

# Birefringences of bio-based liquid crystals

Sherif S. Z. Hindi

Department of Arid Land Agriculture, Faculty of Meteorology, Environment and Arid Land Agriculture, King  
Abdullaziz University, Jeddah, Saudi Arabia

**ABSTRACT:** Birefringence is an optical property of a material having two or three refractive indices and depends on the polarization and propagation direction of light. The material bearing this property is called as birefringent or trirefringent. The birefringence is usually obtained using anisotropic crystals but it can be induced artificially for optically isotropic materials by stress, chemical regeneration, dissolving, electric or magnetic inductions and, finally, by re-alignment and spreading some materials into thin films of amphiphilic molecules. Birefringence can be determined by measuring the changes in the polarization of light passing through the material inserted under crossed polarizers. The best characterized birefringent materials are liquid crystals (LCs) such as nano- and microcrystalline cellulose. Other birefringents such as cellulose, cellulose xanthate, cellulose triacetate, starch and collagen are reported. The LCs material is an intermediate state between liquid and solid can be classified as thermotropic and lyotropic crystals. Nematic and smectic phases are the most common sub-phases of the LCs. The arrangement of molecules in the LCs phases can be used to differentiate nematic, cholesteric and smectic phases. The LCs are essential for liquid crystal displays (LCD), liquid crystal thermometers and optical imaging.

**KEYWORDS:** Birefringence; Nematic phase, Cholesteric phase; Liquid crystals.

## I. INTRODUCTION

### Birefringence definition

When polarized light travels inside a material having two or different indices of refraction, it is splitted into two components (ordinary and extraordinary beams) differed in their speed and refracting angles. This phenomenon is termed as birefringence (double refraction) which is dependent on polarization and propagation direction of light. The material bearing this property is called as birefringent or trirefringent. Crystals possessing birefringence are either uniaxial (hexagonal, tetragonal, and trigonal crystal) or biaxial (orthorhombic, monoclinic, triclinic that have three indices of refraction and known as trirefringent). The birefringence is defined simply as the difference between the maximum and minimum refractive index values. Rutile is highly birefringent materials with a birefringence value of 0.287, while quartz has a low birefringence value of 0.009 [1].

The refractive index ( $n$ ) is defined as the velocity of the light in a crystal divided into the (higher) velocity of light in vacuum. The crystal shown in Figure 1 has two refractive indices. The 1st index has higher value corresponding to slow propagation of light polarized in the direction in which charge can move. On the other hand, the 2nd index has lower value for light polarized perpendicular to the former index [1].

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

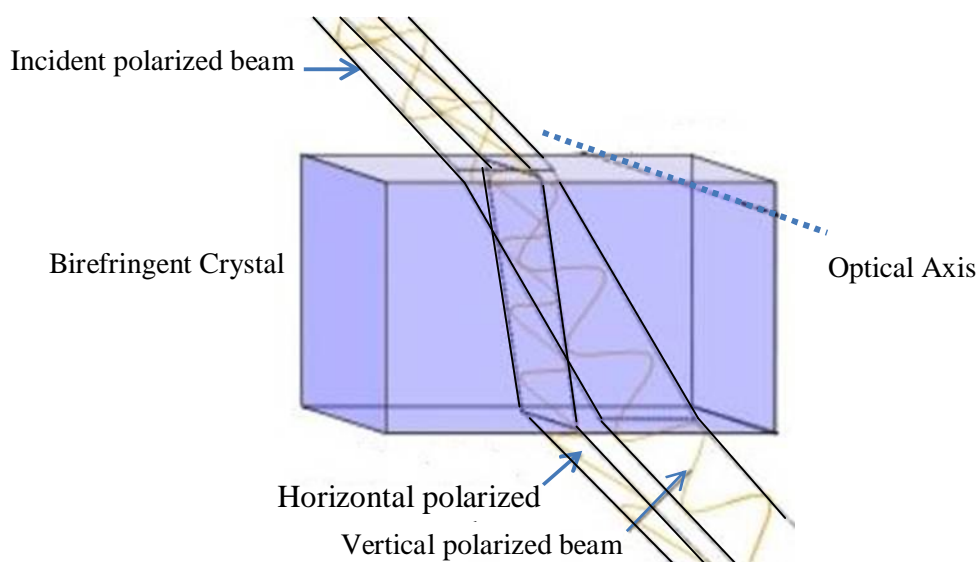


Figure 1. Birefringence arisen due to refraction of polarized light by two optical axis.

Materials can be classified into two divisions, namely isotropic and anisotropic ones. The isotropy property is the uniformity in all orientations (direction-independent), while properties of anisotropic materials vary according to direction. An isotropic material is always homogeneous but the converse is not true. The optically anisotropic materials are termed to be birefringent or birefractive.

## II. SOURCES OF OPTICAL BIREFRINGENCE

Although birefringence is usually obtained using anisotropic crystals, it can be resulted by inducing optically isotropic materials by one of the following methods:

- The stress method: when isotropic materials are stressed, bent or generally deformed until the isotropy is disappeared in one direction, artificial birefringence is induced and is termed as stress birefringence that similar to that occurred for glass studied by de Groot *et al.* [2].
- Chemical regeneration method: modifying chemical structure of a material by addition or substitution reactions, whereby the material has more than one chemical group with differing refractive indices producing intrinsic birefringence [3].
- Dissolving method: since rods or spheres having one refractive index, some materials give form birefringence when are suspended in a media having another refractive index.
- Electric induction (the Kerr effect): applying electric field induces birefringence at optical frequencies through the effect of nonlinear optics [4].
- Magnetic induction (Faraday effect): magnetic field can cause circularly birefringence for some materials until the field is removed [5].
- Re-alignment and spreading some materials into thin films of amphiphilic molecules such as lipids, some surfactants or liquid crystals.

## International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017



Figure 2. Birefringence of a typical liquid crystal.

Since each of director orientation (Figure 5), birefringence, and length are not constant over the entire nematic liquid crystal, some areas appear light and others appear dark due to, taken between crossed polarizers (Figure 2).

It was reported by Horer[6], that three types of birefringence can be arisen due to three different rotational techniques of molecules in solutions, namely flow, electric and magnetic birefringences. The flow type is used to study different biopolymers, while the electric one is used to study the secondary structure of DNA. Furthermore, the magnetic birefringence is used to investigate nucleic acids.

### Measuring the Birefringence

Birefringence and other polarization based optical effects (such as optical rotation as well as linear or circular dichroism) can be determined by measuring the changes in the polarization of light passing through the material inserted under crossed polarizers. Polarized light microscopes, which contain two polarizers that are perpendicular to each other on either side of the sample, are used to visualize birefringence. The addition of quarter wave plates permit examination of circularly polarized light. Birefringence measurements have been made with phase-modulated systems for examining the transient flow behavior of fluids [7; 8].

### Common Birefringent Biomaterials

The best-characterized birefringent materials are crystals. Due to their specific crystalline structures, their refractive indices are well defined. There are many bio-based crystalline and LCs materials can be obtained and were reported extensively for their important industrial applications.

### Cellulose

Crystalline cellulose consists of highly ordered crystallites termed as fringed micelles beside less-ordered domains [9]. Cotton fiber is a birefringent because of its high content of  $\alpha$ -cellulose found in the secondary cell wall. The birefringence of the cellulosic fibers can be recognized by the pseudo color in an image[10]. It was indicated that its birefringence is retained up to 310 °C without any noticeable change indicating that cellulose remains crystalline up to this high temperature [10]. In addition, cellulose becomes less birefringent at around 320 °C, and the birefringence is completely lost at 330 °C. The image becomes brighter as cellulose loses birefringence. The relative brightness stays constant below 310 °C, but increases in the narrow temperature range (310–325 °C), and becomes constant again above 325 °C [10]. The fiber gradually loses birefringence as it is heated, but no significant change is seen in the shape of the fiber. The fiber starts to deform when it almost completely loses

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

birefringence and deforms further at higher temperatures. The large deformation suggests that cellulose becomes plastic upon transformation and the mechanical properties as well as twisting and bending change dramatically upon this transformation.

It is well known that water can only interact with the less ordered domains at ambient conditions [11] but Deguchiet *al.* [10] found clearly that water also interacts with highly ordered domains at high temperatures under pressure leading to crystalline-to-amorphous transformation. It was concluded that water is necessary to induce the transformation because no such transformation is observed in ethanol at 7 MPa and at temperatures up to 350 °C [10].

## Cellulose Xanthate

Several polymers are birefringent due to their molecules are frozen in a stretched conformation upon molding or extrusion [12]. In addition, the bio-based cellophane (cellulose xanthate) is birefringent. From Birefringence measurements of cellophane sheets in the three orthogonal directions, Krishna Iyer[13] indicated that the glucose rings in the amorphous regions align themselves parallel to the film surface if the crystallites are oriented with the '101' plane parallel to the film surface.

## Cellulose Triacetate

Hayakawa and Ueda [14] examined the intrinsic birefringence of a cellulose triacetate (CTA) film using the polarizability of the monomer model using the density functional theory. Since the CTA monomer has three rotational isomers (conformations), namely gg, gt, and tg, the intrinsic birefringence of each isomer was evaluated separately. The CTA with gg and gt structures shows a negative intrinsic birefringence, while the tg structure shows a positive one [14].

## Starch

Starch is a semi-crystalline material having alternating crystalline and amorphous regions [15; 16; 17]. The crystalline regions are predominantly made up of amylopectin while the amorphous regions are constituted of amylose and amylopectin [18]. Starch is insoluble in cold water, while under heating, its amorphous regions absorb water and the crystalline structure is melt leading birefringence to be lost at a certain temperature [19; 20; 21]. This temperature is referred to as gelatinization temperature that is dependent partially on the botanical source of starch [15]. Upon continuous heating, molecular motion is increased leading amylose and amylopectin to be completely separated [22; 23].

The gelatinization of starch can be determined by measuring the birefringence end point, viscosity changes, X-ray diffraction, amylose-iodine binding (blue value), enzymatic digestibility, NMR, light extinction, solubility or sedimentation of swollen granules, and absorption of Congo red [24].

## III. BIREFRINGENCE OF OTHER BIOMATERIALS

### Collagen

Collagen is found in cartilage, tendon, bone, corneas, and many areas in the body. It is birefringent and commonly studied with polarized light microscopy [25]. Some proteins and nucleic acids are also birefringent exhibiting form birefringence [26].

### Liquid Crystals (LCs)

The LCs material is an intermediate state (mesophase) between liquid and solid (Figure 3). The liquid state has the ability to flow, while the solid one has an ordered crystalline structure. Regarding to position and molecular orientation, solid crystals can exhibit short and long-range, while liquids and LCs may show short-range order regarding to position and/or orientation. In addition, positional long-range order disappears for liquid crystals [27]. The most important structural features of LCs molecules can be concluded as reported by Andrienko[28] as follow:

1. The molecules have anisotropic shape (elongated). The LCs features can be arisen when the molecules have flat segments like benzene rings.
2. The LC's backbone is fairly rigid when it contains double bonds along the molecule axis.

3. The existence of strong dipolar groups in the molecule.
4. The groups attached to the extremities of the molecules are generally of lesser importance.

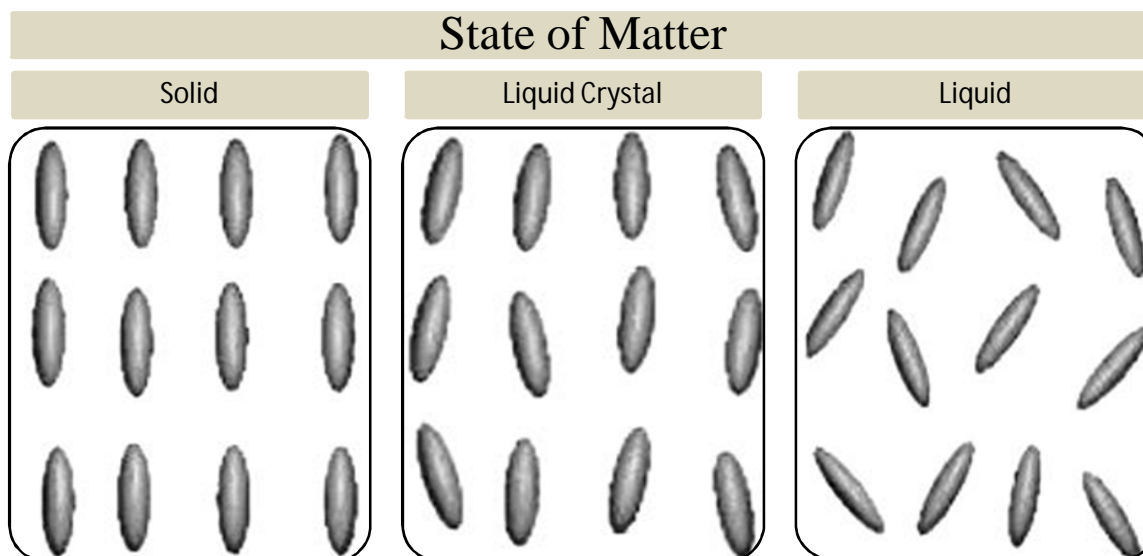


Figure 1Figure 3. Main molecular alignment of the three states of matter.

LCs can show different molecular arrangements than do liquid and solid states. The LCs can be classified as thermotropic and lyotropic crystals. Furthermore, nematic and smectic phases are the most common sub-phases of LCs (Figure 4).

Thermotropic liquid crystals (TLCs) contain large number of organic compounds with anisotropic molecular shapes. The TLCs can be obtained by melting a crystalline solid [28] and lowering temperature of liquid. For the TLC state, too higher temperatures will enhance molecular motion and destroy their crystalline order converting material into isotropic liquid phase [29].

Based on molecular shape of TLCs, they are divided into calamitic (rod like) and discotic (dislike) molecules (Figure 4). Furthermore, calamitic TLCs type are additionally subdivided into nematic and smectic types. The simplest liquid crystals phase is called nematic and is close to liquid phase. The molecules float around as in liquid phase, but are still ordered in their orientation. The nematic phase is seen as the marbled structure. Columnar liquid crystals have a unique construction because they are disclike shaped. Smectic liquid crystals have layered arrangement of orientally-ordered rod-like molecules. The columns are packed together horizontally to form two-dimensional crystalline array [29].

The arrangement of molecules in liquid crystal phases can be used to differentiate nematic, cholesteric and smectic phases. In both nematic and cholesteric phases, the molecules tend to have the same alignment but the molecular positions of nematic phase are not correlated. In addition, for cholesteric phase, the molecular alignment varies regularly through the medium with a periodicity distance (pitch) equals  $p/2$ . Furthermore, in the smectic phase, the molecules tend to lie in the planes with no configurational order within the planes and to be oriented perpendicular to the planes [28].

The cholesteric pitch (Figure 5) may reach about several hundreds nanometers that is comparable to the wavelength of visible light. The spiral arrangement of this phase is responsible for the featured colors in reflection (through Bragg reflection by the periodic structure) and their very large rotatory power. The cholesteric pitch can be quite sensitive to temperature, flow, chemical constitution, and stress-inducing agents applied such as magnetic or electric field [28].

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

Lytotropic liquid crystals (LLCs) are subdivided into two sub-categories, namely lamellar and hexagonal types (Figure 4). The LLCs are formed in solutions rather than in pure substances. Their individual molecules do not align by themselves to create anisotropy but the molecules come together to form anisotropic aggregates which align themselves along the director. Temperature and concentration of substance affects the LLCs behavior. Lyotropic crystals are formed by the amphiphilic molecules termed as surfactants [29]. For more illustration, lyotropic liquid crystals occur as a result of solvent-induced aggregation of constituent mesogens into micellar structure [30].

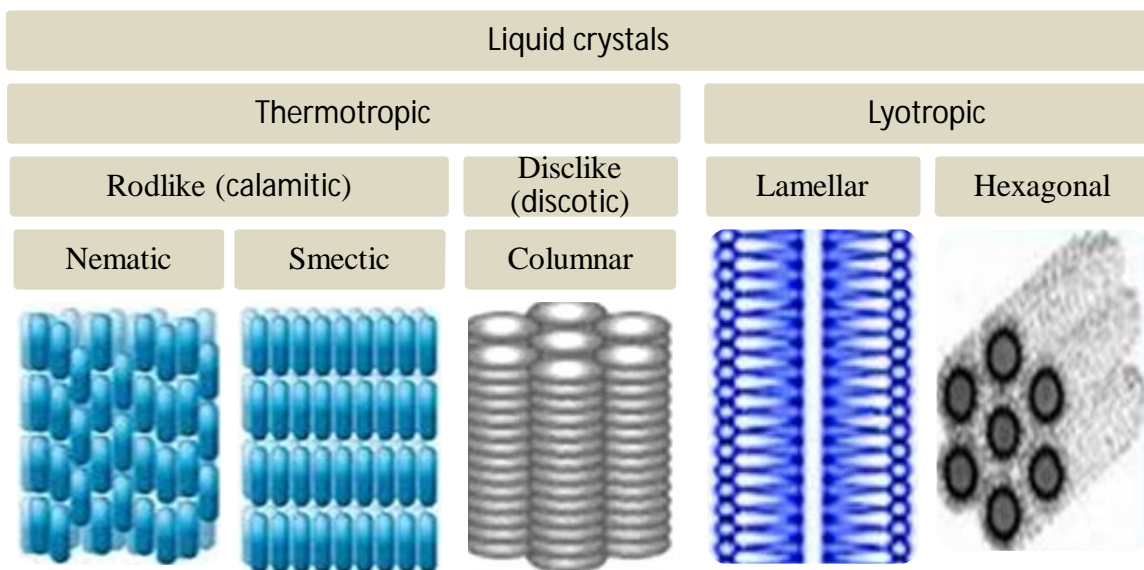


Figure 4. The different molecular arrangements of liquid crystals.

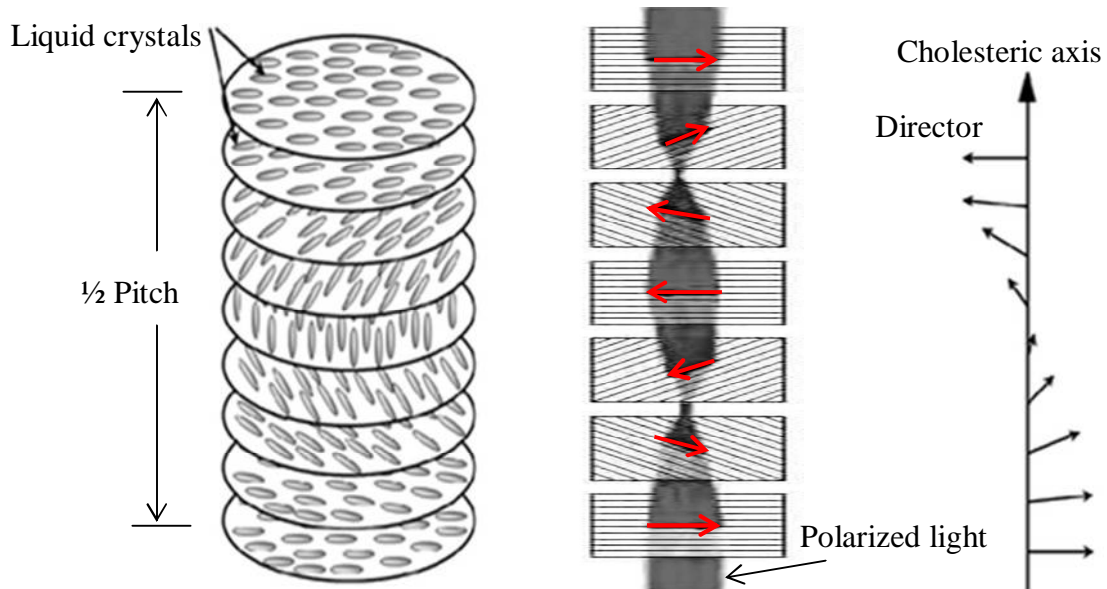


Figure 5. A schematic representative of cholesteric

# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 1, January 2017

## Practical application of birefringence and liquid crystals (LCs)

Polarized light microscopy is commonly used in biological tissue, medical diagnostics as well as to detect stress in plastics such as polystyrene and polycarbonate. In addition, the LCs materials are essential for liquid crystal displays (LCD), liquid crystal thermometers and optical Imaging [29]. In addition, the LCs are used for nondestructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. Furthermore, low molar mass (LMM) liquid crystals are used for erasable optical disks, full color-electronic slides for computer-aided drawing (CAD) and light modulators for color electronic imaging.

## REFERENCES

- [1] Amos, B., "Birefringence for faceters I: what is birefringence?" First published in StoneChat, the Journal of the UK Facet Cutter's Guild. January-March. Edition 2005.
- [2] de Groot, P., Dergevorkian, A. and Erickson, T., "Interferometric analysis of stress-induced birefringence in a rotating glass disk, Part of the SPIE Conference on Laser Interferometry IX: Techniques and Analysis. San Diego, California, Vol. 3478, 227-233, 1998..
- [3] Habibi, Y., Lucia, L. A. and Rojas, O. J., "Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications", Chemical Reviews, Vol.110, 3479-3500, 2010.
- [4] Jellison, G. E., "Electric field-induced birefringence measurements in nuclear detector materials using transmission two-modulator generalized ellipsometry (2-MGE)". Nuclear Science Symposium Conference Record, 2003 IEEE, Vol. 5, 3564- 3568, 2005.
- [5] Rice, S. A., "Advances in chemical physics", John Wiley & Sons, New Jersey, USA, VOL. 129, 2004.
- [6] Hörer, O. L., "The Structure of Biopolymers", Abacus Press, Tunbridge Wells, Kent, England, 293 pp, 1973.
- [7] Fratini, P. and Fuller, G., "A note on phase-modulated flow birefringence: a promising rheo-optical method", Journal of Rheology, Vol. 28 (1), 61, 1984. DOI: 10.1122/1.549768
- [8] Doyle, P., Shaqfeh, E. S. G., Spiegelberg, S. H. and McKinley, G. H., "Relaxation of dilute polymer solutions following extensional flow", Journal of Non-Newtonian Fluid Mechanics, Vol. 86, 79-110, 1998.
- [9] Klemm, D., Heublein, B., Fink, H.-P. and Bohn, A. "Cellulose: Fascinating biopolymer and sustainable raw material". Angewandte Chemie International Edition, Vol. 44 (22), 3358-3393, 2005.
- [10] Deguchi, S., Tsujii, K. and Horikoshi, K., "Cooking cellulose in hot and compressed water", Chemical Communications, Vol. 2006, 3293-3295, 2006. DOI: 10.1039/B605812D.
- [11] Zeronian, S. H., "In Cellulose chemistry and its applications", eds. T. P. Nevell and S. H. Zeronian, Ellis Horwood, Chichester, pp. 139-158, 1985.
- [12] Neves, N. M., Pouzada, A. S., Voerman, J. H. D. and Powell, P. C., "The use of birefringence for predicting the stiffness of injection molded polycarbonate discs", Polymer Engineering and Science, Vol. 38 (10), 1770-1777, 1998.
- [13] Krishna Iyer, K. R., Sreenivasan, S. and Patil, N. B., "Birefringence of stretched cellulose films". Textile Research Journal, Vol. 53 (7), 442-444, 1983. doi: 10.1177/004051758305300709.
- [14] Hayakawa, D. and Ueda, K., "Computational study to evaluate the birefringence of uniaxially oriented film of cellulose triacetate". Carbohydrate Research. Vol. 30 (402), 146-51, 2015. doi: 10.1016/j.carres.2014.10.021.
- [15] Lineback, D. R., "Current concepts of starch structure and its impact on properties", Journal of the Japanese Society of Starch Science, Vol. 33: 80-88, 1986.
- [16] Waigh, T. A.; Hopkinson, I.; Donald, A. M. "Analysis of the native structure of starch granules with X-ray microfocus diffraction". Macromolecules, Vol. 30: 3813-3820, 1997.
- [17] Wang, T. L.; Bogracheva, T. Y.; Hedley, C. L., "Starch: As simple as A, B, C?", Journal of Experimental Botany, Vol. 49: 481-502, 1998.
- [18] Donald, A. M., "Plasticization and self-assembly in the starch granule". Cereal Chemistry, Vol. 78, 307-314, 2001.
- [19] Donovan, J. W., "Phase transitions of starch water system". Biopolymers, Vol. 18, 263-275, 1979.
- [20] Biliaderis, C. G., "Thermal analysis of food carbohydrates". In Thermal analysis of foods; Harwalkar, V. R., Ma, C.-Y., Eds.; Elsevier Applied Sciences: London; pp. 169-220, 1990.
- [21] Parker, R.; Ring, S. G., "Aspects of the physical chemistry of starch", Journal of Cereal Science, 34: 1-17, 2001.
- [22] Keetals, C. J. A. M., van Vliet, T. and Walstra, P., "Gelation and retrogradation of concentrated starch systems: 3. Effect of concentration and heating temperature", Food Hydrocolloids, Vol. 10, 363-368, 1996.
- [23] Levin, H. and Slade, L., "Influence of glassy and rubbery state of thermal, mechanical, and structural properties of doughs and baked products. In Dough rheology and baked product texture, theory and practice; Faridi, H., Faubion, H., Eds.; Van Nostrand Reinhold AVI: New York; pp. 157-330, 1990.
- [24] Lund, D., "Influence of time, temperature, moisture, ingredients, and processing conditions on starch gelatinization", Critical Reviews in Food Science and Nutrition. Vol. 20, 249-273, 1984.
- [25] Wolman, M. and Kasten, F.H., "Polarized light microscopy in the study of the molecular structure of collagen and reticulin". Histochemistry, Vol. 85, 41-49, 1986.
- [26] Sano, Y. 1988. Optical anisotropy of bovine serum albumin. Journal of Colloid and Interface Science, Vol. 124, 403-407, 1988.
- [27] Mueller-Goymann, C. C., "Drug delivery: Liquid crystals in", Encyclopedia of Pharmaceutical Technology, 2013, Chapter 75, 3<sup>rd</sup>, October 2006.
- [28] Andrienko, D., "Introduction to liquid crystals", International Max Planck Research School Modelling of soft matter, 11-15 September, Bad Marienberg: 27-29, 2006.
- [29] Gaikwad, P. P. and Desai, M. T., "Liquid Crystalline Phase & its Pharma Applications", International Journal of Pharma Research and Review, Vol. 2 (12), 40-52, 2013.
- [30] Maiti, S., "Liquid-crystal and Nano-crystal Technology for Solubilization of Poorly Water Soluble Drugs", Journal of Pharma Sci Tech, Vol. 2 (1), 1-4, 2012.