (%)*

Solvent absorptivity percentage was carried out in different solvents such as ethyl methyl ketone (EMK), toluene, chloroform and dimethyl acetamide. The solvent absorptivity percentage of the biopolyesters and their composites has been increases from non-polar to polar solvents. This indicated that the biopolyesters and their composites were hydrophobic in nature. The solvent absorptivity percentage of the biopolyester sheet and their composites were given in Table 2. In the present investigation, the biopolyesters and their composites, the solvent absorptivity percentage was observed in the order SFBSL15 > SFBSL10 > SFBSL5 > SFB.

Table 2 Solvent absorptivity percentage of biopolyester sheet and their sisal fibre composites

| Biopolyesters and their composites | EMK | DMA | Toluene | Chloroform |
|---|---|---|---|---|
| SFB | 15.24 | 55.76 | 18.19 | 26.48 |
| SFBSL5 | 14.81 | 52.21 | 17.93 | 27.09 |
| SFBSL10 | 14.39 | 56.79 | 17.76 | 27.46 |
| SFBSL15 | 13.97 | 55.85 | 17.34 | 27.89 |

*Soil burial test*

Soil burial test was used to find out the environmental resistance of the biopolyester and their sisal fibre reinforced composites. The weight loss percentage of biopolyester and their composites under soil burial test have been presented in Table 3. The percentage of sisal fibre content increases, the degradation rate also increases. They concluded that the sisal fibre reinforced biopolyester composites possesses higher degradation than biopolyester sheet.

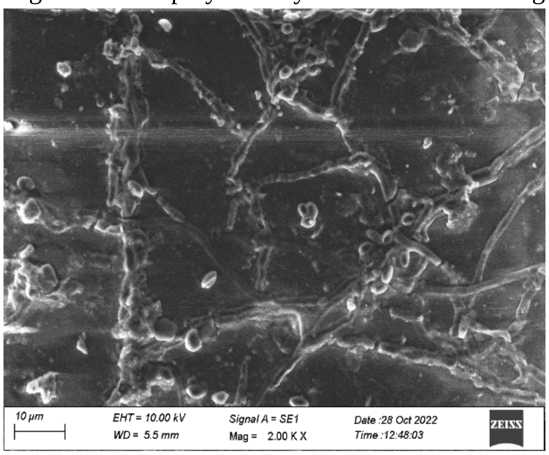
Table 3 Weight loss of biopolyester neat sheet and their composites under soil burial test

| Biopolyesters and their composites | Weight loss (%) |
|---|---|
| SFB | 25.519 |
| SFBSL5 | 29.815 |
| SFBSL10 | 43.717 |
| SFBSL15 | 63.95 |

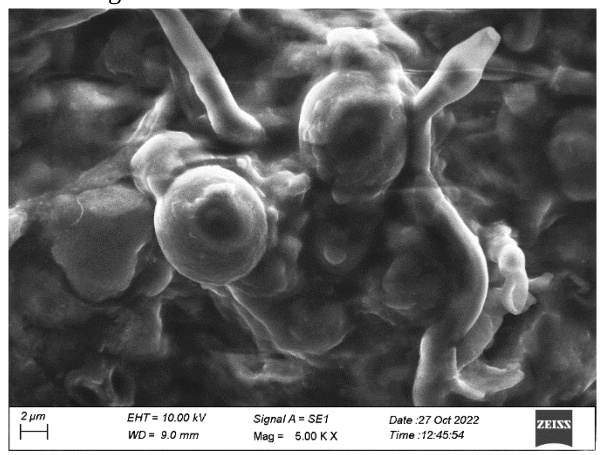
*Scanning electron microscope (SEM) analysis*

Scanning electron microscope analysis was used to study the morphological behavior of biopolyester and their composites. The biopolyester and their composites were analysed which showed that the degradation of polymers by microbial action. Figure 4.8 showed that the SEM micrographs of the SFBSL10 and SFBSL15 before and after degradation.

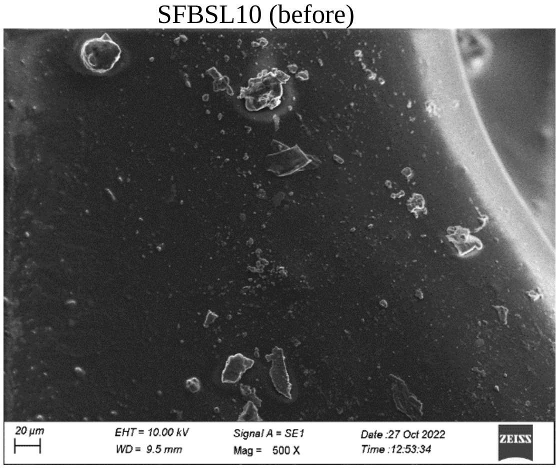
After two months, in the soil, large number of holes, pinholes and cavities were observed in SFBSL10 and SFBSL15 were indicated that the 10% and 15% of sisal fibre reinforced composites were attacked by the microorganism under soil environment.



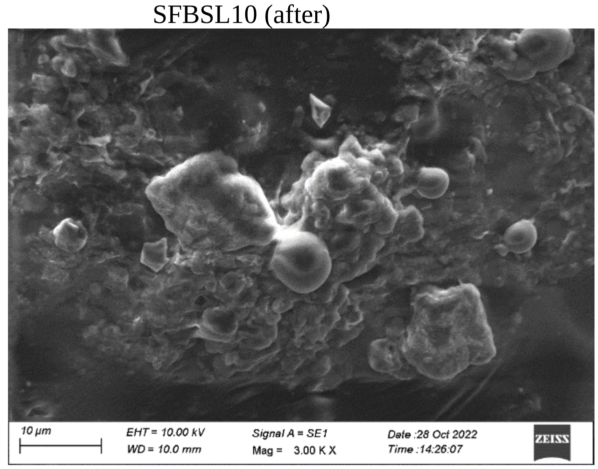

SFBSL10 (before)




SFBSL10 (after)




SFBPSL15 (before)




SFBSL15 (after)

Figure 4.8 SEM images for the biopolyester composites SFBSL10 and SFBSL15 before and after soil burial test

## V. CONCLUSIONS

The synthesis of hydroxylated sunflower oil resin and poly (sunflower oil fumarate) biopolyester resin were confirmed by FT-IR and $^1$H NMR analysis. The synthesis of poly (sunflower oil fumarate) biopolyester and their composites were confirmed by FT-IR analysis. The swelling coefficient of the biopolyester and their composites were high in dimethyl acetamide. The fibre content of biopolyester composites increases, solvent absorptivity can also increases. Soil burial degradation study showed that the biopolyester sheet, 5%, 10% and 15% of sisal fibre reinforced composites were biodegradable. The percentage of sisal fibre content increases, the degradation also increases. The biodegadation of biopolyester and their composites have been confirmed by SEM analysis.

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