University of Alberta

An investigation on interaction between nano crystalline cellulose and water-soluble polymers in aqueous solutions

by

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To my lovely family for always being there to love,

inspire, and support me.

Abstract

In this research, the phase behavior of rod like nano crystalline cellulose (NCC) suspensions has been investigated. NCC suspensions with concentration at 1-4wt.% exhibited isotropic behavior, a mixture of isotropic-nematic behavior at 4 - 6wt.%, and nematic phase behavior at 7- 10wt.%. Then, both phase and rheological behaviors of NCC suspensions were investigated in the presence of polymers such as hydroxyethyl cellulose (HEC), dextran, and carboxymethyl cellulose (CMC) solutions. HEC revealed noticeable impact on phase behavior and induced depletion interaction in NCC-HEC mixtures. Dextran, because of its branched structure did not show thickening behavior in NCC-dextran mixtures. Light polarization and rheological tests showed that CMC can also induce depletion interaction in NCC-CMC mixtures. The effect of ionic strength was also studied by adding NaCl in CMC solutions. Increasing NaCl concentration caused considerable variation in rheological behavior of the samples and they turned into gel-like samples at high NaCl concentrations.

Acknowledgments

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Finally, I thank my beloved family and friends for their love and kindness.

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Chapter 1 Introduction

1.1 Overview

Recently, in our world, nanotechnology has been emphasized for special focus by many governments and using nanomaterials has shown a way to develop innovations in the field of science and engineering. For example, carbon-based nanomaterials and their functional derivatives are implemented in various applications such as to optimize drugs transportations through dense tissues. Also, functionalized nanotubes are utilized as synthetic transmembrane pores. Parallel environmental applications involve targeted delivery of remediation agents, novel membrane structures for water filtration, and engineered removal of hazardous pollutants [1].

A new class of nano materials that are derived from cellulose fibers is known as nano crystalline cellulose (NCC). This novel nano material can be obtained in the form of rod shape particles. The major process for obtaining NCC from cellulose fibers is based on acid hydrolysis. Disordered regions of cellulose are preferentially hydrolyzed and amorphous regions break up; however, crystalline regions with higher resistance to acid attack remain intact [2,3]. Hence, after an acid treatment in which cellulose is hydrolyzed, NCC rod-like particles will be obtained. In comparison to cellulose, NCC has remarkable physicochemical properties such as nano scale dimension, high specific strength and modulus, high surface area and unique optical properties [2]. In addition, this novel nano material in the presence of polymers shows interesting alteration in phase and rheological behavior; these changes depend on parameters such as the polymer type and aspect ratio of NCC. Therefore, NCC and its interaction with polymers can be tailored to develop new smart nano materials to utilize in applications such as drug delivery, new membrane structures for water and wastewater treatment, and reinforcement of polymeric matrix in nanocomposite materials [2,3].

So, this work focused on NCC phase behavior and its critical concentration range as well as change in phase behavior in the presence of water-soluble polymers in aqueous systems.

1.2 Thesis objectives

In this project, at the first step, I investigated NCC suspensions to find the critical concentration for NCC suspensions through testing a wide range of concentrations and phase behavior in this range. At the second step, three polymers were added separately to the system as macromolecules in order to indicate the effect of adding polymer and the possible interactions between polymer chains and NCC rod shape particles on the rheological behavior as well as phase behavior of the mixture. So, it has been shown that based on the polymer type (neutral or negatively charged), polymer concentration, and the electrolyte added to the system the phase and rheological behavior of the final sample could change differently.

In the second chapter, a literature review is presented. Chapter 3 describes materials and methods which have been utilized to conduct this project. In

Chapter 4, the main results and discussion are stated and finally in Chapter 5, conclusions will be given based on the results obtained in this work.

Chapter 2 Literature Review

2.1 Cellulose

Based on literature, cellulose is the most ample natural renewable polymer resource. Being biodegradable and non-toxic can be also considered as some other important properties of cellulose. Cellulose can be obtained from different sources such as wood, cotton and other plant fibres; however, wood pulp is the most common source for cellulose processing. The molecular structure of cellulose is shown in Figure 2.1. As it can be seen, cellulose is a carbohydrate polymer made up of repeating β-D glucopyranose units including three hydroxyl groups per anhydroglucose unit (AGU) and that is where the cellulose gets its high degree of functionality from [3].

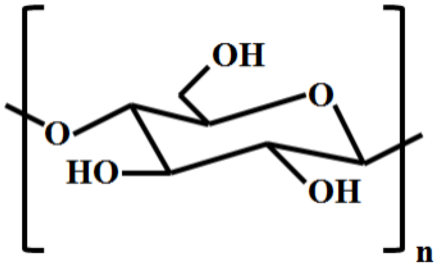

Figure 2.1 Molecular structure of cellulose [4]

Depending on the source and treatment type, degree of polymerization (DP) (number of monomeric units in the cellulose molecule) of cellulose can change. For example, when cellulose is obtained from wood, DP of wood pulp is around 300-1700 and when cellulose is taken from cotton, DP is around 800-10000 [2,4,5].

In order to explain the characteristic properties of cellulose including biodegradability, chirality, hydrophilicity, and also high functionality, obtaining knowledge of cellulose molecular structure is the most prominent challenge. For instance, by having investigation on the structure of cellulose, it can be found that the hydroxyl groups of cellulose introduce partially crystalline (high order) regions interspersed with amorphous regions (low order). This is because hydroxyl groups can create an extensive network of intermolecular hydrogen bonds along the cellulosic chains [2,3,4]. The morphology of cellulose can be described by three distinct fibre structures including elementary fibrils, microfibrils, and microfibrillar bands. For these three distinct fibre structures the length are of the order of a few hundred nanometres and the diameters are in the range of 1.5-3.5 nm for elementary fibrils, 10-30 nm for microfibrils, and around 100 nm for microfibrillar [4].

Cellulose also exhibits different properties in the solution state depending upon the degree of substitution (DS) (average number of substituted hydroxyl groups per glucose), concentration, solvent type and chain length distribution. It is widely known that as a chemical raw material, cellulose has been used in the form of fibers or derivatives for vast range of products and materials in our daily life for almost 150 years [3]. Therefore, considerable amount of investigations have been carried out on different properties of cellulose and its derivatives such as chemical, mechanical and biological properties to get the benefits of these materials in wide area of application such as food, paper production, biomaterials and pharmaceuticals [2,3].

2.2Nano Crystalline Cellulose (NCC)

By acid hydrolysis of cellulose fibres, a new class of nano-materials can be obtained which is called nano crystalline cellulose (NCC). As a result of this acid hydrolysis, the new released material (NCC) has got many advantages in comparison to cellulose fibers. Some of these amazing properties are nanoscale dimension, high specific strength and modulus, high surface area, higher crystallinity, and unique optical properties. NCC is also renewable, strong, lightweight, and low-cost nanomaterial that has been incorporated into renewable polymer matrices for sustainable, environmentally friendly nano-composites [2,3]. In addition, it can be assembled into optically active films which have the ability of reflecting specific wavelengths of light selectively. The optical properties of these NCC assembled films can be adjusted by controlling the cholesteric pitch which can be affected by dispersion composition, temperature, and shear [5,6]. Because of these prominent physicochemical properties, NCC has been of a great interest to many researchers. In particular, Peng and coworkers have done extensive work on NCC in terms of understanding of NCC chemistry and applications [3].

Habibi et al. have published a recent review on NCC (2010); they discussed about the optical and mechanical properties of NCC with respect to chemical structure, composition and their relationship to these properties [2]. As they reported the biopolymeric assemblies of NCC can guarantee considerable attention between researchers not only because of NCCs unsurpassed quintessential physical and chemical properties but also because of their inherent renewability, sustainability, and its abundance.

As it was previously mentioned, NCCs are commonly isolated from native cellulosic materials through acid hydrolysis; therefore, regarding what source has been used for obtaining it and which conditions have been applied for the reaction, the particle size and surface chemistry for NCC can change.

In two other works, researchers have reported lyotropic phase behavior, readily transitioning from isotropic to a biphasic suspension to a liquid crystalline phase with increasing concentration while working with aqueous suspensions of sulfonated NCC [7,8]. In another work, it has been mentioned that the suspension of NCC at high concentrations, can have transition into a birefringent gel-like material [9]. Based on literature, it can be inferred that NCC tends to assemble in cholesteric liquid crystals. In addition, when NCC is mixed with macromolecules such as alginate or inorganic material such as silica, the resultant mixture can contain similar types of ordering [8,10,11].

Other studies with the focus on mechanical properties of NCC when the NCC fibers are blended to calcium alginate are also available. They have shown that the mechanical properties of this kind of NCC depend on the helical assembly of the cellulose crystallites and do not have any dependency cholesteric ordering of CNC suspensions [11,12]. Hence, having knowledge about the rheology and phase behavior of CNC dispersions can be scientifically and practically considered as great interest about NCC. In the transition process of isotropic to biphasic, at the critical concentration, the larger particles form the liquid crystalline phase; however, the smallest stay in the isotropic phase [5].

Indeed, NCC exploitation will make a connection between nanoscience and natural resource products, which could have a great impact on reviving the forest industry in Canada and countries with ample forest resources.

2.2.1 Preparation of NCC

As it has been mentioned previously, the most common process for producing NCC is using acid treatment. That is, through acid hydrolysis, it is possible to obtain crystalline segments from the original cellulose fibers. Native cellulose is composed of amorphous and crystalline regions and the crystalline region has higher density than that of the amorphous region [3]. Therefore, by exposing cellulose fibers to acid treatment, disordered or paracrystalline regions of cellulose are preferentially hydrolyzed and the amorphous regions break up while crystalline regions remain intact because of higher resistance to acid attack. Hence, in acid treatment the hydronium ions cleave the glycosidic linkages hydrolytically which results in releasing the individual cellulose rod-like nanocrystals [3]. Figure 2.2 shows the process.

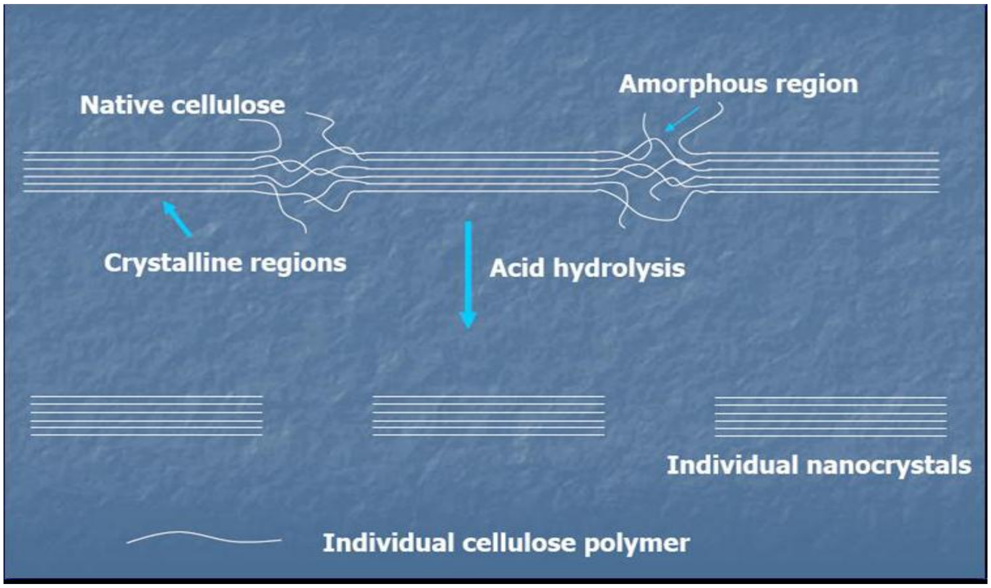

Figure 2.2 Sulphuric acid treatment of native cellulose [13]

NCC obtained from this treatment can have different properties which are contributed to processing condition including applied source, temperature, and retention time. There are many sources that can be employed for obtaining NCC; some of these sources are wood, cotton, sisal, tunicate, microcrystalline cellulose, ramie, and Valonia cellulose. Implementation of these different sources and techniques can result in having NCC with various lengths and diameters; Table 2.1 briefly shows some of these results. More quantitative details on acid treatment of cellulose including the acid type and concentration, range of retention time, and range of applied temperature will be provided later in this Chapter based on different methods people have used in their works.

Table 2.1 Examples of the length (L), diameter (d), and aspect ratio (L/d) of NCCs from various sources obtained via different techniques [3]. TEM: transmission electron microscopy, E-SEM: environmental scanning electron microscopy, AFM: atomic force microscopy, DDLS: depolarized dynamic light scattering.

Source	L(nm)	W (nm)	Aspect ratio	Technique
Cotton	100-150	5-10	10-30	TEM
	150-210	5-11	15-42	E-SEM
MCC	500	10	50	AFM
Ramie	50-150	5-10	5-30	TEM
Sisal	100-500	3-5	20-167	TEM
Tunicate	1160	16	73	DDLS
	100-several 1000	15-30	3-67	TEM
Valonia	>1000	10-20	50-100	TEM
Wood	100-300	3-5	20-100	AFM

This table demonstrates that geometrical dimensions of NCC change considerably by changing the source, techniques, and conditions that are employed for acid treatment of cellulose fibers. Based on this table and another literature, it is found that tunicate is the source which can cause producing NCCs larger in dimensions when compared to those of wood and cotton [14,15]. It happens because tunicate cellulose mostly consists of crystalline regions rather than amorphous regions.

Therefore, breaking the lower number of amorphous regions causes the larger crystallites to be obtained; Figure 2.3 shows TEM images of some NCC samples obtained from various sources [2].

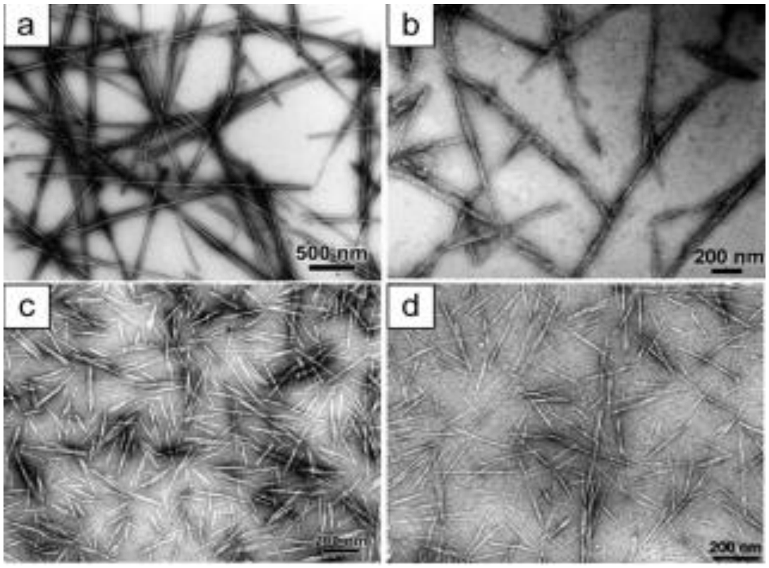

Figure 2.3 TEM image of dried dispersion of cellulose nano crystallites derived from (a) tunicate (b) bacterial (c) ramie (d) sisal [2]

Another study has been done on comparing the properties of NCC obtained from softwood (black spruce) to those of hardwood (eucalyptus) which shows that while working in a same process condition such as same reaction time, temperature, and acid-to-pulp ratios, it results in obtaining NCCs with similar dimensions, surface charge, as well as critical concentrations to form anisotropic liquid phases [16].They have also reported that increasing the reaction time and ratio of acid to pulp result in producing shorter nano crystallites rods with narrow polydispersity index (PDI) (distribution of molecular mass in a polymer sample) and higher critical concentration to form an anisotropic phase [16].

In 2009, Bai and coworkers investigated on a technique to produce narrow size distribution NCC using differential centrifugation [17]. So, they were able to obtain six different narrow PDI NCC fractions via this method which, at a constant centrifugation time, produces relative centrifugal force each NCC fraction. There is also another work focusing on significant parameters reaction conditions for acid hydrolysis of NCC from Norway spruce (Piceaabies). They implemented statistical experimental approach (response surface methodology) in order to optimize reaction conditions [18]. So, in their work, they chose to investigate the effect of concentration of NCC and sulphuric acid, hydrolysis time, temperature as well as ultrasonic treatment time as the variables for the reaction. Eventually, they came to find that temperature, reaction time, and acid concentration are significant factors affecting on the process.

There are also investigations with the focus especially on the effect on temperature on the length of obtained NCC [19,20]. In 1951, Ranby showed that by increasing temperature, the NCC obtained from sulphuric acid hydrolysis of cellulose fibers is shorter in size [20]. Even the acid used to acid hydrolysis treatment in NCC production process plays an important role on the NCC characteristics. Generally, two widely used acids for this process are sulphuric acid as well as hydrochloric acid. Hydrolysis of cellulose fibers using hydrochloric acid results in producing NCC with a limited ability to disperse. Rather they tend to flocculate in aqueous suspensions [2]. However, while using sulphuric acid for hydrolysis process, it reacts with the surface hydroxyl groups of cellulose and produces sulfate esters with charged surface which assists NCC to easily disperse in water [21,22]. Moreover, using any of these two acids can make some differences in thermal properties of the produced NCC. In fact, using sulphuric acid as hydrolysis agent and creating charged sulphate groups on NCC surface can cause the thermal stability of the material to be compromised [23]. The type of acid used in the hydrolysis process also affects the rheological behavior of the resultant NCC suspensions. It has been reported that when NCC is obtained from sulfuric acid hydrolysis, the viscosity has no time dependence; however, suspensions of NCC obtained from hydrolysis by hydrochloric acid exhibited thixotropic behavior at concentrations higher than 0.5% (w/v) and antithixotropic behaviour at concentrations below 0.3%[21].

There is also another method by which NCC is obtained. Cellulose is treated by hydrochloric acid followed by sulfuric acid solution [2]. This method has shown that the resulting material is NCC with the same particle size as it can be obtained from treatment through only sulphuric acid [2]. But, the amount of charge density on the surface of particles will be adjusted by acid sulphuric treatment. Although particle size remains constant in this method, the shape of final particles changes from rod shape to spherical. This change occurs during hydrolysis treatment steps under ultrasonic condition [24,25].

While doing the acid treatment process via acid sulphuric the common amount for acid concentration is around ca.65% (wt.) and it does not change considerably in reaction; however, the temperature can even go up to 70 °C from room temperature and depending on the temperature, the time required for hydrolysis treatment process can alter from 30 min to overnight [2]. But, when acid treatment process is carried out using hydrochloric acid, temperature and acid concentration applied in the system are different. In this case, the process occurs at a reflux temperature and the concentration of acid varies from 2.5Nto 4 N. there is no certain reaction time either in this case and it has its dependence on the source of cellulosic material used for the process [2].

Another way to produce NCC is what is presented by Filson et al. in 2009. This involves the use of recycled pulp as the original source subjected to microwave assisted enzymatic hydrolysis treatment [26]. They reported that this method would give a greater yield of NCC because of the difference in the heating process. This is because selective heating of microwave decreases the reaction time that in turn leads to a greater efficient of NCC production.

2.2.2 General properties of NCC suspensions

NCC suspensions can show different properties depending on the concentration of NCC in the suspension. It has been reported that NCC particles, when the concentration is low, are oriented randomly in the suspension which is called isotropic phase; however, by increasing the concentration the particles get more oriented and NCC suspension starts to transit from isotropic phase. Hence, at critical NCC concentrations, the suspension transforms from isotropic to an anisotropic chiral nematic liquid crystalline phase [3,22].

By increasing the concentration even higher than critical amount, a shear birefringence phenomenon has been shown. Based on the results presented in different literature, the critical concentration of NCC suspension, for sulphated

NCC, depends on important parameters such as aspect ratio of NCC and charge density. So this concentration can vary from 1-10 (wt. %) for different NCC suspensions [3]. Some theories have been presented to clarify this phenomena and its dependency on various parameters, in a work by Stroobants and coworkers (1986), some of these have been shown [27]. They have mentioned that their theory is regarding to the fact available in literature, for concentrations higher than critical concentration, solution of rod-like NCC particles shows a phase separation into an isotropic phase and an anisotropic phase, coexisting in equilibrium. The particles have an organized orientation in the latter phase (lyotropicliquid crystal).

As Stroobants et al. reminded in their work, for the first time, Onsager presented the phase separation phenomenon based on the result of the competition between the orientational disorder caused by orientational entropy and the entropy effect accompanied orientation-dependent excluded volume of the rod-like particles which favors orientational order. For the mono-disperse rigid rods NCC particles, Onsager clearly calculated the concentrations of the coexisting phases.

NCCs' phase behaviour can be influenced by the presence of electrolytes, their counter ions, as well as macromolecules. Adding electrolyte can have impact on the phase behavior of NCC. One of these studies has been done by Dong et al. (1996) [28]. They have shown that addition of electrolytes such as HCl, NaCl, and KCl can considerably lead to decrease in the volume fraction of the anisotropic phase. In case of counter ions impact, another study is carried out by Dong and Gray (1997); adding inorganic counter ions, weakly basic organic counter ions and highly basic organic tetra alkylammonium salts they investigated this impact on the phase separation behaviour and stability of NCC [29]. They reported that phase separation behavior of the NCC suspension can be noticeably influenced by the type of counter ions. As it was mentioned before, another important parameter that can impact on the phase separation behaviour of NCC suspensions is macromolecules addition. To investigate this effect, a study has been carried out by Gray and coworkers [30]. Hence, the impact of dextran and ionic dyes on the phase equilibrium of NCC suspensions was studied. Another issue which is conducted by researchers on the field of NCC suspensions properties is how to enhance dispersity of the NCC particles in non-polar solvents through surfactant coating. For instance, Heuxetet al. (2000), showed that when coating NCC whiskers obtained from two different sources (cotton and tunicate) with Beycostat NA (BNA) surfactant, the result could show desirable dispersity in non-polar solvents [14].As they reported, the presence of surfactant layer around the NCC whiskers did not prevent the formation of chiral nematic phase. Zhou et al. (2009) also reported that NCC shows high dispersity in non-polar solvents when NCC suspension is mixed with adsorbed xyloglucanoligo saccharide poly(ethylene glycol)-polystyrene [31]. In 2009, Elazzouzi-Hafraoui et al. illustrated a comprehensive study on the structure of chiral nematic phase of NCC suspension which Figure 2.4 shows the phase separation they observed through their work by cross polarized experiments for two different concentration of NCC obtained from cotton fibers [32].

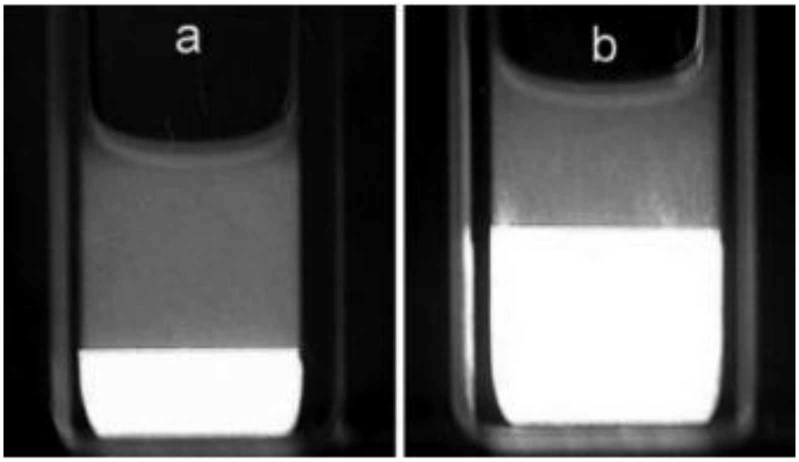

Figure 2.4 Phase separation between cross polarized for different concentrations of NCC suspensions at total concentrations of (a) 19.8 wt% and (b) 25.0wt% [32]

2.2.3Phase classification in a colloidal suspension

As it was mentioned previously, there can be different phases in a colloidal suspension such as NCC suspensions. When the molecules can almost be considered spherical the different phases for the suspension can be indicated by the degree of ordering of the molecules positions. In rod shaped molecules the various phases which can occur consist of two forms of ordering except for fluid and crystalline phases one is positions of the molecules and the other is the orientation of the molecules. Hence, there will be four different phase for a colloidal suspension [33]:

1- Isotropic phase:

This phase refers to the most randomly oriented phase in which the particles can translate and rotate easily with no special order. In other word there is no translational and orientational ordering in this phase. Figure 2.5a shows an isotropic fluid phase.

2- Crystalline phase:

This phase has the highest order of the particles and they all are located in the same direction. In this phase there is both orientational and translational ordering of the particles. Figure 2.5d shows a crystalline phase.

3- Nematic phase:

In this phase, the rod-like molecules translate randomly through space, while pointing on average in a particular direction which is called the nematic director. Nematic phase is one simple example of a meso phase or liquid crystal phase. Figure 1.5b shows a nematic phase.

4- Smectic Phase

This phase is another example of a liquid crystalline phase. In smectic phase, a homogenous two-dimensional layer of oriented molecules creates a piled up sandwich-like structure. The smectic phase, in one direction is considered as crystalline and liquid in the other two directions as a result of the periodicity in director direction. Figure 2.5c shows a smectic phase.

For nematic phase and smectic phase, the properties are something in between of crystals and liquids. For instance, like a liquid these two phases can flow and like similar to a crystal they can diffract.

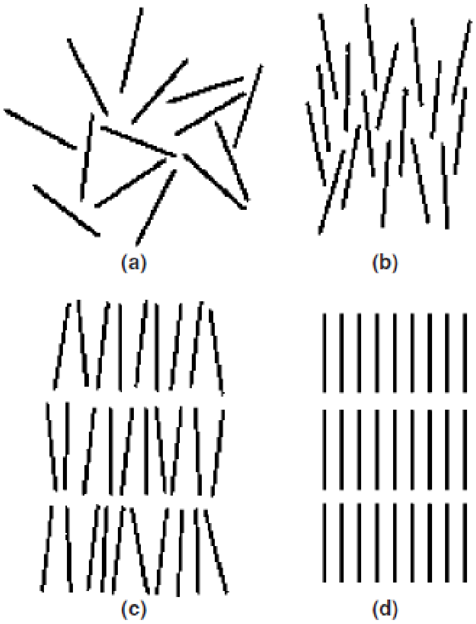

Figure 2.5 Schematic illustrations of typical configurations of rod-like particles in the (a) isotropic, (b) nematic, (c) smectic and (d) crystalline solid phase [33]

2.2.4 Rheological behavior of NCC suspensions

Some investigations have been carried out on alignment of NCC rods by application of shear. For instance, a study has been done by Lima and Borsali (2004) on the rheological behaviour of NCC suspensions from cotton linter source [34]. They investigated the change in viscosity of NCC suspensions in various concentrations while changing the sear rate. Figure 2.6 shows the curve of NCC relative viscosity ($\eta_{rel} = \eta/\eta_s$) versus shear rate where η_s is solvent viscosity [34].

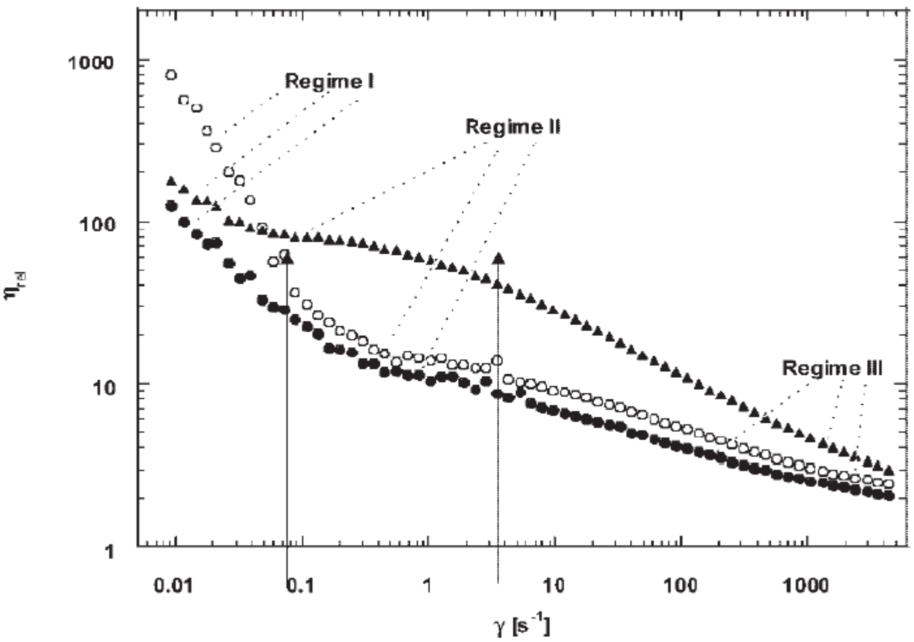

Figure 2.6 Relative viscosity vs. shear rate for different NCC concentrations

(•) 1.2 wt%; (◦) 1.7 wt% and (▲) 2.7 wt% [34]

In the results, as it can be seen in Figure 2.6, they got three different regimes. At low shear rate, shear thinning occurs because of the initial alignment of the NCC crystalline so they called this part as regime 1.

By increasing shear rates up to an intermediate level, a plateau can be seen in the curve which indicates that NCC alignment is the direction of the flow, so they called this region as regime 2.Finally, at the higher amount of shear rates, as a result of breakup of existing NCC crystalline into individual crystals aligning under shear, another shear thinning region occurs. This final region is called regime 3 [34]. As it was mentioned earlier, for NCC suspensions at concentrations higher than critical level, phase separates into an isotropic and an anisotropic phase. Bercea and Navard (2000) conducted a study on the rheological properties of isotropic and anisotropic phases of NCC suspensions [35]. They indicated that for the isotropic-at-rest (0-0.8wt %), below a concentration of 0.4 wt%, the two regimes were observed for solutions and two plateaus at low and high shear rates. At low shear rates, the rods are randomly oriented and viscosity does not change by changing the shear; at high shear rates, the NNC particles seemed to more oriented due to which viscosity becomes independent of shear rate. An isotropic to nematic transition was observed at 0.85 wt%. Figure 2.7 shows these results (viscosity vs. shear rate) for concentration below and higher than 0.8 wt% of NCC [35].

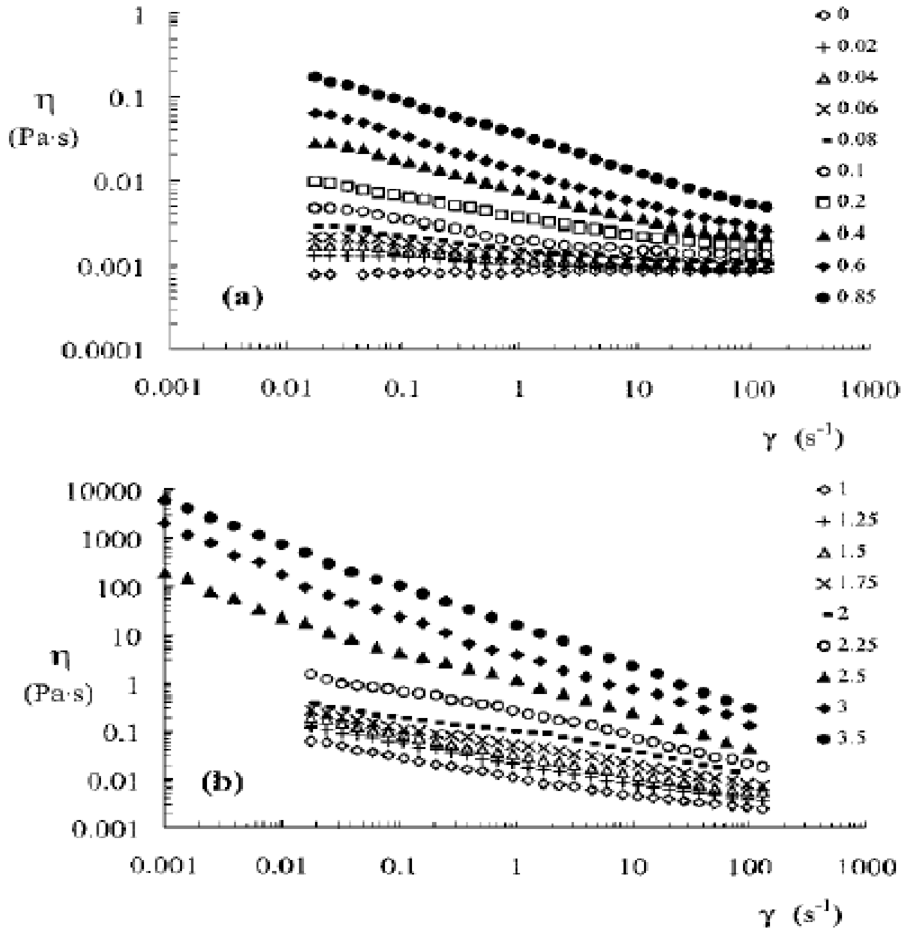

Figure 2.7 Viscosity vs. shear rate at different NCC concentrations [35]

However, when the concentration is higher, in anisotropic-at-rest (1-3.5 wt%) the result for viscosity versus shear rate curve behaves like a conventional liquid polymer solution. so in this range of concentration, a plateau region is surrounded by two shear thinning region. At low shear rates, shear thinning is related to the texture imperfection; however, at high shear rates, shear thinning is related to flow alignment of the suspensions [35].

Now, we know that NCC in different concentrations can show different properties such as variable rheological behaviour. Another question comes to mind is that, when a NCC suspension is mixed with a polymer solution how it behaves or on the other hand what kind of interaction between NCC particles and polymer particles is possible in different conditions.

2.3 Different types of interactions between colloid-polymer mixtures

The interaction between polymer and colloid particles depends on the type of polymer added to the colloid suspension. It means the particles do not exhibit same behaviour for adsorbing and non adsorbing polymers. So, when there is a mixture of colloidal particles and adsorbing polymers, polymers can adsorb on the surface of the colloid particles. In contrast, when a non-adsorbing polymer is added to the system the type of interaction is quite different. In this case, the polymer colloid interaction is called depletion [36]. Figure 2.8 shows a schematic view of these two possible interactions between colloids and polymers [37].

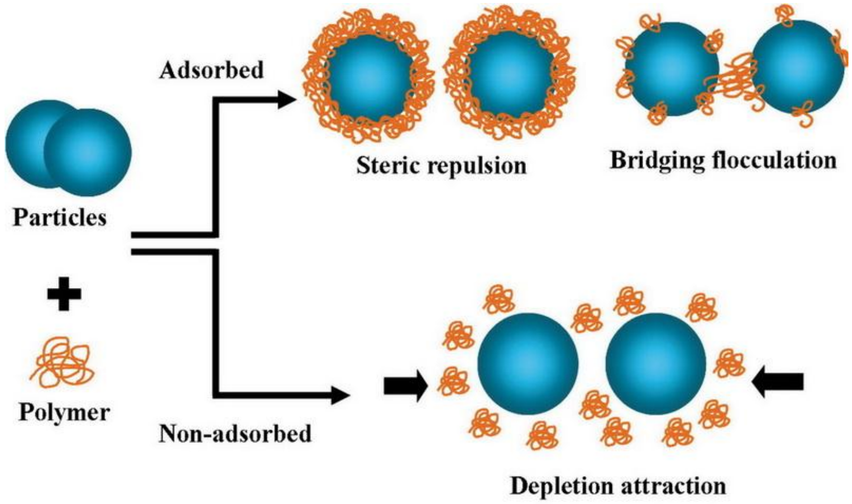

Figure 2.8 Interactions between adsorbing/non-adsorbing polymers and colloid particles [37]

2.3.1 Adsorption interaction

As it was mentioned, one possible phenomenon when adding polymer to a colloidal suspension is polymer adsorption from solution. This phenomenon includes attachment of many polymer segments to the surface of the nanoparticle. The adsorption affinity per segment has to be high enough, in order for the free energy of adsorption of the whole polymer molecule to compensate for the entropy loss that happens during polymer transfer from solution to an interface. The critical adsorption free energy which is required for polymer adsorption is of the order of 0.3 kT per segment [36].

It has been considered that polymer adsorption is strong and irreversible in most cases. While here, irreversible means irreversible to dilution. There is a slight chance for a long polymer chain, that all attached segments becoming detached at the same instant. Figure 2.9 shows an adsorbed polymer chain; as it can be observed, segments attached to the surface in trains, separated by loops which are in fact segments extending into the solution. The tails available at the end of each chain are almost long which are extended into the solution [38].

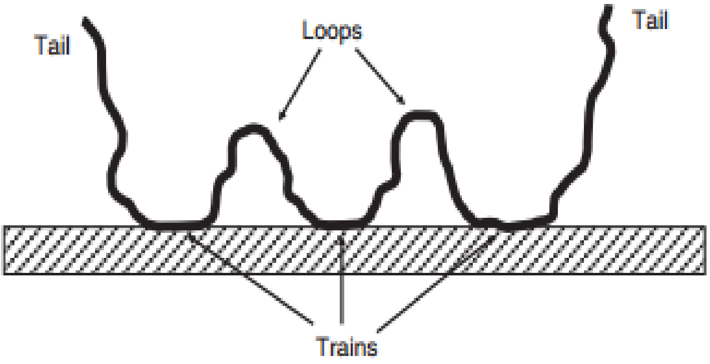

Figure 2.9 Equilibrium conformation of an adsorbed polymer chain [38]

2.3.2 Bridging flocculation

As it has been shown in Figure 2.9 there are some extended loops of polymers in the solution; now, when another particle is available with some vacant adsorption sites so it can attach the polymer tails and extended loops so another kind of adsorption can happen. This aggregation is called polymer bridging flocculation. However, if excess polymer added and adsorbed to the system, the particles will be restabilized by surface saturation and at this time flocc breakup can happen. Figure 2.10 shows a schematic view of polymer bridging.

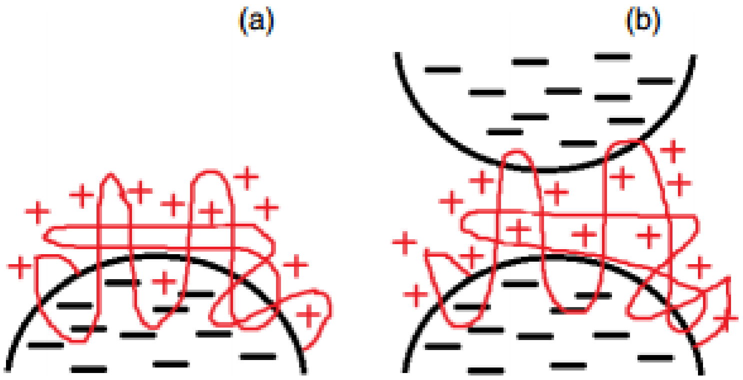

Figure 2.10 Schematics of counter-charge bridge mechanism of flocking: (a) cationic polymer flocculent initially adsorbs onto an anionic particle and (b) the flocculent loops adsorb onto a second anionic particle causing 'bridge' flocculation [39]

2.3.3Depletion interaction

As it was said earlier, when a non adsorbing polymer is added to a colloidal suspension, the interaction between polymer and colloid particles will be depletion which leads to a reduced concentration of polymer in the depletion region [36]. So the space around the particles in which polymers cannot be found is called excluded volume. In some cases, the excluded volume around the colloid particles can overlap when the particles get close together. Therefore, by this overlapping, some free space will be available for the polymers in the system and the colloidal particles aggregate as a result of a net attraction. In other words, we can say that polymers induce depletion interaction in the system. Figure 2.11 clarifies a depletion interaction. As it can be inferred from this figure, the centre of a polymer molecule (coil) is excluded from getting closer than a certain distance (which is almost its radius of gyration: size of the polymer in coil shape) to the colloid surface. This is actually because of the high entropic cost of configurational distortion. So, each particle is surrounded by depletion zone (dotted circle) which is a zone with essentially no polymer centres of mass. When a colloid like particle C is far away from other particles, it exposes to an isotropic osmotic pressure from the polymer. On the other hand, when the surface of two particles (shown as A and B) are closer than twice depletion zone size, there will be no polymer in the overlapping region. In this case, the net (osmotic) force pushes the particles together is called the depletion attraction [40].

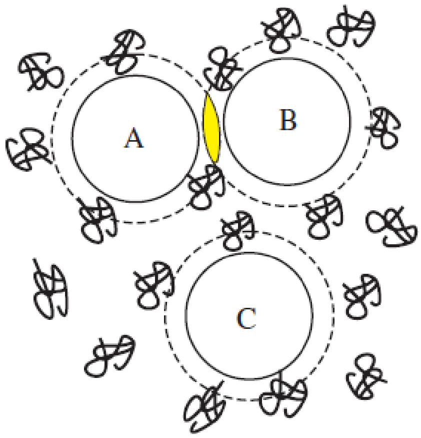

Figure 2.11 Schematic illustration of the depletion interaction for a polymer colloid system [40]

Chapter 3 Materials and Methods

3.1 Materials

3.1.1 NCC

NCC used in this research was supplied from Alberta Innovates Technology Futures (AITF) and it was NCC batch No. 100421. Based on the characterizations carried out in our research group, it was found that this NCC has the length of 130 (nm) and the diameter of 6 (nm). So, the aspect ratio (L/d) was 21.66. Also our research group reported that the source of this NCC is Whatman cotton paper.

3.1.2 Hydroxy Ethyl Cellulose

Hydroxy ethyl cellulose or HEC is a water-soluble cellulose derivative which is applied in food and cosmetic industry as thickeners. HEC also can be used in polymerization processes as protective colloids and very recently as thickeners in water-based paints. The aqueous solutions of HEC possess high viscosity. This cellulose based polymer is neutral unless it is chemically modified. The HEC used in this work was purchased from Aldrich; the molecular weight was 720 kDa and it was a neutral polymer. For this polymer, based on the calculations reported by Boluk et al., the radius of gyration (R_G) was 80 nm, degree of substitution (DS) was 1.0, molar substitution (MS) (average number of hydroxyl group per glucose) was 2.0, critical overlapping concentration (c*) was 0.005 (g/ml) [53]. Figure 3.1 shows the structure of HEC [41].

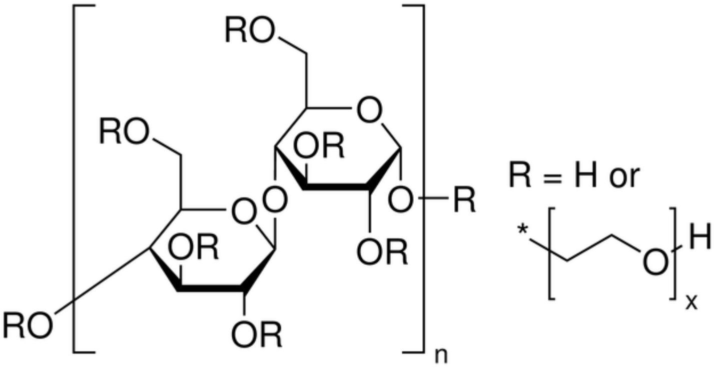

Figure 3.1 Chemical structure of hydroxyl ethyl cellulose (HEC) [41]

3.1.3 Carboxy Methyl Cellulose

Carboxymethyl cellulose, which is known as CMC, is a carboxymethyl ether of cellulose. In order to obtain this material from cellulose, Carboxy methylation has to be initiated using an alkali to activate the cellulosic chains and then react with monochloro acetic acid (or its sodium salt) to produce carboxy methyl groups. So, this linear, anionic water-soluble polymer can exist as free acid or its sodium salt or mixtures. CMC has been widely used for various applications in industry. As a case in point, extra pure CMC grade is used in food industry, pharmaceuticals and toothpastes whereas, semi purified and technical grades have applications in oil drilling muds, paper coatings, textile sizing, mining operations, as well as detergents. The CMC used for this work was purchased from Aldrich with the molecular weight of 700 kDa. Again based on the calculations in Boluk et al. work, R_G was 280 nm, DS was 0.7, and c* was 0.002(g/ml) [53]. Figure 3.2 illustrates chemical structure of CMC [42].

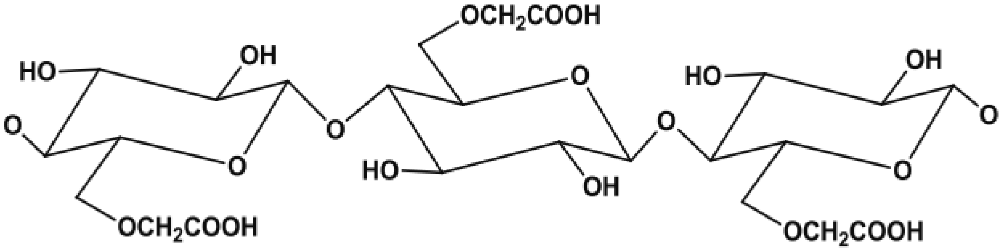

Figure 3.2 Chemical structure of CMC [42]

3.1.4 Dextran

Dextran is a bacterial polysaccharide produced from sucrose by extracellular Dextransucrases. Commercial dextrans are commonly obtained from the bacteria Leuconostocmesenteroides,strainB-512F including a backbone of consecutive α-1,6 linkages, with the remaining being branched α-1,3 linkages[43]. Dextran can be also derived from other strains of the L. mesenteroides as well as other bacteria, leads to have products which include either different percentages of the branched α-1,3 linkages or branching at either position 2, 3 or 4. The dextran obtained from the strain B-512F are known to contain almost 5% randomly distributed α-1,3 branched linkages of varying lengths (up to 50–100 residues) [44]. The significant factor in indicating the rheological properties of dextran are actually these long branches. The dextran used in the present work was purchased from Sigma with the molecular weight of 2000 kDa. Based on the information obtained from Edgar and Gray (2002), the R_G of 2000 kDa dextran is 34 nm [30]. Figure 3.3 shows chemical structure of dextran [45].

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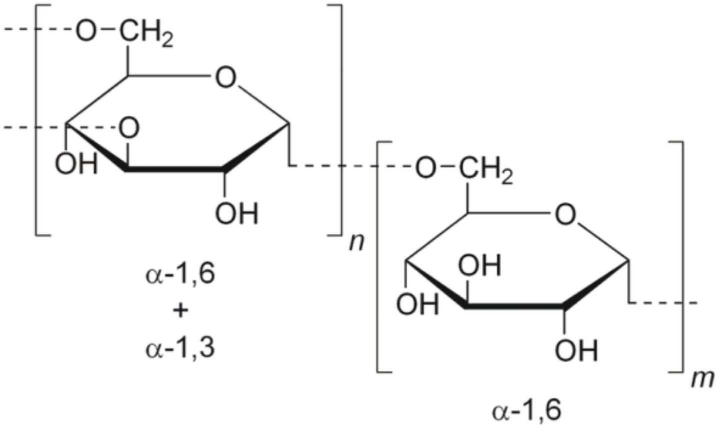


Figure 3.3 Chemical structure of dextran [45]

3.2 Methods

3.2.1 Rheology

Rheology is the science of deformation and flow of matter under controlled testing conditions. The matter can be either in the liquid state as well as soft solid. Which means the flow behaviour of solids under conditions which make them to behave like a plastic flow instead of elastically deform as a result of an applied force. Rheology can be implemented for materials with complicated structure; for instance, polymers, suspensions, mud, silicates, and biological materials can be mentioned as the examples of this complicated structure [46].

Fluids can be divided into two major classes based on their rheological behaviour. One of these classes includes fluids which show the constant viscosity in the response of changing strain rate [46]. But this behaviour can be observed just for a small number of fluids and this class is called Newtonian fluids. However, for the next class of fluids, the viscosity of the fluid does not remain constant by the change of strain rate. The fluids show this behaviour, are called non- Newtonian fluids. Generally, the term rheology is applied for characterizing the behaviour of non-Newtonian fluids and by using rheology it is possible to indicate the relation between viscosity of the fluids with strain or strain rate [46].

Rheometer is implemented in order to do the rheological test. In this work, AR-G2 was purchased and applied which is most advanced rheometer with combined motor and transducer (CMT). AR-G2 has a main unit as well as separate control box which contains electronics. Figure 3.4 shows the schematic diagram of this instrument.

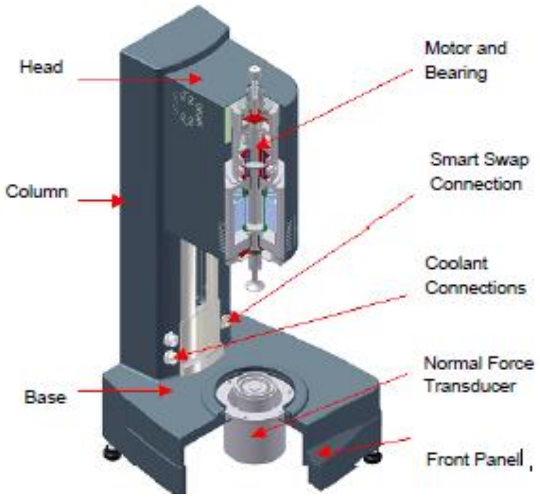


Figure 3.4 Schematic diagram of AR-G2 rheometer [47]

In this work this instrument was applied to do flow test and oscillation test for a wide range of concentrations of samples.

3.2.1.1 Flow test

This test is a very commonly used test for the target of obtaining flow curve of the material. By this test, it is possible to plot the flow behaviour of the tested material by showing the change of the viscosity versus shear rate [47].

3.2.1.2 Oscillation test

3.2.1.2.1 Oscillatory shear testing

This test is used to characterise and measure the presence, rigidity and integrity of internal structure which can be as a result of flocculation of dispersed particles or droplets, or cross-linking and entanglement of dissolved polymers.

Typically measured parameters include: Complex modulus (G*) Elastic (or storage) modulus (G') and viscous (or loss) modulus (G'') phase angle (δ) and tangent of the phase angle (tan δ) [46,47].

3.2.1.2.2 Oscillation Stress Sweeps

Oscillation stress and strain sweeps provide information about the soft-solid rigidity and yield stress (gel strength) of even delicately-structured fluids such as suspensions which are resistant to sediment [46,47].

3.2.1.2.3 Oscillatory Frequency Sweeps

Oscillatory frequency sweeps are employed to investigate and recognize the nature of the structuring mechanisms present in a fluid. The sample is exposed to small-deformation oscillations covering a range of frequencies to assess the structural response to deformations of longer or shorter timescales. This technique can demonstrate a valuable tool when attempting to match textures and flow behaviours in thickened systems [46,47].

3.2.2 Polarized Optical Microscopy

Polarized Optical Microscopy (POM) which is also known as polarized light microscopy is a technique with enhanced contrast which helps to advance the image quality of birefringent materials. This instrument possesses a high sensitivity and can be employed for both quantitative and qualitative studies targeted at a wide range of anisotropic samples. In fact, it can be used for the samples which are visible mainly due to their optically anisotropic character. Figure 3.5 depicts the process of light polarizing which occurs in the instrument. As it can be inferred from the figure, the microscope has a polarizer and an analyzer. The polarizer is located in the light path before the specimen, and the analyzer (a second polarizer) is located in the optical pathway between the objective rear aperture and the observation tubes or camera port. The polarized filter placed after the specimen (polarizer) is able to rotate and allows the polarized light to pass through the microscope and specimen. If the analyzer and polarizer are placed at a 90 degree angle, all light will be blocked out and a dark image will be observed. If a specimen with double refraction is placed between the 90 degree located filters, as a result of a change in transmitting light, an image will be appeared. The light refraction depends on the specimen’s thickness, orientation of minerals and its birefringence [48].In this work, polarized optical microscope was utilized in order to investigate the phase regime in NCC and NCC-polymer samples.

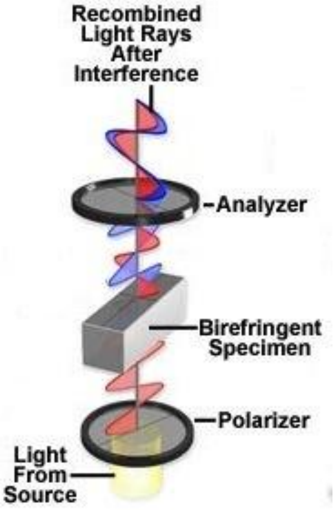


Figure 3.5 Light polarization [49]

3.2.3 Cross polarized experiment

In this simple experiment which is based on the main procedure of light polarization microscopy, two films and a flash light as a light source is used to do the light polarization. The method is simply placing the sample between two films in a dark room in which the only light source is the flash light. The second film is in vertical direction; so when there is no sample between two films the light comes from the flash light cannot go through the films and it will be polarized then the only thing can be seen after the second film is darkness. But when there is a sample in between, it can different; when a sample includes some liquid crystals so the light can be rotated by the sample and can go through the second film so the result of cross polarized is not darkness. By this simple method it is possible to approximately indicate the phase behaviour of the sample.

Chapter 4 Results and Discussion

In this chapter, the first part is mainly focused on NCC solutions phase behaviour for a wide range of concentrations. In the next parts, result of adding polymers to NCC suspensions will be investigated and reported. Based on all results, the interpretations for the samples phase and rheological behaviour and the possible type of interaction will be made.

4.1Cross polarized experiments for NCC suspensions

In order to investigate the phase behaviour of NCC suspensions, light transition through cross polarized filters was implemented. It is possible to find the concentration range where NCC suspensions go through a very randomly oriented phase (isotropic) to a chiral nematic phase and there will be a phase transition behaviour as reported in the literature [50, 51, 52]. So, different concentrations of NCC have been tested through cross polarized experiment. All concentrations for NCC suspensions were reported in weight%. So, a wide range (2,4,6,7,8,10wt.%) of NCC suspensions in water were prepared for the cross polarized experiment. Figure 4.1 shows NCC suspensions in different concentrations.

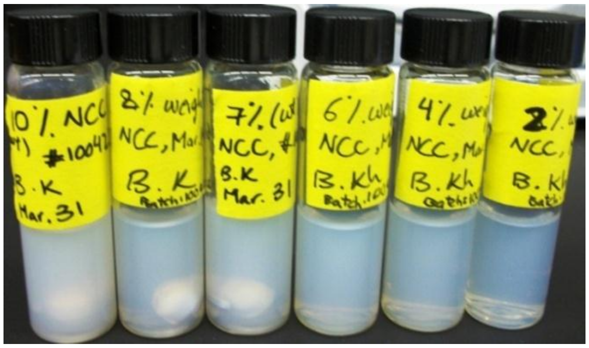
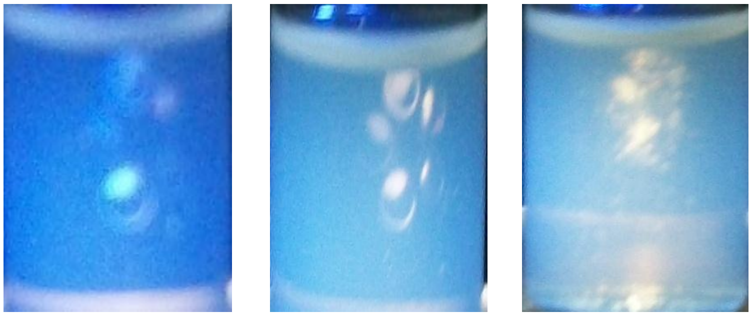


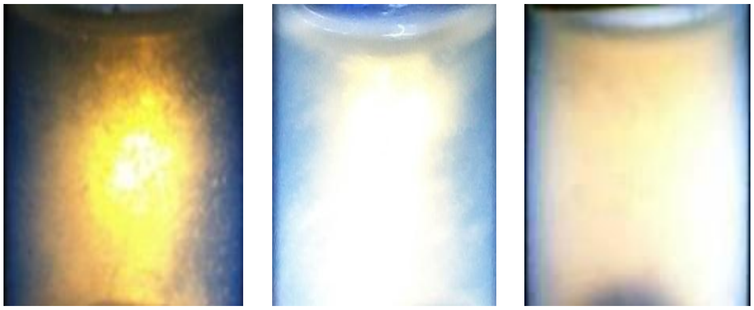
Figure 4.1 NCC suspensions in water

The results of cross polarized showed that by increasing the concentration of NCC suspensions, a considerable change in phase behavior of the samples can occur. Figure 4.2 reveals what has been observed through a crossed polarized experiment for NCC suspensions. Respecting to the mechanism of this method, when a crystalline sample can rotate the light and be seen after cross polarization so it means the sample no longer behaves as an isotropic suspension; it can be assumed either in a transition phase or a chiral nematic phase base on the observed light through the sample. Whereas, when the result of cross polarized experiment is dark the sample can be simply considered in a randomly oriented isotropic phase regime.

Therefore, as it can be observed from Figure 4.2, for the investigated range in cross polarized experiments, NCC suspensions with concentration of 2 and 4 wt. % were dark (based on the cross polarization results) which indicated phase behavior. However, by increasing the concentration from 4 to 6 wt%, it can be inferred that the phase behavior of the sample is changing and the result of the cross polarization cannot be assumed as a dark sample anymore. So, it means the sample is going through an isotropic phase to a more oriented phase. For 6 wt% NCC sample respecting to this result, it can be surely said that sample is not in an isotropic phase but it is still hard to decide whether it is in transition phase or a chiral nematic phase. For sample 7-10wt%, it can be observed that NCC suspensions are behaving like a chiral nematic sample as compared to the literature [50,51,52]. So, these experiments helped to obtain important ideas about the phase behavior change in NCC samples has been used in this project by increasing the concentration. In order to make sure about the point that transition region starts and the point that sample shows nematic behavior, polarized light microscopy as a more accurate method has been implemented for a wider range of the concentrations (1,3,5,9 wt% also added).



a)2%wt. NCC **b)**4%wt. NCC **c)**6%wt. NCC

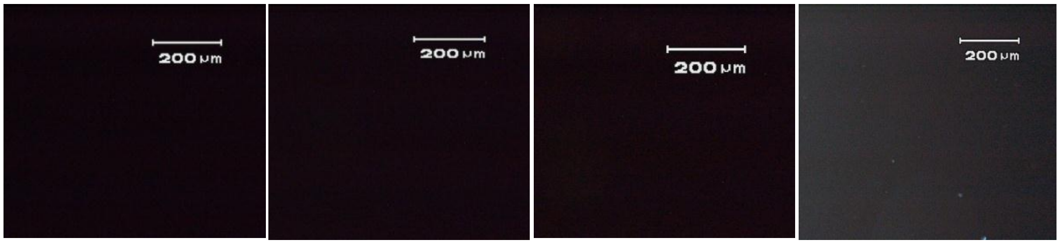


d)7% wt. NCC **e)**8% wt. NCC **f)**10% wt. NCC

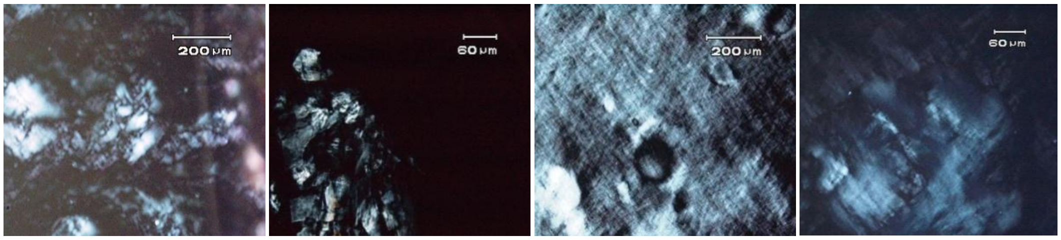
Figure 4.2 Results of cross polarized for NCC suspensions

4.2 Light Polarization Microscopy for NCC suspensions

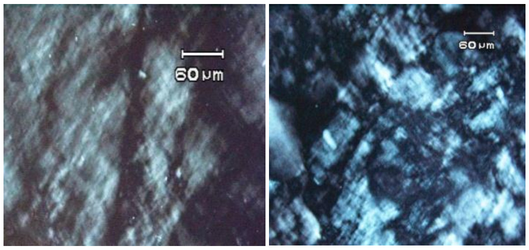
NCC suspensions were tested by light polarization microscopy (POM). This time four more concentrations were added to the investigation range as mentioned in the previous part. The results of the experiment are presented as follows (see figure 4.3)



a)1wt. % NCC **b)** 2wt.% NCC **c)** 3wt.% NCC **d)**4wt.% NCC



e)5wt.% NCC **f)**6wt.% NCC **g)**7wt.% NCC **h)** 8wt.% NCC



i) 9wt.% NCC **j)** 10wt.% NCC

Figure 4.3 Light polarization of NCC (POM experiment)

The results of POM in Figure 4.3 shows that at low concentrations of NCC such as samples a-d, the only thing can be observed is darkness after light polarization process. So this darkness means there is no liquid crystal in the sample to rotate the light then make the whole sample or part of it visible even after polarization. Therefore, it can be said that for this range of concentrations (1-4wt%) NCC suspensions are definitely in isotropic phase and no liquid crystal has been formed in the NCC suspensions. All samples investigated in this range are considered to have no specific orientation and the NCC rod like particles are located totally in random locations. The viscosity of the samples here were almost low then samples (a) and (b) could be considered as runny fluids. But in samples (c) and (d) the viscosity was getting somewhat increased; however, they could not be considered as high viscous suspensions.

However, by increasing the concentration of NCC suspensions the liquid crystals started to be formed in the sample; so, that is the reason the light can be observed after polarization. The crystals inside the sample rotate the light and the result of the experiment is not just darkness as it was for low concentrations. Therefore, respecting to the results showed in Figure 4.3 (e-f) it can be said that in these range of concentration which includes concentrations higher than 4wt.% up to 6 wt.%, the sample is not behaving as an isotropic sample because it is not all dark; also, it is not showing a complete nematic behaviour because it is not bright in the whole area. Based on these facts, this area (4-6 wt% NCC suspensions) is in transition phase; so, it can be called a phase which is a combination of isotropic and nematic phase, it is also called I+N phase. In this transition area, NCC rod like particles are located somewhat oriented and the suspension can no longer be assumed as randomly oriented sample. The viscosity of the samples in this region was partially high; however, they could not be considered as gel like samples.

By increasing concentration up to 10 wt. % (Figure 4.3 g-j), it can be inferred that liquid crystal is formed in this range of concentrations so the samples are all bright. All samples in this range are behaving as a nematic sample; then it can be concluded that for samples with concentration higher than 6wt.% the phase behaviour changes from a combined (I+N) to a nematic behaviour and here NCC rod like particles are completely oriented. The viscosity of the samples in this range was quite high and they all could be considered as gel. All of them showed exactly gel like behaviour. Figure 4.4 shows a simple way of phase behaviour diagram for NCC suspensions.

Figure 4.4 Phase behavior of NCC suspensions for concentration of 1-10 wt.%

Also, Table 4.1 summarizes the result of phase behaviour for this work and those of reported by Dong et al. [29].

Table 4.1 Phase transition of NCC suspensions in pure water

L (nm)	D (nm)	Aspect ratio (L/D)	$\phi_{I \rightarrow I+N}$	ϕ_N	Ref.
115	7	~16.4	4.55% (wt.)	13.13% (wt.)	[29]
130	6	~21.6	~4% (wt.)	~7% (wt.)	this work

Where $\phi_{I \rightarrow I+N}$ is the suspension concentration when the sample enters the mixture phase behaviour (isotropic+ nematic) and ϕ_N is the sample concentration for the nematic phase. So based on the results summarized in table 4.1 it is obvious that by changing the aspect ratio the phase transition behaviour of the colloidal particles has been changed. As Dong et al. reported for NCC suspensions with approximate aspect ratio of 16.4 which is lower than the one applied in my work [29]. Hence, it means increasing the aspect ratio has decreased the concentration in which phase transition happens in NCC suspensions. The reason is rods with higher aspect ratio are easier to align with each other to form the liquid crystal.

4.3 NCC-Polymer mixtures

After investigating effect of concentration on the behaviour of NCC rod like particles in the aqueous suspensions and obtaining the phase behaviour of the samples; in the next step, polymers were added to the systems to investigate the difference in phase behaviour for a mixture compared to NCC suspensions. In this section, both phase behaviour and rheological behaviours of the samples were studied to investigate the interactions between NCC rod shape particles and polymers. Three different polymers have been used: HEC 720 kDa, CMC 700 kDa, and dextran 2000 kDa. The results have been reported and discussed. Table 4.2 shows a quick view of the experiments carried out for NCC in the presence of these three polymers.

Table 4.2 Methods used to discuss phase and rheological behavior of NCC-polymer mixture

Mixture	Light polarized/phase diagram	Rheology
NCC/HEC720k	√	Boluk et. al. [53]
NCC/dextran	Edgar et al. [30]	√
NCC/ CMC 700k	√	√

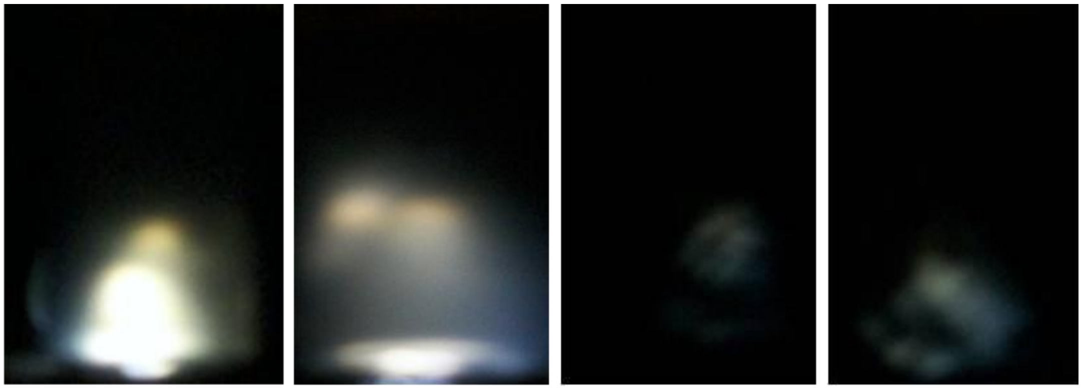
Based on this table for NCC-HEC mixture, cross polarized experiment was applied and phase diagram was obtained but the rheological behaviour was discussed using Boluk et al. work results. For NCC-dextran, rheological experiment was done but the phase behaviour explained by using the results of Edgar et al. work. For NCC-CMC both POM and rheological experiments were carried out.

4.3.1 NCC- HEC mixture

HEC 720k was used as a neutral cellulose based polymer. For investigating the phase behaviour of NCC–HEC mixture in the first step, the solutions have been prepared for constant concentration of NCC (1wt.%).The critical overlapping concentration for HEC 720 as reported in a study by Boluk et al. (2012), is 0.005 g/mL (0.5 wt.%); so, the concentration range of 0.15,0.3,0.45,0.6 wt.% was selected for HEC 720k solutions which included two samples below the critical overlapping concentration, one sample around that critical concentration as well as one sample higher than critical overlapping concentration [53]. Figure 4.5 shows the final mixture of NCC-HEC solutions.

Figure 4.5 NCC-HEC 720 solutions (cons. NCC at 1wt.%)

These low concentrations have selected because no effective background viscosity was desirable from the polymer. The cross polarized test was carried out for this range and the results of this experiment are showed in Figure 4.6.



a)1wt.% NCC-0.15 wt.% HEC **b)** 1wt.%NCC 0.3 wt.% HEC **c)** 1wt.% NCC 0.45 wt. % HEC **d)** 1wt.% NCC 0.6 wt.% HEC

Figure 4.6 Cross polarized experiment for NCC-HEC720 mixtures (1wt.% colloid particles)

Based on the results of cross polarized and the explanation was provided for the previous part (NCC cross polarized experiments), Figure 4.6 shows that for this range of HEC (a-d) and 1wt.% NCC rod like particles all pictures can be considered as dark. So in this part, it can be said that NCC –HEC mixtures (a-d) are all in isotropic phase area because no liquid crystals can be observed after putting the second film (polarizer) in front of the sample so there is no rotation of light by the sample, and the poor light which can be seen in the picture just comes from the flash light source. Therefore, there is no special orientation for the particles in the solutions (a-d) and the particles are located randomly in the sample. As it was shown in the previous section (4.2), the low concentration of NCC (1wt%) behaved as an isotropic sample with low viscosity and adding low HEC concentration to this sample has not changed the phase behavior. Hence, this HEC concentration has not been enough to make the NCC suspensions transit from isotropic phase to combined phase (I+N) or nematic phase. On the other hand, it is not easy to determine the exact effect of increasing HEC amount in a constant concentration NCC.

Now, it is found that a higher concentration is needed which can be obtained by increasing the HEC concentration or NCC concentration. So, it was decided to examine the same range of HEC but just change the concentration of NCC to 2wt% (figure 4.7). So, the viscosity of the samples might increase because of increasing the NCC concentration.

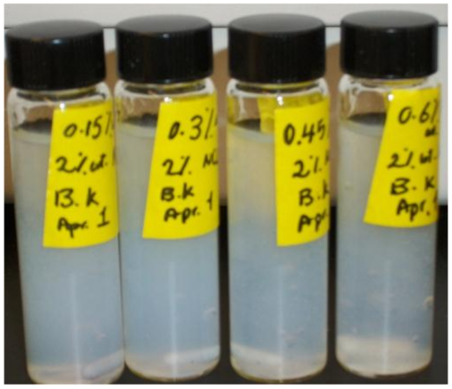
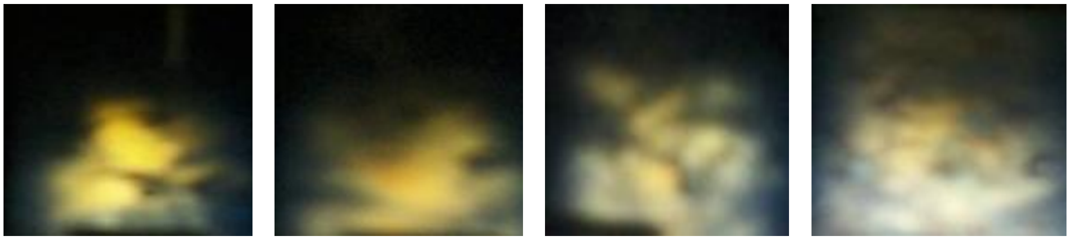


Figure 4.7 NCC-HEC 720 mixtures (cons. NCC at 2wt.%)

Results of cross polarized experiment have been shown in the following figure (Figure 4.8).



a)2 wt.% NCC-0.15 wt.% HEC

b) 2 wt.% NCC 0.3 wt.% HEC

c) 2 wt.% NCC 0.45 wt. % HEC

d) 2 wt.% NCC 0.6 wt.% HEC

Figure 4.8 Cross polarized experiment for NCC-HEC720 mixtures (2wt.% colloid particles)

Based on the results obtained from crossed polarized experiment, it can be said that the effect of increasing NCC concentration (2wt% NCC) is obvious in comparison to the results of lower concentration (1wt.% NCC- Figure 4.6).

As it can be observed in Figure 4.8 (a-d) the polymer-colloid mixture is changing its phase behavior by changing the polymer concentration. So, in sample (a) for a low concentration of HEC some liquid crystals are visible after putting the second film (polarizer) in front of the sample. The liquid crystal rotated the light then for almost half percentage of the sample cloudy bright parts can be seen which means the sample is not in the isotropic phase anymore if it is compared to the sample (a) in figure 4.6. Therefore, increasing the concentration of NCC from 1 wt.% to 2 wt% at the presence of HEC caused a considerable change in phase behavior which is moving the sample from an isotropic phase to a combined phase (I+N). Particles then change from randomly oriented positions to partially oriented positions .Another change in the sample contributed to the rheological behavior; which means in this higher level of NCC (2wt.%), although sample still is not viscous but it is not that runny as it was for the lower level of NCC (1wt.%) and it still can be considered as low viscous sample.

By increasing the concentration of the polymer, in sample (b) (see Figure 4.8), it can be inferred that the cloudy bright part which represents the formation of liquid crystal is almost wider in comparison to the sample (a). However, the polymer-colloid mixture is still showing dark in same parts so the mixture can be considered in combined (I+N) phase region. Similar to the sample (a) the liquid crystals which are formed in the suspension made some parts of sample to be seen cloudy bright after putting the second film (polarizer) in front of the sample in the cross polarized experiment. Therefore, the particles are assumed to have partial orientation in the sample. When this sample (b) with higher amount of NCC (2wt.%) is compared to the sample (b) with same amount of polymer (HEC) and lower amount of NCC (1wt.%), it can be concluded that increasing NCC concentration with the order of 1wt% can make obvious effect on the phase behavior of the final sample. Therefore, similar to the previous part, the impact of increasing NCC shifted the sample from isotropic region to (I+N) combined region.

In sample (c) (Figure 4.8), more change can be observed. In fact, the bright parts showing the presence of liquid crystals are expanded. It means that for this level of NCC (2wt.%), an increased amount of polymer caused more change in phase behavior of the polymer-colloid mixture. So, by looking at the picture taken from sample (c), after putting the polarizer in front of the sample in crossed polarized experiment, it can be said that the sample is almost behaving like a nematic suspension. As the change in polymers concentration was not so much and in sample (b) it could be said that mixture is in I+N phase. So, for this sample, it can be concluded that the mixture is just entering the nematic area. Hence, by considering the mixture in nematic region, it is logical to expect the particles in the mixture should have specific orientation. Again, comparing this sample to the one revealed in Figure 4.6 with the same polymer (HEC) concentration and lower NCC concentration (1wt.%) it indicates that for this level of polymer (0.45 wt.%) increasing NCC concentration can have even more impact than a lower level of polymer; as it caused to move the mixture from an isotropic phase to a nematic phase. This shift can be explained by both increasing NCC and polymer concentration in the mixture for a non-adsorbing polymer when there are more colloidal particles (NCC rod-like particles) and more polymer chains so it causes stronger interaction between particles and chains.

For sample (d) (Figure 4.8), again based on the picture taken from the sample during cross polarized experiment, it has been revealed that the amount of liquid crystal is the suspension is increasing and the sample is behaving like a nematic suspension. The difference between this sample (d) and sample (c) is that in this sample because of higher concentration of polymer (HEC), the bright part in the picture is wider and it can be said that more liquid crystal has been formed in the mixture. But when comparing this sample to the sample (d) in Figure 4.6, it shows that in this level of polymer concentration (0.6wt.%) which is not very low concentration, increasing NCC concentration from 1wt% to 2 wt.% caused a huge difference in phase behavior of the final polymer-colloid mixture; which was described in an isotropic phase area for that lower amount of NCC. In fact, the particles went from randomly oriented positions to a phase which has a complete orientation.

Regarding to these results, it found that increasing NCC concentration could have a significant effect on the phase behavior of the system but in these experiment just two concentrations of NCC were tested and in each run. The NCC concentration was constant while the polymer (HEC) concentration was changing. All concentrations selected for polymers range were lower than 1wt.%; therefore, another investigation can be increasing the HEC concentration to a higher level such as 1 wt.% and keep it constant while changing the NCC concentration. NCC concentrations even lower than 1wt.% were tried. So, the range of 0.5, 0.75,1 (all in wt.%) were selected to be mixed with 1wt.% HEC for the cross polarized experiment and investigation on polymer- colloid mixture phase behavior. Figure 4.9 shows the results of cross polarized experiments.

a)0.5 wt.% NCC- 1 wt.% HEC

b) 0.75 wt.% NCC 1 wt.% HEC

c) 1 wt.% NCC 1 wt. % HEC

Figure 4.9 Cross polarized experiment for increasing NCC concentration (at1wt.% cons, HEC)

From what can be observed in Figure 4.9, the first conclusion is that none of the mixtures are behaving like an isotropic suspension. For the lowest concentration of NCC it is clear that a substantial amount of liquid crystal has been formed which showed like bright cloud in the picture. However, there are still some parts of the mixtures which turned dark in the cross polarized experiment after putting the polarizer. Thus, the mixture in Figure 4.9 (a) can be considered as a sample in I+N region then the particles in such sample are fairly oriented. It definitely expressed that even at a low level of NCC concentration it is possible to move the mixture from a very runny isotropic one to a mixture which is located in a phase transition area. In compare to the both previous experiment were discussed for constant NCC and a low concentration range for polymer (HEC) it demonstrates that a high concentration of polymer can lead the mixture to move from randomly oriented particles to somewhat oriented ones. It can be because of excess amount of polymer chains added to the system and the interactions between these chains and NCC rod-like particles.

In mixture (b), the picture discloses that apparently more liquid crystals have been formed in the sample. This mixture includes the same concentration of polymer (HEC) but higher concentration of NCC compared to the mixture (a). So, this higher concentration of NCC colloidal particles made the mixture to have more aggregation of liquid crystals which is caused by the interaction between polymer chains and NCC particles. As almost the whole sample could rotate the light in cross polarized experiment; hence, it can be inferred that the sample is behaving as a nematic suspension and there are just a few small parts in the sample showing dark. In addition, the other point is that the particles in this mixture are located in an oriented manner. Then, the higher concentration of NCC in a 1wt.% polymer (HEC) leaded to a shift from transition (combined: I+N) phase to a nematic phase.

Figure 4.9 also gives information about mixture (c); based on this picture, it can be said that the result of cross polarized experiment for this mixture is almost similar to sample (b). However, it is also acceptable to say that the percentage of bright area which can be observed in the picture is a bit more than what can be seen for sample (b) and it is reasonable because the concentration of colloidal part is increased. Therefore, it is expected to see more crystalline parts than it was formed for sample (b). Thus, sample (c) can be considered as a nematic polymer-colloid mixture which also shows more viscous behavior than the other samples previously have been discussed. The particles are located in an oriented manner which again proves that having a higher concentration of HEC can really have significant impact on the phase behavior of the mixture.

With respect to the obtained results for phase behavior of NCC-HEC mixtures for these three ranges, a simple phase distribution diagram can be plotted. Figure 4.10 shows the phase diagram for NCC-HEC mixtures.

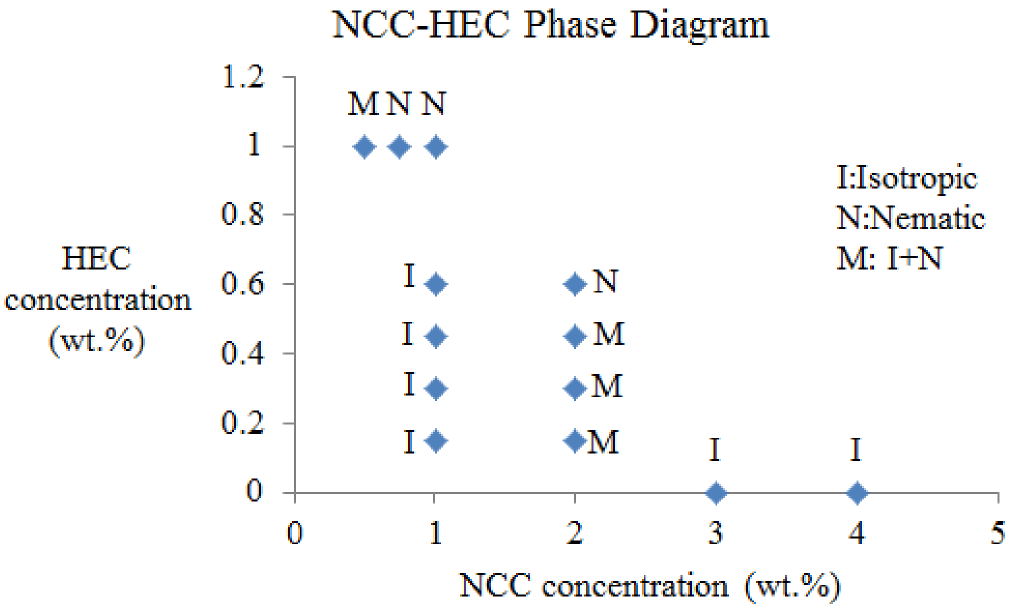


Figure 4.10 Phase diagram for NCC-HEC mixtures

In order to investigate how much viscosity background have been obtained from the polymer part in the mixture, it was necessary to investigate rheological behavior of HEC solutions when they are not yet mixed with NCC suspensions. So, rheology tests were carried out for a range of HEC solutions. As the solutions of HEC below 0.5 wt% were too runny, so, this range was selected for the experiment: 0.5, 1, 1.5, and 2 (all in wt. %). Figure 4.11 demonstrates the rheological behavior of the HEC solutions.

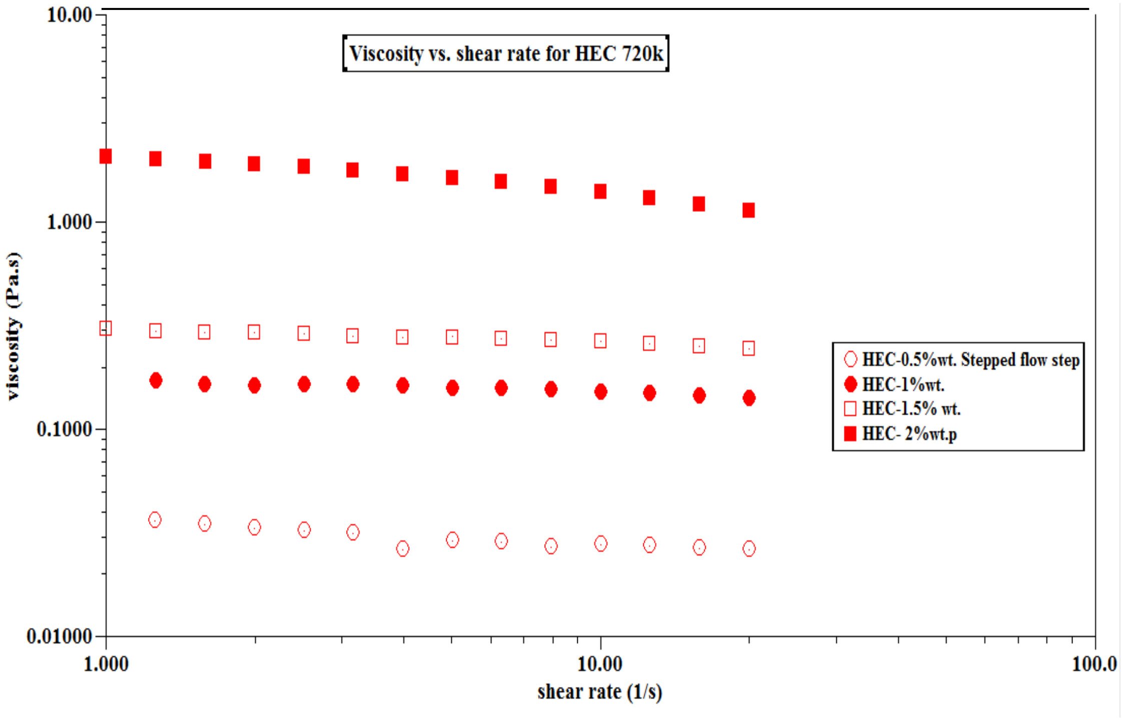


Figure 4.11 Viscosity vs. shear rate for HEC solution in different concentrations

The above figure shows the rheological behavior of HEC in different concentrations. As it can be understood from the figure, in general viscosity is almost constant by increasing the shear rate for all HEC concentrations investigated for the test. However, the amount of viscosity is increasing by increasing the HEC concentration. For the lowest concentration of HEC (0.5 wt.%), in the applied shear rate, viscosity smoothly decreases from 0.036 (Pa.s) to 0.0260 (Pa.s).

By increasing the concentration to 1wt.%, in overall the viscosity is higher than it was for 0.5 wt.% concentration. Again, there is a smooth decrease (from 0.169

Pa.s to 0.140 Pa.s) in viscosity by increasing shear rate which is obviously higher than the previous sample. It can be said that the viscosity is almost independent of the shear rate and shows Newtonian behavior.

When the HEC solution concentration is increased to 1.5wt.% viscosity is higher than two previous samples. For this sample also the viscosity shows very small change (decrease) by increasing the shear rate. Thus, rheological behavior of the solution can be almost considered as a Newtonian fluid.

For the last sample which includes 2wt.% HEC, viscosity results is obviously higher than those of other three samples and the curve shifted up. The whole range of obtained viscosity for applied shear rate is changing from 2.063-1.136 (Pa.s) which is totally different from the other samples. In this case, again viscosity is decreasing by increasing the shear rate. Therefore, respecting to this whole results obtained from rheological behavior of this polymer, it can be found that in a very low range of concentration (which is any concentrations equal or lower than 1wt.%), there is no strong viscosity background from the polymer while mixing polymers in this range to colloidal suspension (NCC samples).

In a study by Boluk et al. (2012), they showed that for NCC- HEC mixtures with 0.66 volume % NCC and 1 wt.% HEC the result for visco-elastic oscillation test within linear deformation rangewas as presented in Figure 4.12 [53].

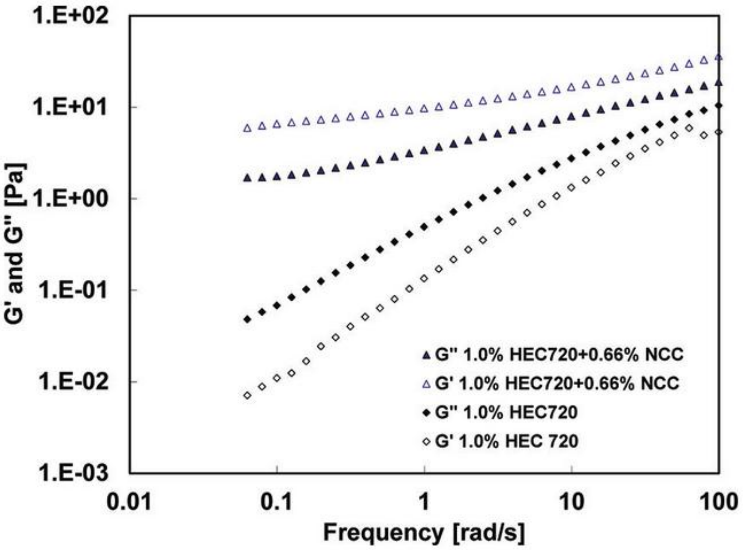


Figure 4.12 G’(ω) and G”(ω) 1wt.% HEC with and without presence of NCC [53]

From what can be observed in Figure 4.12, the HEC solution without the presence of NCC showed the loss modulus (G”) much higher than the elastic modulus (G’). For the measured frequency range, in HEC solutions without NCC, the dominant component is the viscous component; however, by increasing the frequency the increase in elastic component was steeper than viscous component.For this concentration of HEC (1wt.%) that they tried and the measured frequency range there could not be found any point with G’=G” which is also called cross over point. As they also indicated no terminal relaxation times and plateau regions can be observed in the measured frequency region [53].But when NCC was added to the system as can be inferred from Figure 4.12, G’ values of NCC-HEC mixture showed a plateau region and it was higher than the G” values at the measure frequency range. It can even be indicated that loss and storage modulus be inclined to converge at higher frequencies. When there is a plateau region in the G' curve it can be explained as most likely presence of some internal structures, such as aggregated fractal-like structures which discloses the gelation character of the NCC particles [53].

According to the fact that G' $\approx \omega^a$ and G" $\approx \omega^b$ and based on gel theory when $a = b = 0.5$ the gel point is obtained and when $a = 0$ and $b = 1$ final gel state is reached; they reported that for NCC-HEC mixture in the plateau range $a = 0.21$ and $b = 0.76$ which shows that the mixture is between gel point and final gel state [53].

As Boluk et al. explained there are two mechanisms which can be used to elucidate the remarkable enhancement in the rheological behaviour of NCC-polymer mixtures [53]. The first mechanism states that polymer-bridging of particles can cause weak NCC networks. At low ionic strength NCC suspensions which include negatively charged NCC particles are stable; but, by adding polymer to the system, polymer can adsorb on the NCC rod particles surfaces if NCC surfaces prefer macromolecules to aqueous medium. When polymer chains are long enough, some segments adsorb in the form of trains whereas tails extend into the solution and can adsorb on the other particles. The distance which long tails of macromolecules (polymers) can extend is about radius of gyration RG of polymers. So when the polymer concentration in the mixture increases the interparticle interactions by polymer bridging grow weaker. But, in Boluk et al. work they also tried isothermal titration calorimetry as a technique to indicate the thermodynamic parameters of interactions in the NCC-HEC mixture. This method is used to investigate the binding of macromolecules to small molecules. They reported that the interaction potential of HEC-NCC mixture is zero and rejected the possibility of adsorption of HEC on NCC [53]. As they indicated HEC macromolecules have no preference to replace surface bound water molecules by adsorption on NCC surface. Respecting to the fact that HEC is neutral polymer and can either accept or donate proton similar to NCC surface; so, there is just a slight chance of very weak adsorption of HEC on NCC surfaces through hydrogen bonding [53]. Hence, flocculation by bridging cannot be acceptable to elaborate rheological behavior of NCC-HEC mixture.

So, the second mechanism is the NCC particles flocculation by the depletion of nonadsorbing polymers. Then the rheological behavior of NCC-HEC mixture can be clarified by depletion flocculation. This means when macromolecules (polymers) do not adsorb at particle interfaces, the exclusion of the polymer segments from the particulate volumes leads to an effective "entropic" attraction between the particles and this called as the depletion interaction [53].

The qualitative depletion analysis was first formulated by Asakura and Oosawa [54,55].So, they first suggested the model which stated that the exclusion of polymer molecules leads to an effective attractive interaction between the particles. This model (also called AO model) and most of experimental works are for the regime in which the size of colloidal particles (diameter, r) is much bigger than the size of polymers (radius of gyration, R_G). This regime, where $r >> R_G$ is called "colloid limit". But there is also another regime (opposite limit) in which $r \leq R_G$ and this regime has been mainly investigated for the case of adding polymer to protein solutions to assist protein crystallization and is called as “protein limit” [56].This second regime ($r \leq R_G$) can be applied not only in proteins case but also for all nanoparticles when the size of the particles is smaller than R_G of nonadsorbing polymers. As Boluk et al. indicated for this second regime ($r \leq R_G$) instead of the term “protein limit” it is better to say “nanoparticle limit” which can better elucidate the situation [53]. NCC rods in one direction have an infinite plane profile and in the other direction they have a profile of sphere. So, in parallel orientation, with the condition of L (length) > R_GNCC rods still meet the colloid limit whereas in perpendicular orientation with w (width) <<R_G the rods are considered in nanoparticles (protein) limit [53].

In my work, the HEC 720k which was applied, as previously mentioned in chapter 3, had the R_G of 80 nm and NCC particles had length of 130 nm and diameter of 6 nm. Therefore, $r \ll R_G$ and the mixture falls into “nanoparticles limit”. In comparison to Boluk et al. work (1wt.% HEC and 0.66% volume fraction of NCC) in my work, for example, when NCC was used in 1wt% concentration (≈0.60% volume fraction) and HEC was 1wt.% the concentrations are almost the same. As it was showed in the cross polarized results in figure 4.9 it was completely obvious that there is an interaction in the system. So, it can be indicated that gel-like structure of NCC dispersion in polymer solutions was occurred as a result of the attractive interactions of particles in the presence of depleted nonadsorbing polymer (HEC 720k). Then, all the explanations were made for the Boluk et al. work can also fit in my case. Another point here is that the transition from dilute to semi dilute concentration for nano particles occurs at the volume fraction of $\Phi \leq (\Pi/4)\ (d/L)^2$ where d is diameter and L is the length of NCC rod shape particles. Therefore, in my work Φ or the volume fraction of transition concentration for NCC is 0.16 %. It means that even for the lowest concentration of NCC that I used in the mixtures (0.5wt.% NCC) the volume fraction is 0.3 % which is higher that the transition volume fraction and indicates that the NCC concentration is in semi dilute range and is above the dilute concentration range where the particles can scarcely contact each other.

4.3.2 NCC –dextran mixture

A high molecular weight dextran (2000kDa) was selected for the experiments. It was used as a non adsorbing neutral polymer to be mixed with NCC suspensions. As dextran was so runny in low concentrations even with this high molecular weight, so it was decided to prepare high concentration of dextran (10wt.%) for mixing with a range of (0.5,1,1.5 wt.%) NCC to more likely gets viscose NCC-dextran mixtures.

Rheological tests were carried out for the final samples. The results of flow test are all shown in Figure 4.13.

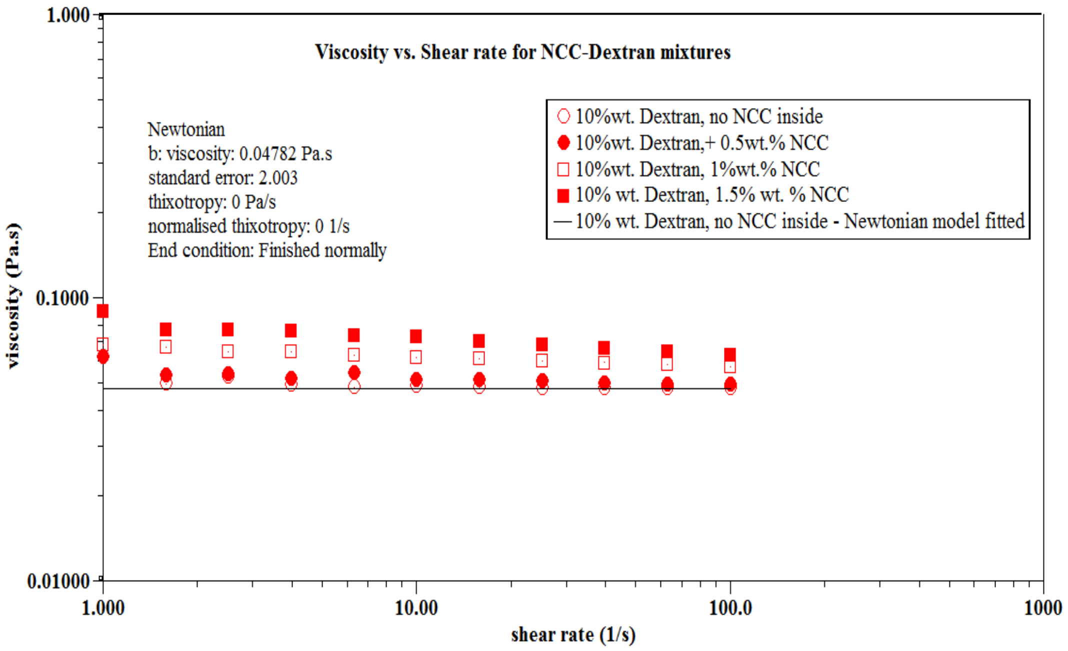


Figure 4.13 Rheological behavior of 10wt% dextran with and without NCC

Based on the results represented in Figure 4.13, rheological behavior of dextran can be discussed. First of all, although the concentration of dextran was high the samples were not showing the thickening behavior in rheological tests; this also could be found by easily shaking the samples. This fact is confirmed with rheology test which for the 10wt.% dextran solution with no NCC inside showed a very low amount of viscosity (0.0497 Pa.s) and no thickening behaviour. Another interesting point which can be inferred from the curve for dextran viscosity vs. shear rate is that the viscosity is almost totally independent from the shear rate. This Newtonian behavior is also proved with fitting a Newtonian model to the rheological data achieved for dextran with no NCC. In the figure, it can be seen that the data are well fitted to the line.

When 10 wt.% solution of dextran is mixed with a low concentration of NCC suspension (0.5wt.% of rod-like particles), it can be observed that for the applied range of shear rate (1-100 (1/s)), the rheological behavior of the colloid-dextran mixture is approximately the same as of dextran with no colloid particles in it. Which means by adding NCC suspensions to the polymer solutions no gel like or thickening behavior was observed. The overall viscosity is still too low and as the Figure 4.13 reveals the Newtonian model fitted to the data for dextran with no rod-like particles can be considered as an appropriate fit for these data (10wt.%Dextran-0.5wt.%NCC) as well. So in this applied shear rate range these two curves are behaving the same except the first point for the mixture which shows higher viscosity which might be because of instrumental error.

By increasing colloidal particles to 1wt.%, the overall viscosity is still too low which indicates the mixture is a runny fluid. However, the viscosity is a bit higher than two previous samples which included 0 and 0.5 wt% NCC. So, here, the total number of colloidal rod-like particle increased which leaded to a higher viscosity for the mixture. It can also be said that the viscosity is independent of shear rate (for the given shear rate range) and the fluid is showing Newtonian behavior for the applied experiment condition.

By adding higher amount of NCC (1.5wt.%), the viscosity getting increased but still too low to be considered as a viscose sample. As it is shown in the figure, the viscosity even in the higher amount of it which obtained for the lowest applied shear rate (1.0, 1/s) is 0.9010 Pa.s. This one is also close to a Newtonian fluid behavior but not as much as it was for the previous mixtures which lower amount of NCC rod-like particles (0.5 and 1 wt.%). So no gel-like or thickening behavior was seen for tested dextran and the previously mentioned range of NCC.So, in order to indicate the phase region for each sample was tested here and to explain the phase behavior the result of a same study by Edgar et al. has been reported here. They studied the effect of2000 kDa dextran (Rg =34 nm) on the phase behaviour of cellulose nanocrystals (average length L = 110 nm, D = 10 nm), prepared by acid hydrolysis of cotton filter paper [30].So they obtained the partial phase diagram of dextran-NCC suspensions by number density of coils (multiplied by R_G^3) versus number density of rods (multiplied by R_G^3). They used R_G^3 to make the density numbers dimensionless [30]. Later, in a book written by Lekkerkerker et al. this phase diagram is redrawn in a simpler way and a new phase diagram for dextran-NCC mixture based on the Edgar et al. results is provided in volume fraction of polymer (dextran solutions) versus volume fraction of NCC suspensions [57]. Figure 4.14 shows the phase diagram for dextran –NCC suspensions drawn by Lekkerkerker et al. [57].

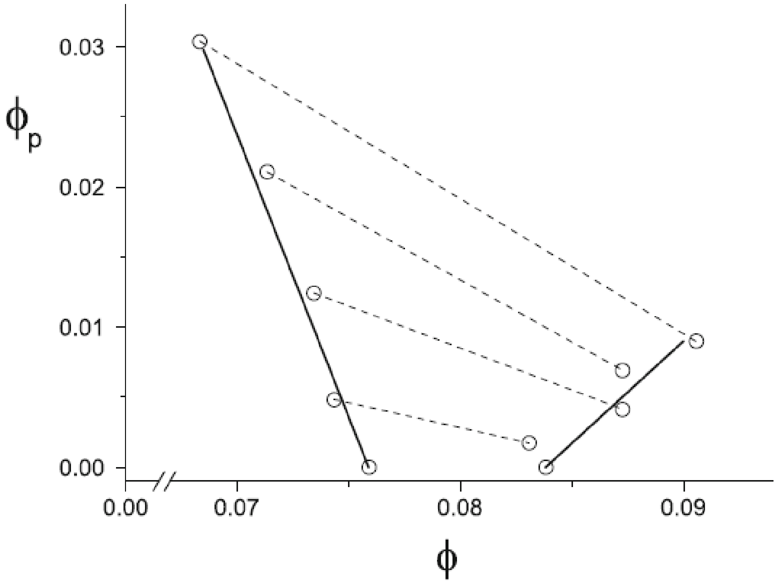


Figure 4.14 Dextran-NCC phase Diagram; Φp: polymer volume fraction,

Φ: NCC volume fraction [57]

Regarding to this phase diagram (Figure 4.14) and Edgar et al. work, adding dextran to the NCC suspensions in biphasic region caused a considerable widening of coexistence region in the phase diagram [30,57]. In this phase diagram, the dextran volume fraction (Φp) is changing from 0-0.03 and the NCC volume fraction (Φ) is changing from 0.07-0.09 and the diagram has been divided into three different regions the left side region is the isotropic area (I), the middle region is the combination area (I+N), and the right side region is the Nematic phase area. In my work, the same dextran (MW=2000 kDa and R_G=34nm) is used but the concentration of dextran is constant for all the samples and as previously mentioned that is 10wt%. The density of dextran in applied molecular weight (2000kDa), for 10wt.% is reported in literature to be 1034 (kg/m^3) by Akashi et al. (2000) who measured acoustic properties of aqueous dextran solutions for six different molecular weights (10400-2000000 Da) and in four different concentrations(5-20wt.%) [58].So, respecting to the dextran density (1034kg/m^3), the volume fraction of dextran which is used in my work can be calculated as $\Phi p=9.66*10^{-3}\approx 0.009$. The volume fractions of the NCC suspensions used in three concentrations 0.5, 1, and 1.5 wt.% can also be calculated as 0.3, 0.6, and 0.9 respectively. Now the mixtures can be compared to the results provided by Edgar et al. and redrawn phase diagram of those results by Lekkerkerker et al.

Therefore, it can be said that with respect to Figure 4.14, the mixtures tested in my work ($\Phi p\approx 0.009$ and $\Phi=0.3$-0.9) can be considered either in the combined phase region (I+N) or nematic region and they are not in isotropic region definitely. The reason that the thickening behavior was not observed in my work is because of the dextran structure. If POM tests were considered for these mixtures the I+N and nematic phase behavior could be proved by the pictures. Therefore, for dextran-NCC mixtures, with respect to the Edgar and Gray work, it can be said that the exclusion of dextran chains occurs in the solution from the aggregated NCC nanoparticles [30].

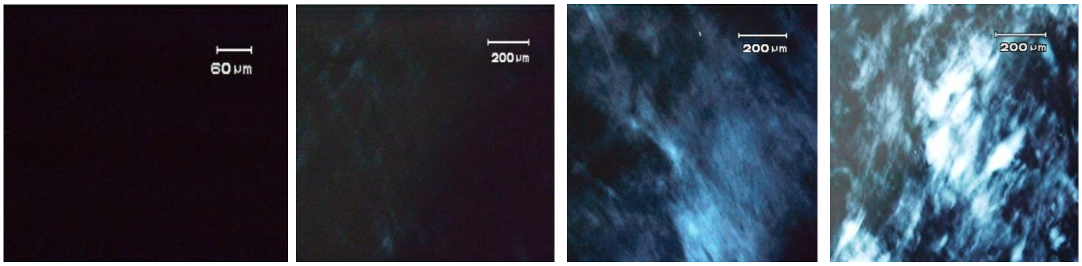
4.3.3. NCC-CMC Mixtures

CMC with molecular weight of 700k was selected for the experiments. As this polymer is a cellulose base negatively charge which is the same charge as rod-like particles so it is more likely to get the depletion interaction for the mixtures include CMC and NCC in different range of concentration. For the first set of experiments a constant concentration for NCC (1wt.%) and a range of 0.5,1,1.5, and 2 (all in wt.%) for CMC were selected and for all samples 10mMNaCl was added as ionic strength. Figure 4.15 shows the final samples.

Figure 4.15 NCC –CMC700k mixtures including 10mM NaCl

4.3.3.1 Phase behavior

As it was previously indicated NCC 1wt% is an isotropic suspension; so, for these new NCC-polymer mixtures POM was implemented to see the effect of adding a negatively charged non-adsorbing polymer on the phase behavior of the system. The results of POM experiment is presented in the following figure (see Figure 4.16).



a)1 wt.% NCC 0.5 wt.% CMC

b)1 wt.% NCC 1 wt.% CMC

c) 1 wt.% NCC 1.5 wt.% CMC

d) 1 wt.% NCC 2 wt. % CMC

Figure 4.16 POM results of NCC –CMC700K mixtures (including 10mM NaCl)

By looking at the results obtained from POM for these mixtures the first possible conclusion is that all phases from an isotropic to a nematic can simply be observed. For sample (a) the result shows that the sample does not include any liquid crystal and it all turned dark while doing light polarization microscopy. This can be because of the amount of CMC which lower than the concentration is needed for the mixtures to have the strong interaction to change the phase behavior of colloidal particles. Therefore, this mixture is considered as an isotropic sample which does not have specific orientation. The macroscopic rheological behavior does not express a runny sample; however, it does not look like a gel like sample which makes sense because of low concentration for both polymer and NCC. The rheological properties and behavior of the sample will be discussed later in this chapter.

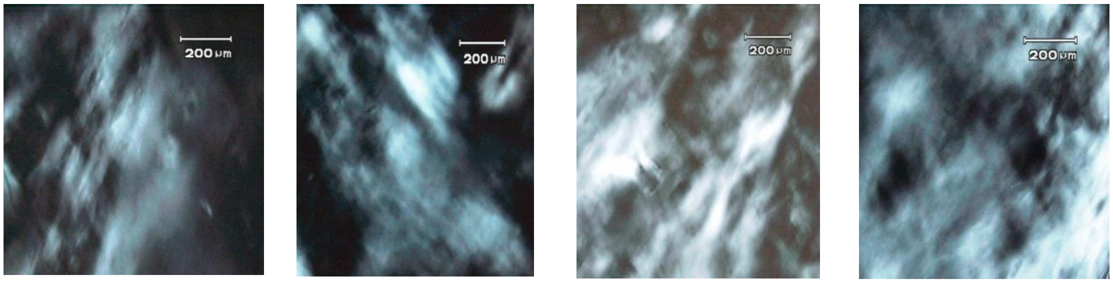
Sample (b) based the results in Figure 4.16, has not turned to a complete dark picture while doing applying polarization by microscope. However, the figure is not disclosing a significant amount of liquid crystals. Everything is the same as it was for sample (a) except the CMC concentration which was increased to 1 wt.%; and this caused to a change in phase behavior of the system however, it is not that recognizable. But these bright areas in the picture especially in the left side of picture for sample (b), indicate that the mixture is starting to form liquid crystals even though the amount is low. So, based on this fact it can be said the increasing the CMC concentration has influenced the phase behavior of sample. This can be the start point of the biphasic phase (combination of isotropic and nematic: I+N) and it can be concluded that this concentration is exiting from isotropic phase area. Therefore, it is logical to consider a little change in the orientation of particles.

Sample (c), based on the POM result strongly proves that liquid crystals have been formed in the mixture. Here, the CMC concentration is increased to 1.5 wt.% which apparently is high enough to move the mixture totally toward the biphasic phase (I+N). In compare to sample (b) it can be found that a bit change in CMC concentration can have a significant impact on phase behavior of the mixture. Main area in the picture turned to bright which is an evidence of liquid crystals; though, there are still parts in the picture which showed up dark. Hence, the mixture cannot be considered as a nematic sample but is it acceptable to state that particles are partially oriented. The effect of CMC enhancing in the mixture can be assumed as causing stronger interaction in this case (both negatively charged rod-like particles and polymer). This interaction is a function of different parameters such as polymer molecular weight, particles and polymer concentration and also the rheological behavior of the mixture.

For the highest CMC concentration, sample (d) the phase behavior of the mixture is noticeably changed. The CMC concentration was 2wt.% which is definitely the reason of shifting the sample to a new phase region. Respecting the POM result, almost the whole area of the picture taken by microscope is bright which can be the evidence of high amount liquid crystals formation in the sample. Thus, a significant interaction between polymers and rod-like colloidal particles must be expected. In fact, the increase in polymer concentration has leaded to this noticeable interaction. Sample (d) can be assumed in nematic region so the phase is totally oriented for this sample. Also the rheological behavior of the sample can be related to the interaction between particles and polymers; however, the relationship between rheological behavior and interaction are not discussed that much in the literature [3]. The rheological properties of this sample and the other ones (a-c) will be discussed later in this chapter.

As it was found, although the range did not include very high concentrations, enhancing CMC concentration in the mixture for this level of NCC (1wt.%) caused considerable impact on the phase behavior of the final mixture. It is also interesting to find out how increasing CMC concentration impacts on the polymer-NCC mixture for a lower level of NCC concentration. Then a lower NCC concentration (0.5wt.%) was prepared and mixed with CMC to investigate the effect. The new range of CMC selected as 1.5, 2, 2.5, and 3 wt.%; again, 10 mM NaCl was added to each sample (see Figure 4.17).This time experiments started from higher CMC just to increase the possibility of having nematic phase and more noticeable interaction between particles and polymer. Figure 4.18 illustrates the POM experiment results for this new range.

Figure 4.17 NCC-CMC700k mixtures for cons. NCC at 0.5wt.% (including 10 mMNaCl)



a)0.5 wt.% NCC 1.5 wt.% CMC	**b)**0.5 wt.% NCC 2 wt.% CMC	**c)** 0.5 wt.% NCC 2.5 wt.% CMC	**d)** 0.5 wt.% NCC 3 wt. % CMC

Figure 4.18 POM results of NCC-CMC700K (including 10 mM NaCl)

Based on the results showed in figure 4.18, first conclusion is that none of the solutions are behaving as an isotropic one. Because as it is obvious in the figure, during the light polarization experiments none of them turned totally to a dark picture.

For sample (a), there 1.5wt.% of CMC in the sample which made the solution not to locate in isotropic phase area. The amount of NCC is low in this sample and if there was no CMC in it would definitely locate in isotropic region. But this experiment shows that how significant can 1.5wt.% CMC adding act in the mixture. In fact, the interaction between NCC rod-like particles and CMC has leaded to form liquid crystals in the sample and then these crystals could rotate the light in light polarization experiment. Although the picture is bright in some parts; there is still another dark area in the picture. This means that sample (a) is in biphasic region which is a combination of isotropic and nematic behavior. When this sample is compared to sample (c) in figure 4.16, it can be included that both sample is almost behaving similarly however they have different amount of NCC. It can be explained as they have same amount of CMC which seems high enough to have impact on the final interaction between particles and polymers in the mixture. So, for sample (a), particles are involved in partial orientation. The rheological behavior of the sample and the possible relation between the rheology and interactions which eventually caused biphasic phase behavior will be discussed later.

For sample (b), a change in phase behavior can be recognized from the Figure 4.18. In compare to sample (a), sample (b) shows more bright area in the picture which is the sign of more liquid crystal formation in the mixture. Therefore, the increase in CMC concentration from 1.5wt.% to 2 wt.% could lead to form this higher amount of liquid crystals and eventually cause the mixture shift from I+N combined phase to a nematic phase region. This behavior can be also compared to that of sample (d) in Figure 4.16.This comparison indicates that the nematic behavior in sample (d) (Figure 4.16) is more noticeable and that is logical because the rod-like particles concentration is higher in that sample and for a high concentration of CMC it leads to formation of more liquid crystals. So, sample (b) here, based on nematic phase behavior has complete orientation for the particles.

In sample (c), again the CMC concentration is increased for the same amount of NCC. As it was expected, the picture shows almost totally bright area which is a nematic phase behavior. Respecting to higher amount of CMC, the stronger interaction has been occurred in the system which is resulted in formation of more liquid crystals. The final mixture is very viscous; the rheological behavior investigation will be discussed later in this chapter.

For sample (d), still same concentration of NCC is interacting with higher concentration of CMC which is increased from 2.5wt.% to 3 wt.%. So based on the information was obtained from previous sample, this new one with higher amount of CMC should express extremely nematic behavior in light polarization. This expectation was confirmed by the experiment and the picture (Figure 4.18 d) demonstrates this fact. So, sample (d) is in nematic phase region with total orientation. Again it can be explained by effect of adding more CMC on the final interaction between polymers and rod-like particles. This sample also shows high viscose behavior while working with sample.

Regarding to the results obtained through POM experiment, for the tested range of the mixture a simple phase diagram can be plotted. Figure 4.19 depicts NCC-CMC mixtures phase diagram.

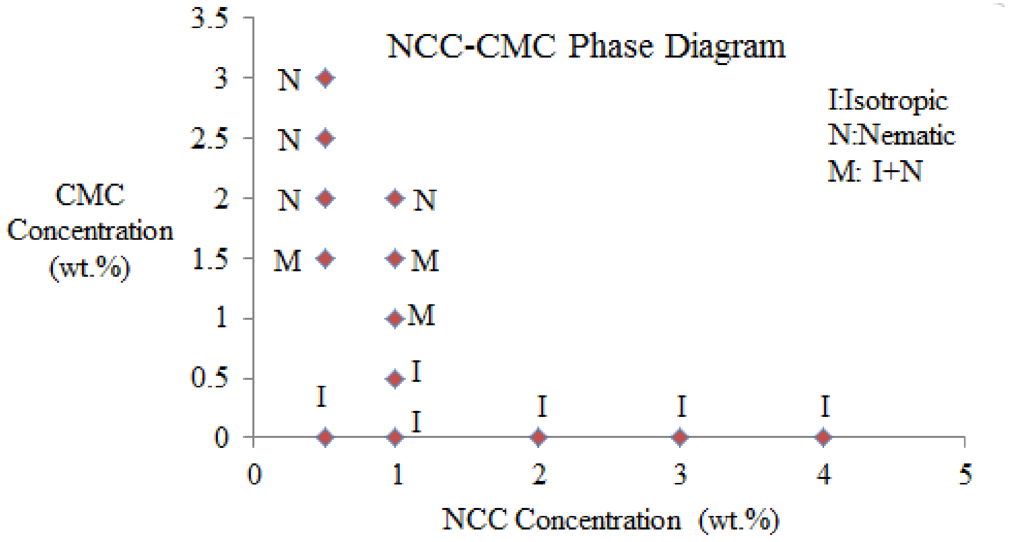


Figure 4.19 Phase diagram of NCC-CMC 700 kDa mixtures

As it can be seen, different phase behavior of NCC-CMC mixture is summarized. The points shown by (I) label introduce the isotropic phase behavior, the points labeled by (M) introduce combined phase behavior (I+N), and the points labeled by (N) reveal nematic behavior.

In order to find the relation between phase behavior and rheological behavior of the sample, rheology experiments were carried out for NCC-CMC700k mixtures. Results are shown and discussed in the following section.

4.3.3.2 Rheological behavior

4.3.3.2.1 Effect of changing CMC and NCC concentration in the mixture

For further investigation on the impact of adding CMC 700kDa to the NCC solutions, it can be useful to examine the rheological behavior of CMC solutions to see what happens in rheological behavior of CMC 700k when the concentration is increasing. Thus, a wide range of CMC was selected as following: 0.5, 1, 1.5, 2, 2.5, 4, 6 (all in wt.%).

The oscillation frequency step test was carried on for CMC samples and the results for elastic modulus (G’) and loss modulus (G”) are exhibited in Figure 4.20. In order to recognize them better, G’ and G” are shown separately in figure 4.20 (a) and Figure 4.20 (b) respectively. So, based on the results obtained from the frequency step oscillation test for CMC samples (Figure 4.20 (a)), it can be said that elastic modulus is increasing for each CMC concentration by increasing the angular frequency. For the lowest concentration, G’ changes from 1.264 E-3 (Pa) to 4.056 (Pa) for the range of angular frequency tested (0.1-100 rad/s). When the CMC concentration increased to 1wt% the G’ increased considerably as it can be inferred from the figure. The G’ curve shows an increasing behavior by increasing the angular frequency.

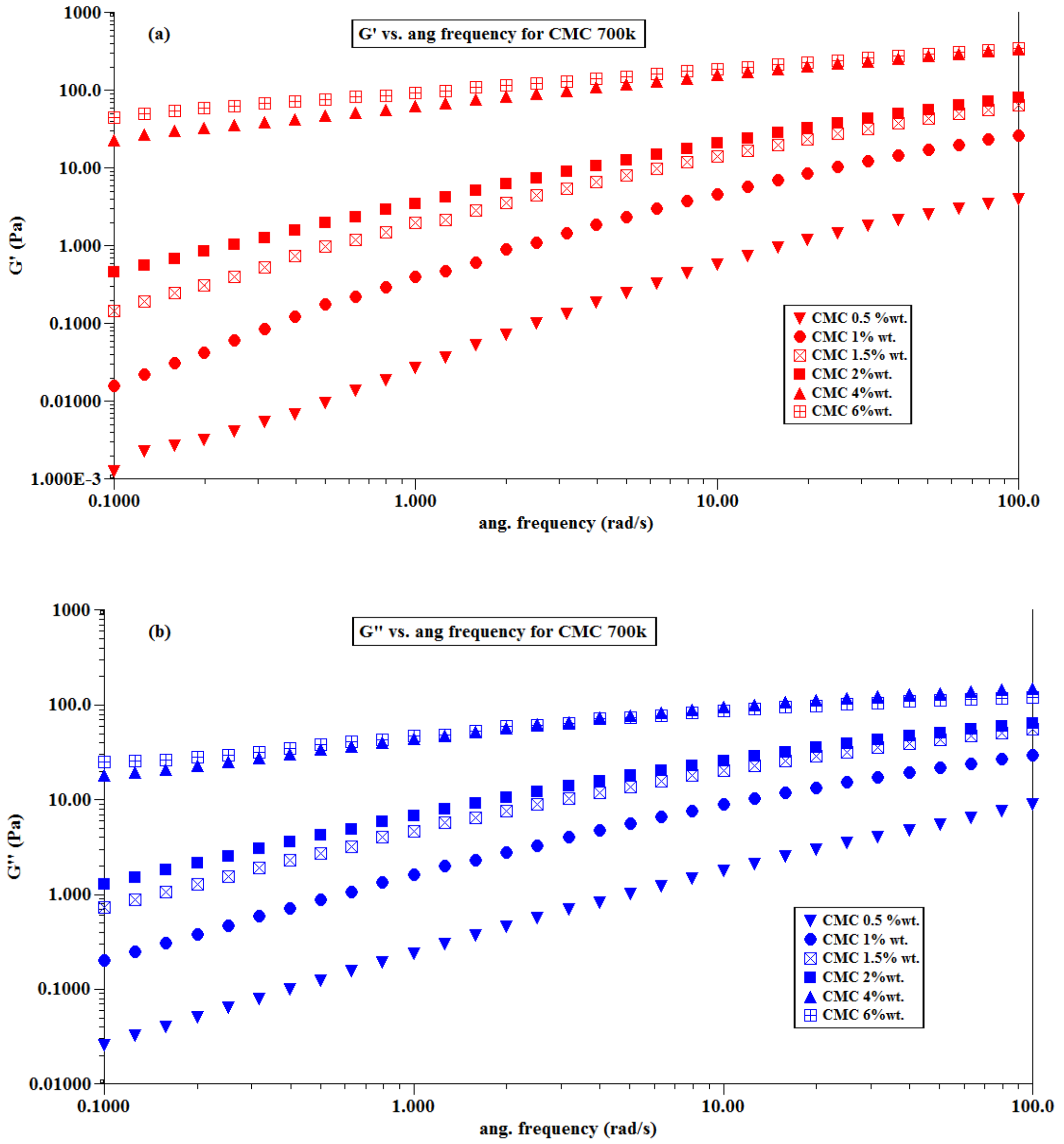


Figure 4.20 Changing elastic modulus and loss modulus vs. angular frequency:

a) G’ vs. angular frequency b) G” vs. angular frequency

For this concentration the curve is as steep as it was for the previous one (0.5 wt.%). This time in the tested range of frequency the elastic modulus is changing from 0.01556 Pa to 25.85 Pa which shows a significant increase for G’. For the next CMC sample which includes 1.5 wt.% of CMC solutions the same trend can be observed and G’ is changing from 0.1462 Pa to 55.54 Pa for the tested range of frequency. When the concentration is increased more, the 2wt% CMC sample shows higher G’; however, the slope of the curve is different. In fact, based on the results, the data for 2wt% CMC are so close to those of 1.5wt.% CMC when the frequency reaches to 4 rad/s and after that they are even closing more but not completely overlapping.

By increasing polymer concentration to higher steps such as 4 and 6wt.% the elastic modulus shows the same behavior and increases by increasing the angular frequency; however, the distance between 4wt.% CMC G’ curve and 2wt.% CMC G’ curve is more than that of between 2 wt.% and 1.5 wt % CMC. In addition, the data for 4wt.% and 6wt.% are so close together and when the frequency increases the distance between the two curve decreases. For 4wt.% G’ changes from 22.8 Pa to 338 Pa and for 6wt.% G’ changes from 45.26 Pa to 346.6Pa.

Now, by looking at Figure 4.20 (b), it can be inferred that G” is also increasing by increasing the angular frequency. In 0.5 wt.% concentration curve, G” changes from 0.02538 (Pa) to 8.999 (Pa) for the same range of angular frequency mentioned previously. This numbers for G” demonstrate loss modulus is much higher than elastic modulus. By increasing CMC concentration to 1wt% the G” has the same behavior as steep as the lower concentration; however, the curve has noticeable distance with previous one. G” changes from 0.1972 Pa to 28.92 Pa. which in compare to the G’ for the same CMC concentration shows that the viscous component (loss modulus) is the dominant component; nevertheless, the results for G’ and G” are getting too close as the frequency increases.

When the CMC concentration is increased to 1.5 wt.% G” changes from 0.7314 Pa to 55.54 Pa but for the G’ in the same concentration the start point and end point were 0.1462 Pa to 64.38 Pa which shows that by increasing frequency G’ increases more than G” and in that range elastic component is the dominant component.

For 2wt.% CMC concentration, G” changes from 1.29 Pa to 64.53 Pa which is obvious that in higher frequencies it is getting so close to that of 1.5wt.% CMC. For this one, G’ as it shows in Figure 4.20 (a) is also reached to a higher final point (0.4560 Pa to 81.23 Pa) which means again for a range of frequency G” is the dominant component and once the frequency is increased more G’ becomes the dominant one.

For 4wt.% G” is still having the same behavior which is getting increased by increasing the frequency (from 18.20 Pa to 148.5 Pa). However, in compare to range of changing G’ for the same tested range of frequency in the whole range G’ is higher than G” which means the dominancy of elastic modulus for this high concentration of CMC. By increasing the CMC concentration to 6wt.%, G” goes from 24.82 Pa to 120.6 Pa which is in some parts even lower than the result for 4wt.% and this can be inferred from the figure. Besides, for this high concentration of CMC,G’ plays the dominant role as it is obviously higher than G”. 4 and 6wt.% of CMC are totally viscose samples and they behave like gel. It means selecting 3wt.% CMC as the highest concentration for the previous section and preparing mixtures with NCC was an appropriate choice.

After the rheometry results for CMC in different concentrations were known; the effect of having NCC and CMC together could be investigated. So, the oscillation frequency step tests were carried out first for the mixture of 1wt.% NCC and 0.5, 1, 1.5, 2 (all in wt.%) CMC. Figure 4.21 shows the results of this experiment.

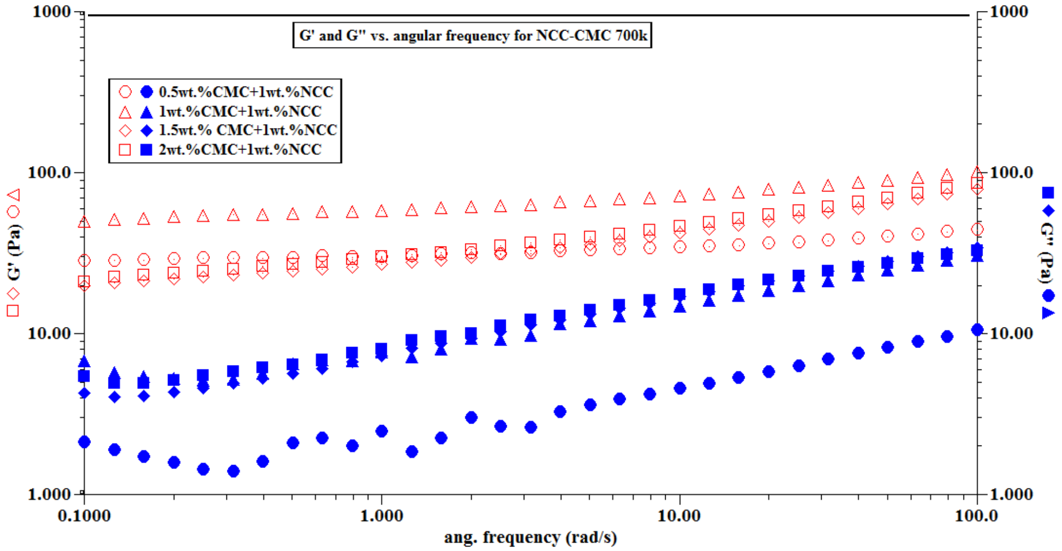


Figure 4.21 Visco-elastic behavior of NCC-CMC 700 mixture for const. 1wt,% NCC

Based on the results obtained from oscillation tests for NCC-CMC mixtures, the first obvious conclusion is that for all mixtures tested the G' data are located upper than G" data which demonstrates that elastic (storage) modulus is the dominant component for all of them. In addition, it can be found that there is no cross over point (G'=G") for this range of NCC-CMC mixtures. Furthermore, the results show that for lowest CMC with 1wt.% NCC inside, the amounts obtained for viscose (loss) modulus are considerably lower than those of higher CMCs with 1wt.% NCC inside. Once the CMC concentration is increased from 0.5 wt.% to 1, 1.5, 2 wt.% the other three higher concentrations behave almost the same and for some frequencies they are extremely close to each other. Comparing these G” results to the results obtained from POM for these mixtures, it reminds that through POM the behavior of the mixture with lowest CMC was noticeably different from the rest of samples and it completely turned to a dark picture. However, to explain the sample behavior both G’ and G” results should be considered. By looking at the results for G’ (elastic-storage modulus), it can be inferred that the higher amount obtained for G’ belongs to 1 wt.% CMC with 1wt.% NCC inside and it is increasing slightly by increasing the frequency. The behavior of mixtures including 1.5 and 2wt.% CMC are very close to each other; they both have slight increase by increasing the frequency. However, the curves for 1.5 and 2 wt.% CMC (1 wt.%NCC inside) are a little steeper than the curve for 1 wt.% CMC. The G’ result for the mixture with lowest amount of CMC (0.5wt.%) shows that for this mixture G’ is almost independent of frequency and for frequencies lower than 2rad/s G’ is higher than those of mixtures with 1.5, 2wt.% CMC and when the frequency is more than 2 rad/s G’ curve is located below the curves of those two mixtures. Generally, in all the G’ curves in for this range of mixtures, a plateau region can be observed especially for the mixtures including 0.5 and 1wt.% CMC solutions (1wt.% NCC inside); the presence of this plateau region in G’ curve states the possibility of existence of some internal structures, for instance, the aggregated fractal like structure which reveals the gelation character of NCC rod-like particles [53].

To consider the behavior of both G’ and G” for each mixture, another component can be implemented. This component is defined as tan δ=G”/G’, where δ is the phase angle. So for the set of tested mixture, Figure 4.22 illustrates the change in tan δ by increasing angular frequency.

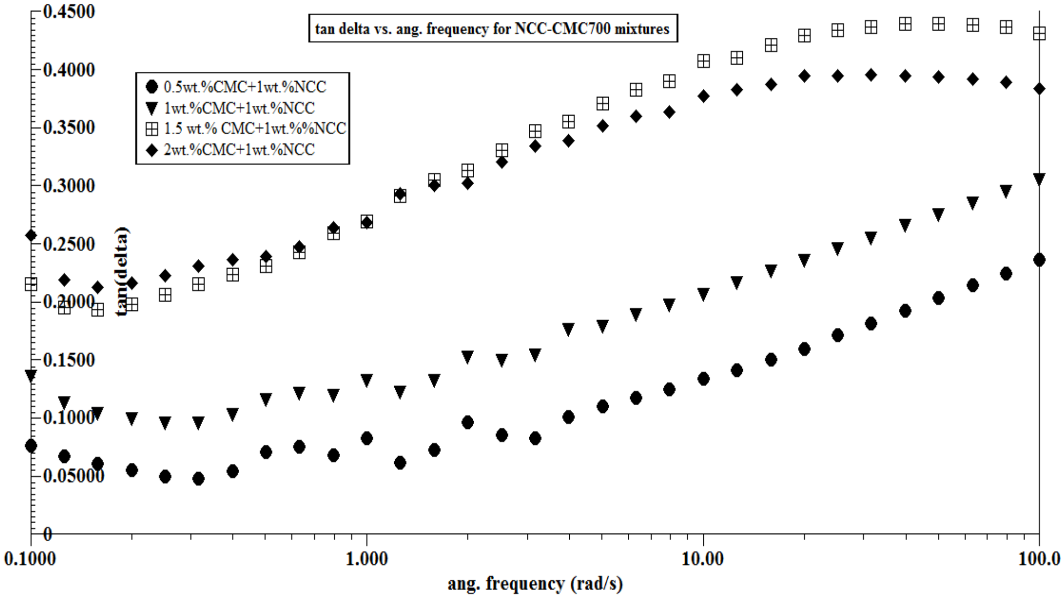


Figure 4.22 Angular frequency dependence of tan δ vs. for CMC700- NCC 1wt.%

With respect to these results, it can be inferred that tan δ is increasing by increasing the angular frequency for all mixtures. However, when the CMC concentration increased from 0.5 to 1 wt.% and then to 1.5 there is a distance between curves and the amount of tan δ increase but for the highest concentration of CMC the behavior of the curve and tan δ is almost close to the mixture with 1.5wt.% CMC except for the frequencies greater than 1.5 rad/s which tan δ for the mixture with 2 wt.% CMC is lower than the result for mixture with 1.5wt.% CMC. All the results show that for all samples tan δ is lower than 1 which means

G”/G’ <1 and this confirms that the storage modulus is the dominant component. Also for the POM results of these mixtures, sample (a) behaved as an isotropic mixture, and by increasing the concentration sample (b) moved from isotropic region and just entered the biphasic area, sample (c) completely showed the behavior of I+N phase and by more increase in polymer concentration, sample (d) showed a nematic phase behavior. The POM result for sample (c) and (d) were too close to each other and different from lower polymer concentration. Another consideration which can be taken into account is that by comparing these rheological results to those of CMC (no NCC inside) it is obvious that adding NCC to CMC samples make the CMC solutions show different rheological behavior. For instance, when CMC solutions (no NCC) were tested for low concentration such as 0.5 and 1wt.% G”/G’ was greater than 1 which means (tan δ)>1 and dominancy of viscose modulus. But, when 1wt.% NCC is added to the system the interactions between rod-like particles and CMC make the mixture to have tan δ<1 for the whole range of tested frequency and the dominancy of storage modulus. For 1.5 and 2wt% CMC (no NCC) first the tan δ>1 and then by increasing the frequency it becomes equal to 1 (cross over point) and then tan δ<1 which shows the dominancy of viscose modulus in the first part and dominancy of storage modulus in the second part. But by adding 1wt.% NCC to the samples the only dominant component for the whole frequency range tested is just storage modulus.

The rheological behavior of the mixtures with 0.5wt.% NCC suspensions and 1.5,2,2.5,3, 3.5 wt.% CMC solutions were also tested for further investigation. Figure 4.23 shows the oscillation frequency step results.

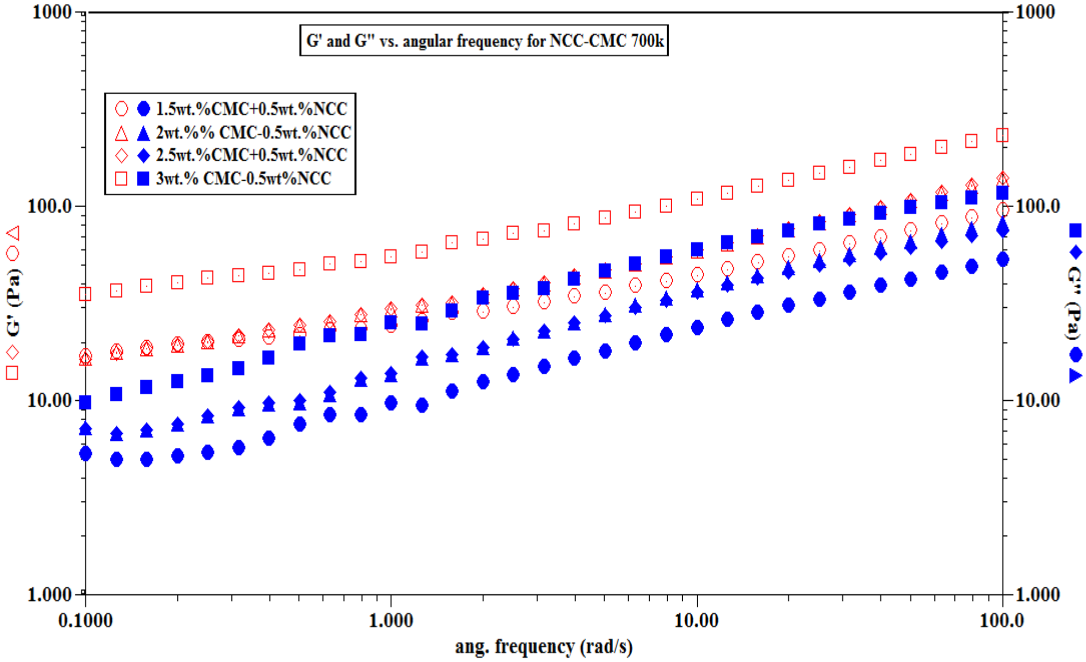


Figure 4.23 Angular frequency dependence of G’ and G” for CMC-NCC mixtures

Regarding to the Figure 4.23, it is obvious that for each sample G’ is higher than G”. Hence, the dominant component for all samples in this range is again storage modulus. Except a few points for all samples it can be observed that G’ and G” are increasing by increasing the frequency. For sample (a) G” has the lowest amounts in whole range of tested frequency. By increasing the concentration to sample (b) G” also increases and there is a distance between the curve of G” for sample (b) and sample (a). However, when the concentration is increased more, the results G” for sample (c) is almost the same as the result for sample (b) and there is kind of overlapping. By increasing the polymer concentration to the highest level, again G” is getting increased and makes a distance between these new results and those of sample (b) and (c).

For G’ analysis, it can be observed that for sample (a), (b), and (c) the beginning points of the curve is almost the same till the frequency gets around 0.25 rad/s and after that the curve for sample (a) does not behave as steep as those of sample (b) and (c). However, sample (b) and (c) have almost the same results for G’ for the tested frequency range. In sample (d), the G’ curve gets higher amount than the previous samples and there is a noticeable distance. So, the storage modulus has the highest amount in sample (d) which includes the highest CMC concentration. Again, in this set of samples, it can be seen that G’ has a plateau region; this time plateau region is in the beginning of the G’ curve. Similar to the previous set of samples (1wt.% NCC-CMC) the presence of this plateau region in G’ curve might be because of some internal structure such as aggregated fractal-like structure in the system which shows the gelation behavior of the NCC particles [53].

Thus, adding NCC even in this low concentration made the polymer solutions showing different rheological behavior. Figure 4.24 shows comparison of rheological behavior between two CMC concentrations including 0, 0.5, and 1 wt.% NCC.

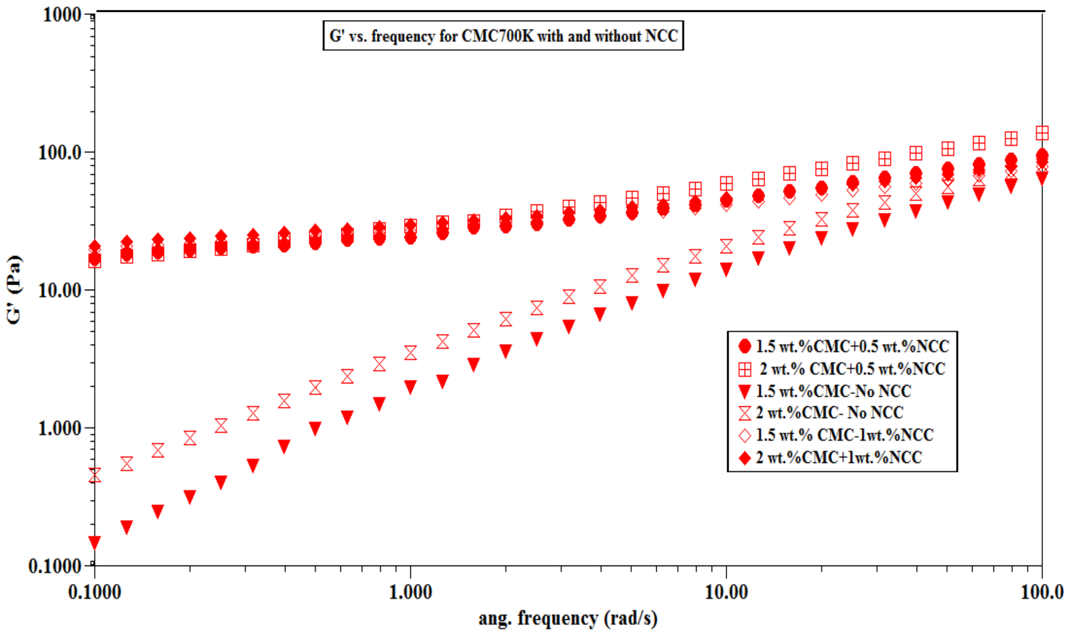


Figure 4.24 Comparing G' for two concentrations of CMC 700k with and without NCC

As it is illustrated in the figure, the elastic modulus is low for polymer samples without NCC inside them and there is strong dependency between G' and angular frequency; so that is why the curve for the polymer samples is sharp. On the other hand, by adding NCC to the samples, G' increases while the dependency on angular frequency reduces. As it is clear from this figure, the impact of adding NCC to CMC samples (1.5 and 2 wt.%) on the rheological behavior does not make that much change for from NCC 0.5 wt.% to NCC 1wt.% as the results of POM even showed almost the same configuration. Hence, it can be said that adding NCC to the polymer samples leaded to a strong interaction between rod-like particles and polymers which caused considerable change in both phase and rheological behavior of the system. NCC-CMC mixtures exhibited totally viscose behavior while doing rheological measurements and the appearance of plateau region in G’ curve after adding NCC to the CMC solution is also another reason for the presence of internal and aggregated structure in the system.

4.3.3.2.2 Interaction between NCC and CMC

As it was previously mentioned in this chapter the transition from dilute to semi dilute concentration for nano particles occurs at the volume fraction of $\Phi \leq (\Pi/4)(d/L)^2$ where d is diameter and L is the length of NCC rod shape particles. It also mentioned that in my work Φ or the volume fraction of transition concentration for NCC is 0.16 % and the volume fraction of NCC suspension in these two range of NCC-CMC mixtures were 0.3 % and 0.6 % which are both in semi dilute region. So it can be said that the rheological and viscoelastic characterization of suspensions of semi-dilute NCC in CMC polymer solutions demonstrated that addition of rod-shaped nanoparticles, even at the onset of semi-dilute concentration, significantly altered the rheological behaviour of the CMC solutions. As it was explained for the NCC-HEC mixtures, again for explaining the interaction between NCC particles and CMC chains two possible mechanisms can be considered [53]. The first mechanism indicates that polymers bridging of particles can lead to have weak NCC networks. So when the polymer is added to the system, in case NCC surfaces rather macromolecules to aqueous medium polymer can adsorb on the NCC rod particles surfaces. When there are long enough polymer chains in the mixture, some parts adsorb in the form of trains but tails extend into the solution adsorbing on the other particles [53]. And as was also mentioned previously, long tails of macromolecules (polymers) can extend into a distance about R_G of polymers. Therefore, increasing the polymer concentration in the mixture decreases the polymer bridging interactions [53]. CMC is an anionic polymer and it logically it is predicted that it does not adsorb on the surface of NCC particles because the adsorption of this negatively charged polymer on the anionic sulphate groups contained NCC cannot be desirable electro-statically [53]. And as it is explained in Boluk et al. work, when there is adsorbing polymer in the system, 1% wt. concentration of polymer is too high to observe bridging flocculation because polymer bridging happens at low surface coverage and polymer addition of 0.0001 wt.% [53].

The second mechanism indicates depletion of non-adsorbing polymers which causes the flocculation of NCC particles. This mechanism, AO model, and three different terms: “colloid limit”, “protein limit”, and “nanoparticle limit” was explained in the NCC-HEC mixtures section in this chapter. So, regarding to those definitions, in my work, the CMC 700k, as previously mentioned in chapter 3, had the R_G of 280 nm and NCC particles had length of 130 nm and diameter of 6 nm. Hence, $r \ll R_G$ and the mixture falls into “nanoparticles limit”. Therefore, it can be stated that gel-like structure of NCC dispersion in polymer solutions was happened because of the attractive interactions of particles in the presence of depleted non-adsorbing polymer (CMC 700k). In other words, this high range of CMC concentration (0.5-3 wt.%) can only induce depletion interactions in the mixture of CMC and NCC particles. As it is depicted in Boluk et al. work, the semi-dilute NCC particle suspension exhibits behaviour like that shown in Figure 4.25 in the presence of CMC 700k solutions [53].

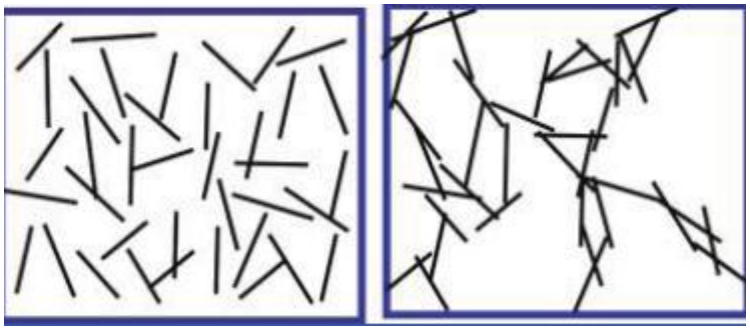


Figure 4.25 Semi-dilute NCC suspensions: (left side) without nonadsorbing polymer; (right side) percolated NCC network with depleted nonadsorbing polymer [53]

4.3.3.2.3 Effect of ionic strength

In addition to concentration, another parameter that can be considered to have a significant impact on rheological behavior for a NCC-CMC mixture is ionic strength of the mixture. So, it was decided to change the NaCl concentration in the mixtures to investigate this possible effect. As previously mentioned all the NCC-CMC mixtures tested before were containing 10 mM NaCl. So this time, a wider range for NaCl was selected as 10, 30, 50, and 70 mM; all these concentrations applied to a constant mixture concentration (1wt.% NCC and 1wt.% CMC). Figure 4.26 shows the rheological results. The results demonstrate that increasing electrolyte concentration can increase both G’ and G” of the sample. For the range of NaCl tested in all samples the dominant component is storage modulus; all samples behave as a very viscose material for higher concentration of electrolyte it can be said that the sample is a complete gel. For the lowest NaCl concentration (10mM) storage modulus change from 49.80 Pa to 101.0 Pa and the loss(viscose) modulus starts from 6.777 Pa and ends to 30.78 Pa however, there are some data with G” amount for the tested frequency range (the lowest is 5.161 Pa). For the sample with 30mM electrolyte concentration storage modulus changes from 52.52 Pa to 187.2 Pa; which in compare to the previous sample the start point is close but the end point is obviously higher and shows more dependency on angular frequency. The range of changing loss modulus for sample with 30mM electrolyte is from 14.08 Pa to 43.54 Pa; however, again there are a few data lower than this range and the lowest one is 13.08 Pa. It is obvious that the range is higher that it was for previous sample but with less dependency on frequency.

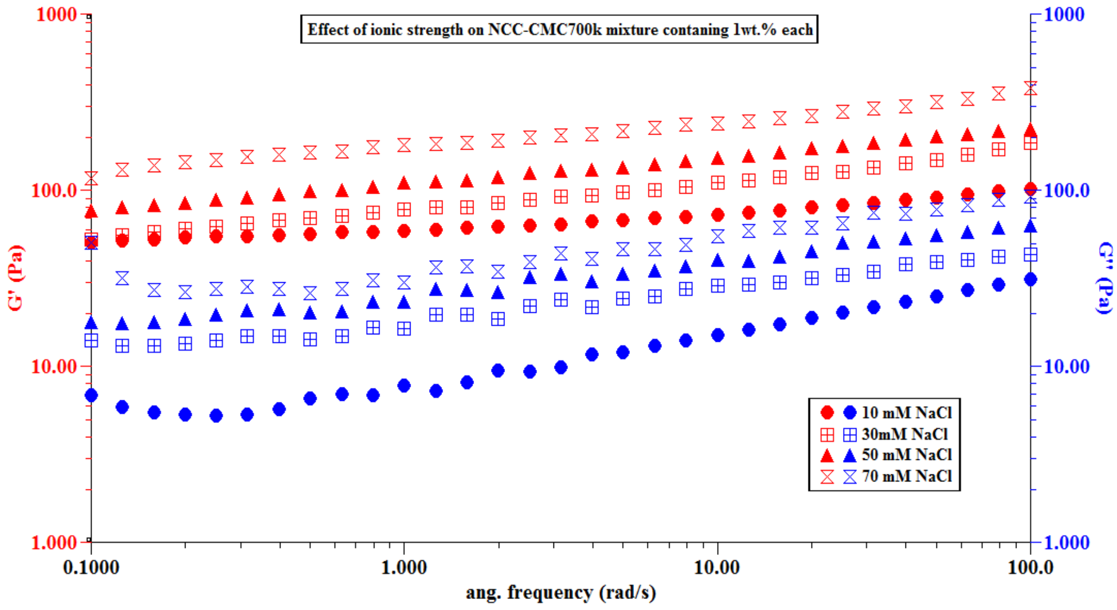


Figure 4.26 Effect of ionic strength on G’ and G” for 1wt% NCC+1wt% CMC

By increasing the electrolyte concentration to 50mM, the storage modulus varies from 76.60 Pa to 224.9 Pa which shows increase in compare to the previous sample but is follows the same dependency on angular frequency. In fact the same behavior as it was for 30 mM NaCl and higher dependency in compare to 10 mM

NaCl. For this electrolyte concentration loss modulus alters from 17.83 Pa to 67.70 Pa which is almost like the behavior seen for the 30mM sample but just with higher amounts.

For the sample with highest electrolyte concentration (70 mM), it was observed that both G’ and G” are higher than those of the three previous samples.

Therefore, the results indicate that by increasing the ionic strength in a sample, the sample starts to behave like a gel and G’ still remains as dominant component. There is obviously no cross over point in the system for any samples tested. All these salt concentrations were tested in the samples with constant amounts of NCC–CMC. It is concluded that at high ionic strength polymer can have more impact on the rheological behavior of the mixture. In fact, this impact is relevant to the polyelectrolyte behaviour with salt addition.

As it is known NCC and CMC all have negative charge, and roughly can be treated as polyelectrolytes in the solution. When there is no salt in the solution, the negative charge along the chains will repulse them from each other, and leading to a well dispersion. In this case, the chains are separate from each other; even though, there could be some entanglements or association of the chains, this entanglements or association could not be so compact, and the 3-d network composed of chains and NCCs is not so strong. But when salt added, there could be another situation. Here there is an electrostatic shielding effect. Namely, the added salt will weaken the charges along the chains, and the electrostatic repulsion of the chains and NCCs would be reduced. So, the chains could be closer to each other with more salt and the 3-d network could be more compact with more salt.

Chapter 5 Conclusion

Based on the results presented and discussed in the previous chapter, the most important points which can be concluded from the entire data set are:

For the NCC particles used in this project, as expected, increasing its concentration in the suspension changes the phase behavior of the suspension. At low concentrations (1-4wt.%) the results obtained from cross polarized and POM experiments showed that the suspensions behave as an isotropic sample, indicating that no liquid crystals here formed. In other words, the NCC rod-like particles were randomly dispersed in the solution.

By increasing the NCC concentration above 4wt. % both cross polarized and POM results showed that liquid crystals were formed partially in the suspensions. It means that by increasing the number of particles, the inter-particle interactions leaded to a partial orientation of the rod-like particles in the suspensions. This behavior happened for the particles in the range of 4-6 wt.%. This region was called I+N transition.

When the samples tested for concentration higher than 6wt.%, the phase behavior entered to a new region. The almost totally bright pictures proved that the samples with concentration in the range of 7-10 wt.% are in the nematic region. Meaning that rod like particles exhibited similar orientation. When the results were compared with Dong et al (1997), it was found that changing the aspect ratio can change the transition concentrations Φ_{I+N} and $\Phi_{I+N->N}$[29].

In the second section, where different polymer samples were added to the suspensions at low concentrations it was observed that the polymer had changed the phase behavior and rheological behavior of such mixtures significantly. These changes occurred as a result of the interaction between polymer chains and NCC rod-like particles. Such interactions depend obviously on the polymer type and concentration. For the first polymer (HEC) as a neutral cellulose base polymer when a low range (0.15-0.6 wt.%) tested in the presence of 1 wt.% NCC, it showed that all the interactions between polymer chains and rod-like NCC particles are not strong enough to change the isotropic behavior of this low amount of NCC. But when for the range of polymer just the NCC particle concentration was increased to 2wt.% the phase behavior showed noticeable change. Two samples revealed I+N transition phase behavior and the other two showed nematic behavior. Hence, it can be concluded that by adding polymer to a colloidal system like NCC, it is possible to see the change in phase behavior when there is enough concentration of both polymer and colloid. As it presented previously, 2wt.% NCC behaved as an isotropic sample when there was no polymer in the system.

In addition, while testing another range of HEC-NCC mixtures with constant HEC and variable NCC, the results showed that for a constant concentration of HEC (1wt.%) which is higher than the levels tested in the previous runs, by adding even a low concentration of NCC (0.5wt.%) the mixture is placed in I+N transition phase. Following that by increasing the NCC concentration a bit more (0.75wt.%) the mixture showed nematic phase behavior which means this little increase in particles concentration caused to a change in phase behavior. Needless to add that the third sample with higher NCC (1wt.%) was also in nematic phase. All these facts show the effect of having enough polymer chains in the system to cause strong interaction between the rod-like particles and polymer chains. So an increased polymer concentration can lead to change in phase behavior. This also can be concluded based upon rheological behavior of comparable HEC samples previously showed in that section. The rheological test showed that by increasing HEC concentration viscosity increased and its dependency on shear rate decreased even for very low shear rates. Hence, this could be one of the reasons for observing the change behavior in a mixture of NCC-HEC when the polymer concentration was increased. Based on the POM results obtained here and with respect to the results of Boluk et al., it was concluded that the interaction between HEC macromolecules and NCC rod-like particles in HEC-NCC mixtures is depletion interaction and the possibility of adsorption interaction was rejected in their work. Then NCC particles flocculation happens by depleted HEC chains [53].

When another neutral polymer was tested for investigating rheological behavior it showed that for a high molecular weight (2000 kDa) and at a high concentration (10wt.%) adding NCC could not make any change in rheological and phase behavior of the system and did not show any thickening behavior because in comparison to HEC, dextran is a branched polymer. By implementing the phase diagram reported by lekkerkerker et al. based on the work by Edgar et al. it was found that the dextran-NCC mixtures which tested in my work were mostly located in I+N and nematic region of the phase diagram [30,57].

Moreover, trying a negatively charged polymer like CMC (700k) revealed considerable changes both in phase and rheological behavior of the samples. While testing CMC, for a constant NCC concentration at (1wt.%) by varying polymer concentration from 0.5wt.% to 2wt.% all three phase behavior were observed which leaded to conclude that increasing CMC concentration can increase the interaction between rod-like particles and polymer chains especially for this case as both polymer and particles are negatively charged the probability of observing depletion interaction was higher. I+N and nematic phase behavior both were observed while testing lower amount of NCC and an increased range of CMC. From the rheological runs (oscillations tests) it could be concluded that for CMC samples with no NCC there is not a cross over point in the system (G'=G") for low concentration (0.5 and 1wt.%-) and the dominant component is loss modulus. Nevertheless, by increasing the concentration (1.5-2.5 wt.%), the cross over point was observed and the elastic modulus started to be dominant. For concentration again there was no cross over point and elastic modulus became the absolute dominant component. From these all it can be concluded that increasing CMC concentration can have a huge effect on the rheological behavior which can also have impact on the interactions in the presence of colloidal particles. Hence by adding NCC (1wt.%) to the system, as it was expected the dominant component for all samples was storage modulus. The rheological results of second range of NCC-CMC mixtures with lower NCCs also exhibited that G' is the dominant component. Based on these results and comparing to the results of Boluk et al., it was concluded that CMC macromolecules has induced depletion interaction in the NCC-CMC mixtures and NCC particles flocculation occurred by the depleted polymer chains [53].

In the last part of the project, we investigated the effect of ionic strength by testing a range of salt concentrations (10-70 mM NaCl). For a system of negatively charged CMC and negatively charged NCC particles with no salt, the CMC chains will be repulsed as a result of this negative charge which can finally cause well dispersion. Hence, although the chains are separate from each other; still some entanglements or association of the chains can occur. However, the entanglements or association could not be so compact, and the 3-d network composed of chains and NCCs is not so strong. But by adding the salt to the system, it can cause an electrostatic shielding effect that means the salt will weaken the charges along the chains, and the electrostatic repulsion of the chains and NCCs would be reduced. So, the chains could be closer to each other with more salt and the 3-d network could be more compact with more salt.

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