Studies on X-Ray Diffraction (XRD) patterns of Soya-hulls for Interpretation of Crystallinity Index

Preeti Soni[1] Jitendra Kameliya[2] and Shweta Vyas[*3]

1,2,3Department of Pure and Applied Chemistry, University of Kota, Rajasthan 324005,India

Abstract

X-Ray diffraction (XRD) technique is a prominent & nondestructive tool, used for the determination of crystallographic structure of any material. The technique follows the Brag's Law and measures the intensities and scattering angles of the X-rays that leave the material to provide information on phases, preferred crystal orientations, crystal defects, crystallinity, and many other parameters. Crystallinity Index (CI), which is a quantitative indicator of crystallinity of any material, can also be calculated using XRD data and applying Segal's method. In the present study, XRD patterns of Alkali/Acid treated soya-hulls are recorded and used for the calculation of CI. Results indicated wide variation of CI ranging from 22%-76% with lowest value for sodium hydroxide treated and highest for ascorbic acid treated soya hulls which may be due to maximum removal of hemicelluloses and amorphous lignin type structure. This study reveals that organic acids which are more eco-friendly can work better to increase CI and cellulose content of any lignocellulosic waste biomaterials like soya hulls for the application in composite and nanocomposites material synthesis.

Keywords*: Biomaterials, X-ray techniques, Composite materials, Nanocomposites*

1. Introduction

X-Ray Diffraction (XRD) technique is a prominent & nondestructive tool, used for the crystallographic structure determination of any material. When incident beam of X-rays fall on any material, atomic planes of a crystal cause interference of an incident beam of X- rays, as they leave the crystal and produce X-ray Diffraction (XRD) pattern [1]. During X-ray diffraction, every substance gives a pattern; which is specific for a given substance and depends up on the scattering angles of x-rays by the material. Planes of compounds act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. The interaction of the incident X-rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy **Bragg's Law** [2] as shown in equation (i)-

$$n\lambda = 2d \sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Where n= Order of Reflection; d= Plane spacing; θ = Bragg Angle

This law relates the wavelength of electromagnetic radiation (λ) to the diffraction angle (θ) and the lattice spacing in a crystalline sample (d). By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. The diffracted X-rays are then detected by X-ray diffractometer to generate the XRD pattern.

Crystallinity index (CI) of any material, which is a quantitative indicator of crystallinity [3] have been measured by using several methods like Solid-state 13C NMR, infrared (IR) spectroscopy, Raman spectroscopy including XRD technique [4]. In current study CI is calculated using XRD data and applying Segal's method [5] of maximum peak height determination by following relationship-

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \ldots\ldots\ldots\ldots \text{(ii)}$$

Where CI is Crystallinity Index; I_{002} is maximum intensity of the principle peak of crystalline form; and I_{am} is minimum intensity for amorphous form. Generally CI of any lignocellulosic material depends on the ratio of cellulose, hemicelluloses, lignin etc. any physic-chemical treatment may alter the ratio of cellulose, lignin, hemicellulose, etc. [6] which may be clearly seen in the XRD patterns. In the present study, CI of alkali/acid treated soya hulls is calculated with the help of equation (ii) using Segal's peak height method.

2. Materials and Method

2.1 Materials

Sodium hydroxide pellets (anhydrous), ≥ 98%(Fluka), Orthophosphoric acid, ACS reagent, ≥85 wt. % in H2O(Sigma-aldrich), L-Ascorbic acid reagent grade(Sigma-aldrich), Oxalic acid reagent grade(Sigma-aldrich), Deionised distilled Water, Soya hull wastes.

2.2 Method

Soya hulls are agro-industrial wastes generated at soya-oil manufacturing units and are collected from local small scale industry of Kota, Rajasthan, India. Washed soya hulls are oven dried at 60ºC for 24 hours, crushed in a kitchen blender and sieved through 120 mesh to get powered form. Four types of chemical treatments are carried out by using 05 g powdered soybean hulls, first sample alkali treated soya hulls ASH is prepared by performing alkali treatment with 2% sodium hydroxide while acid treatments are given using 0.5 M acid solutions of phosphoric acid, oxalic acid, and ascorbic acid, to prepare PASH, OASH, and AASH respectively. X-ray diffraction studies are carried out (Rigaku Ultima-X-ray diffractometer with Cu-Kα, λ = 0.1542 nm) to identify the crystalline nature of the soya hull materials. The maximum intensity of the principle peak of 200 (I_{002}, 2θ= 22°) and the intensity of diffraction of 110 peaks ($I_{am,}$ 2θ=16°) was noted and calculation for the crystallinity index (CI) were performed using Segal's method, I_{002} denote highest intensity for crystalline form and I_{am} denotes the amorphous material. XRD patterns obtained are shown in fig.2.

3. Result and Discussions

X-Ray diffraction pattern of native cellulose contains sharp as well as defused bands as shown in fig. 1 [4].Sharp bands correspond to orderly arranged crystalline regions and defused bands correspond to amorphous regions. Crystalline structure is formed due to regular arrangement of atoms. Cellulose contains both crystalline and amorphous phases, arranged randomly. When beam of X-Ray passed through the sample, some of the regularly arranged atoms reflect the X-ray beam constructively and produced enhance intense patterns.

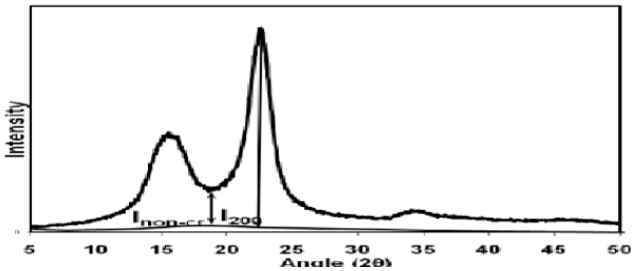

Fig. 1 XRD Pattern of Native Cellulose

X-Ray analysis of alkali/acid treated soya hulls is shown in fig. 2, evidently an increase in ordered crystalline cellulose content is seen and was achieved by the solubilization of the amorphous cellulose, hemicellulose and lignin etc. present in soya hulls-

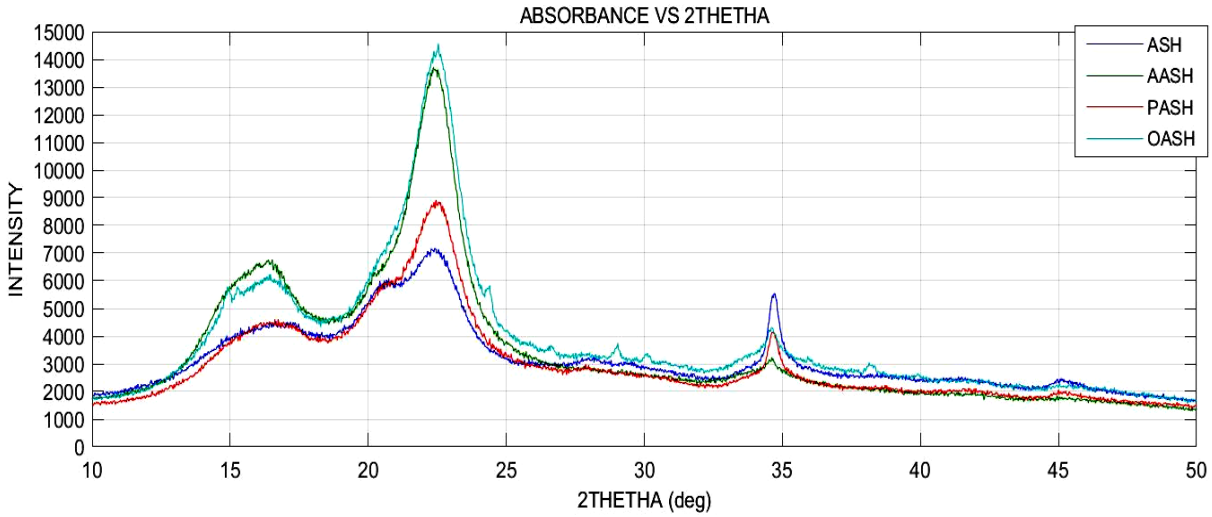

Fig. 2 XRD Pattern of Acid/Alkali Treated Soya-hulls

Many researchers reported that acid treatment tends to increase CI [3,6,8] and same has been observed by us as for treated soya hulls are depicted in the Table1 -

Table 1 Values of Crystallinity index (CI) for Lignocellulsic Materials

S.No.	Material	Crystallinity index (CI %)	Reference
1.	Raw material NaOH-treated	16% 50%	3
2.	CML-1T CML-2T CML-3T	63.82% 43.10% 61.42%	6
3.	Raw Fibers Alkali Treated Fibers Bleached Fibers Acid Hydrolysis Fibers	25% 54% 57.5% 60.3%	8
4.	Alkali treated Soya hulls (ASH) Phosphoric acid treated Soya hulls (PASH) Oxalic acid treated Soya hulls (OASH) Ascorbic acid treated Soya hulls (AASH)	22.65% 54.82% 70.39% 76.16%	**Our Study**

4. Conclusion and Future Aspects

Crystallinity Index of lignocellulosic materials depends upon the cellulose, lignin, hemicellulose, etc. contents of material any physicochemical treatments may alter the ratio of cellulose, lignin, hemicellulose, etc. for instance acid hydrolysis treatments given to soya-hulls lead to increase the cellulosic contents of materials & remove amorphous lignin, hemicellulose etc. the values of CI showed vast variations from 22.65% to 76.16%. Hence calculating CI using XRD patterns may lead to give useful information about cellulose contents of lignocellulosic materials and provide useful information about the

impact of any physical or chemical treatment applied. This study reveals that organic acids like ascorbic acid and oxalic acid which are more eco-friendly can work better to increase CI and cellulose content of any lignocellulosic waste biomaterials like soya hulls for the application in composite and nanocomposites material synthesis.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Acknowledgements

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