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Bionanocomposite films and coatings: current applications in advanced technology

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Abstract

Polymers, which are suitable for use for various purposes, are decorative, chemically inert and corrosion-free, have long periods of destruction in nature and are generally known as chemically produced substances, have gained importance in green chemistry and green production. Composite materials are obtained by combining materials such as natural biopolymers or synthetic biodegradable polymers, inorganic or organic nanomaterials, nanoscale minerals with different materials. The aim of this review is to briefly investigate the biopolymers used in the production of composite materials and the film coating techniques related to these materials, to determine what can be done for the future, and to reveal the environmental importance of the use of biopolymers as binders of composite materials that can be produced in the future.

Keywords: *Biocomposite, biodegradable polymer, film coating*

Biyonanokompozit filmler ve kaplamalar: gelişen teknolojideki mevcut uygulamaları

Öz

Çeşitli amaçlarla kullanıma uygun, dekoratif, kimyasal olarak inert ve korozyona uğramayan, doğada uzun süre yok olan ve genel olarak kimyasal olarak üretilen maddeler olarak bilinen polimerler, yeşil kimya ve yeşil üretimde önem kazanmıştır. Kompozit malzemeler, doğal biyopolimerler veya sentetik biyobozunur polimerler, inorganik veya organik nanomalzemeler, nano ölçekli mineraller gibi malzemelerin farklı malzemelerle birleştirilmesiyle elde edilir. Bu derlemenin amacı, kompozit malzemelerin üretiminde kullanılan biyopolimerleri ve bu malzemelerle ilgili film kaplama tekniklerini

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kısaca araştırmak, geleceğe yönelik neler yapılabileceğini belirlemek ve biyopolimer kullanımının çevresel önemini ortaya koymaktır.

Anahtar kelimeler: *Biyokompozit, biyolojik olarak parçalanabilen polimer, film kaplama*

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1. Introduction

Biomaterials science is one of the branches of science where great progress has been made in recent years and detailed research has been concentrated. Compared to previous years, natural materials produced from materials such as wood, glue and rubber, gold, iron, glass and zinc have been used for biomaterial purposes to bring new life forms to living tissues. In the last decade, serious progress has been made in the development of new materials to understand the interaction of materials with biological systems. Biomaterials are materials of natural or synthetic origin used to increase or support the functionality of living tissues that have lost their function in the human body [1,2]. Contrary to their high potential and properties, industrial polymers create pollution as they cannot be destroyed through a natural process and can only be disposed of as a result of costly degradation processes. However, the fact that they are obtained from exhaustible resources such as petroleum resources has led to new searches in terms of sustainability and environmental harmony in the polymer industry.

Biopolymers have come to the fore as alternative materials in many areas, especially in the packaging industry, as a result of the disadvantages of industrial polymers such as being obtained from exhaustible resources and being difficult to dispose of. They obtained from natural and sustainable sources have properties equivalent to those of industrial polymers, thanks to their mechanical and thermal properties [3–5].

Characterization techniques bionanocomposite materials are divided into four. The first of these characterization techniques is microscopy-based characterization techniques. They are scanning electron microscope, transmission electron microscope, atomic force microscope and scanning tunneling microscope. The second is X-ray related characterization techniques. This category also includes X-ray diffraction and X-ray photoelectron spectroscopy. The third and fourth characterization techniques of bionanocomposite materials are spectroscopic techniques, namely UV-VIS spectrophotometry, Raman/FT-IR spectroscopy [6].

In the production of bionanocomposite films, natural or synthetic biodegradable polymers are generally preferred. The properties and applications of bionanocomposite-coated films depend on the nanoscale material's characteristics. In previous studies, in the production of films coated with bionanocomposite, the structures were determined by molecular arrangement, reaction activity. Natural polymers are divided into classes based on functional groups, bonding properties, thermal behavior, and solubility in different solvents. Materials such as some natural minerals and clay minerals have also been preferred recently. Studies have been conducted with these minerals in different disciplines.

In this review, we focused on the different properties of bionanocomposites and different characterization techniques for analysis, and discussed the latest developments in both technical and scientific matters for the applications of bionanocomposites. Additionally, this article aims to review studies on the formation of polymer-based nanocomposite coating films and their properties.

Most of the synthetic polymers used today are petrochemical products and are not biodegradable. Therefore, when socioeconomic life is considered, the production of degradable plastics instead of conventional plastics is an important process. It has become increasingly accepted that long-lasting polymers are not sufficient for applications intended for short-term use. This process will accelerate further when concerns about the protection of ecological systems are also taken into account. When bioplastics are obtained, a biologically derived material is used as raw material. This material can be of plant origin such as starch or corn, or it can be a microorganism such as bacteria or yeast that performs biotransformation using this plant. Mass energy cycles are closed. When they decompose in nature, they are separated into their basic components and mixed back into the carbon cycle. When their lifespan is over, if they are used to obtain heat, they produce energy, which has a neutral effect on the climate. Especially considering the increase in recent years, it is a very important feature that it protects fossil-based raw material reserves and reduces dependence on oil. By composting bioplastics, carbon-rich compost is obtained that can be used in farms, agricultural lands, etc. This process is also important in terms of reducing chemical fertilizer consumption [7].
As for the disadvantages of bioplastics, they are still produced in relatively small quantities, which is one of the reasons why they are expensive. This will change when bioplastic production begins on a large scale and production costs will decrease. Biopolymers, which are less durable than traditional plastics, may not provide sufficient performance in some applications. Especially for the production of single-use products, the choice of biopolymers may lead to durability problems. The manufacturing process can sometimes be complex and energy intensive, which can limit the potential of biopolymers to reduce their environmental impact [8,9].

2. Component materials involved in the production of biodegradable composite matrix

High molecular weight compounds with a long chain or branched structure, formed by many identical or different atomic groups connected by chemical bonds in a small or regular manner [10,11]. These long chains are held together by cross-links, Van der Waals bonds, hydrogen bonds or primary covalent bond forces. The properties of polymers vary greatly depending on their monomers, which are their building blocks. Therefore, the selection of appropriate biomaterials for the application area should be made carefully. Starch, chitosan, cellulose, natural rubber, albumin, lginate, protein, shellac, lignin and polyhydroxyalkanotes, gelatin and DNA (genetic material) belong to the group of natural polymers. There are also many synthetics available today. The types of nanoscale materials, their importance and loading levels into the matrix, as well as the impact of nanoscale materials on coating application are discussed. Additionally, this review explores various applications and properties of film-forming materials [12,13].

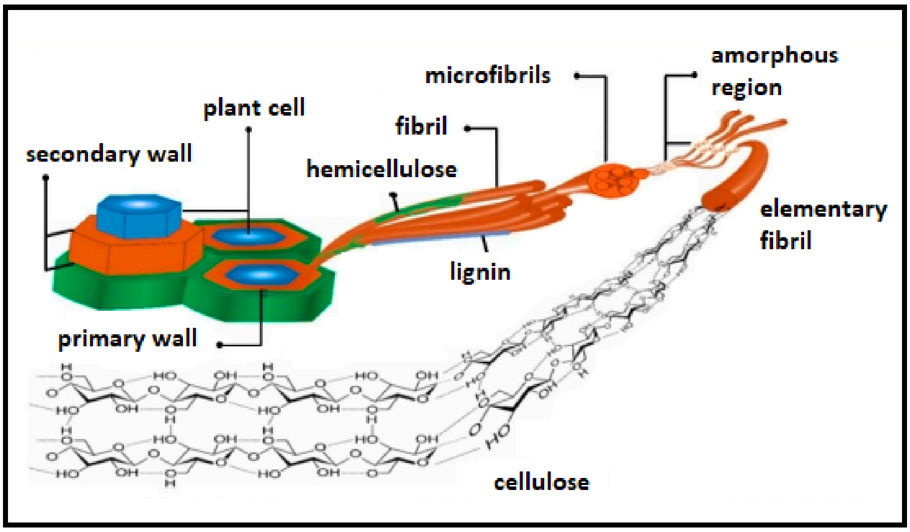

Figure 1. Schematic representation of the hierarchical structure of cellulose obtained as a result of the extraction process from plants [14]

Lignin, hemicellulose, waxes, extracts and trace elements are among the materials that form the composite in plant materials. Cellulose exists as a cellular hierarchical biocomposite within some structures such as these materials. [14]

2.1. Natural Polymers and in situ Polymerization

Polymers are long-chain molecules composed of small repeatable units. The low molecular weight units used to start the synthesis are called "monomers". Natural polymers used in polymeric biomaterials used in the biomedical field can be classified as hydrogels, inorganic polymers, biodegradable polymers, smart polymers, fabrics, grafts and coatings. Natural polymers are grouped into three classes: proteins, polysaccharides and polynucleotides. In this review, functional groups, chemical structures and technological applications of natural polymers such as cellulose, chitosan, lignin, pullulan, polyhydroxyalkanoate and protein were investigated.

The advantages of natural polymers are that they are very similar to macromolecules in the biological environment. It does not have the toxicity and chronic inflammation problems encountered with synthetic polymers. They are degraded by enzymes in the biological environment (biodegradation). Disadvantages of natural polymers: They have an effect that disrupts the body's immune system (immunogenic). Disadvantages of natural polymers: These polymers, no matter how natural they are, have an immunogenic effect that disrupts the body's immune system. The living body is protected by many defense systems consisting of very different molecules, cells and tissues. All molecules that stimulate the immune systems of living beings and are not their own are called "antigens" or "immunogens". With their protective elements, the living being first prevents "antigens" that are foreign to its structure from entering the body. This protection is a system that is increased layer by layer, its members are; surface barriers, innate and acquired immune system [15]. If any antigen can overcome the surface barriers such as the skin, respiratory and digestive system, which are the first barrier, and enter the living being, the second defense system is immediately activated. Because the immune system is the sum of the processes that protect against diseases in a living being, recognize pathogens and tumor cells and destroy them. The immune system can distinguish substances with very similar properties from each other, for example; it has the ability to distinguish even proteins with one amino acid different from each other. This distinction is complex enough to cause pathogens to find new ways to infect despite the host's defense system and to make some adaptations. In order to survive in this struggle, some mechanisms have developed that recognize pathogens and neutralize them [15,16]. Since they have a more complex structure than synthetic polymers, their technological manipulation is difficult. They are degraded by enzymes in the biological environment. In particular, protein structures decompose at high temperatures. Thermoforming and sterilization are difficult are difficult. Their composition varies depending on the source from which they are obtained [17].

As seen in Figure 2, monomers polymerize in the presence of nanoclay. These biomaterials first swell in liquid monomer solution and the polymerization process takes place between the intermediate layers formed [18]. However, it is a disadvantage that some inorganic particles in the structure tend to separate rapidly from the polymer formed and precipitate. To eliminate this disadvantage, certain groups must be attached to their surfaces [19,20].

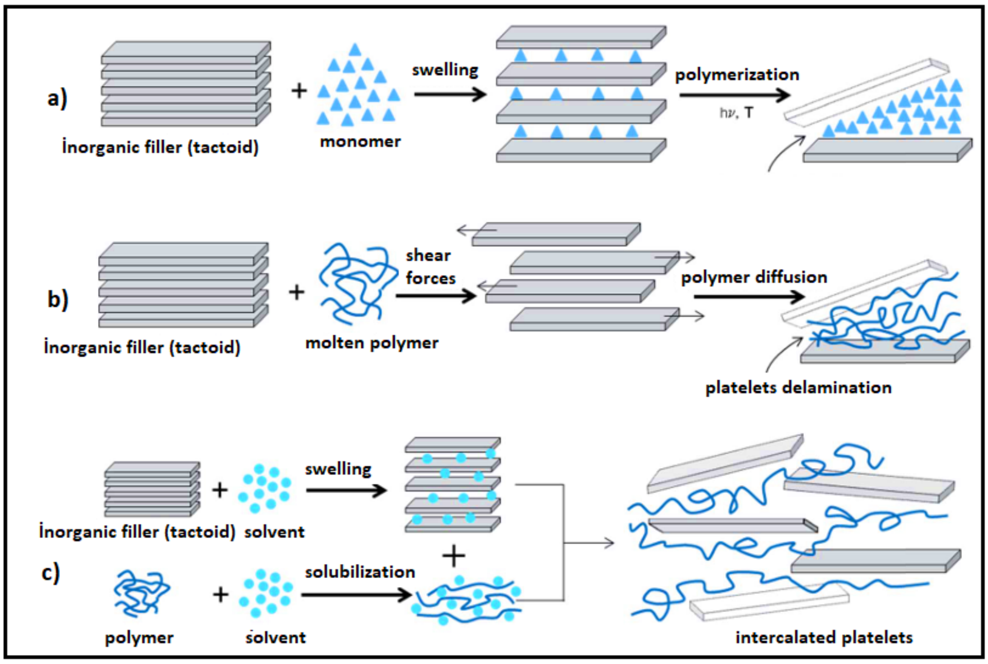

Figure 2. Schematic representation of the polymerization process of monomers in the presence of nanoclay via (a) in situ polymerization, (b) melt processing, and (c) solution casting [18]

Some instability may occur during processing, such as PLA-, chitosan- and pullulan-based bionanocomposites. To eliminate this situation, the process can be accelerated with nanocomposites containing organically modified clay. While these processes have been conducted, some parameters must be carefully optimized during the process of some biopolymers that may degrade in heat [19].

2.1.1 Cellulose-based bionanocomposites

Natural polymers are divided into classes based on functional groups, bonding nature, thermal behavior, and solubility in different solvents has a linear chain of several hundred to over ten thousand (1→4) linked d-glucose units. Different derivatives made with cellulose are used as optical films, coatings, controlled release systems, biodegradable plastics, and composite materials in different applications in the field of biomedical materials. Such derivatives include cellulose ethers such as methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC) and cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB). In this study by Swain, cellulose nanobiocomposites were formed by intercalating boron nitride with cellulose matrix by solution method. Boron nitride dispersion and nanobiocomposite formation showed significant reduction in oxygen permeability [21]. By adding cellulose into polymer films, moisture barrier properties are further improved. The presence of crystalline fibers within the composite creates a lower diffusion process and therefore lower permeability. It has been stated that nanosized cellulose fibrils also improve the thermal properties of polymers. It has been stated that the thermal stability of polymers in nanocomposites with cellulose hair-crystals is improved compared to similar polymer clusters.

Cellulose is used in many applications when creating composite films due to its superior properties such as water absorption capacity, strong reinforcement and excellent dimensional stability, as well as its strength and durability [22]. Since coatings made using cellulose are less damaged by environmental effects, stable and high-performance nanocomposite films have attracted widespread attention [23,24]. Wu et al., observed that when they developed polyurethane with cellulose nanofibrils, its elongation decreased due to conventional micro-sized cellulose filling [25]. These differences may be related to different degrees of matrix-cellulose interactions. According to the study by Wang et al., the addition of weakly interacting nano-reinforcements containing matrix causes elongation. Due to this elongation, the strength of the material decreases [26].
As shown in Figure 3, cellulose nanocrystals or nanoparticles (CNCs) are crystal structures that have an amorphous structure within the crystal regions and are well organized and coordinated within the cellulose fibers themselves.

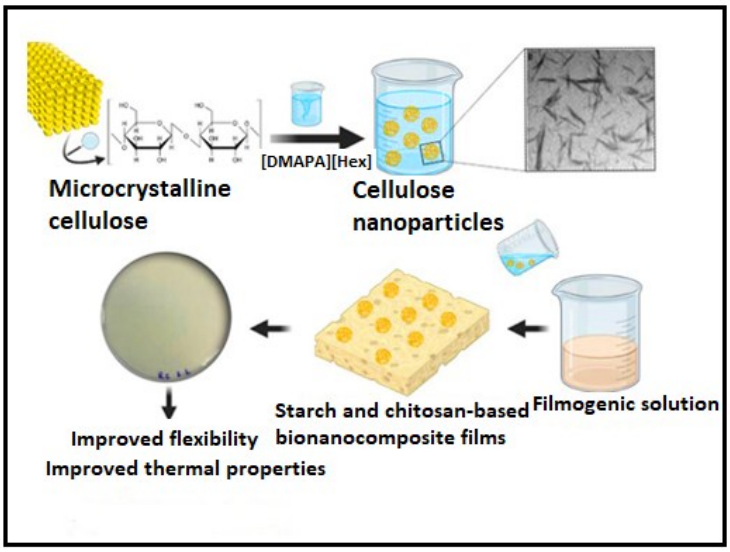

Figure 3. Schematic representation of the bionanocomposite formed by cellulose nanoparticles in an amorphous structure [27]

These structures, the molecular arrangement of cellulose and their bond structures with each other, were clearly revealed by Habibi et al. CNCs have recently been investigated as microcrystals, nanofibers or nanofibrils obtained using different mechanical and chemical processes [27]. The advantages of these fibers such as high thermal stability, high aspect ratio, relatively high strength, low density, excellent tensile strength and mechanical strength are determined by the formation of polymer-based nanocomposites. In addition to these features, surface modification processes also improve the properties of CNCs. In the study conducted by Habibi et al., surface coating processes and mechanical properties with CNCs were examined [28,29]. Cellulose derivative-based films for creating bionanocomposites show good tensile strength, acting as an effective barrier protecting the material against O_2 or CO_2 [30,31].

2.1.2 Starch-based bionanocomposites

Starch consists of granules in which polymer chains are tightly interlocked. The chains in the granules, which water cannot normally penetrate, move away from each other at high temperatures and become capable of interacting with water. Under the influence of water and temperature, the polymers in starch bind to water instead of forming hydrogen bonds with each other. As water penetrates into the starch, the order of the overall polymer structure begins to deteriorate and the granular regions become smaller and amorphous. Amylose interacting with water leaches out of the starch grain [32]. In recent years, there has been a significant increase in studies on water absorbent polymers. Starch-graft copolymers have a significant percentage in these studies. However, many of its applications are limited due to its poor mechanical properties, such as lack of barrier properties and film gloss caused by high intermolecular forces [33,34]. After extrusion, starch typically turns into a thermoplastic material with low mechanical strength and poor protection against oxygen and moisture.

Quintavalla et al., prepared hybrids of nanoclay and thermoplastic starch (TPS)[35] and when they examined their final properties, they found that the strong interaction between TPS and nanoclay improved the tensile strength and had lower water vapor permeability compared to the pure TPS matrix [36]. When the amorphous regions that enable the separation of crystalline lamellae, which are more resistant to hydrolysis, are hydrolyzed, native starch granules are formed. It can be subjected to long-term hydrolysis at temperatures below the gelatinization temperature [37].
Turmeric nanofilm (TNF) film was prepared to create bionanocomposite and change its functional properties to compare with each other. A schematic representation of the preparation steps of these films is presented in Figure 4.

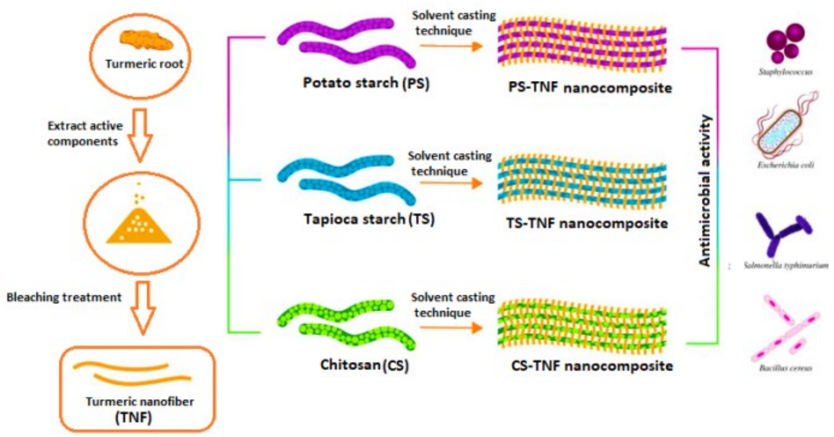

Figure 4. Schematic representation of the preparation of bionanocomposites obtained with starch-based materials and their antibacterial activities [38]

Antibacterial activities of biopolymer matrices and antibacterial performance of the prepared bionanocomposite were investigated by adding TNF to B. cereus, E. coli, S. aureus and S. typhimurium [38].
In a study by Sorrentino et al., it was observed that both the tensile strength and elongation at break of TPS increased in the presence of small amounts of sodium montmorillonite (less than 5%). Additionally, while the relative water vapor diffusion coefficient of TPS decreased, the decomposition temperature increased. Starch/clay nanocomposite films were obtained from the dispersion of montmorillonite nanoparticles using the polymer melting process technique. Mechanical characterization results showed an increase in modulus and tensile strength. The compliance of the final material sample with the actual regulations on biodegradable materials was confirmed by migration tests [39].

Pea starch/α-ZrP(PS/ZrP) nanocomposite films prepared by casting and solvent evaporation method are formed through hydrogen bonds. The structure, thermal and mechanical properties of pea starch-based films were modified and improved by incorporating αZrP [25].

3. Chitin/Chitosan based bionanocomposites

Chitosan is a partially N-deacetylated derivative of chitin. It is theoretically possible to completely remove the acetyl groups, the branched group of chitin, but n-deacetylation almost never occurs completely. Methods for obtaining chitosan are divided into chemical and enzymatic. Osuna et. al., prepared a magnetically recoverable biopolymer-based nanocatalyst via covalent immobilization of chitosan-linked 2-hydroxynaphthaldehyde Pd complex on the surface of superparamagnetic nanoparticles [40]. Liu et al., and Sriupayo et al., prepared chitin hair-crystals by acid hydrolysis of chitin [41,42].

The average sizes of bristle-crystals were calculated according to Liu et al., as 500 nm in length and 50 nm in diameter, and by Sriupayo et al., [42] as 417 nm in length and 33 nm in diameter. Liu et al., [41] incorporated chitin hair-crystals into soy protein isolate thermoplastics and the hair-crystals significantly improved not only the tensile properties (tensile strength and elastic modulus) of the matrix but also its resistance to water. Due to the hydrophilic character of chitosan, its weak mechanical properties in the presence of water and humid environments limit its use. Therefore, by adding chitosan chains to the inner layers of the silicate, chitosan layered silicate nanocomposites were created, that is, by adding $MMTNa^+$ to the chitosan matrix by increasing it to 5 wt%, its mechanical properties were improved. Surface roughness increased with the addition of a small amount of nanoclay, which improved the mechanical and thermal properties of the resulting films compared to Cloisite 30B [43].

Chitosan/tripolyphosphate nanoparticles tend to fill the empty spaces within the pores of the HPMC matrix and, when added to hydroxypropyl methylcellulose films, significantly improved the thermal, mechanical and barrier properties [44].

4. Oil-based bionanocomposites

Hydrophobic oil-based materials such as neutral lipids, fatty acids or waxes are added to biopolymer films to improve moisture barrier properties. High strength and hard composites and nanocomposites based on epoxidized soybean oil (ESO) were formed through flax fiber and organic clay reinforcement, and ESO/clay nanocomposites were observed to develop in an intercalated structure [45].

Triglyceride oil-based polymer-silver nanocomposites were obtained through electron transfer reaction and free radical polymerization processes. Due to the antibacterial effect of silver, these nanocomposite films showed good antibacterial effects against gram-positive (S. aureus), gram-negative (P. aeroginosa) and spore-form (B. subtilis) bacteria, and an inhibition zone was created. Nanocomposite samples showed better film properties than polymers other than silver nanoparticles [46].

5. Protein-based bionanocomposites

Edible films made from proteins are the most interesting films. The first reason for this is; secondly, increasing the nutritional value. It has impressive gas barrier properties compared to lipid and polysaccharide films. Therefore, the properties of edible films, especially protein films, are greatly improved by the addition of nanoclay [47].

Nanocomposite films between wheat gluten and montmorylnonite (WG/MMT) were obtained by casting method. It was confirmed by transmission electron microscopy that MMT particles were homogeneously distributed in the composite film. While the O_2 and CO_2 permeability of the films remained unchanged when the MMT content was higher than 5%, significant changes were observed in their permeability to water vapor and aroma components [48].

Nanofibers obtained from soybeans were added to polymers such as polyethylene, polyvinyl alcohol and polypropylene, and these nanofibers have diameters between 50 nm and 100 nm and micro-sized lengths. The increased stiffness of soybean nanofibers reinforced with 5% (wt) PVA is very promising. The addition of nanofibers significantly changed the tensile behavior of the composites, and the tension of the nanofibers coated with ethylene-acrylic oligomer emulsion as a dispersant increased, but the amount of nanofiber elongation decreased [49].

Plasticized protein coating was prepared on polypropylene (PP) film, and its optical and tensile properties were examined to determine the effect of protein and plasticizer type in utilizing a new composite film for food packaging applications. The film coated with the composite obtained with different plasticizers such as propylene glycol, glycerol, polyethylene glycol, sorbitol, sucrose and different proteins such as soy protein isolate, milk protein isolate and corn casein has more transparency and tensile strength and more excellent visual quality than other coated films. and has been found to have mechanical properties. Thanks to these properties, it has great potential for applications in active packaging systems [50].

6. Nanocellulose-reinforced natural rubber composite

The results of using natural rubber as a reinforcement material in bionanocomposites are shown in Figure 5. It has been shown that due to its very good flexibility, it can be used in the dispersed aqueous phase as a nanofiller reinforcement to examine the healing effects and is an excellent candidate for this system [51].

As shown in Figure 5, hydrodynamic effects occur between the filler and natural rubber.

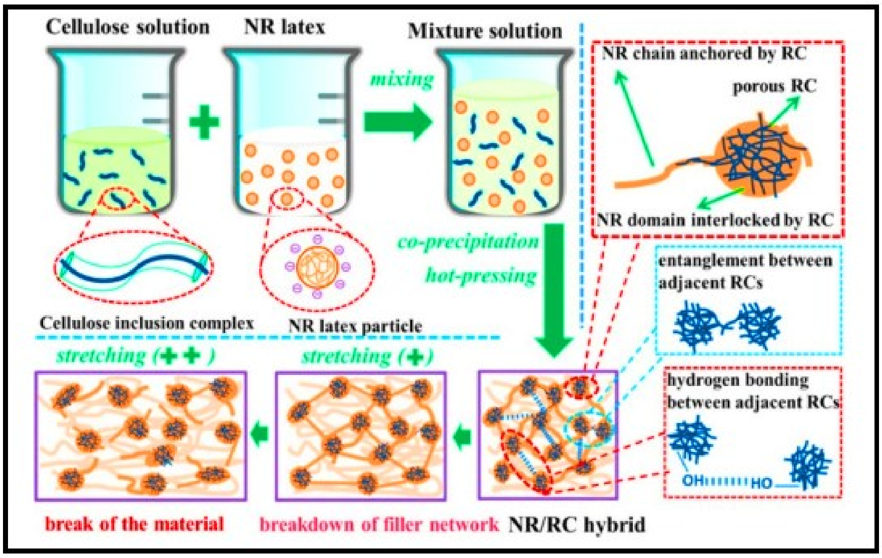

Figure 5. Schematic representation of bionanocomposite formed by cellulose of natural rubber reinforced with regenerated cellulose in alkaline urea-aqueous system [51]

Additionally, strong interactions and percolation effects contribute to stress distribution, leading to remarkable improvements in tensile strength by up to 8.5 times and spherical modulus by up to 29 times [51].

7. Conclusions

In recent years, the field of bio-based nanocomposite coating films has been developing rapidly and these materials are synthesized by various methods. This review aims to provide information about different synthesis approaches, bionanomaterials with various shapes and sizes, and the production of composite films created with them. These films are used in many different applications due to their recyclable properties such as both external factors and biodegradability. Especially in recent studies, improvement techniques to increase the quality of the materials forming this bionanocomposite coating film are being investigated.

Different bionanocomposite coating film formation approaches have improved the physicochemical, thermal and mechanical properties of the structures as well as their application areas. However, in order for biopolymers to compete with stronger and more formable commercial polymers such as polyethylene or polypropylene, different techniques must be developed to improve their functional properties. Market research supports the idea that biopolymers will play a significant role in many industrial sectors in the coming years.

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