

Crystalline Structure of Starch Based Nano Composites

Farid Amidi Fazli, Afshin Babazadeh, Farnaz Amidi Fazli

Abstract—In contrast with literal meaning of nano, researchers have been achieved mega adventures in this area and every day more nanomaterials are being introduced to the market. After long time application of fossil-based plastics, nowadays accumulation of their waste seems to be a big problem to the environment. On the other hand, mankind has more attention to safety and living environment. Replacing common plastic packaging materials with degradable ones that degrade faster and convert to non-dangerous components like water and carbon dioxide have more attractions; these new materials are based on renewable and inexpensive sources of starch and cellulose. However, the functional properties of them do not suitable for packaging. At this point, nanotechnology has an important role. Utilizing of nanomaterials in polymer structure will improve mechanical and physical properties of them; nanocrystalline cellulose (NCC) has this ability. This work has employed a chemical method to produce NCC and starch bio nanocomposite containing NCC. X-Ray Diffraction technique has characterized the obtained materials. Results showed that applied method is a suitable one as well as applicable one to NCC production.

Keywords—Biofilm, cellulose, nanocomposite, starch.

I. INTRODUCTION

IN recent years synthetic polymers have been commonly used; plastics have been used more and more for many kinds of applications in the food industry due to their inexpensive production as well as profit properties of plastics. Nowadays selling food materials out of plastic covers is rare and sometimes impossible. The main problem with synthetic polymers is their non-degradable properties. A suitable way to overcome this problem is using biodegradable polymers that are degraded easily by natural microorganisms flora existing in the environment. These polymers should ensure functional properties that are needed for food packaging materials. Starch is a cheap and renewable source of biofilm production but needs mechanical and barrier properties improvement. Fillers like nano cellulose could achieve the improvement of starch biofilm.

Nevertheless, the used packaging materials, such as shopping bags, are still easily visible in the environment in many countries. So biodegradable materials offer a possible alternative to the traditional non-biodegradable polymers, especially in short lifetime application and when their recycling is difficult and/or not economical [1]. The term 'biodegradable' materials is used to describe those materials

which can be degraded by the enzymatic action of living organisms such as bacteria, yeasts, fungi and the ultimate end-products of the degradation process, like CO₂, H₂O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions [2].

Among the biomaterials present, today in the market, those derived from renewable resources such as starch-based products are the most widespread and economic biomaterials. Starch is a semi-crystalline polymer stored in granules as a reserve in most plants. It is composed of repeating 1,4-a-D D glucopyranosyl units: amylose and amylopectin. The amylose is almost linear, in which the repeating units are linked by a (1-4) linkages; the amylopectin has a (1-4)-linked backbone and ca. 5% of a (1-6)-linked branches. The relative amounts of amylose and amylopectin depend upon the plant source. Corn starch granules typically contain approximately 70% amylopectin and 30% amylose [3]. The ratio of the two components characterizes materials with very different properties. In the food packaging sector, the starch-based material has received great attention owing to its biodegradability, wide availability and the low cost (less than 1 euro per kg). Several studies are concentrated on the development of starch-based materials, for the reasons mentioned above [4]. Unfortunately, the starch presents some drawbacks, such as the strong hydrophilic behavior (poor moisture barrier) and poorer mechanical properties than the conventional non-biodegradable plastic films used in the food packaging industries.

The recent interest in using stiff nanometric particles as reinforcement materials in polymeric matrixes, composites or nanocomposites, has been increasing. Two good examples of these types of particles are carbon nanotubes and cellulose nanocrystals. Cellulose nanocrystals, also reported in the literature as whiskers, nanofibers, cellulose crystallites or crystals, are the crystalline domains of cellulosic fibers, isolated by means of acid hydrolysis, and are called in this way due to their physical characteristics of stiffness, thickness, and length. [5]

Samir et al. report that cellulose whiskers are regions growing under controlled conditions, which allows individual high-purity crystals to form. Their highly ordered structure may not only impart high resistance, but also make significant changes to some important properties of materials, such as electrical, optical, magnetic, ferromagnetic, and dielectric nature, as well as concerning conductivity [6].

The cellulose polymer constituting the whiskers is formed by units of glucose containing three free hydroxyl groups bonded to carbons 2, 3, and 6, which are responsible for the

Farid Amidi is with the Department of Food Science and Technology Soofian branch, Islamic Azad University, Soofian, Iran (phone: +98-411-3859676; fax: +98-472-3343556; Ext. 6; e-mail: amidi_f@yahoo.com).

Afshin Babazadeh is a M.Sc. student of Food Science and Technology, Tabriz University, Iran.

intermolecular interactions, which successive structures are formed from, giving rise to the cell wall of the fiber: micelles, chain grouping into bundles; microfibrils, micelle aggregates; and fibrils, microfibrils aggregates that can be also called microfibrils. Therefore, the microfibrils composing the fibers, resulting from the cellulose molecule arrangement, are constituted by crystalline, highly ordered; and amorphous, disordered regions [7].

II. MATERIALS AND METHODS

There are different techniques to produce nanocrystalline cellulose; these methods have been reviewed by [8]. In this work chemical method has been employed. After cutting cotton linter to small piece about 2 cm to eliminate impurities cotton linter treated with soda then acid treatment took place by H₂SO₄ (65% w/w) for 3 hours then neutralization step took place by 10% (w/w) sodium hydroxide solution. The final pH of the suspension was adjusted about 6.5. Suspension

drained by deionized water for 1 hour. The washing water was being replaced every 15 minutes. Finally, Nanocrystalline Cellulose was obtained by ultrasonic treatment at 40 KHz for 15 minutes.

Various techniques can be used in the production of nanocomposites. Applied method will be varied, depending on the initial materials, facilities, and expected functional properties of the polymer. The casting method was used in this study. To produce starch nanocomposite, 5% starch suspension in water was prepared for this purpose 5 g of starch was solved in 100 ml cold distilled water.

Glycerol is a conventional plasticizer in the starch-based film production [9]. Mechanical properties of starch films by adding glycerol will be improved. However, the inhibitory properties of starch films may weaken [10]. The applied amount of glycerol as a plasticizer was 0.8 g/g, which was added to the starch suspension. For gelatinization, the suspension was heated at 90 °C for 60 min in a water bath.

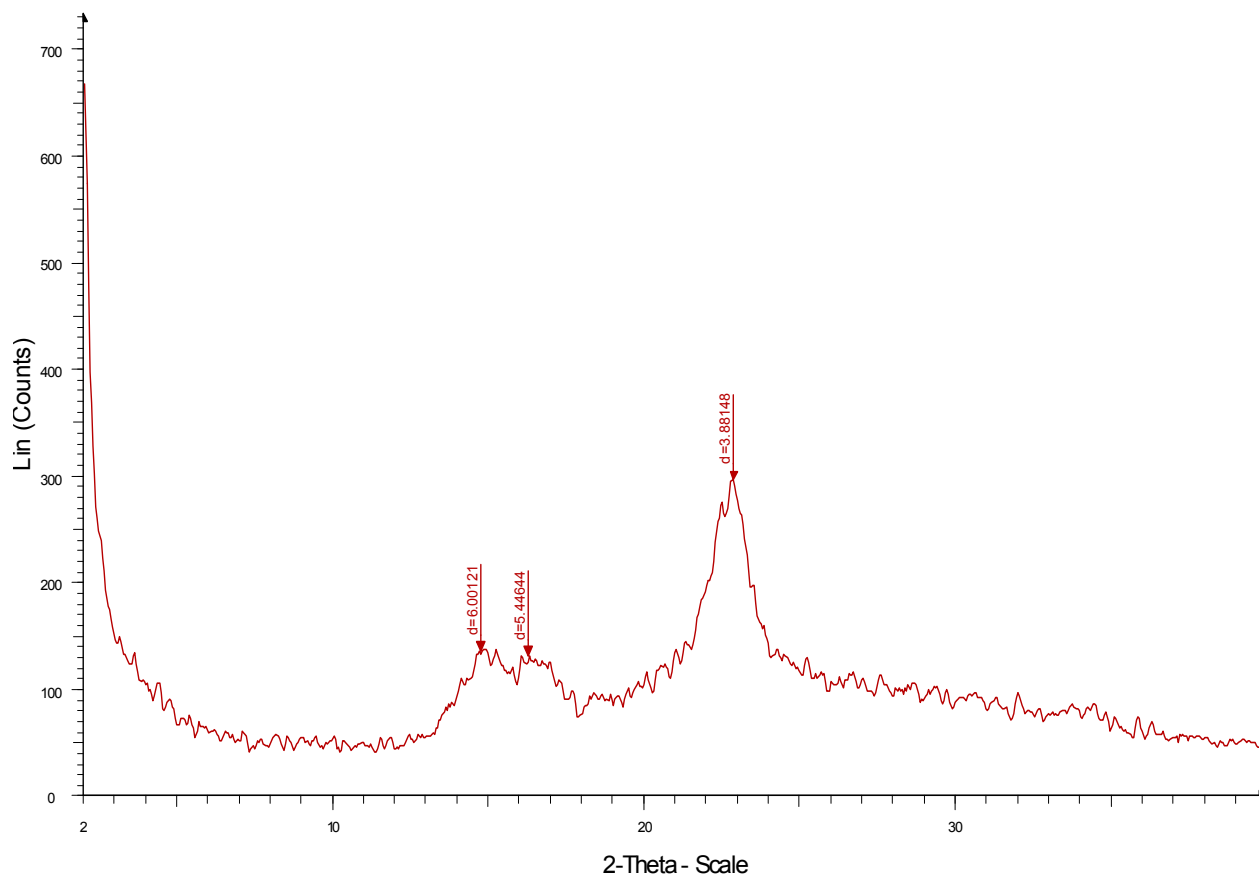


Fig. 1 X-Ray diagram for obtained nanocrystalline cellulose

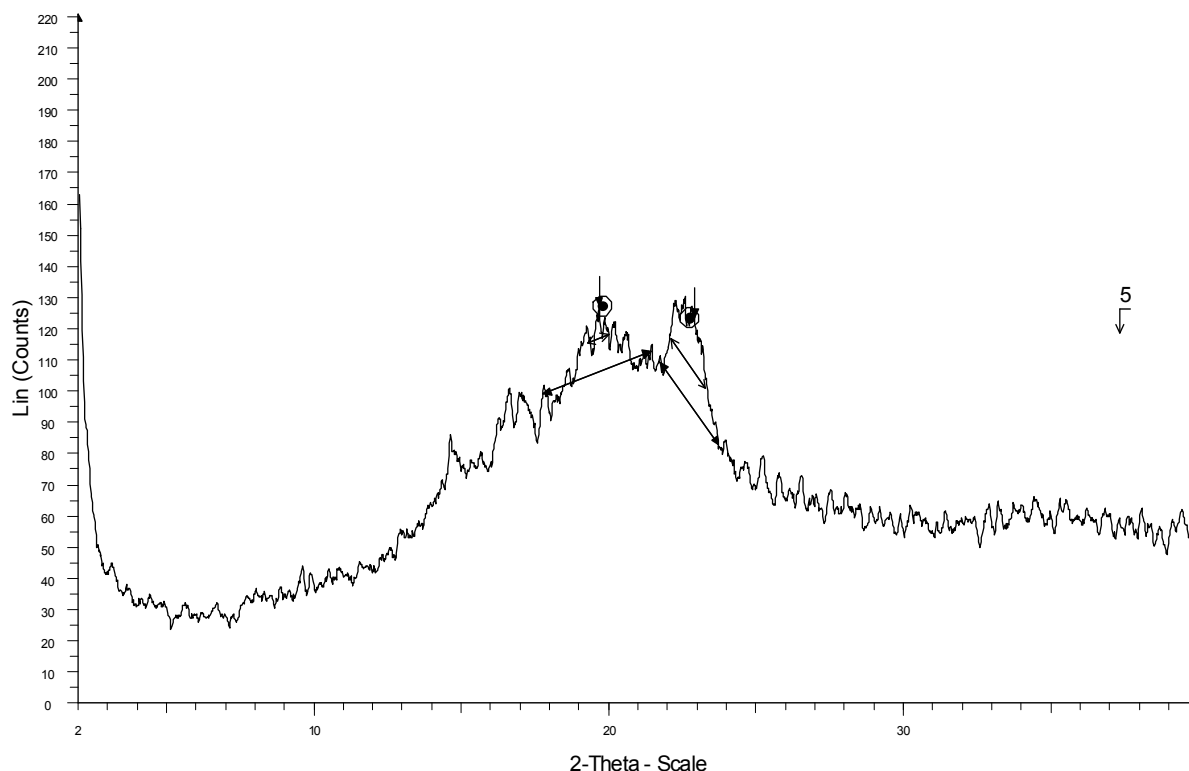


Fig. 2 X-Ray diagram for obtained starch nanocomposite containing NCC

To study of nanocrystalline cellulose effects on the properties of starch films, nanocrystalline cellulose solution was homogenized by ultrasound and was added to gelatinized starch. The used NCC was 8% (w/w) of the starch weight. To obtain homogeneous solution the obtained mixture was stirred at 70 °C for 15 min. then the mixture has cooled, and gently spread over the polystyrene surface. Finally, extra water of film was evaporated by drying in an oven at a temperature of 55 °C for 16 hours. The obtained biofilm removed from the surface of polystyrene.

X-Ray Diffraction (XRD) was applied to determine production of nanocrystalline cellulose. Scanning took place at $2\theta = 2-40$ by 0.05° step and step time was 1 second. The experiment was done at 25° degrees of siliceous.

III. RESULTS AND DISCUSSION

Regarding diagram obtained through X-Ray Diffraction analysis (Fig. 1) it was confirmed that nanocrystalline cellulose has been obtained during mentioned process above. As there were three peaks in 14.7 , 16.5 and 23.2° . It seems that nanotechnology has the potential to change and improve the food packaging industry through designing new applications of cellulose with different properties. It is known that cellulose is the most abundant, natural, renewable and biodegradable polymer that occurs as a nanostructure in plants, giving resistance. The most important aspects of this material are its bioavailability [11].

Fig. 2 shows X-ray diffraction results of the starch biofilm.

Three peaks were observed in Fig 2. Showing that crystalline structure of nanocrystalline cellulose is maintained.

Engineering fiber and design of lignocelluloses or rod-like cellulose nanoparticles and microfibrils to get high value-added products with special performance can reach new markets through nanotechnology [12], [13]. According with Lima and Borsali charged rod-shaped cellulose whiskers are a good model for understanding the rod-particles behavior with polyelectrolytic properties. Mechanical behavior was pointed out as an important feature of the cellulose whiskers as fillers for reinforcements in different polymer matrices; this reinforcing effect is mainly because of the percolation effect [14].

A recent review showed that nanocrystalline cellulose exhibited intriguing scientific and engineering discoveries and advancements. However, the authors pointed out that, the field is still in its infancy and open to opportunities for new advancements and discoveries [15]. Other authors showed that cellulose nanocrystals are attractive material to incorporate into composites because they can introduce additional strength gains with highly versatile chemical functionality [16].

REFERENCES

- [1] Maurizio Avella, Jan J. De Vlieger, Maria Emanuela Errico, Sabine Fischer, Paolo Vacca, Maria Grazia Volpe. Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*, 2005, 93: 467–474.
- [2] Doi, Y. & Fukuda, K. (Eds.). *Biodegradable plastics and polymers*. Amsterdam: Elsevier.1994, pp. 479–497.

- [3] Lambert, J. F., & Poncelet, G. Acidity in pillared clays: origin and catalytic manifestations. *Topics in Catalysis*, 4: 43–56.
- [4] Pelissero, A. (Ed.). *Le materie plastiche e ambiente*. Bologna: AIM 1990, pp. 129–138.
- [5] Souza Lima, M.M., Borsali, R. Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromol. Rapid Commun.* 2004, 25: 771-787.
- [6] Samir, M.A.S.A., Alloin, F., Dufresne, A. Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacromolecules*. 2005, 6: 612-626.
- [7] Deusanilde de Jesus Silva, Maria Luiza Otero D'Almeida. Cellulose whiskers. *O PAPEL*, 2009, 70 (07): 34 - 52
- [8] Nelson durán, ana p. Lemes, marcela durán, juanita freer, jaime baeza. A minireview of cellulose nanocrystals and its potential integration as co-product in bioethanol production. *J. Chil. Chem. Soc.* 2011, 56, 2.
- [9] Myllarinen, P., R. Partanen, J. Seppala and P. Forssell. 2002. Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymer*, 50, 4: 355–361.
- [10] Garcí'a, M.A., M.N Martino and N.E. Zaritzky. 2000. Microstructural characterization of plasticized starch-based films. *Starch-Starke*, 52, 4: 118–124.
- [11] M. Postek, E. Brown, Proc. SPIE 10.1117/2.1200903.1474 2009.
- [12] W. Hamad, Can. *J. Chem. Eng.* 2006, 84: 513.
- [13] D.G. Gray, In *Towards Understanding Wood, Fibre, and Paper-deeper knowledge through modern analytical tools*. Final seminar of COST Action E41 & Workshop of Action E50 2008.
- [14] M.M.S. Lima, R. Borsali, *Macromol. Rapid Commun.* 2004. 25: 771.
- [15] Y. Habibi, L.A. Lucia, O.J. Rojas, *Chem. Rev.* 2010, 110: 3479.
- [16] X. Cao, Y. Habibi, W.L. E. Magalhães, O.J. Rojas, L.A. Lucia, *Curr. Sci.* 2011, 100: 1172.