



## Significance of Casein Fiber in Textile Technology

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### Abstract

Textile businesses have begun to adopt synthetic material alternatives in the interest of sustainability and eco-friendly manufacturing. They are either researching new natural materials, recycling industrial or agricultural waste or, in some cases, reducing the use of synthetics and chemicals. Casein fibers are milk-derived regenerated protein fibers. Recently, environmentally friendly techniques for manufacturing casein fibers have been discovered. Casein fiber offers several qualities that make it particularly valuable in textile technology due to its superior moisture absorption, smooth texture, and resistance to UV radiation. Furthermore, casein fiber has antibacterial properties. This opens up a slew of new options for the medical business. Casein fiber utilization is expected to increase soon due to its minimal environmental impact.

**Keywords:** casein fabric, antibacterial, sustainability, milk-derived, UV radiation, textile technology.

### Introduction

casein fiber is a new generation of innovative fiber and a kind of synthetic fiber made of milk casein through a bio-engineering method with biological health care function, natural and long-lasting antibacterial effect, which has got valid certification for international ecological textile certification of Oeko-Tex Standard 100 Authentication approved it in April 2004. It is most comfortable with excellent water transportation and air permeability. It is also more healthy, light, soft, and colorful being resistant to fungus, insects, and aging [1].

Skimmed milk is used to make milk protein fiber. Casein proteins derived from cow's milk are the main components of this fiber. Casein fiber includes eighteen amino acids and combines the benefits of natural and synthetic fibers. The pH of milk fiber is 6.8, which is the same as the pH of human skin. Milk protein fiber is a combination of nature, science, and technology that combines the benefits of natural and synthetic fiber. It is extremely comfy and has good water and air permeability. It is renewable and biodegradable. Casein is mostly used in technical, non-food applications such as wood adhesives, paper coating, leather finishing, food packaging, and synthetic fibers, as well as plastics for buttons, buckles, etc [1].

Casein (CAS) is a protein composed of three polypeptide chains ( $\alpha$ S1,  $\alpha$ S2, and  $\beta$ ) that represent 80% of milk composition. The chemical structure includes phosphoproteins in a random spiral configuration with polar groups (phosphate groups bound to serine units), displaying significant lipophilic characteristics[2, 3].

Its structure comprises the presence of amino acids. Amino acids have a variety of chemically reactive groups like phenolic hydroxy groups, and the presence of peptide bonds. Casein also includes amino groups, ketones, and hydrazine groups. As shown in **scheme (1)**[4], casein could only be used in combination with other additives for the production of regenerated protein fibers. The reason responsible for the white is the opaque appearance of milk in which it is combined with calcium and phosphorus as clusters of casein molecules, called micelles (CMs) due to their poor solubility properties. CMs are roughly spherical, colloidal structures with diameters ranging from 50 to 600 nm. Their broad size distribution can be described by a log-normal distribution[5]. CMs are complex association colloids composed of four natively unfolded phosphoproteins  $\alpha$ S1-,  $\alpha$ S2-,  $\beta$ -, and  $\kappa$ -casein and colloidal calcium phosphate[3, 6]. Their primary structure shows distinct hydrophilic and hydrophobic

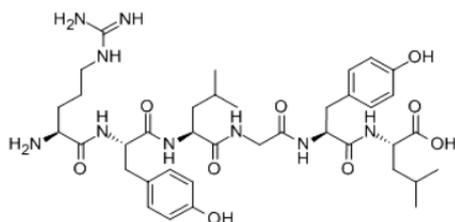
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Receive Date: 05 July 2023, Accept Date: 06 August 2023

DOI: 10.21608/JTCS.2023.221107.1212

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regions, which led to their consideration as diblock copolymers within the dual binding model of hydrophilic and hydrophobic interactions[7]. According to the model, the hydrophobic regions of the caseins associate with each other, while phosphoserine-rich spots in the hydrophilic blocks associated with colloidal calcium phosphate particles are distributed in the micelle.



**scheme 1. Structure of casein**

**Table (1)** shows that casein has a chemical composition that is very similar to wool protein. However, wool and casein fibers can be easily distinguished from each other because wool fibers have scales while regenerated casein fibers do not. Casein fibers contain less sulfur than wool fibers, which explains why they have fewer or no disulfide bonds in their fiber structure[8]. This also results in reduced fiber strength and lesser resistance to chemicals than wool fibers. The major amino acids in casein are leucine (19%), glutamic acid (22%), proline (11%), and lysine (8%)[9]. the physical properties of casein fibers with other natural protein fibers such as silk and wool. Casein fibers have similar tenacity (0.8-1.1 g/den), density (1.30 gm/cm<sup>3</sup>), and moisture regain (14%) properties as silk and wool fibers. Casein fibers have good resistance to acids but poor resistance to alkalis and ultraviolet rays[8].

**Table 1. Chemical composition of casein and wool fibers**

Elements	Casein fiber	Wool fiber
Carbon (%)	53.0	49.2
Hydrogen (%)	7.50	7.6
Oxygen (%)	23.0	23.7
Nitrogen (%)	15.0	15.9
Sulfur (%)	0.70	3.6
Phosphorous (%)	0.80	-

While Chemical Properties represent[10]:

- Effects of Acids: Casein is stable to aid moderate strength under normal conditions.
- Effects of Alkalis: Casein is sensitive to alkalis.
- Effects of Organic Solvents: Dry cleaning solvents do not cause damage.
- Insects: Casein fiber is not attacked by moth grubs to the same degree as wool.

Microorganisms: Casein fibers are attacked by mildews, particularly when moist.

- Electrical Properties: Dielectric strength of casein fibers is low.

It has been claimed that CAS fibers represent a significant challenge in manufacturing non-toxic and biodegradable materials for biomedical and textile applications[3]. Due to their resistance to UV radiation can be feasibly blended with other fibers such as cotton. In addition, it is biocompatible in contact with skin and presents antimicrobial characteristics[11]. However, the processing of CAS fibers could be compromised due to low mechanical properties, poor water resistance, and brittle texture; therefore, required to add additives to maintain the intrinsic properties and durability of the final product, such as plasticizers, binders, and crosslinker agents[12]. The primary function of plasticizers (i.e., glycerol) is the conformation of a porous 3D network structure with enhanced permeability, elasticity, and swelling properties, producing an appealing platform for specific biological applications[13]. The advantages of casein fiber Milk protein is hygienic and flexible. It is highly smooth, sheen, and delicate. It is moisture-absorbent, permeable, and heat-resistant. It is colorfast and easily dyeable and requires no special care because of its natural protein base. It can be blended with other fibers. It is a renewable, biodegradable, and eco-friendly fabric. Disadvantages of casein fiber It gets wrinkled easily after washing and needs to be ironed every time. It has a low durability though caseins can be laundered with care same as wool but they lose strength when wet and must be handled gently. It is expensive. They cannot be kept damp for any length of time due to quick mildewing[1].

#### Types of casein fiber

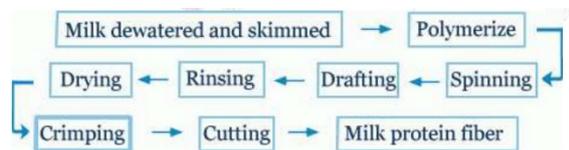
Commercial casein is generally made in two forms: Rennet Casein and Acid Casein

Acid Casein: is used for spinning textile fibers. Acid casein may be made either by precipitation from milk by mineral acids or by separation after allowing the milk to sour. The dried product is made into a solution using dilute caustic alkali. The process followed in manufacturing is similar to that of other synthetic fibers, the solution being extruded through fine holes into a coagulating bath. The chemicals used, however, are different and an essential part of the process consists of a treatment to render the casein fibers insoluble, and resistant to the various textile baths[1].

Rennet Casein: is a phosphorus-protein complex (micelles) resulting from milk coagulation by the action of enzymes (chymosin and pepsin) contained in the calf's abomasum. The micellar structure and the presence of calcium give the rennet casein its texturizing properties[14].

#### The manufacturing process of milk fibers

Milk protein fiber is dewatered and skimmed milk which is manufactured into the protein spinning fluid suitable for the wet spinning process as shown in **scheme (2)** employing new bioengineering techniques, chemically they are known as casein fibers.



**Scheme 2. Flowchart of Milk fiber production.**

### Pre-treatment

The mass-specific resistance of milk protein fiber is larger, so there—treatment before scorching is more important. After opening bales, the milk protein fibers need some water and an antistatic agent. Pretreatment and the process condition of milk protein blended fabric and elastic fabric were introduced. Owing to the strong yellowing of milk protein fiber, its bleaching process was adopted reductant bleaching or hydro peroxide + reductant bleaching according to the shade, for light shade brightening process was used.

### Manufacturing of casein fabric

Casein is obtained by the acid treatment of skimmed milk. The curdy precipitate is washed free of acid, dried, and then ground to a fine powder. 1kg casein is produced from about 35 – 37 liters of skimmed milk[10].

### Spinning

The casein made as explained above is dissolved in a caustic soda solution and allowed to stand to reach a predetermined viscosity (ripening). This solution is pumped to spinnerets and under pressure, the filaments are extruded into a coagulating solution.

coagulating solution (Bath)[10]:

2 parts Sulphuric acid

5 parts Formaldehyde

20 parts Glucose

100 parts Water

During coagulation, the filaments are stretched to some extent. During the spinning operation, the molecules are aligned to some extent but are not crystallized hence they are weak and soft if handled will break, and also water can enter the fiber and push the molecules apart hence it has got little use in textiles. To make it stronger, the casein is cross-linked which will hold the molecule together. Cross-linked casein acquires an increased resistance to the effect of water, retaining a higher degree of tensile strength and resistance to swelling[10].

### Wet Processing

- Desizing: If water-soluble sizes have been utilized, desizing is not required when using enzyme products, which are best used at pH 4.0 to 6.0.
- Scouring: Synthetic detergents should be used preferably under acidic conditions.
- Bleaching: Because casein fiber is typically white, bleaching is not normally required. Under controlled conditions, a light perborate or peroxide bleach should be applied if necessary. Under slightly acidic conditions, casein fibers retain optimum strength and minimal swelling. If alkaline processing is utilized, it must be followed by thorough washing and acidification with acetic acid.
- Dyeing: in general, casein can be dyed with dyestuffs used for wool. Acid, basic, direct, and disperse dyes are used where good washing fastness is not a prime essential. After dyeing, loose stocks and yarns may be centrifugally hydro-extracted before being dried in a conventional plant.
- Printing: Casein blend fabrics can be printed very effectively. Fabrics containing casein may be printed by block, roller, surface roller, and modified paper printer methods[10].

### Finishing

- Singeing: If singeing is needed, a light treatment with a slow burner will be sufficient.
- Crease Resistant Finish: The crease-resistant finishing agents have more choices and the environmental finishing with a good crease resist effect should be selected.
- Softening: During dyeing and after crease-resistant treatment fiber feels hard in high temperature and tension, to make fabric full and soft, softening is needed, and softening with a suitable softening agent is an effective method.
- Carbonizing: Casein will withstand carbonizing treatment when carried out with the minimum strength of sulphuric acid necessary for the effective removal of vegetable matter. Then the material should be well-rinsed and adjusted to pH 4 with sodium carbonate[10].

Casein fibers were first introduced in 1930 and since then there are several investigations for improving the mechanical properties of fibers and also pursuing eco-friendly production passways. Casein fibers production is principally possible through several methods including extruding, cross-linking, and electrospinning[15, 16].

- In the extruding process, Casein powder is dissolved in sodium hydroxide to obtain a

sufficient concentration solution. As a result, the solution was extruded into a coagulation bath containing sodium sulfate and acetic acid. Although the fibers generated have qualities similar to wool, they are more susceptible to alkali conditions and would swell in water. Furthermore, these fibers wrinkle easily and must be regulated and hung out. Aralac, called, Cargan, Tiolan, Lactofil, Fibrolane, and Silkool were brand names for casein fibers manufactured in several nations.[17].

- Due to low tensile strength and their high solubility in water, cross-linking of casein fiber is necessary[18]. Crosslinking agents like glutaraldehyde, formaldehyde, and toluene diisocyanate are used for casein crosslinking but they all have toxicity problems. Yang and Reddy produced casein fibers through wet spinning and after-treatment crosslinking carried out using citric acid. But there is still a cytotoxic effect because of using crosslinker[16].

#### **Eco-friendly Techniques for Producing Casein Fiber**

1. To overcome the toxicity of formaldehyde, there is another method to create casein fibers by cross-linking. Firstly, casein powder was mixed with water in different proportions, mixed, slowly heated up to 75 °C, and spun as well as used as a coating layer on different textile fabrics[19]. To reduce the brittleness of the resulting fibers and coating layers, different amounts of glycerin or hyaluronic acid were added to the solution. To increase the water resistance of the casein fibers and coatings, cross-linking was performed using chitosan or carboxymethyl cellulose and calcium chloride. Secondly, another chemical approach was tested, using 4 g casein powder + 50 ml cold water, 2 ml sodium hydroxide (2 mol/L) + 2 ml glycerin (50 %). This mixture was heated to 50 °C under stirring and afterward used for fiber extrusion as well as coating of different textile fabrics. the second approach seems to be more promising, the disadvantage of this method is the necessity to use sodium hydroxide. On the other hand, both approaches have shown the principle possibility to create casein fibers and coatings without using formaldehyde[19].
2. The process used to produce milk fiber is not environmentally friendly because it uses too many chemicals including some carcinogenic chemicals like formaldehyde. So a new type of milk fiber is invented which uses 100% natural and renewable resources, is called Qmilk. Here only two liters of water and 80 deg Celsius temperature is only needed. It is made of 100% organic polymer without plasticizers, solvents, and chemical cross-linkers, it is home compostable and breaks down free of residues within a few months on the environment. The manufacture of these organic fabrics, which involves heating powdered casein and adding ingredients like zinc and beeswax, is environmentally friendly. The casein is extracted from dried milk powder and then heated up in a type of meat-mincing machine with other natural ingredients. The fibers come out in strands and are then spun into yarn on a spinning machine. Qmilk fills a gap in the market that might unwittingly turn a blind eye to sustainable options. This process is considered an eco-friendly process of producing casein fiber because there is no use of formaldehyde in the processing of casein fiber. It ensures a particular level of cost efficiency and ensures a minimum of CO2 emissions[10].
3. In another study of producing casein fiber eco-friendly, casein powder was mixed with water in different proportions, stirred, slowly heated up to 75 °c, and spun by hand extrusion through nozzles of different diameters as well as used as coatings on different textile fabrics. To reduce the brittleness of the resulting fiber, different amounts of glycerine were added to the solution. This resulted in significantly different viscosities depending on the casein-water proportion. In all cases, the necessity to add the casein to heated water in small amounts during stirring emerged. Independent of the mixing ratio, the resulting fibers or textile coatings were quite hard and brittle[20]. Technical casein from bovine milk containing 90 % protein (was ground in a mortar and filtered through a sieve with a 200 μm mesh size was used. Viscous paraffin oil and glycerol (99.8 %) were added. Partly, glucose or wax for all compositions, glycerol was mixed with equal amounts of distilled water. Casein was added under stirring at 500 rpm at room temperature. The pH value of this mixture was carefully adjusted to pH 6.5, using 0.5 m NaOH since casein is soluble in water only above pH 6.4. After the casein was completely dissolved, the mixture was heated to 65 °c to decrease viscosity and allow the formation of fibers through a spinning nozzle. The mechanical properties are significantly lower than in other biopolymers, but one order of magnitude higher than foams from microcrystalline chitosan, suggesting their use in medical applications which do not necessitate high mechanical strength, e.g. In wound healing, drug delivery, or for tissue engineering. Chemical modifications, as well as temperature treatment,

resulted in significantly increased water resistance, showing a way to possible eco-friendly production methods of casein fibers without formaldehyde or cytotoxic citric acid[20].

4. Electrospinning is a simple and effective method for producing superfine and continuous fibers with a diameter of about several micrometers to a few ten nanometers and also can apply to producing nanocomposites, hollow, and core-shell fibers[21]. This method relies on concepts of electromagnetic forces, and its main idea refers to more than 70 years ago, but from the 1990s when nanotechnology gained more attention[22], electrospinning as a simple production method for nanofibers gets more attention. more than a hundred types of different polymers either in solution or melted form have been successfully spun into the superfine fibers by using this method[23]. Producing yarns from nanofibers is a new investigation area that could bring valuable properties of nanostructure polymers to the field of yarn application. Nanostructure yarn could be used in sutures and medical applications. Few methods introduced for producing nano yarns[24].

#### Merits of Casein Fabric

casein-based products are rendering different advantages that make them suitable for different applications such as plastic, color, medical and dental goods, glue, and fibers industry. casein fibers are eco-friendly, high strength, and much finer as compared to manmade fibers. Some of the gains of having milk fiber are listed below[8]:

- The graft polymerization technique makes it environmentally friendly.
- It can be regarded as a “Green Product” as no formaldehyde is present in the final product.
- Milk protein fiber is made from milk casein instead of fresh milk. The varieties of acid, reactive or cationic dyes could be used for their coloration.
- As casein fibers are bio-degradable, they can be explored in medical textiles as an aid in wounds, surgical sutures, etc.
- These fibers are more comfortable, with excellent air permeability and water transport properties.
- Some of these advantageous properties are including UV resistance
- high moisture transferring ability, good resistance against tiny insects and fungi (increasing the fabric lifetime), high moisture absorption due to the presence of amide and carboxylic groups, fast and simple colorant adsorption during the dyeing process, suitable performance in contact with the

skin especially for humans with allergenic problems due to the pH equality.

- The natural antibacterial effect of casein fibers also, makes it possible to have several hygienic features[25].

#### Good moisture – absorption, and conduction

The fiber base body does not have regular channels, which makes the fiber have as fine moisture absorption as natural fiber and better moisture conduction than synthetic fibers – milk fiber is both comfortable and permeable.

#### Excellent dyeability

The fibers can be dyed in bright colors using reactive, acid, or cationic dye technology[8].

#### Antimicrobial properties

A unique spinning solvent utilization zinc ion is used in the spinning solvent when the fibers are produced. After drying and treatment, this solvent produces zinc oxide, giving the fibers an inherent bacteriostatic property.

- They are comfortable white, fluffy, and springy.
- PH of 6.8 (same as the human skin)
- Can be blended with almost any fiber

#### Thermal and tensile properties of Casein protein fiber

The tested and analyzed thermal properties of casein protein fiber with DIG and DSC. The results showed the low hygroscopicity of this fiber, and the thermal cracking began at 262.7°C and reached its peak at 317.6°C. The tensile experiment showed that the wet tensile strength and breaking elongation of this fiber are weaker than they are in the dry state[8].

#### Drawbacks of Casein Fabric

- The main drawback is the higher expense of producing casein fiber.
- It is not hard and it has low durability.
- It gets wrinkles very easily after washing and needs to be ironed every time.
- The use of formaldehyde to make the fiber stiff, as the formaldehyde is carcinogenic.
- The coagulation bath is contagious in our environment if it is not handled in a safe way[10].

#### Fabrics Blended with Casein Protein fiber

The features of breaking strength, bursting strength, wear-resistant fastness, wrinkle flexibility, drape, pilling, property, permeability, and heat retention are analyzed and compared for milk protein fiber. The outcome demonstrates that milk protein fiber can be combined with silk, cotton, cashmere, or other natural or synthetic fibers. When milk fiber is blended with various fibers, the resulting fabric takes on some new traits from other fibers, but one

property is retained in every blend: being a healthy and environmentally friendly fiber. Among them, the cotton-blend fabric is soft, has good heat retention and permeability, and is appropriate for undergarments, socks, and other clothing textiles[1].

#### **Blend with silk and bamboo**

It is the cool, free-of-moisture, sweat-exhibitor, comfy, and aerated fiber that has the chattel of coolness. It is soft and silky with an attractive sheen. The dazzling grace is reflected in the personality of wearing this fabric[1].

#### **Blend with wool and cashmere**

It is a heat-protective fiber. Milk fiber has a type of three-dimensional arrangement ie. With permeability and humidity-resistant properties, the milk fiber when combined with wool and tepid cashmere, turns out to be an extremely warm material and it is a comfy and healthy fabric. Blended fabrics combining milk protein fiber with cashmere increase garment strength and glossiness[1].

#### **Blend with cotton and cashmere**

It is suitable for comfortable undergarments. The milk protein contains ample amino acid and moisture-protecting genes. It is competent enough of resisting microorganisms. Natural cotton and cashmere fibers also contain similar characteristics and combined with milk fiber, these traits churn together to make healthy and comfy under clothing[26].

#### **The major uses of casein fibers**

Casein fibers can be used in a variety of textile industries. They are used to create eco-friendly clothing items such as T-shirts, undergarments, sportswear, sweaters, children's clothing, eye masks, socks, and headgear. Additionally, they are employed in hygiene diaphragms, household textiles, the automotive sector, and other specialized textile applications.[8].

#### **Applications of Casein Fabric**

Caseins are largely random coil polypeptides with a high degree of molecular flexibility and the ability to form typical intermolecular interactions (hydrogen, electrostatic, and hydrophobic bonds) due to the low frequency of secondary structures (-helix and -sheets)[27]. This gives caseins good film-forming and coating properties. Caseins have a strong amphipathic character due to the balance of polar and non-polar amino acid residues, which leads them to concentrate at interfaces to create a protein film. This gives casein excellent emulsifying and stabilizing characteristics. Caseinate has good adhesion to various substrates such as wood, glass, or

paper due to their high polar group content, and this hydrophilicity makes caseinate films ideal barriers to non-polar molecules such as oxygen, carbon dioxide, and aromas[28].

Chemical modification of casein can change protein-protein interactions as well as protein-environment interactions to influence specific features. Crosslinking agents are difunctional chemicals that react with free reactive groups in protein chains to produce covalent bonds, resulting in the development of a three-dimensional network. Crosslinked materials have better physical and mechanical qualities in general. Caseinate-based polymers can be utilized in a variety of technological applications, including protective coating and foams, paper coating, adhesives, and injection molding disposables. Casein's particular characteristics important to technical applications are listed in **Table (2)**.

#### **Casein as a coating or sizing agent**

Casein serves as a binder for the coating material, which is often a mineral mixture that is deposited as a thin layer on the material's surface[29].

#### **In the Leather industry**

Polyol plasticized casein is used in the leather industry's finishing processes in combination with other components such as acrylates, phenol derivatives, pigments for colored products, or binders such as gelatine or sulfonated castor oil. The solution is applied to the leather before it is mechanically processed (brushed, ironed, glazed, etc.)[29].

#### **Casein as an adhesive**

According to Tague[30], casein was used to make cement and wood glues as early as the Egyptians and into the Middle Ages. Casein glues were created in the early nineteenth century and were mostly utilized in woodworking. Casein glues were developed at the turn of the twentieth century for the military airplane industry (plane structures were made of wood).

To date, many formulations for casein-based glues have been published or patented: most casein glues are accessible as a powder having two major elements, namely casein, and alkali, which are combined in water before use (less than 24 h).

According to the formulas, a third mixing chemical ingredient may be added: lime or copper chloride to give water-resistant glues by promoting crosslinking of casein molecules, resulting in insoluble material; dissociating agents such as ammonia or urea to limit the viscosity of the adhesive through lowered H-bonds between caseinates; sodium silicate to extend working life, tannate or alkali tannate to increase adhesion.

**Table 2. Principal technical applications of caein and caseinates**

Product	Property	Applications	Remarks/importance
Coating	Film forming ability Adhesion Technical properties	Paint	Still used in some paints
		Ink	Still used
		Paper	Still used
		Packaging	To be developed
		Leather finishing	Historical
		Textile coating	Historical
Adhesive	Good processability Bond strength Water resistance obtained by crosslinking	Water based glue	Historical Still used in some few applications
Plastic	Strength Good mechanical properties Water resistance obtained by crosslinking	Rigid plastic	Historical
		Disposable	Historical
		Fibre	Historical
		Coating Film/foil in packaging application	To be developed Laboratory scale
Surfactant	Surface tension Stability of interface	Emulsifier, detergent	Enhancement by chemical modification

Casein glues are still used in labeling adhesives, the bottling industry, interior woodworking (plywood, door panels, Formica laminates...), bonding paper, and pressure-sensitive adhesives, despite being displaced by synthetic glues in exterior woodworking[30].

#### Casein in the Paper industry

Casein's hydrophobic/hydrophilic equilibrium improves its pigment affinity, ink-binding capabilities, and adherence to diverse substrates. Casein is used in the paper industry as a size for high-quality glazed sheets or exquisite halftone illustrations. Exposure to formaldehyde vapors or dipping in strong formaldehyde solutions might result in water resistance. Crosslinking chemicals such as formaldehyde or dialdehyde bond free amino groups to proteins to form a three-dimensional network. For example, putting a layer of casein solution brushed over with a formaldehyde solution makes wallpaper water washable[29]. Coating solutions with high solid contents (china clay, kaolin, chalk...) become overly viscous, hence flow modifiers are used in specific applications to improve the casting process. Viscosity can be reduced by lowering casein molecular weight and denaturing the protein. This can be accomplished through the addition of urea, alkaline or enzymatic hydrolysis, or the use of disulfide bond-reducing agents such as mercaptoacetic acid or 2-mercaptoethanol. Pigments can be put straight into the mixture to create colored sizes and coatings. Casein's main applications in the mid-twentieth century were paper and board coating. Casein is still used in high-quality paper finishing and enamel grades of paper today. When hardened,

such casein coatings increase abrasion resistance, improve pigment binding, and make the cloth moisture-resistant. Casein size is used in the textile industry due to its film-forming and adhesive properties. Caseins mixed with acrylates form a protective layer against cotton greying. Chemically modified caseins, either grafted with acrylate esters or crosslinked, are used to finish natural (wool, cotton, and silk) and synthetic (polyester) textile fibers[29].

#### Casein in the Textile industry

Casein was first used like that of the paper industry: textile fabrics are soaked with a casein solution and cross-linked using either formaldehyde vapors or dipping into a crosslinker solution. When hardened, such casein coatings increase abrasion resistance, improve pigment binding, and make the cloth moisture-resistant. Casein size is used in the textile industry due to its film-forming and adhesive properties. Caseins mixed with acrylates form a protective layer against cotton greying. Chemically modified caseins, either grafted with acrylate esters or crosslinked, are used to finish natural (wool, cotton, and silk) and synthetic (polyester) textile fibers[29].

#### Casein-based packaging films and biomaterials

Because of their transparency, biodegradability, and high technical qualities, casein-based packaging films and biomaterials are innovative packaging materials. They do, however, have two significant disadvantages with conventional protein-based biomaterials: low mechanical characteristics and

water sensitivity. Plasticizers are added to improve workability, elasticity, and flexibility to address these difficulties. Polyols, sugars, and starches are the most commonly used plasticizers in casein-based products. The addition of polyol-type plasticizers (glycerol and sorbitol) to protein-based films reduces tensile strength while increasing ultimate elongation. Milk protein-based films outperform starch-based materials in terms of mechanical characteristics. However, when compared to synthetic films (from 150% for plasticized PVC to 500% for LDPE), the maximum elongation in protein-based samples is quite low (less than 85%), which may limit the application domains for protein-based films[31].

The second disadvantage of caseinate films is their water sensitivity and vapor permeability. It is simple to lower water sensitivity by combining the protein with oils, waxes, or acetylated monoglycerides. Casein can also be hydrophobized by the addition of hydrophobic ligands, most often alkyl groups introduced through esterification or the use of monofunctional aldehydes. Crosslinking with calcium ions, transglutaminase, -irradiation, and formaldehyde or dialdehydes can also lower water sensitivity in caseinate films. The resulting three-dimensional casein network, on the other hand, produces a stiff material with higher Young's modulus and tensile strength but lower elongation at break than plasticized casein[32].

Casein-based films are hydrophilic, making them good gas barriers to nonpolar molecules such as oxygen, carbon dioxide, and smells. Casein-based films' barrier characteristics are highly influenced by additions such as plasticizers or chemical modification. Casein-based films and biomaterials derived from caseinates have a wide range of applications, including edible films and coatings for fruits and vegetables, as well as mulching films.

#### **Casein as an additive**

Because of their amphipathic character, caseins are frequently utilized as emulsifiers or stabilizers in a variety of compositions when casein is not the primary element[29].

#### **Casein in other industrial applications**

Casein has good metal- and ion-binding capabilities, making it suitable for absorbing and recovering chromate from wastes generated during manufacturing processes such as electroplating and water purification. Casein has been utilized as a strengthening agent and a stabilizer in rubber tires. Casein and caseinate are also utilized in a variety of non-food applications, including dishwashing detergents[29].

#### **Casein-treated cotton as flame retardant**

Faheem *et al.* manages to study the effect of casein treatment on Thermo oxidative stability, flame

retardant properties, and physiological comfort of cotton fabrics. Furthermore, the short-term durability of casein-treated cotton textiles was examined against water washing and ultraviolet rays aging [33].

#### **Preparation of Casein Solution**

The aqueous suspension of casein was prepared by dissolving the casein powder in various concentrations under magnetic stirring. The suspension was subsequently heated at 80 °C and the pH was adjusted to 9. The casein suspension was later cooled to 30 °C before applying to cotton fabric. The casein suspension was applied on cotton fabric using a padder by adjusting the pressure and speed at 80 % pick up. The casein-treated samples were dried at 100 °C by air dryer. It was found that the casein protein was applied on cotton fabrics to provide an environment-friendly flame-retardant finish without loss of physiological comfort and mechanical properties. Due to the release of phosphoric acid from their macromolecules, the casein treatment favored cellulose dehydration[33]. The thermogravimetric study revealed a higher production of thermally stable char with the appearance of the local intumescent flame retarding mechanism. Flame-retardant effectiveness while maintaining acceptable physiological comfort and mechanical qualities. Finally, the persistence of flame-retardant characteristics against washing and aging was determined to be insufficient for long-term usage. However, it is predicted that in the future could improve it by combining casein, TiO<sub>2</sub> nanoparticles, and hydrophobic agents. As a result, casein treatment appears appealing for preventing second-degree burns from low-intensity heat flux events such as cigarette fires[33].

#### **Casein as antibacterial textile**

##### ***Casein as an antibacterial agent***

Hydrolysis of casein was achieved by using white casein powder, and hydrochloric acid (HCl) solution was used as the hydrolysis medium. The casein showed high efficiency as an antibacterial material; its antibacterial activity value was found to be higher than 6.4. For comparison, silver and ZnO are widely used as antibacterial agents in textile materials. So it is possible to replace some currently used antibacterial agents that are not natural, non-renewable, and harmful to the environment as well as to human health, with a product from a renewable source, while promoting the recycling of dairy waste[34].

##### ***Casein in Wound Dressing***

Casein used in hydrogels formula as casein sodium salt and acid casein were prepared via free radical polymerization of acrylamide (AAm) and coagulation of casein micelles. Two different formulations were used: formulation cs with casein

sodium salt, and formulation c with acid casein. High levels of enzymes like lysozyme and proteases were identified in infected and chronic wounds. The lysozyme concentration has been reported to be 13–24 times higher in infected wound fluid than in uninfected wounds. This enzyme, produced by the human immune system, is capable of catalyzing the hydrolysis of glycosidic bonds of mucopolysaccharides in bacterial cell walls[35]. Furthermore, it is known that lysozyme can strongly associate with  $\alpha$ -casein, and this is the reason for using lysozyme in the degradation assays. Then casein hydrogel is used as wound dressings to treat chronic wounds. Additionally, these dressings were loaded with antiseptics, aiming to ensure a more rapid and efficient wound care treatment. Two casein hydrogel formulations were tested: casein sodium salt (cs) and acid casein (c). The hydrogels presented with high swelling capacity, low degradation in simulated exudate solution, and adequate mechanical properties to be used as wound dressings. Although the properties of both hydrogels were similar, some differences were found. The hydrogel of formulation c was characterized by a lower elasticity and a higher resistance to degradation. When loaded with polyhexanide, the hydrogels were able to release the drugs in a sustained manner for, at least, 48 h. Both antiseptic-loaded materials presented good antimicrobial properties and were demonstrated to be non-irritant, highly haemocompatible, and non-cytotoxic. Three-layer dressings based on casein hydrogels (formulation c) loaded with octiset® led to an efficient healing process. Altogether, the obtained results indicate that the developed casein hydrogels appear to be promising wound dressing materials[35].

### Conclusion

Experts have been devoted to research on enhanced fibers for many years, and they have now succeeded in developing the globally advanced milk protein fiber, a milestone in the international textile business. Milk Fabrics, as the ideal conjugation of nature and technology, are so skin-friendly that they make us feel better. Scientific progress is also assisting in the creation of tomorrow's green clothing. These textiles will be the source of future advancements. It's elevating fashion to a whole new level where it's about more than just looking good. It's also about feeling comfortable. Milk protein fiber is a new product that is an excellent green, nutritious, and pleasant fiber that will undoubtedly become popular in the market.

### Conflicts of interest

There are no conflicts to declare

### Funding sources

There is no fund to declare

### Acknowledgments

The authors are gratefully-grateful to acknowledge the Faculty of Applied Arts, Benha University. Furthermore, the authors are gratefully grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

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## أهمية ألياف الكازين في تكنولوجيا النسيج

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### الملخص

بدأت شركات النسيج في اعتماد بدائل للمواد الاصطناعية لصالح الاستدامة والتصنيع الصديق للبيئة. إنهم إما يبحثون عن مواد طبيعية جديدة ، أو يعيدون تدوير النفايات الصناعية أو الزراعية ، أو في بعض الحالات ، يقللون من استخدام المواد التركيبية والمواد الكيميائية. ألياف الكازين هي ألياف بروتينية متجددة مشتقة من الحليب. في الأونة الأخيرة ، تم اكتشاف تقنيات صديقة للبيئة لتصنيع ألياف الكازين. توفر ألياف الكازين عددا من الصفات التي تجعلها ذات قيمة خاصة في تكنولوجيا النسيج نظرا لامتناسها الفائق للرطوبة وملمسها الناعم ومقاومتها للأشعة فوق البنفسجية. علاوة على ذلك ، فإن ألياف الكازين لها خصائص مضادة للبكتيريا. هذا يفتح عددا كبيرا من الخيارات الجديدة للأعمال الطبية. من المتوقع أن يزداد استخدام ألياف الكازين في المستقبل القريب بسبب الحد الأدنى من التأثير البيئي.

**الكلمات المفتاحية:** نسيج الكازين ، مضاد للبكتيريا ، الاستدامة ، مشتق من الحليب ، الأشعة فوق البنفسجية ، تكنولوجيا النسيج