

Preparation and Characterization of Chitosan Binary Blend

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Abstract- Chitosan biopolymer represents an attractive alternative to other bio materials because of its significant physico-chemical behaviours. In order to improve chitosan's performance, chemical modification has been carried out. Chemical modification that lead to the formation of chitosan derivatives, grafted chitosan and chitosan composites have gained much attention, extensively studied and widely reported in the literature. In this work, the properties of chitosan are modified by blending with silk fibroin which is another natural polymer which is produced by the silk worm larvae of *Bombyx mori*. Chitosan/silk fibroin binary blend is synthesized and characterized by FTIR, TGA and XRD. The results showed that the proper blending has been taken place between the polymers.

Index Terms- Chitosan, Silk fibroin, Binary blends.

I. INTRODUCTION

Chitosan, poly- β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose, is an aminopolysaccharide derived from the N-deacetylation of chitin (see **Figure 1**), which is a structural element in the exoskeleton of crustaceans (crabs, shrimps, etc.) and cell wall of fungi and it is also classified as a natural polymer because of the presence of a degradable enzyme, chitosanase. The relative amount of the two monosaccharides in chitosan may vary, giving samples of different degrees of deacetylation (75-95%), viscosities, pKa values and molecular weights (50-2,000 kDa) [1-3]. Therefore, chitosan not only refers to a uniquely defined compound but also refers to a family of copolymers with various fractions of acetylated units.

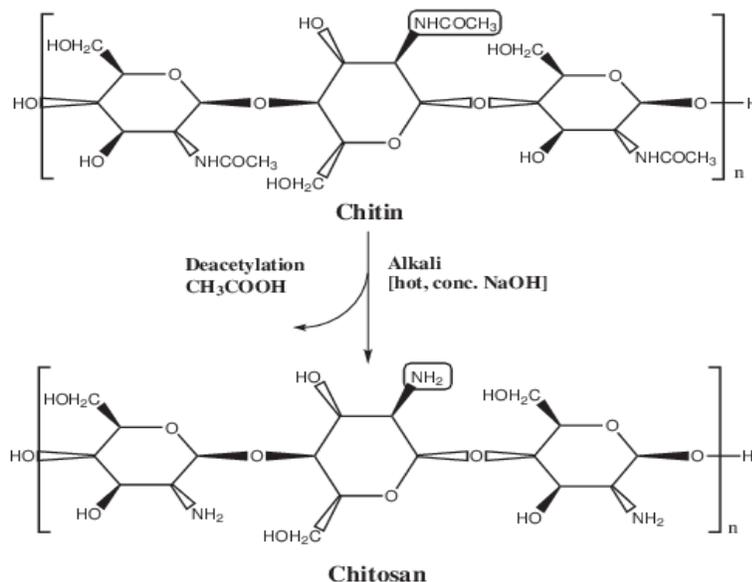


Figure 1: Chemical structure of chitosan and its production from chitin.

Chitosan is a biopolymer which has many interesting properties that have been utilized in many pharmaceutical applications [4]. Improving the fragile nature of films and membrane permeability are the key challenges that need to be addressed for improving chitosan as a biomaterial. In addition, chitosan is expected to be useful in the development of composite materials such as blends or alloys with other polymers, since chitosan has many functional properties [5]. There have been many studies on the blends of chitosan with various kinds of polymers [6-10] in order to obtain some improved properties.

In recent years, polymer blending has received much attention. This is mainly due to the fact that new materials can be observed with better physicochemical properties when the original polymers are compatible [11,12].

In order to satisfy the growing needs of new materials with specific properties such as engineering materials, new polymers have been developed [13-15] and chemical modifications in conventional polymers have also been proposed [16,17]. The characteristics of polymeric blend will mainly depend on the miscibility of the constituent polymers, the properties of its polymeric components, and its composition [18]. Miscibility has been known as one of key factors influencing the structure and properties of a polymer blend which are important in applications. Therefore, miscibility, structure and properties have been important issues in the studies regarding polymer blends [19].

In some cases, by synergistic effects, the blend provides better properties than the pure components [18,20]. Since chitosan has many functional groups, it can be modified by blending with other polymeric materials which is expected to be useful for some applications. The formation of polymeric blends constitutes a perspective way of making materials with new properties, especially from natural polymers that are of special importance.

Numerous investigations have been reported on the studies of films made from chitosan [21-25] and chitosan blends with natural polymers [7,26-29] or synthetic polymers [9,30].

II. MATERIALS AND METHODS

A. Preparation of Chitosan Solution

Chitosan (from crab shells) was obtained from India Sea Foods, Cochin, Kerala. About 50 gms of chitosan was slowly added to 1000 ml of 1:1 formic acid with constant stirring. The mixture was heated to set a whitish viscous gel of chitosan – formic acid mixture. *Bombyx mori* silk was boiled in 0.5 wt% of Na_2CO_3 solution for 40 mins to remove the sericin, then rinsed three times successively in distilled water and soaked in distilled water overnight. The degummed silk was dried for 7 hrs. Silk fibroin solution was prepared by dissolving 50 g of degummed silk in 1000 ml of 15% lithium chloride in formic acid. The chitosan/silk fibroin blends were prepared by mixing solutions of chitosan with silk fibroin solution in the weight ratio 1:1. The solutions were stirred well and were stored at 5 °C overnight and then allowed to dry to get chitosan/silk fibroin blends.

B. FTIR Studies

Fourier Transform infrared (FTIR) spectral analyses of chitosan/silk fibroin blend were performed with Thermo Nicolet AVATAR 330 spectrophotometer in 4000 – 400 cm^{-1} wave length range, using KBr pellet method.

C. Thermo Gravimetric Analysis

Thermogravimetric analysis was conducted to measure the thermal weight loss of the chitosan/silk fibroin blend on a SDT Q600 V8.0 Build 95 instrument at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. The weight losses at different stages were analysed.

D. X – Ray Diffraction Studies

X-ray diffraction (XRD) patterns of chitosan/silk fibroin blend were studied using X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered $\text{Cu K}\alpha$ X-ray radiation source. The relative intensities were recorded within the range of 10° – 90° (2θ) at a scanning rate of 5° min^{-1}

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy

The IR spectra of chitosan (**Figure – 2**) showed a strong absorption band at 3454 cm^{-1} due to OH and amine N-H symmetrical stretching vibrations. A peak at 2923 cm^{-1} was due to symmetric $-\text{CH}_2$ stretching vibration attributed to pyranose ring [31]. A peak at 1156 cm^{-1} was assigned to the structure of saccharide. The sharp peak at 1384 cm^{-1} was assigned to CH_3 in amide group [32]. The broad peak at 1021 and 1098 cm^{-1} indicated the C-O stretching vibration in chitosan and peaks at 1628 and 1540 cm^{-1} were due to C=O stretching (amide I) and NH stretching (amide II). The absorption bands at 1151 cm^{-1} was assigned to the anti-symmetric stretching of C-O-C bridge, and 1098 and 1021 cm^{-1} were assigned to the skeletal vibrations involving the C-O stretching [33].

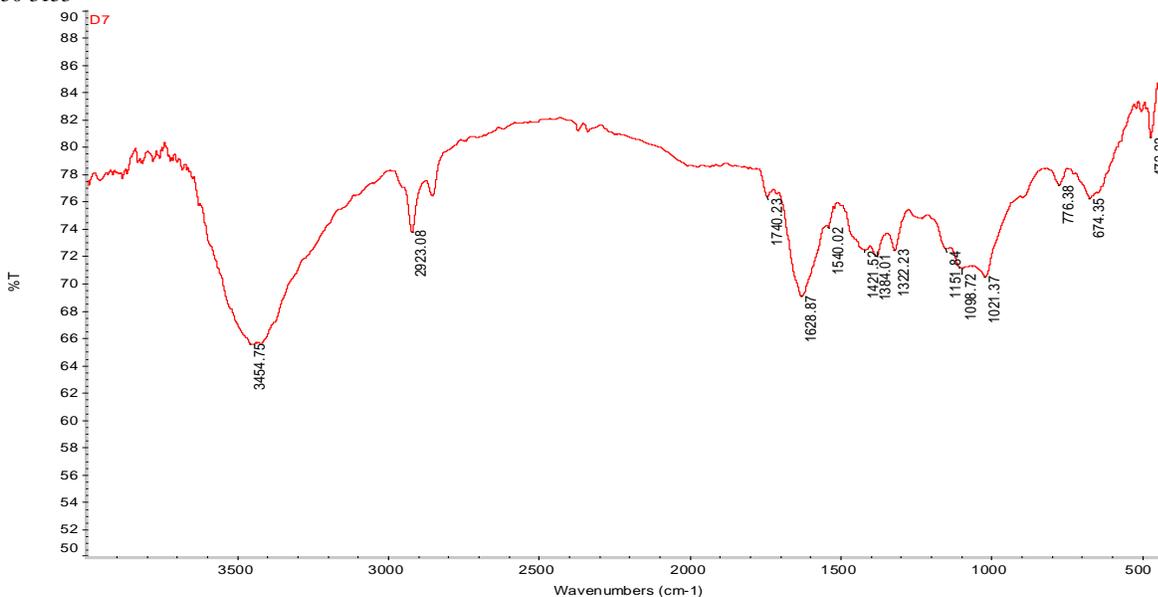


Figure 2: FTIR spectra of Pure Chitosan

In the FTIR spectra of 1:1 CS/SF blend (**Figure-3**), the absorption band at 3434.94 cm⁻¹ corresponds to –OH and NH stretching frequency. The band at 2927.01 cm⁻¹ corresponds to –CH₂ vibration and was assigned to the –CH stretching vibration of the pyranose ring. The band at 1598.33 cm⁻¹ corresponds to C=O stretching vibration and 1426.93 cm⁻¹ corresponds to C-H and O-H deformation vibrations. Another absorption band at 1230 cm⁻¹ could be attributed to C-OH stretching. A peak at 777.96 cm⁻¹ band showed CH₂ rocking. The peak 680.40 cm⁻¹ corresponds to N-H bending.

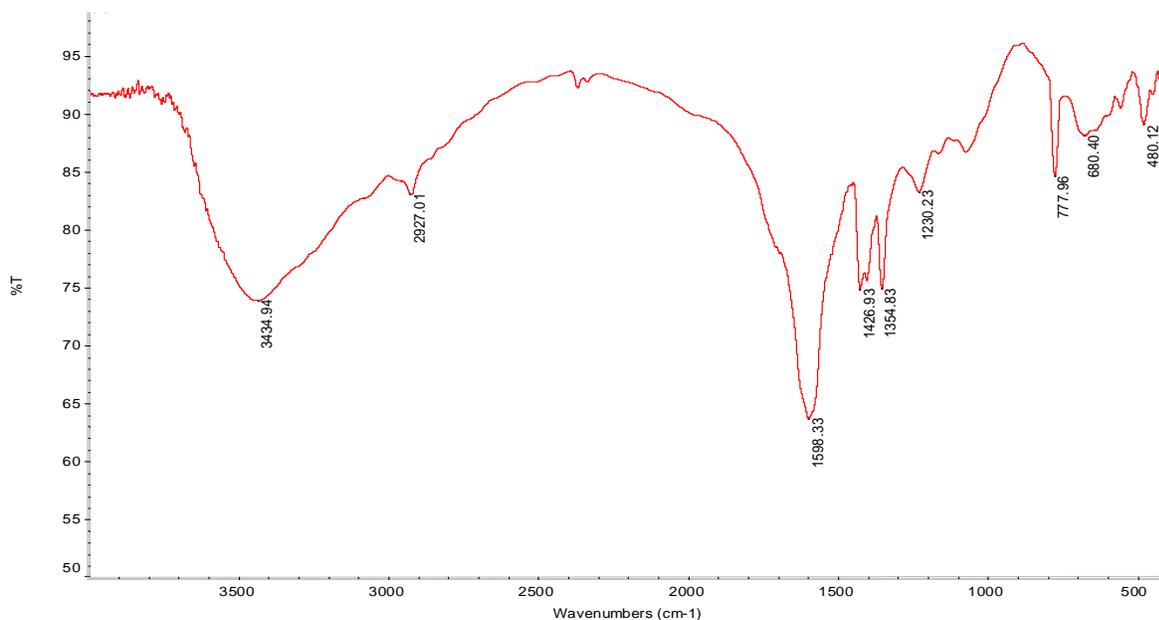


Figure 3: FTIR spectra of 1:1 CS/SF blend

The IR spectrum of chitosan showed absorption bands at 3454 cm⁻¹ and 1628 cm⁻¹ correspond to OH, NH stretching and C=O in amide group stretching vibration. For the 1:1 CS/SF blend, the absorption band at around 3454 cm⁻¹ concerned with OH stretching vibration for pure chitosan broadened and shifted to a lower wave number 3434 cm⁻¹. Compared with chitosan, the blend showed disappearance of the C=O in amide group at 1628 cm⁻¹ concluded that a certain degree of interaction between silk fibroin and chitosan molecules may be due to the formation of intermolecular hydrogen bands [34].

B. Thermogravimetric Analysis

TGA thermal details of chitosan with 92% degree of deacetylation is shown in **Table I and Figures 4 and 5**. It can be seen from **Figure 5** that three consecutive weight loss steps were observed in the pure chitosan. The first weight loss was about 6.733 wt% at 55 – 191 °C which was responsible for the loss of moisture content indicating its hygroscopic nature. The second weight loss was about 38.35 wt% in the range of 230 to 327 °C, which was due to scission of the ether linkage in the chitosan backbone. In the third stage, the weight loss was about 24.85 wt% in the range of 327–840 °C, which corresponds to the thermal decomposition of glucosamine residues [35].

Table 1: TGA Thermal studies of pure chitosan

Percentage Decomposition (%)	Decomposition Temperature (°C)
10	276
20	300
30	330
40	450
50	715
60	800
70	840

The thermal decomposition details of chitosan given in **Table - 1 and Figure – 4** represent the percentage decomposition of the sample at different temperatures. At the end of the experiment nearly 30% of the sample was remained as residue showing the higher thermal stability of chitosan. The degradation of chitosan in fact started with the amino groups and formed an unsaturated structure [36].

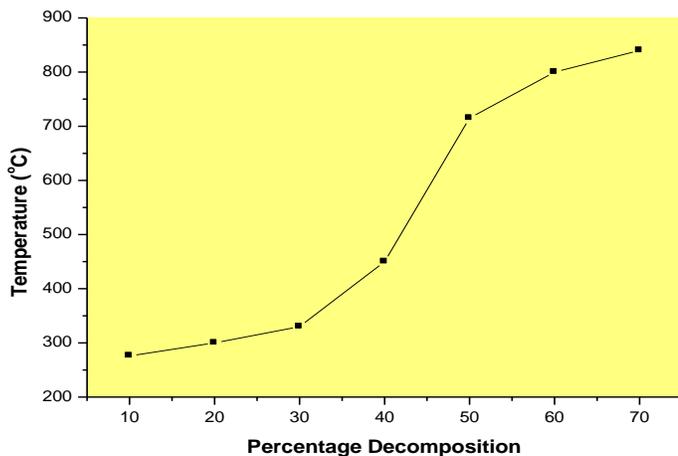


Figure 4: TGA Thermal studies of pure chitosan.

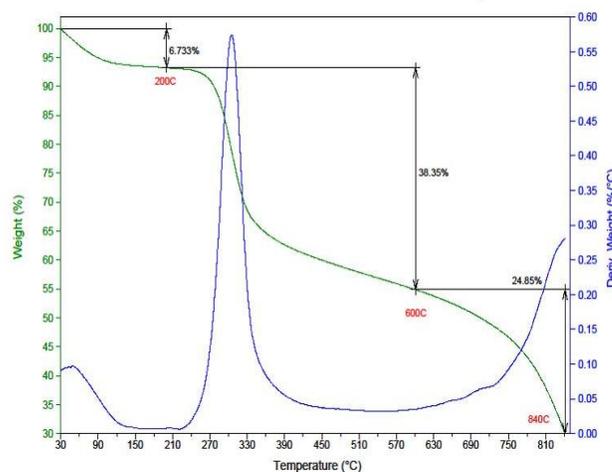


Figure 5: TGA thermogram of pure chitosan.

Table - II and Figure - 6 represent the TGA thermogram details of chitosan/silk fibroin composite (1:1). **Figure 7** shows the thermogravimetric curves of 1:1 chitosan/silk fibroin blend. The blend exhibited two weight loss steps. The initial weight loss fallen in the range of 100–230 °C and was due to the evaporation of water. The second weight loss began at about 350 °C that was due to degradation of blend. Similar weight loss has been observed in the case of chitosan/polyaniline blend by Thanpitcha and his group [37].

Table II: TGA thermal studies of chitosan /silk fibroin blend (1:1).

Percentage decomposition (%)	Decomposition temperature (°C)
10	148
20	188
30	245
40	280
50	338
60	400
70	444
80	464
90	635

TGA thermogram details of CS/SF (1:1) blend showed that 90% of the blend disintegrated at 635 °C. Maximum weight loss of the blend occurred at the temperature range of 188–400 °C. During heating above 150 °C, the degradation rate sharply increased to reach its maximum at 400 °C (**Table - II and Figures – 6 & 7**). At the end of the experiment (at 788 °C) only 7.89% of the blend remained. Residual weight was found to be 0.381 mg.

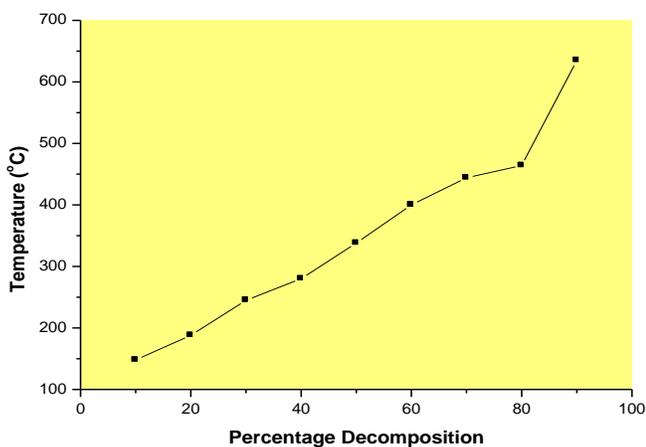


Figure 6: TGA thermal studies of 1:1 CS/SF blend.

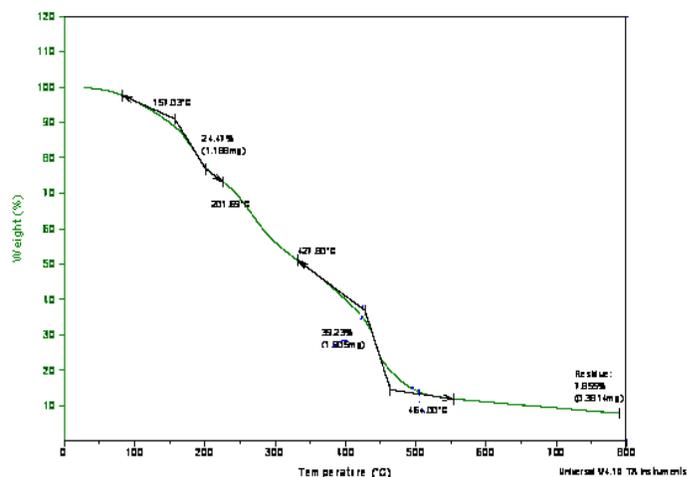


Figure 7: TGA thermogram of 1:1 CS/SF blend.

From **Table–III and Figure-8**, it is evident that the percentage decomposition of chitosan/silk fibroin blend 1:1 was greater compared to that of pure chitosan. As the temperature increased, the percentage decomposition of the blend also increased drastically. The main observation on the blended system was that the decomposition temperature of blends was higher than those of pure chitosan. In the case of CS/SF blend, the degradation was about 15–40% higher when compared to pure chitosan. This is an unusual behavior because generally the related system may have the greater thermal stability than the pure one [38,39] and this anomaly could be related with crystalline and/or morphological variations in blend with respect to those of the pure polymers [40].

Table III: Rate of thermal decomposition (%) of CS and CS/SF blend

Temperature (°C)	CS	CS/SF (1:1)
100	6	4
200	8	23
300	20	44
400	38	61
500	43	86
600	45	89
700	50	91

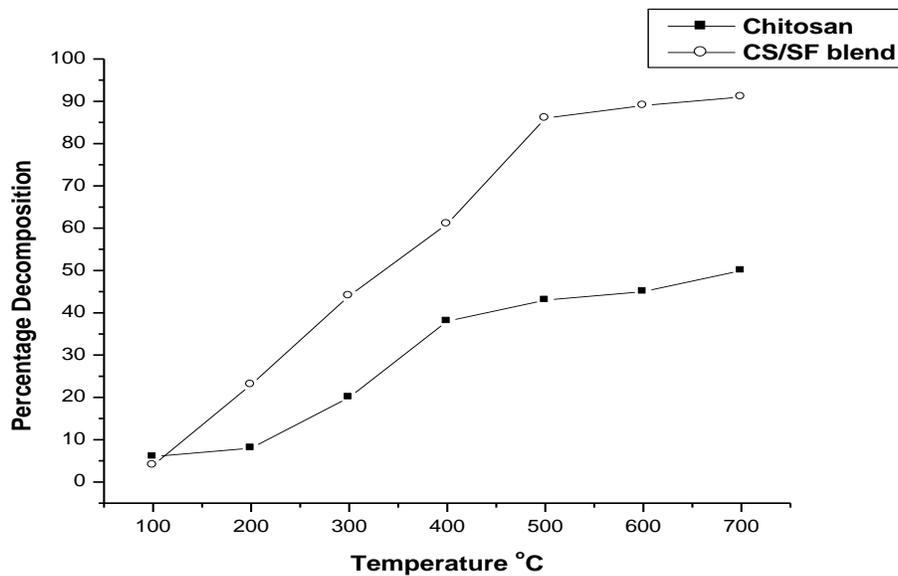


Figure 8: Rate of thermal decomposition (%) of CS and CS/SF blends

C. X-Ray Diffraction Studies

Figure 9 shows the X-ray diffraction pattern of chitosan which showed distinct crystalline peaks at around 2θ values 10° and 20° . This is because of presence of plenty of $-OH$ and $-NH_2$ groups in the chitosan structure, which could form stronger inter and intramolecular hydrogen bonds and the chitosan structure has certain regularity, so that the molecules form crystalline regions easily which was similar to the results reported by Duan and his co-workers.

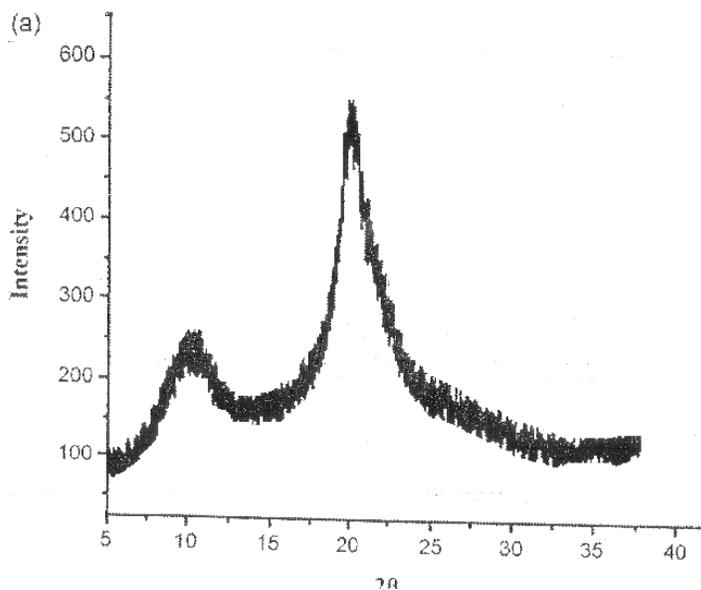


Figure 9: X-ray diffraction pattern of pure chitosan

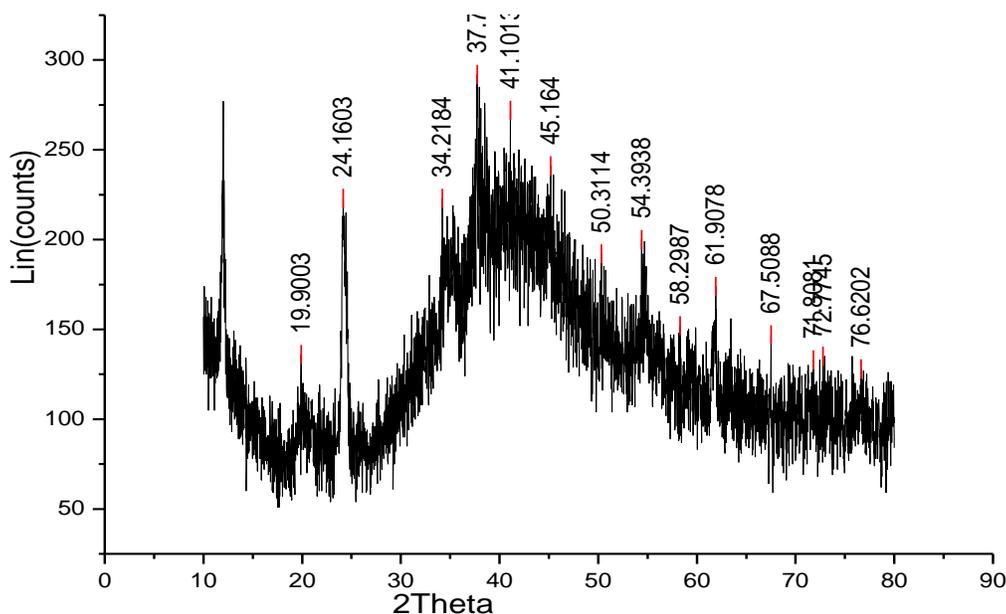


Figure 10: X-ray diffraction pattern of 1:1 CS/SF blend

Figure 10 present the XRD pattern of CS/SF blend under study. For the pure chitosan, there were two peaks around 2θ value 10° and 20° [7]. The peak of chitosan at $2\theta = 10^\circ$ became weak until disappearing in the blend and the peak at 20° weakened and the intensity of the peak became low. These evidences suggested that strong interaction occurred between CS and SF molecule in the blend. A new peak was observed in all the blends at 2θ around 40° which may be the characteristic peak of silk fibroin. The significant shift in the diffraction peaks and the diffraction pattern with a broad amorphous peak indicated that there was a molecular miscibility and interaction between the components [42]. The XRD results thus, provided supporting evidence to the FTIR results that some specific chemical interaction between CS and SF existed in the blend.

IV. CONCLUSION

In this present research, chitosan/silk fibroin binary blend was developed successfully and characterized using FTIR spectra, thermograms and XRD. The characterization results proved that there was an interaction between the polymers. The binary blend may have both the characteristics of chitosan and silk fibroin, which can be used for various applications like biomedical application and waste water treatment.

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