الجـــمهورية الجـــزائرية الــديمقراطية الشـــعبيـة

People's Democratic Republic of Algeria

وزارة التـــعليم العـالي والبـحث العـلمي

Minister of Higher Education and Scientific Research

جامعة البليدة - 1-

University SAAD DAHLAB BLIDA-1-

كلية العلوم

Faculty of science

قسم الكيمياء

Department of chemistry

A thesis submitted in fulfillment of the Requirements for MASTER'S degree

<u>Option</u>: Applied Chemistry

Theme

Synthesis of thin films based on hydroxypropyl cellulose doped with zinc oxide by solvent casting method

Presented by:

ADJEZ Sabrina

SOUAT Nesrine

Supported on: 13/10/2020

Dr M.KARS	MCA	University BLIDA -1-	President
Dr A.OURADI	MCB	University BLIDA -1-	Examiner
Dr S.HAMMANI	MCA	University BLIDA -1-	Thesis supervisor
Dr M.FETTAKA	MCB	University BLIDA -1-	Thesis Co-supervisor

2019-2020

Abstract

The aim of this thesis is to study thin films based on hydroxypropyl cellulose HPC doped with nanoparticles of zinc oxide ZnO by the solvent casting method. In our study, we want to investigate the influence of ZnO on HPC film performance, an attempt to improve its properties even at extremely low ZnO loadings. This thesis focused on three major parts, the first part is devoted to the study of nanocomposites based on HPC (matrix) and ZnO (reinforcement agent), the second part is addressed to show the importance of state dispersion/distribution of ZnO in the matrix due to the agglomeration of ZnO NPs, this will prevent their good dispersion within the polymer matrix, the third part is aimed to show the effect of CTAB on the performance of the film. The study will be completed by the following analyzes: IR spectroscopy, X-ray diffraction, scanning electron microscopy (SEM) analysis, and UV-vis spectroscopy. The results showed that our HPC film is rich with ZnO NPs with the size of a micrometer, the formation of $Zn(OH)_2$ and that the surfactant CTAB plays a very important role in directing the morphology of NPs.

Key words: Thin films, HPC, ZnO, nanocomposites, dispersion/distribution, agglomerate, CTAB, IR, XRD, UV-vis; SEM analysis, morphology.

Résumé

L'objectif de cette thèse est d'étudier des films minces à base d'hydroxypropyl cellulose HPC dopé avec nanoparticules de l'oxyde de zinc ZnO par la méthode de coulée au solvant. Dans notre étude, nous voulons étudier l'influence de ZnO sur les performances du film HPC, une tentative d'améliorer ses propriétés même à des charges ZnO extrêmement faibles. Cette thèse a porté sur trois grandes parties, la première partie est consacrée à l'étude des nanocomposites à base de HPC (matrice) et de ZnO (agent de renforcement), la deuxième partie est adressée pour montrer l'importance d'état de dispersion / distribution du ZnO dans la matrice due à l'agglomération des ZnO NPs, cela empêchera leur bonne dispersion au sein de la matrice polymère, la troisième partie vise à montrer l'effet du CTAB sur l'exécution du film. L'étude sera complétée par les analyses suivantes : spectroscopie IR, diffraction des rayons X, analyse par microscopie électronique à balayage (MEB) et spectroscopie UV-vis. Les résultats ont montré que notre film HPC est riche en NPs ZnO de la taille d'un micromètre, la

formation de Zn(OH)₂ et que le surfactant CTAB joue un rôle très important dans l'orientation de la morphologie des NPs.

Mots clés : films minces, HPC, ZnO, nanocomposites, dispersion/distribution, s'agglomérer, CTAB, IR, XRD, UV-vis, MEB, morphologie.

ملخص

الهدف من هذه الاطروحة هو دراسة الأغشية الرقيقة المبنية على هيدروكسي بروبيل السليلوز HPC المدمجة بجزيئات نانوية من أكسيد الزنك ZnO بطريقة الصب بالمذيب. في دراستنا ، نريد التحقق من تأثير ZnO على أداء فيلم HPC ، في محاولة لتحسين خصائصه حتى في حالات تحميل ZnO منخفضة للغاية. ركزت هذه الأطروحة على ثلاثة أجزاء رئيسية ، الجزء الأول مخصص لدراسة المركبات النانوية القائمة على HPC (المصفوفة) و ZnO (عامل التقوية) ، أما الجزء الثاني فقد تناول إظهار أهمية حالة تشتت / توزيع ZnO في المصفوفة بسبب تكتل ZnO NPs ، وهذا سيمنع تشتتها الجيد داخل مصفوفة البوليمر ، ويهدف الجزء الثالث إلى إظهار تأثير CTAB على أداء الفيلم. سيتم استكمال الدراسة بالتحليلات التالية: مطيافية الأشعة تحت الحمراء ، حيود الأشعة السينية ، تحليل المجهر الإلكتروني (SEM) والتحليل الطيفي للأشعة فوق البنفسجية. أظهرت النتائج أ فيلم HPC الخا بنا غني بـ ZnO NPs بحجم ميكرومتر ، وتشكيل Zn (OH)₂ وأ الفاعل بالسطح CTAB يلعب دورًا مهمًا للغاية في توجيه مورفولوجية NPs.

** كلمات مفتاحية :** الأغشية الرقيقة, HPC, ZnO, المركبات النانوية, التشتت / التوزيع, يتكتل, CTAB, التحليل الطيفي للأشعة تحت الحمراء IR ، حيود الأشعة السينية XRD ، تحليل المجهر الإلكتروني (SEM) والتحليل الطيفي للأشعة فوق البنفسجية UV-vis, مورفولوجية.

Dedication

I dedicate this work to:

my loving parents and my sweet

family, I could never have done

this without you guys.

I LOVE YOU

SOUAT NESRINE

Dedication

Thanks to Allah almighty who enabled me to complete this thesis in such difficult time.

I dedicate this work

with a deep sense of reverence, my gratitude towards my parents who have supported me morally and also economically.

To all people that I love the most,

Thank you for your unconditional love and encouragement.

ADJEZ Sabrina

Table of contents

Abstract

Acknowledgment

Dedication

List of abbreviations

List of figures

List of tables

List of symbols

Table of contents

Chapter II : Polymer-matrix nanocomposites.

Chapter III: Materials and methods.

Chapter IV: Results and discussion.

Acknowledgment

"If you can't figure out your purpose, figure out your passion. For your passion will lead you right into your purpose."

—Bishop T.D. Jakes

LIST OF ABBREVIATIONS

CA: **C**itric **A**cid

CTAB: **C**etyl **T**rimethyl **A**mmonium **B**romide

DNA: **D**eoxy **N**ibonucleic **A**cid

FED: **F**ield **E**mission **D**isplay

FFS: Film forming system

FTIR: **F**ourier-**T**ransform **I**nfrared spectroscopy

HPC: **H**ydroxy **P**ropyl **C**ellulose

HPMC: **H**ydroxy **P**ropyl **M**ethyl **C**ellulose

H$_2$O: **W**ater

IPA: **I**sopro**p**yl **A**lcohol

IR: **I**nfrared **S**pectroscopy

KDa: **K**ilo **Da**lton

MW: **M**olecular **W**eight

NPs: **N**ano-**P**article**s**

N$_2$: **N**itrogen

O$_2$: **O**xygen

PE: **P**olyethylene

PET: **P**oly (**E**thylene **T**erephthalate)

pH: **P**otential hydrogen

PLA: **P**oly (**L**actic **A**cid)

SEM: **S**canning **E**lectron **M**icroscope

TSC: **T**ri-**S**odium **C**itrate

USA: **U**nited **S**tates of **A**merica

UV-vis : **U**ltraviolet **V**isible

XRD : **X** **R**ay **D**iffraction

ZnO : **Z**inc **O**xide

Zn (OH)$_2$ **:** **Z**inc **H**ydroxyde

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

Nm: Nanometer

g: Gramm

g/cm³: Gramm per cubic centimeter

g/mol: Gramm per mole

g/ml: Gram per milliliters

°C: Degree Celsius

Ev: Electron-volt (s)

h: hour

Mev: Mega-electronvolt (s)

ml: Milliliters

MPas: Millipascal-second

a_0: Mech parameter

c_0: Mech parameter

K: kelvin

Cm: Centimeter

Cm³: Cubic centimeter

Pa: Pascal

MPa: Mega Pascal

%: Percentage

μm: Micrometer

n: An integer parameter

λ : X-ray Wavelength

d: Interplanar spacing between rows of atoms

L: Dimension of the particle

θ: Angle of the X-ray beams

β: Peak width

θ: Scattering angle

mA: Milliamperes

kV: kilo volt

mol/cm^3: Mole per cubic centimetr

mol-1/cm^2: Mole per square centimeter

I. General introduction

In recent years, the interest in the study of polymer composite system has been continuously growing due to their various potential applications in sensors, dielectrics, biomedical field, food packaging, bioplastics, and coatings.

The researchers suggested that the addition of inorganic nanofillers into polymers results in improved polymer properties that greatly differ from the properties of conventional polymers. It has been revealed that the nanoparticles **(NPs)** significantly influence the properties of base polymers when they are introduced into it to generate nanocomposite **[1].**

The peculiar characteristics of **ZnO NPs** is its chemical stability, low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicines. Moreover, **ZnO** is a low-cost material that has been used in conductive glass, white paint and commercial sunscreens **[1]**, all these characteristics make **ZnO NPs** a great reinforcement agent that can provide improved thermal, mechanical or optical properties for different matrices.

All advantages of **HPC** are countless, **HPC** is a biodegradable, non-toxic, and solid polymer, besides, **HPC** is a very renewable resource that has several traditional applications including biological, medical, and pharmaceutical fields **[2]. HPC** is a good candidate as a matrix for the production of nanocomposites reinforced by nanoparticles of **ZnO.**

These promising nanocomposites will revolutionize the entire nanotechnology, by covering the overall applications in electronic, mechanical and chemical sectors **[1].**

The aim of our thesis is to study the **HPC/ZnO** nanocomposites according to the impact of **ZnO** on **HPC** films performance, an attempt to improve their properties.

Particular attention was also paid to the state of dispersion/distribution of particles in the matrix, also, the effect of surfactant Cetyltrimethylammonium Bromide **(CTAB)** on the film preparation.

This thesis also considers the modifications and improvements in thin films based on biopolymers including the recent progress in the field.

This work consists of a theoretical part and an experimental study.

The theoretical part focuses on two main chapters:

The first chapter "Nanotechnology and biopolymers: generalities" is a literature review about nanotechnology and how it's helping to revolutionize so many industrial sectors, and then, we briefly talk about biodegradability and biopolymers and reveal the reason behind their extensive commercial interest in both pharmaceutical and commercial applications, last but not least, a brief description of cellulose and **HPC** and their physicochemical properties, finally, we end this chapter by talking about thin films based on biopolymers, their endless applications in our daily life in pretty much every industrial sector.

The second chapter "Polymer-matrix nanocomposites" aims to review the main topics and recent progresses related to polymer nanocomposites and their applications.

The chapter presents the most important concept about nanocomposites, an approach on different types of reinforcement agents that can be incorporated in different types of matrices, after that, we highlight some potential applications that have been achieved in polymer nanocomposites.

The chapter also provides a review of **HPC** as matrix, and **ZnO (NPs)** as reinforcements, and the objectives of incorporating **NPs** into polymers.

Finally, we talk about the state of dispersion/distribution of **NPs** into the matrix and the difficulty to attain a homogenous dispersion due to agglomeration/aggregation.

The third chapter "materials and methods" was addressed to the description of the materials and experimental techniques to the preparation and characterizations.

The fourth chapter "Results and discussion" is devoted to the discussion of the results and the interpretation. We finish our thesis by a conclusion gathered with the main results, observations and future perspectives.

I.1.History of nanotechnology

The concept of a ''nanotechnology'' was first mentioned during the **1959** by Richard Feynman when he presented a lecture titled, ''There's Plenty of Room at the Bottom'', in which he introduced the concept of manipulating matter at the atomic level **[3-4].**

This speech outlined a vision for manipulating and observing things on a small scale and how this would revolutionize many industries as well as provide answers to many fundamental questions, particularly in the context of understanding biology **[5].**

Almost 15 years after Feynman's lecture, a Japanese scientist, Norio Taniguchi, was the first to use ''nanotechnology'' to describe semiconductor processes and he defined nanotechnology as being able to manipulate a single nanoscale object **[3-5]**.

The golden era of nanotechnology began in the 1980s when Binning and Rohrer developed the scanning tunnelling microscope and Binning developed the atomic force microscope **[5].**

I.1.1. Nanotechnology

The nanotechnology exactly means any expertise performed on a nanoscale it incorporates the production and application of physical, chemical, and biological systems like semiconductor technology, information technology or cellular and molecular biology **[6].**

Nanotechnology is the study, understanding and control of matter at dimensions approximately between **1** and **100 nm [5]**.
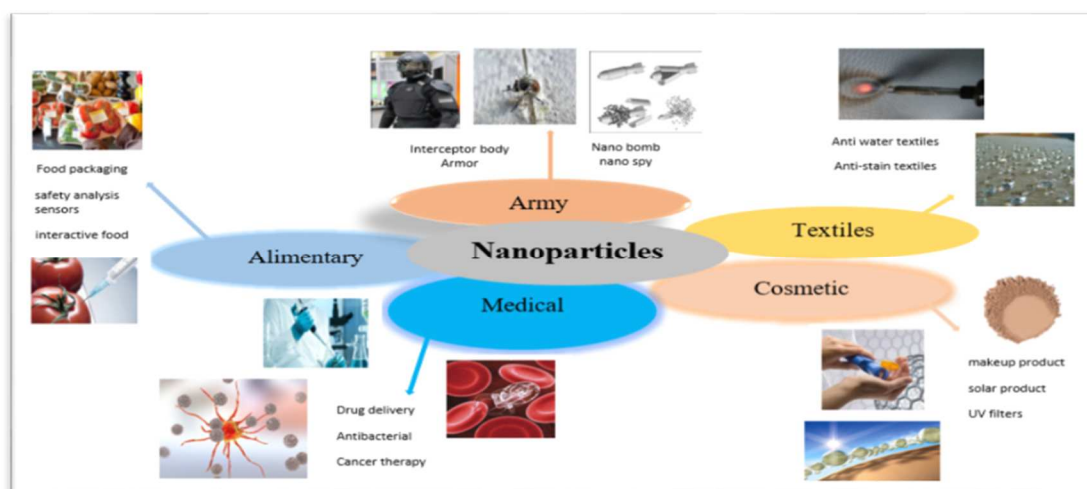
Figure I.1: Applications of nanotechnology in daily life.

I.2. Nanoparticles

Nanoparticle is combination of two words Nano and particles. nano in the International System of Units means one-billionth of metre 10^{-9}, and particle means a small portion of matter. So, we can say that nanoparticle is an ultrafine particle his diameter was between **1** and **100** nanometre **(nm).**

I.2.1. Nanoparticle Properties

The use of nanoparticles for the production of materials can increase material strength, reduce material weight, and enhance material thermochemical properties **[7].**

I.2.2. Nanoparticles Sources

There are a variety of nanoparticle sources:

- **a- Natural nanoparticles:** nanoparticles are present in the environment naturally we have for example dust emitted by combustion or by volcanoes (volcanic fumes).

- **b- Man-made nanoparticles**: this type is divided into two sections, non-manufactured nanoparticles and manufactured nanoparticles.

Non-manufactured nanoparticles are those produced unintentionally by humans for example from burning of fossil fuels like diesel vehicles, petrol vehicles or particles from welding fumes.

Manufactured nanoparticles are those produced intentionally for new properties **[8].**

I.2.3. Synthesis Methods of nanoparticles

There are two methods to synthesis of nanoparticles: top-down and bottom-up approaches.

a) Top-Down Approach

The Top-down approach involves the breaking down of the bulk material into nano sized particles.

b) Bottom-Up Approach

The Bottom-up approach refers to the build-up of a material from the bottom: single atoms and molecules are assembled into larger nanostructures. This method is very powerful for creating identical structures with high atomic precision **[9].**
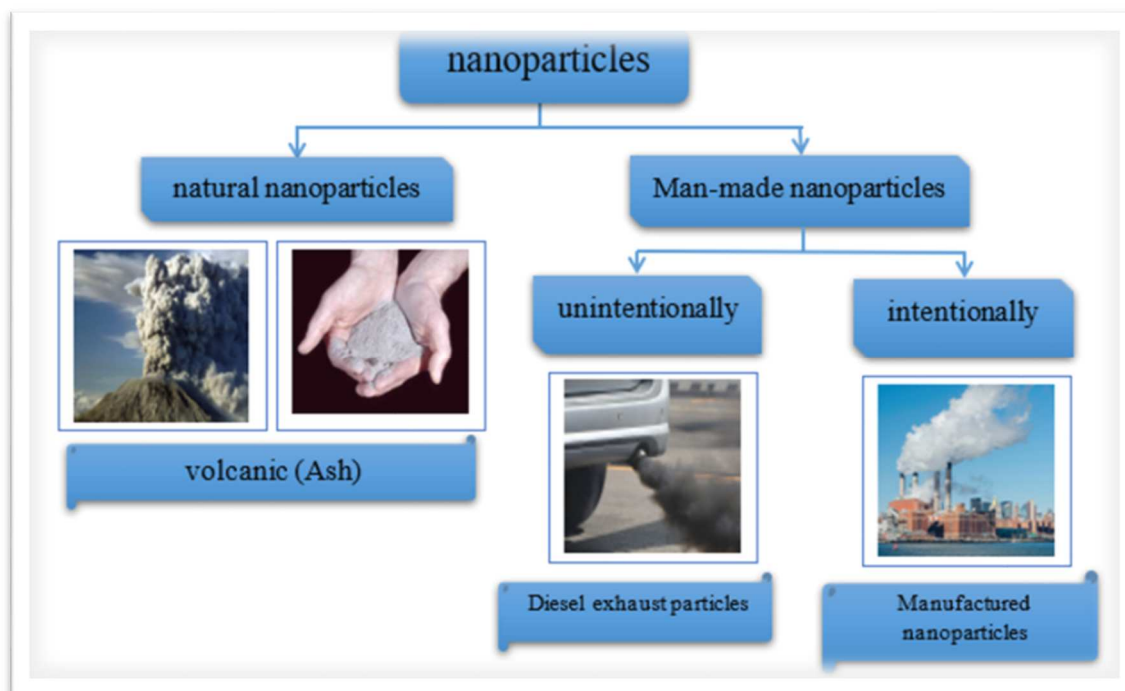
Figure I.2: Different sources of the generation of nanoparticles.

I.3. Biodegradability

Biodegradability refers to the ability of a material to decompose after interactions with biological elements.

Biodegradability is the capacity for biological degradation of organic materials by living organisms down to the base substances such as water, carbon dioxide, methane, basic elements and biomass [10].

I.3.1. Biopolymers

Biopolymers are chain-like molecules made up of repeating chemical blocks produced from renewable resources which could be degraded in the environment [11].

Biopolymers are roughly divided into two sections: polymers with natural origin and polymers produced by chemical synthesis (Fig.I.3).

Natural biopolymers are produced within living organisms. These include mainly proteins and polysaccharides. From all biopolymeric proteins the most popular is collagen.

Commonly used polysaccharides include cellulose [12].
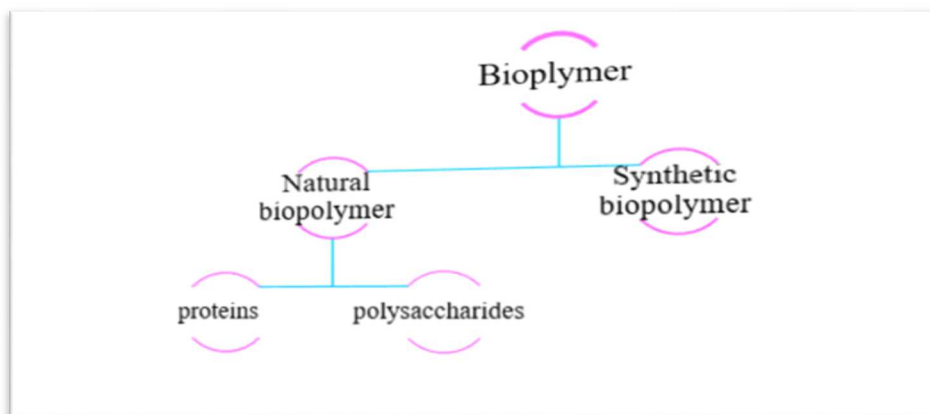
Figure I.3: Biopolymers classification.

I.4. Polysaccharides

Polysaccharide, such as starches and celluloses, are formed by polymerization of monosaccharides and oligosaccharides **[13].**

Polysaccharides and their derivatives (starch, cellulose, chitosan, alginates, pectin, carrageenan, etc.) are widely used in the production of biodegradable packaging materials.

Polysaccharides are great materials for the film formation, as they show excellent mechanical and structural properties due to hydrophilic nature of these molecules, the application of biopolymers based on polysaccharides is limited because they show poor barrier properties against water vapor. Good barrier properties to gases and aromas, good mechanical properties and ability to carry active components are their major potential **[14].**

Many polysaccharides are non-toxic, and for this reason there is extensive commercial interest in the use of polysaccharides in cosmetic and pharmaceutical applications **[15]**.

I.5. Cellulose

Cellulose is the most abundant polymer on earth, because it is considered as the principal constituent of all plant life because it is the building material of long fiber cells. These cells can be found in the stem, the leaves, or the seeds of plant **[16].**

Powdered cellulose is manufactured by the purification and mechanical size reduction of a-cellulose obtained as a pulp from fibrous plant materials so we can say powdered cellulose$(C_6H_{10}O_5)_n$ is a natural polymer with high strength , it occurs as a white or almost white, odorless and tasteless powder of various particle sizes **[17]**.

Powdered cellulose is a stable, slightly hygroscopic material, and is generally regarded as a nontoxic and non-irritant material. It is commercially available in several different particle sizes **[17].**

Cellulose pertains to the class of carbohydrates. It contains **44.4 %** of carbon, **6.2 %** of hydrogen and **49.4 %** of oxygen. The chemical structure of cellulose is given in Figure.**I.4 [16].**
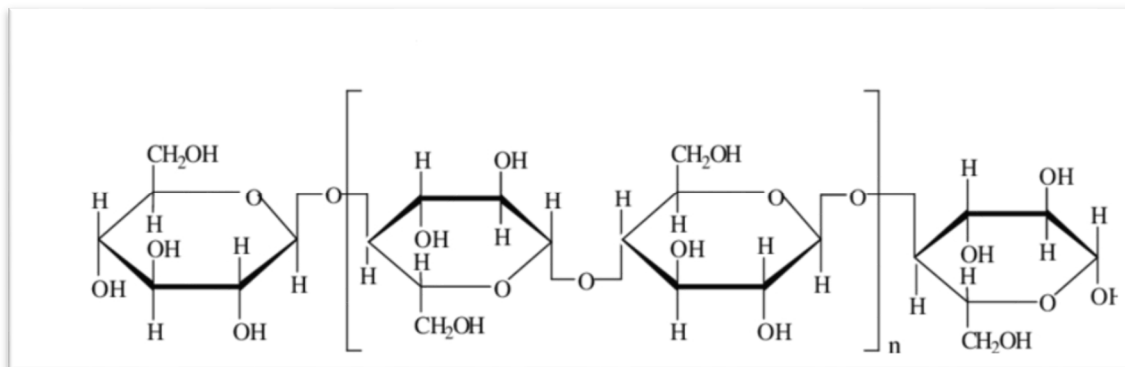
Figure I.4: The structure of cellulose [16].

I.5.1. Physicochemical properties of cellulose

The physicochemical properties of cellulose were summarised on table.**I.1.**

Table I.1: Properties of cellulose.

Property	Value
Molecular Formula	• $(C_6H_{10}O_5)n$ **[17].**
Molecular weight (for n=500)	• 243000 **[17].**
Density	• 1.5 g/cm^3**[17].**
Solubility	• Insoluble in (water, dilute acids and most organic solvents)**[17].** • Soluble in most liquids **[17].**

I.5.2. Application of cellulose

Cellulose has widely been used for two centuries in commodity and industrial products such as pulp and paper, textile, and coatings it is also used in oral pharmaceutical formulations and food products because it has enormous potential in developing bio-friendly, and sustainable technological products [18].

Cellulose has various cellulose ethers derivation such as hydroxypropyl cellulose (HPC) and hydroxypropyl methyl cellulose (HPMC) [19].

I.6 Hydroxypropyl methylcellulose "HPMC"

Biopolymer composites are very promising materials because they are easy to process, eco-friendly in nature, and offer better properties. **HPMC,** being a biodegradable and biocompatible polymer, has also been used to prepare bio composites.

Hydroxypropyl methylcellulose **(HPMC)** belongs to the group of cellulose ethers in which hydroxyl groups have been substituted with one or more of the three hydroxyl groups present in the cellulose ring [20].
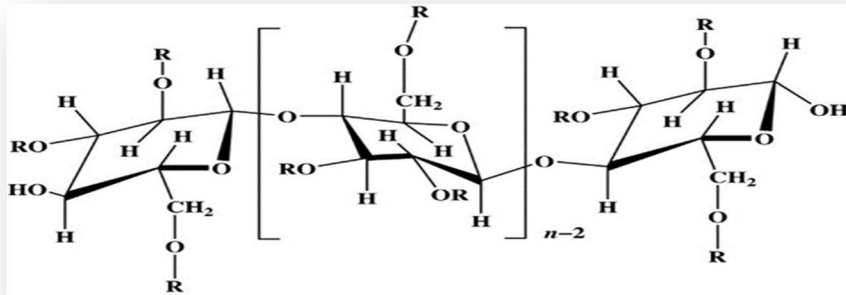
Figure I.5: Chemical structure of hydroxypropyl methylcellulose (HPMC) [20].

Hydroxypropyl methyl cellulose is synthesized from methyl cellulose by the action of alkali and propylene oxide. The resultant product is a water-soluble ether derivative of cellulose containing both methoxy and hydroxypropyl groups [21].

Methyl substitution of HPMC is performed using the substitution of free hydroxyl groups of glucose with hydroxypropyl groups. Such modifications tend to improve the cellulose backbone regarding viscosity, solubility, gelation, and film-forming performance [22].

I.6. 1. Physicochemical properties of HPMC

- **H**ydroxypropyl methylcellulose is odorless, flavorless, transparent, stable, oil-resistant, nontoxic, and edible material with good film-forming properties. It is a nonionic polymer with a linear structure of glucose molecules, in which its matrix is stabilized using hydrogen bonds **[22]**.

- **HPMC** is hydrophilic (water soluble) in the cold water, but after heating they form a thermally reversible and relatively hard gel by heating process at **50–80°C [22]**.

- **HPMC** is also soluble in polar organic solvents, making it possible to use both aqueous and nonaqueous solvents. It has unique solubility properties with solubility in both hot and cold organic solvents. **HPMC** possesses increased organo-solubility compared to other methyl cellulose counterparts **[20]**.

- **pH** is described as a basic factor for solution property control, which can affect on physicochemical properties of **HPMC** molecules and interactions with other molecules. The pH of pure **HPMC** solution without additives is **6.47–7.87 [22]**.

I.6. 2. Flow behavior of HPMC film (apparent viscosity, shearing stress)

Rheology of biopolymer can control the thickness, uniformity of matrix, and film-forming properties of film. In addition, evaluation of rheological behavior is required for processing and preparation of biopolymers such as shearing rates. The viscosity is depended on the **HPMC** concentration, type, and the temperature of solution.

Pure **HPMC** solution has apparent viscosity about **15 (MPa.s)** at concentration of **2%** at **25°C [22]**.

I.6. 3. HPMC films application

The first application of hydroxypropyl methylcellulose (**HPMC**) for film coating appeared in **1962.** Film coatings using **HPMC** have become popular, taking the place of the conventional sugar coating of tablets, because they give a superior appearance, act as protection for fragile tablets.

The main reason for the extensive use of **HPMC** as a film-coating polymer is that it is soluble in some organic solvents and also in water over the entire biological **pH** range. Film coating can therefore be done using an organic solvent system, and the film formed will dissolve in the digestive juices, leading to complete release of the active ingredients **[23]**.

HPMC forms flexible and transparent films from aqueous solution. **HPMC** films are generally odorless and tasteless and can be effectively used in reducing absorption of oil from fried products because of their resistance to oil migration. It is extensively used in the food industry as a stabilizer, as an emulsifier, as a protective colloid, and as a thickener **[20].**

Hydroxypropyl methylcellulose cellulose, is available in several grades that vary in viscosity and extent of substitution. It is widely used in pharmaceutical formulations:

- in oral products,
- as a tablet binder,
- in film-coating and as a controlled-release matrix **[24].**

Moreover, the application of film coating to the surface of pharmaceutical solid-dosage forms, particularly tablets, has been practiced for more than **100 years**. Film coating is used for reasons ranging from the aesthetic to a desire to control the bioavailability of the drug. The drivers for use of film coating include:

- to mask unpleasant taste and odor;
- to improve product stability;
- to facilitate handling;
- to modify drug-release characteristics **[24].**

I.7. Thin films of biopolymers

Thin film is not a recent formulation, the first use of thin films for optical purposes can be dated back to **1912** and the first introduced in the pharmaceutical field was in late **1970** to overcome swallowing difficulties exhibited by tablets and capsules**.** **G**enerally, thin films can be referred as a thin and flexible layer of polymer **,** or Materials with thicknesses ranging from nanometres to micrometres are called thin films**[25-26].**

Thin film technology is a mature field encompassing a wide range of applications such as electronics, optical communications, and bio-systems. The list of potential applications is practically endless with an impact in nearly every industrial sector **[27].**

Figure I.6: Different applications of thin films.

I.7.1. Film forming system

Film forming system **(FFS)** is a novel approach which can be used as an alternative to conventional topical and transdermal formulations. It is defined as non-solid dosage form that produces a film in situ, i.e. after application on the skin or any other body surface. These systems contain the drug and film forming excipients in a vehicle which, upon contact with the skin, leaves behind a film of excipients along with the drug upon solvent evaporation. The formed film can either be a solid polymeric material that acts as matrix for sustained release of drug to the skin or a residual liquid film which is rapidly absorbed in the stratum corneum **[28].**

I.7.2. Thin film formulation advantages

Thin film formulations offer several advantages including **[26]:**

- Convenient administration through non-invasive routes.
- Ease of handling during manufacture and transportation.
- Cost effectiveness in the development of formulations.

I.7.3. Storage

A film should not be exposed for too long time since it is prone for being damaged. If possible, it should be cut and packed immediately after the preparation to keep its stability **[26].**

II.1. Composite material

A composite material is an assembly of two non-miscible materials, consisting of two (or more) non-miscible phases with different properties and roles, one continuous, is called matrix and the other, discontinuous, called reinforcement agent, the components must be physically identified, there must be a distinct interface between them [29].

II.2. Nanocomposite

A nanocomposite is defined as a material consisting of several phases including at least one matrix (polymer, ceramic or metallic) in which objects, having at least one of their dimensions less than 100 nm (reinforcing phase) are incorporated.

We are looking for generally by this association a complementarity to have a synergy of properties, leading to a material with improved overall performance [29-30].
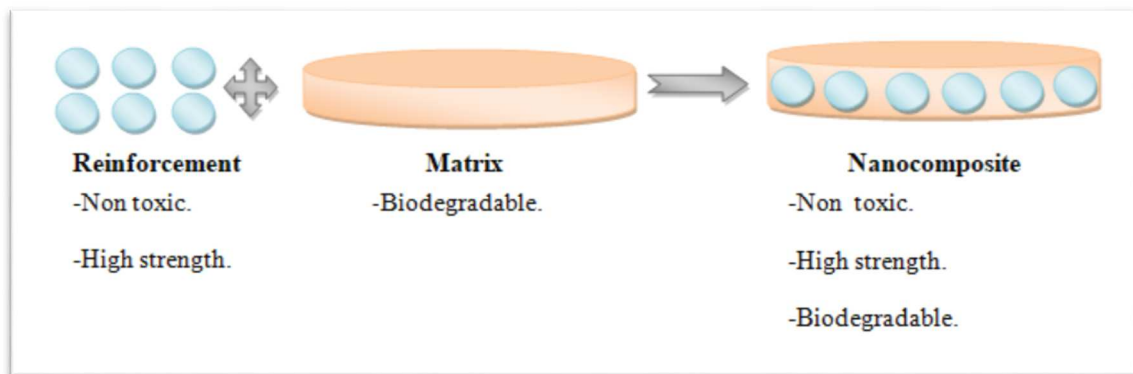
Figure II.1: Schematic representation of a nanocomposite.

II.3. Types of Biopolymers Matrix

Bio-based polymers, which are considered the matrix base during preparation of nanocomposite films, have many advantages. They are renewable, biodegradable, multi-functional, and biocompatible.

Bio-based polymers can be classified into two major categories:

1. Natural bio-based polymers, including:

- Polymers extracted from agricultural resources:

- ▪ polysaccharides:
  - • neutral: e.g., cellulose, hemicellulose, starch
  - • cationic: e.g., chitin, chitosan

- anionic: alginic acid, hyaluronic acid

- bacterial origin: e.g., pullulan, carrageenan;

- proteins: e.g., gelatin and whey protein;

2. Other bio-based polymers: e.g., lipid, lignin, natural rubber, **DNA,** etc. polymers produced directly from microorganism's bacterial cellulose; polyhydroxyalkanoates, poly-ε-caprolactones.

3. Synthetic bio-based polymers, including:

- natural-based or bio-based synthetic polymers, the monomers of which are derived from renewable resources (**e.g**., **poly** (lactic acid)-**PLA);**

- partially bio-based polymers such as polyethylene **(PE),** poly (ethylene terephthalate) **(PET)**, etc…. **[31].**

II.4. Reinforcement agent

At first, it is important to differentiate the term filler from the term reinforcement agent. Reinforcement (or reinforcing charge) is defined as any immiscible body capable of modifying mechanical, electrical or thermal properties of a polymer. Filler term is used to qualify a body to improve the surface appearance or decrease the price of the final composite**.** Fillers are generally solid, inorganic or organic substances, which are dispersed in a polymer matrix in the form of powders or fibers**.** They vary greatly depending on their price, composition and their physical and chemical characteristics. While for a given polymer, the choice of a filler is determined by application of finished product **[29-30].**

II.4.1. Types of reinforcement agents

There are three main types of reinforcements:

- Organic reinforcements (flax fibers, organic fibers, carbon, graphene...).

- Inorganic reinforcements (mica, glass fibers, silica.).

- Metal reinforcements (boron fibers, aluminum...).

These reinforcements can be in the form of particles, short or long fibers, woven or not. Each type of reinforcement having benefits (improved stability against UV ageing for loads particulate matter) and disadvantages (inability to extrude long fibers, difficulty impregnating fibers in thermoplastics…) **[30].**

II.5. Objective of incorporating a nano-object into a polymer

The intrinsic properties of an object (micrometric or nanometric) can give the material specific properties such as magnetic or electrical and/or changing its thermal, mechanical or optical properties **[29].**

Polymer nanocomposites have advantages:

- Their barrier properties are improved compared with the neat polymer.
- Their mechanical and thermal properties are potentially superior and exhibit excellent flammability properties **[32]**.

These materials are particularly present in the automotive industry (reinforced paints, engine parts, etc.), textiles (flame retardant fibers, conductors, etc.), health (implants, medical treatments, etc.) or in the field of sport (skis, bicycles, tennis rackets, etc.) **[30].**

II.6. Hydroxypropyl cellulose

Hydroxypropyl cellulose **(HPC) i**s one of a family of water-soluble cellulose ethers **[33]** in which hydroxyl groups was hydroxy propylated on the cellulose backbone **[34].** Actually **HPC** was developed by Dr Eugene Klug at Hercules Chemical and marketed as Klucel **[33].** Hydroxypropyl cellulose is a white to slightly yellow coloured, odorless and tasteless powder, it is a non-ionic, water-soluble polymer **[17-19-35].**

HPC is commercially available in different viscosity grades, with an average molecular weight **(MW)** grades ranging from **20** to **1500 kDa [34]**.
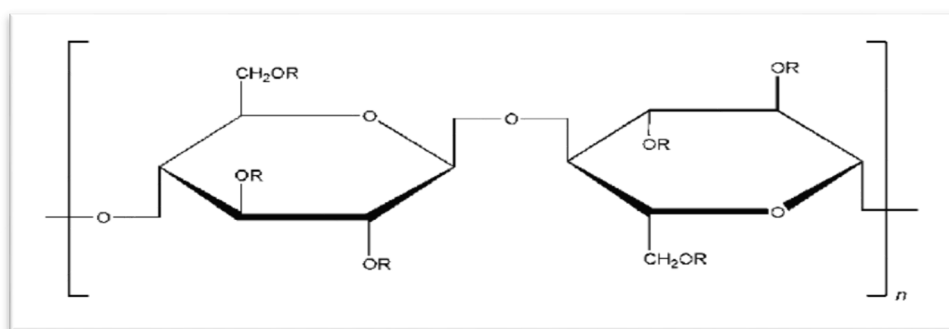
Figure II.2: Chemical structure of hydroxypropyl cellulose "HPC"

(R= CH$_2$-CH-CH$_3$) [36].

OH
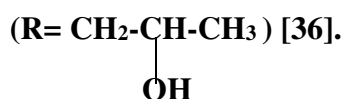
II.6. 1. Physicochemical properties

The physicochemical properties of **HPC** were summarized in table **II.1.**

Table II.1: Properties of hydroxypropyl cellulose.

Properties	Value
Molecular formula	• $C_{36}H_{70}O_{19.}$
Molecular weight	• 50 –1 250 kDa [26].
Synonyms	• Cellulose,2-hydroxypropyl ether; Klucel; E463 [17].
Appearance	• Hydroxypropyl cellulose is a white to slightly yellow-coloured, odorless and tasteless powder [35].
Solubility	• Soluble in polar organic solvent (methanol, ethanol, isopropyl alcohol (IPA), and acetone) [34] at any temperature [37]. • HPC is soluble in water at room temperature but it is insoluble in water above 45°C [35].
Softening temperature	• 100–150 °C [37].
Burnout temperature	• 450–500 °C in N2 or O2 [37].
Cloud point	• approximatevly 42°C [33].
Freezing point	• 0 °C [37].
pH	• 5 – 8.5 [17].
Density	• 0.5 g / cm^3[17].
Storage	• Hydroxypropyl cellulose powder should be stored in a well closed container in a cool, dry place because it absorbs moisture from the atmosphere [17].

II.6. 2. Solubility and viscosity of hydroxypropyl cellulose

For pure hydroxypropyl cellulose, the solubility in water is limited to the cold temperate range **0–38 °C.** When an aqueous **HPC** solution is further heated, there is a precipitation. In other side the viscosity of an aqueous **HPC** solution decreases as the temperature of the solvent is increased. This effect is known and is considered normal for polymers in solution.

Temperatures above **40–45 °C** lead to precipitation of **HPC** from aqueous solutions and the precipitation is completely reversible (reversed by cooling).
The presence of other substances in the **HPC** solution may strongly influence the flocculation temperature (the temperature at which the **HPC** precipitates).

The solubility of hydroxypropyl cellulose in alcohol–water mixtures depends on the composition of the mixture with respect to its alcohol content and the viscosity of hydroxypropyl cellulose in aqueous alcoholic solutions varies with the solvent composition.

Owing to the presence of alcohol in the system, the solubility of hydroxypropyl cellulose is improved compared to that in pure water. This results in an increase in flocculation temperature and leads to an increase of the viscosity (thickening power). In some cases, **HPC** can be heated to boiling without precipitating. With high alcohol concentrations (e.g. at least **45%** by volume of ethanol, methanol, and propylene glycol) dissolved HPC can be heated to the boiling point without flocculation **[38].**

II.6. 3. Hydroxypropyl cellulose (HPC) applications

The general properties of **HPC** has a number of traditional applications including biological, medical and pharmaceutical fields **[2]** such as oral and topical pharmaceutical formulations **[19]** in oral products is primarily used as a film former or in tableting as a binder and film coating and it is used in transdermal patches and ophthalmic preparations **[35].**

HPC is also used in cosmetics such as (hair styling products, emulsion creams, lotions and shampoos) **[37]** and in food products as an emulsifier and stabilizer **[17].**

II.7. Zinc oxide (ZnO)

Zinc oxide is an inorganic compound, white in color and available in a powdered form. Its chemical formula is **"ZnO".** It is insoluble in water, however, completely soluble in acids such as hydrochloric, phosphoric and fatty acids. Zinc oxide is produced synthetically but it is also available naturally in the form of zincite **[39].**
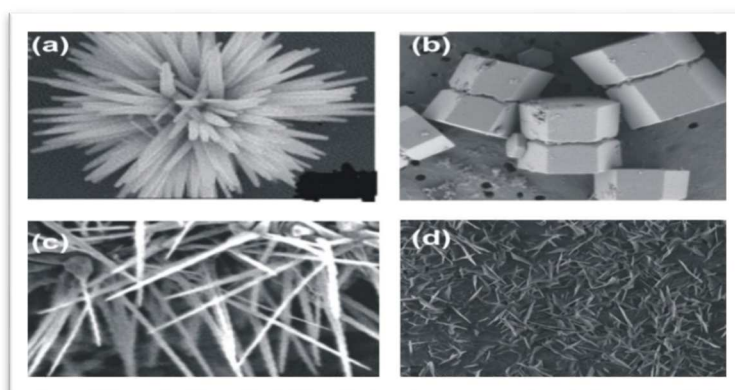
Figure.II.3: Examples of zinc oxide structure: flower (a); rods (b); wires (c, d) [40].

II.7. 1.ZnO Properties

a) Electrical properties

As for its electrical properties, zinc oxide is a semiconductor with a large prohibited band **(3.37 eV)** corresponding to a transition in the near ultraviolet **(UV)** and a high exciton binding energy **(60 meV).**

It is transparent in the visible and near-infrared which has earned it an interest in potential applications in photovoltaics, light-emitting diodes for lighting, oxides transparent conductors, photonics or sensors. It also has properties of the **II-VI** family: hardness, stability of the exciton **[40].**

b) Crystal structure

Zinc oxide exists in the so-called wurtzite crystal structure which may be viewed as a network of tetrahedra formed by the oxygen atoms in a structure reminiscent of that of diamond **[41].** The first crystallographic studies of some zinc oxide go back up to the thirties. This material crystallizes in a hexagonal network of type wurtzite, in which ions of oxygen are willing to a network of compact hexagonal type, and where ions of zinc occupy the half of positions interstitials tetrahedral having the same arrangement that the ions of oxygen. An example of the hexagonal structure of the powdered **ZnO** is shown Figure **II. 4**, Sizes "a" and "c" correspond to mesh parameters and have for 0.3249 nm and **0.5206 nm** respectively **[42].**
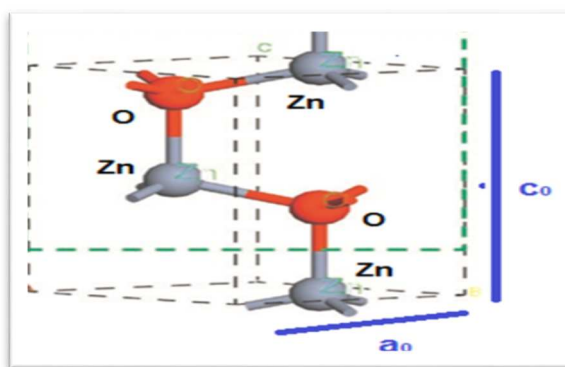
Figure II.4: The wurtzite structure model of zinc oxide (ZnO) [43].

Table II.2: Physical properties of zinc oxide [44].

Property	Value
Lattice parameters at 300 K	
a_0 c_0 a0/c0	**0.32469 nm** **0.52069 nm** **1.602 (1.633 for ideal** **hexagonal structure)**
Density	**5.606 g.cm^{-3}**
Fusion point	**2248 K**
Relative dielectric constant	**8.66**
Gap energy	**3.37 eV, direct**
Exciton binding energy	**60 meV**
Effective electron mass	**0.24**
Effective hole mass	**0.59**

c) Optical properties

The optical properties of zinc oxide have been studied by several techniques.

They concern the study of optical absorption, transmission, reflection, photoluminescence or the optical gap **[42].**

ZnO shows high light absorption in **the UVA (315–400 nm)** and **UVB (280–315 nm)** regions, which are beneficial for applications, such as skin care products **[45].**

II.7. 2. ZnO application

Zinc oxide was first studied in the **1970s**. It is again studied over the past few years due to its attractive fundamental properties in particular the field of spintronics for the production of medicines, photovoltaics, sensors, biology, or lighting **[42].** Because of its diverse properties, both chemical and physical, zinc oxide is widely used in many areas. It plays an important role in a very wide range of applications, ranging from tyres to ceramics, from pharmaceuticals to agriculture, and from paints to chemicals.

Figure **II.5** shows worldwide consumption of zinc oxide by region **[40].**
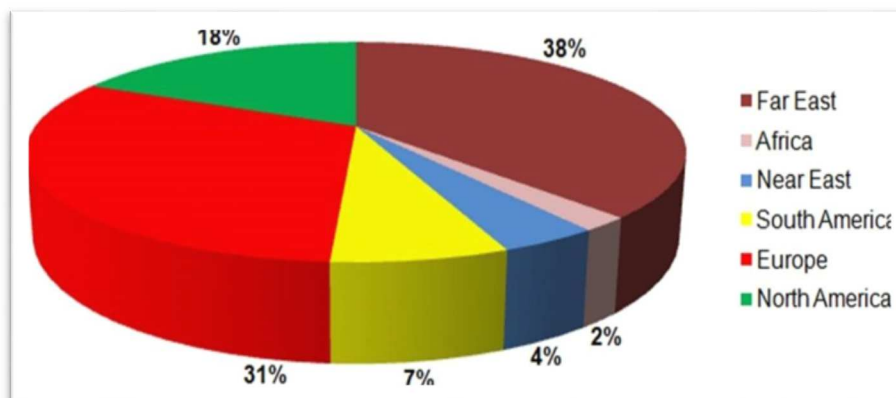
FigureII.5: Worldwide consumption of zinc oxide [40].

a) Rubber Industry

Global production of zinc oxide amounts to about **105** tons per year, and a major portion is consumed by the rubber industry to manufacture various different cross-linked rubber products.

b) The Pharmaceutical and Cosmetic Industries

Due to its antibacterial, disinfecting and drying properties, zinc oxide is widely used in the production of various kinds of medicines. It was formerly used as an orally administered medicine for epilepsy, and later for diarrhea. At the present time it is applied locally, usually in the form of ointments and creams, and more rarely in the form of dusting powders and liquid powders. **ZnO** has properties which accelerate wound healing, and so it is used in dermatological substances against inflammation and itching. In higher concentrations it has a peeling effect. It is also used in suppositories. In addition, it is used in dentistry, chiefly as a component of dental pastes, and also for temporary fillings. **ZnO** is also used in various types of nutritional products and diet supplements, where it serves to provide essential dietary zinc.

c) The Textile Industry

The textile industry offers a vast potential for the commercialization of nanotechnological products.

For textile applications, not only is zinc oxide biologically compatible, but also nanostructured **ZnO** coatings are more air-permeable and efficient as **UV-blockers** compared with their bulk counterparts. Therefore, **ZnO** nanostructures have become

very attractive as **UV-protective** textile coatings. Different methods have been reported for the production of **UV-protecting** textiles utilizing **ZnO** nanostructures.

d) The Electronics and Electrotechnology Industries

Zinc oxide can be used in photoelectronic and electronic equipment, in devices emitting a surface acoustic wave, in field emitters, in sensors, in **UV** lasers, and in solar cells. **ZnO** also exhibits the phenomenon of luminescence, because of this property it is used in **FED** (field emission display) equipment, such as televisions. The photoluminescent properties of zinc oxide depend on the size of crystals of the compound, defects in the crystalline structure, and also on temperature.

e) Photocatalysis

Numerous studies prove that **ZnO** offers unique photocatalytic properties, making it possible for this oxide to be used as a photocatalyst in the process of degradation of various substances.

f) Miscellaneous Applications

Apart from the applications mentioned above, zinc oxide can also be used in other branches of industry, including for example concrete production. The addition of zinc oxide improves the process time and the resistance of concrete to the action of water, and also improves the whiteness and final strength of the cement.

Zinc oxide is also used in pigments to produce shine. It is added to many food products, including breakfast cereals. **ZnO** is used as a source of zinc, which is an essential nutrient. Thanks to their special chemical and antifungal properties, zinc oxide and its derivatives are also used in the process of producing and packing meat products (e.g., meat and fish) and vegetable products **[40].**

II.8. Nano composite HPMC-ZnO

Polymer nanocomposites with inorganic nanoparticles, gaining greater importance because of their tunable properties, simple preparation methods and relatively low cost **[4].** Very few studies have reported the addition of inorganic oxide nanoparticles into **HPMC**. The advantages of using these inorganic oxide nanoparticles as antimicrobial agents are less toxicity and heat resistance. In addition, they provide mineral elements essential to human cells and even small amount of them exhibit strong activity among metal oxide nanoparticles **[20].** The bio nanocomposite prepared by addition of **ZnO** nanoparticles into **HPMC** polymer films has additional antibacterial activity **[46].**

II.9 State of dispersion/distribution

The macroscopic properties of a nano composite depend heavily on the state of dispersion of the reinforcement agents in the matrix. Therefore, dispersion control and characterization are very important for the understanding of the final properties of the material **[30].**

However, nanoparticles can be easily aggregated and agglomerated when added to polymer matrix. The aggregation/agglomeration can be formed during the production process of nanoparticles or incorporating them in polymer. Also, agglomeration is when particles are combined loosely which can be simply broken by mechanical forces. The aggregation/ agglomeration prevents the obtaining of improved properties and thus, the achieving of various applications by nanostructured materials. The aggregation/agglomeration has been attributed to the direct mutual attraction between nanoparticles via van der Waals forces or chemical bonds.

The strategies for avoiding aggregation/agglomeration is by using optimal parameters in production process that can lead to an effective breaking of aggregates **[47].**
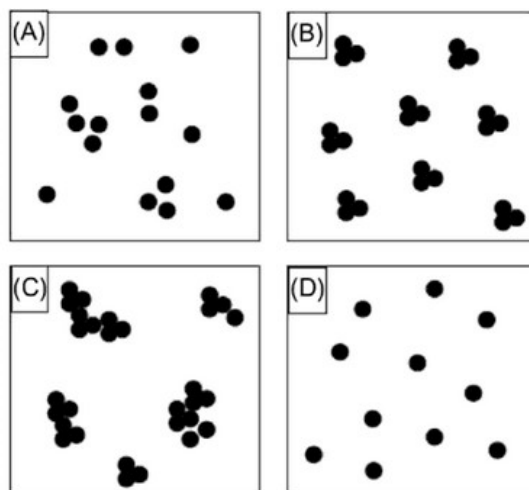
Figure II.6: Schematic representation of the degree of dispersion and distribution of nanoparticles in a polymer matrix: **(A)** good dispersion, poor distribution; **(B)** poor dispersion, good distribution; **(C)** poor dispersion, poor distribution; **(D)** good dispersion, good distribution **[48]**.

III. Materials and characterisation methods.

This chapter is devoted primarily to the presentation of the products used as well as the description of the different steps and procedures for preparing films based on **HPC** doped by nanoparticles. **A** brief overview of the various analytical techniques and characterization used will then be provided.

III.1. Used materials

Film formation involves the use of:

III.1.1. The matrix.

At least one constituent capable of forming a matrix with sufficient cohesion and continuity. They are generally polymers or compounds which, under the conditions of preparation used, have the property of forming continuous crystalline or amorphous structures. We chose hydroxypropyl cellulose **HPC** for its excellent film-forming properties and quality as a food additive.

The **HPC** used in our study is a modified cellulose ether of the type **EXF** Pharm marketed by **KLUCEL (USA),** the choice of the type of this **HPC** powder is based on the EXF which indicates a combination of the type of viscosity followed by the size of particles whose **E** refers to a very low viscosity and **X** a fine size of particles that make them more easily soluble and can give better solutions.

The following table includes some physical and chemical characteristics of **HPC.**

Table III.1: Some physical-chemical properties for HPC Klucel.

Characteristics	Values
pH	5 - 8
Softening temperature, °C	100 - 150
Viscosity (mPa · s)	300 - 600
Weight (Daltons)	80 000

III.1.2. The reinforcement agent

Our film based on **HPC** (matrix) will be incorporated with nanoparticles of **ZnO** (reinforcement agent), **ZnO** nanoparticles show chemical stability, thermal resistance, robustness, and long shelf life.

Table III.2: Physicochemical properties of zinc oxide [39].

Property	Value
Molar mass	**81.38 g/mol**
Odor	**Odorless**
Density	**5.606 g.cm^{-3}**
Melting point	**1975°C**

III.1.3. The solvent

    A solvent in which the polymer disperses or solubilizes to form film-forming solutions of controlled concentration. These concentrations represent a compromise between the optimum solvency and extension of polymer molecules on the one hand, and good viscosity on the other. The solvent used influences the cohesion of the film. We chose a mixture composed of water and methanol as our solvent.

    Methanol **(CH$_3$OH)** is a colourless, volatile liquid and flammable, with a distinctive odor **[49].**

Methanol is toxic, and very corrosive substance. It is miscible in water **[50].** It is used as antifreeze, solvent, fuel, and denaturant for ethanol **[49].**

Methanol is among the best solvents for all types of Klucel **HPC,** as this latter has excellent solubility with body fluids and provides clear solutions at room temperature, helps to dry films for a reasonably short time, which is why our choice was based on this solvent whose characteristics are grouped in the following table.

Table III.3: Characteristics of methanol.

Properties	Value
Structure	CH₃OH.
Molecular Weight	32,04 g/mol [51].
Synonyms	methyl alcohol, wood alcohol [52].
Density	0,7915 [51].
Boiling point	64,5°C [51].
Appearance	colourless liquid with a distinctive odor (pungent odor) [52].
Solubility	Soluble in water. Soluble in ethanol. Soluble in ether. Soluble in acetone. Soluble in chloroform [52].

III.2. Solvent casting method

Preparation of biopolymer films includes biopolymers dissolution or dispersion in different solvents; solution evaporation and, finally, drying. This method is called as "solvent casting"**[53].**

Solvent casting method is the most commonly used techniques for the preparation of thin films **[54].**

III.2.1. Solvent casting method principle

The films were formed with the solution/solvent casting method**.**

- **T**he preparation of solutions/dispersions and the film casting were performed at room temperature **[19].**

- **S**olutions/dispersions were prepared by very carefully and gradually dissolving polymer (**HPC**) into a solvent or a mixture (methanol and buffer solution (**75/25**) (i.e., **75%** methanol solution) **[19].**

- **T**he mixture stirred at ambient temperature overnight by an agitator until the uniformity of the dispersions could be confirmed visually (**~24 h** in total) **[19].**

- **T**he mixture or the gel was poured (casted) into a plastic Petri dish **[55].**

- **A**fter casting the solution into a suitable substrate, they are left for drying to allow the solvent to evaporate that just leaves a polymeric film with a drug on it **[26].**

The technique of solvent casting exhibits advantages and drawbacks.

III.2.2. Advantages

Solvent casting is widely used method mainly due to the several advantages such as:

- Low costs **[54].**

- Shorter preparation time **[54].**

- Most importantly easy variation in reaction conditions **[54].**

- The straightforward manufacturing process **[26].**

- Better physical properties, easy processing **[26].**

- And excellent uniformity of thickness are observed with the film obtained by solvent-casting**[26].**

III.2.3. Disadvantages

Solvent casting has certain disadvantages, these include:

This process suffers from some limitation. For instance, a polymeric thin film prepared by solvent casting method was brittle upon storage, as marked by decrease in the percent elongation due to evaporation or loss of the residual solvent in the film over time.

Another issue under scrutiny associated with this method is the requirement of using organic solvents. The presence of organic solvent system is a serious problem because it causes a hazard to health and environment. As a result, strict regulations have been adopted by many countries regarding the use of an organic solvent **[26]**.

III.2.4. Solvent casting in the future

The production of films is one of the biggest challenges because many factors such as heating, mixing speed, and temperature could bring variability in quality and consistent formation of films in commercial scale may not be possible.

Therefore, in the future sufficient endeavour should be invested to optimize the various parameters such as the speed of casting, drying time, and final thickness of the dried strip, which may affect the production of films from commercial scale output **[26].**

III.3. Film preparation

III.3.1 Preliminary HPC solubility tests in the chosen solvent

Several tests of **HPC** powder solubility in methanol were carried out to ensure better dissolution as well as the quality of film to be prepared.

To do this, we prepared a bi-phasic mixture of methanol and distilled water **(50/50)** and another of **(75/25)** from which we remove 20 ml for each film casting solution prepared and to which we add each time a different amount of powder and leave for 24 hours under magnetic agitation.

Among the trials we managed to have a single film of concentration of **1.25g/ 20ml** of methanol/water solvent **(75/25).**

The following two figures represent the solution as well as the film made.
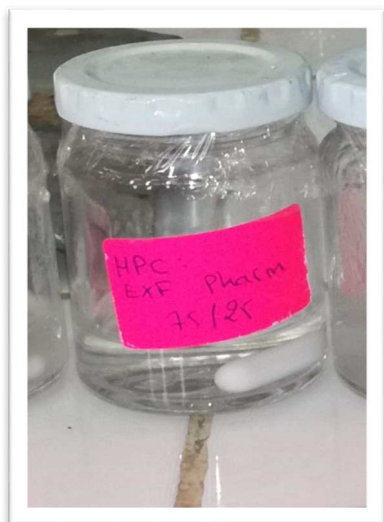
Figure III.1: HPC solution 1,25g/ 20ml (75/25) .

Figure III.2: HPC film 1,25g /20ml(75/25).

III.3.2 Zinc oxide (ZnO) based dispersions

The dispersive solutions used in film preparation are listed as follows:

Table III.4: Composition of dispersions used in film preparation.

Solution Numbers	Composition
1	**HPC/buffer solution/CTAB/ZnO**
2	**HPC/buffer solution**

III.3.3. Preparation of buffer solution

In order to prepare the buffer solution, we need **2** main components:

III.3.3.1. Citric acid

Citric acid **($C_6H_8O_7$)** is a fine white crystalline powder **[17]** it is a weak organic acid soluble in water. We can find it naturally in various fruits and vegetable, especially in the citrus fruits.

Citric acid is the most produced organic acid it is versatile and widely used in the field of food such as flavouring agent and as emulsifying agent in ice cream and used like cleaning agent in chemical industry, it is also used in pharmaceutical industries and cosmetics **[56].**
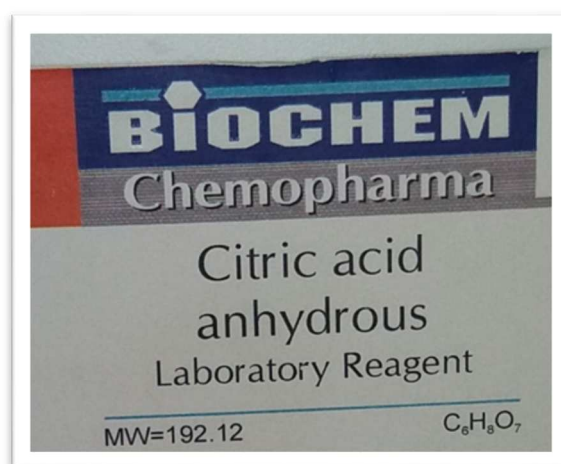
Figure III.3: citric acid.

a- Structural Formula
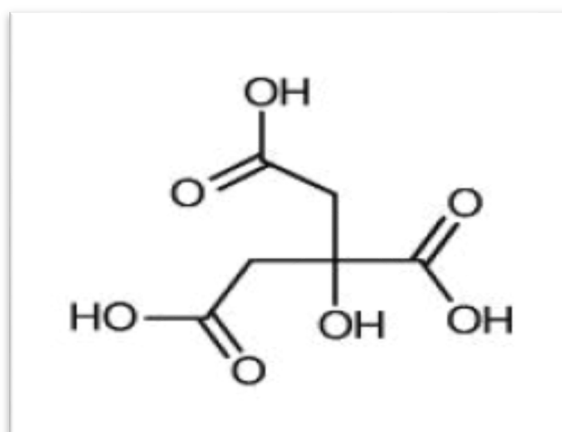
Figure III.4 : Chemical structure of citric acid [57].

b- Physicochemical properties

Some selected physicochemical properties for Citric acid are listed in table **III.5.**

Table III.5: Physicochemical properties of citric acid.

Properties	Values
Structure	$C_6H_8O_7$ [56].
Molecular Weight	192.12 g/mol [17].
Synonyms	2-hydroxypropane 1,2,3-tricarboxylic acid ; E330 [17].
Density	1.66 g/cm^3[17].
Melting point	153 °C[17].
Boiling point	175 °C [57].
Appearance	white crystalline powder, almost odourless [17].
Solubility	soluble in Water and ethanol [17].

III.3.3.2. Tri-sodium citrate

Trisodium citrate **($C_6H_5Na_3O.2H_2O$)** is a white granular to fine powder odourless with a saline taste**.** It is soluble in water and insoluble in ethanol. We can use trisodium citrate like emulsion stabilizer, buffer**.** It is widely used in pharmaceutical formulations (for example to relieve the painful irritation caused by cystitis, and also, to treat dehydration and acidosis due to diarrhoea it is also used in food products, to adjust the pH of solutions **[17-58].**
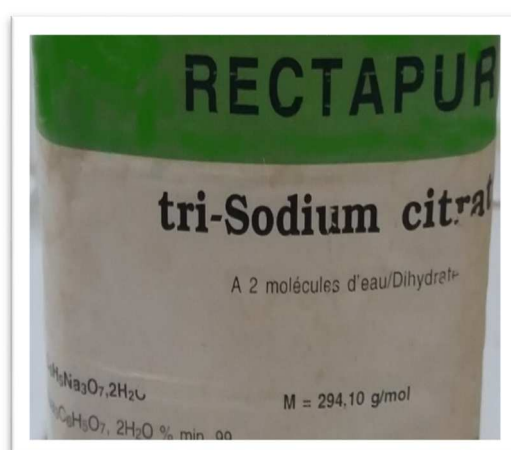
Figure III.5: tri-sodium citrate.

a- **Structural Formula**
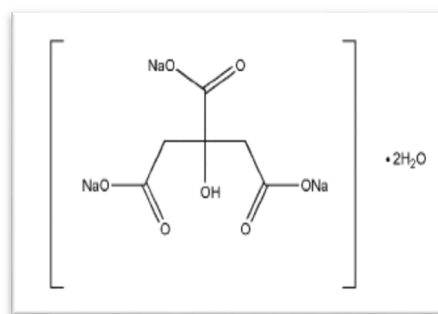
Figure III.6: Chemical structure of tri-sodium citrate [17].

b- **Physicochemical properties**

Some selected physicochemical properties for tri-sodium citrate are listed in table.

Table III.6: Physicochemical properties of trisodium citrate.

Properties	Value
Structure	$C_6H_5Na_3O.2H_2O$[17].
Molecular mass	**294.10 g/mol[17].**
Synonymes	**trisodium citrate dihydrate ; trisodium salt and E331[17-59].**
pH	**8.0 - 8.7[59].**
Melting point	**150 ºC [17].**
Solubility	**freely soluble in water, and insoluble in ethanol[59].**
Storage	**stored in an airtight container in a cool, dry place[17].temperature range of 10–30 °C[59].**

c- **Cetyltrimethylammonium Bromide (CTAB)**

CTAB is a quaternary ammonium surfactant that has been used for applications from nanoparticle synthesis to cosmetics. Due to its use in human products, along with other applications **[60].**
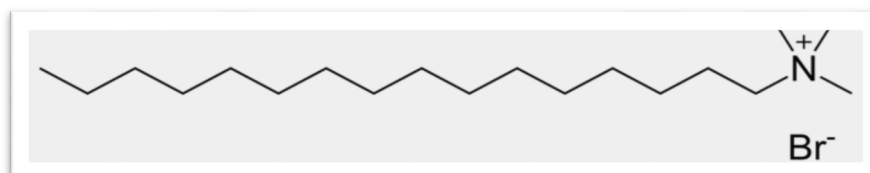
Figure III.7: Chemical structure of CTAB [60].

III.3.3.3. Procedure

To prepare the buffer solution at required **pH (pH=5).**

- **Trisodium citrate solution**

7.35 g of trisodium citrate is dissolved in 250 ml of distilled water.
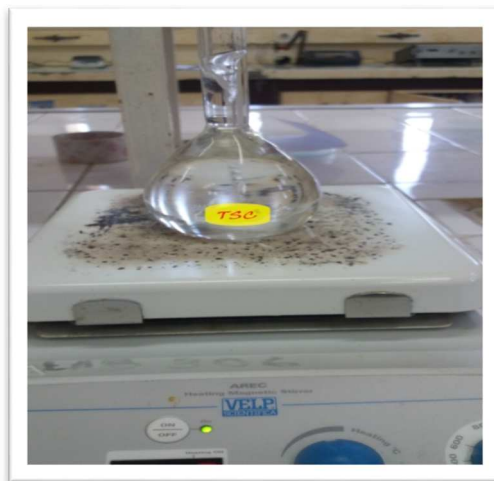
Figure III.8: Trisodium citrate solution.

- **Citric acid solution**

4.8 g of citric acid is dissolved in **250 ml** of distilled water.
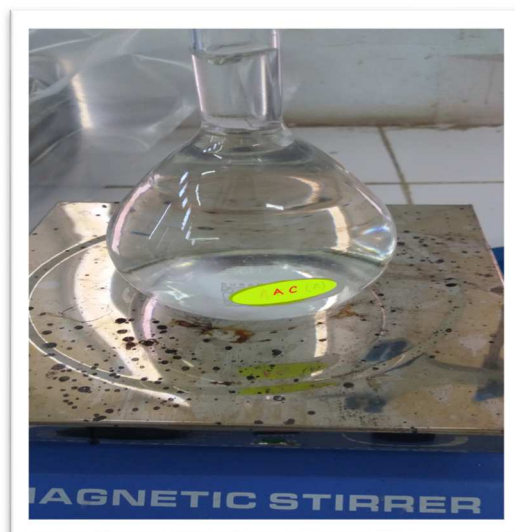
Figure III.9: Citric acid solution.

We add **35 ml** of citric acid solution to **65 ml** of trisodium citrate solution, we put the solution under a magnetic agitation for **10 min.**

The buffer solution is prepared at **pH=5.**

Table III.7: citrate buffer.

pH	Citric acid solution (ml)	Trisodium citrate (ml)
3	82.0	18.0
4	59.0	41.0
5	35.0	65.0
6	11.5	88.5

Table III.8: samples preparation.

Solution Numbers	Solutions (100 ml)	Conditions	Results
1	pH=5, ZnO=0.1%	**Under magnetic stirrer (15 min) + ULTRASOUND (15 min).**	**Good dispersion**
2	pH=5, ZnO=0.1%, CTAB= 0.1%		

III.3.4. The protocol for producing films doped with zinc oxide

First, the buffer solution was prepared at **pH=5.** An amount of 0**.1% of CTAB** was added to **100 ml** of buffer solution and stirred under a magnetic agitation at ambient temperature to get a clear solution. After that **0.1% of ZnO** is added into the previous solution, the mixture was put under magnetic stirrer for **15 min**.

The solution will be taken after that in the ultrasound **(BRANSON 2800)** for **30 min**.

We prepare the mixture of (methanol/buffer mixture) **(75/25).**

We add **1.25g of HPC** in 20ml of (methanol/buffer mixture).

The mixture solution (hydrogel) was put under magnetic agitation for **24 h** until it was homogenized.

Finally, this solution was casted onto a glass petri dish then was dried in a hot air oven at **70° for 2h.**

Figure III.10: ultrasound (BRANSON 2800).

III.3.5. Organizational chart

0.1% CTAB

100 ml Buffer
solution (pH=5)

Magnetic stirrer

0.1% of ZnO

Buffer sol + 0.1%
surfactant

Buffer sol+0.1%
surfactant+0.1% ZnO
(buff mix)

BRANSON
2800

Ultrasonication

Agitation

1.25g HPC

25% (buff mix)

75% Methanol

Methanol/buff mix
(75/25)

Solvent evaporation and drying

Solvent casting in a petri dish

Magnetic stirrer

Thin film
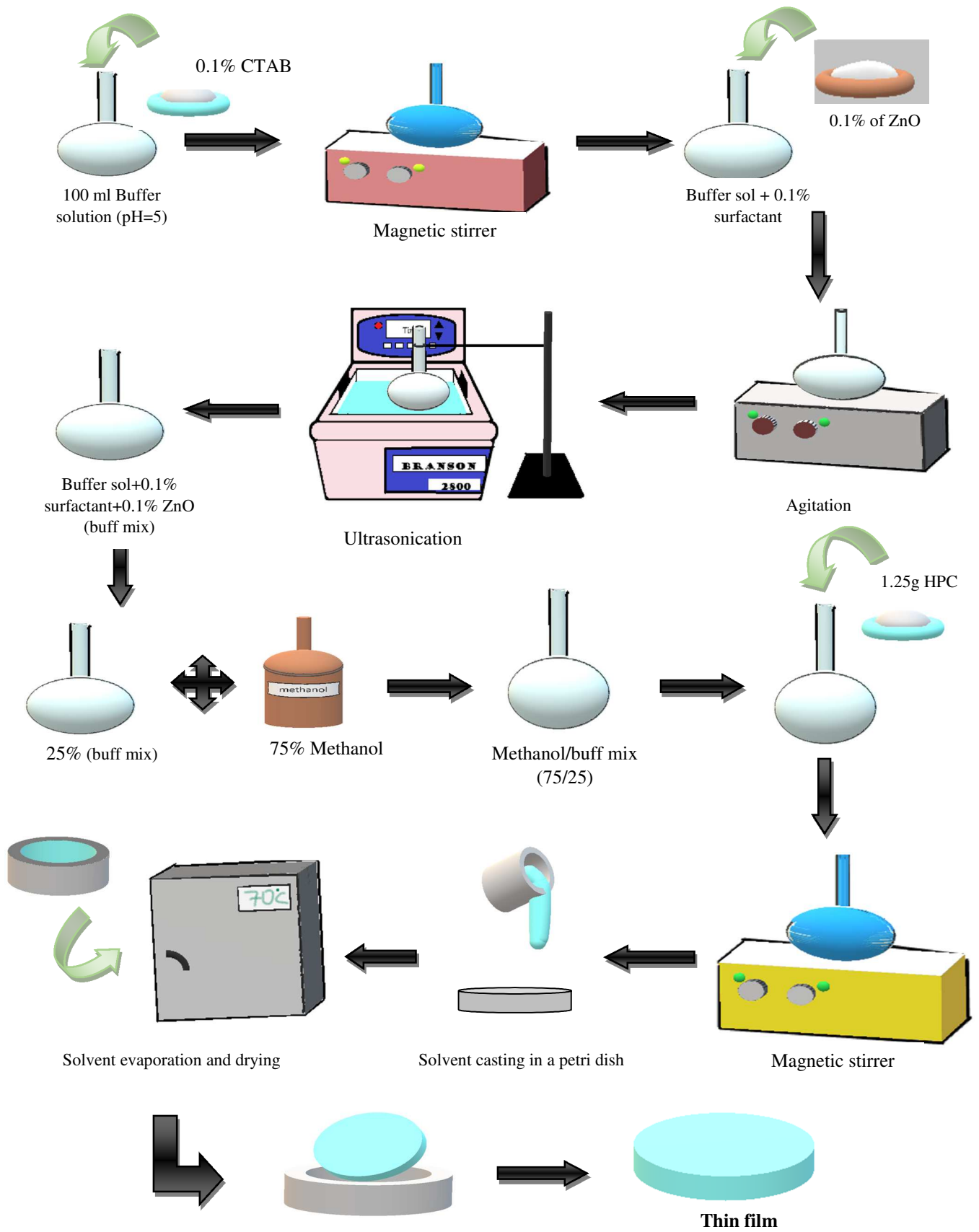
III.4. Characterization techniques

III.4.1. Fourier transform infrared (FTIR) spectroscopy

Infrared spectroscopy studies the interactions between matter and electromagnetic fields in the **IR** region. In this spectral region, a molecule can be excited to a higher vibrational state by absorbing **IR radiation. IR spectroscopy** is, therefore, a very useful technique, which provides fingerprint information on the chemical composition of the sample.

Infrared **(IR)** spectroscopy is one of the most important and common spectroscopic techniques used by chemists for structural elucidation and compound identification. IR spectroscopic analysis is used to determine the various chemical functional groups present in the sample. Different functional groups absorb characteristic frequencies of IR radiation **[61].**

III.4.1.1. The Beer-Lambert Law

The Beer-Lambert Law (also called Beer's Law) is a relationship between the attenuation of light through a substance and the properties of that substance.

The Beer-Lambert law is a linear relationship between the absorbance and the concentration, molar absorption coefficient and optical coefficient of a solution **[62].**

$$A = \varepsilon.l.c$$

A **(no units):** absorbance.

ε **(mol^{-1}/cm^2) :** molar extinction coefficient.

c (mol/cm^3): molar concentration.

l (cm): optical pathlength.

III.4.1.2. Regions of the Infrared spectrum

Most of the bands that indicate what functional group is present are found in the region from 4000 cm^{-1} to 1300 cm^{-1}. Their bands can be identified and used to determine the functional group of an unknown compound **[63].**

Figure III.11: Infrared spectrum regions [63].

Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from **1300 cm^{-1}** to **400 cm^{-1}**. These bands are only used to compare the spectra of one compound to another.

The samples used in IR spectroscopy can be either in the solid, liquid, or gaseous state **[63].**

III.4.1.3. Principle of Infrared Spectroscopy

The **IR** spectroscopy theory utilizes the concept that molecules tend to absorb specific frequencies of light that are characteristic of the corresponding structure of the molecules. The energies are reliant on the shape of the molecular surfaces, the associated vibronic coupling, and the mass corresponding to the atoms.

For instance, the molecule can absorb the energy contained in the incident light and the result is a faster rotation or a more pronounced vibration **[63].**

III.4.1.4. IR Spectroscopy Instrumentation

The instrumentation of infrared spectroscopy is illustrated below. First, a beam of **IR** light from the source is split into two and passed through the reference ant the sample respectively.
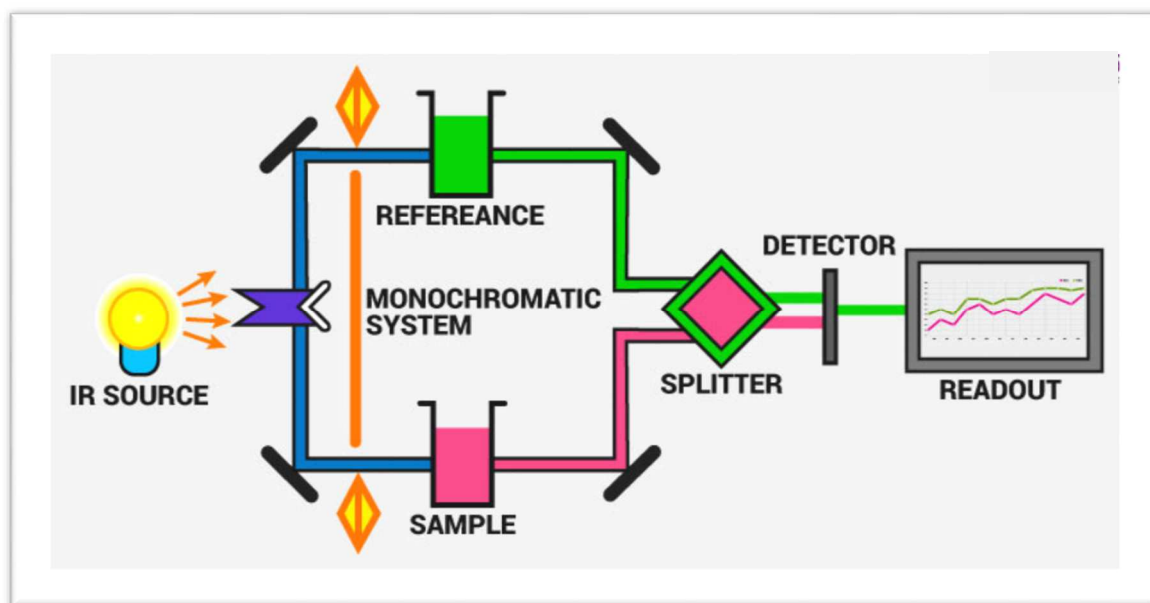
Figure III.12: IR Spectroscopy Instrumentation [63].

Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector **[63].**

The tested films were prepared under the conditions mentioned above. The analyses were carried out on a Perkin Elmer type device, assisted with a   microcomputer in **Château-neuf EL- BIAR.**

Figure III.13: infrared spectroscopy instrumentation « PERKIN ELMER ».

III.4.2. X-ray diffraction (XRD)

X-ray diffraction is a powerful non-destructive technique used to analyse all kinds of matter ranging from fluids, to powders and crystals, and with the advent of new optical systems thin film analysis can also be carried out using **XRD**.

XRD is a unique method for the determination of the crystallinity of different compounds. From research to fabrication and engineering, **XRD** is an indispensable technique for material characterization and quality control**.**

It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects **[64-65].**

The **X-ray** diffractograms **(XRD)** of the **ZnO** dispersed in polymer samples were recorded using **BRUKER "D2 PHASER" [67].**

Generally, **X-ray** diffractogram of BRUKER is recorded on an **X-ray** diffractometer operating at known voltages

 (10 mA) and current **(30 kV)** using a **Cu Kα X-rays (λ = 1.5406 nm)** over the **2θ** range from **10** to **100** degrees.

Figure III.14: x-ray diffraction (BRUKER "D2 PHASER").

III.4.2.1. Fundamental Principles of X-ray Diffraction

The **XRD** technique is based on the constructive interference of monochromatic **X-rays** and a sample.

The **X-rays** are generated using a cathode ray tube, filtered to construct monochromatic radiation, collimated to concentrate the radiation, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (a diffracted ray) **[65].**

In simple words a monochromatic beam of **X-rays** is allowed to incident on a sample, and reflected **X-rays** are detected by a detector **[68].**

The next figure shows schematic diagram of a typical **XRD** detection system.
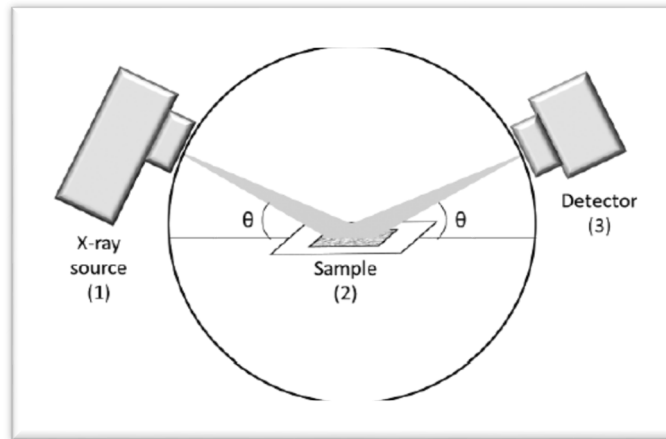
Figure III.15: Schematic diagram of X-ray detection system used in XRD technique. [69].

III.4.2.2. Bragg's law

The technique uses Bragg's law of diffraction as was discussed earlier.

In fact, Bragg's law is one of the keystones to understanding **X-ray** diffraction:**[65]**

$$n\ \lambda = 2\ d\ \sin\theta$$

With**:**

n: is an integer,

λ: is the characteristic wavelength of the **X-ray** beams impinging on the crystallize sample,

d: is interplanar spacing between rows of atoms.

θ: is the angle of the **X-ray** beams with respect to these planes.

Within the crystalline lattice, a set of parallel atomic planes can be described that are separated by a distance (d). **X-rays** striking the first plane are reflected at the incident angle**, θ**, as shown In Figure **III.16.**

Diffraction of the incident **X-ray** beam by atomic planes in a crystalline solid **[69].**
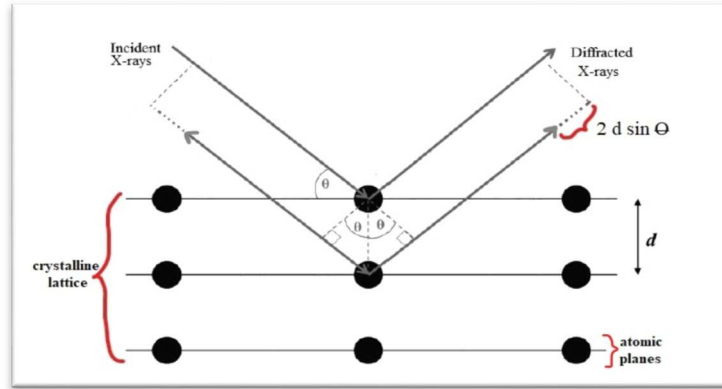
Figure III.16: Bragg's law [69].

III.4.3. Ultraviolet visible spectroscopy

UV-visible spectroscopy is one of the important characterization techniques to study the optical properties.it used in order to acquire absorption measurements for different materials or fluids. By measuring the absorption of different wavelengths by a sample, a spectrum is obtained by plotting a graph between the wavelength of the whole region and the absorption of each wavelength.

The ultraviolet region can be further divided into two regions: far **UV** (**100-200nm)** and near-**UV (200-400 nm).**

UV-visible spectroscopy primarily is a quantitative analytical technique concerned with the absorption of near-**UV (200-400 nm)** or visible (**390–780 nm)** radiation **[65].**
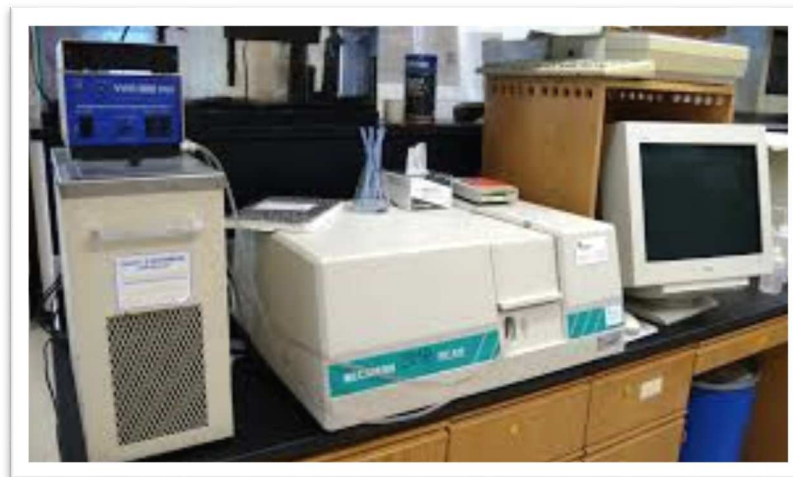
Figure III.17: UV-Visible spectrophotometer [70].

III.4.3.1 Principle of UV-Visible spectroscopy

Spectrophotometer is an instrument used to measure the absorbance of light by a sample. This instrument works on the principle of Beer-Lambert Law. In this instrument, wavelength of light to be passed through sample is selected using prisms or gratings and absorption of light by the unknown sample is measured. Light source should emit a strong bond of radiation over the entire wavelength range for which instrument is designed. Power of radiation should be sufficient for adequate detector response **[71].**
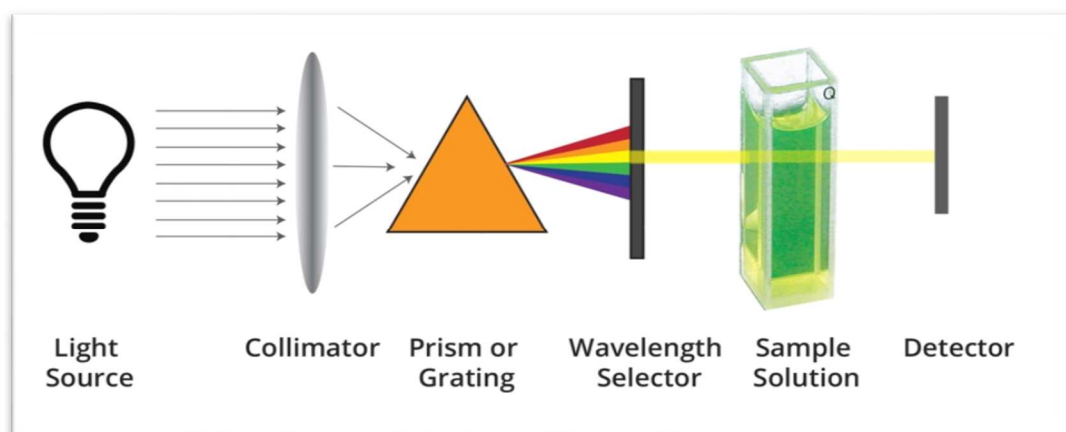
Figure III.18 : Schematic diagram of spectrophotometer system used in UV-visible spectroscopy technique [71].

It helps to understand the interaction between the matrix and the nanofiller and analyses the role of nanofillers in enhancing the property of the nanocomposites. Coupled with other characterization methods, **UV-Vis** spectroscopy is an indispensable tool to evaluate the desired optical properties of nanofillers in a polymer matrix.

The optical properties of hydroxypropyl cellulose films were determined by measuring the light transmission spectra of the films using a **SHIMADZU 1800 UV**-visible spectrophotometer.

Film samples **(7cm-7cm)** were placed directly into the spectrophotometer test cell and air was used as a reference.

III.4.4. Scanning electron microscopy (SEM)

Scanning electron microscopy **(SEM),** which is also recognized as **SEM** analysis or **SEM** technique, has been used worldwide in many disciplines. It can be regarded as an effective method in analysis of organic and inorganic materials on a nanometer to micrometer (µm) scale. **SEM** works at a high magnification reaches to **300,000x** and even **1000000** (in some modern models) in producing images very precisely of wide range of materials **[72].**

Scanning electron microscopy **(SEM)** with a secondary electron detector can visualize crystal shape, surface morphology, dispersed and agglomerated nanoparticles, and surface functionalizations. **SEM** can examine each particle, including the aggregate particles, individually; thus, the method is considered to be an absolute measurement of particle size. It can be coupled to image analysis computers for examination of each field for particle distribution **[73].**

III.4.4.1. SEM equipment

SEM is widely used to investigate the microstructure and chemistry of a range of materials. The main components of the **SEM** include a source of electrons, electromagnetic lenses to focus electrons, electron detectors, sample chambers, computers, and displays to view the images. Electrons, produced at the top of the column, are accelerated downwards where they passed through a combination of lenses and apertures to produce a fine beam of electrons. The electron beam hits the surface of the sample mounted on a movable stage under vacuum. The sample surface is scanned by moving the electron-beam coils. This beam scanning enables information about a defined area of the sample. The interaction of the electron beam with the sample generates a number of signals, which can then be detected by appropriate detectors **[73].**

41
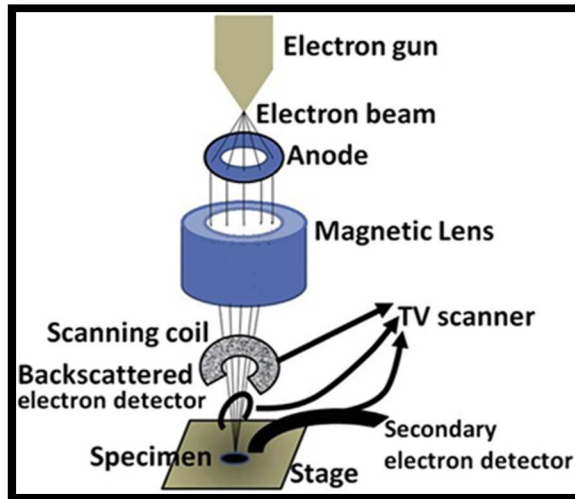
Figure III.19: Components of scanning electron microscopy (SEM) [73].

IV. Results and discussion.

In this chapter, the results of the study are presented and discussed, we will present our results of research and give reasonable interpretations.

IV.1. Characterization by Fourier transform infrared (FTIR) spectroscopy

The characterization by infrared spectroscopy is a major importance, due to its usefulness in determining structures of compounds and identifying them.

IV.1.1. FTIR of HPC/ZnO film

The analyses by **FTIR** were carried out firstly on **HPC/ZnO.**

The characteristic peaks of the different groups of **HPC/ZnO** film are shown in figure **IV.1:**

- **B**etween **3400-3200 cm $^{-1}$**: we mainly see broad band corresponding to stretching vibrations of the hydroxyl groups located on the surface of **Zn (OH)$_2$** of **HPC**.

- **A**t **2976 cm^{-1}**: strong peak corresponding to stretching vibrations of **sp^3** of **C-H** and **-CH$_2$** of **HPC.**

- **P**eaks around **1432 cm^{-1}** corresponding to deformation vibrations of CH- CH$_2$.

- **A**t **1070 cm^{-1}**: strong and sharp peak corresponding to stretching vibrations of **C-O (Ether group) of HPC.**

- **A**t **839-750 cm^{-1}:** at lower wavenumbers, **Zn-OH** bending is observed.
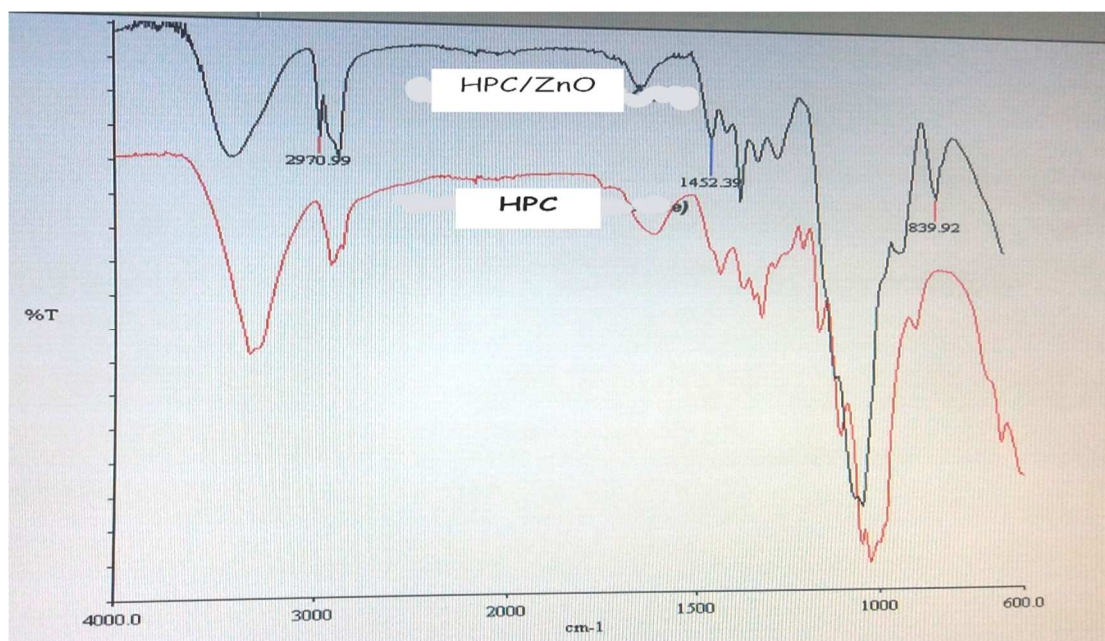
Figure IV.1: FTIR spectrum of HPC/ZnO film.

IV.1.2. FTIR of HPC methanol (pH=5, CTAB, ZnO) film.

The analyses by **FTIR** were carried out secondly on **HPC** methanol (**pH=5, CTAB, ZnO).**

The characteristic peaks of the different groups of **HPC** methanol (**pH=5, CTAB, ZnO**) film are shown in figure **IV.2:**

- **B**etween **3500 cm** **-1:** we mainly see a broad band corresponding to stretching vibrations of the hydroxyl groups located on the surface of **Zn (OH)$_2$.**

- **A**t **2976 cm^{-1}** strong peak corresponding to stretching vibrations of **sp^3 C-H** bond of **-CH$_2$ and -CH$_3$ of HPC.**

- **P**eaks around **1432 cm^{-1}** corresponding to deformation vibrations of CH-CH$_2$.

- **A**t **1090-1070 cm^{-1}:** strong and sharp peak corresponding to stretching vibrations of **C-O of HPC.**

- **A**t **840 cm^{-1}**: weak to medium peak observed in the low energy region (fingerprint) is formed by the stretching vibrations modes of **Zn-OH.**
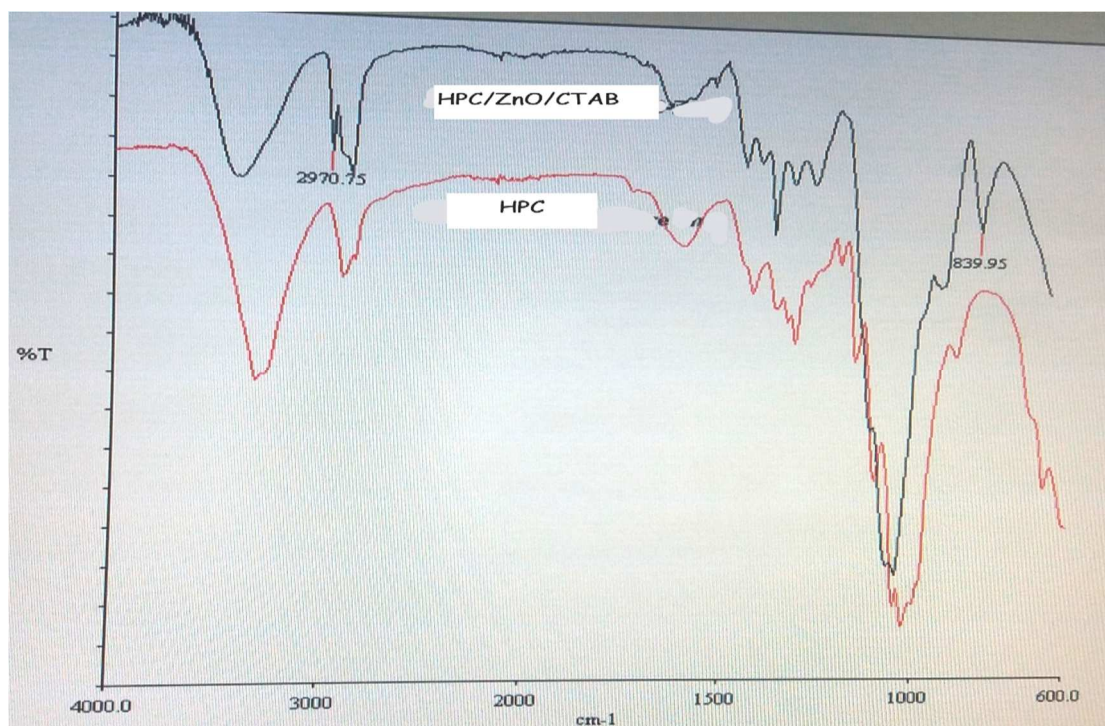
Figure IV.2 : FTIR spectrum of HPC methanol (pH=5, CTAB, ZnO).

IV.2. Analysis of X-ray diffraction spectra

The structural properties of hydroxypropyl cellulose films were determined by measuring the crystallinity of the samples using **BRUKER "D2 PHASER.**

Figures **IV .3** and **IV .4** shows the **X-ray** diffraction spectra of the samples.
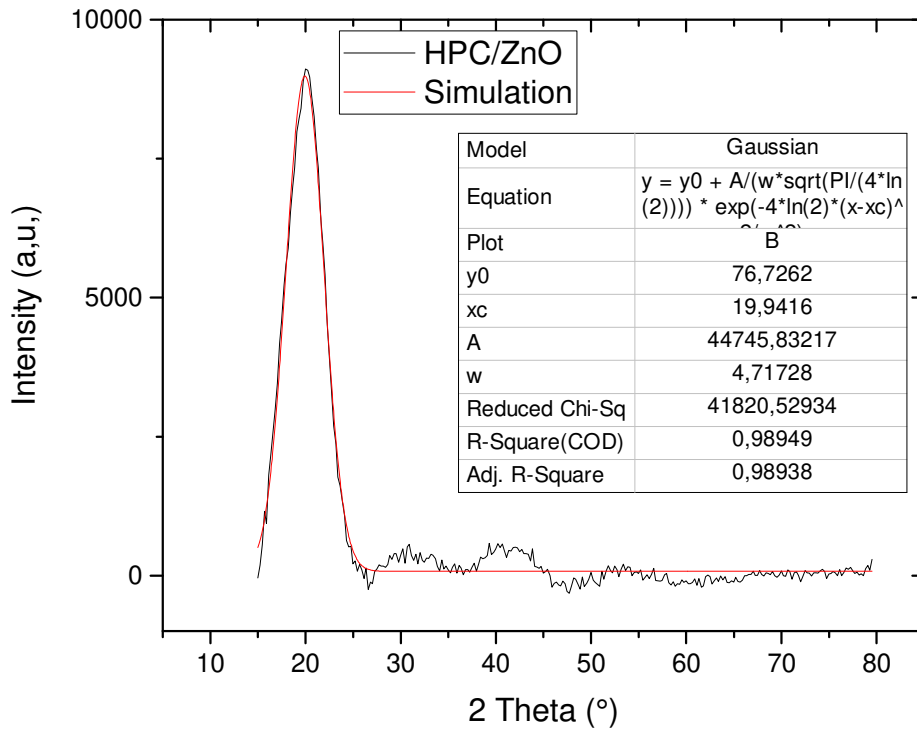
Figures IV .3: XRD scan of HPC/ZnO film.

IV.2.1. Interpretation

The figures (**IV.3.** and **IV .4**.) shows the **DRX** diffractograms of **HPC/ZnO** and **HPC/ZnO/CTAB** films.

The patterns of the film **HPC/ZnO** show that broad peak corresponding to the Bragg angle **2θ=19.94°** in (Figure **IV .3**.).

Figure **IV.3** show the film of **HPC/ZnO**, we notised the presense of high band of the amourphous part of **HPC**, the air of the amorphous part is equal to **44745, 83.**

We have noticed the absence of crystalline peaks even though our films are incorporated by **ZnO** nanoparticles.

Our hypothesis is that the hydroxypropyl cellulose enveloped the particles of zinc oxide, that's why there is no crystallite phase.

Figure **(IV. 4)** represents high band with different peaks into the band. The band represents the amorphous phase of **HPC** and the peaks in presents the intense peak of **Zn(OH)₂.**
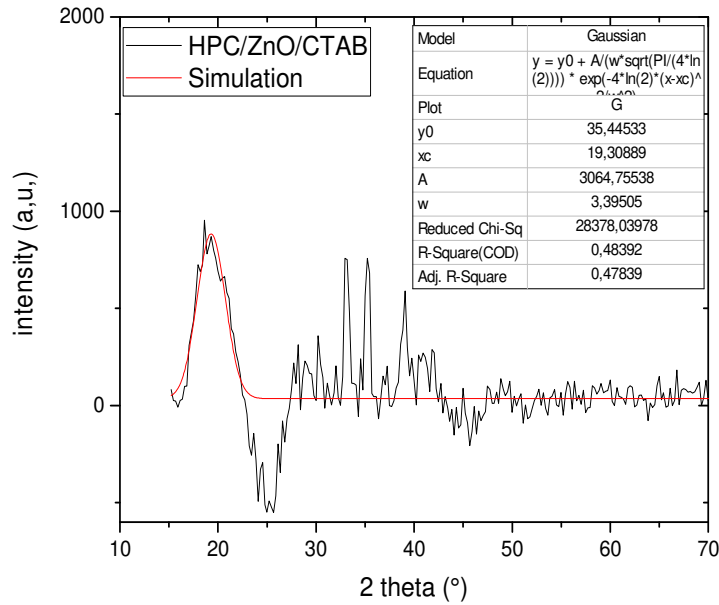
Figure IV.4: XRD scan of HPC/ZnO/CTAB sample.

IV.2.2. Calculation of the mean size of the crystalline

Sherrer equation serves to calculate the coherent scattering region, which is usually considered as being equal to crystallite size:

$$L = \frac{K.\lambda}{\beta.\cos\theta}$$

Where:

L: is a measure of the dimension of the particle in the direction perpendicular to the reflecting plane.

λ: is the X-ray wavelength (nm).

K: is a constant (often 1).

β: is the peak width (rad).

θ: is the scattering angle (rad) **[74].**

$$L = \frac{1.5418 \times 1}{3.3951 \times \cos(9.6544)}$$

$$L = 26.41 \text{ nm}$$

Then the dimension of the particle is **26.41 nm.**
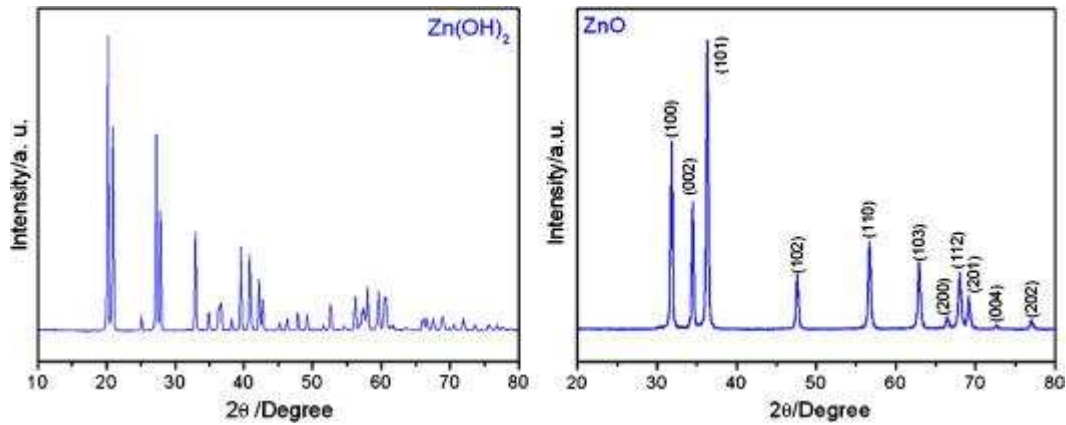
Figure IV.**5**: **XRD scan of ZnO nanoparticles (a), Zn(OH)₂ nanoparticles [75].**

IV.2.3. Interpretation

The **XRD** diagram of **HPC/ZnO/CTAB** films (Figure **IV.4**.) shows a number of Bragg reflections with **2 θ** ° the values of: **19.31** °, **28.69** °, **31.84** °, **34.02** ° in the range of **(0** ° to **70** °)**.**

According to figure **IV .5** we notice that the peaks of the values **19.31** °, **28.69** °, show a diagram of **DRX** of **Zn(OH)₂** on the other hand the peaks which corresponding to the values: **31.84** °, **34.02** ° show a diagram of **XRD of ZnO**.

From the results of **X-ray** diffraction we can conclude that in our films of **HPC/ZnO/CTAB** there is the coexistence of **ZnO** and **Zn(OH)₂** crystals.

In the films which contain the dispersant **(CTAB)** the **DRX** analysis shows the presence of a crystallite phase so from these results we can say that there is an effect of the dispersant (despite the concentrations are very low **(0.1%)** on the dispersion of particles.

IV.3. Characterization by Scanning electron microscopy (SEM)

The scanning electron microscope used is a «Cambridge Zeiss», StereoScan 240, (United Kingdom) coupled with a computer allowing the image to be taken. The microscopic observations were made in the laboratory of the Faculty of Medical Physics of the University of **Saad Dahlab**.

IV.3.1. HPC/ZnO film micrographs

Figure.**IV.6** shows the micrographs of the surface of the **HPC/ZnO** film without surfactant with magnification of **3000, 8000** and **30,000**.

The size of the particles is in the order of micrometer and the shape of the particles is homogenuoes and circular.
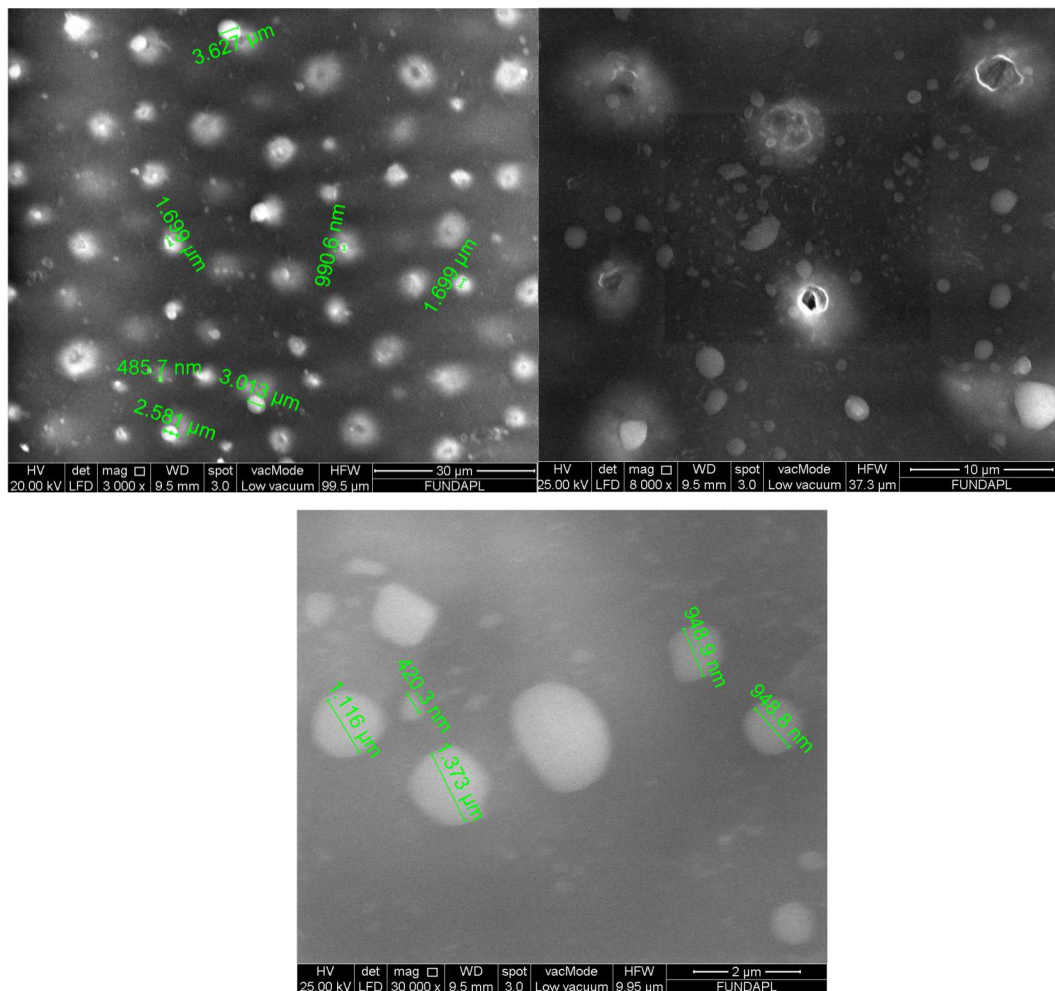
Figure IV.6: HPC/ZnO film micrographs with 3000, 8000 and 30,000 magnifications.

According to the literature, when the energy of primary electrons is high, other electrons can be removed from the material. These are back-scattered electrons that have a lot of energy. This method gives information on the density of the sample. The heavier the elements studied, the greater the amount of electrons returned. On the screen, this phenomenon results in a greater intensity of light in the densest areas, that is to say where the elements are heavier. This density is proportional to a colouration between gray levels. The denser the material, the more the white colour prevails and vice versa. This observation suggests that the **HPC/ZnO** film is rich in particles with sizes of the order of the micrometer.

IV.3.2. Surface micrographs of HPC/ZnO films in the presence of CTAB

The microstructure **HPC/ZnO** in the presence of CTAB films were observed by **SEM** and gave the micrographs shown in Figure **IV.7:**
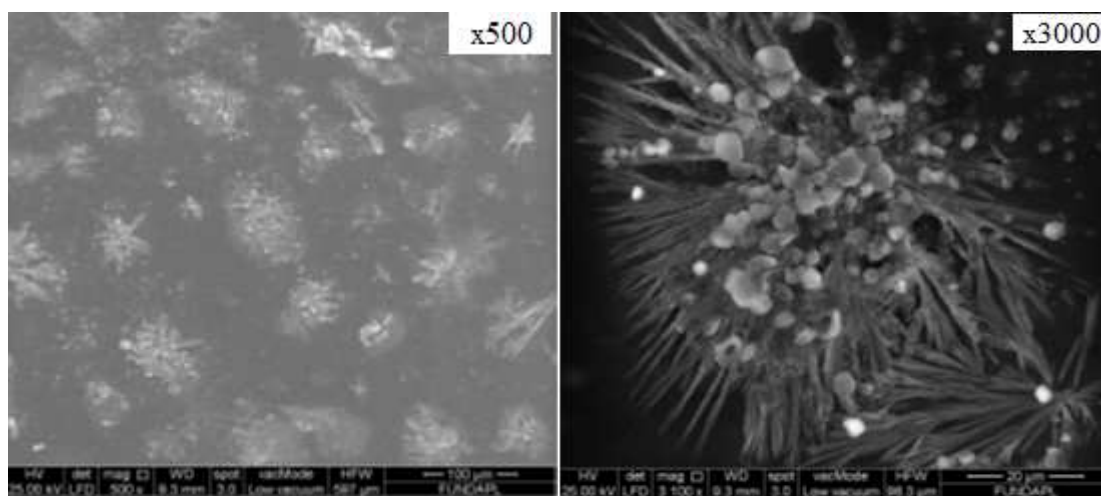
Figure IV.7 : Surface micrographs of hydroxypropyl cellulose HPC/ZnO films in the presence of CTAB at X500 magnification and X3,000.

The micrograph with mgnification **(x500)** showed a good distribution of aggregate **ZnO** in the matrix **HPC**. With high manification **(x3000),** micrograph showed clearly the effect of **CTAB** on the morphology of **ZnO** particles aggregation within the film. **A** coexistence of flower and prism morphologies in cationic environment is the major

finding for this part of the work. The size of the flower is pratically the same in film and the shape of the **ZnO** particles is circular. We can note that the aggregation is a bad phenomenon in the preparation of the microcomposite.

IV.4. Characterization by UV-visible spectrophotometer

IV.4. 1.Optical properties of hydroxypropyl cellulose films

The hydrogel of **HPC** was prepared in two different forms; one of theme was without a dispersant and the other form with a dispersant **"CTAB". CTAB** solution has a white color while the other one without dispersant was transparent.

Our films were transparent and clear for both forms, with and without dispersant. The optical properties of hydrogel films were determined by measuring the light transmittance in the range of **200** to **800 nm.** The spectral results on light transmittance and visual appearance of films have been presented inuv Figure **IV .8.**
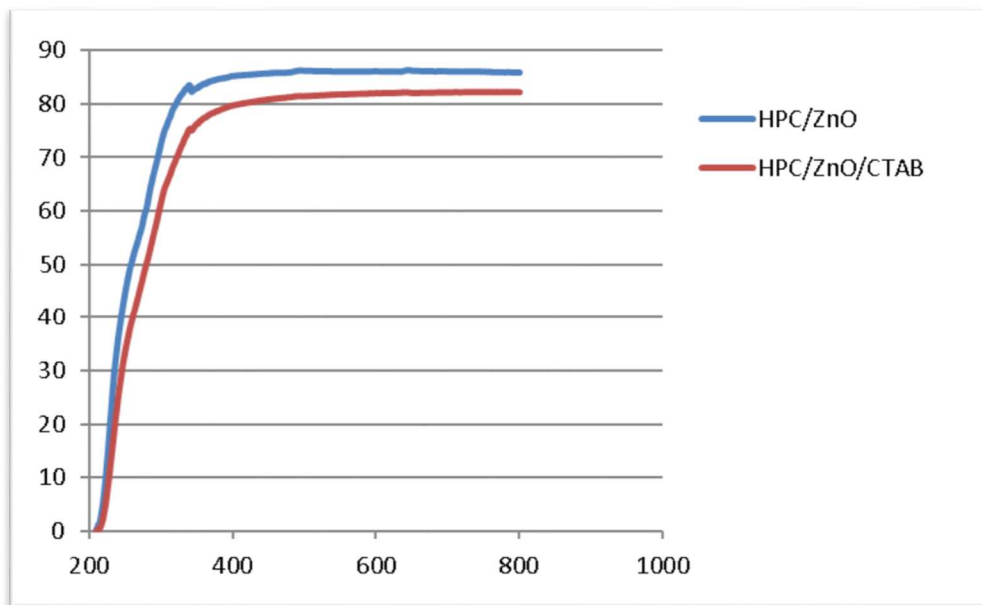
Figure IV .8: Transmission spectrum of hydrogel HPC films with 0.1%
ZnO/ZnOH$_2$ without surfactant (1), with CTAB (2).

IV.4. 2.Interpretation

The **HPC** film without active material is transparent with the highest transmittance of **86%** at **660 nm**. The transparency of our film was slightly decreased to **83%** by incorporating **CTAB.**

Interestingly, the decrease in the light transmittance of composite films incorporating metallic **NPs** and surfactant has been mainly attributed to the interference with the passage of light by metallic **NPs**.

However, we can say that the surfactant/nanoparticle combinations and the presence of aggregation of **(ZnO/ZnOH₂)** may be responsible for this more pronounced decrease which could be due to the **ZnO** crystallized in the film. In the two film have a good optical propreties (**≥ 80%** of transmission).

Conclusion

The main objective of our work was the synthesis of films based on **HPC** doped by nanoparticles of zinc oxide to improve their properties even at extremely low **ZnO** loadings.

The characterization of the **HPC/ZnO** and **HPC/ZnO/CTAB** films was achieved by Fourier Transform Infrared spectroscopy **(FTIR), X** ray diffractions (**XRD** analysis), UV spectroscopy, and scanning electron microscope **(SEM).**

The **FTIR** characterization showed that the band between **(3200- 3500cm^{-1})** in the **HPC/ZnO/CTAB** is larger than that of **HPC/ZnO**. It is may be due to the formation of **Zn(OH)$_2$** favored by the presence of **CTAB**. At low wavenumbers **(840- 750 cm^{-1})** presents **Zn-OH** bending and **OH** liberation.

The presence of the **CTAB** has a remarkable effect on the movement of bands towards a larger wavelength due to the attenuation of the interaction bonds between the macromolecular chains and **CTAB.**

The **XRD** diffractogram **HPC/ZnO** film showed the absence of crystalline peaks even though our films are incorporated by **ZnO** particles as a result, the hydroxypropyl cellulose has wrapped the particles of zinc oxide, that's why there is no crystallite phase. Through the **XRD** results of **HPC/ZnO/CTAB** film, we can conclude that there is a coexistence of **ZnO** and **Zn(OH$_2$)** crystals in our films of **HPC/ZnO/CTAB**.

The **SEM** micrographs of **HPC/ZnO** film is rich in **ZnO** particles with sizes of the order of the micrometer.

The **SEM** Characterization of **HPC/ZnO/CTAB** film showed the presence of flower shape with same size, with high magnification the presence of mineral particle with reflection **(ZnO and Zn(OH)$_2$).** The particles with flower shape were very well distributed on the surface of the film but very bad dispersed.

The **HPC** film without active material is transparent with the highest transmittance of **86%** at **660 nm**. The transparency of our film was slightly decreased to **83%** by incorporating **CTAB.**

UV-visible spectroscopy was used to investigate the dispersion and stability of zinc oxide nanoparticles in aqueous media with and without dispersants.

Most researches in recent years work in field of polymer nanocomposites because of their wide range of applications.

PERSPECTIVES

In addition to this work, it would be interesting to carry out:

- **T**he use of other types of surfactants to attain a homogenous dispersion and good distribution.

- **T**he use of another cellulose **HPMC** to explain the effect of the matrix on the distribution of the nanoparticles.

- **A** rheological study to confirm dispersion.

- **E**nrich the study using alternative characterization methods such as **RAMAN** spectroscopy.

.

References

[1] Ponnamma, D., Cabibihan, J.-J., Rajan, M., Pethaiah, S. S., Deshmukh, K., Gogoi, J. P., … Cheng, C. (2019). Synthesis, optimization and applications of ZnO/polymer nanocomposites. Materials Science and Engineering: C. doi: 10.1016/j.msec.2019.01.081

[2] Y. Yang, Y. Zhou, F. Boey, and Y. Long, "Temperature-responsive hydroxypropylcellulose based thermochromic material and its smart window application," R. Soc. Chem., p. 13, 2016, doi: 10.1039/C6RA12454B.

[3] J. E. Hulla, S. C. Sahu, and A. W. Hayes, "Nanotechnology: History and future," Hum. Exp. Toxicol., vol. 34, no. 12, pp. 1318–1321, 2015, doi: 10.1177/0960327115603588.

[4] B. Y. Wyser *et al.*, "Outlook and Challenges of Nanotechnologies for Food Packaging," no. June, pp. 615–648, 2016, doi: 10.1002/pts.

[5] L. Leon, E. J. Chung, and C. Rinaldi, A brief history of nanotechnology and introduction to nanoparticles for biomedical applications. Elsevier Inc., 2020.

[6] J. Huot, Nanostructured Materials, no. 9783319351063. 2016.

[7] M. Nasrollahzadeh, S. M. Sajadi, M. Sajjadi, and Z. Issaabadi, Applications of Nanotechnology in Daily Life, 1st ed., vol. 28. Elsevier Ltd., 2019.

[8] S. Lanone and J. Boczkowski, "Les sources de nanoparticules," *Rev. Fr. Allergol.*, vol. 50, no. 3, pp. 211–213, 2010, doi: 10.1016/j.reval.2010.01.039.

[9] M. Bouloudenine and M. Bououdina, Toxic Effects of Engineered Nanoparticles on Living Cells, no. January. 2016.

[10] Goswami, P., & O'Haire, T. (2016). Developments in the use of green (biodegradable), recycled and biopolymer materials in technical nonwovens. Advances in Technical Nonwovens, 97–114. doi:10.1016/b978-0-08-100575-0.00003-6

[11] M. Mohiuddin, B. Kumar, and S. Haque, *Biopolymer Composites in Photovoltaics and Photodetectors*. Elsevier Inc., 2017.

[12] M. Ekiert, A. Mlyniec, and T. Uhl, "The influence of degradation on the viscosity and molecular mass of poly(lactide acid) biopolymer," Diagnostyka, vol. 16, no. 4, pp. 63–70, 2015.

[13] Mukherjee, P. K. (2019). Extraction and Other Downstream Procedures for Evaluation of Herbal Drugs. Quality Control and Evaluation of Herbal Drugs, 195–236. doi:10.1016/b978-0-12-813374-3.00006-5

[14] Šuput Danijela ORCID, Lazić Vera, Popović Senka ORCID, Hromiš Nevena, Bulut Sandra (2017) BIOPOLYMER FILMS SYNTHESIS AND CHARACTERISATION SINTEZA I KARAKTERIZACIJA BIOPOLIMERNIH FILMOVA, Journal on Processing and Energy in Agriculture, 21 (2017), p 9-12

[15] PARTAIN, E. M. (2000). INDUSTRIALLY IMPORTANT POLYSACCHARIDES. Applied Polymer Science: 21st Century, 303–323. doi:10.1016/b978-008043417-9/50018-0

[16] T. Al Mobarak, "MATERIAL PROPERTIES OF ACETYLATED JUTE-MAT COMPOSITES M . Phil Department of Physics Faculty of Engineering B angladesh U niversity of E ngineering and T echnology (BUET) Dhaka-1000 , Banglade Thesis," 2017.

[17] P. S. Siân, Owen;C, Raymond Rowe,;J, Handbook of Pharmaceutical Excipients, no. 1. 2006.

[18] V. S. Raghuwanshi and G. Garnier, "Cellulose Nano-Films as Bio-Interfaces," Front. Chem., vol. 7, no. July, pp. 1–17, 2019, doi: 10.3389/fchem.2019.00535.

[19] Y. Takeuchi, K. Umemura, K. Tahara, and H. Takeuchi, "Formulation Design of Hydroxypropyl Cellulose Films for Use as Orally Disintegrating Dosage Forms," J. Drug Deliv. Sci. Technol., 2018, doi: 10.1016/j.jddst.2018.05.002.

[20] Deshmukh K, Basheer Ahamed M, Deshmukh RR, Khadheer Pasha SK, Bhagat PR, Chidambaram K (2017). Biopolymer Composites With High Dielectric Performance: Interface Engineering. Biopolymer Composites in Electronics, pp. 27–128. doi:10.1016/b978-0-12-809261-3.00003-6.

[21] https://www.chemicalbook.com/ChemicalProductProperty_EN_cb3225318.htm

[22] Ghadermazi, R., Hamdipour, S., Sadeghi, K., Ghadermazi, R., & Khosrowshahi Asl, A. (2019). Effect of various additives on the properties of the films and coatings derived from hydroxypropyl methylcellulose—A review. Food Science & Nutrition. doi:10.1002/fsn3.1206

[23] Application of HPMC and HPMCAS to Aqueous Film Coating of Pharmaceutical Dosage Forms Sakae Obara and Hiroyasu Kokubo Cellulose and Pharmaceutical Excipients Department, Shin-Etsu Chemical Co., Ltd

[24] Guo JH, Skinner G, Harcum W, Barnum P (1998). Pharmaceutical applications of naturally occurring water-soluble polymers. Pharmaceutical Science & Technology Today, 1(6), 254–261. doi:10.1016/s1461-5347(98)00072-8.

[25] K. Mylvaganam, Y. Chen, W. Liu, M. Liu, and L. Zhang, "Hard thin films: application and challenges," in Anti-Abrasive Nanocoatings, 2015, pp. 543–567.

[26] S. Karki, H. Kim, S. J. Na, D. Shin, K. Jo, and J. Lee, "Thin films as an emerging platform for drug delivery," Asian J. Pharm. Sci., vol. 11, no. 5, pp. 559–574, 2016, doi: 10.1016/j.ajps.2016.05.004.

[27] M. Benelmekki and A. Erbe, "Nanostructured thin films background , preparation and relation to the technological revolution of the 21st century," in Nanostructured thin films, 2019, pp. 1–34.

[28]　　Kathe, K., & Kathpalia, H. (2017). Film forming systems for topical and transdermal drug delivery. Asian Journal of Pharmaceutical Sciences, 12(6), 487–497. Doi : 10.1016/j.ajps.2017.07.004.

[29]　　LASMI SOFIANE (2014).　Effets des taux de l'agent traitant et de l'agent compatibilisant sur les propriétés des nanocomposit es Polypropylène /Silice. [diplôme de MAGISTER]. UNIVERSITE SETIF-1.

[30]　Alexandra Siot. ELABORATION ET CARACTERISATION DE POLYMERES NANOCHARGES. Polymères. IMT - MINES ALES - IMT - Mines Alès Ecole Mines - Télécom, 2018. Français. ffNNT : 2018EMAL0001

[31]　　Jamróz, Kulawik, & Kopel. (2019). The Effect of Nanofillers on the Functional Properties of Biopolymer-based Films: A Review. Polymers, 11(4), 675. doi:10.3390/polym11040675

[32]　　Dantas de Oliveira, A., & Augusto Gonçalves Beatrice, C. (2019). Polymer Nanocomposites with Different Types of Nanofiller. Nanocomposites – Recent Evolutions. doi:10.5772/intechopen.81329

[33]　M. H. Godinho, D. G. Gray, and P. Pieranski, "Revisiting (hydroxypropyl) cellulose (HPC)/water liquid crystalline system," *Liq. Cryst.*, vol. 44, no. 12–13, pp. 2108–2120, 2017, doi: 10.1080/02678292.2017.1325018.

[34]　T. Dürig and K. Karan, "Binders in wet granulation," in Handbook of Pharmaceutical Wet Granulation: Theory and Practice in a Quality by Design Paradigm, 2018, pp. 317–349.

[35]　ashland, "hydroxypropylcellulose," *chempoint*, 2017. .

[36]　P.S.Siân, Owen;C,Raymond Rowe,;J,Handbook of pharmaceutical Excipients , no.1.2006.

[37]　T. Wüstenberg, "Hydroxypropylcellulose," in Cellulose and cellulose derivatives in the food industry: fundamentals and application., 2015, pp. 319–342.

[38**]**　T. Wüstenberg, "Hydroxypropylcellulose," in *Cellulose and cellulose derivatives in the food industry: fundamentals and application.*, 2015, pp. 319–342.

[39]　　https://www.corrosionpedia.com/definition/2454/zinc-oxide

[40]　　Kołodziejczak-Radzimska, A., & Jesionowski, T. (2014). Zinc Oxide—From Synthesis to Application: A Review. Materials, 7(4), 2833–2881. doi:10.3390/ma7042833

[41]　　Darvell BW (2018). DSc CChem CSci FRSC FIM FSS FADM. In: Materials Science for Dentistry (10th Edition), Duxford, UK, Cambridge, MA, Woodhead Publishing.

[42]　　Liu Yang. Caractérisation de couches minces de ZnO élaborées par la pulvérisation cathodique en continu. Autre. Université du Littoral Côte d'Opale, 2012. Français. ffNNT : 2012DUNK0334ff. fftel-00919764

[43] Dai S, Park HS (2013). Surface effects on the piezoelectricity of ZnO nanowires. Journal of the Mechanics and Physics of Solids, 61(2), 385–397. doi:10.1016/j.jmps.2012.10.003.

[44] Norton DP, Heo YW, Ivill MP, Ip K, Pearton SJ, Chisholm MF, Steiner T (2004). ZnO: growth, doping & processing. Materials Today, 7(6), 34–40. doi:10.1016/s1369-7021(04)00287-1.

[45] Recent trends in nanostructured particles: synthesis, functionalization, and applications Ahmed Barhoum, ... Guy Van Assche, in Fundamentals of Nanoparticles, 2018.

[46] Lakshmeesha Rao, B., Madhukumar, R., Sharath Chandra, K., Neelakandan, R., Wang, Y., & Sangappa, Y. (2018). Physicochemical and Antimicrobial Properties of Gamma Irradiated HPMC-ZnO BNC Films. Materials Today: Proceedings, 5(10), 21398–21405. doi:10.1016/j.matpr.2018.06.546

[47] Zare, Y. (2016). Study of nanoparticles aggregation/agglomeration in polymer particulate nanocomposites by mechanical properties. Composites Part A: Applied Science and Manufacturing, 84, 158–164. doi:10.1016/j.compositesa.2016.01.020

[48] Albrecht, Kaspar. (2018). Redispersibility of Cellulose Nanofibrils.

[49] O. Kurtas et al., "The evaluation of deaths due to methyl alcohol intoxication " Biomed. Res., vol. 28, no. 8, pp. 3680–3687, 2017.

[50] Muhammet Kayfeci ; Ali Kecebaş, "Hydrogen storage," in *Solar hydrogen production*, 2019, pp. 85–110.

[51] inrs, "Méthanol," 2018.

[52] VAL.TECH, "Methanol," 2012.

[53] D. Suput, V. Lazic, S. Popovic, N. Hromis, and S. Bulut, "Biopolymer films synthesis and characterisation," *J. Process. Energy Agric.*, vol. 21, no. 2, pp. 9–12, 2017, doi: 10.5937/jpea1701009s.

[54] F. Wahid, T. Khan, Z. Hussain, and H. Ullah, "Nanocomposite scaffolds for tissue engineering; properties, preparation and applications," in *Applications of Nanocomposite Materials in Drug Delivery*, Elsevier Inc., 2018, pp. 701–738.

[55] S. K. Owusu-ware, J. S. Boateng, B. Z. Chowdhry, and M. D. Antonijevic, "Glassy state molecular mobility and its relationship to the physico- mechanical properties of plasticized hydroxypropyl methylcellulose (HPMC) film," *Int. J. Pharm. X*, vol. 1, no. August, p. 9, 2019, doi: 10.1016/j.ijpx.2019.100033

[56] P. K. Kanse, Nitin G. .,Mokal Deepali ., "A REVIEW ON CITRIC ACID PRODUCTION AND ITS APPLICATIONS," *Int. J. Curr. Adv. Res.*, vol. 6, no. 9, pp. 5880–5883, 2018.

[57] Interchim, "Citric Acid."

[58] F. Uses, "Trisodium citrate," 2002.

[59]   P. D. Sheet, "Trisodium Citrate Dihydrate," 2015.

[60]   https://en.wikipedia.org/wiki/Cetrimonium_bromide

[61]   Sonia, T. A., & Sharma, C. P. (2014). Experimental techniques involved in the development of oral insulin carriers. Oral Delivery of Insulin, 169–217. doi:10.1533/9781908818683.169

[62]   //www.edinst.com/blog/the-beer-lambert-law/

[63]   https://byjus.com/chemistry/infrared-spectroscopy.

[64]   C. Outline, "Methods for Assessing Surface Cleanliness," in Developments in Surface Contamination and Cleaning, Volume 12, vol. 12, 2019, pp. 23–105.

[65]   M. Nasrollahzadeh, M. Atarod, M. Sajjadi, S. M. Sajadi, and Z. Issaabadi, "Plant-Mediated Green Synthesis of Nanostructures: Mechanisms, Characterization, and Applications," in Interface Science and Technology, 1st ed., vol. 28, Elsevier Ltd., 2019, pp. 199–322.

[66]   S. Nasrazadani and S. Hassani, "Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries," in Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry, Elsevier Ltd., 2016, pp. 39–54.

[67]   R. S. A. S. B. LAKSHMEESHA RAO, MAHADEVIAH, S. ASHA, "EFFECT OF ZnO NANOPARTICLES ON STRUCTURAL, MECHANICAL, OPTICAL AND SURFACE PROPERTIES OF HPMC POLYMER FILMS," *Appl. NANO Mater. Electron. ENERGY Environ.*, pp. 101–106, 2012.

[68]   J. P. Patel and P. H. Parsania, "Characterization, testing, and reinforcing materials of biodegradable composites," in Biodegradable and Biocompatible Polymer Composites: Processing, Properties and Applications, Elsevier Ltd, 2017, pp. 55–79.

[69]   J. V. Smith and J. V. Smith, "X-ray Diffraction Techniques," in *Feldspar Minerals*, 1974, pp. 179–216.

[70]   https://en.wikipedia.org/wiki/Ultraviolet%E2%80%93visible_spectroscopy

[71]   Orbit Biotech, " Ultraviolet visible spectroscopy, "Molecular analysis usinUV/Visible spectroscopy", 2018. [Online]. Available: https://orbitbiotech.com/molecular-analysis-using-uv-visible-spectroscopy-spectroscopy-uv-absorption-reflection-spectra-electromagnetic-radiation/

[72]   Mohammed, Azad & Abdullah, Avin. (2019). Scanning Electron Microscopy (SEM): A Review.

[73]   Singh, A. K. (2016). Experimental Methodologies for the Characterization of Nanoparticles. Engineered Nanoparticles, 125–170. doi:10.1016/b978-0-12-801406-6.00004-2

[74] Irina V.Krasnikova, Ilya V.MishakovAlexey, A.Vedyagin, "Functionalization, Modification, and Characterization of Carbon Nanofibers, " in Carbon-Based Nanofillers and Their Rubber Nanocomposites, Elsevier Ltd., 2019, pp. 75–137.

[75] PrabhakarRai, Yeon-TaeYu, "Citrate-assisted hydrothermal synthesis of single crystalline ZnO nanoparticles for gas sensor application," in Sensors and Actuators B: Chemical, 2012 , vol 173, pp 58-65.