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EFFICIENCY OF XRD METHOD FOR STUDYING FRC COMPOSITES – A REVIEW

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Abstract- The appropriate and proficient management of different types of fibrous materials is one of the major concerns by the agricultural countries. The plenty of natural as well as synthetic fibres from the last few decades are used by researchers for different civil engineering applications. The properties of fibres differ from each other depending upon their growing condition, harvesting and extraction method. The different fibre reinforced concrete are similar as of their texture apparently but differs structurally. Microscopic examination plays a vital role in identification of mineral composition. The microscopic study to explore micro-structure of fibre reinforced composites (FRC) needs to be done. A variety of methods are available for studying the material characterization at micro-level. This paper preliminary focuses on the characterization and efficiency of fibre reinforced composites through X-ray diffraction (XRD) test. XRD test is widely used to determine the cellulose and lignin composition. XRD test is most suitable for identification of crystallographic structure providing the crystallinity index as well. Similarly, Composition of lignin, cellulose and can be detected by use of XRD analysis. The detailed discussion on structural characterization is made.

Keywords- X-ray diffraction, Fibre Reinforced Concrete, Material Characterization.

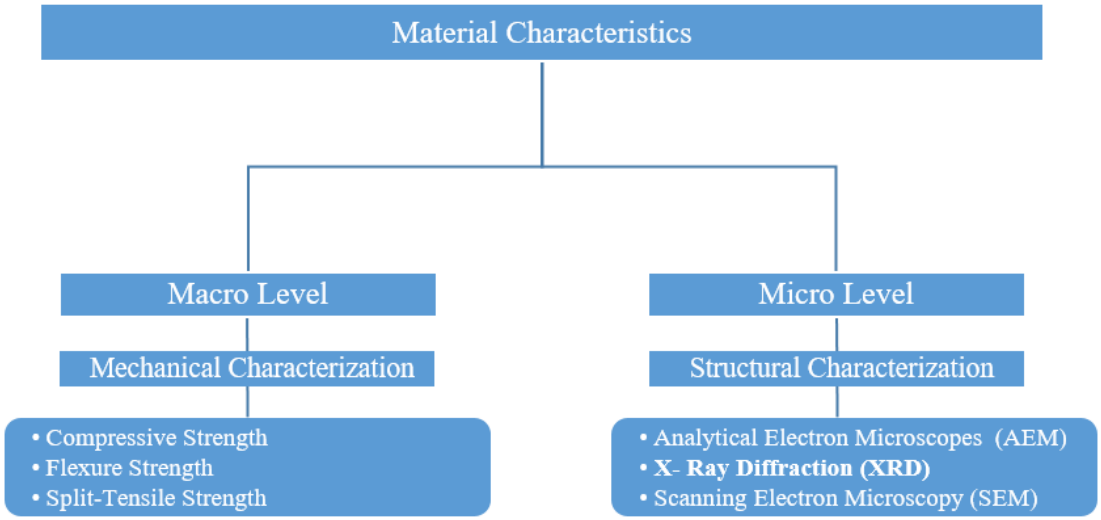
1 INTRODUCTION

The innovation of X-rays in 1895 by Wilhelm Conrad permitted the new applications possible in all major disciplines of engineering as well as scientific making the use of X-rays more beneficial. (Roentgen, 1895) [1]. The objective of this work focuses on the efficiency of XRD test for analyzing the material characterization at micro-level as shown in Figure 1. In particular, Laue, Knipping and Friedrich initiated the study of crystals by X-rays and opened new possibilities to study the crystalline materials by using the X-ray diffraction to explore material characterization (Friedrich et al., 1913) [2]. The advancement in technological phase promoted use of X-rays like X-ray radiography, X-ray computer tomography, X-ray fluorescence spectroscopy etc. [4] The advance technologies are used for different composites study. The application of XRD method on crystals is a precise study of crystalline phase structure in a characteristic manner by the ability of crystals to diffract X-rays [5].

To date, having environment friendly materials is one of the current trends in the construction industry with the help of effectively utilization of natural fibres as an alternative of man-made or synthetic fibres in concrete [6-8]. Fiber reinforced concrete (FRC) for the use of structural applications has proven itself to be a comparable material due to its improved mechanical properties [9-11]. The use of fibres are seeking attention because of their light weight and improved mechanical properties [26]. Different industries like ceramic, polymer and construction industry have several applications of nanotechnology producing composites which are more improved and comparable mechanical and physical properties. [12]. The improvement of cementitious matrices and polymers for improving their fracture resistance and strength properties is greatly influenced by the use of cellulose and natural fibres [13,14]. Natural fibres are biodegradable, lighter and cheaper, than its equivalent man-made fibres. Wheat straw, cotton, rice straw, sisal, bagasse, flax, bamboo, hemp, banana, coir, and others are some of the examples of natural fibres [15-17]. Indeed, some obstacles which have limited the applications of fibres in the composites despite of all their advantages of fabrics and natural fibres. The FRC composites look apparently same because of presence of fibres but actually they differ structurally. Hence, having the different bond behaviour and different mechanical characteristics. The material characterization of natural fibres like jute, kenaf, hemp, coir, sisal and flax and their composites are explored by significant amount of research works and can be find on. The natural fibres particularly are in raw form having impurities in it. The fibres can be amended and make more effectively

incorporated. Physical and chemical methods are most adopted methods by which the surface of natural fibres can be modified which can make significant improvement in material characteristics.

Figure 1: Material Characterization Techniques



In engineering and material science field, the application of XRD method on crystals is a precise study of crystalline phase structure in a characteristic manner by the diffraction of X-rays and by the ability of crystals. The patterns recorded by diffraction analysis of the sample contains the influence of numerous micro- and macro structural features. With the, space group, macro stresses, peak position and lattice parameters the qualitative phase analysis or chemical composition can be examined. The information about the structure of crystals including occupancy, atomic position and temperature as well as quantitative phase including the texture can be obtained by the peak intensity. Therefore, the peak shape gives the detailed information about the sample micro-strains and crystallite sizes (Dinnebier and Billinge, 2008) [5]. In this study, the method of XRD and its material characterization with different composition level of crystalline and amorphous state of FRCs are discussed. The evaluation of XRD is emphasized on FRC in order to better understand the structural characterization in FRCs. The determination of crystallinity index of FRCs is also explained.

2 OVERVIEW OF XRD METHODOLOGY

2.1 Sample preparation.

One of the most important requirements for XRD analysis is proper sample preparation. Sample preparation includes not only to remove undesirable substances by the precise sample treatments, but also appropriate and efficient techniques to get desirable thickness, orientation and particle size etc. To achieve good signal without distortion and fluctuation extremely fine grained sample are required for the analysis of XRD, and minimize preferred orientation to avoid spottiness. As reported by Brindley, 1980 and Cullity, 1978) [17], The recommended range of size for sample is around 1 µm to 5µm The mesh size of sieve 325 (45µm) is usually used for the sample sieving for the use qualitative evaluation of mineral components.

2.2 Technology involved in XRD laboratory equipments.

Generally, in labs stationary equipment is used. The main parts of the instruments for XRD are a sample holder, goniometer, primary and secondary optics with and an X-ray source having a detector as shown in Figure 2. Goniometer is essential part of the equipment and all XRD equipments are equipped with a goniometer, The X-ray source are allowed to move through the goniometer which is the dominant part of the diffractometer, similarly in a very precise manner the detector and sample are placed relative to each other. While, the generation and acceleration of electrons is necessary for the generation of X-ray photons coming which can be done by the use tungsten filament. Generally, for the acceleration of electrons the voltage range between 20 to 60 kV are used (Spieß et al., 2009) [4]. For the production of X-rays 99% of the energy is dissipated in the form of heat and only 1% of the available energy is used for the generation of the radiation.

Moreover, the consideration of heating is a major issue which affecting the efficiency of the X-rays. Therefore, it is mandatory to cool down the system and instrument by using anode having continuous water cooling. While, limiting the beam intensity to 60mA and low current can be used in X-ray tubes.

Figure 2: XRD equipment (D8 Bruker-AXS Advance Diffractometer [18]

2.3 Employment Technique.

Goniometer being the crucial part of the diffractometer which allows the movement of X-rays hereby all laboratory equipments of XRD are equipped with it. According to the purpose and required need of the measurement, particular sample holders e.g., automatic sample changing, continuous translation or sample rotation to achieve automatic sample positioning, etc., or considering the sample geometry a controlled preparation environment can be used. The use of glass plated can be done for powdered samples of amorphous polymer for carrying the powder. The additional rotation axes are generally required for the texture and residual stresses measurements, in addition to position these investigations of the sample are needed for these investigations.

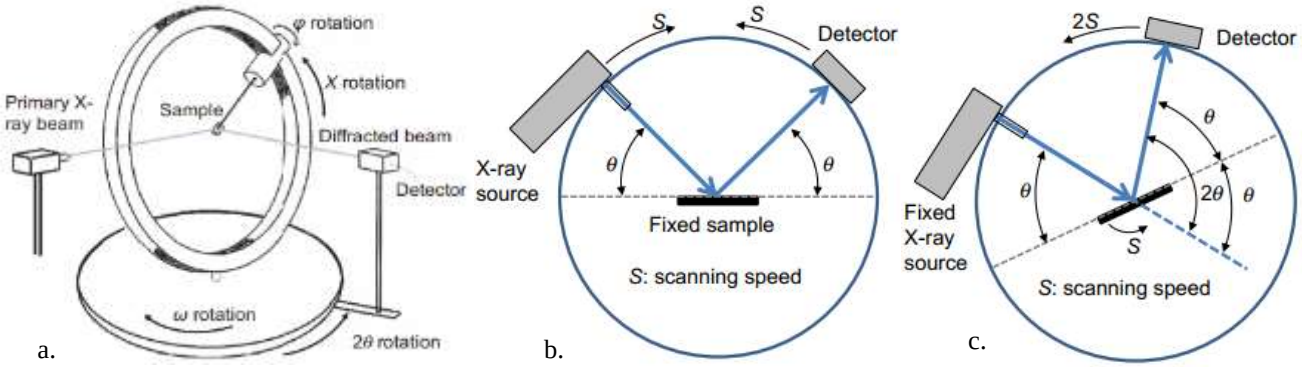


Figure 3: Employment Technique, a. principle of goniometer, b. Θ/ Θ goniometers, c. Θ/ 2Θ goniometers [18]

The basic method of employment is shown in Figure 3. where the sample is fixed while, the detector as well as X-ray source moves, and at a fixed position Similarly, for the next round sample and detectors are moving with goniometer and the X-ray source is fixed. Both the actions can be done simultaneously depending upon the ability of detectors to read.

2.4 Employment Technique.

According to the peak height from the X-ray diffractogram, the Crystalline Index (CI) or degree of Crystallinity in cellulosic material technique can be determined by the established Segal empirical equation (Segal et al. 1959) [19], as shown in equation 1.

$$C.I = \frac{I200 - IAM}{I200} \qquad (1)$$

Where: I_{200} is the maximum intensity of reflection by the crystalline plane of the cellulose at 2Θ and I_{am} is the maximum intensity of the amorphous part at 2Θ.

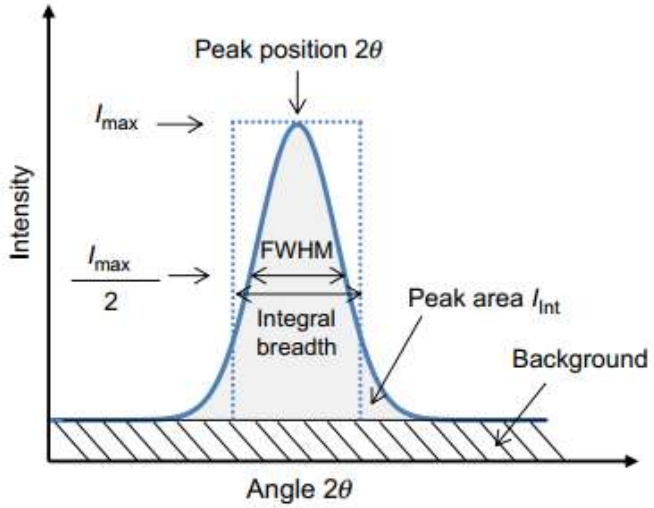


Figure 4: Information about diffraction peak [18]

In general, as a function of angle 2Θ the intensity distribution is extracted from the diffraction data. The information that can be extracted from the diffraction peaks is represented in Figure 4.

3 REVEALED CHARACTERISTICS OF FRC THROUGH XRD

2Θ The mineral constituents as well as the textures (i.e. size, shape and arrangement of mineral constituents within the groundmass for both concretes are largely similar. However, microstructurally they are quite distinct. Many research by various researchers to study the change in the microstructure and surface morphology after the treatment of fibres are studied. The interfacial bonding can be improved by removing the cementing substances and impurities which can increase the effective area providing better interlocking and improved properties. [20-21]. Punyamurthy et al.[22] reported that the by the treatment of fibres the surface roughness can be increased this is because of the removal of hemicellulose and lignin removal . Symington et al. reported that excessive treatment of fibre can lead towards fibre cracking phenomena and can have adverse effect on mechanical properties of natural fibres. The examples of over treated fibres are kenaf, abaca, flax and sisal fibres

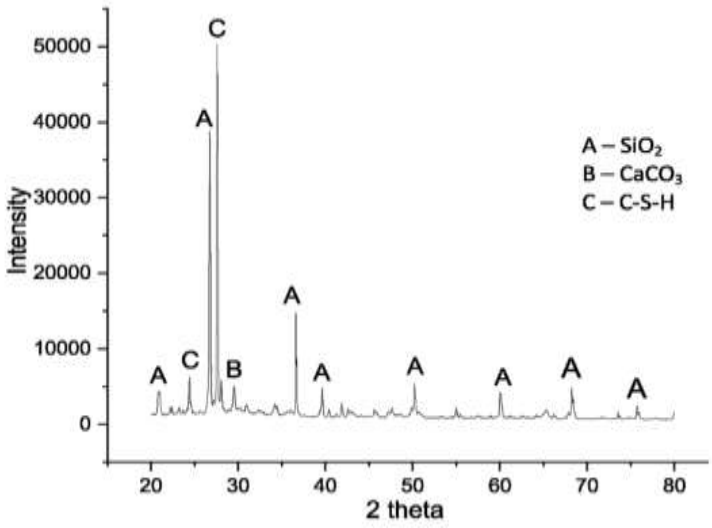


Figure 5: XRD pattern of Bagasse Fibre Composite [25]

Fiore et al. subjected to the treatment of kenaf fibres improve surface morphology, which leads to increase the mechanical properties by the removal of surface impurities and other cementitious impurities, this was done by alkaline treatment of 48 hours [23].

The XRD analysis of the composites after the curing time of 28 days in water is shown in Fig. 5. Most commonly produced X-ray patterns are of crystalline materials like cristobalite and quartz. In the diffraction analysis both O and Si have long-range atomic number and are arranged differently this arrangement of O and Si are reflected in the diffraction analysis. The O and Si atoms are organized differently, but both have atomic order of long range and the difference of their crystals structure are is reflected in the observed diffraction peaks. The broad scattered pattern of XRD analysis if observed by the amorphous glass because it does not have long-range atomic order. Fig. 6 shows the Quartz (SiO2) effect in the diffraction peaks. There is small presence and effect of hydrated compounds such as $Ca(OH)_2$, C–S–H, and $CaCO_3$. The content present of SiO2 in the mixture can increased due to the presence of micro-silica affecting its content ratio. Similarly, in the presence of water, reaction of silica (SiO_2) with calcium hydroxide ($Ca(OH)_2$) leads to the formation of C–S–H gel in the concrete mix. The peak of $Ca(OH)_2$ in the diffraction can be disappeared. The formation of C–S–H gel can turn to increase the strength of composites because the amount of SiO_2 decreases and more silica is used to react with Ca(OH)2 in the presence of water. Thus, calcite being the filler material in form of calcium carbonate contributes to enhance the strength of composites. This implies the formation of C–S–H gel comes in hydration reaction in which silica plays and important role. The presence of by-products such as calcium carbonate and calcium hydroxide are present but are in less ratio.

One of the challenging part is the phase identification of nanoscale material by XRD because of nearly indistinguishable patterns obtained by the diffraction analysis. For example, Ag and Au have similar structure lattice and both are face-centered cubic metals, which have broadened and scattered peaks obtained by XRD and is a tedious job which cannot be differentiated by XRD. Similarly, the XRD patterns of magnetite Fe_2O_3 and magnetite Fe_3O_4 two forms of iron oxide, are sufficiently similar with broad peaks, and they cannot be distinguished by XRD patterns. Differentiating the nitrides Ni_3N and nickel carbides Ni_3C or any hexagonal close-packed form can be similarly challenging. In these particular and other similar cases, the phase identification for additional characterization techniques are important [24].

4 RESEARCH FINDINGS/ FINDINGS DRAWN/ LESSON LEARNED

Material characterization under the influence of various condition like treatment methods, absorption of water and loading methods etc.is an important aspect for the natural fibres and its composites to understand their behaviour. A visual or manual control and selection of peak needs to be done once the preselection of possible phases are defined for the selected pattern. The intensity variation from the ideal peak and due to the solid part or strain needs to be taken in part. The macroscopic strains as well as texture effects can be avoided for the case of fine powder samples, and therefore measurements and can actually match up to some extent with the theoretical patterns precisely. In contrast to all of these,

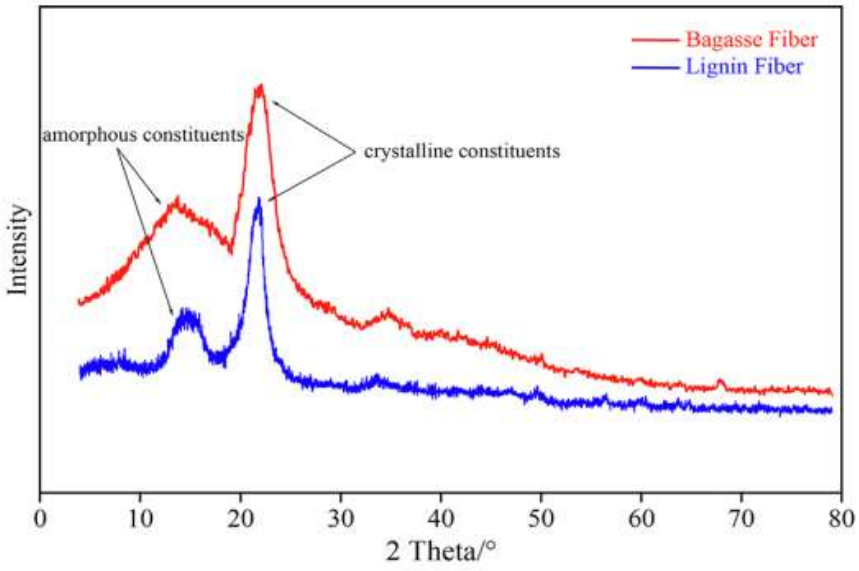


Figure 6: XRD pattern of Bagasse Fibre Composite [24]

the engineering mechanisms and samples which are more solid can reveal the textures more strongly, large grains and therefore the poor diffraction and irregular peak shape or due to high conditions of microscope the peaks shift or scatter. The adoption of the present final phase selection by the user to be performed only, based on the required results and of this understanding about measurement conditions and measurement conditions of the investigated sample. For an ideal case of diffraction, all the peaks measured of diffraction obtained from XRD should be assigned to a phase.

Crystallographic structure of sisal fibres was analyzed by Sahu [27] and reported that fibers mainly contain lignin, hemicellulose and cellulose. Cellulose is mainly composed of crystalline and that of amorphous structures, whereas the hemicellulose and lignin shows amorphous behavior. Development of the new hydrogen bonds among cellulose enhance crystalline percentage and crystallinity index of the natural fibers by treatment of fibres. The lignin part has amorphous structure and cellulose are crystalline in nature. The elimination of non-cellulosic parts makes fibre more crystalline and this is learned from XRD pattern.

Table 1: .Variation of crystalline index and crystalline percentage of treated and untreated fibre composite

Fibre Studied	Maximum Intensity	Angle (2-Theta) at I_{200}	Maximum Intensity	Angle 2 Theta at Iam	Crystallinity Index	Percentage of Crystallinity
	I_{200}	2 Θ – I_{200}	I_{am}	2Θ –I_{am}	CI	%
Sisal	4085	22.42	2246	15.98	0.45	64.52
Treated Sisal	5814	22.38	2688	16.22	0.53	68.30

Based on the prominent analysis of the FRCs, by the XRD pattern the source of the peaks can be confirmed. The observed peaks are represented in Fig. 6. The XRD pattern of the fibre reinforced composites show a peak at 2Θ, which represents the cellulose in form of crystalline constituents, the peak of amorphous denotes constituents like amorphous, lignin, and hemicelluloses. The treatment of natural fibres irrespective of any method the crystallinity index also tends to increase with their treatment. Most of this carbonation has taken place at the interface of the aggregates and few of them are associated with micro cracks and voids. On the basis of present investigation, it is concluded that the use of calcium stearate as admixture can enhance the strength and durability properties of concrete due to batter microstructure, formation of additional C-S-H gels and infilling of pores. Therefore, peak intensity tends to increase with the pretreatment of natural fibres and this pretreat of fibres can be done by various techniques such as chemical, alkaline treatments etc.

5 CONCLUSION

Since from the first experiment of XRD and the innovation of X-rays used for the crystals, among one of the most prevailing technique of art to explore material characterization is by mean of XRD methods. The design of high performance materials and their components have been strongly improved by the improved knowledge about properties of components, crystal structure and microstructure. Based on the review of XRD for FRC composites following conclusions are drawn

- The sample preparation requires to be extremely fine grained to achieve good signal without distortion and fluctuation extremely fine grained sample are required for the analysis of XRD, and minimize preferred orientation to avoid spottiness. The recommended range of size for sample is around 1 µm to 5µm.
- The interfacial bonding can be improved by removing the cementing substances and impurities which can increase the effective area providing better interlocking and improved properties
- The crystallinity index may vary because of the present impurities and can be removed by treatment of fibres.
- XRD is recommended to observe crystals behaviour, but for detailed investigations digital image processing techniques can be applied because of their advance revealing properties.

On the other side, In the present era present studies and new developments still ongoing, especially for the exploration of geometries, bonding of materials, complex material investigations and their applications. The advancements in the field of the high resolution XRD and energy-dispersive methods are opening new possibilities of investigations.

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