

**MECHANOCHEMICAL RADICAL FORMATION IN
CELLULOSE BALL MILLING AND PRODUCTION OF
CELLULOSE-METAL NANOPARTICLES COMPOSITES**

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MECHANOCHEMICAL RADICAL FORMATION IN CELLULOSE BALL
MILLING AND PRODUCTION OF CELLULOSE-METAL
NANOPARTICLES COMPOSITES

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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

MECHANOCHEMICAL RADICAL FORMATION IN CELLULOSE BALL MILLING AND PRODUCTION OF CELLULOSE-METAL NANOPARTICLES COMPOSITES

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Cellulose is the most abundant biopolymer in nature, which contains linear chains of repeating D-glucose molecules connected by β -1,4-glycosidic linkages. Over the past decades, due to growing interest in sustainability and green chemistry, cellulosic materials have received much attention. Since cellulose is highly abundant, light weight, strong, biodegradable, and nonabrasive, composite materials including cellulose can be environmental friendly, biocompatible, low cost, low weight, and multifunctional. Cellulose composites including metal nanoparticles (cellulose-metal NPs composites) find application in many fields due to the combined properties of both metal NPs and cellulose matrices. However, current production methods of cellulose-metal NPs composites have generally multistep, long, and non-environment friendly procedures due to their requirement for hazardous chemicals to reduce the metal ion precursor and stabilize the metal NPs that form.

This thesis work focuses on the investigation of cellulose mechanoradicals formation produced by ball milling qualitatively and quantitatively with the changes occurred in cellulose samples after mechanical treatment, and using formed cellulose mechanoradicals as reducing agent to reduce metal cations in cellulose matrices to obtain cellulose-metal NPs composites. Firstly, formation of cellulose mechanoradicals -free radicals that are formed by the homolytic breaking of the bonds in cellulose chains under mechanical input (ball milling)- was analyzed

qualitatively and quantitatively. Qualitative analysis of cellulose mechanoradicals by ESR spectroscopy showed that, formed radicals could be generally peroxy and alkoxy types. The numbers of mechanoradicals formed by milling cellulose samples (cotton and microcrystalline cellulose) in wet and dry conditions were detected by using DPPH solutions with UV-Vis spectroscopy. It was shown that, dry grinding method led to the higher number of mechanoradicals formation. Changes in cellulose samples occurred after milling probed by using SEM, XRD, and FTIR-ATR analyses were found to follow the mechanoradical formation. Due to more efficient grinding in dry conditions, with increasing milling time, the progressive decrease in fiber size leading more accessible regions with smaller particle size of cellulose samples, and forming mostly amorphous cellulose samples were observed. FTIR-ATR analyses of ground cellulose samples, especially dry ground samples, showed the breaking of intra and intermolecular hydrogen bonds and β -1,4-glycosidic linkages. Lastly, cellulose-metal NPs composites were produced by using cellulose mechanoradicals as reducing agent for the first time. The composites were characterized by SEM, EDX, XRD, and XPS analyses. Au, Ag, Pt, and Pd NPs in their metallic forms, and Cu NPs in its metallic form Cu^0 or in 1+ oxidation state as Cu_2O , and Co in 2+ oxidation state as CoO NPs are successfully produced in cellulose matrices. This mechanochemical method can be proposed as a new and green method for cellulose-metal NPs composites production. Consequently, our findings can contribute to the area of mechanochemistry and composite materials.

Keywords: *mechanoradicals, cellulose composites, ball milling, cryomilling, mechanochemistry*

ÖZET

BİLYELİ ÖĞÜTME İLE SELÜLOZDA MEKANOKİMYASAL RADİKAL OLUŞUMU VE SELÜLOZ-METAL NANOPARÇACIK KOMPOZİTLERİNİN ÜRETİMİ

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Selüloz, tekrar eden β -1,4-glikosidik bağlarla birbirine bağlı D-glikoz moleküllerinden oluşmuş doğada en çok bulunan bir biyopolimerdir. Son on yılda sürdürülebilirlik ve yeşil kimya alanına olan artan ilgi nedeniyle selülozlu malzemeler dikkat çekmektedir. Selülozun bol miktarda bulunması, hafif, dayanıklı ve biyobozunabilir olması nedeniyle selüloz içeren kompozit malzemeler de doğa dostu, biyoyumlu, düşük maliyetli, hafif ve çok fonksiyonlu olabilmektedir. Metal nanoparçacıkları (NP) içeren selüloz kompozitleri (selüloz-metal NP kompoziti), metal NP ve selüloz matrisinin birleşmiş özelliklerinden dolayı birçok kullanım alanına sahiptir. Ancak selüloz-metal NP kompozitlerinin mevcut üretim metotları, metal iyonlarını indirgemek ve stabilize etmek için kullanılan zararlı kimyasalları gerektirdikleri için, genellikle çok adımlı, uzun ve çevre dostu olmayan yöntemler içermektedirler.

Bu tez çalışması, bilyeli öğütme ile selüloz mekanoradikalleri üretiminin kalitatif ve kantitatif olarak, mekanik etki sonrası selüloz örneklerinde meydana gelen değişiklerle birlikte incelenmesi ve üretilen selüloz mekanoradikallerinin metal katyonlarını selüloz matrislerinde indirgenmesi için indirgen madde olarak kullanılarak selüloz-metal NP kompozitlerinin elde edilmesine odaklanmaktadır. İlk olarak, selüloz mekanoradikalleri -selüloz zincirindeki bağların mekanik etki altında (bilyeli öğütme ile) homolitik olarak kırılması sonucu oluşan

serbest radikaller- kalitatif ve kantitatif olarak analiz edilmiştir. ESR spektroskopisi ile yapılan kalitatif analiz, oluşan radikallerin genellikle peroksil ve alkoksil radikalleri olduğunu göstermiştir. Selüloz örneklerinin (pamuk ve mikrokristal selüloz) ıslak ve kuru koşullarda öğütülmesi ile oluşan mekanoradikallerin sayısı DPPH çözeltisi kullanılarak, UV-Vis Spektroskopisi ile tayin edilmiştir. Kuru öğütme yönteminin daha fazla sayıda mekanoradikal üretimine neden olduğu gösterilmiştir. Öğütme sonrasında SEM, XRD ve FTIR-ATR analizleri ile izlenen selüloz örneklerinde meydana gelen değişikliklerin mekanoradikal oluşumu ile paralellik gösterdiği rapor edilmiştir. Kuru koşullarda öğütmenin daha etkili olmasından dolayı, artan öğütme zamanı ile selüloz liflerinin boyutlarının sürekli azalması sonucu erişilebilir alanların artması yanında daha küçük parçacık boyutlu selülozun ve çoğunlukla amorf selülozun oluştuğu gözlemlenmiştir. Öğütülmüş selüloz örneklerinin, özellikle de kuru olarak öğütülmüş örneklerin FTIR-ATR analizleri, moleküller içi ve moleküller arası hidrojen bağları ve β -1,4-glikosidik bağların kırıldıkları göstermiştir. Son olarak selüloz mekanoradikalleri ilk defa indirgen madde olarak kullanılarak selüloz-metal NP kompozitleri üretilmiştir. Bu kompozitler SEM, EDX, XRD ve XPS analizleriyle karakterize edilmiştir. Au, Ag, Pt ve Pd NP metalik formlarında, Cu NP metalik veya +1 yükseltgenme basamağında ve Cu₂O formunda, Co ise 2+ yükseltgenme basamağında ve CoO NP formunda selüloz matrislerinde başarıyla üretilmiştir. Bu mekanokimyasal yöntem, selüloz-metal NP kompozitleri üretimi için yeni ve yeşil bir metot olarak önerilebilmektedir. Sonuç olarak bulgularımız mekanokimya ve kompozit malzeme alanına katkı sağlayabilmektedir.

Anahtar sözcükler: mekanoradikaller, selüloz kompozitleri, bilyeli öğütme, soğuk öğütme, mekanokimya

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LIST OF ABBREVIATIONS

VC: Vegetable Cellulose

BC: Bacterial Cellulose

NFC: Nanofibrillated Cellulose

DPPH: 2,2-Diphenyl-1-picrylhydrazyl

MCC: Microcrystalline Cellulose

SEM: Scanning Electron Microscopy

EDX: Energy Dispersive X-ray

ESR: Electron Spin Resonance

EPR: Electron Paramagnetic Resonance

XRD: X-ray Diffraction

XPS: X-ray Photoelectron Spectroscopy

FTIR-ATR: Fourier Transform Infrared Attenuated Total Reflectance

NP: Nanoparticle

NPs: Nanoparticles

C: Crystallinity or Crystallinity Index

fcc: Face Centered Cubic

hcp: Hexagonal Close Packed

SERS: Surface Enhanced Raman Scattering

HIRES: High Resolution

CHAPTER 1

INTRODUCTION

1.1 Cellulose: as a Promising Material

In recent times, due to the problems of petroleum deficiency and environmental pollutions resulted from non-degradable polymers, there has been a great interest in products obtained from renewable, environmentally friendly and sustainable resources. At this point cellulose has become a promising material. It is the most abundant biopolymer in the world with its annual production of around 10^{12} tons [1], [2]. In addition to high abundance of cellulose, it has many desirable properties. Despite its high strength, stiffness, good mechanical properties, it has low cost due to worldwide availability [3]. Its properties of biodegradability, renewability, low abrasive and nontoxic nature, low density and low weight make cellulose polymer a good chemical for being used in composite or cellulose based materials [4]. Moreover, using cellulose in structural engineering materials is proper due to its rigidity, high crystallinity, and insolubility in common organic solvents [5], [6].

1.2 Brief History, Important Derivatives and Application Areas of Cellulose

After the French chemist Anselme Payen in 1838 did an experiment with the tissue of plants and woody materials by applying different treatments using various acids and bases, he recognized that, the plants' cell wall composed of the same

substance, which is cellulose [3], [7], [8]. The name of cellulose as a term was used by the French Academy in a report including Payen's work in 1839 [9], [10]. In 1920 Hermann Staudinger identified cellulose structure as a polymer consisting of repeating glucose units connected to each other by covalent bonds [11], [12].

Before the discovery of cellulose in cell wall of plant cells, it was used generally in the form of wood and cotton and other plant fibers. For almost 200 years, cellulose has been used in various applications as a raw material in pulps, papers, cardboards, building materials, textiles, composites, personal care products, and in pharmaceutical industry [7], [9]. With the improvements achieved in chemical methods, cellulose could be extracted from plants and then modified with various chemical groups. These modified celluloses or cellulose derivatives also have extensive application areas. In 1832 cellulose nitrate (also known as nitrocellulose, guncotton) was discovered by esterification reaction with nitric acid. Cellulose acetate, cellulose acetate butyrate and propionate are now other important cellulose ester derivatives [11]. In 1870 the first thermoplastic polymer called celluloid was produced by Hyatt Manufacturing Company using nitrocellulose, camphor, and other additives. Rayon (known as artificial silk), cellophane (known as viscose), carboxymethyl cellulose (cellulose gum), methyl cellulose, and hydroxyalkyl cellulose are other important derivatives of cellulose. These kinds of derivatives are also called as "first-generation cellulosic material" or "traditional cellulosic material". All these produced cellulose derivatives have shown that, modification of the cellulose structure is possible. With modified cellulose samples, the application areas including cellulosic materials can be increased. For example, in the production of optical films, filters, coatings, cosmetics, foods additives, and laminates, cellulosic materials have been used [1], [7], [13]. These first-generation

materials produced from cellulose are among the material groups, which are commonly used worldwide. There are fair enough reasons of such an inclination towards cellulose and materials produced from cellulose. For instance, cellulose is natural and the most abundant polymer in the world, cellulosic materials are much lighter than their equivalents, there is considerable amount of knowledge on chemical, physical, electrical and mechanical properties of cellulose, and it is the raw material that can be used in wide range of areas from textile to industrial productions. Apart from the traditional cellulosic materials produced from cellulose mentioned above, it is also possible to produce extraordinary but very useful materials for humanity. As an example, for such materials “diagnostic sheet” can be made mention of. This material is produced by saturation of sheets with biochemical materials and it can provide early diagnosis of critical diseases. These diagnosis kits are made up of paper. Therefore, diseases can be diagnosed easily, quickly and cheaply without needing complex medical equipment and procedures. Thus, they can be used in the regions like Africa and South Asia where access to medical supply and services are limited. The other technology product like “diagnosis sheet” is “paper robots”. These are produced by using cellulose-based materials, which make them lighter than the other robots, and thus they will be much more energy-efficient and easier to use. The products for point of care diagnostics such as urine, diabetes, and pregnancy test strips, paper chromatography for detection of amino-acids in protein [14], paper based microfluidics [15], paper based bioassay for detection of glucose in urine [16], paper based immunoassays [17], [18], and pathogen detection [19], [20] can be given as the examples of paper based technology products [6]. It is crucial to easily

obtain cellulosic (composite) materials for all of these applications and for future technologies.

1.3 Sources, Types, and Properties of Cellulose

Cellulose is present on the cell walls of almost all plants as a structural component. Cotton linters (as plant source) and wood pulp are used as the conventional cellulose sources [21]. Turkey is one of the largest cotton producer country in the world. More than 90% of cotton and 40%-50% of wood are cellulose. Cellulose in cotton is almost pure, but in woody plants it is present with other materials such as lignin and hemicellulose [7], [21]. Although the whole structure of lignin has not clearly defined yet, it is a polymer with nonlinear structure and phenyl propanoid units. While cellulose forms the main skeleton of the wood, lignin acts as a cement binding the cells of the wood together. It attaches to the hemicellulose covalently and it gives stiffness and rigidity to woody plants [6], [21]. Hemicellulose is a heteropolymer with branched chains of many different sugar units such as glucose, mannose, galactose. Its sugar units differ for all plants. It provides the compatibility between cellulose and lignin in plants [6]. In addition to plants, cellulose is also obtained from some marine animals, algae, fungi, bacteria, and amoeba [9]. Cellulose's annual production is around 10^{12} tons, and it is seen as 'an inexhaustible raw source' [1], [2]. Thus, the cellulose sources can be grouped into plant, wood, tunicate, algae and bacteria [1]. Plant sources could be reclassified according to their origins [3]. These are summarized in Table 1.

Plant Origin	Examples of Cellulose Source
Leaf	sisal, pineapple, cantala, abaca, date palm, henequen, banana
Seed	cotton
Bast	ramie, hemp, flax, jute
Fruit	oil palm, kapok, coir
Grass	bamboo, bagasse, alfa
Stalk	straw or cereal

Table 1. Examples of cellulose sources from plant origins.

Cellulose can be extracted from plant sources with purification. In addition to wood as mentioned before, tunicates are another cellulose source. They are sea animals having a shell containing cellulose polymer in a protein matrix. They are also called as “sea squirts” (*Ascidacea*). The most used tunicate species as a cellulose source are *Metandrocarpa uedai* [22], *Halocynthia roretzi* [23], and *Halocynthia papillosa* [1], [24], [25]. Cellulose can also be produced by some green, red, and grey algae species such as *Boergeresia*, *Valonia*, *Caldophora* [1]. Lastly, cellulose can be secreted by some bacteria called *Gluconacetobacter xylinus* [1], [26].

Cellulose samples used for composite preparation can also be classified as vegetable cellulose (VC), bacterial cellulose (BC), and nanofibrillated cellulose (NFC) in terms of morphological and mechanical characteristics [27]. BC and NFC have nanosized fibers, which leads to new properties gained by the composites containing BC and NFC. There is an increasing interest towards using BC in composites and other application areas such as food and medical industry due to its desirable properties. The properties of crystallinity (60-90%), purity, degree of

polymerization (up to 8000), mechanical stability, elasticity, and water content are high [7], [26]–[30]. With the developed methods including chemical treatments cellulose can be obtained as nanofibers called NFC from VC sources. NFC is obtained as an aqueous suspension. It has high aspect ratio with the fibers with 5–30 nm diameters and micrometer lengths. Moreover, it is highly attractive due to its characteristics such as high surface area ($>100\text{m}^2/\text{g}$), low density (1.6 g/cm^3), high strength and flexibility, and low thermal expansion. In short, the types of cellulose obtained from different sources display different properties.

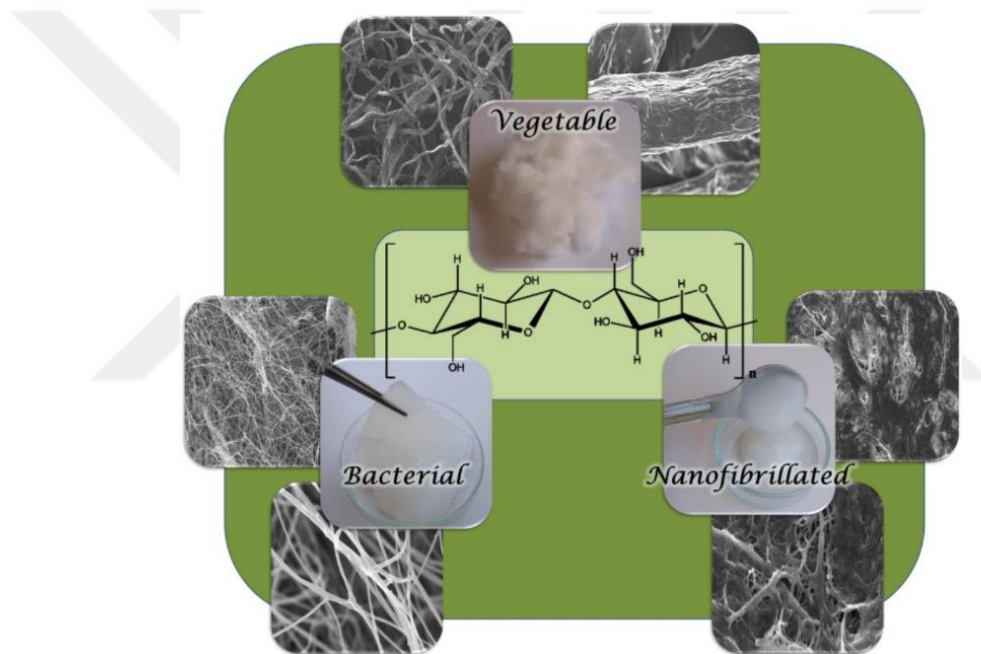


Figure 1. Morphological properties and structure of different types of cellulose [27].

Apart from these some differences observed in the types of cellulose mentioned above, cellulose fibers have generally desirable properties. They possess excellent tensile strength, elastic modulus, , low density, and high durability [3]. For example, the mechanical characteristics of the fibers obtained from wood and flax are similar with E-glass fibers that are alumino-borosilicate glass fibers used

mainly in glass reinforced plastics. Therefore, cellulose fibers have been used as the reinforcing agents in polymer composites, as well. In addition, they show recyclability, good moldability, biodegradability, renewability, low abrasive, and nontoxic nature. It should be noted that, the properties of fibers are affected by some factors such as cellulose source and the conditions of purification or extraction processes. Therefore, it can be possible to obtain cellulose fibers with desired and modified properties.

1.4 Molecular and Supramolecular Structure of Cellulose

The interesting properties cellulose result from its specific chemical structure. Cellulose (poly (β -1,4-D-anhydroglucopyranose)) is a natural linear polymer, with a structure shown in Figure 2.

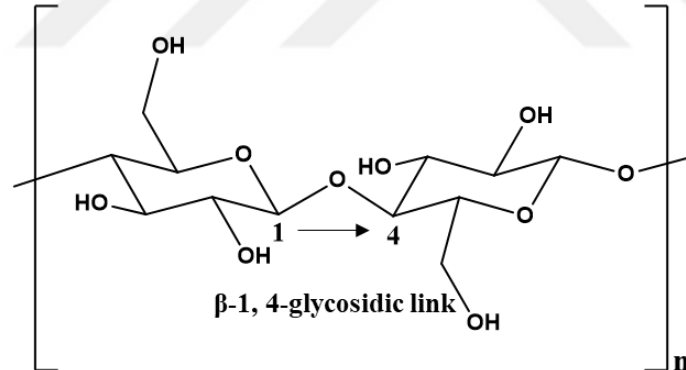


Figure 2. Molecular structure of cellulose (n: degree of polymerization).

Cellulose is composed of repeating units of two connected β -D-anhydroglucopyranose rings (β -D-glucose rings) [9]. The degree of polymerization value of cellulose can be in the range of 300-15000, depending on cellulose source and extraction process. For example, for cotton and other plant sourced cellulose samples this value is between 800-10000 [6]. β -D glucose molecules are connected

to each other by 1-4 glycosidic linkages. In other words, D-glucose rings are connected to each other through β -1-4 glycosidic linkages. These glucose molecules are linked when water is eliminated by combining -H and -OH groups. Therefore, the prefix of anhydro is used generally. When just two glucose molecules are connected to each other, a disaccharide called cellobiose forms. The 6-membered glucose rings in cellulose chains are called glucopyranose rings. They are connected through the oxygen atoms (ether bond, acetal link) between the equatorial group of C1 (anomeric) carbons of one glucopyranose ring and C4 carbons of the adjacent ring, which forms cellulose polymer. The stereochemistry the group at C1 carbon determines the whether the polymer is in α or β anomeric form. In cellulose structure, the oxygen atom at C1 carbon is at equatorial position, leading to β -linkage. Therefore, this linkage is called as β -1,4 glycosidic link.

The equatorial position of the groups at C1 carbon and of the all other groups at carbon atoms on the ring leads to the linear alignment of the cellulose chains, which makes cellulose a good fiber forming polymer. Because of this linearity of the cellulose chains, the groups on the rings can approach together. Therefore, the hydroxyl groups on the chains can easily form strong hydrogen bond networks between and within the cellulose chains, which provides cellulose polymer high cohesive energy. Figure 3 represents the cellulose chains forming inter and intramolecular hydrogen bonds for common native cellulose (cellulose I).

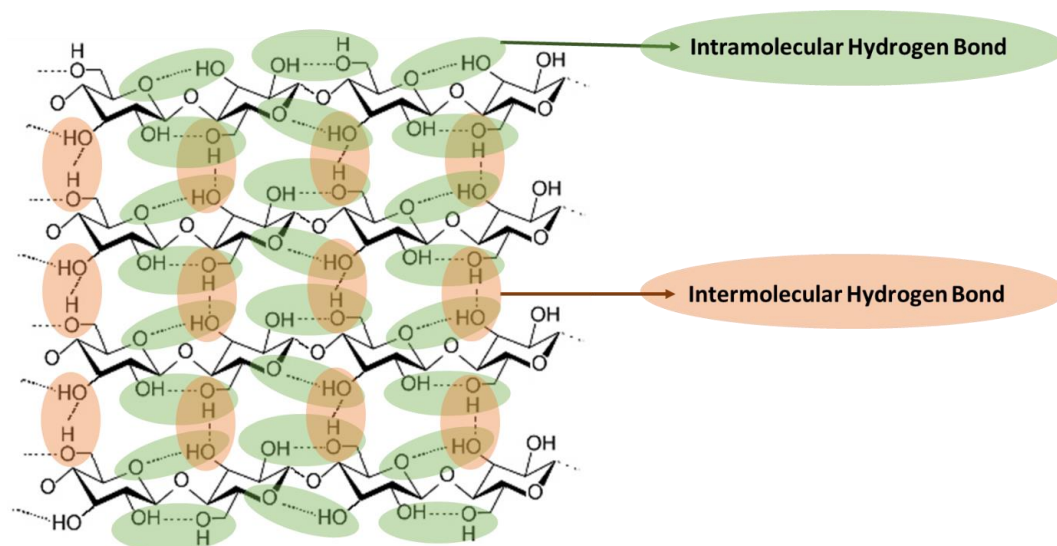


Figure 3. Cellulose chains forming inter and intramolecular hydrogen bonds.

As can be seen in Figure 3, there are intramolecular hydrogen bonds between the atoms of O(3)H-O(5) and O(2)H-O(6), and intermolecular hydrogen bonds between the atoms of O(6)H-O(3) [6]. These hydrogen bonding networks determine the physical properties of cellulose. Due to these intramolecular hydrogen bonds, cellulose chains have linear configurations. Moreover, these bonds stabilize the glycosidic linkages, and provide thermal stability and good mechanical properties. Intermolecular hydrogen bonds also lead to strong cellulose fibers with insoluble nature [3]. The parallel aggregation or stacking of the cellulose chains forming cellulose fibrils arises from the combined effect of intermolecular hydrogen and van der Waals forces [1]. The regularity of these bonds might determine the ordered or disordered regions in cellulose chains. Therefore, the different crystalline structures (allomorphic forms of cellulose) are originated because of different supramolecular arrangements resulted from different hydrogen bonding formations. Thus, both inter- and intramolecular hydrogen bonds provide the cellulose fibers the characteristic properties of high stiffness and chains with parallel arrangements.

There are four known polymorphic or allomorphic forms of cellulose crystallites. These are cellulose I, II, III, and IV. Native cellulose found in nature has cellulose I crystalline structure that has chains with parallel orientations. Cellulose II shows antiparallel orientations of chains. It is energetically more stable. Cellulose III has two forms, which are cellulose III_I and cellulose III_{II}. These are produced from cellulose I and cellulose II, respectively. Liquid ammonia or some amine derivatives are used to produce cellulose III. Two forms of cellulose IV that are cellulose IV_I and cellulose IV_{II} are produced from cellulose III_I and cellulose III_{II}, respectively. High temperature treatment (260 °C) in glycerol is applied for production of cellulose IV [31], [32], [2]. Among these forms of cellulose, cellulose I and cellulose II have become focus of interest. The transformation from cellulose I to cellulose II was achieved by mercerization process, which is alkalization of cellulose I with sodium hydroxide and regeneration of cellulose II, and by treatment of cellulose I in subcritical water [33], [34], [35], [31]. Moreover, amorphous cellulose that still has cellulose I structure was recrystallized to cellulose II by water absorption and heat treatment [36]–[38]. Different supramolecular arrangements of cellulose chains form the different crystalline structures, as mentioned above. The specific crystalline structures of cellulose I and cellulose II are attributed to different intermolecular hydrogen bonds they have. The intramolecular hydrogen bonds O(3)H-O(5) are common for both crystalline form, but the O(2)H-O(6) bonds present in only cellulose I structure. While the intermolecular hydrogen bonds at O(6)H-O(3) occur in cellulose I, the O(6)H-O(2) bonds present in cellulose II structure, which can be seen in Figure 4.

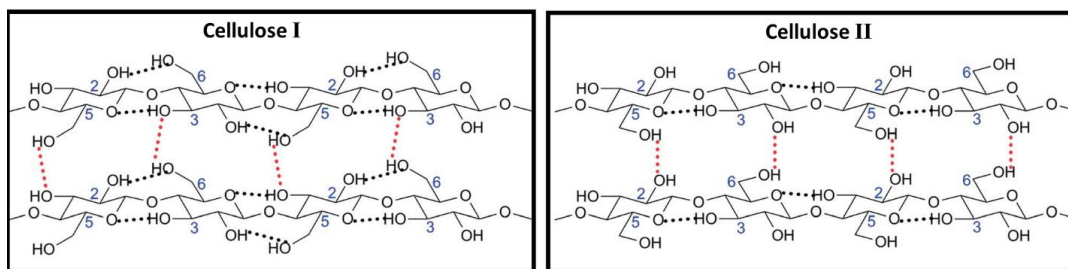


Figure 4. Supramolecular arrangements of the chains of cellulose I and cellulose II crystalline structures [6].

Cellulose has both crystalline regions having extensive hydrogen bonding and amorphous regions having weak hydrogen and van der Waals interactions. These regions can be shown as in Figure 5, cellulose fibers possessing ordered and disordered regions. The chemical reactivity and accessibility of cellulose are hindered by its high crystallinity. Therefore, pretreatment processes leading to the decrease in cellulose crystallinity have been applied to cellulose samples to obtain better reactivity and efficient reaction. To decrease crystallinity of cellulose, applied processes are ball milling [39], liquid acid and base treatments [40], [41], [42], and microwave irradiation treatments [43], [44], [45].

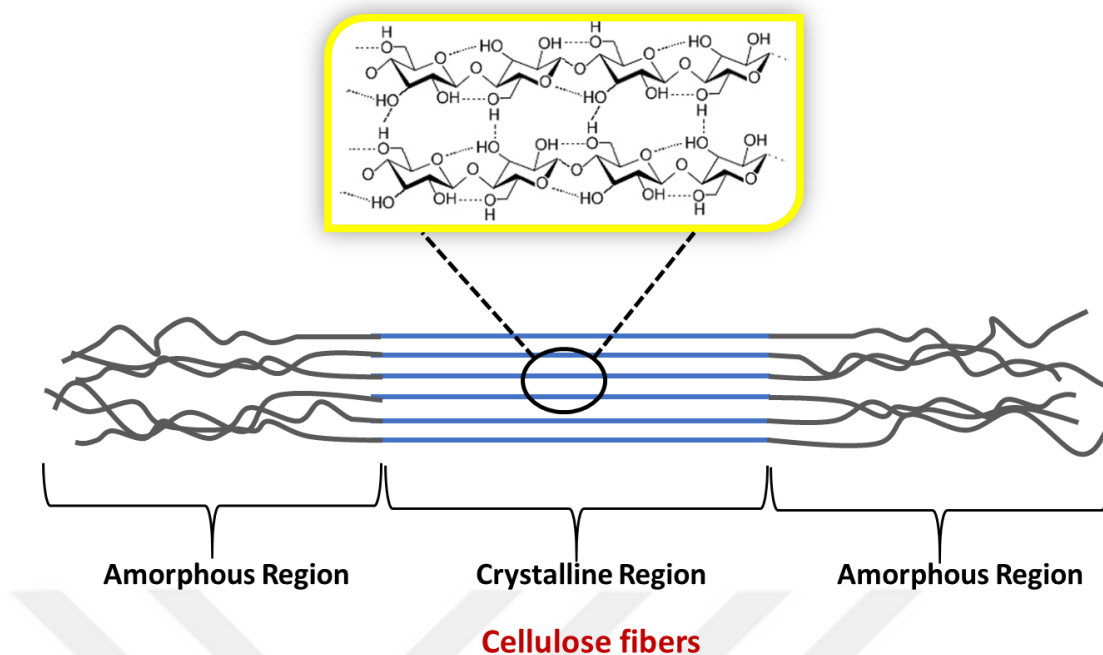


Figure 5. Schematic illustration of cellulose fibers.

1.5 Cellulose Composites

In recent years, with the developments in material field, cellulose has started to be the center of interest in producing cellulose particles and composite materials, which are also called as “new generation cellulose materials”. These new generation cellulose materials differ considerably from traditional materials by means of mechanical and physical features as well as in their area of utilization. Composite materials possess the properties of the constituent materials they have. In other words, they show combined properties. Because of the desirable properties of cellulose, its composites have been produced to impart the features coming from cellulose itself. Petroleum deficiency and environmental concerns led to a great interest on products obtained from renewable, environmentally friendly and sustainable resources. Therefore, composite materials including cellulose, which

are environmentally friendly, biodegradable, renewable, low abrasive and nontoxic nature have been getting an increased attention [1]–[5].

Cellulose materials have other advantageous properties, too. Good mechanical properties, low cost, low weight, and low density are some of these properties. As striking examples showing excellent properties of cellulose materials, one might show; nanofibers of cellulose in crystal state resemble Kevlar polymer with respect to Young's modulus, and cellulose in the form of nanoparticles shows higher tensile strength than cast iron [46]. Having the edge on diverse range of applications due to the mentioned features, the number of studies on both new generation cellulose and their composites is rising day by day. Soon, it is expected that applications of these materials can be improved in the areas such as antimicrobial and transparent films, flexible screens, reinforcement for polymeric materials, biomedical implants, pharmaceutical materials, drug delivery systems, textiles, and batteries.

1.5.1 Cellulose-Metal Nanoparticle Composites

The films including metal nanoparticles (NPs) have begun to get more attention progressively due to their use in many areas. Depending on features of metal ion they include, these composites can be used, for instance, in anti-bacterial textile and kitchenware [47], [48], medical devices [49], electronic parts [50], [51]. Similarly, cellulosic composites bearing metal NPs as the filler material find application in many fields spanning from diagnostics to state-of-the art new generation paper robots due to their light and multifunctional nature. The properties of cellulose- metal NPs composites depend on the metal NPs employed as fillers and on the type of cellulose matrix used. Therefore, it is possible to make materials

with combination of different properties and biocompatibility due to cellulose matrix [52]. For example, silver NPs in cellulose matrix give the antimicrobial properties to the composite, so that it can be used in applications of artificial skin, food packaging, water treatment [27]. Gold, platinum, palladium, copper NPs enable to be used cellulose composites in catalytic applications [27].

In order to prepare such composites, diverse methods were developed. Some of these methods are electrostatic assembly [53]–[56], surface pre-modification of cellulose [57], [58], blending of components [59]–[61], and reduction of metal NPs by adding external reducing agents [56], [61]–[65], by using UV light [66], and by using high temperature conditions some chemical treatments [67]–[69].

Among these preparation methods, the most popular one is the one in which metal ions are reduced in cellulose matrix with external reducing agent to obtain metallic NPs in the matrix, and stabilizers are used to prevent NPs from aggregation. Due to the reducing chemical use, this method is *toxic* and environmentally *hazardous*. Moreover, the method necessitates generally multi-step and long processes, and the chemicals used in the method lead to contamination in later applications; e.g., if the composite material is to be used in the sensor field, the contaminations lead to unreliable measurements with the sensor. Another common method for preparation of cellulose-metal NPs composites is reducing the metal ions with UV light. This method is straightforward and contamination-free but it can *only* be used for Ag NPs.

An efficient “green synthesis” that uses mechanochemical method to form such cellulose-metal NPs composites, possessing advantages of 1) having ‘naked’ nanoparticles (without using stabilizers), 2) using cellulose mechanoradicals

formed by mechanical action to reduce the metal ions (without using external reducing agents) 3) in a straightforward way (no multistep procedures) is shown in this thesis.

1.5.1.1 Application Areas of Cellulose-Metal Nanoparticle Composites

As mentioned above, cellulose-metal NPs composites bare the characteristics of the metal NPs embedded in them, so they can be used in applications emerging from these properties. Therefore, with changing metal NPs in cellulose matrix, the properties and application areas of the composite can be changed. These application areas are summarized in Table 2. The most notable characteristics of the metal NPs in cellulose matrix are; anti-microbial/anti-fungal characteristics of Ag and Cu NPs, catalytic action of Au, Ag, Pt, Pd, Cu NPs and magnetic property of Co NPs. Also, as Au and Ag NPs was proven suitable for Surface Enhanced Raman Scattering (SERS), composites made of the mentioned NPs are convenient for chemical and biochemical detection platforms. When these features of Au and Ag particles are joined with easy-accessibility, biocompatibility and cheapness of the cellulose matrix, ideal material could be obtained for sensor applications [59], [70]. Cellulose-metal NPs composites' features do not only depend on metal NPs they include, but also on cellulose type (VC, BC or NFC) [27]. For instance, when the composite of Ag NPs in BC matrix was compared with the composite of Ag NPs in VC matrix, the former surpassed the latter in terms of detection of amino acids [71]. For this very reason, in addition to using different metal cations, at the same time, we aim to work with two different cellulose matrices (cotton and microcrystalline cellulose (MCC)) and to compare these composites in our project.

Metal NPs	Application
Au	Catalytic, Conducting, Biosensors, Electronic devices, Medical (drug and protein delivery), SERS, Smart papers and textiles
Ag	Biosensors, Catalytic, Paper industry, Textiles, SERS, Anti-counterfeiting, Antimicrobial (artificial skin, water treatment, wound dressing, food-packaging)
Pt	Fuel cells, Catalytic (electrocatalytic, photocatalytic)
Pd	Catalytic
Cu	Antimicrobial, Catalytic
Co	Electronic actuators, Magnetic, Microfluidics devices

Table 2. General application areas of cellulose-metal NPs composites [27].

1.6 Polymer Mechanochemistry

Mechanochemistry as a research field examines the chemical transformations induced by mechanical force such as friction, stress, deformation, milling or grinding. Polymer mechanochemistry is based on breaking of long polymer chains, with mechanical effect such as pulling, bending, pressing, milling or grinding [72]–[75]. Although the history of the method reaches back to Staudinger’s mastication experiments (“mastication”, making chemical reaction by pressing) [76], [77], it can be said that, innovative research in polymer mechanochemistry have been conducted only in the last decades.

The studies on polymer mechanochemistry can be categorized in two groups: In the first group, chemical groups, which can selectively react upon mechanic effect in the mentioned polymer chains (called as mechanophores), are added into

the polymer chains by organic synthesis, and polymers are exposed to mechanical effect to observe polymer's reactions [78]–[82]. With these studies, it was shown that some products were produced, which could not have been obtained previously through thermal and photochemical methods (e.g. anti-Woodward-Hoffmann products), and new methods were developed.

In the second group of studies [83], [84], easy-accessible and synthetic general-use polymers are used. Mechanochemical reactions are made by exposing polymers to pulling, pressing and rubbing, and through mechanical effect, homolytic and heterolytic chemical bond breakages take place in the bulk or on the surface of the polymer. Homolytic bond-breakage leads to mechanoradicals (polymer radicals formed through mechanic effect), and heterolytic bond cleavage leads to mechanoions (polymer cations and anions formed through mechanic effect). This second group of studies showed that through mechanochemistry of general polymers (without any specially designed mechanophores) it is possible; to change rheologic features of rubber, to obtain intended output of molecular weight [85]–[87], to dehalogenate environmentally hazardous halogenated polymers [88], to polymerize and co-polymerize synthetic polymers [89] and in mechanochromism [90], to obtain conductive polyaniline on other polymer surfaces [91], to activate and pattern adhesive surfaces toward nanoparticle deposition [92], and to drive lab-scale chemical reactions with mechanoradicals [84], [93].

General-use polymers have cumulative production amounts of 245 million tons and their sales reach up to 454 billion dollars annually with growth rate between 2012 and 2017 of 3.8% (2009, World polymer production) [94]. Mechanochemistry of polymer materials, have begun to be attractive research field,

because of this large ‘feedstock’ and also because of the diverse applications of polymer materials. For all that researches conducted in the last decades, still polymer mechanochemistry studies are not sufficient enough, to uncover the real potential of the mechanochemical method.

1.6.1 Polymer Mechanoradicals

Polymer mechanoradicals (products of homolytic mechanochemical polymer chain scission) were firstly detected and identified in 1960-1970s with the enhancement of the Electron Spin Resonance (ESR) method. “Mechanoradical” term was first used by Sohma [95] and it was defined as radicals produced by mechanical impact. The first and subsequent research on mechanochemical bond-breakages were conducted by Butyagin, Tomashevskii, Peterlin, DeVries, Kausch and Sohma, in polymers such as polypropylene [96], poly(tetrafluoroethylene) (PTFE) [97], polyethylene [98], poly(vinyl chloride), poly(vinylidene chloride), poly(oxymethylene), poly(ethylene terephthalate), poly(caprolactone), and the formation of mechanoradicals were analyzed. In Table 3, a summary of these efforts, i.e. formation methods of mechanoradicals in polymers, ambient conditions, types of bonds broken through mechanic effect, chemicals composition of consisted primary mechanoradicals and the methods used to observe consisted mechanoradicals are shown [99]. In short, to form mechanoradicals in polymers, ball milling, mastication, ultrasound waves and extrusion are used as primary methods.

If we would think about a reaction, in which the mechanically formed radicals can be used, we would come up first with the idea to use these mechanoradicals as initiators to launch polymerization of some monomer. A few examples of such

studies can be found in the literature, where mechanoradicals formed at the surface of poly(tetrafluoroethylene) (PTFE), were used to (co)polymerize methyl methacrylate, vinyl acetate and ethylene [97]. The formed copolymer hosts the features of each of the two polymer components. As it can clearly be seen from these studies, mechanoradical formation is an effective and straightforward method in making surfaces functional or to make reactions in the surfaces.

Mechanoradical formation was also found to be critical for the static electricity research. Static electrification, accumulation of static charges on polymers, is a big problem faced in industry. With two studies published in *Science* it was shown that mechanoradicals (the uncharged species) and mechanoions (the charges on the polymer surfaces) interact with each other and removal of mechanoradicals ceases static charge accumulation on surfaces. With these studies, the academical and technological interest in polymer mechanochemistry field was revived [100], [101].

The earlier studies of Baytekin *et. al* in the field of polymer mechanochemistry were inspirational for the topic of this thesis [84], [91]–[93]. In one of these studies elastomeric polymers were exposed to simple mechanical input, such as squeezing by hand, to produce mechanoradicals within the polymers. These mechanoradicals then migrated and led to the formation of hydrogen peroxide H_2O_2 at polymer-water interface, when the polymers are exposed to water. This H_2O_2 could then drive the several chemical reactions e.g. gold nanoparticle synthesis, bleaching of an organic dye, formation of a fluorescence with dye from its non-fluorescent derivative [84], [93]. Exposing the mechanically treated polymers to water, one can make use of mechanoradicals but mechanoions are eliminated in reactions with water. In a subsequent study, this time, without using

water, but now in organic solvents, it was shown that, the created mechanoions could make nonconductive polyaniline conductive [91]. In more recent studies from Baytekin group, gold, palladium, copper and silver nanoparticles were produced by the mechanoradicals formed on the surface of adhesive tapes after mechanical pulling [92]. So far, all these studies included synthetic polymers and no biopolymer. This thesis focuses on using a biopolymer (cellulose) to drive similar reactions.

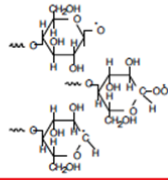
Polymer Type	Mechanical input	Medium nature	Type of split bond	Type of primary radical	Method of radical investigation	Stimulated mechano-chemical reaction
Polyethylene	vibratory milling mastication	inert air	>C-C<	$\text{~CH}_2\text{-}\dot{\text{C}}\text{H}_2$ $\text{~CH}_2\text{-CH}_2\text{-O}\dot{\text{O}}$	- radicalic acceptors - grafting	mechano-degradation block copolymerisation
Poly(vinyl chloride)	vibratory milling ultrasonation (in solution and suspension) two roll mixing	inert air	>C-C<	$\text{~CH}_2\text{-}\dot{\text{C}}\text{H}$ ~CH-CH_2 $\text{~CH}_2\text{-CH-O}\dot{\text{O}}$ $\text{~CH-CH}_2\text{-O}\dot{\text{O}}$	- radicalic acceptors - grafting – block copolymerisation	mechano-degradation block copolymerisation grafting reticulation elimination of HCl
Poly(vinylidene chloride)	vibratory milling	inert	>C-C<	$\text{~CH}_2\text{-}\dot{\text{C}}(\text{Cl}_2)$ $\text{~C}(\text{Cl}_2)\text{-CH}_2$	- grafting – block copolymerisation	mechano-degradation block copolymerisation grafting elimination of HCl
Poly(oxymethylene)	vibratory milling	inert air		$\text{~CH}_2\text{-}\dot{\text{O}}$ ~O-CH_2 $\text{~O-CH}_2\text{-O}\dot{\text{O}}$	-ESR -radicalic acceptors - grafting	mechano-degradation block copolymerisation grafting elimination of CH_2O
Poly(ethylene terephthalate)	vibratory milling cryolysis	inert	$\text{~O-CH}_2\text{-}$	~C(=O)-C(=O)-O $\text{~O-CH}_2\text{-CH}_2\text{-O}$ ~C(=O)-C(=O)-O $\text{~O-CH}_2\text{-CH}_2\text{-O}$	-ESR -radicalic acceptors - grafting	-mechano-degradation -block and graft copolymerisation -mechano-chemical polycondensation and hydrolisis
Poly(ϵ -caprolactam)	vibratory milling shearing in capillary	inert polar liquids	>C-C< >C-N<	~OC-NH-CH_2 $\text{~OC-NH-(CH}_2\text{)-CH}_2$	-radicalic acceptors - grafting	-mechano-degradation -block and graft copolymerisation -polycondensation -hydrolisis
Cellulose and derivatives	vibratory milling cryolysis	inert air			-radicalic acceptors - grafting	-mechano-degradation -block and graft copolymerisation -mechano-chemical polycondensation -hydrolisis
Lignine	vibratory milling	inert air	>C-C< >C-O-C<	—	-ESR -radicalic acceptors -grafting	-mechano-degradation -block and graft copolymerisation -

Table 3. Types of mechanoradicals formed under mechanical input in different mediums [99].

1.7 Mechanochemistry of Cellulose

Biopolymer mechanochemistry is as much attractive and applicable as synthetic polymer chemistry. Mechanical effect upon high pressure homogenization and milling/purifying has sizably used to obtain cellulose, from various natural sources mentioned above, through isolation. However, this method is rather a physical isolation than being a chemical reaction. It has been known since 1921 that, when cellulose is subjected to mechanical input, its fibrils disintegrated. However, it was also shown that, when cellulose was subjected mechanical input with ball milling, the intermolecular hydrogen bonds, and covalent bonds were broken and mechanoradicals were produced [102]–[104]. Thereby, it is possible to divide mechanochemistry of cellulose into two as; 1) breaking of intermolecular bonds and 2) breaking of covalent bonds. Among these two groups, in the studies of the former, it was possible to make esterification reaction by using free OH groups formed after breaking hydrogen bonds in cellulose chains through mechanical effect [105]–[107]. In the second group of studies; mechanoradicals formed by ball milling were characterized by ESR, and mass spectrometry analyses [102]. The broken bonds by applying mechanical input in the cellulose chains are C-O-C glycosidic bonds and C-C bonds, forming alkyl (carbon centered) and alkoxy (oxygen centered), and peroxy radicals (if breaking takes place in oxygen atmosphere) [102].

In addition to the studies mentioned above, recent research also showed, by using cellulose mechanoradicals, formed by ball milling, it is possible to start polymerization of several monomers such as methylmethacrylate [108], [109], hydroxyethyl methacrylate [110], styrene [111] by using cellulose

mechanoradicals as polymerization initiators and to obtain cellulose-synthetic polymer copolymers.

1.8 Aim of Thesis

This thesis focuses on 1) the investigation of cellulose mechanoradicals produced by ball milling qualitatively and quantitatively, together with the changes occurred in cellulose structure during mechanical treatment, and 2) production cellulose-metal NPs composites by using cellulose mechanoradicals. Cellulose mechanoradicals are characterized qualitatively by using electron spin resonance spectroscopy (ESR) and this characterization is combined with the quantitative analyses of the mechanoradicals by using radical scavenger 2,2-Diphenyl-1-picrylhydrazyl (DPPH) molecule, using UV-Vis spectroscopy (first time in the literature with respect to cellulose mechanoradicals characterization and also with respect to using the method developed and used (dry grinding method) in ball milling studies). Moreover, the changes in cellulose structure after mechanical treatment is analyzed by using scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy.

In this thesis, we are reporting formation of cellulose-metal NPs composites through formation of mechanoradicals. These composites are characterized by SEM, energy dispersive X-ray (EDX), XRD, and X-ray photoelectron spectroscopy (XPS). In the formation of composites, two cellulose samples are used; commercially available cotton and microcrystalline cellulose (MCC). They have different morphologies, and MCC is produced by mild acid hydrolysis, which will be discussed in next sections. By using two cellulose sources for both radical

production analyses and composites production, it is possible to see the effect of cellulose morphology on its mechanochemistry. Furthermore, for cellulose-metal NPs composites six different metal ion precursors are used with the two different cellulose sources (vide supra) as matrices, to obtain different combined properties. Mechanical input is applied to cellulose samples by using Retsch Cryomill, which has an integrated cooling system that enables us to do mechanochemistry at low temperatures, eliminating the heating of the sample (thermal reactions) and to elongate the life time of the formed radicals. Our starting point is illustrated in Figure 6, which basically shows the formation of cellulose mechanoradicals on broken fibers of cellulose after cryomilling.

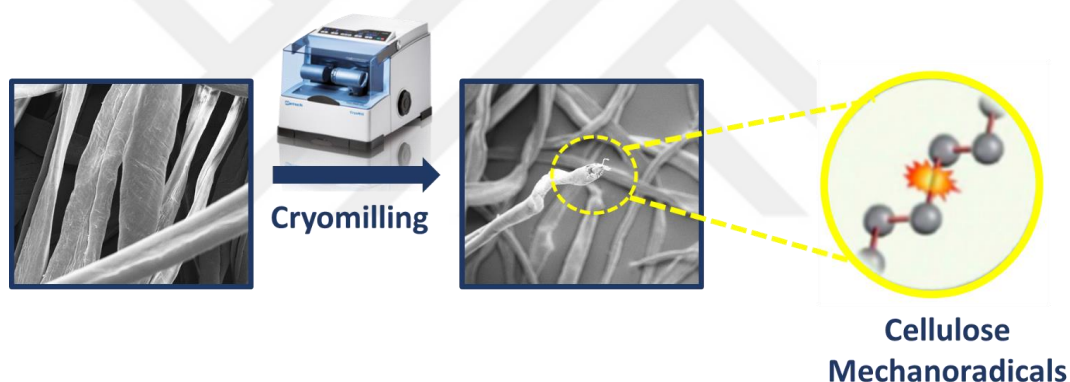


Figure 6. The illustration of the formation of cellulose mechanoradicals on broken cellulose chain after cryomilling of cotton sample.

As mentioned above in part 1.5.1, cellulose-metal NPs composite production methods usually involve multistep procedures and long processes, they are not environmentally friendly due to used chemicals such as stabilizing or reducing agents to form metal NPs. In this thesis work, cellulose mechanoradicals are used as reducing agent to produce metal NPs in cellulose matrices and both cellulose polymer chains and radicals are used as stabilizers of the in-situ formed ‘naked’

nanoparticles. Thereby, this research can be proposed as a “green”, mechanochemical method.



CHAPTER 2

EXPERIMENTAL

2.1 Materials

As cellulose sources, cotton (100% pure) from direct commercial source and microcrystalline cellulose (MCC) from Acros Organics were used. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) and acetonitrile solvent were supplied by Sigma-Aldrich. DPPH stock solution in acetonitrile solvent was prepared for quantitative determination of the mechanoradicals by UV-Vis Spectroscopy. For the preparation of cellulose-metal nanoparticles composites, metal precursors: chloroauric acid HAuCl_4 , palladium (II) acetylacetonate $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, potassium (II) tetrachloroplatinate K_2PtCl_4 , cobalt (II) acetylacetonate $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$ and silver nitrate AgNO_3 from ABCR; copper (II) acetylacetonate $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ from Acros Organics were utilized.

2.2 General Experiment Conditions and Setup

Samples are milled with 6 zirconia balls with 10.06 mm diameter as grinding medium in zirconia chamber using Retsch Cryomill instrument. In a typical experiment, the cellulose samples are milled at 30 Hz frequency for an indicated time at 77 K (cryo condition). This low temperature is achieved by liquid nitrogen that circulates through the milling chamber keeping the temperature at 77 K. Due to low temperature, life times of produced radicals can be enhanced and samples in

the chamber can be milled without sticking on the wall of the chamber. Moreover, using balls and chamber made up of zirconia allows us to mill the samples in the chamber without contamination due to wearing and sticking of zirconia on cellulose samples. Zirconia milling medium also prevents unwanted electron transfer between the milling medium and the reactants and rapid decaying of produced radicals.

2.2.1 Wet Grinding of Cellulose Samples

500 mg of cotton and MCC were separately milled with 2.5 mL of 1.3×10^{-4} M of DPPH solution prepared in acetonitrile solvent for 10, 20, 30, 40 and 60 minutes at 30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K by using Cryomill instrument. At the end of the cryomilling for each indicated times, the mixture of cellulose source and DPPH solution were diluted to 10 mL by adding 7.5 mL of acetonitrile solvent in the sample chamber and the mixture was mixed at 5 Hz frequency for 30 seconds by using Cryomill instrument. By this way, the concentration of the DPPH solution became 3.2×10^{-5} M (as if DPPH were not consumed at all). Then, the mixtures of cryomilled cellulose and DPPH solution were taken into tubes and separated from each other by centrifugation. The liquid part of the mixture, containing DPPH solution cryomilled with cellulose source for indicated times, was used for quantitative analysis of the produced mechanoradicals by using UV-Vis Spectroscopy. Reference DPPH solution that has concentration of 3.2×10^{-5} M was prepared. From the difference of the absorbance of the reference DPPH solution and the cryomilled DPPH solution with cellulose source, the amount of produced mechanoradicals was calculated. The precipitate part of the mixture containing cellulose source was

washed several times and dried in vacuum. Then it was utilized to examine the morphological, structural, compositional changes and changes in crystal structure after milling for indicated times by using SEM, FTIR-ATR, XPS and XRD analyses.

2.2.2 Dry Grinding of Cellulose Samples

In a typical dry grinding experiment, 500 mg of the cellulose samples (cotton and MCC) were separately milled for 10, 20, 30, 40 and 60 minutes at 30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K by using Cryomill. After the cryomilling, 2.5 mL of 1.3×10^{-3} M DPPH solution prepared in acetonitrile solvent were added on to the milled sample. (In an initial experiment, after dry grinding of cellulose source for 60 minutes, 2.5 mL of 1.3×10^{-4} M DPPH solution was added to the sample chamber and it was observed that dark purple color of the DPPH solution immediately turned into yellow color, as it came into contact with cryomilled cellulose source, which meant that all DPPH radicals were depleted by cellulose mechanoradicals produced from dry ground cellulose source. Therefore, in order to determine the amount of all produced radicals and to prevent the reaction of all DPPH, DPPH solution with 10 times higher concentration than those used in wet grinding was used in dry grinding experiments). Then the mixture was diluted to 10 mL by adding 7.5 mL of acetonitrile solvent in the sample chamber, and mixed again and taken to the tubes. Cellulose precipitated at the bottom of the tubes after centrifugation and the 0.5 mL of liquid part containing DPPH solution on the precipitated cellulose was diluted to 5 mL with acetonitrile solvent to obtain $[DPPH] = 3.2 \times 10^{-5}$ M (as if DPPH were not consumed at all) for UV-Vis Spectroscopy analysis. To determine the amount

of mechanoradicals that have formed in the bulk of the cellulose and migrated to the cellulose surface, UV-Vis spectra were taken after indicated hours of diffusion time ('waiting time'). After all UV-Vis analyses, cryomilled cellulose sources were washed several times and dried in vacuum. They were utilized to examine the morphological, structural, compositional changes and changes in crystal structure after dry milling for indicated times by using SEM, FTIR-ATR, and XRD analyses. Qualitative investigation of the mechanoradicals were made by ESR Spectroscopy of 500 mg of cotton that was cryomilled for 60 minutes.

2.3 Experiment Conditions and Setup for Production of Cellulose–Metal NPs Composites

Since more radicals were obtained through dry grinding of cellulose, in both cotton and MCC matrices metal NPs were produced by using cellulose radicals formed with dry grinding. 500 mg of cotton and MCC were separately cryomilled for 40 minutes at 30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K. After grinding the cellulose samples, 3 mL 5.1×10^{-3} M of metal solution was added and the formed mixture is mixed at 5 Hz for 30 seconds. For both cotton and MCC matrices, 6 metal solutions were used. These are chloroauric acid HAuCl_4 , palladium (II) acetylacetonate $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, potassium (II) tetrachloroplatinate K_2PtCl_4 , cobalt (II) acetylacetonate $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$, copper (II) acetylacetonate $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$, and silver nitrate AgNO_3 . HAuCl_4 , AgNO_3 , and K_2PtCl_4 , which were prepared in water; $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$, and $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$, which were prepared in acetonitrile. The mixture of cellulose and the metal ion solution was then diluted to 6 mL with the solvent that was used to prepare corresponding metal solutions, was taken to a polypropylene tube, and stored in

dark. Small samples were taken out after 1 day, 1 week and 2 weeks waiting time. These were washed several times with the solvent, dried in vacuum, and characterized by SEM, EDX, XRD, and XPS analyses.

2.4 Instrumentation

2.4.1 Cryomill

In all experiments cryogenic grinding of cellulose samples were performed by using Retsch Cryomill instrument while cooling with liquid nitrogen from the integrated cooling system.

2.4.2 UV-Vis Spectroscopy Analysis

In order to detect the radical amount quantitatively Cary 300 UV-Vis Spectrophotometer was utilized.

2.4.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Analyses

The surface morphology of cellulose samples and cellulose-metal NPs composites was imaged and analyzed with a Quanta 200F model SEM with an accelerating voltage of 5 kV.

2.4.4 Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) Spectroscopy Analysis

After dry grinding of cotton samples (vide supra), produced cellulose mechanoradicals were characterized by means of room temperature measurement with Bruker ELEXSYS E580 model ESR spectrometer.

2.4.5 Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) Spectroscopy Analysis

The chemical structure changes in cellulose after wet and dry grinding of samples were investigated by infrared spectroscopy. FTIR spectra of the samples were obtained in the range of 4000-400 cm^{-1} with a Bruker Alpha model spectrometer with Platinum ATR crystal.

2.4.6 X-Ray Diffraction (XRD) Analysis

The changes in crystalline structure of the wet and dry cryomilled cellulose samples were monitored by X-ray diffraction (XRD). The XRD measurements were performed on an X'Pert PRO, PANalytical model X-ray diffractometer with Cu $K\alpha$ radiation. 40 mA applied current and 45 kV accelerating voltage were used.

2.4.7 X-ray Photoelectron Spectroscopy (XPS) Analysis

Proofs of complete reduction of metal ions into metal nanoparticles in the cellulose matrix were obtained by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectrograms were measured using an ESCALAB 250 (Thermo Scientific K-Alpha X-Ray Photoelectron Spectrometer system with a Al $K\alpha$

microfocused monochromator source). C1s signal were referenced to at 284.8 eV for all measurements.



CHAPTER 3

RESULTS & DISCUSSION

3.1 Investigation of Radical Production and Radical Amount

3.1.1 Quantitative Determination of Produced Radicals by UV-Vis Spectroscopy

DPPH (2,2-diphenyl-1-picrylhydrazyl) was used in order to determine the amount of cellulose mechanoradicals. DPPH is a stable free radical, which can be used as a radical scavenger. When there is a radical ($R^\bullet$ or $H^\bullet$) in the medium, DPPH reacts with this radical to form DPPH-R or DPPH-H, respectively. DPPH forms deep violet colored solutions in organic solvents with absorption band at about 520 nm. When it traps a radical molecule, its color bleaches and when all DPPH is consumed and turns into DPPH-R or DPPH-H, the color of the solution turns to pale yellow. This reaction can be followed by UV-Vis spectroscopy. When DPPH molecule reacts with other radical molecules, the absorption band of the DPPH molecule at about 520 nm decreases. This decrease in the absorption band is directly proportional with the amount of radical molecules in the medium. From the difference between the absorption of a reference DPPH solution and that of the DPPH solution which reacted with other radicals in the medium, concentration, and then the initial number of the radicals ($R^\bullet$ or $H^\bullet$) in the medium can be calculated.

During milling of the cellulose samples, covalent bonds are broken, and cellulose mechanoradicals are produced. During wet milling these radicals can react

immediately with DPPH solution in the milling chamber. In dry milling, samples are introduced to DPPH solutions, once the milling is completed. Some mechanoradicals formed in the bulk of the samples, cannot interact with DPPH molecules immediately but can diffuse to the surface of the sample and can react with DPPH after several minutes, hours, and even after some days. From the UV-Vis analysis of the DPPH solutions, the number of radicals for each cryomill run was calculated. In the literature there are studies on using DPPH molecule as a radical trap during milling (wet milling). In this thesis, we also used this quantification method with DPPH also in dry grinding. Quantification of cellulose mechanoradicals with DPPH and also using developed dry grinding method in ball milling studies were also done first time in the literature with this thesis work.

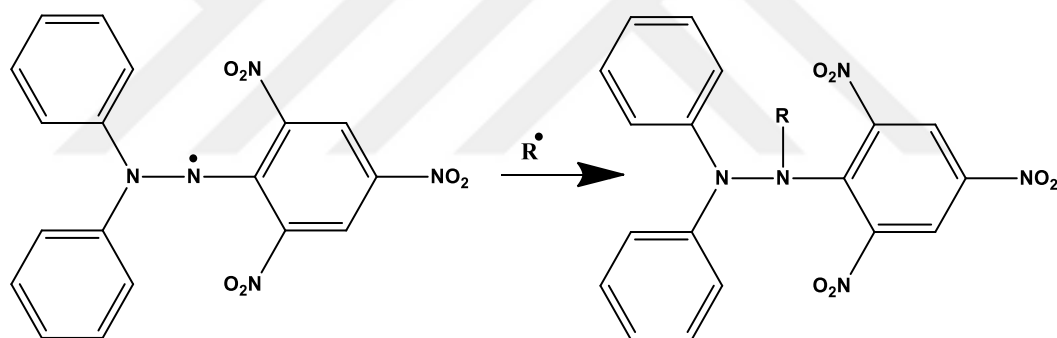


Figure 7. DPPH reaction with radical $R^\bullet$.

3.1.1.1 Cellulose Mechanoradicals From Wet Grinding Method

After cryomilling of the cellulose sample (cotton or MCC) and DPPH solution for 10, 20, 30, 40, and 60 minutes (and proper dilutions, see above, Experimental section), the number of radicals were calculated using UV-Vis spectrums as follows: Figure 8 shows the UV-Vis spectra of the DPPH solutions that were cryomilled with cotton samples for 10, 20, 30, 40, and 60 minutes (Figure

8A). It can be seen that, with increasing milling time from 10 minutes to 60 minutes, the absorption of the DPPH solution at 519 nm decreased. This means that, with increasing milling time the number of cellulose radicals increases, as shown in Figure 8B. The increase in the number of radicals with increasing milling time was faster for the first 10, 20, 30, and 40 minutes. However, the increase in the number of radicals got slower from 40 minutes to 60 minutes. It was found that, 9.8×10^{16} and 1.1×10^{17} radicals per gram of cryomilled cellulose were produced after wet grinding for 40 minutes and 60 minutes, respectively.

Figure 9 represents the UV-Vis spectra of the DPPH solutions that were cryomilled with MCC samples as a cellulose source for 10, 20, 30, 40, and 60 minutes (A) and corresponding radical amounts per gram of MCC (B).

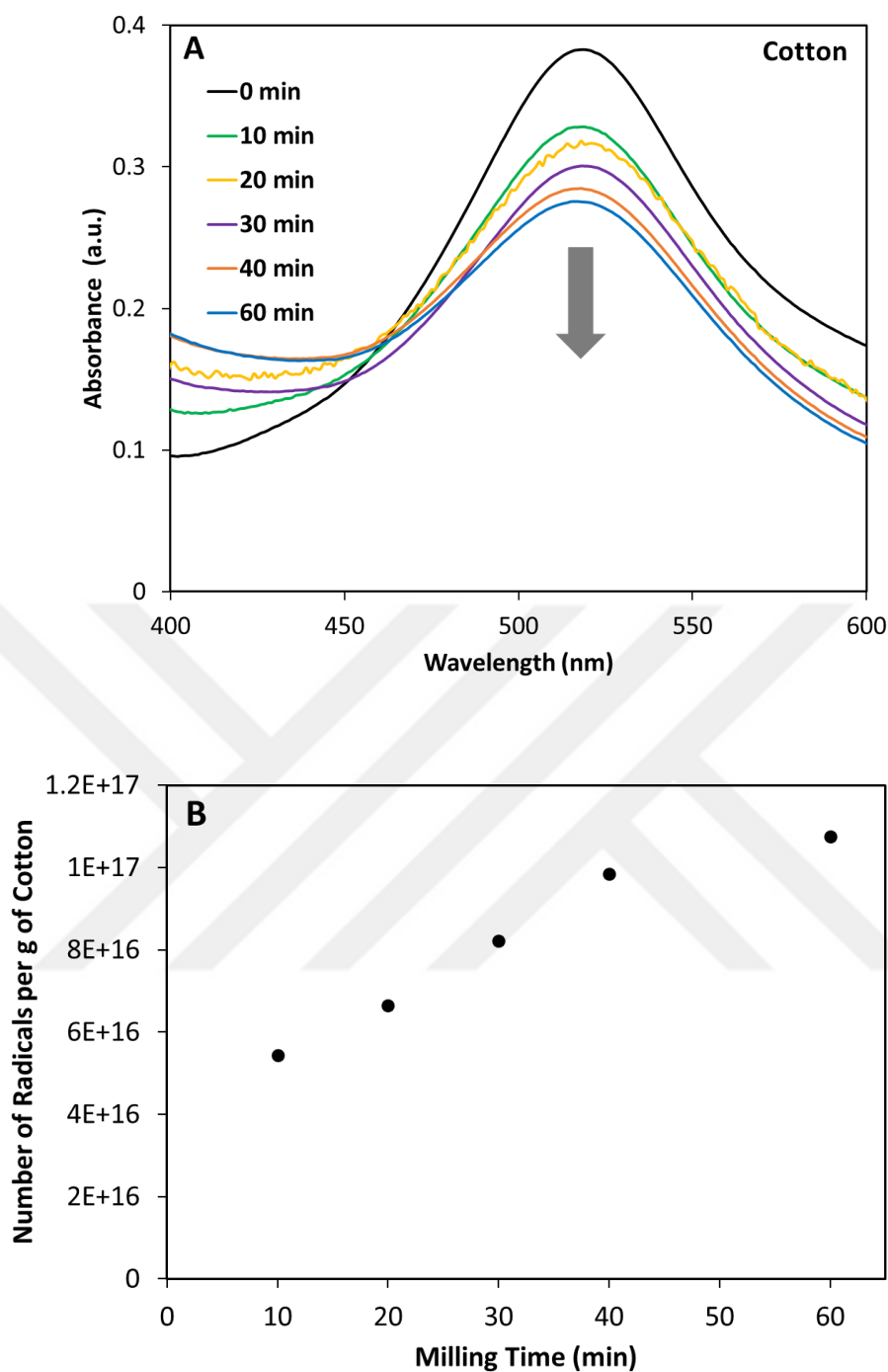


Figure 8. (A) UV-Vis spectra of the DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) that were wet cryomilled (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) with 500 mg cotton samples for 10, 20, 30, 40, and 60 minutes, and (B) calculated number of radicals per gram of cotton from the UV-Vis measurements for each milling time.

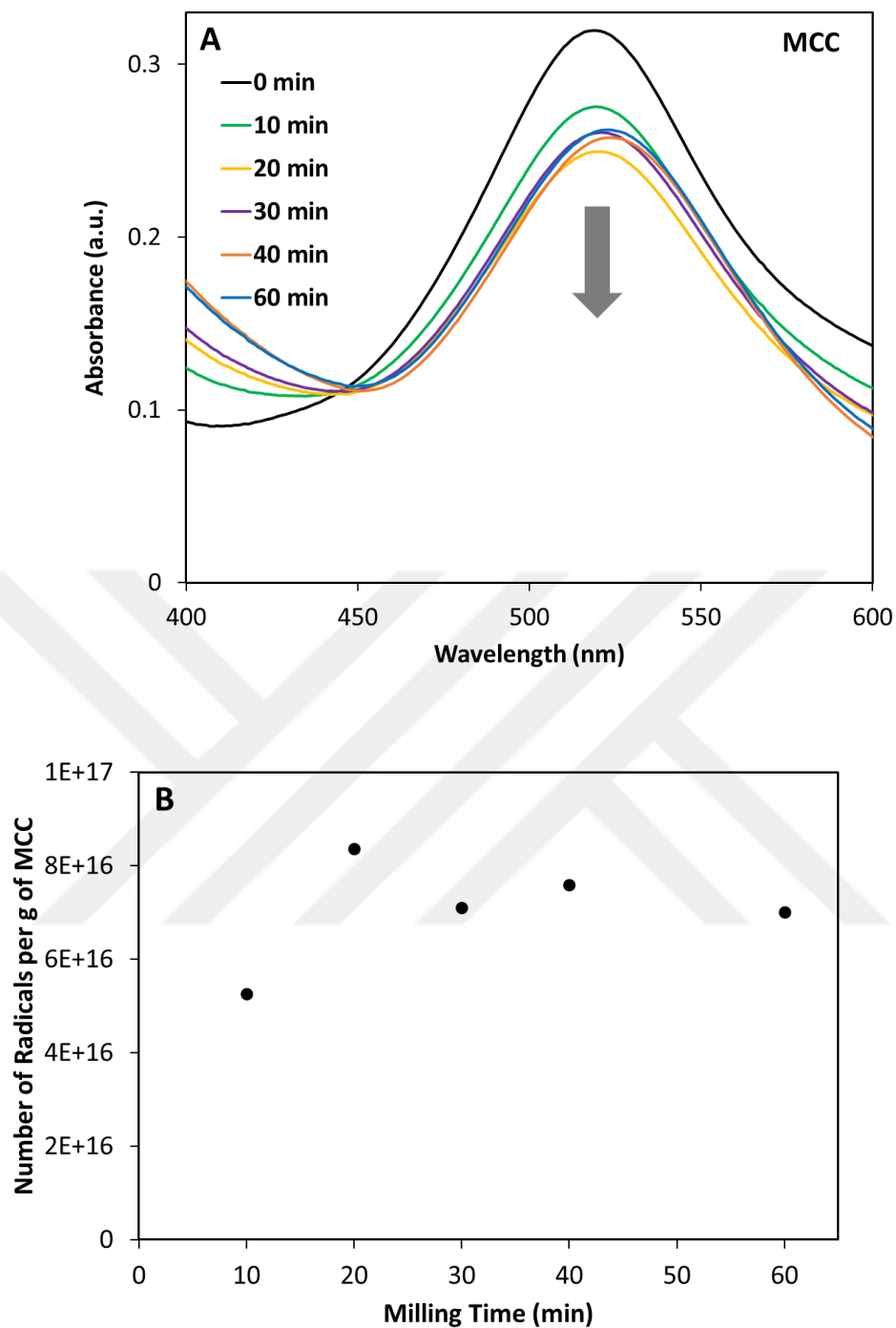


Figure 9. (A) UV-Vis spectra of the DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) that were cryomilled (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) with 500 mg MCC samples for 10, 20, 30, 40, and 60 minutes, and (B) calculated number of radicals per gram of MCC from the UV-Vis measurements for each milling time.

Similar to the results of the experiment with cotton sample, DPPH solutions cryomilled with MCC samples showed lower absorbance than the reference DPPH solution (indicated as '0 min' in the graph). This indicates that, grinding of the MCC samples, too, formed mechanoradicals that were scavenged by DPPH molecules. MCC samples could form around 7.5×10^{16} of mechanoradicals after milling for 40 minutes. There is not much difference observed between the radical amounts of the MCC samples cryomilled for 20, 30, 40, and 60 minutes. Also, MCC samples formed slightly lower number of radicals than cotton samples for 30, 40, 60 minutes milling (Table 4). This observation can be explained by taking particle size of milled cellulose sample into account: Milling of the cellulose samples leads to the bond breaking and the decrease in the particle size of the samples with new open ends. These new open ends of the particles are the location of the produced mechanoradicals. The particle size of the MCC is lower than the cotton samples, (SEM images in morphological characterization part 3.2). Cotton sample have millimeter-long fibers that slowly degrade to smallest possible particles microns during milling. On the other hand, MCC particles are already small (average size a couple of hundreds of microns), so they can reach to the minimum particle size possible in shorter times than cotton samples in wet conditions, which eventually means less number of bond-breakages and hence, less mechanoradicals.

Wet Grinding Time	Number of Radicals from Cotton	Number of Radicals from MCC
10 min	5.43×10^{16}	5.26×10^{16}
20 min	6.65×10^{16}	8.37×10^{16}
30 min	8.21×10^{16}	7.11×10^{16}
40 min	9.84×10^{16}	7.59×10^{16}
60 min	1.07×10^{17}	7.01×10^{16}

Table 4. Numbers of the mechanoradicals per gram of cellulose formed by wet grinding of (500 mg) cotton and MCC samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.1.1.2 From Dry Grinding Method

Contrary to wet grinding method, in dry grinding method after cryomilling of the cellulose for 10, 20, 30, 40, and 60 minutes, DPPH solutions were added. In addition to an immediate analysis of the number of mechanoradicals, after designated waiting times - the samples were allowed to stay in DPPH solution for designated waiting times to allow the diffusion of mechanoradicals to the surface (diffusion coefficients of mechanoradicals in polymeric matrices were calculated in [84]) and to give enough time to complete the reaction between mechanoradicals and DPPH- cellulose mechanoradicals were analyzed. In dry grinding method, we are exposing the samples to air before the addition of DPPH solutions. This causes peroxy cellulose radicals to form through the reaction between oxygen in the environment and some reactive cellulose mechanoradicals (see ESR analysis part

3.1.2). This type of radicals can give slower reaction with DPPH than initially formed carbon or oxygen based radicals. Also, it was reported that cellulose mechanoradicals showed high stability at room temperature for a long period of times [103], [104].

As mentioned in the experimental part, after cryomilling of the cellulose for 60 minutes, DPPH solution, that has the same concentration and the amount with the one used in wet grinding method, was added to the sample chamber and it was observed that deep violet color of the DPPH solution immediately turned into pale yellow color, as it came into contact with dry cryomilled cellulose. This indicated that, all DPPH was consumed by cellulose mechanoradicals produced from dry ground cellulose. Therefore, DPPH solution with 10 times higher molarity than those used in wet grinding method was used in dry grinding method, in order to detect the amount of all cellulose mechanoradicals.

Figure 10 shows the number of radicals per gram of cotton calculated from the UV-Vis spectra just after the addition of DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) on dry cryomilled cotton samples (A), and after several hours (B) for 10, 20, 30, 40 and 60 minutes milling.

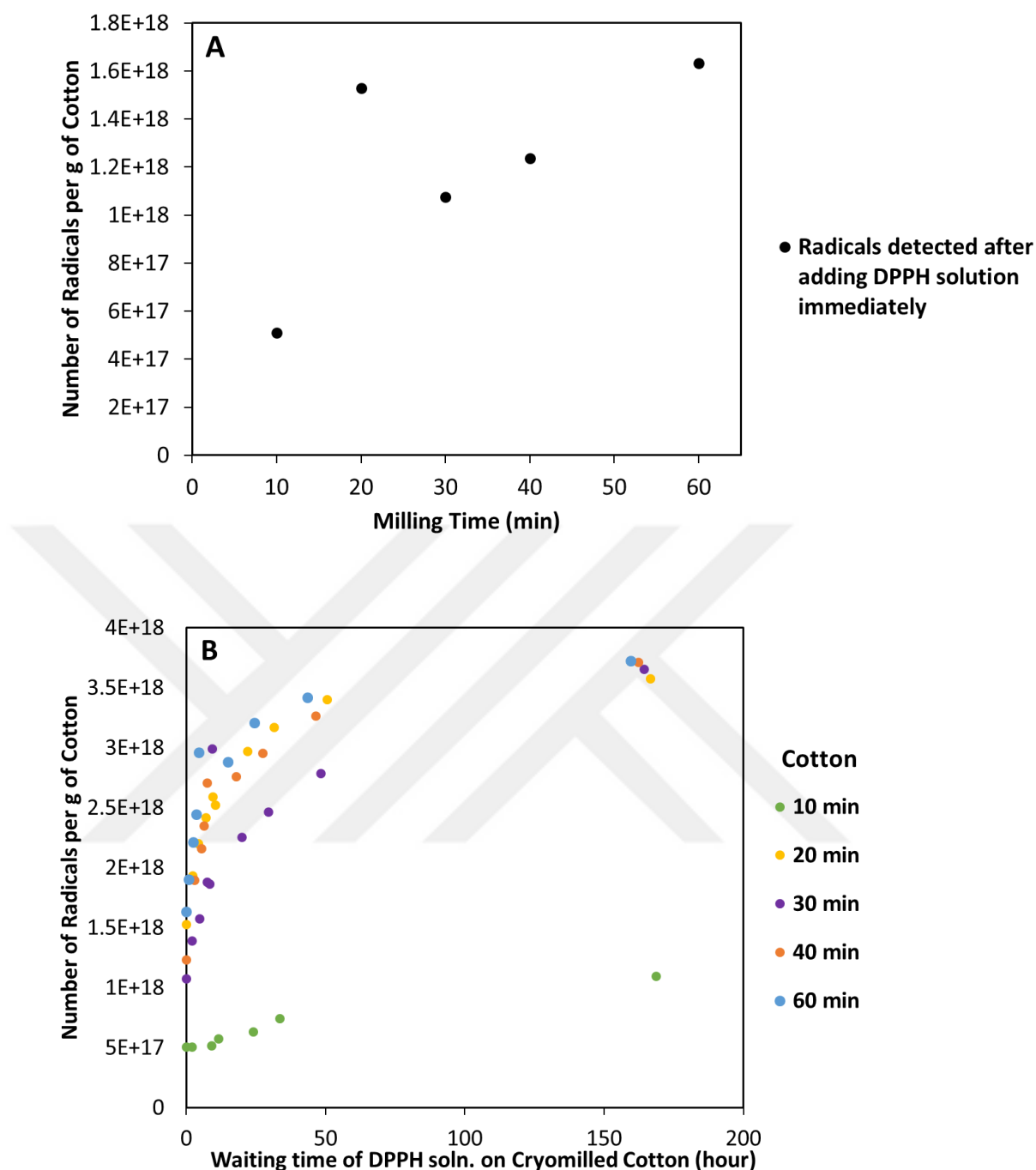


Figure 10. (A) Number of radicals per gram of cotton calculated just after the addition of DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) on dry cryomilled 500 mg of cotton samples for 10, 20, 30, 40 and 60 minutes of milling (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K), and (B) number of radicals calculated after designated waiting times.

Milling Time of Cotton	Number of Radicals from Wet Grinding	Number of Radicals from Dry Grinding	Ratio of the Radicals from Dry Grinding to Wet Grinding
10 min	5.43×10^{16}	5.10×10^{17}	9.38
20 min	6.65×10^{16}	1.53×10^{18}	22.99
30 min	8.21×10^{16}	1.08×10^{18}	13.11
40 min	9.84×10^{16}	1.24×10^{18}	12.55
60 min	1.07×10^{17}	1.63×10^{18}	15.19

Table 5. Number of mechanoradicals per gram of cotton formed by wet and dry cryomilling of 500 mg cotton samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) and their ratio at 10, 20, 30, 40, and 60 minutes milling time.

Table 5 shows the number of mechanoradicals formed by wet and dry cryomilling of cotton samples. As it can be seen from the Table 5, dry grinding method led to the 9.4 to 23.0 times more mechanoradicals than wet grinding.

Figure 11 represents the number of radicals per gram of MCC calculated from the UV-Vis spectra just after the addition of DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) on cryomilled MCC samples (A), and after several hours (B) for 10, 20, 30, 40 and 60 minutes milling.

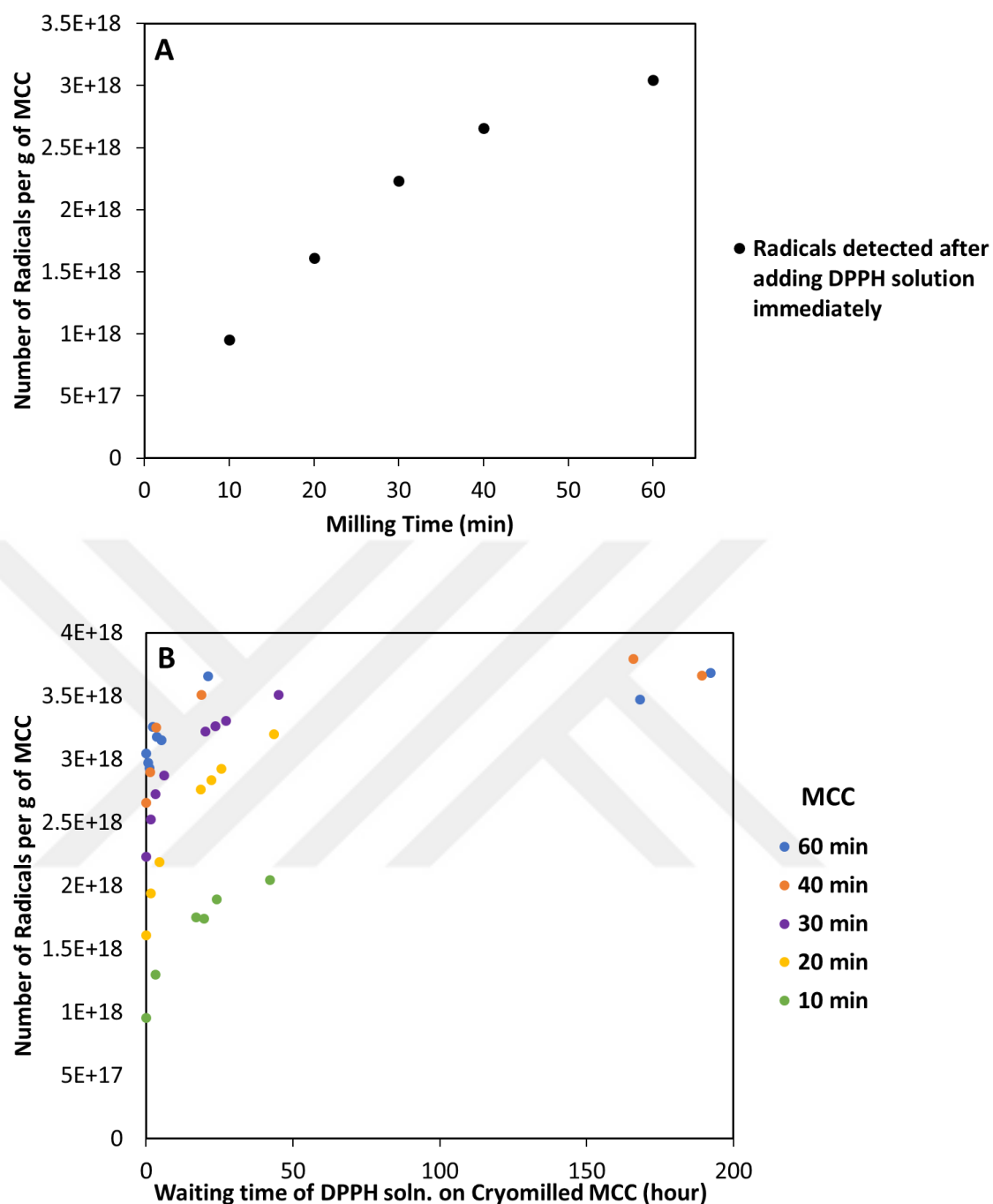


Figure 11. (A) Number of radicals per gram of MCC calculated just after the addition of DPPH solutions (initial concentration after dilutions was 3.2×10^{-5} M) on dry cryomilled 500 mg of MCC samples for 10, 20, 30, 40 and 60 minutes of milling (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K), and (B) number of radicals calculated after designated waiting times.

Table 6 shows the numerical amounts of radicals formed by wet and dry cryomilling of MCC samples. Results show that dry grinding method produces 18-43 times more number of mechanoradicals than wet grinding method.

Milling Time of MCC	Number of Radicals from Wet Grinding	Number of Radicals from Dry Grinding	Ratio of the Radicals from Dry Grinding to Wet Grinding
10 min	5.26×10^{16}	9.56×10^{17}	18.18
20 min	8.37×10^{16}	1.61×10^{18}	19.23
30 min	7.11×10^{16}	2.23×10^{18}	31.4
40 min	7.59×10^{16}	2.66×10^{18}	35.01
60 min	7.01×10^{16}	3.05×10^{18}	43.42

Table 6. Number of mechanoradicals per gram of MCC formed by wet and dry cryomilling of 500 mg MCC samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) and their ratio at 10, 20, 30, 40, and 60 minutes milling time.

In the light of these results, it is clear that dry grinding method led to more mechanical activation of cellulose particles, led to more number of bond cleavages and created more number of radicals than wet grinding method. This difference might be attributed to the higher efficiency of solventless grinding in this method. We have proven that in the presence of solvent or any solution, it is not possible to obtain fine grinding, which will be discussed in the morphological characterization by SEM part 3.2 in details. Therefore, in dry conditions cellulose samples can be milled effectively and dry milling can form more active particles with lower particle size and with more open ends i.e. more number of mechanoradicals.

Another reason for the difference in number of mechanoradicals formed through wet and dry grinding might be a reaction of solvent with the initially formed, active radicals. In literature DPPH was used to detect mechanoradicals formed on wet ground alumina and quartz [112], [113]. In these studies, solvent was reported to contribute in reactions with the formed mechanoradicals. In dry grinding the mechanoradicals formed react with oxygen and form peroxy radicals, which do not react with the solvent of DPPH solution (acetonitrile) [84].

3.1.2 Qualitative Determination of Produced Radicals by Electron Spin Resonance (ESR) Spectroscopy Analysis

In addition to quantitative investigation of cellulose radicals by UV-Vis analysis, qualitative investigation has been studied by Electron Spin Resonance spectroscopy (ESR). ESR provides a useful method to identify free radicals and it has been utilized in many studies [114]–[116]. Mechanoradicals formed using ball milling were examined with ESR spectroscopy firstly by Butyagin *et. al* in 1964 [117]. Later, a ball milling apparatus was designed special for ESR analysis by Sakaguchi and Sohma [118]. In their setup, there is a direct connection between an ESR sample tube and the sample chamber and design of this apparatus allows milling in vacuum or in any gas and at low temperatures, which makes taking ESR measurement easier, without any exposure to air. This way, the temperature of the sample tube does not increase before the ESR measurement, either. It was reported that, mechanical treatment applied to cellulose samples led to the production of cellulose mechanoradicals by breaking of β -1,4 glycosidic bond in cellulose chain [102]–[104], [108], [109], [111]. Figure 12 shows the structures of produced

cellulose mechanoradicals due to bond scission caused by ball milling or cryomilling.

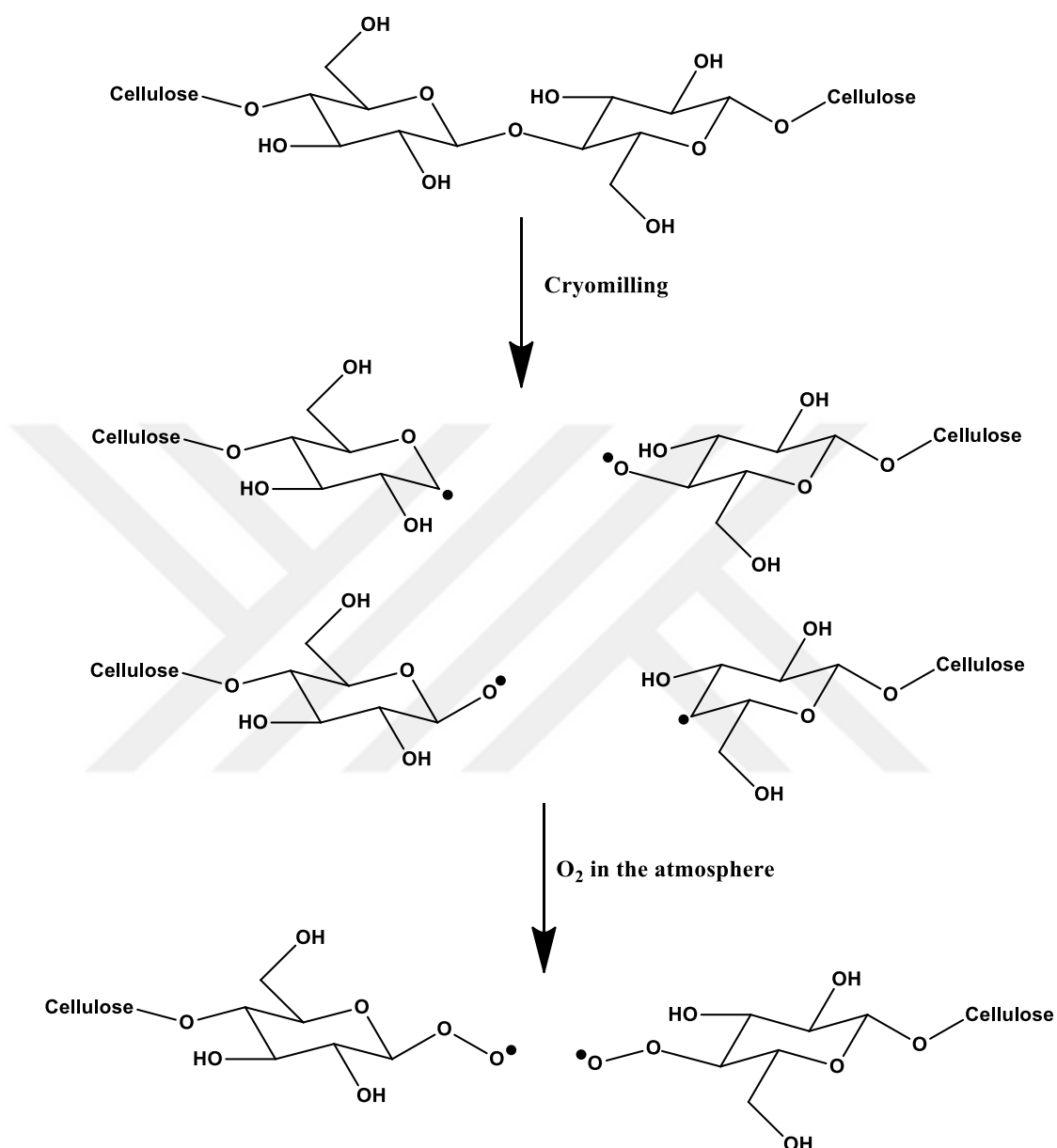


Figure 12. Structures of cellulose mechanoradicals produced by ball milling, Modified from [108], [119], [120].

After dry grinding of cotton sample (500 mg) for 60 min (see Experimental section 2.2.2 for more details), the sample was subjected to ESR measurement at room temperature (Figure 13).

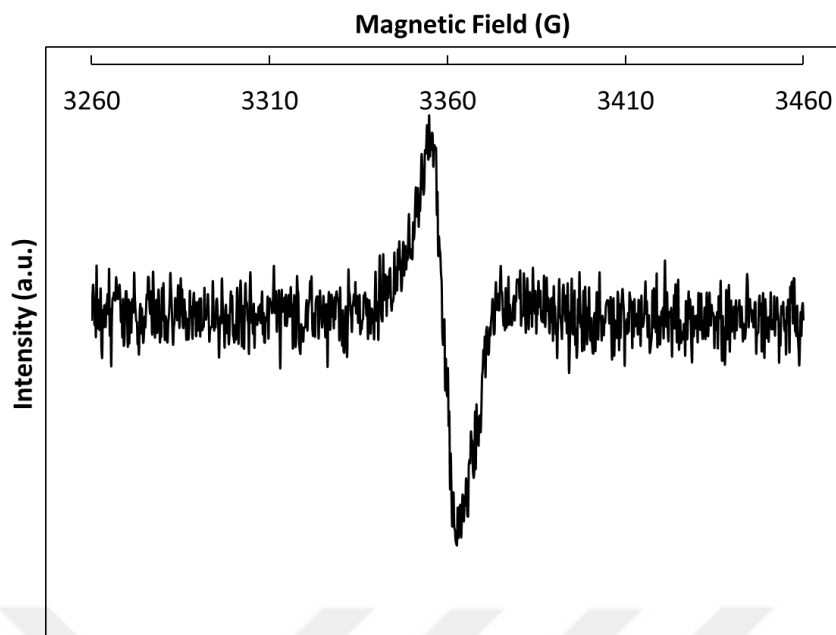


Figure 13. Room temperature ESR spectrum of cryomilled cotton (500 mg) sample (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K).

ESR spectrum of the cryomilled cotton sample shows a singlet signal with g -value of 2.00558 ($g\beta B_0 = h\nu$). Solala *et. al* reported the study including an identical ESR result [111]. In this study, 40 min cryomilled cotton sample had the similar single ESR pattern at room temperature. However, the corresponding chemical structures of the cellulose radicals were not reported exactly in this paper. As can be seen in Figure 12, four types of the cellulose mechanoradicals -two alkyl type-carbon centered radicals and two alkoxy type-oxygen centered radicals- are produced due to mechanical breaking of the glycosidic bond of cellulose chain. In the literature, studies including cellulose mechanoradicals had the ESR measurements generally taken at 77K after milling in vacuum atmosphere at 77K. Their ESR patterns had lower noise, so the small humps that appeared near the main singlet signal are visible. In these papers, when cellulose mechanoradicals were let to warm up, it was seen that these humps disappeared and only the singlet signal

was obtained, which is identical with our result [102], [108], [119]. This might have been the same for our cellulose samples as they warmed up to room temperature (we had to let the samples come to room temperature as we took them out of the milling chamber). If the milling is not done under vacuum, initially formed cellulose mechanoradicals react with oxygen in the atmosphere to form secondary peroxy cellulose radicals that have singlet signal with g-value of around 2.006 [120], [102], [108], [121], which is similar to the g-value we obtained (2.00558). Formed peroxy radicals have higher stability due to more resonance stabilization of the unpaired electron. In the light of these studies, after the cryomilling of the cellulose sample in air atmosphere at 77K and the ESR measurement at room temperature, the main cellulose mechanoradicals can be assigned as the long lived and stable peroxy cellulose radicals and maybe some alkoxy type radicals (alkoxy radicals also show a singlet ESR signal with close g-value to our result [102], [104], [108]).

3.2 Morphological Changes in Cryomilled Cellulose Samples by Scanning Electron Microscopy (SEM) Analysis

After cryomilling of cotton and MCC samples, changes in samples' morphology was investigated to evaluate the effects of the initial morphology of the samples on mechanoradical production. As shown before, mechanical energy is adsorbed by cellulose samples and then, cellulose chains break and radicals form. Here we show, decrease in the particle size of the samples parallels the formation of radicals: As the particle size is reduced, fresh surfaces form and more 'open ends' form. These new open ends and surfaces of the particles is where mechanoradicals form.

3.2.1 Morphological Changes in Cryomilled Cellulose Samples by SEM Analysis - Wet Grinding Method

After cryomilling of the cellulose samples with DPPH solutions for indicated times, cellulose samples were washed and dried in order to investigate morphological changes by SEM analysis. Figures 14 and 15 show the SEM images of cotton and MCC samples, respectively, after given milling times. MCC is produced by mild acid hydrolysis of native cellulose or pulp [122], [123], therefore, the initial morphology of the MCC is different than that of cotton, i.e., cotton has millimeters-long-fibers with approximately 20.4 μm width. MCC has shorter (103.8 μm) fibers of approximately 27 μm width. SEM images (Figure 14 and 15) show, for both cotton and MCC samples, with increasing milling time particle sizes decreases. The images also show, during wet milling of cotton particles size is reduced gradually. On the other hand, MCC can reach to the minimum particle size in shorter time than cotton, due to MCC's lower initial particle size. As was shown in Table 4, milling of MCC samples produced slightly lower number of radicals than cotton samples for 30, 40, and 60 minutes milling, under same conditions. We believe this difference is a result of a smaller change in particle size of MCC after especially 30 minutes milling compared to that in cotton - smaller number of bond-breakages yields smaller number of radicals. In addition to this observation, we may also surmise that the distribution of the mechanical energy on cotton samples may be easier than that of the MCC samples in wet conditions because of the longer fiber length of the cotton samples.

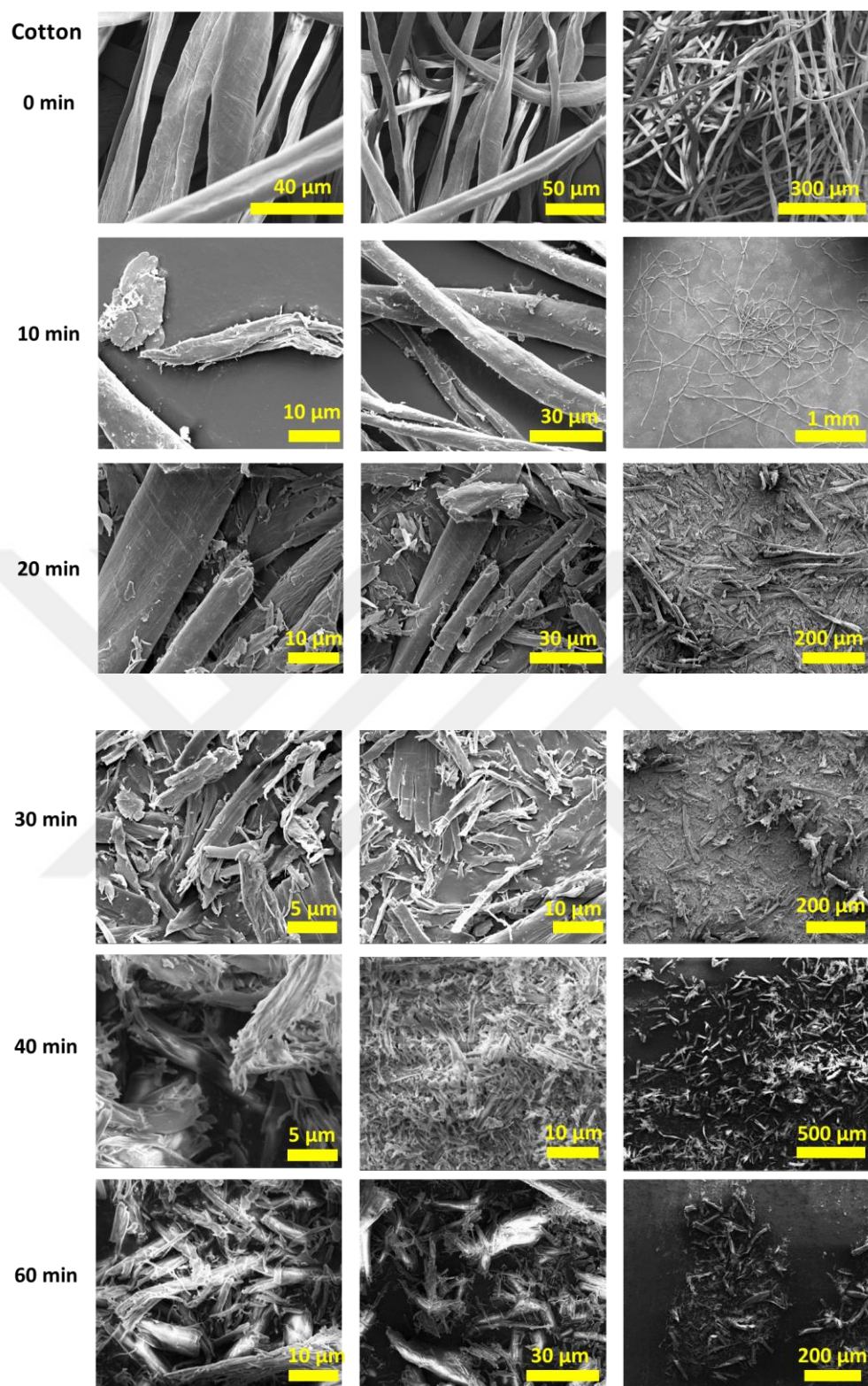


Figure 14. SEM images of cotton and wet cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

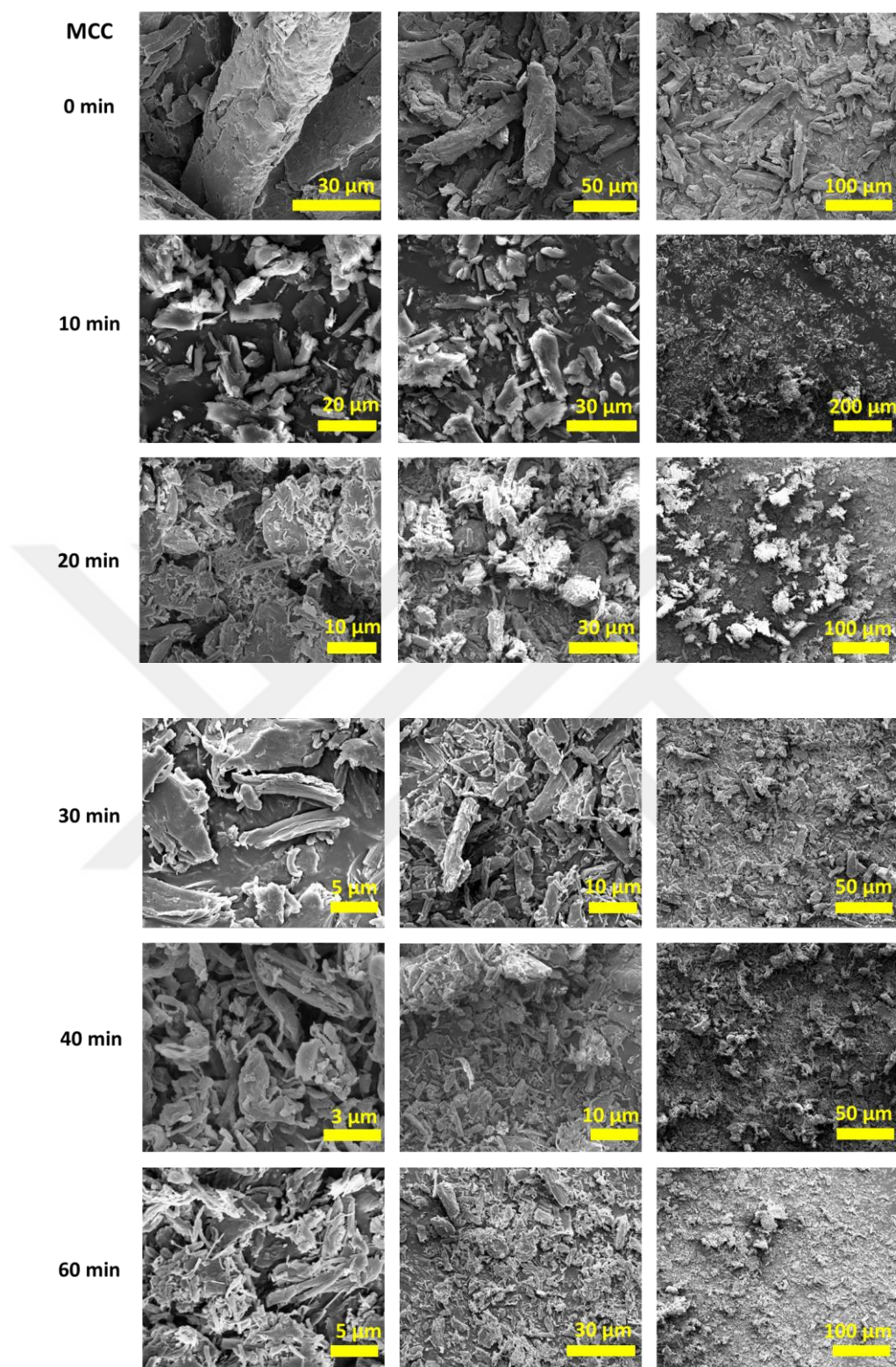


Figure 15. SEM images of MCC and wet cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.2.2 Morphological Changes in Cryomilled Cellulose Samples by SEM Analysis - Dry Grinding Method

After dry cryomilling (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) of the cellulose samples for indicated times, the morphological changes in the samples upon grinding were investigated by SEM analysis. Figure 16 and 17 show the SEM images of cotton and MCC samples after given milling times, respectively. As expected, both cotton and MCC showed a decrease in particle size with the increase in milling time. This decrease is much more in dry milling condition than that observed in wet milling condition. This can be due to the fact that, the presence of solution during wet milling preventing the efficient transfer of mechanical energy to cellulose samples. In contrast to cotton samples that were milled in wet condition, the cotton samples milled in dry condition lost their fiber morphology after milling for 20 minutes, implying that mechanical impact was transferred more efficiently to the cellulose. Fiber morphology of MCC samples were lost by milling, too. The particle size of the cellulose samples decreases faster in dry grinding method and accessibility of the cellulose surfaces increased due to the formation of the new surfaces. The faster particle size reduction imaged by SEM can also be correlated with more number of radicals produced in dry grinding compared to wet grinding (Table 5,6).

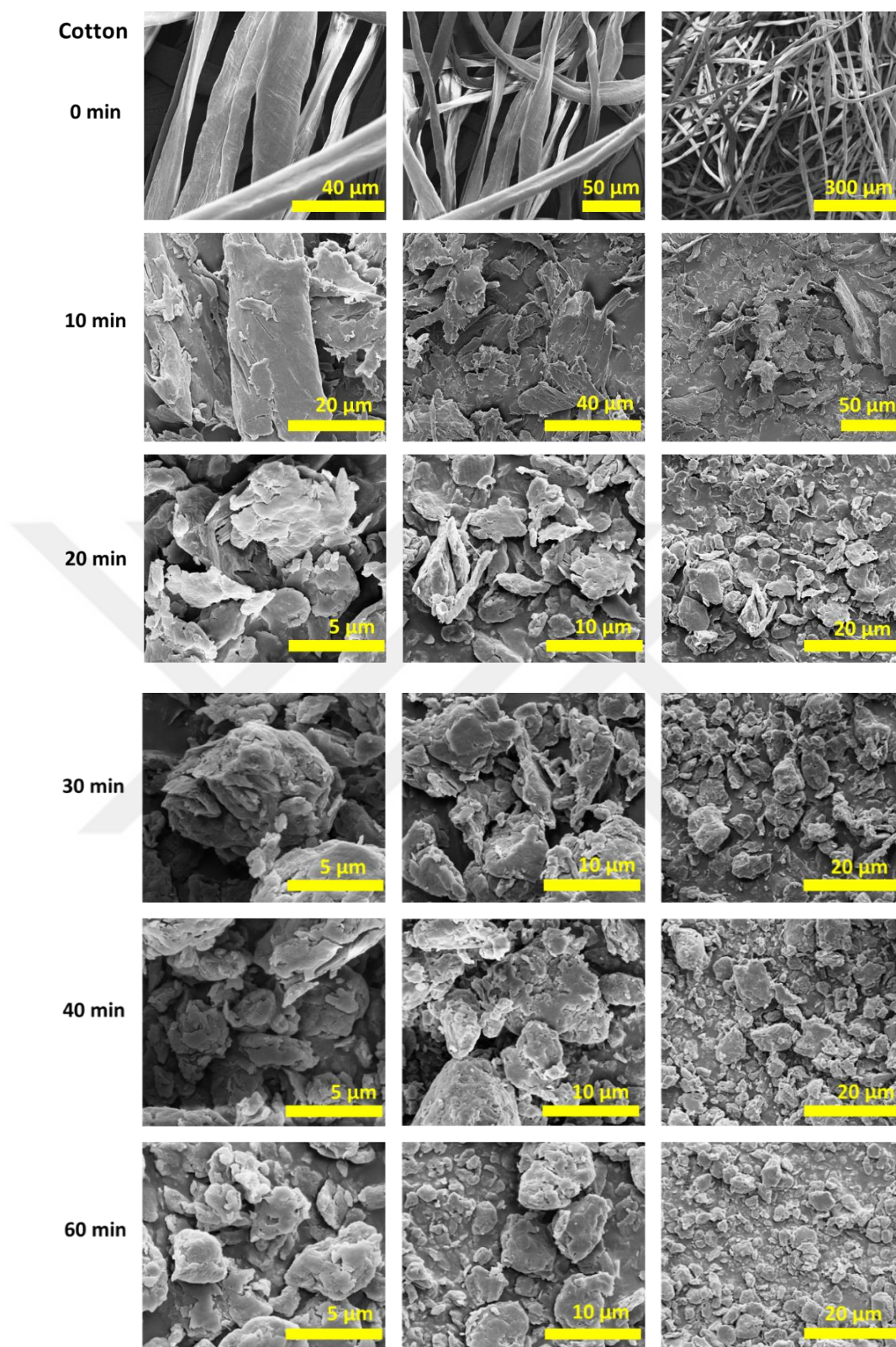


Figure 16. SEM images of cotton and dry cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

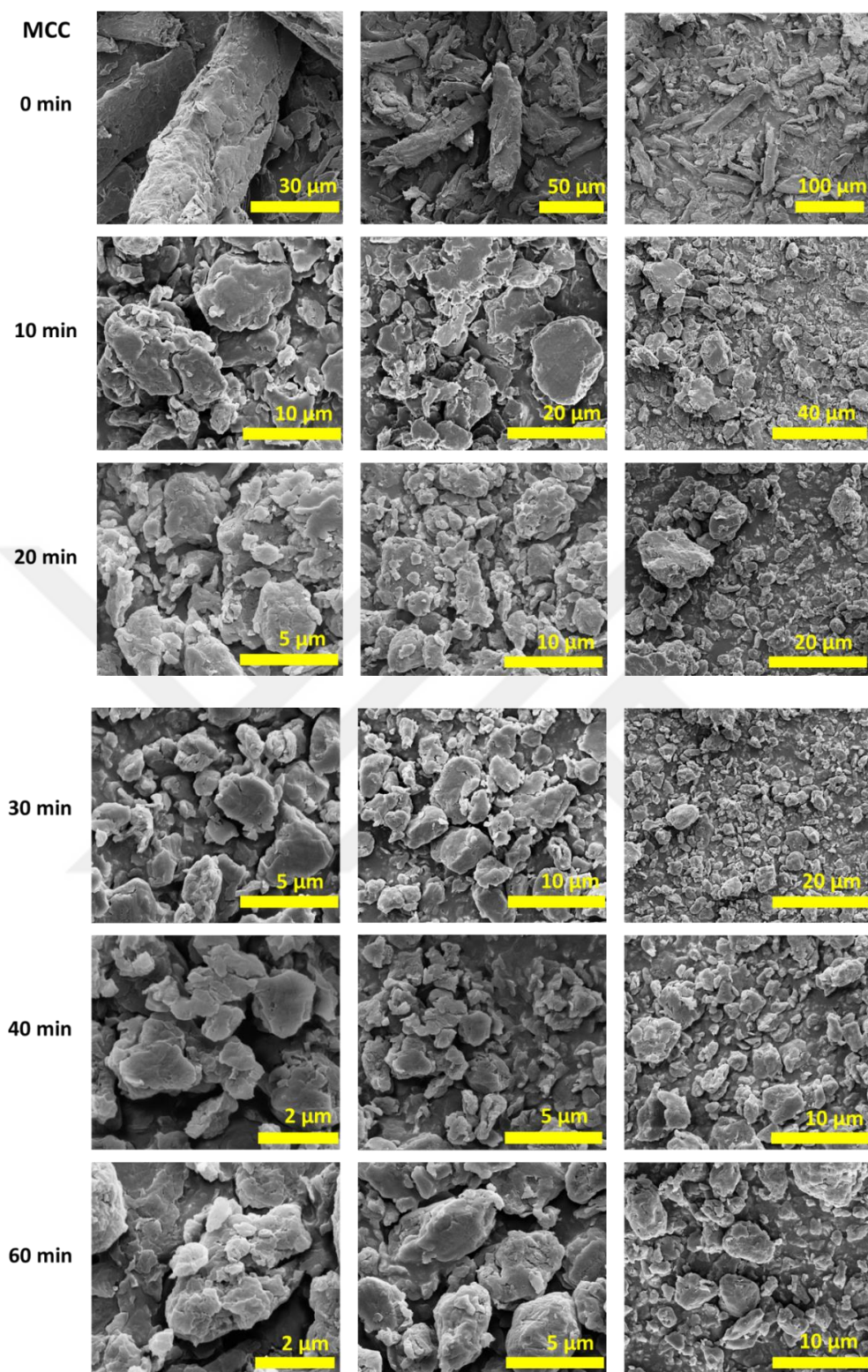


Figure 17. SEM images of MCC and dry cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.3 Changes in Crystalline Structure of Cryomilled Cellulose Samples by X-Ray Diffraction (XRD) Analysis

Cellulose is a semicrystalline polymer. It has crystalline regions including strong intra and intermolecular hydrogen bonds, and amorphous regions including weak van der Waals forces. XRD measurement of cellulose shows strong signals from crystalline parts of the cellulose structure. Non-crystalline or amorphous parts of the cellulose structure give broader or less clearly defined signals in XRD patterns. When mechanical treatment is applied to cellulose, it can absorb this mechanical energy. This absorbed mechanical energy can bring about the changes in crystalline structure, which can be observed by X-ray diffraction (XRD) analysis. After wet and dry grinding of cellulose samples (cotton and MCC), the changes in crystalline structure of cryomilled cellulose samples was investigated by XRD analyses.

3.3.1 Changes in Crystalline Structure of Cryomilled Cellulose Samples by XRD - Analysis Wet Grinding Method

As mentioned in the experimental part, after cellulose samples were wet cryomilled with DPPH solution, they were washed and dried for XRD analysis. Figure 19 and 20 show the XRD diffractograms of wet cryomilled cotton and MCC cotton for 10, 20, 30, 40, and 60 minutes, respectively. In these diffractograms cotton gave the diffraction lines approximately at 2θ : 15.25° , 16.88° , 23.18° , 34.89° and MCC samples showed the diffraction lines approximately at 2θ : 15.03° , 16.40° , 22.54° , 34.62° . These diffraction lines match closely with the reported values of cellulose I crystalline structure showing corresponding crystallographic planes of $(1\ 1\ \bar{0})$, $(1\ 1\ 0)$, $(2\ 0\ 0)$, and $(0\ 0\ 4)$, respectively [124], [125], [126]. As

mentioned before, cellulose I is one of the polymorphic forms of cellulose crystallites, which shows parallel orientation of chains. The diffraction lines appeared as a doublet at 2Θ : 15.25° and 16.88° for cotton and at 15.03° and 16.40° for MCC samples corresponding to lattice or crystallographic planes of $(1\ 1\ \bar{0})$ and $(1\ 1\ 0)$ respectively, come from the two crystalline forms of native cellulose (allomorphs of cellulose I), that are $I\alpha$ and $I\beta$ [127]. (Cellulose I structure has the mixture of $I\alpha$ and $I\beta$ forms, the distribution of $I\alpha$ having triclinic unit cell and $I\beta$ having monoclinic unit cell depends on the origin of the cellulose [127]. $I\alpha$ form is thermodynamically less stable that, it can be converted to $I\beta$ form by annealing at 260°C [31].) In two forms of cellulose I, the repeating unit is cellobiose and both forms have strong intramolecular hydrogen bonds with same characteristics. However, intermolecular hydrogen bonds and packing of the crystal characteristics show difference in the two forms [31]. The main diffraction line approximately at 2Θ : 23.18° for cotton and at 22.54° for MCC samples are due to the lattice plane of $(2\ 0\ 0)$, which arises from the distance between the sheets having hydrogen bonds [124], [127]. Moreover, the last diffraction line at approximately at 2Θ : 34.89° for cotton and at 34.62° for MCC samples corresponds to the lattice plane of $(0\ 0\ 4)$, which results from the orientation along the fiber direction, which are affected by the alignment of chains into the fibrils [124], [126], [127].

As can be seen in both XRD patterns of wet cryomilled cotton and MCC samples, there was no crystal structure change observed after cryomilling of the cellulose samples for indicated times. In order to explain properly, the crystallinity or crystallinity index (C) of wet cryomilled cellulose samples for indicated minutes were calculated. XRD analysis has been used in order to calculate the crystallinity of cellulosic materials extensively [122], [128]–[130]. The most extensively

utilized method to determine crystallinity from XRD measurement is the peak height method [122]. This method was developed by Segal and coworkers [129]. According to this method, the crystallinity (C) is calculated by this equation;

$$C = 100 \times (I_{200} - I_{\text{non-cr}}) / I_{200} [\%]$$

where I_{200} is the maximum intensity of the 200 lattice plane at 2θ angle between 22° - 24° and $I_{\text{non-cr}}$ express the intensity of amorphous or non-crystalline portions in cellulose, minimum intensity of the valley between the lattice planes of 110 and 200 approximately at angle 2θ : 18 - 19° in XRD pattern [122]. I_{200} has the contribution from mainly crystalline and some amorphous portions in cellulose but, $I_{\text{non-cr}}$ represents only the amorphous portions in cellulose structure. Therefore, subtraction of the intensity coming from amorphous portions ($I_{\text{non-cr}}$) from the intensity coming from crystalline and amorphous portions (I_{200}) give the value due to only crystalline portions in cellulose structure. Dividing this value to the intensity due to both crystalline and amorphous parts (I_{200}), then by multiplying with 100 results the percent crystallinity of cellulose. Figure 18 shows the XRD pattern of cotton sample having the intensities used in peak height method.

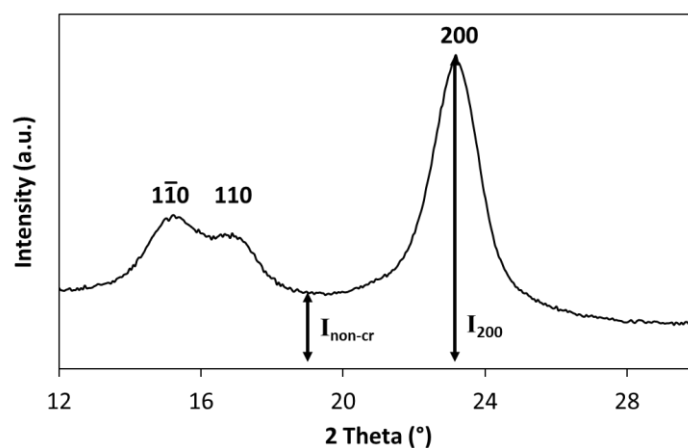


Figure 18. XRD pattern of cotton sample having the intensities used in peak height method for percent crystallinity analysis.

Using the peak height method (Figure 18 and Equation 1), percent crystallinities of cotton and MCC before and after wet cryomilling for 10, 20, 30, 40 and 60 minutes were calculated. These are shown in Table 7. The crystallinity of cotton sample is 75.91% and that of MCC sample is 73.84% before milling. These values are consistent with the reported crystallinity values of cotton and MCC samples (cotton: 56-78%, MCC: 65-83%) [122]. It can be said that, there was no significant change in crystallinities after wet cryomilling of both cotton and MCC samples. When mechanical treatment in a form of milling is applied to the cellulose samples, they can absorb this mechanical energy. When this mechanical energy is high enough, this can lead to the slippage of the bonds, breaking of intra and intermolecular hydrogen bonds and scission of the glycosidic linkages in cellulose structure. When cotton samples were cryomilled, percent crystallinity did not decrease as can be seen in Table 7, but it increased slightly, presumably because of the chain alignment caused by mechanical treatment. In contrast to cotton samples, the percent crystallinity was decreased slightly for MCC with cryomilling.

As seen in SEM imaging and analysis of mechanoradical production, wet grinding could not provide efficient milling to break appreciable amount of bonds in both cotton and MCC. Here this trend is also followed in insignificant changes in percent crystallinity after milling. We believe this inefficiency is because of the presence of a solvent in the grinding chamber, which prevent the transfer of mechanical milling energy directly to cellulose during wet milling. Under this condition, mechanical energy could reach only to the amorphous parts of the cellulose samples. It is likely that, mechanical energy can only be absorbed by amorphous parts in the cellulose chains, leading to no significant changes in crystalline structures or crystallinity of cellulose samples.

Cryomilling Time	Percent Crystallinity for Cotton	Percent Crystallinity for MCC
0 min	75.91%	73.84%
10 min	78.74%	73.13%
20 min	80.49%	70.17%
30 min	79.34%	69.97%
40 min	80.63%	63.75%
60 min	79.09%	60.81%

Table 7. Percent crystallinities of cotton and MCC (500 mg) samples before and after wet cryomilling (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes, calculated from peak height method. For details of milling conditions, see experimental part.

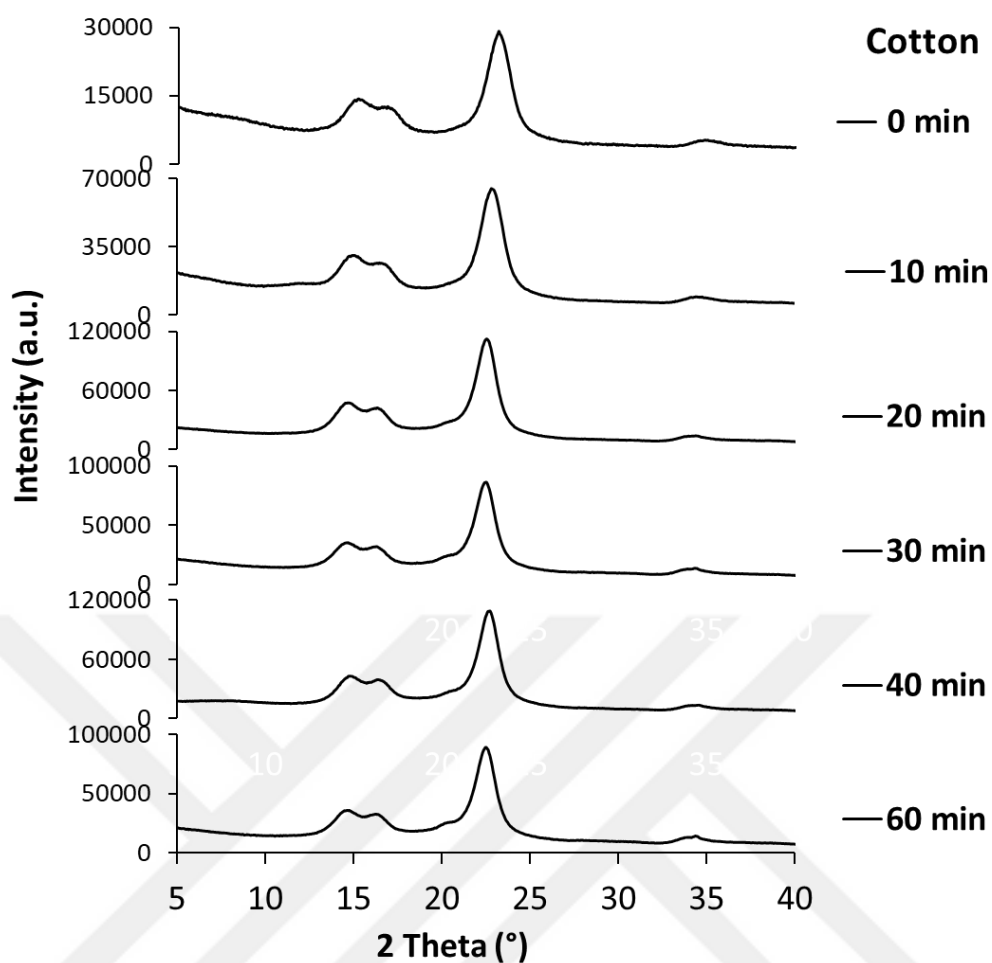


Figure 19. XRD patterns of cotton and wet cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

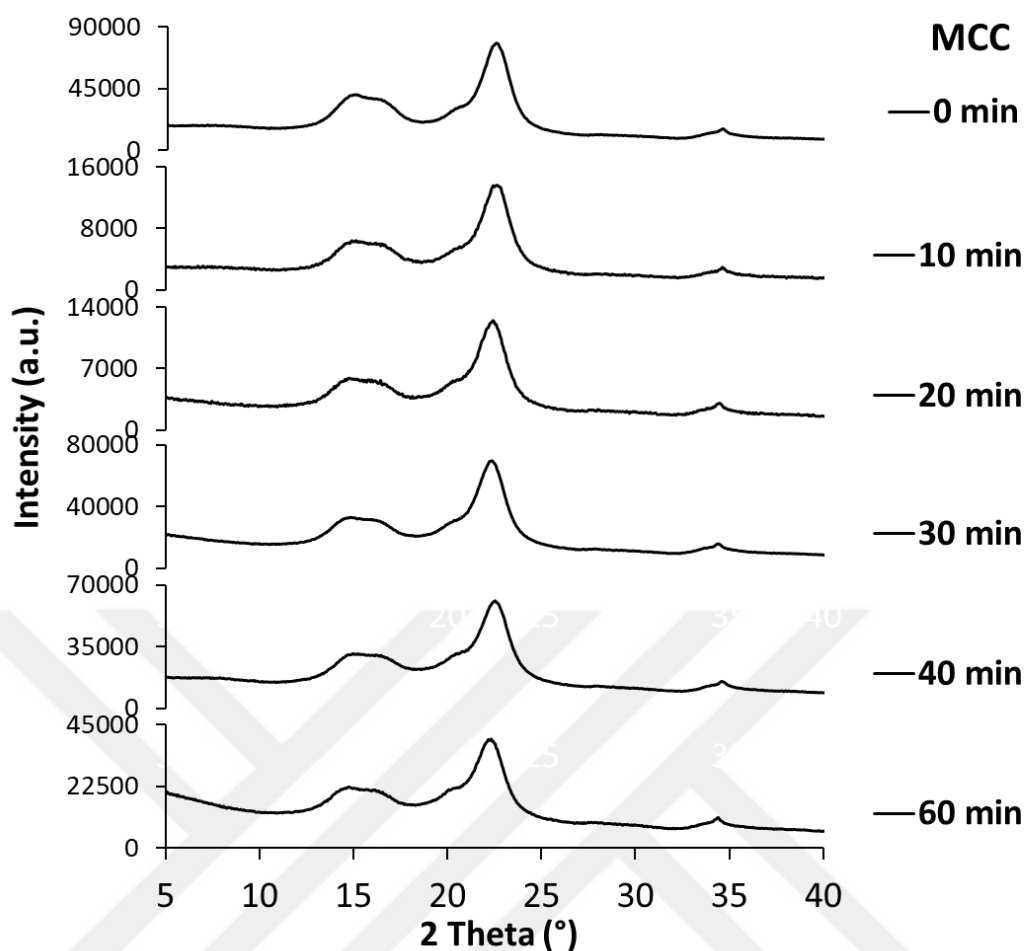


Figure 20. XRD patterns of MCC and wet cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.3.2 Changes in Crystalline Structure of Cryomilled Cellulose Samples by XRD - Dry Grinding Method

As mentioned in experimental part, after cellulose samples were cryomilled in dry condition, they were analyzed by XRD. Figure 21 and 22 show the XRD diffractograms of cotton and MCC dry cryomilled 10, 20, 30, 40, and 60 minutes, respectively. As mentioned in wet grinding method, cotton and MCC samples have cellulose I crystalline structure with characteristic diffraction lines and

crystallographic planes before cryomilling. When mechanical treatment was applied to cotton, typical crystalline diffraction lines disappeared after dry cryomilling for 20 minutes. For MCC samples mechanical treatment led to the disappearance of the characteristic crystalline diffraction lines after 10 minutes. This new formed diffraction line including broad band approximately at 2θ : 19° after dry cryomilling indicated the formation of mostly amorphous cellulose samples [35], [42], [131], [132]. The formation of mostly amorphous cellulose after cryomilling of cotton sample for 20 minutes is compatible with the result observed by SEM analysis of the dry cryomilled cotton sample, showing the loss of fiber morphology of the cotton sample after milling for 20 minutes. This time period is 10 minutes for MCC sample. Since the cotton sample has longer fibers, it has to be milled for a longer time than MCC sample so that mechanical impact affects the crystalline regions. All these results showed that, in dry condition mechanical energy or impact could dissipate in larger areas in cellulose chains and this energy was absorbed by crystalline parts in cellulose structure. This energy absorption led to the rearrangements of the chains. In dry ball-milling, mechanical energy is high enough to disorder the crystalline regions and break the bonds in crystalline parts. These findings are also supported by the radical formation analyses in dry condition (Table 5, 6), which indicated the formation of more accessible regions and more number of mechanoradicals in dry grinding.

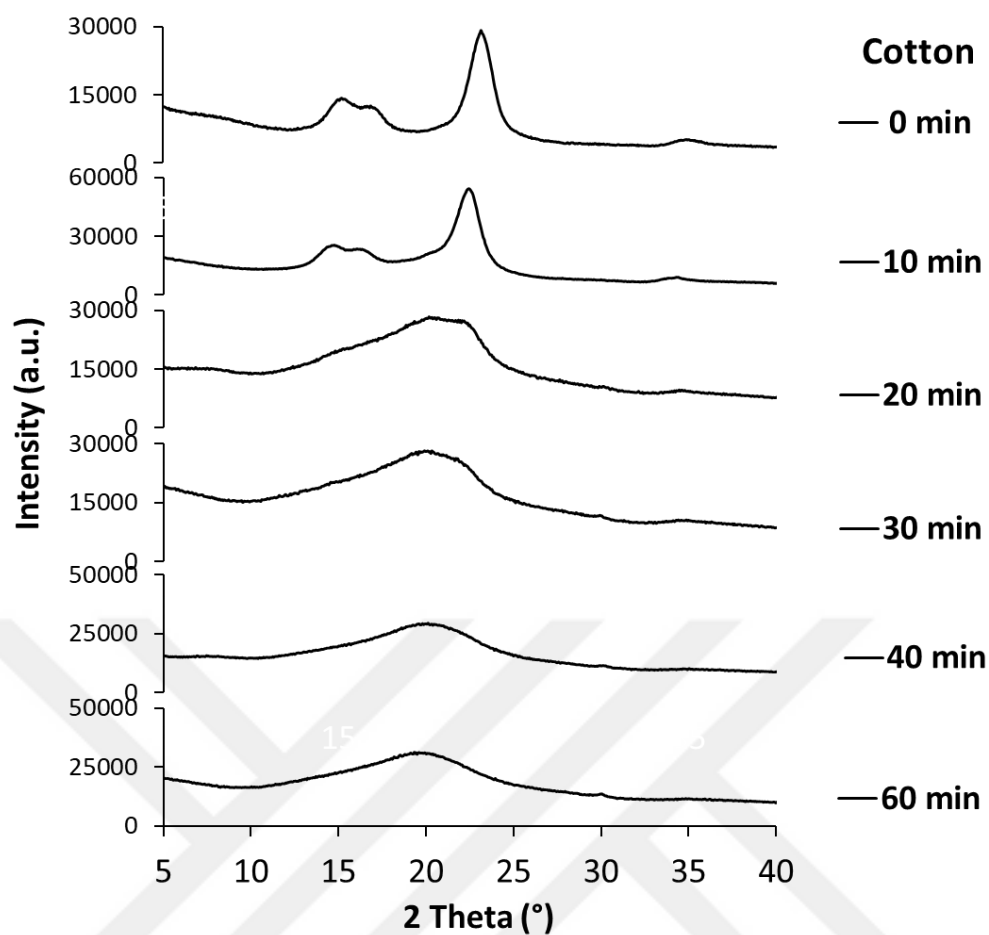


Figure 21. XRD patterns of cotton and dry cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

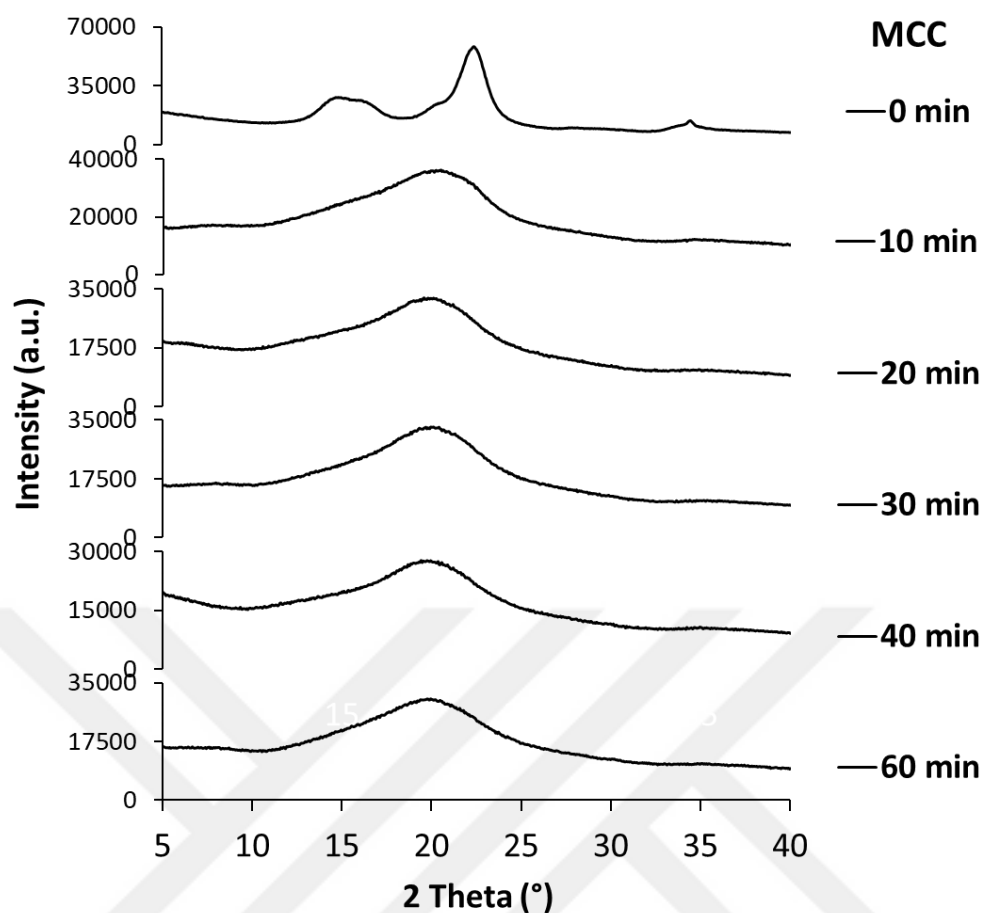


Figure 22. XRD patterns of MCC and dry cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.4 Structural Changes of Cryomilled Cellulose Samples by Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) Spectroscopy Analysis

The structural changes in cryomilled cellulose samples have been investigated by FTIR-ATR analyses after wet and dry grinding of cellulose samples.

3.4.1 Structural Changes of Cryomilled Cellulose Samples by FTIR-ATR Spectroscopy Analysis - Wet Grinding Method

As mentioned in experimental part, after cellulose samples were cryomilled with DPPH solution, they were washed and dried for FTIR analysis. Figures 24 and 25 show the FTIR spectra of wet cryomilled cotton and MCC, respectively. IR bands observed for cotton and MCC samples are shown in Table 7. Bands assignments of FTIR spectrum of cotton is displayed in Figure 23. The strong bands with two maxima at 3335 cm^{-1} and 3282 cm^{-1} for cotton, and at 3335 cm^{-1} and 3293 cm^{-1} for MCC are attributed to the characteristic O-H stretching vibrations. The bands at lower wavenumbers (3282 cm^{-1} for cotton and 3293 cm^{-1} for MCC) are due to intermolecular hydrogen bonds between O(6)H-O(3), and the bands at higher wavenumbers (3335 cm^{-1} for cotton and 3339 cm^{-1} for MCC) are attributed to intramolecular hydrogen bonds between O(2)H-O(6) and O(3)H-O(5) in cellulose chains [133]–[136]. After cryomilling of cotton samples for 20 minutes, the peak corresponding to OH stretching vibrations due to intermolecular hydrogen bonds became less pronounced. Like cotton, MCC showed the less defined peak of intermolecular hydrogen bonds after cryomilling for 10 minutes. These results are due to the scission of intermolecular hydrogen bonds after mechanical treatment. Moreover, the bands due to both intra and intermolecular hydrogen bonds in cotton and MCC shifted slightly to higher wavenumbers after mechanical milling was applied. For example, cryomilling of cotton sample for 60 minutes led to the shift of the peaks due to intra and intermolecular hydrogen bonds from 3335 cm^{-1} and 3282 cm^{-1} to 3339 cm^{-1} and 3302 cm^{-1} . Cryomilling of MCC for 60 minutes resulted in the shift of the both peaks corresponding to intra and inter molecular hydrogen bonds from 3294 cm^{-1} and 3335 cm^{-1} to 3304 cm^{-1} and 3343 cm^{-1} . These findings

indicated that, cryomilling of cellulose samples induced the increase in free hydroxyl groups or decrease in the number of inter and intramolecular hydrogen bonds between cellulose chains [137]–[139]. In addition to the changes in O-H stretching region, after cryomilling of cotton for 20 minutes and MCC samples for 10 minutes, bands visible as weak shoulders around 1000 cm^{-1} and 984 cm^{-1} disappeared. These bands are due to -CH- rocking, C-O and ring stretching [140]–[143], and therefore, implying that milling breaks these intramolecular covalent bonds. Overall, FTIR-ATR results prove again that, when mechanical treatment was applied to cellulose samples, it leads to the breaking of intra and intermolecular hydrogen bonds, chain scissions (in glycosidic bonds or in cellulose rings at C(2)-C(3) position [102]).

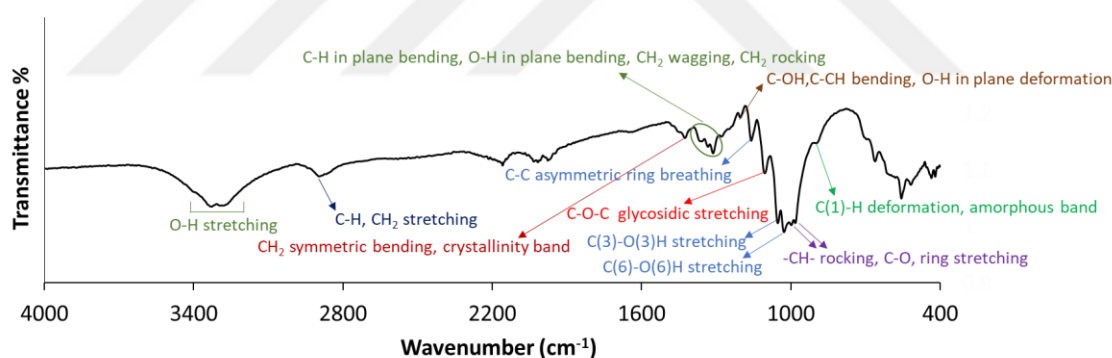


Figure 23. FTIR spectrum of cotton with band assignments from corresponding literature (also in Table 7).

Wavenumber (cm⁻¹)	Vibration	Reference
3520-3060	O-H stretching	[133]–[139]
~2900	C-H and CH ₂ stretching	[130], [136], [139], [45]
1425-1430	CH ₂ symmetric bending, scissoring (crystallinity band)	[136], [139]
1360-1370	C-H in plane bending	[136], [144]
~1335	O-H in plane bending, CH ₂ wagging	[136], [140]
~1314	CH ₂ rocking	[136], [140]
~1204	C-OH and C-CH bending, O-H in plane deformation	[136], [140]
~1160	C-C asymmetric ring breathing	[140], [145], [146]
~1105	C-O-C glycosidic stretching	[140], [146]– [148]
~1053	C(3)-O(3)H stretching	[137], [140], [145]
~1029	C(6)-O(6)H stretching	[137], [140]
~1000, 984	-CH- rocking, C-O and ring stretching	[140]–[143]
~897	C(1)-H deformation (anomeric vibration, amorphous band)	[13], [136], [146], [149]

Table 7. FTIR band assignments for cotton and MCC samples from corresponding literature.

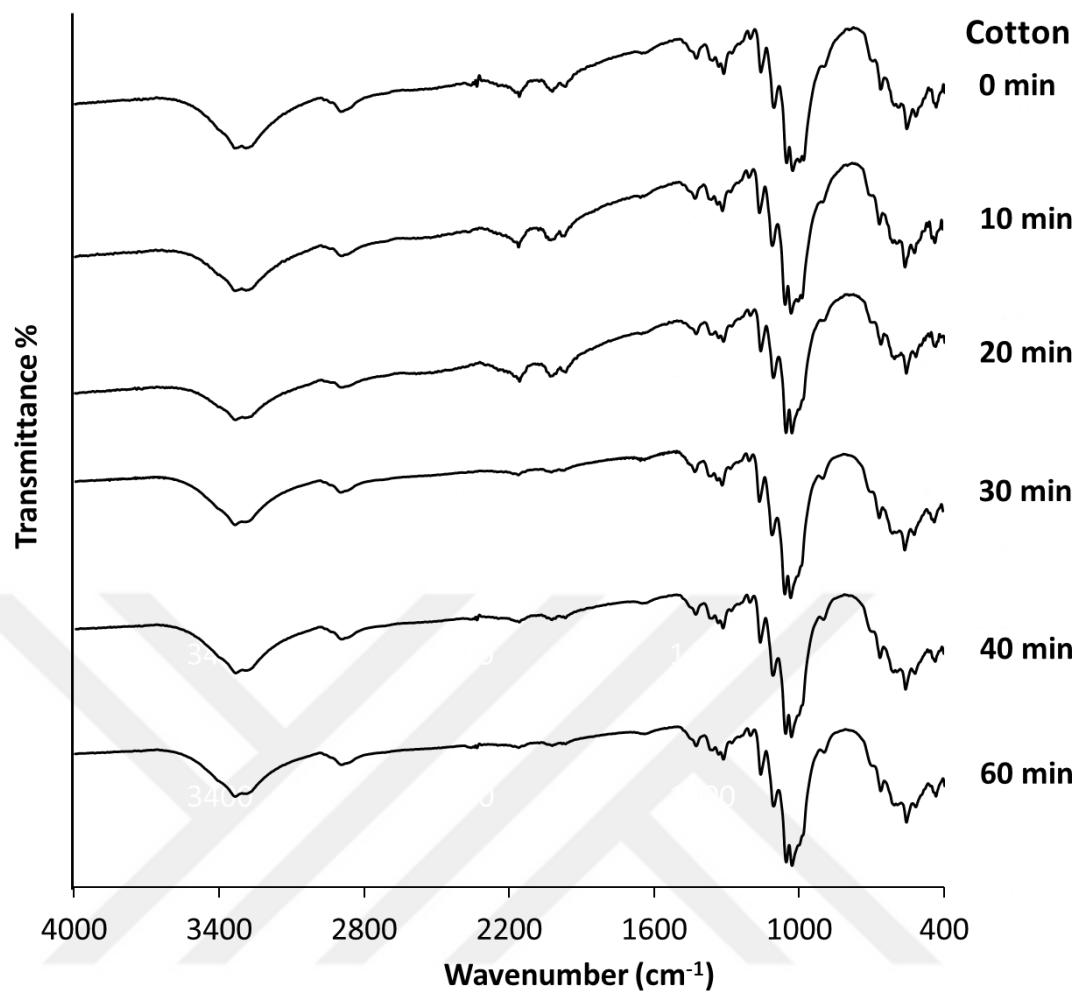


Figure 24. FTIR spectra of cotton and wet cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

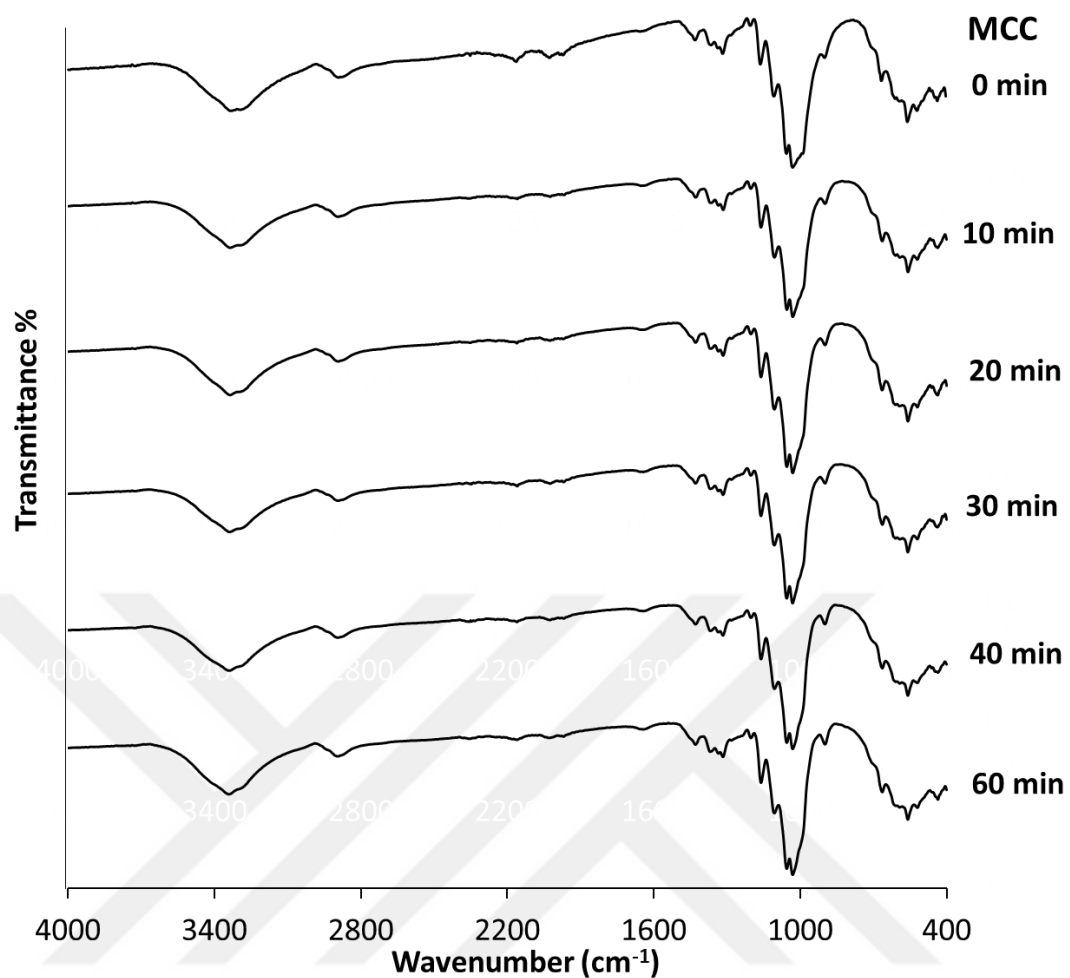


Figure 25. FTIR spectra of MCC and wet cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.4.2 Structural Changes of Cryomilled Cellulose Samples by FTIR-ATR Spectroscopy Analysis - Dry Grinding Method

After cellulose samples were cryomilled in dry condition, they were analyzed by FTIR spectroscopy. In Figures 26 and 27, FTIR spectra of dry cryomilled cotton and MCC are presented, respectively. Similar to wet grinding, with dry grinding, the O-H stretching vibration bands with two maxima due to intra and inter molecular hydrogen bonds in the region of 3520-3060 cm^{-1} disappeared for cotton and MCC after 20 and 10 minutes of cryomilling, respectively. It is clear that, center of the O-H band shifted to the higher wavenumber with milling. For cotton samples the center of the OH band around 3301 cm^{-1} , shifted to 3314 cm^{-1} , 3332 cm^{-1} , 3336 cm^{-1} , 3346 cm^{-1} and 3348 cm^{-1} after cryomilling for 10, 20, 30, 40 and 60 minutes, respectively. For MCC samples the center of the OH band at 3301 cm^{-1} , shifted to 3332 cm^{-1} , 3346 cm^{-1} , 3352 cm^{-1} , 3360 cm^{-1} and 3363 cm^{-1} after cryomilling for 10, 20, 30, 40 and 60 minutes, respectively. Upon dry milling, the intensity of the band the band around 1053 cm^{-1} resulting from C-O stretching of C(3)-O(3)H groups decreased, too, and became visible as a very small shoulder after cryomilling. This change in the literature is also attributed to the broken intra and intermolecular hydrogen bonds after milling [137]. These findings supported breaking of the some intra and intermolecular hydrogen bonds in cellulose chains and formation of free hydroxyl groups [137]–[139].

Like the results obtained from wet grinding process, in dry cryomilling of cotton and MCC samples for 10 minutes led to the disappearance of the bands visible as a weak shoulders around 1000 cm^{-1} and 984 cm^{-1} resulting from -CH-rocking, C-O and ring stretching [140]–[143], suggesting the breaking of intramolecular covalent bonds. Under dry cryomilling of cotton this transition

happened around 10 minutes milling time, which is less than 20 minutes needed under wet cryomilling conditions. This decrease verifies again that in dry milling mechanical energy is more efficiently transferred to the sample.

In the literature there are also some attempts linking the crystallinity changes in cellulose to observed FTIR bands in cellulose. For example, symmetric CH_2 bending band in the region of $1425\text{--}1430\text{ cm}^{-1}$ is assigned as ‘crystallinity band’ in cellulose. The intensity of this band decreased in dry milling of both cotton and MCC, which again shows the decrease in crystallinity and formation of less ordered cellulose samples by ball milling. (Similar results are reported in the literature for different cellulose samples after milling [131], [139], [150]). Another band around 897 cm^{-1} due to C(1)-H deformation known as ‘amorphous band’ [13], [136], [139], [146], [149] increased slightly after cryomilling, indicating the increase in amorphous regions in cellulose samples.

Finally, the most important band in the whole spectrum related to milling-induced changes is the C-O-C glycosidic stretching band around 1105 cm^{-1} [140], [146]–[148]. The intensity of this band was reduced gradually upon milling, indicating that, cryomilling of cellulose samples caused to the breaking of glycosidic bonds in cellulose chains in addition to the breaking of intra and intermolecular hydrogen bonds. Like other changes observed in XRD and SEM analyses, these changes in IR bands due to mechanical treatment were clearly seen after cryomilling of cotton samples for 20 minutes and cryomilling of MCC samples for 10 minutes. It is clear that, more number of glycosidic bonds were broken in dry grinding method than in wet grinding method, since the intensity of C-O-C glycosidic band did not change significantly by wet grinding of the samples.

In the light of these results, it can be said that, the activation energy from mechanical energy produced in ball milling process is high enough to overcome the forces including intra, intermolecular hydrogen bonds and covalent bonds that are glycosidic bonds holding cellulose polymer together. Specifically, dry grinding is can break all, whereas wet grinding is effective more on the former. Of all the covalent bonds in the cellulose structure, glycosidic bonds are more open to mechanical rupture because they are the weakest bonds in cellulose chain with respect to bond energies [120]. When mechanical energy was transferred to the cellulose samples, they absorbed this energy, leading to disaggregation of cellulose chains, the decrease in crystalline regions and formation of mostly amorphous samples. At the end of the dry grinding process, cellulose chains with lower number of intra and intermolecular hydrogen bonds and with lower degree of polymerization - due to broken glycosidic linkages - were formed. These findings support why more mechanoradicals are produced upon dry grinding. In the next section, I describe how we used these cellulose mechanoradicals formed by cleavage of glycosidic bonds upon dry cryomilling to produce of cellulose-metal nanoparticle composites.

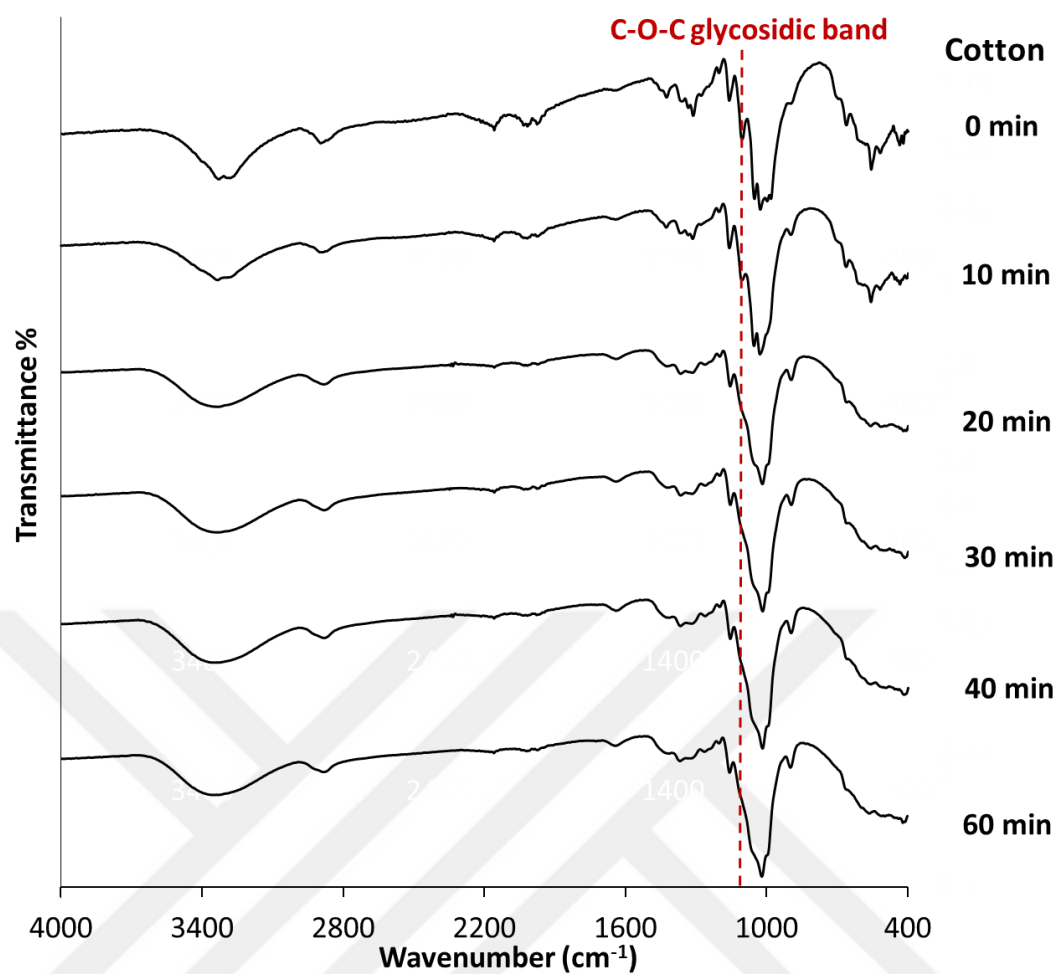


Figure 26. FTIR spectra of cotton and dry cryomilled cotton (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

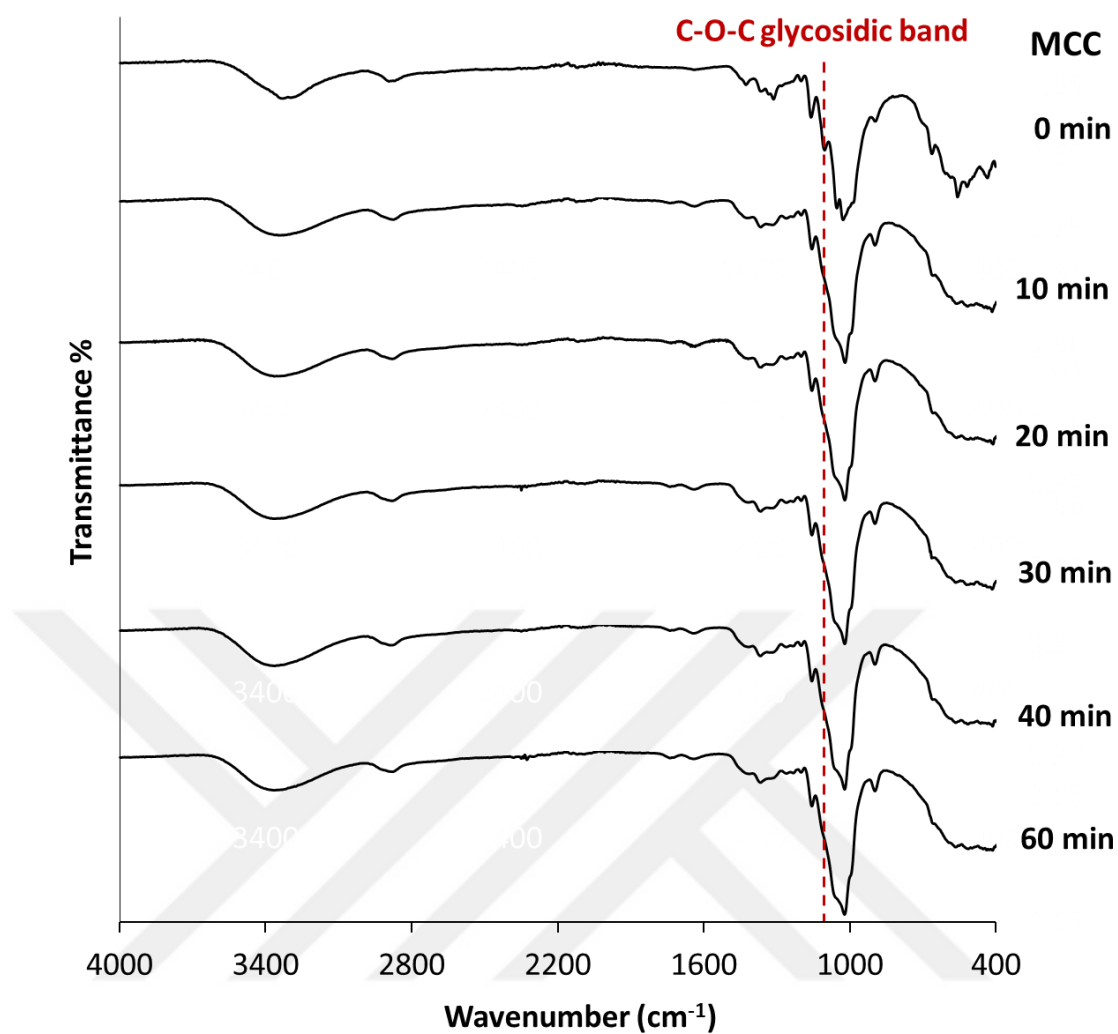


Figure 27. FTIR spectra of MCC and dry cryomilled MCC (500 mg) samples (30 Hz frequency in the presence of 6 zirconia balls in the zirconia sample chamber at 77 K) for 10, 20, 30, 40, and 60 minutes.

3.5 Production of Cellulose-Metal NPs Composites by in-situ Reduction with Cellulose Mechanoradicals

One of the main aims of this thesis is to make cellulose-metal nanoparticle composites by reducing metal ions in cellulose matrices using cellulose mechanoradicals produced by milling. The reduced metal is surrounded and stabilized by the cellulose chains. This method provides not only a straightforward way of making NPs but also eliminates the usage of toxic reducing and stabilizing agents. Since dry grinding of cellulose samples led to higher number of mechanoradicals, the following composites of cellulose-metal NPs were prepared by using cellulose mechanoradicals produced by dry cryomilling. The experimental procedure, which was explained in detail in the experimental part was used to obtain the mechanoradicals. We used both MCC and cotton in order to assess the effects of the initial cellulose morphology on the resulting composites.

In a typical experiment, cellulose mechanoradicals from 500 mg cotton or MCC was produced by dry cryomilling for 40 minutes. Then metal ion solution was added onto the cellulose samples. The mixture of cellulose samples and metal solution were stored in dark. After 1 day, 1 week and 2 weeks, small samples were taken out, washed in order to get rid of metal precursor solution or metal NPs that are not stabilized in cellulose matrix, and dried. Finally, the resulted composites were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses.

3.5.1 Cellulose-Gold Nanoparticles Composite

To obtain cellulose-Au NP composites, after dry grinding of the cellulose sources, gold ion (Au^{3+}) precursor solution (HAuCl_4 chloroauric acid in water, $5.1 \times 10^{-3} \text{ M}$) was added on the cellulose samples. The mixture of cellulose samples and metal solution were stored in dark. After 1 day, 1 week, and 2 weeks, small samples of cellulose were taken out, washed, and the resulting composites were dried. Within this time, cellulose powder changed its color from white to intense pink-purple (in a few minutes!), implying that the Au NPs had been formed (surface plasmon absorption of gold NPs is around 550 nm) in cellulose samples.

SEM images and EDX spectra of the composites of gold NPs both in cotton matrix and in MCC matrix are shown in Figures 28 and 29, respectively. In the SEM images, gold nanoparticles are spotted as bright spherical particles. As seen from the images, gold nanoparticles were formed even after 1 day, and remained at about the same concentration for the rest of the time. The regular distribution of the bright spots show that nanoparticles were distributed homogeneously, without any aggregation, in the cellulose matrix. This suggests that, Au NPs were stabilized in the cellulose matrices due to fibrous and porous cellulose structure and strong ion-dipole interactions between Au NPs and hydroxyl and ether groups on cellulose structure. EDX spectra of these composites showed the presence of Au atom, which appears as a main signal at 2.12 eV. Since Cl atom that could come from the metal ion precursor (HAuCl_4) did not appear in the EDX spectra, it was expected that, all gold nanoparticles are in reduced metallic Au^0 form.

In order to confirm that the deposited material (NPs) is in the metallic form, XPS was employed. By XPS, it is possible to determine the oxidation states of the

metal components on the surface. HIRES XPS spectra of the Au 4f region of the composites are shown in Figure 31. Two peaks, which arise from the spin orbit splitting of the Au 4f_{7/2} and 4f_{5/2} levels were observed for both composites. The binding energies of Au 4f_{7/2} electrons centered approximately at 84.08 eV for both cotton and MCC-Au NPs composites, and the binding energies of Au 4f_{5/2} electrons appeared approximately at 87.88 eV for cotton-Au NPs composite and 87.98 eV for MCC-Au NPs composites. These values are consistent with the reported values (84.0 eV and 87.7eV) for gold in metallic state Au⁰ [151]. In addition, since the peaks coming from Au³⁺ at 86.9 eV and 90.6 eV were not observed in the spectra, it can be said that all precursor gold ion (Au³⁺) were reduced by cellulose mechanoradicals and stabilized as metallic gold NPs in cellulose matrices [152].

XPS results are also supported by the X-ray diffraction (XRD) patterns of the composite of cotton-Au NPs with pure cotton sample (A) and the composite of MCC-Au NPs with pure MCC sample (B), as shown in Figure 30. The composite of cotton-Au NPs showed the diffraction lines different from pure cotton sample, approximately at 2 θ : 38.26°(1 1 1), 44.77°(2 0 0), 64.98°(2 2 0) ,and 77.85°(3 1 1). The diffraction lines of the composites of MCC-Au NPs, different from the lines of pure MCC sample, appeared approximately at 2 θ : 38.05°(1 1 1), 44.77°(2 0 0), 64.83°(2 2 0) and 77.90°(3 1 1). These new lines emerge from corresponding (as indicated on the figure) crystallographic planes reflections. The detected lines match closely with the reported values for face centered cubic (fcc) structure of metallic gold Au⁰ nanoparticles [153].

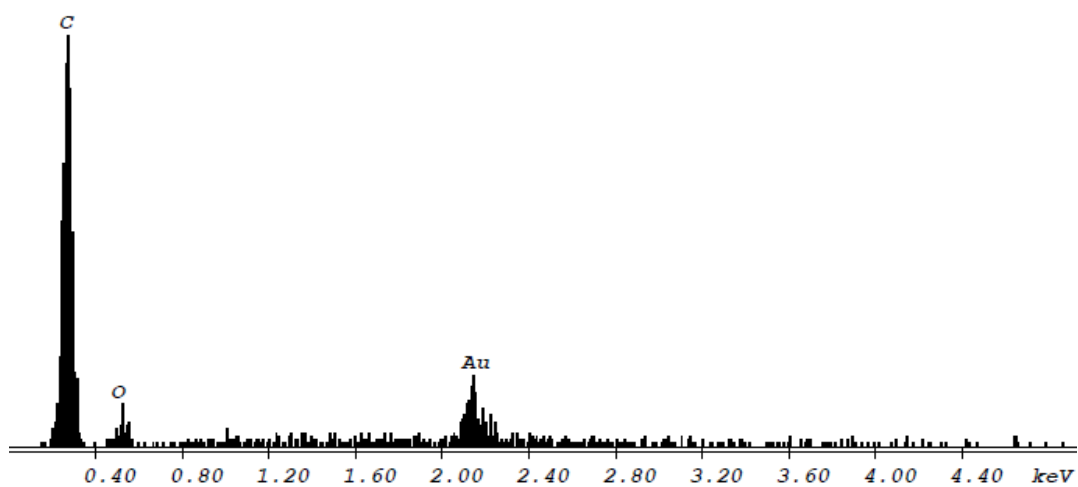
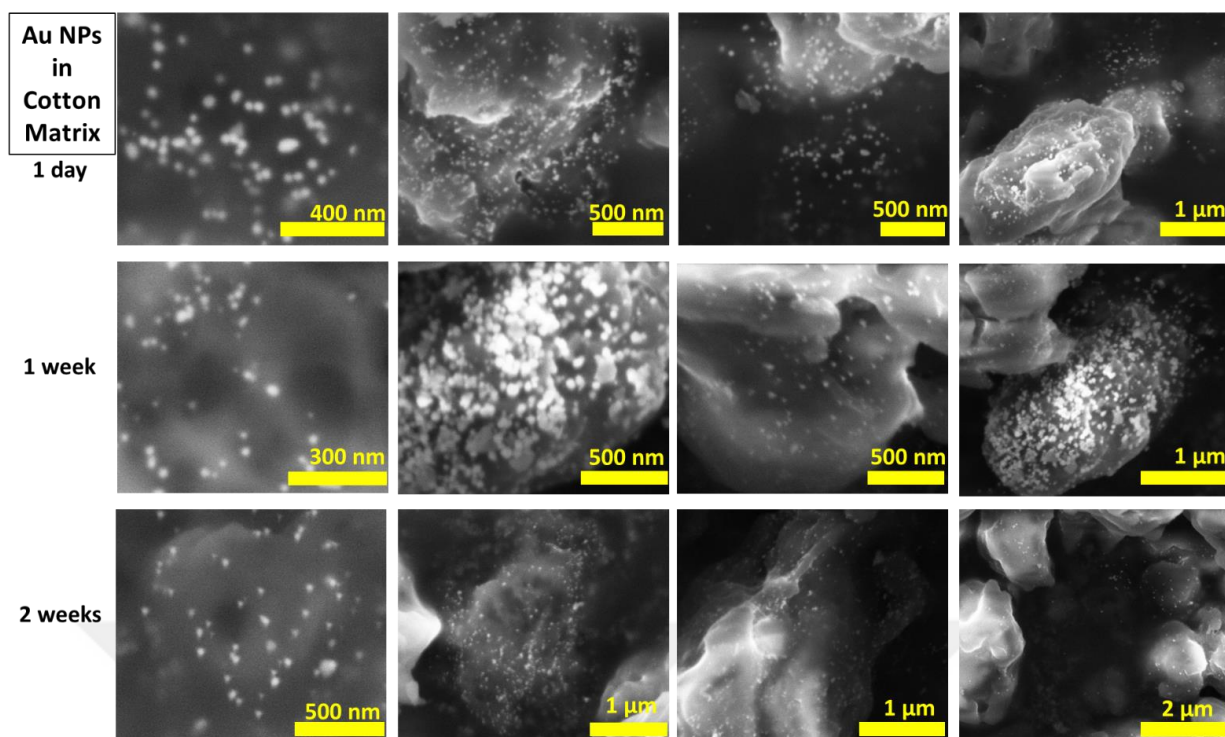


Figure 28. SEM images and EDX spectrum of the cotton-Au NPs composite, showing formed Au NPs as bright spots in the cotton matrix, and the presence of Au atoms in the chemical structure.

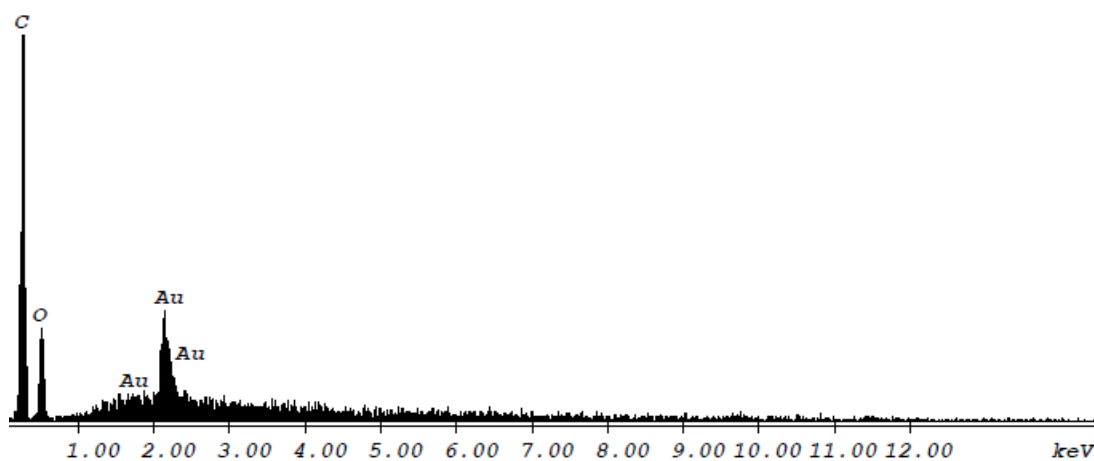
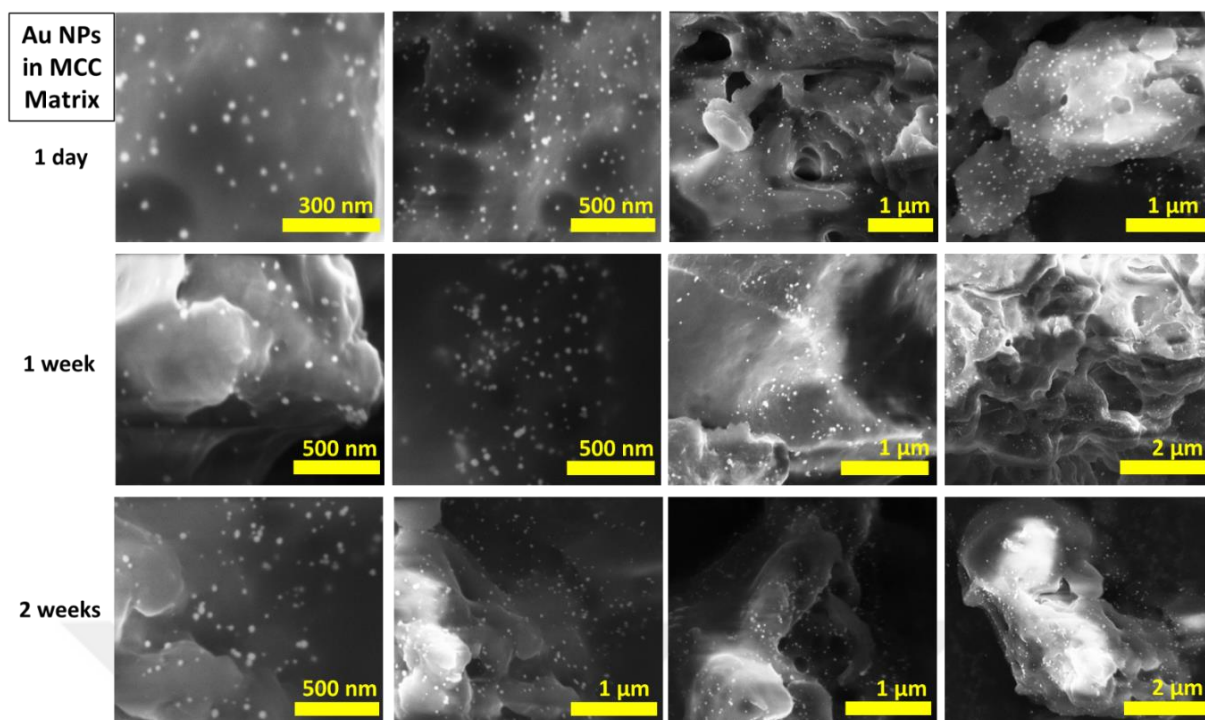


Figure 29. SEM images and EDX spectrum of the MCC-Au NPs composite, showing formed Au NPs as bright spots in the MCC matrix, and the presence of Au atoms in the chemical structure.

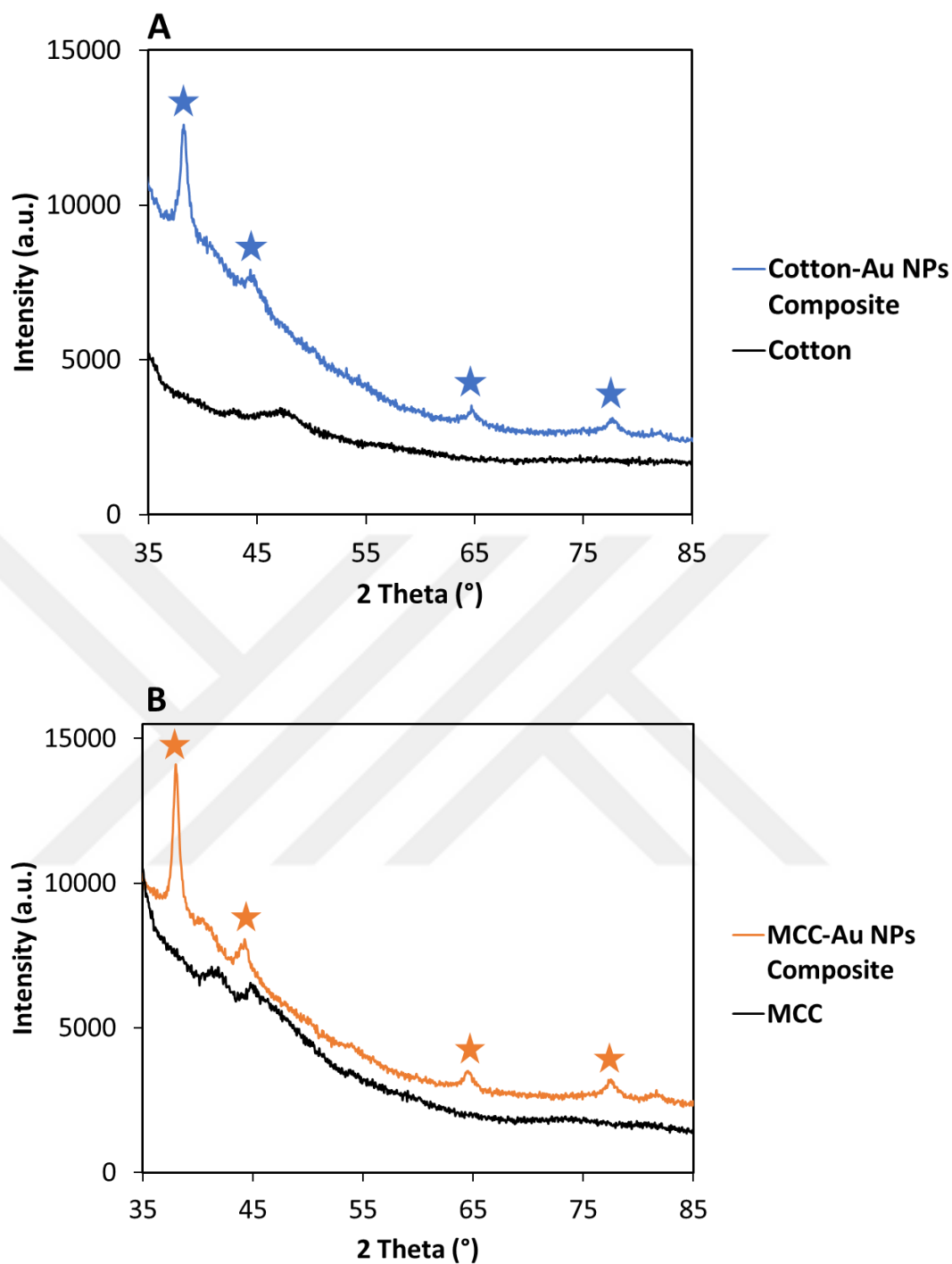


Figure 30. XRD pattern of (A) cotton-Au NP composite (blue line) in comparison to that of pure cotton (black line), and (B) MCC-Au NP composite (orange line) in comparison to that of pure MCC (black line). Diffraction lines for metallic gold Au^0 with fcc structure are marked with stars.

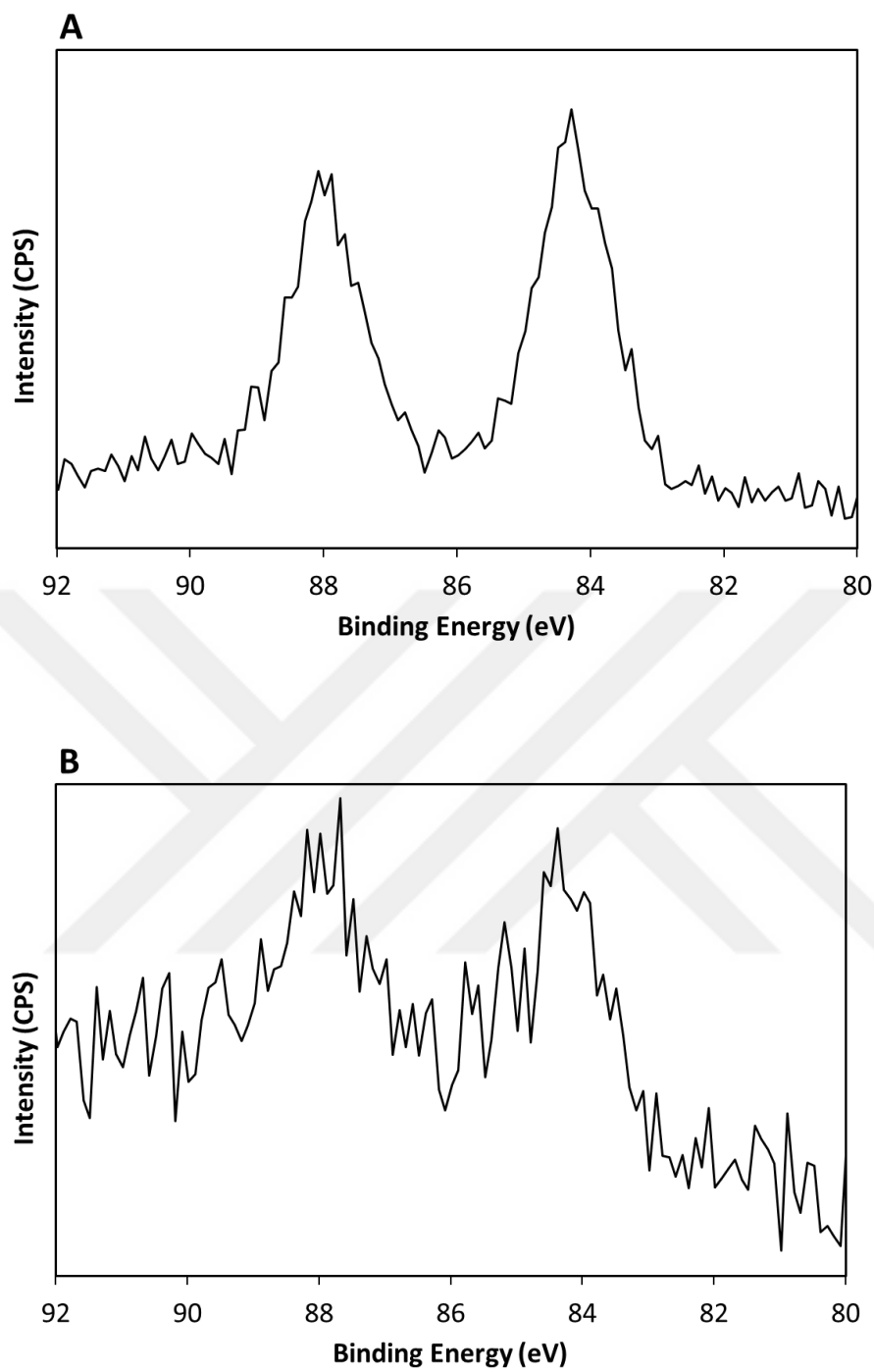


Figure 31. Au 4f Hires XPS spectra of the composites of (A) cotton-Au NPs, and (B) MCC-Au NPs.

3.5.2 Cellulose-Silver Nanoparticles Composite

After dry cryomilling of 500 mg of cotton or MCC, silver ion (Ag^+) precursor solution (silver nitrate AgNO_3 in water, 5.1×10^{-3} M) was added on the cellulose sample. The mixture of cellulose samples and metal solution were stored in dark. After 1 day, 1 week and 2 weeks, small portions of the solid were washed, dried, and characterized.

Like cellulose-Au NPs composite, the cellulose powder changed color from white to light brown during the waiting time, due to surface plasmon absorption of Ag NPs (ca. 400 nm) formed on cellulose.

Figures 32 and 33 represent the SEM images and EDX spectra of the composites of Ag NPs in cotton and in MCC matrix, respectively. Bright spherical spots in SEM images are Ag NPs in both cotton and MCC composites. It can be said that, the number of Ag NPs was increased in progress of time from 1 day to 2 weeks. This can be due to slower reaction between the cellulose mechanoradicals and silver ions compared to gold ions described above. It is known that, standard reduction potential of the silver ion to its metallic form (0.80 V) is lower than that of the gold ion (1.5 V). Therefore, reduction of silver ions can be slightly harder than that of gold ions and this can take a longer time. Ag NPs, too, were stabilized in the cellulose matrices without aggregation due to fibrous and porous cellulose structure and strong ion-dipole interactions between Ag NPs and hydroxyl and ether groups on cellulose structure. The presence of Ag atoms in the matrix was initially confirmed by EDX spectra of these composites with Ag peaks as a main signal at 2.984 eV. Since N atom that could come from the metal ion precursor (AgNO_3) did not appear in the EDX spectra, it was expected that silver nanoparticles are in

reduced metallic Ag^0 form. However, the proof that the deposited metal is metallic could only be obtained by XPS. Figure 35 shows the Ag 3d XPS spectra of the composites of Ag NPs in cotton matrix (A), and Ag NPs in MCC matrix (B). Spin orbit pairs of 3d peak for both cotton and MCC composites are namely $3d_{5/2}$ and $3d_{3/2}$. The binding energies of Ag $3d_{5/2}$ electrons were observed approximately at 368.08 eV in cotton matrix and 368.18 eV in MCC matrix. And Ag $3d_{3/2}$ peaks occurred at binding energies of 374.08 eV in cotton matrix and 374.38 eV in MCC matrix. These values are consistent with the reported values (368 eV and 374 eV) for silver in metallic state Ag^0 [154].

Figure 34 shows the XRD patterns of the composite of cotton-Ag NP and MCC-Ag NP composites. The composite of cotton and Ag NPs showed diffraction lines different than those from pure cotton sample, approximately at 2θ : $38.25^\circ(1\ 1\ 1)$ and $45.18^\circ(2\ 0\ 0)$. The diffraction lines of the MCC-Ag NP composite, different from the lines of pure MCC sample, appeared approximately at 2θ : $38.10^\circ(1\ 1\ 1)$, $65.14^\circ(2\ 2\ 0)$ and $77.69^\circ(3\ 1\ 1)$. These diffraction lines (indicated crystallographic planes are shown on the figure) are consistent with the reported values for fcc crystal lattice structure of metallic silver Ag^0 [155].

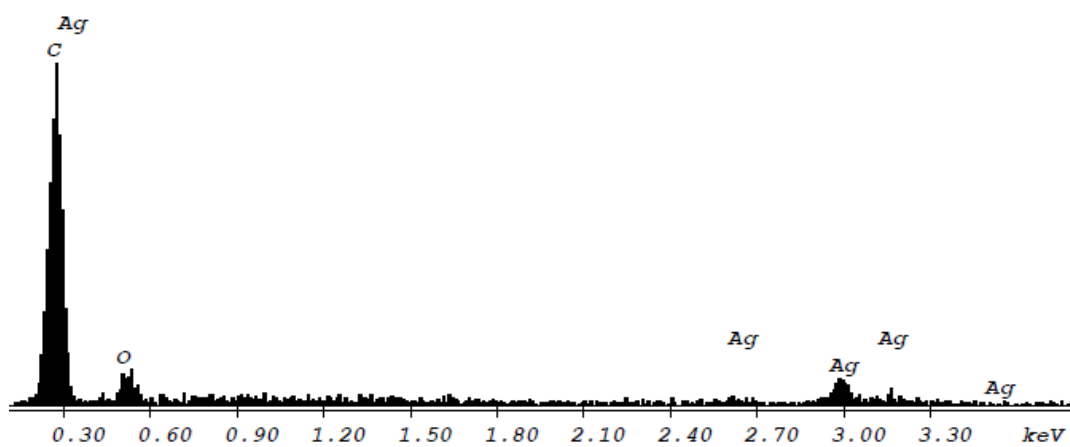
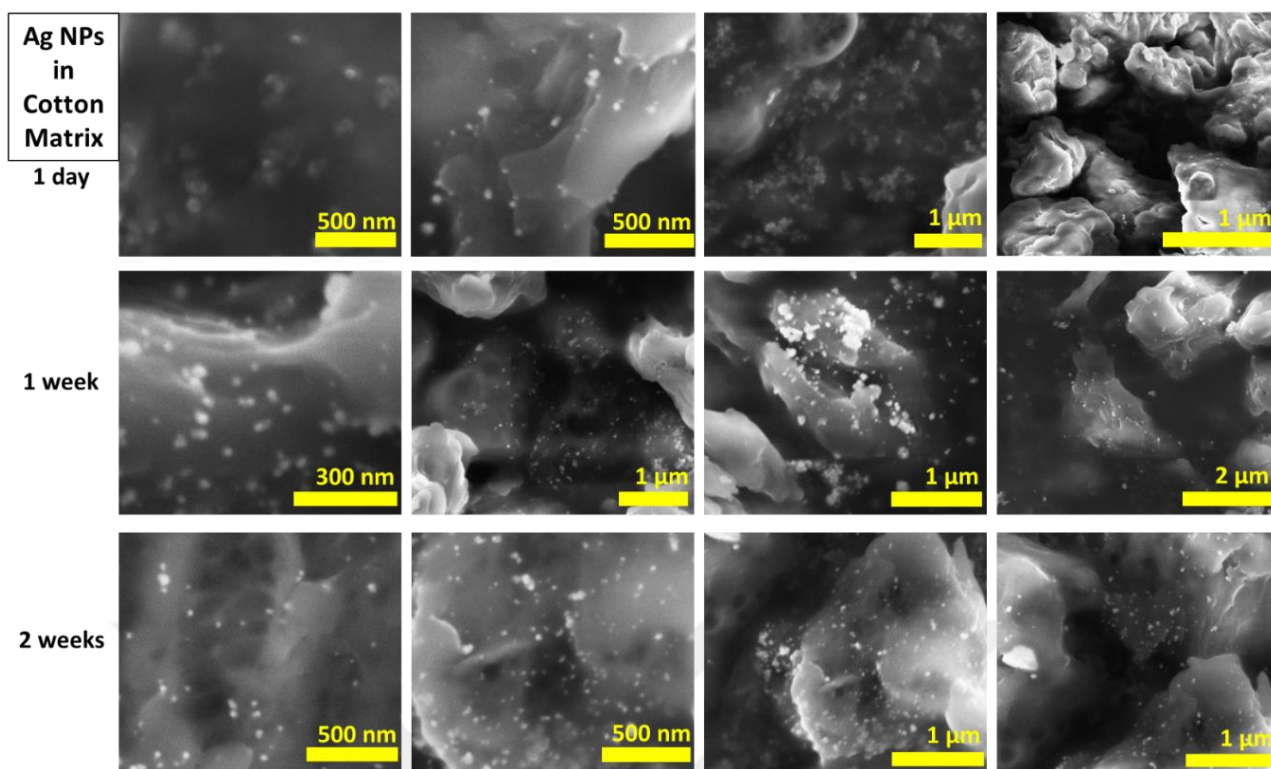


Figure 32. SEM images and EDX spectrum of the cotton-Ag NPs composite, showing formed Ag NPs as bright spots in the cotton matrix, and the presence of Ag atoms in the chemical structure.

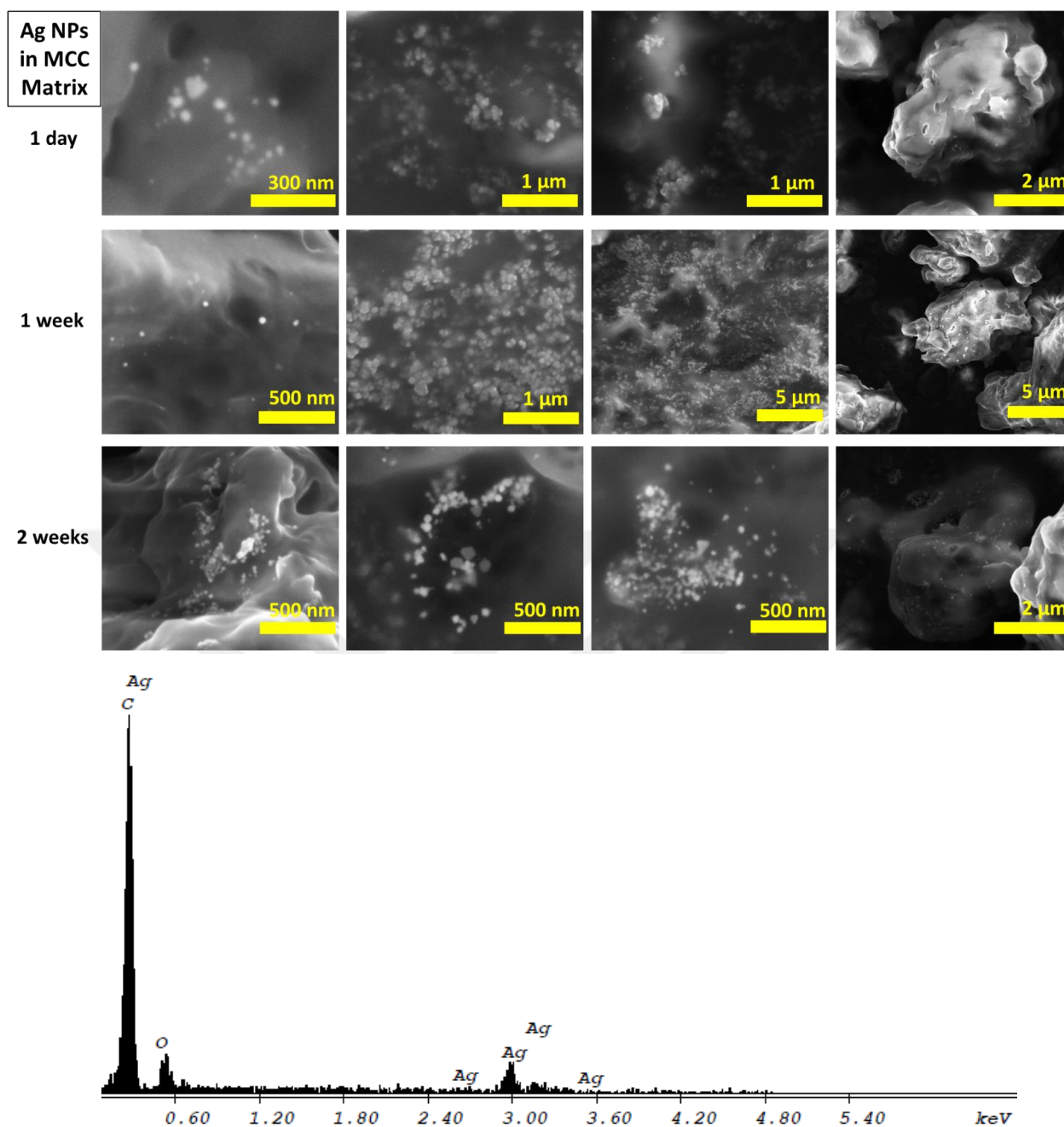


Figure 33. SEM images and EDX spectrum of the MCC-Ag NPs composite, showing formed Ag NPs as bright spots in the MCC matrix, and the presence of Ag atoms in the chemical structure.

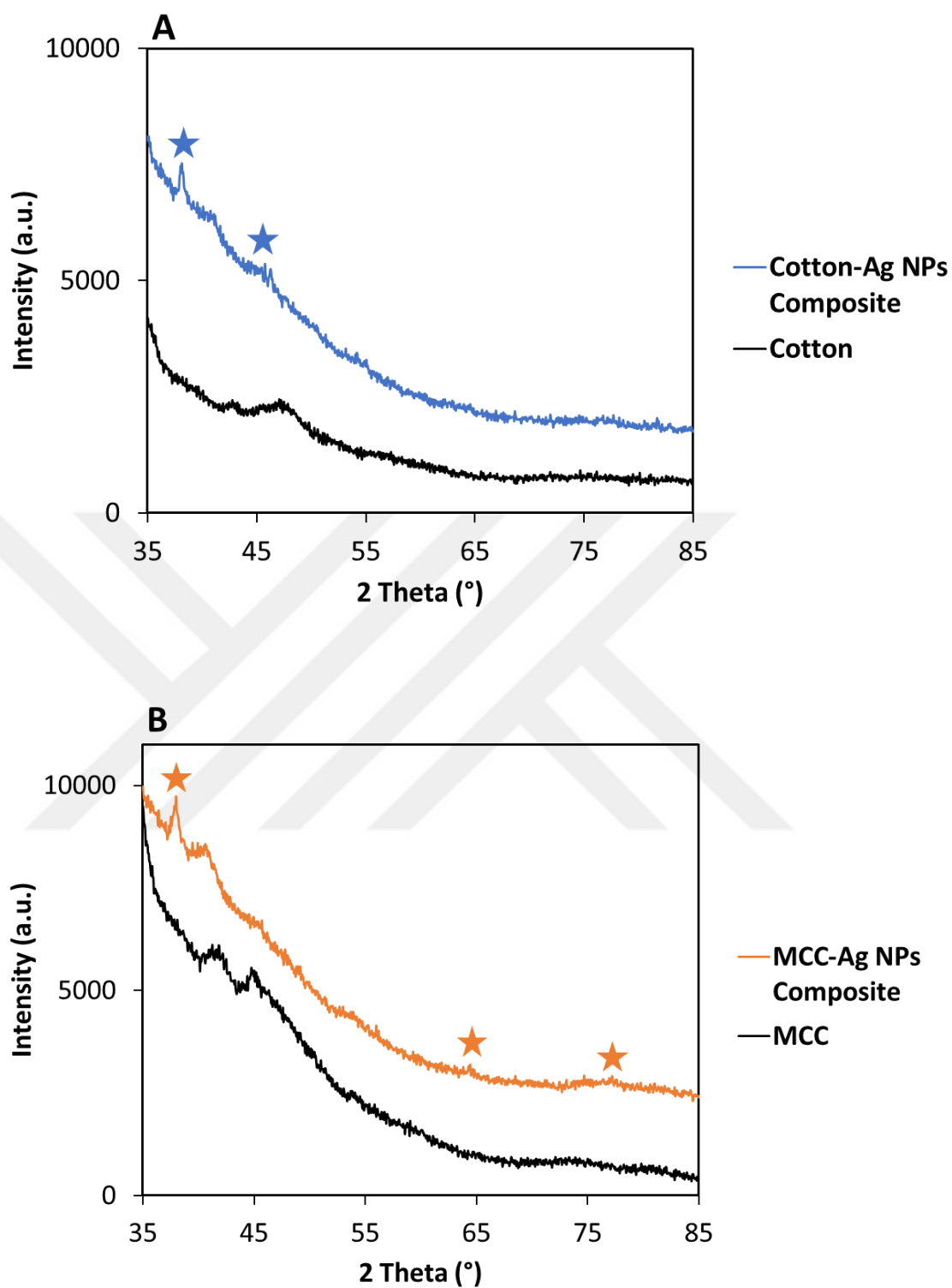


Figure 34. XRD pattern of (A) cotton-Ag NP composite (blue line) in comparison to that of pure cotton (black line), and (B) of MCC-Ag NP composite (orange line) in comparison to that of pure MCC (black line). Diffraction lines for metallic silver Ag^0 with fcc structure are marked with stars.

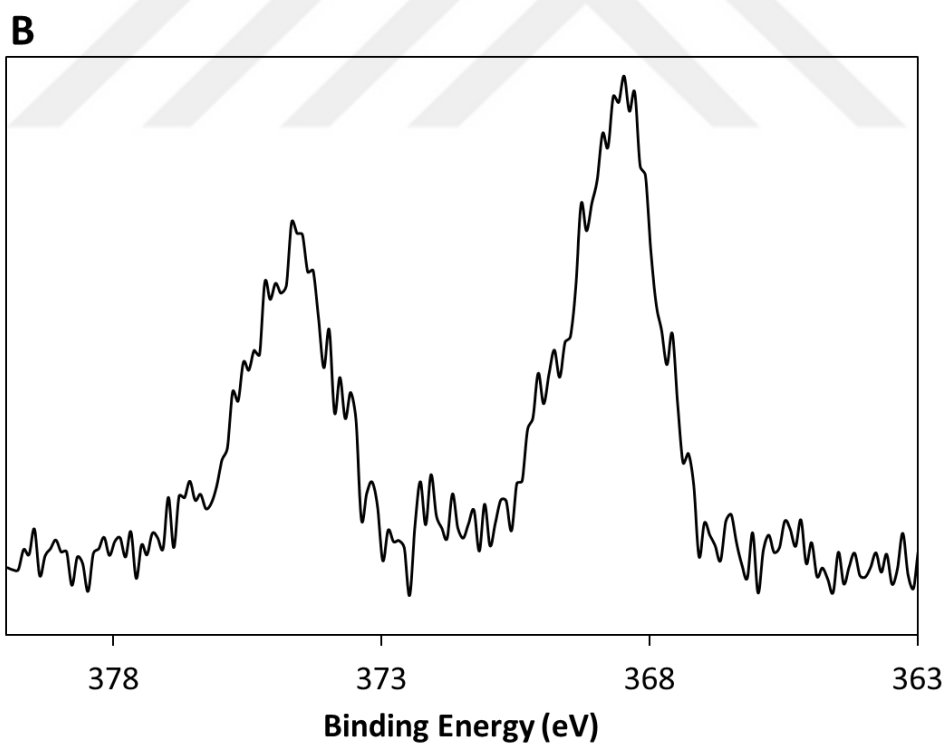
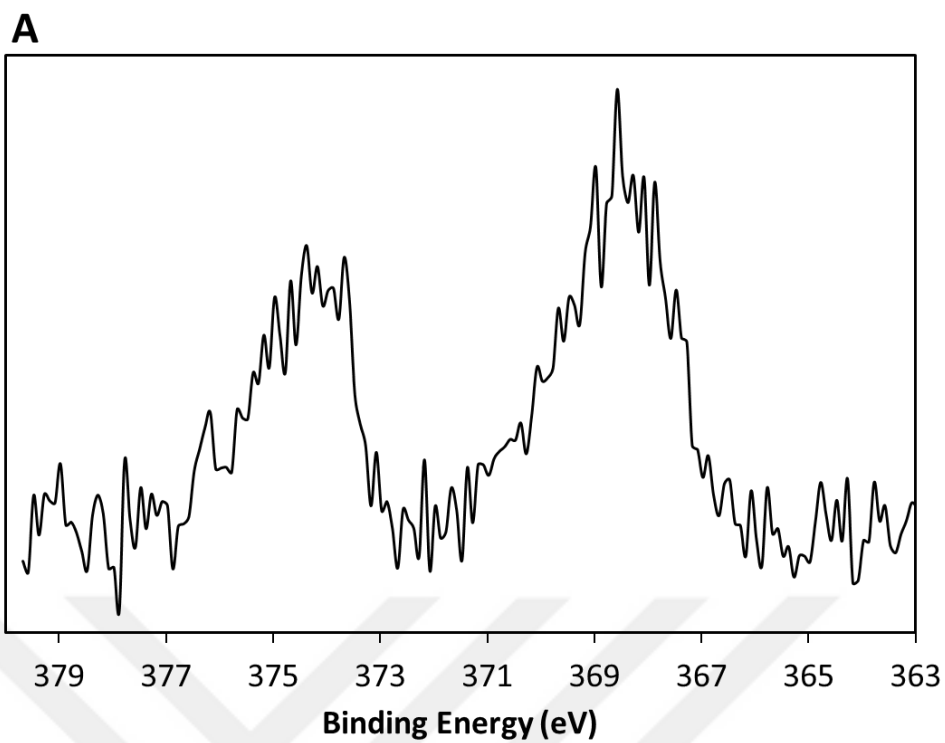


Figure 35. Ag 3d Hires XPS spectra of the composites of (A) cotton-Ag NPs, and (B) MCC-Ag NPs.

3.5.3 Cellulose-Platinum Nanoparticles Composite

Like other cellulose-metal NPs composites, same procedure was applied for the production of cellulose-platinum NPs composites. Potassium (II) tetrachloroplatinate (K_2PtCl_4) (5.1×10^{-3} M in water) was used as a metal ion (Pt^{2+}) precursor solution.

At the end of the waiting period for formation of the NPs, light grey colored composites were obtained, which was the first indication of the Pt NPs in cellulose matrices. The SEM images and EDX spectrum of the composites of Pt NPs in cotton and in MCC matrix are shown in Figure 36 and 37, respectively. The morphology of the NPs was spherical in both cotton and MCC matrices as evident from the spherical bright spots in the SEM images. Pt NPs were distributed homogeneously and stabilized in the cellulose matrices without aggregation due to cellulose fibers and strong ion-dipole interactions between Pt NPs and hydroxyl and ether groups on cellulose structure. The presence of Pt atom can be seen from the EDX spectra of these composites. Pt peaks appeared as a main signal at 2.048 eV. It can be said that Pt NPs should be in reduced metallic Pt^0 form because K and Cl atoms that could come from the metal ion precursor (K_2PtCl_4) did not appear in the EDX spectra of the composites.

The oxidation state of Pt NPs in cotton and MCC matrices was confirmed by XPS analysis as well. Figure 39 shows the Pt 4f Hires XPS spectra of the composites of Pt NPs in cotton matrix (A), and Pt NPs in MCC matrix (B). Spin orbit pairs of 4f peak for both cotton and MCC composites are namely $4f_{5/2}$ and $4f_{7/2}$. The binding energies of Pt $4f_{5/2}$ electrons were observed approximately at 74.48 eV and the binding energies of Pt $4f_{7/2}$ electrons were observed

approximately at 71.18 eV for both cotton and MCC matrices. In the literature the values of binding energies of metallic platinum Pt^0 were reported as $4f_{5/2}$:74.5 eV and $4f_{7/2}$:71.2 eV. Furthermore, the binding energies of Pt^{2+} ion that could come from metal ion precursor (K_2PtCl_4) were reported as $4f_{5/2}$:76.1 eV and $4f_{7/2}$:72.8 eV [156]. These results indicate the Pt NPs are in their metallic Pt^0 forms.

Figure 38 illustrates the XRD patterns of the composite of cotton-Pt NPs and the composite of MCC-Pt NPs (B). The composite of cotton-Pt NPs showed the diffraction line approximately at 2θ : $39.98^\circ(1\ 1\ 1)$. The diffraction line of the composite of MCC-Ag NPs appeared approximately at 2θ : $40.51^\circ(1\ 1\ 1)$. These values are consistent with the reported value for fcc structure of metallic platinum Pt^0 [157]. Other diffraction lines of Pt NPs which should appear approximately at 2θ : $46.60^\circ(2\ 0\ 0)$, $67.50^\circ(2\ 2\ 0)$, $81.20^\circ(3\ 1\ 1)$, and $86.70^\circ(2\ 2\ 2)$ could not be seen in the XRD spectra [157]. The reason for this can be that, the formed Pt NPs were not sufficiently dense to be detected by XRD measurement. It is known that, XRD measurements are useful for bulk analyses, not surface analysis. Since the formed Pt NPs located on the surface of cellulose samples not as densely as Ag on Au NPs (vide supra), some of their less intense characteristic diffraction lines could not be seen. All these results showed that Pt NPs in their metallic state were successfully formed in the reduced form in both cotton and MCC matrices.

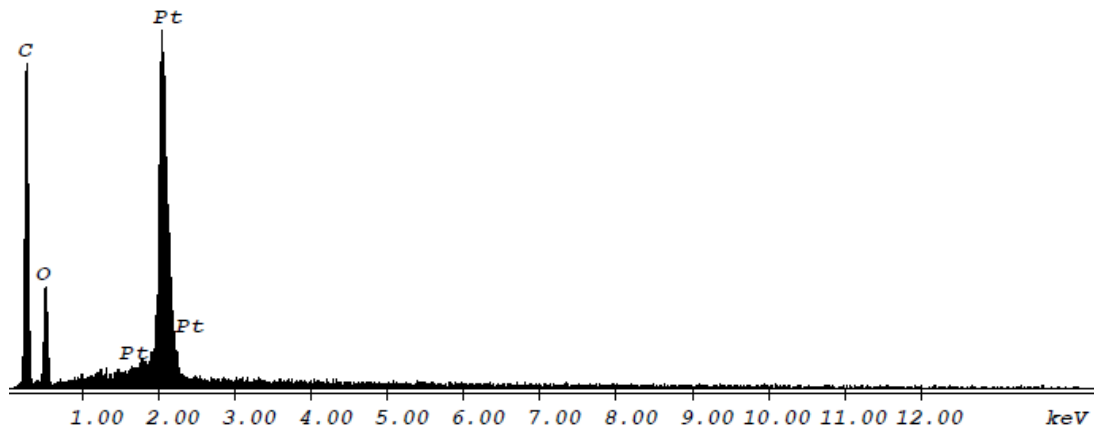
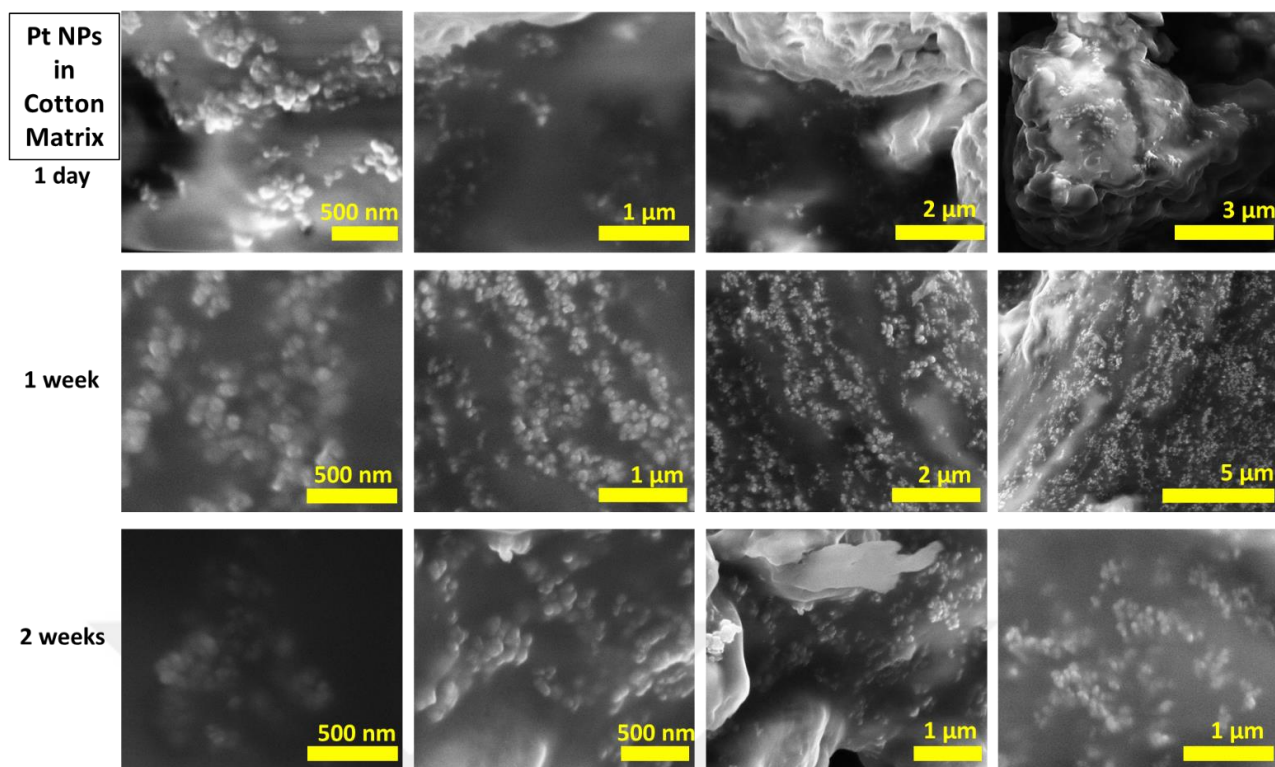


Figure 36. SEM images and EDX spectrum of the cotton-Pt NPs composite, showing formed Pt NPs as bright spots in the cotton matrix, and the presence of Pt atoms in the chemical structure.

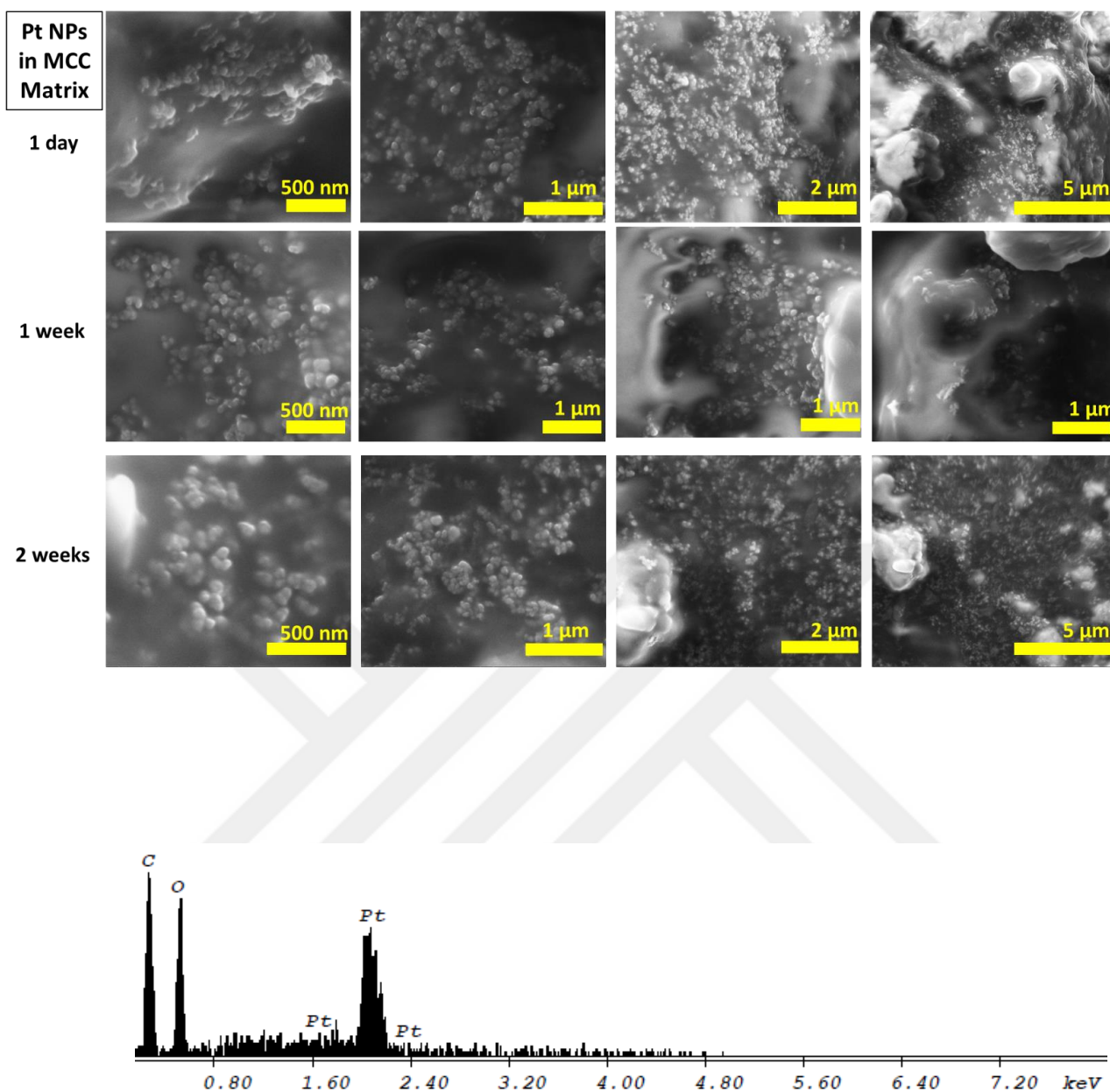


Figure 37. SEM images and EDX spectrum of the MCC-Pt NPs composite, showing formed Pt NPs as bright spots in the MCC matrix, and the presence of Pt atoms in the chemical structure.

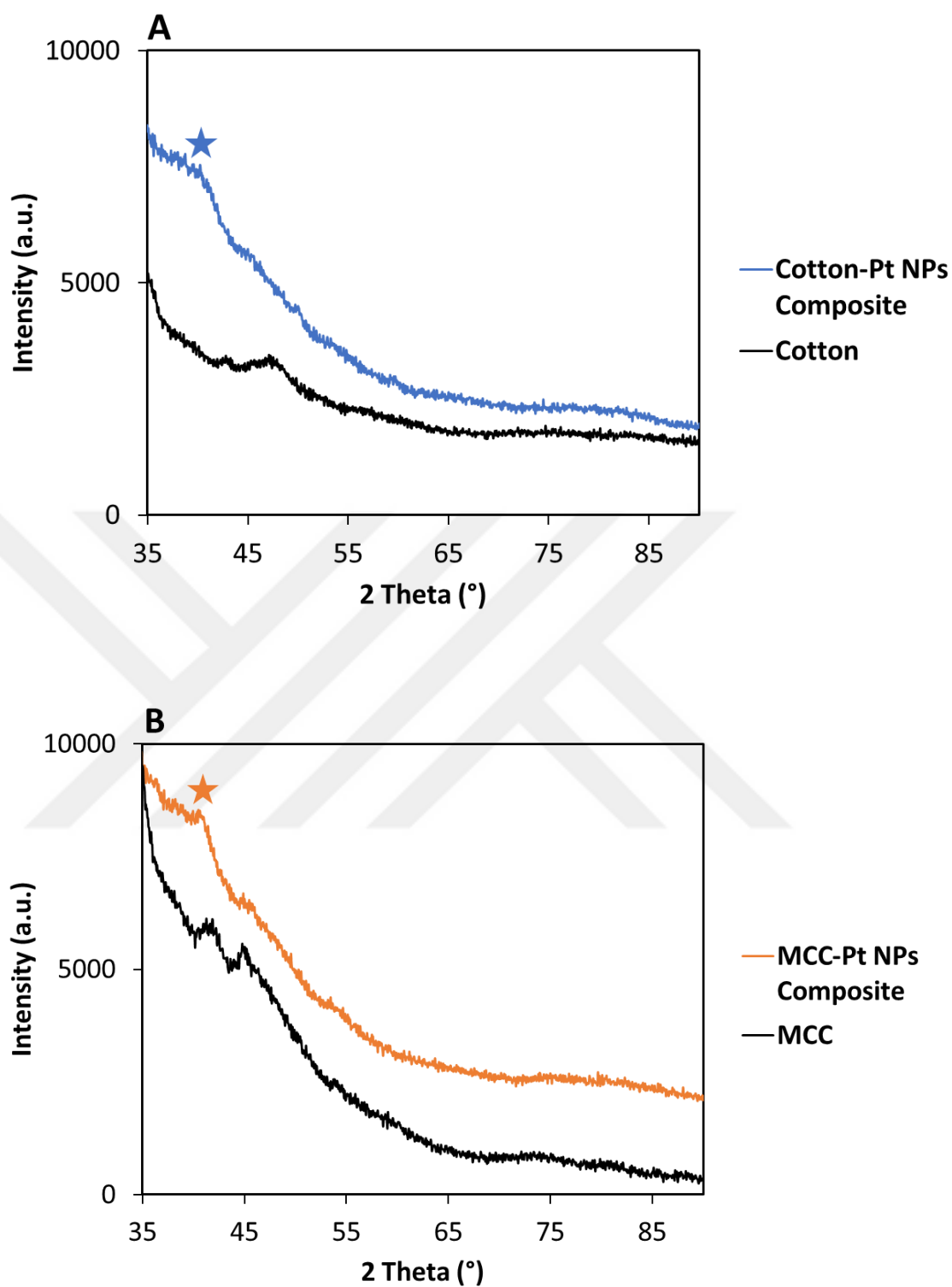


Figure 38. XRD pattern of (A) cotton-Pt NP composite (blue line) in comparison to that of pure cotton (black line), and (B) of MCC-Pt NP composite (orange line) in comparison to that of pure MCC. Diffraction line (for 111 planes) for metallic platinum Pt^0 with fcc structure is marked with a star.

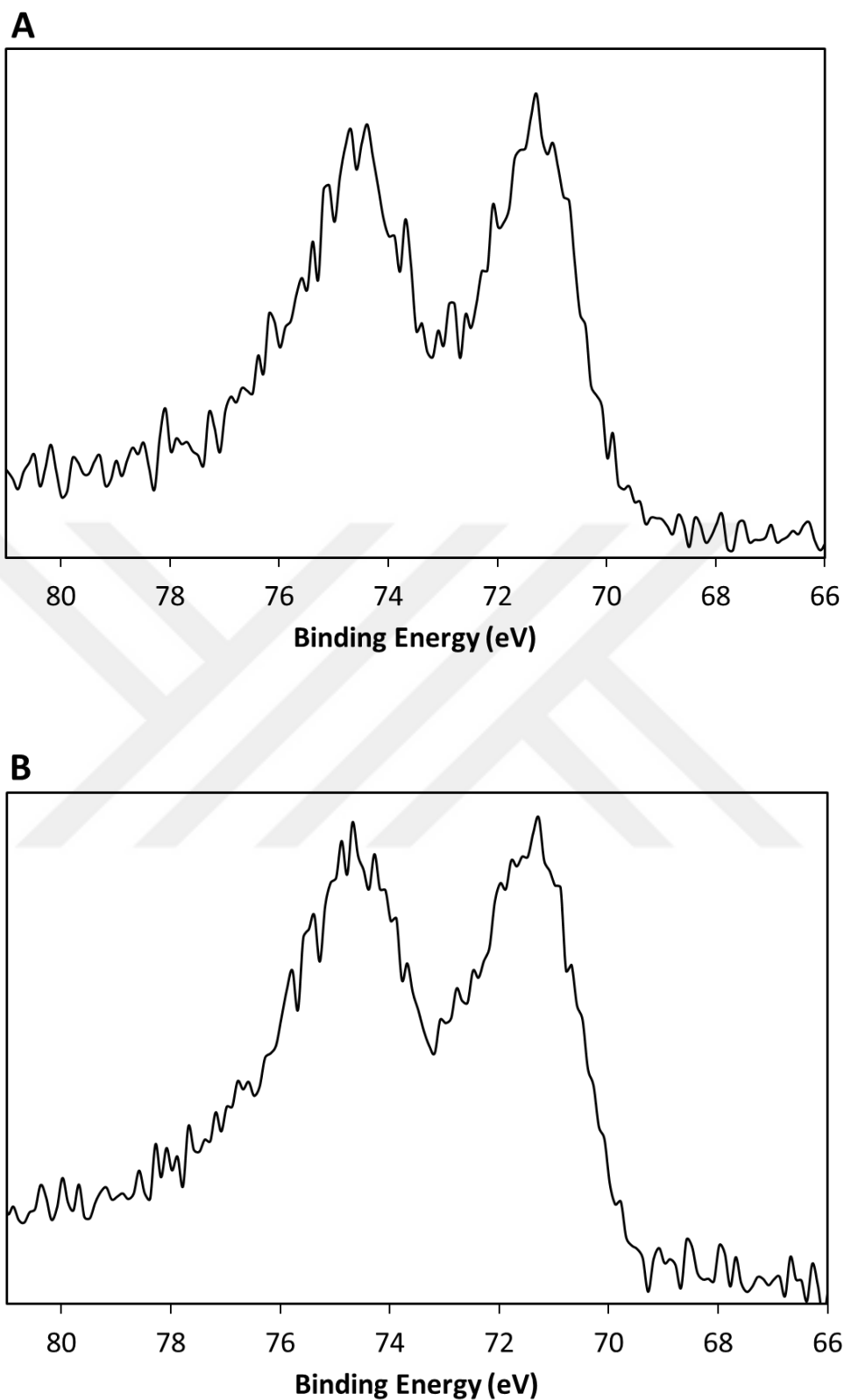


Figure 39. Pt 4f Hires XPS spectra of the composites of (A) cotton-Pt NPs, and (B) MCC-Pt NPs.

3.5.4 Cellulose-Palladium Nanoparticles Composite

The procedure mentioned above was applied for the production of cellulose-palladium NPs composites, too. Palladium (II) acetylacetonate ($\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, $5.1 \times 10^{-3} \text{ M}$ in acetonitrile) was used as a metal ion (Pd^{2+}) precursor solution.

Light grey colored composites were obtained at the end of the waiting period, which was the first indication of the Pd NPs in cellulose matrices. The SEM images and EDX spectrum of the composites of Pd NPs in cotton and in MCC matrix are shown in Figures 40 and 41, respectively. The morphology of the NPs was spherical in both cotton and MCC matrices as evident from the bright spots in the SEM images. The density of Pd NPs imaged increased in progress of time, from 1 day to 2 weeks. This can be related with the fact that, the reduction potential of Pd^{2+} ion to its metallic form (0.83 V) is not as high as the reduction potential of Au^{3+} ion (1.5 V). Thus, Pd NPs could not be formed as much as Au NPs using cellulose mechanoradicals in a short time. However, after 1 week, the number of Pd NPs increased for both in cotton and MCC matrices. Pd NPs in MCC matrix were found to lay closer to each other than Pd NPs in cotton matrix. This may be a result of the longer fiber length of the cotton sample, which could prevent NPs from coming close to each other. EDX spectra of the composites showed the presence of Pd atoms in the matrices with a main signal at 2.838 eV.

The composites of cotton-Pd NPs and MCC-Pd NPs were analyzed by XPS, as well, to prove the metallic nature of the deposited NPs. Figure 43 shows the Pd 3d XPS spectra of the composites of Pd NPs in cotton matrix (A), and Pd NPs in MCC matrix (B). The peaks centered approximately at binding energies of 335.18 eV in cotton composite, and at 335.48 eV in MCC composite were attributed to Pd

$3d_{5/2}$ electrons. Also, the peaks appeared approximately at binding energies of 340.08 eV in cotton composite, and at 340.68 eV in MCC composite were assigned to Pd $3d_{3/2}$ electrons. It was reported that, metallic Pd⁰ showed the peaks at the binding energies of Pd $3d_{5/2}$: 335.2 eV or 335.7 eV, and Pd $3d_{3/2}$: 340.1 eV or 341.0 eV [156], [158]. XPS spectra were noisier compared to those obtained for Au, Ag, and Pt, which may be a result of lower density of the formed Pd NPs.

Figure 42 shows the XRD patterns of the composite of cotton-Pd NPs (A) and the composite of MCC-Pd NPs (B). The diffraction lines at 2θ : 39.72° in cotton-Pd NPs composite and at 39.25° could be ascribed to (1 1 1) reflection of metallic fcc structure of Pd NPs [159]. Other diffraction lines of Pd metal, that are approximately at 2θ : $46^\circ(2\ 0\ 0)$, $68^\circ(2\ 2\ 0)$, $82^\circ(3\ 1\ 1)$, $87^\circ(2\ 2\ 2)$, could not be seen in the XRD patterns of the composites [159]. Since the density of Pd NPs was not very high on the surface of the cellulose samples, these lines could not be detected by XRD analysis properly, which is a bulk analysis method. Above all, the results showed that, Pd NPs in their metallic state were successfully formed in both cotton and MCC matrices.

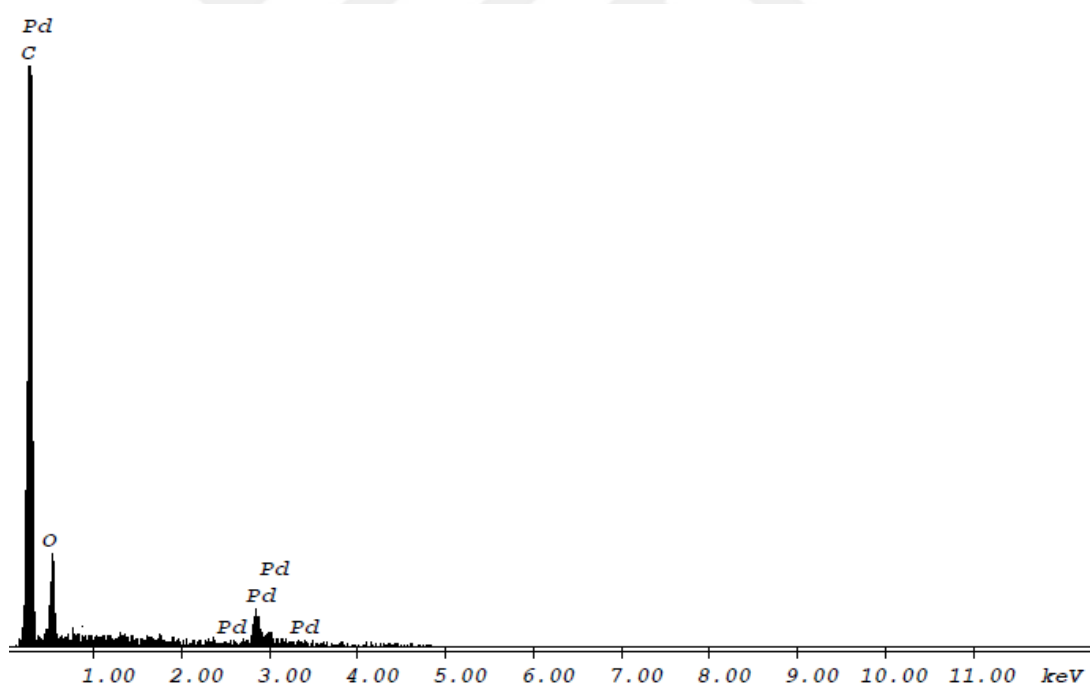
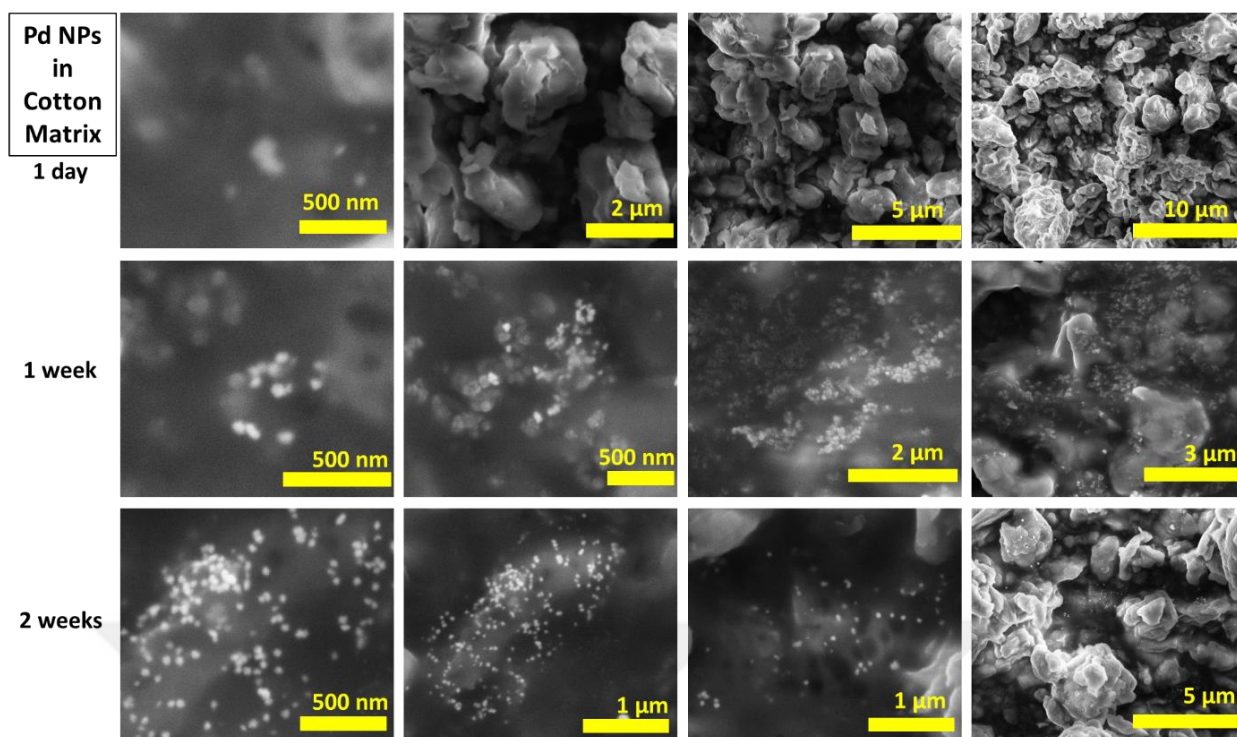


Figure 40. SEM images and EDX spectrum of the cotton-Pd NPs composite, showing formed Pd NPs as bright spots in the cotton matrix, and the presence of Pd atoms in the chemical structure.

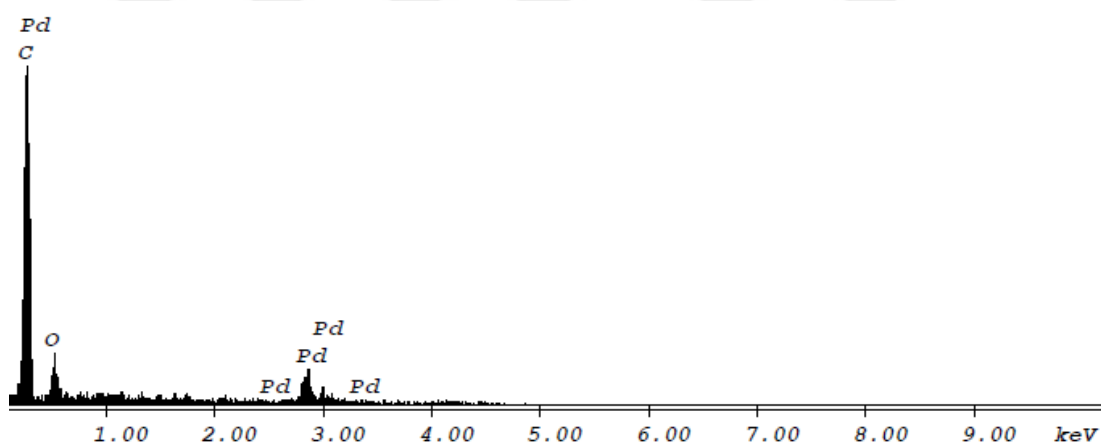
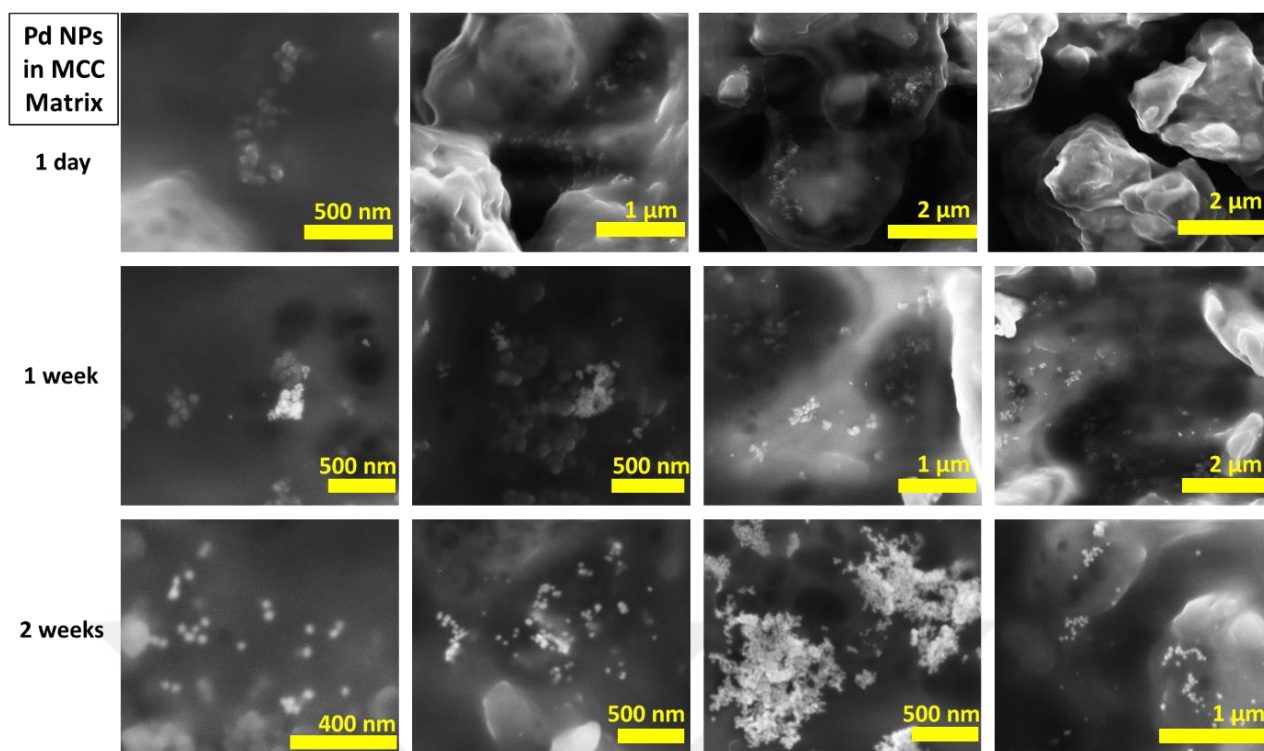


Figure 41. SEM images and EDX spectrum of the MCC-Pd NPs composite, showing formed Pd NPs as bright spots in the MCC matrix, and the presence of Pd atoms in the chemical structure.

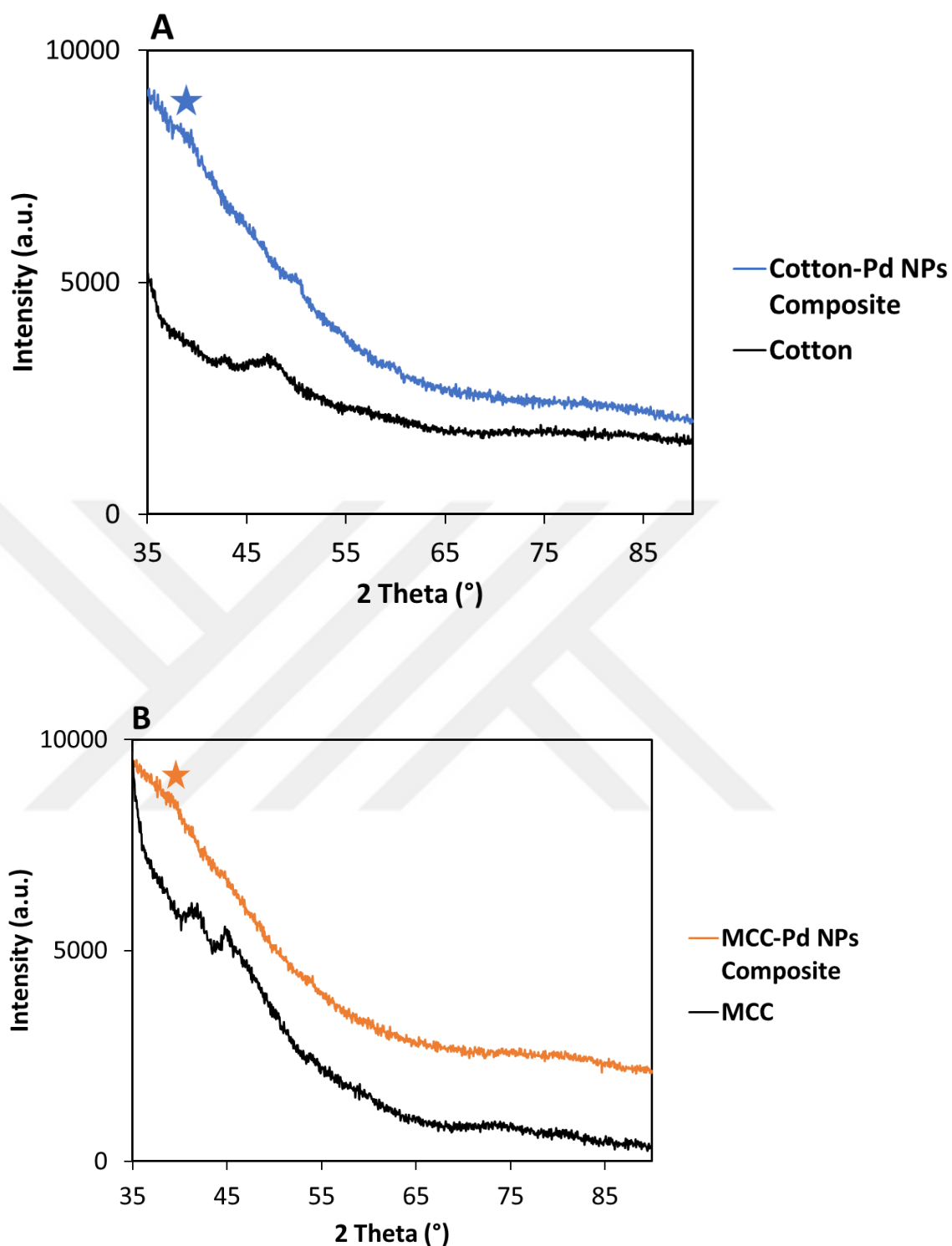


Figure 42. XRD pattern of (A) cotton-Pd NP composite (blue line) in comparison to that of pure cotton (black line), and (B) of MCC-Pd NP composite (orange line) in comparison to that of pure MCC. Diffraction line (for 111 planes) for metallic palladium Pd⁰ with fcc structure is marked with a star.

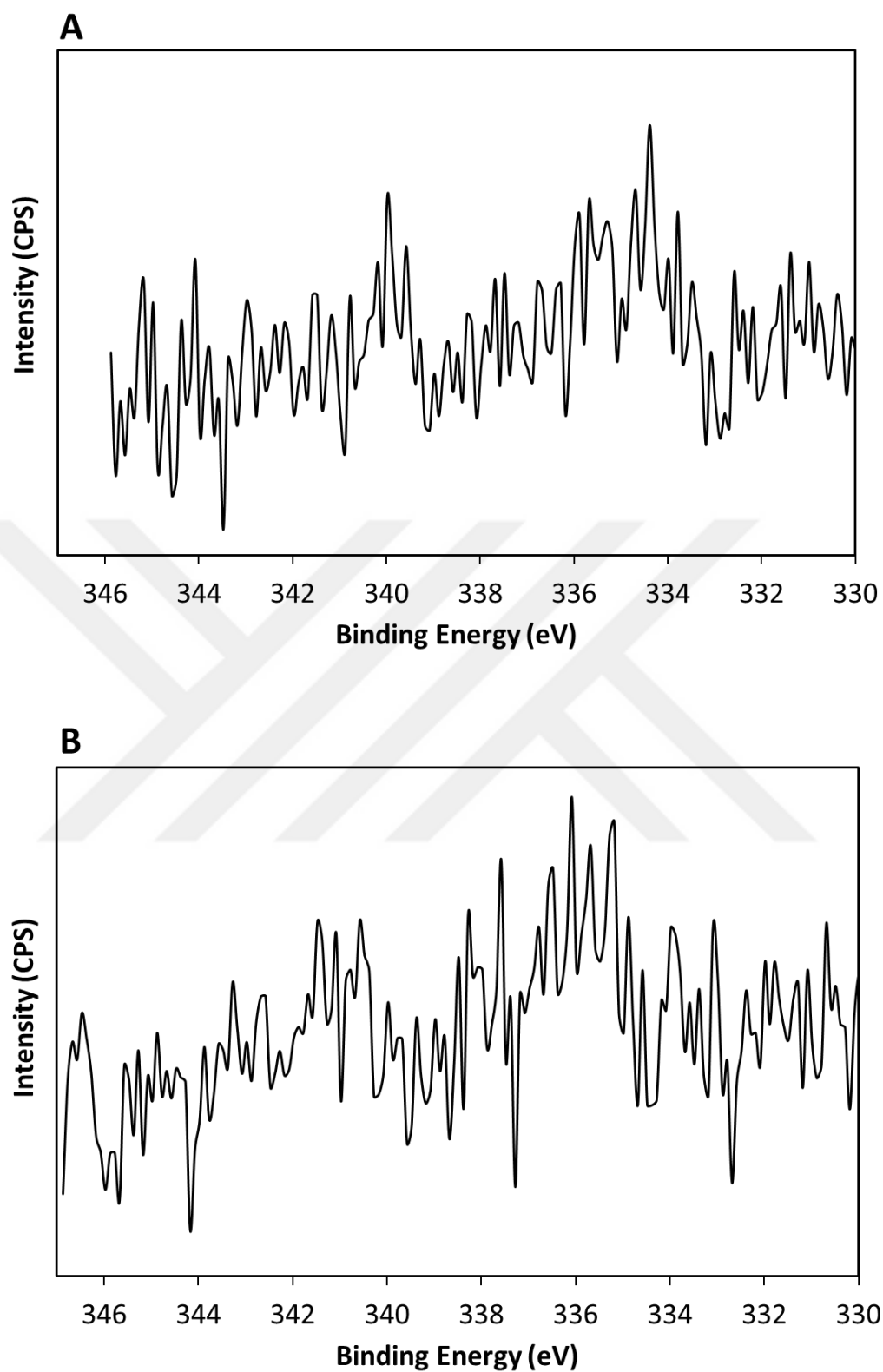


Figure 43. Pd 3d Hires XPS spectra of the composites of (A) cotton-Pd NPs, and (B) MCC-Pd NPs.

3.5.5 Cellulose-Copper Nanoparticles Composite

Copper (II) acetylacetonate ($\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ in acetonitrile $5.1 \times 10^{-3}\text{M}$) was used as a metal ion (Cu^{2+}) precursor solution in the experiment and the procedure mentioned above was applied. Later, produced cellulose-Cu NPs composites were characterized by SEM, EDX, XRD and XPS analyses.

At the end of the designated waiting time, yellowish colored composites were obtained. The SEM images and EDX spectrum of the composites of Cu NPs in cotton and in MCC matrix are shown in Figures 44 and 45, respectively. The morphology of the NPs was spherical in both cotton and MCC matrices as seen in SEM images. There was no Cu NPs in cotton matrix after 1 day. Also in the following days, the Cu NPs composites in cotton and MCC matrices showed lower number of metal NPs than other composites, which were formed. This can be due to the lower standard reduction potential of Cu^{2+} ion (0.34V) than Au^{3+} , Ag^+ , Pd^{2+} , and Pt^{2+} . Thus, the reduction of Cu^{2+} ion by cellulose mechanoradicals, is harder, and it takes longer time. Therefore, Cu NPs could be formed in only small area of the cellulose matrices, and the amount of metal NPs with respect to cellulose matrix could be low, which leads to harder detection by the instruments useful generally for relatively bulk analyses such as EDX (expected Cu main signal at 0.930 eV) and XRD (2θ : $43.2^\circ(1\ 1\ 1)$, $50.3^\circ(2\ 0\ 0)$, and $73.9^\circ(2\ 2\ 0)$ [160]).

These composites were analyzed by XPS for the oxidation state of the deposited metal. Figure 47 represents the Cu 2p Hires XPS spectra of the composites of Cu NPs in cotton matrix (A), and Cu NPs in MCC matrix (B). The peaks appeared approximately at binding energies of 932.68 eV in both cotton and MCC composite; and at 952.58 eV in cotton and MCC composite (clearer for cotton

composite) were attributed to Cu 2p_{3/2} and Cu 2p_{5/2} electrons, respectively. These peaks could be ascribed to the metallic Cu⁰ according to the binding energies of Cu⁰ in the literature, that are at Cu 2p_{3/2}: 932.7 eV and 2p_{5/2}: 952.6 eV [161]. However, the difference in binding energies between Cu(0) and Cu(I) is approximately 0.3 eV [161]. Therefore, it is hard to identify the exact oxidation state of Cu metal. Proposed formation mechanism of NPs is likely that, cellulose mechanoradicals reduced Cu²⁺ precursor ion to Cu⁰. Later, some or all Cu⁰ can oxidize easily by atmospheric oxygen, Cu¹⁺ ions were formed and stabilized as Cu₂O NPs.

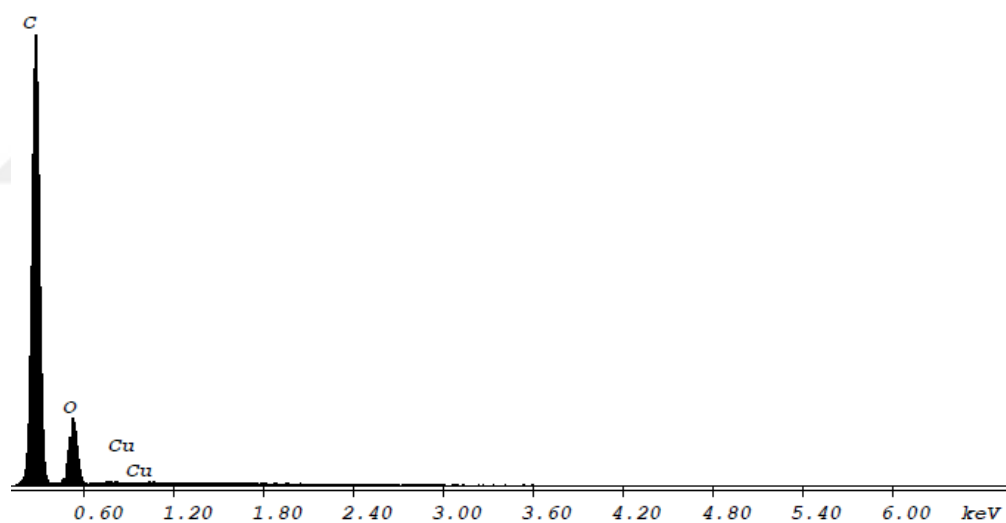
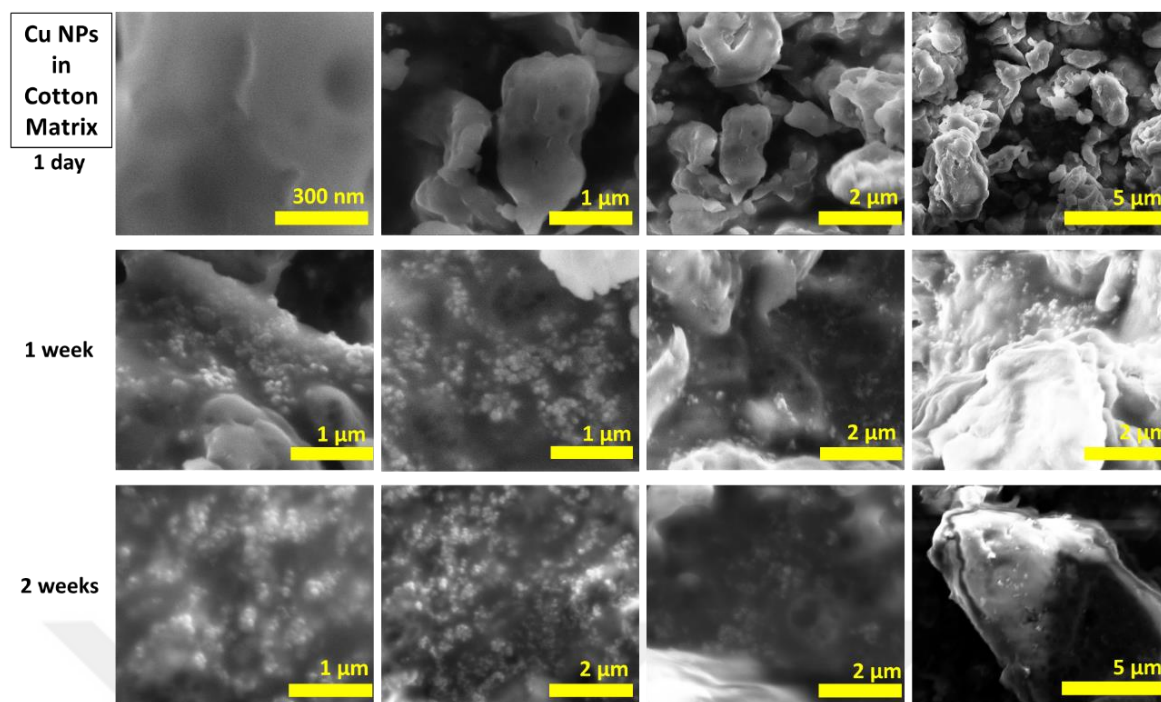


Figure 44. SEM images and EDX spectrum of the cotton-Cu NPs composite, showing formed Cu NPs as bright spots in the cotton matrix. The presence of Cu atoms in the chemical structure is only slightly seen in the EDX spectrum.

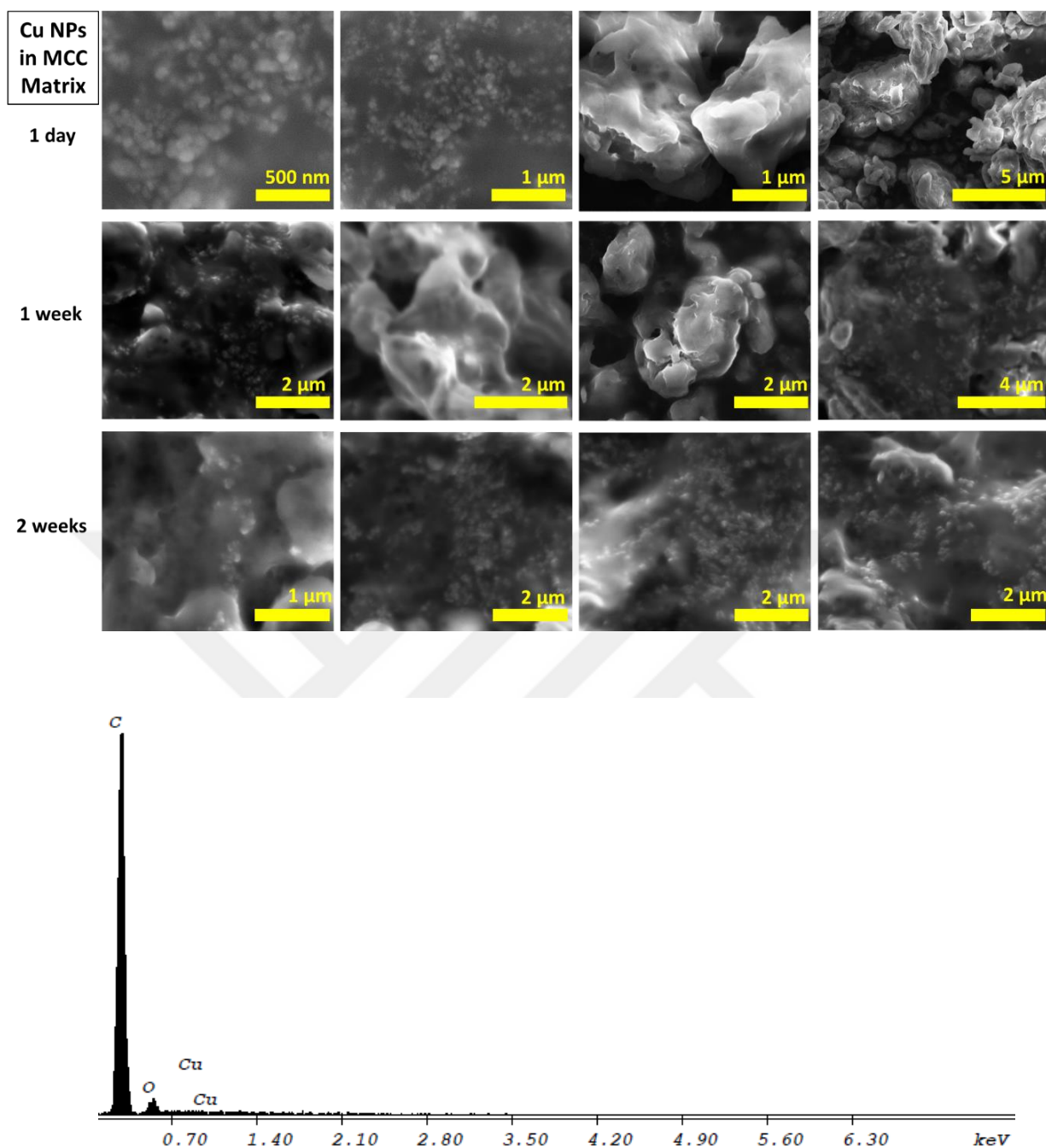


Figure 45. SEM images and EDX spectrum of the MCC-Cu NPs composite, showing formed Cu NPs as bright spots in the MCC matrix. Cu atoms are not seen in the EDX spectrum, presumably because of their low density in the cellulose matrix.

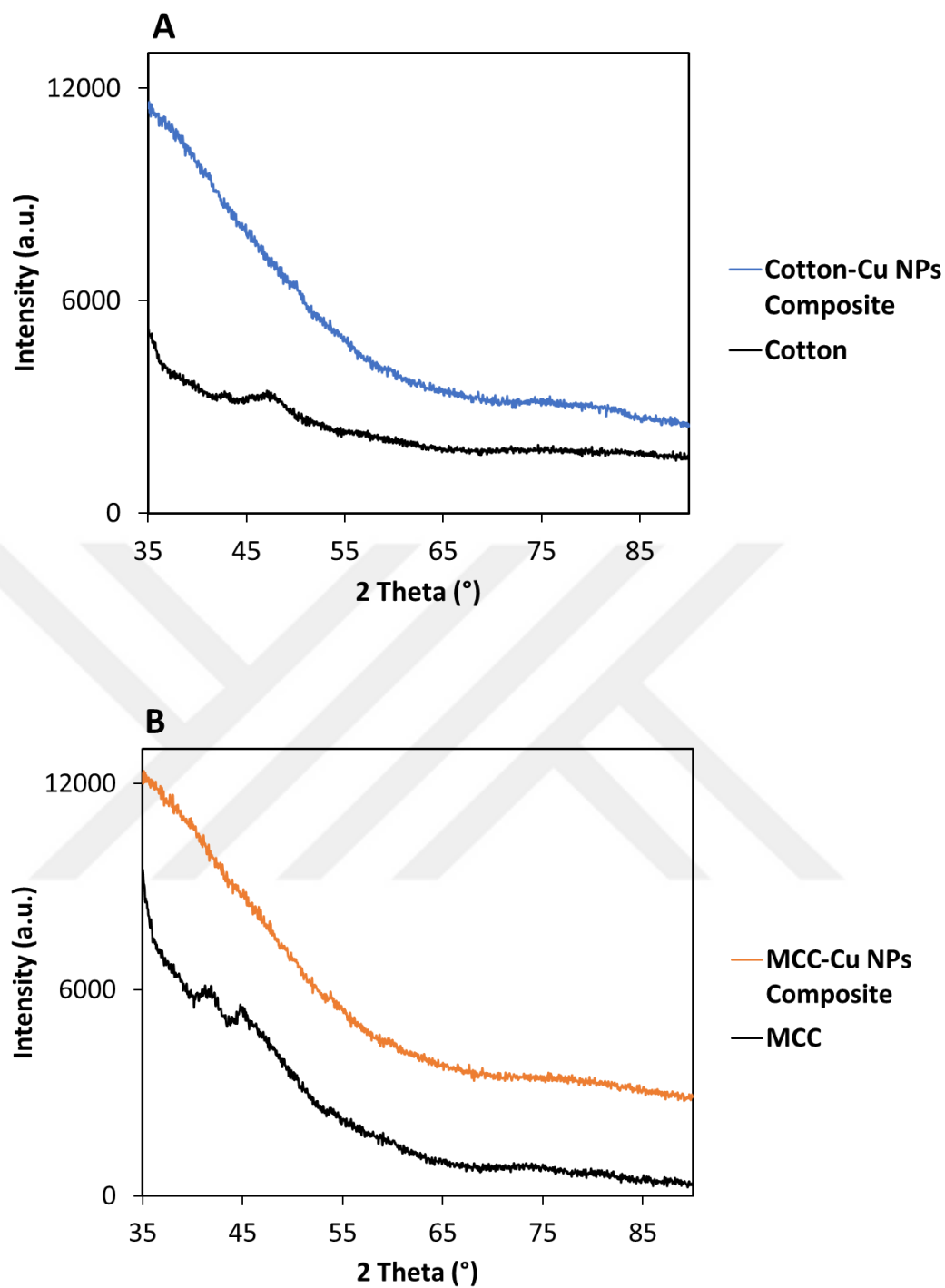


Figure 46. XRD pattern of (A) cotton-Cu NP composite (blue line) in comparison to that of pure cotton (black line), and (B) of the MCC-Cu NP composite (orange line) in comparison to that of pure MCC. Because of the low amount of the Cu (Cu₂O) NPs in the matrices, the crystal lines are not visible in the XRD diffractograms.

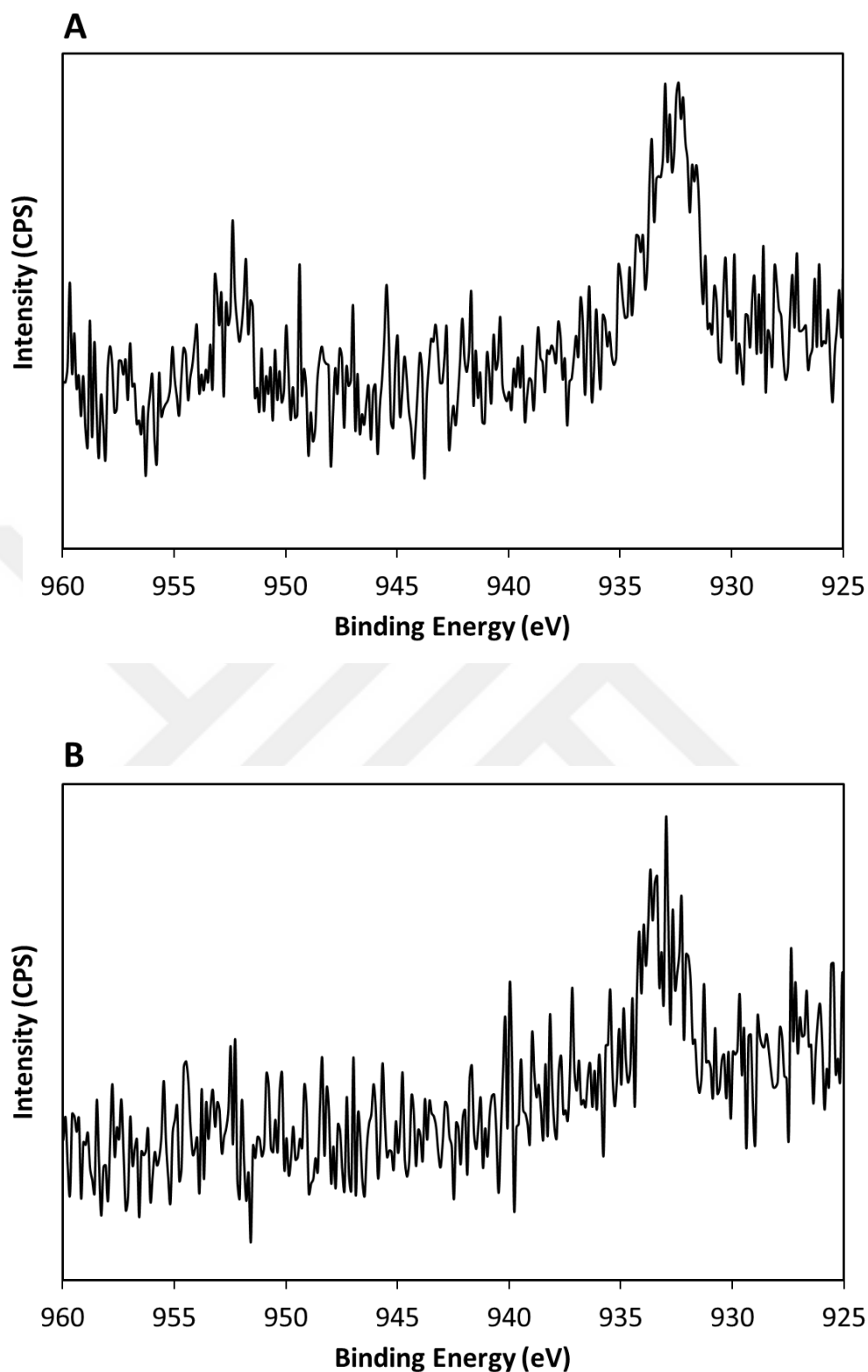


Figure 47. Cu 2p Hires XPS spectra of the composites of (A) cotton-Cu NPs, and (B) MCC-Cu NPs (B).

3.5.6 Cellulose-Cobalt Nanoparticles Composite

As a metal ion (Co^{2+}) precursor solution cobalt (II) acetylacetonate ($\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$ in acetonitrile $5.1 \times 10^{-3}\text{M}$) was used in the standard procedure described above. Then, produced cellulose-Co NPs composites were characterized by SEM, EDX, XRD and XPS analyses.

Yellowish colored composites were obtained at the end of the waiting time. SEM images and EDX spectra of the composites of Co NPs in cotton and in MCC matrix are shown in Figures 48 and 49, respectively. Spherical NPs were obtained in both cotton and MCC matrices, as shown in the SEM images. The intensity of NPs in cotton and MCC matrices was lower than that of NPs in other composites with Ag, Au, Pt, Pd, and Cu, probably because Co^{2+} ion has the lowest standard reduction potential (-0.28 V) among all other ions (Au^{3+} , Ag^+ , Pd^{2+} , Pt^{2+} , and Cu^{2+}). Because of this, the reduction of Co^{2+} is harder and lower number of NPs form in cellulose matrices, as evident from only a very weak Co main signal at 0.776 eV detected by EDX.

Figure 50 shows the XRD patterns of the composite of cotton-Co NPs (A) and the composite of MCC-Co NPs (B). Any diffraction lines corresponding to the Co NPs in metallic state Co^0 with hexagonal close packed structure (hcp), that should centered approximately at 2θ : 41° , 47.2° [162] were not observed. The reason for this can again be the lower amount of NPs with respect to cellulose samples in the composites.

These composites were analyzed by XPS, for the oxidation state of the deposited Co atoms. Figure 51 shows the Co 2p HIRES XPS spectra of the composites in cotton matrix (A), and in MCC matrix (B). Co $2p_{3/2}$ electrons

appeared approximately at binding energy of 781.38 eV in both cotton and MCC matrix. The smaller peaks, which are clearer for cotton composite and due to Co 2p_{1/2} electrons centered approximately at 797.08 eV in both cotton and MCC composites. Furthermore, the peaks approximately at 785.38 eV and 802.38 eV were attributed to the satellite peaks. All these values of binding energies were consistent with the reported values of Co²⁺ ions, that have the peaks at Co 2p_{3/2} : 781.0 eV, 2p_{1/2} : 796.9 eV, satellite peaks at 786.8 eV and 802.7 eV [163]. In the literature the values of binding energies for metallic Co⁰ were reported as 2p_{3/2}: 778 eV and 2p_{1/2}: 793 eV [164]. Thus, it can be said that, the formed Co NPs were in 2+ oxidation state. It is known that the standard reduction potential of Co²⁺ metal is very low (-0.28 V) so its reduction by cellulose mechanoradicals can be hard, and may not take place at all. Another possibility is that, firstly Co²⁺ precursor ions were reduced by cellulose mechanoradicals. Then, formed Co⁰ NPs were immediately oxidized to Co²⁺ by atmospheric oxygen to form CoO NPs.

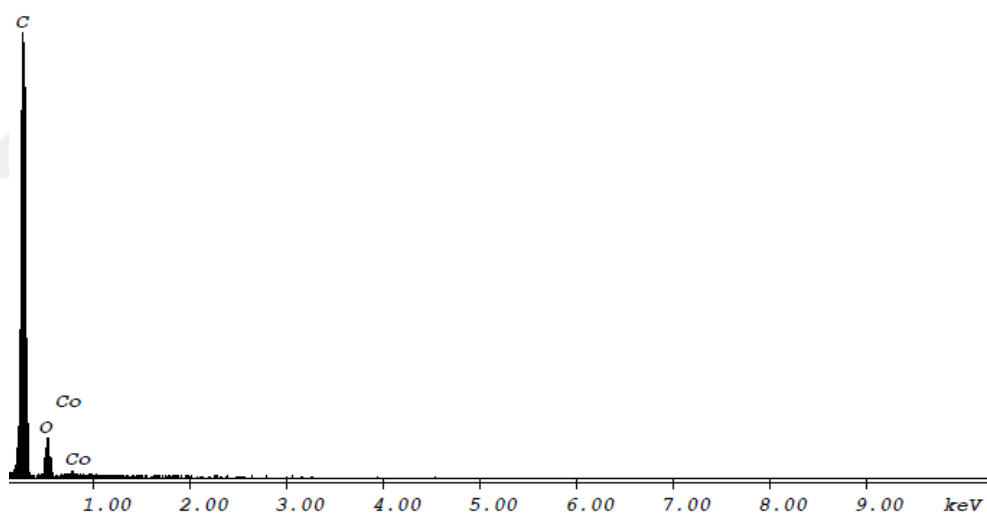
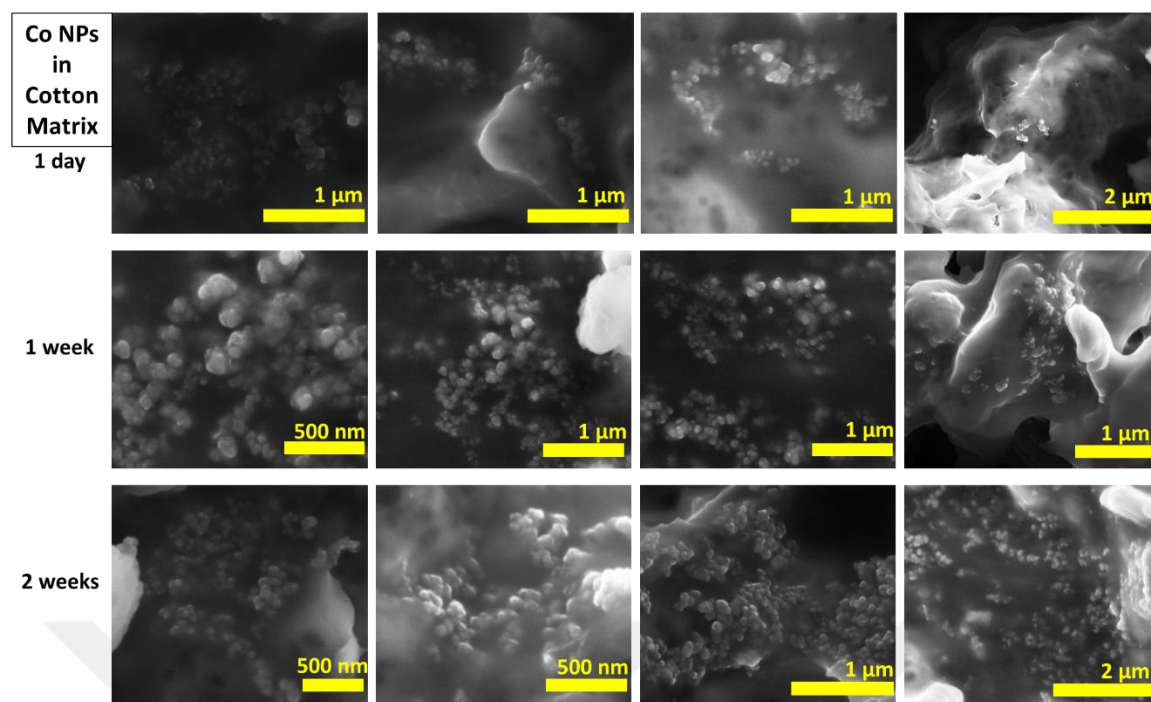


Figure 48. SEM images and EDX spectrum of the cotton-Co NPs composite, showing formed Co NPs as bright spots in the cotton matrix. The presence of Co atoms in the chemical structure is only slightly seen in the EDX spectrum.

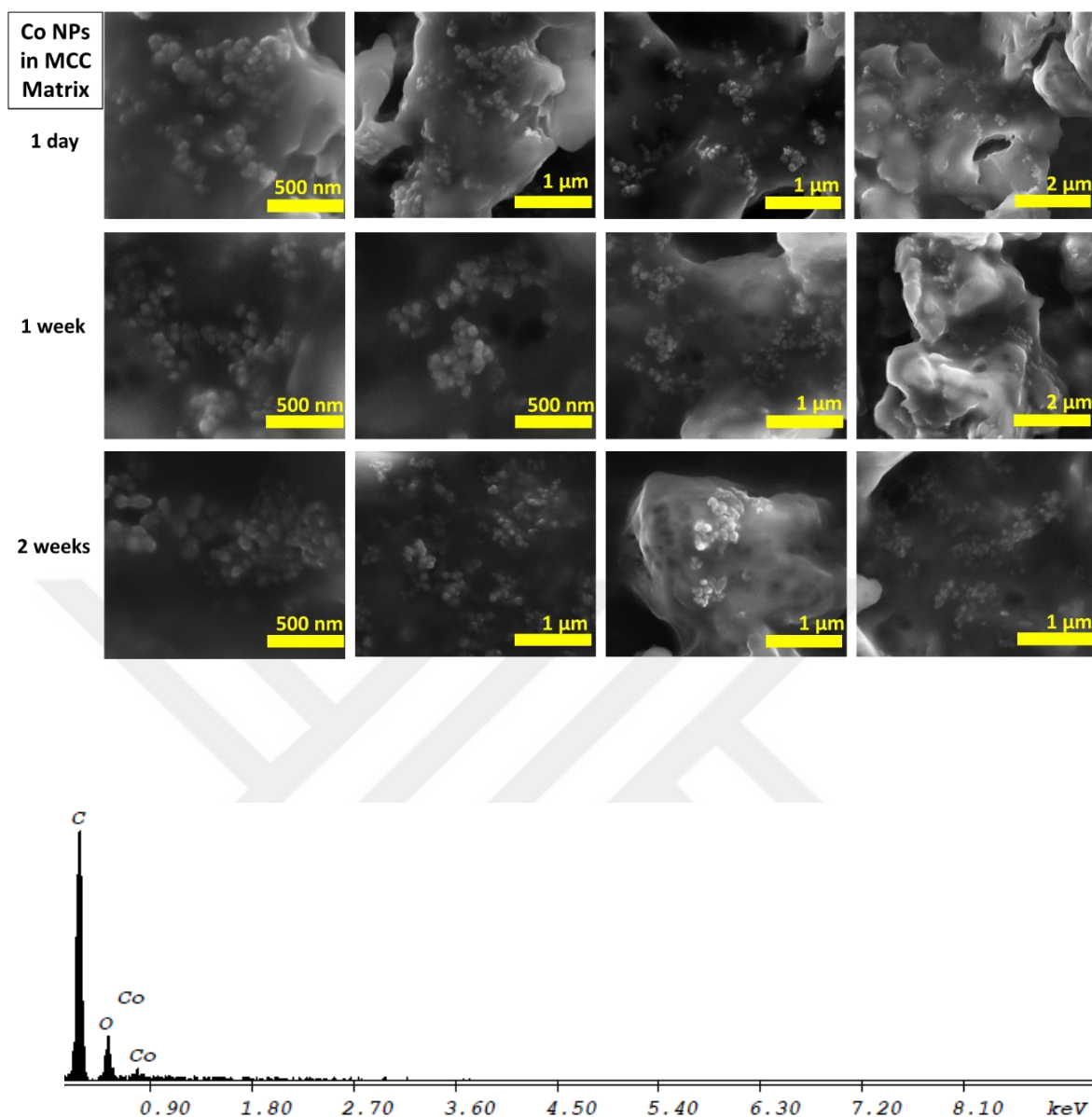


Figure 49. SEM images and EDX spectrum of the MCC-Co NPs composite, showing formed Co NPs as bright spots in the MCC matrix. The presence of Co atoms in the chemical structure is only slightly seen in the EDX spectrum.

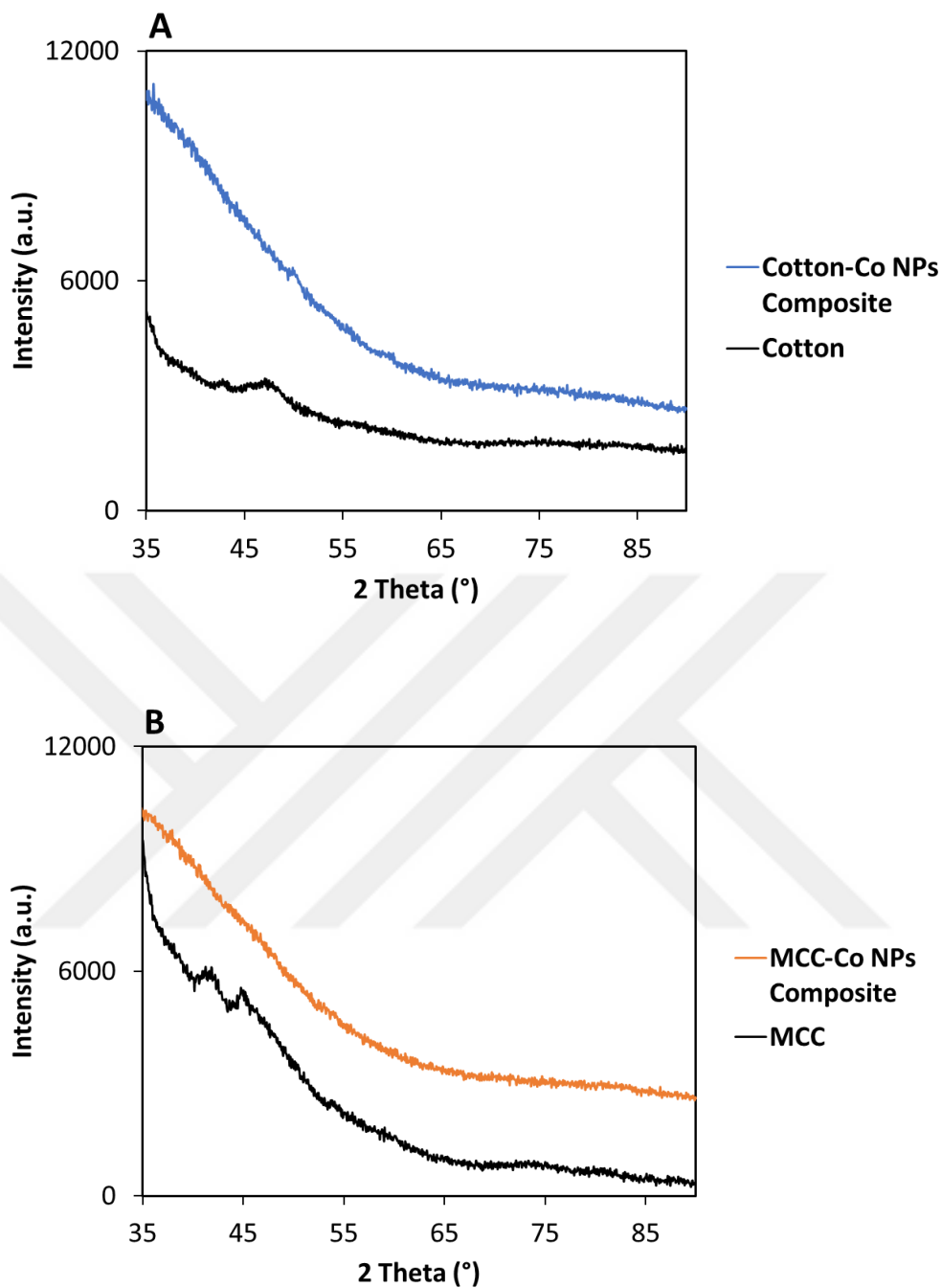


Figure 50. XRD pattern of (A) cotton-Co NPs composite (blue line) in comparison to that of pure cotton (black line), and (B) of the MCC-Co NPs composite (orange line) in comparison to that of pure MCC. Because of the low amount of the Co (CoO) NPs in the matrices, the crystal lines are not visible in the XRD diffractograms.

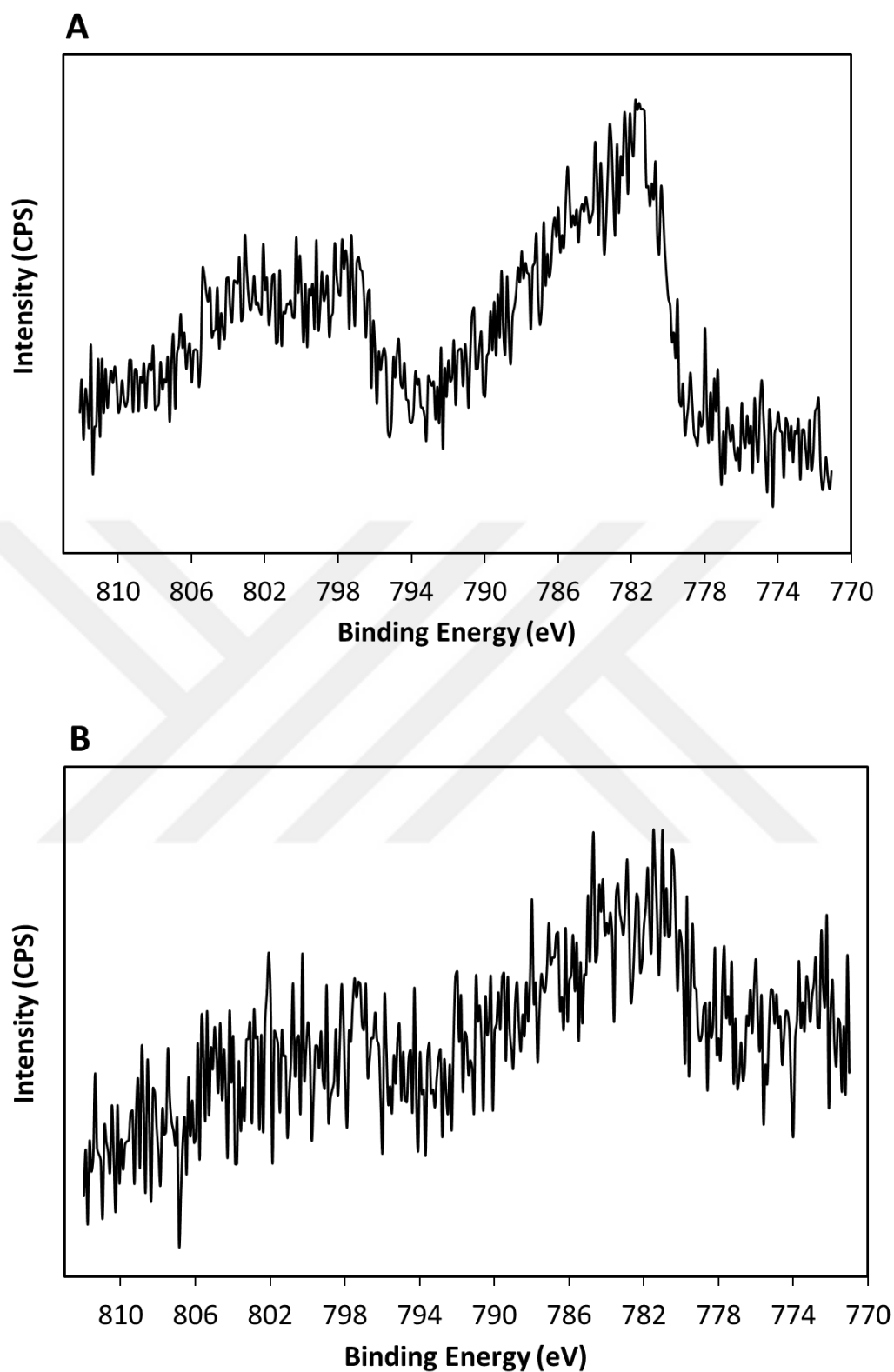


Figure 51. Co 2p Hires XPS spectra of the composites of cotton-Co NPs (A), and MCC-Co NPs (B), implying that Co atoms are deposited as Co^{2+} . See text for further discussion on XPS spectra.

3.6 Possible Formation Mechanism of Cellulose-Metal NPs Composites

All these results for cellulose-metal NPs composites showed that, cellulose mechanoradicals, that were formed by using cotton and MCC samples from dry grinding in cryomill, could reduce metal ions to their metallic state - apart from the cases for Cu and Co, which may be reduced to the metallic state and then could be further oxidized by the oxygen in the environment.

Figure 52 represents a possible production mechanism of cellulose-metal NPs composites by cryomilling. When cryomilled cellulose samples and metal ion solutions come into contact, firstly strong electrostatic interactions occur between the electro positive metal cations and the electron rich oxygen atoms (in hydroxyl and ether groups) in the cellulose structure and cellulose mechanoradicals. Because of these strong interactions, metal ions are attached to the cellulose fibers. Then, metal ions are reduced by cellulose mechanoradicals in an electron transfer reaction. Reduced metal NPs are impregnated into the pores of the cellulose fibers and stabilized due to the cellulose fiber structure and strong ion-dipole interactions between metal NPs and hydroxyl and ether groups in the cellulose structure. These interactions and fiber structure of the cellulose also prevent the aggregation of metal NPs in cellulose matrix. By this method, cellulose mechanoradicals are used as reducing agents and cellulose chains act as stabilizing agents.

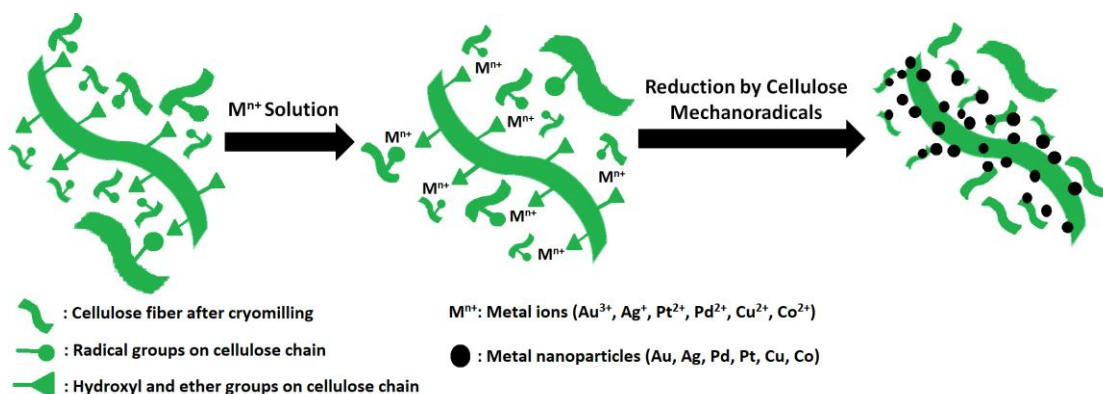


Figure 52. Representation of the production of cellulose-metal NPs composites by cryomilling.

3.7 Crystalline Transformation from Cellulose I to Cellulose II

As mentioned in the part of investigation of the changes in crystalline structure of the cryomilled cellulose samples, dry cryomilling of cellulose samples gave rise to formation mostly amorphous cellulose from both cotton and MCC samples. However, while characterizing the cellulose-metal NPs composites by XRD, it was realized that the diffraction lines different from the characteristics of amorphous cellulose I were observed for some composites. After literature research, these new diffraction lines were ascribed to the cellulose II structure. In our experiment, metal ion solutions of gold, silver, platinum were prepared in water, and metal ion solutions of palladium, copper, cobalt were prepared in acetonitrile solvent. As mentioned in experimental part, after cryomilling of cotton and MCC samples, metal ion solutions were added on the cellulose samples. Then the cellulose sources and metal ion solutions were mixed in cryomill at 5 Hz frequency for 30s. After dilution with corresponding solvent, these composites were stored. XRD analyses of the composites were reported above between the

range of 2θ : 35° - 90° in order to see the diffraction lines coming from metal NPs clearly. However, all measurements were taken between the range of 2θ : 5° - 90° . Therefore, it could be seen that, new diffraction lines were observed for the composites that were formed by metal ion solutions having water solvent. Figure 53 and 54 shows the XRD patterns of the cotton sample and the composites of Au, Ag, Pt, Pd, Cu, and Co NPs in cotton matrix. XRD patterns of the MCC sample and the composites of Au, Ag, Pt, Pd, Cu, and Co NPs in MCC matrix are shown in Figures 55 and 56. As can be seen in Figures 53 and 55, new diffraction lines (different from the characteristic cellulose I amorphous pattern) were obtained, which were resulted when water was used as the solvent in the metal ion solution. These diffraction lines, for cotton composites the diffraction lines approximately at 2θ : 12.45° , 20.55° , 21.66° ; for MCC composites the diffraction lines approximately at 2θ : 12.05° , 20.19° , 21.76° , are consistent with the reported values of cellulose II structure, which has diffraction lines approximately at 2θ : $12.1^\circ(1\ 1\ \bar{0})$, $20.0^\circ(1\ 1\ 0)$, $21.7^\circ(0\ 0\ 2)$ [34], [165], [166]. In the experiment even 30 seconds mixing of cellulose sources and metal ion solution containing water as a solvent (total 6 mL of water after dilution), was enough to recrystallize the mostly amorphous cellulose having cellulose I structure to cellulose II structure. In a similar study, Ago *et al.* reported a crystalline transformation from cellulose I to cellulose II by ball milling of native cellulose with specific amount of water [35]. The presence of water results in the new planar orientation and the formation of hydrogen bonds [167]. After folding of molecule chains, antiparallel and more stable cellulose II structure is formed from parallel cellulose I structure [168].

When acetonitrile was used as a solvent in composites preparation, there was no transformation to cellulose II, only mostly amorphous cellulose was obtained, which can be seen in Figures 54 and 56. Similar phenomena was observed in the literature that when toluene or 1-butanol was used during ball milling of cellulose [137].



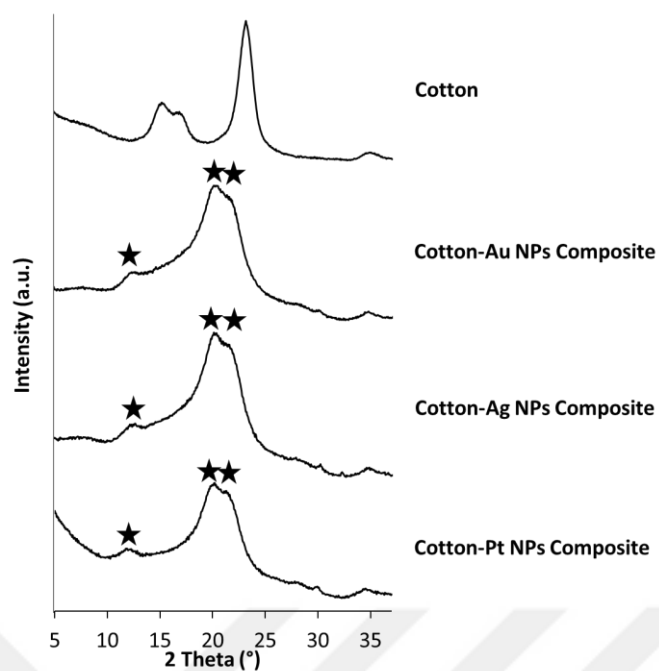


Figure 53. XRD patterns of the cotton sample and the composites of Au, Ag, Pt NPs in cotton matrix. Stars indicate the diffraction lines coming from cellulose II structure.

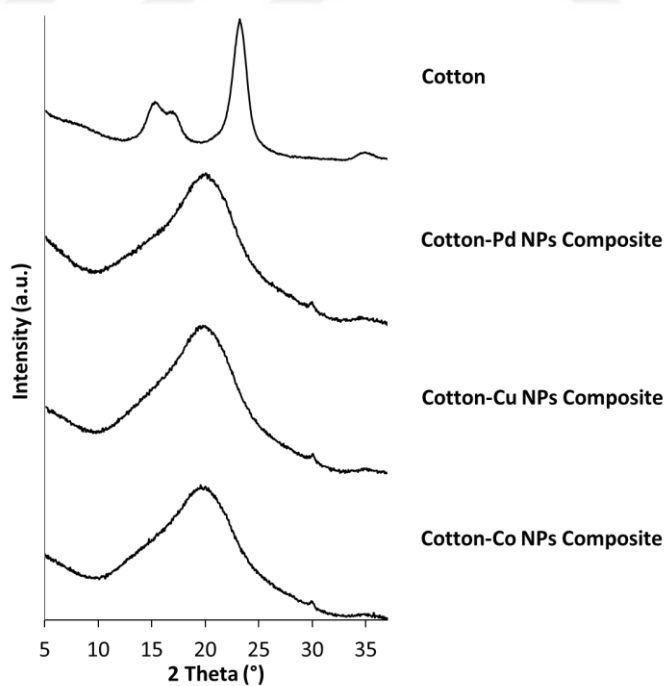


Figure 54. XRD patterns of the cotton sample and the composites of Pd, Cu, Co NPs in cotton matrix.

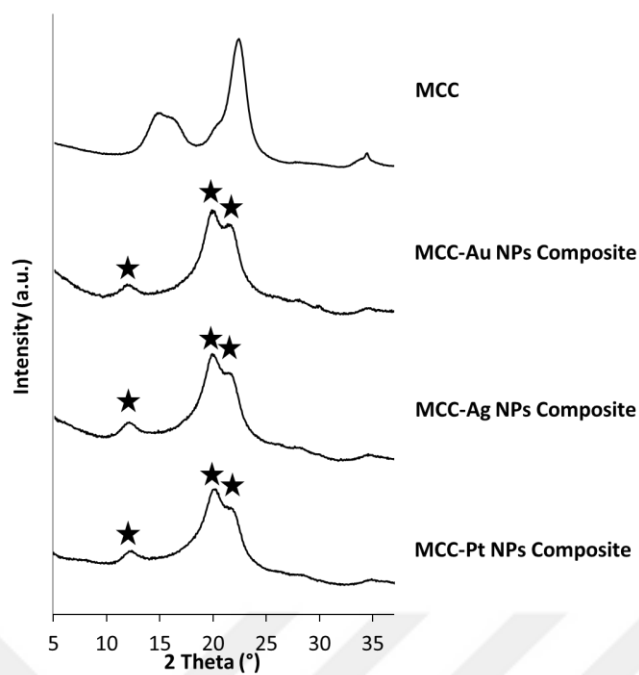


Figure 55. XRD patterns of the MCC sample and the composites of Au, Ag, Pt NPs in MCC matrix. Stars indicate the diffraction lines coming from cellulose II structure.

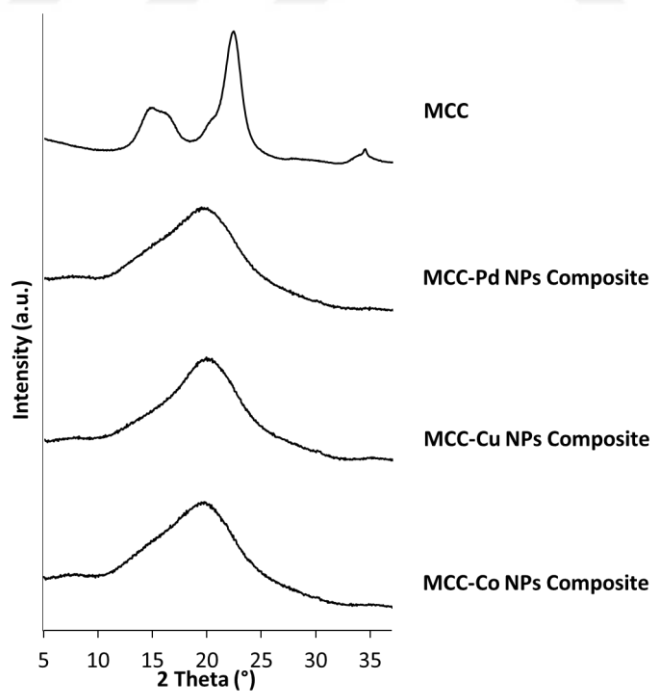


Figure 56. XRD patterns of the MCC sample and the composites of Pd, Cu, Co NPs in MCC matrix.

CHAPTER 4

CONCLUSION

With this thesis work; *for the first time in the literature*, 1) we analyzed the formation of cellulose mechanoradicals produced by ball milling qualitatively and quantitatively, vis a vis the morphological changes occurred in cellulose structure during mechanical treatment, and 2) we showed a mechanochemical method to obtain cellulose-metal NPs composites by using cellulose mechanoradicals.

In the first part, we have shown that, the obtained mechanoradicals are of peroxy and alkoxy type by using electron spin resonance spectroscopy (ESR), and that we can obtain the number of mechanoradicals produced by using radical scavenger DPPH molecule, using UV-Vis spectroscopy. Of the two grinding methods we used, we showed that dry grinding method produces 9-43 times more number of radicals than wet grinding method. The bond-breakages leading to mechanoradical formation was monitored by FTIR-ATR spectroscopy, which also showed differences in bond breakages in wet and dry grinding of cotton and MCC cellulose samples; in the former, it was shown that, mostly intra and intermolecular hydrogen bonds were broken, while in the latter together with the intra and intermolecular hydrogen bonds, significant amount of glycosidic bonds (covalent linkages in cellulose chains) are cleaved. Crystallinity of cellulose was also affected by the mechanochemical treatment. With increasing milling times and especially with dry grinding, in FTIR-ATR amorphous band ($\sim 897\text{ cm}^{-1}$) was more pronounced, and crystallinity band ($\sim 1427\text{ cm}^{-1}$) was less pronounced for both

cotton and MCC samples, as also supported by XRD analyses. Also, with XRD it was shown that, in presence of the solvent crystalline regions stayed intact during milling, but dry milling causes the disintegration of crystalline regions at lower milling times. SEM analyses showed especially in dry milling conditions the progressive decrease in particle sizes of cellulose samples, formation of new, active, and accessible surfaces.

In the second part, cellulose-metal NPs were produced by using cellulose mechanoradicals formed by cryomilling, for the first time in the literature. These composites were characterized by SEM, EDX, XRD, and XPS analyses. Au, Ag, Pd, Pt NPs were successfully produced as in their metallic forms in both cotton and MCC matrices. Cu NPs could mainly be in the form of Cu^0 NPs or Cu^{1+} as Cu_2O NPs. Finally, the composites of Co NPs were obtained as CoO NPs stabilized in cotton and MCC matrices. Cellulose mechanoradicals were used as reducing agent to reduce metal cations and cellulose chains led to the stabilization of reduced metal NPs in cellulose matrices, which kept NPs stable without any aggregation. By this way, in the production composites, we not only excluded the use of any external hazardous reducing and stabilizing agents, but also obtained ‘naked’ NPs in cellulose matrices without any contaminants. Further studies of using these cellulose-metal NP composites in catalysis and for SERS applications are continued, with positive preliminary results.

With this work, we have drawn many structure/chemistry relationships in the mechanochemistry of cellulose, which are valuable for using green methods to prepare these composites of this abundant and versatile material. I hope that, the future chemistry brings more environment-friendly composites, made through non-hazardous, green chemical methods.

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