547 *Egypt. J. Chem.* **Vol. 66** No. 11 pp.637-652 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Biopolymer Applications for Different Treatments of the Historical Paper Manuscripts and Leather Bindings: A Review

Gomaa Abdel-Maksoud[1,*] Hanaa El-Sayed Nasr[2], Mahmoud Saad-Edeen kassem[3]

[1]Conservation Department, Faculty of Archaeology, Cairo University, 12613 Giza, Egypt.
[2]Polymers and Pigments department, National research Centre, Egypt.
[3]Manuscript Conservation Department, Al-Azhar El-Sharif Library, Cairo, Egypt.

Abstract

Biopolymers materials exhibit outstanding potential in various conservation applications of historical paper manuscripts and bookbinding due to their flexible functionalization and various characteristics. This study aims to make an integrated study for the different application purposes of natural and synthetic biopolymers that can be used in the conservation of historical paper manuscripts and leather bindings. This study discussed the different sources of biopolymers such as plants, animals, and microorganism sources. The different applications of biopolymers such as consolidation, adhesive, retanning, cleaning, gap filling, and lubrication, antifungal were explained. The chemical composition, advantages, disadvantages, and application techniques of biopolymers were also discussed. This study showed that there are many biopolymers used in the field of treatment of paper manuscripts and leather binding. Still, the most common was polysaccharides-based materials, which were used in the bio-consolidation of paper, and this was due to the compatibility in their characteristics with paper. Essential plant oils (tea tree, lavender, and thyme oils) and Chitosan are the most common biopolymers used as antimicrobials. Japanese papers and bacterial cellulose are the most appropriate materials for consolidation and completion of the missing and fragile parts of the papers and leathers. Polyurethanes, a synthetic biomaterial, were used as a coating to protect the leather from gas pollution. Beeswax protects the leather from pollution such as sulfur dioxide. This study is considered a guide for all conservators working on paper manuscripts and leather binding.

Keywords: Historical manuscripts, leather bindings, deterioration, biopolymers, conservation, consolidation, cleaning, disinfection.

1. Introduction

Libraries and museums have huge numbers of historical manuscripts and books with leather bindings. Historical paper Manuscripts consider important records of cultural heritage in different historical periods [1, 2]. Leather bindings are designed to protect manuscripts and books from the harmful effects of the environment, In addition to the artistic values represented in calligraphy, bookbinding, decorations, pigment, etc. [3-8]. Therefore, the study of the conservation of historical paper manuscripts with leather bindings has become vital in the conservation field [9].

Historical Papers are made of plant fibers, which contain cellulose, and sometimes contain hemicelluloses and lignin [10, 11]. There are fillers, Additives, and sizing, which are usually added to writing to enhance usability such as reducing water permeability and brightness [12]. Leather is a protein structure based on the collagen fibril made of animal skins such as goats, and calves [6]. Through tanning, the skins of animals are converted into a durable material called leather [13]). Vegetable tannage was the most common tanning material used in historical leather bindings [3].

Deterioration is one of the significant problems for different collections in libraries, museums, and storage worldwide due to unsuitable storage and display conditions [14-19]. There are different types of deterioration factors in historical paper

*Corresponding author e-mail: gomaa2014@cu.edu.eg.; (Gomaa Abdel-Maksoud).
Receive Date: 27 July 2023, **Revise Date:** 21 August 2023, **Accept Date:** 04 September 2023
DOI: 10.21608/EJCHEM.2023.225573.8320

manuscripts and bookbinding. These factors are biological factors such as insects and microorganisms, and Physical and chemical factors such as relative humidity, heat, and air pollution gases [20]. They cause the appearance of some aspects of deterioration such as weakness, tears, fragility, bores, holes, stains and etc (Fig. 1), It can be added that the deterioration factors can also lead to deformation and sometimes loose ink and pigments found on historical manuscripts [21-24].

The role of conservation processes is to protect the objects from adverse chemical action, increase their chemical stability, improve the appearance of the objects, give future resistance against unappropriated conditions, improve the mechanical properties, and reveal the aesthetic values [25- 32].

Recently, with the advancement of the science of archaeological conservation, many chemicals have appeared on the market. Sometimes non-specialists apply some of these materials to historical manuscripts and other archaeological materials without prior knowledge of their chemical composition, different characteristics, advantages and disadvantages, and other critical criteria that must be taken into account at the time of application, and the end result is the deterioration of the archaeological materials, or lost them as a result of irreversible damage [33, 34].

In recent years significant advances have been made in using and developing polymeric materials for different treatments of historical manuscripts such as consolidation, adhesive, filler, coating, etc. Biopolymers are natural polymers produced and synthesized by plants or organisms [35]. Biopolymers have different specific physical, chemical, biological, biomechanical, and biodegradable properties additionally, they are natural renewable materials environmentally friendly [36]. Biopolymers can be classified differently based on different scales. Based on their origin, biopolymers can be traditionally distinguished into plants, microorganisms, and animals. [37]. Degradability can be used to classify biopolymers; they can be divided into two broad groups, namely biodegradable and non-biodegradable. Biopolymers can be classified according to the biopolymer family: polyesters, polysaccharides, Proteins, Lipids/ Surfactants Polyphenols, and Specially polymers [38, 39].

This study aims to produce an integrated study that focuses on biopolymers materials and their derivatives used in the conservation of historical paper manuscripts and leather bindings according to the main source of biopolymers.

2. Classification of biopolymers used in the treatments of the historical paper manuscripts and leather bindings

2.1. Biopolymers materials from Plants

Cellulosic materials

Cellulose is a polysaccharide $(C_6H_{10}O_5)n$ consisting of linear glucose chains [40] (Fig. 2). It is the main component of plants, such as wood, cotton, flax, etc. [38]. Derivatives of cellulose can be created by adding different functional groups. Cellulose and Cellulose derivatives are used to form a variety of fibers, powders, thickening solutions, and gels to be used in different treatments of historical paper and leather artifacts as follows:

Cellulose powder: Cellulose powder in both micro and nano size cellulose is white and has been used as an adhesive, coating, and an effective cleaning method for historical papers [41] and leather [42]. Cellulose nanocrystal was used as a consolidant with 1-3 % concentration to improve the mechanical properties of paper [29]. It was also used as a cleaner gel for removing degradation products, soils, and dust from the paper. It can minimize damages caused by water use. Cellulose Nanocrystals loaded with ZnO were used as a coating to increase the color stability of the paper and make the paper antimicrobial [43]. Cellulose powder in standard size was used with ethyl acetate to remove labels, the advantage of this method is the label could be removed in one piece, but this method required the use of moderately large amounts of solvent, and placing blotter paper over areas beside label to absorb excess solvent which results in tide lines. Cellulose powder is useful for filling small holes in paper [44].

Japanese paper and pulp: Japanese papers are one of the most common materials from Cellulose fibers used for restoring, conserving, and treating books [46] such as damaged papers, and leather binding [47]. There are three types of Japanese papers made from Japanese plants [48]. Kozo paper is made from the tree of the mulberry family. The Kozo paper has long fibers and strength which make it ideal for treating paper objects [46].

Mitsumata and Gampi papers are made from the tree of the Daphne family. Mitsumata paper has shiny fiber. Fibers of Gampi paper have a higher viscosity, luster, or shiny texture, which creates a semitransparent or translucent paper [49]. Japanese papers, known as ‘‘washi papers’’ are commonly used in paper restoration by lining old papers with them (Fig. 3 a, b) [48], closing splits and breaks [44], and re-backing the old partially degraded leather.

Fig. 1. Some aspects of deterioration for some historical rare manuscripts from Al-Azhar El-Sharif Library such as weakness, tears, fragility, bores, holes, stains, pressure-sensitive tape

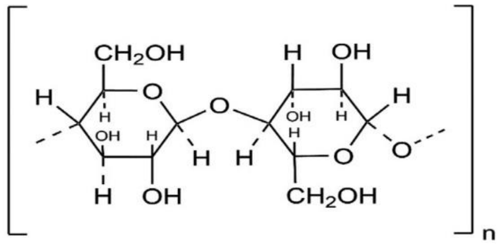

Fig. 2. Chemical structure of cellulose [45]

Japanese paper selected for this technique should be strong and long-fibred, and it should be reasonably transparent so the color of the leather will be shown through the finished repair [50]. Japanese papers can be dyed or colored to reduce the color difference between the Japanese paper and the original color of the manuscript [51].

Paper pulp is a fiber from different sources such as cotton and linen. It was used to make Hand-made paper. Handmade paper is used in the completion of the missed parts of the historical paper and leather (Fig. 3 a, b)[51, 52].

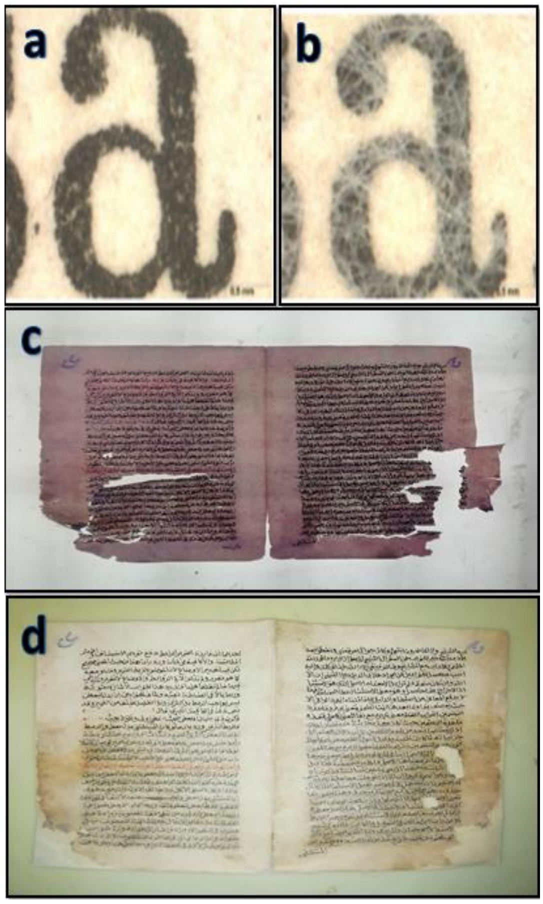

Fig. 3. The use of Japanese paper in the restoration process of historical manuscripts: (a) Unlined book paper, (b) Lined book paper with Japanese paper, (c) Under a stereoscopic microscope [48]. Missed parts from a historical manuscript from the Al-Azhar El-Sharif Library, (d) the historical manuscript after the completing the missed parts using the hand-made paper from the paper pulp.

Methylcellulose (MC): Methylcellulose is non-ionic ether created by treating cellulose fibers with methyl chloride (Fig. 4). MC was used as a Consolidation and adhesive in paper conservation. This was due to its flexibility, which improve the mechanical properties of the paper. It is considered the most widely material used in current practice in paper conservation. MC is soluble in cold water, but not in hot [53-55]. It is used in solutions of 1, 2, and 3% for consolidating; it is preferable to dilute it with alcohol to improve penetration and enhances drying time. In 0.5 % concentration, it can be used as sizing in paper pulp used in conservation, which can repel oil and grease, and enhance the fiber bonding [44]. Some disadvantages of MC are the distortions of the surface with re-application more than once on the same surface [56], It does not give enough strength if it was used alone in tear repairing. It is not really strong enough to be used as an adhesive [54]. At higher concentrations such as 5 % with acetone, it removes labels from leather, but it leaves some remains on the surface and is irreversible. It was also not effective because the methylcellulose acted as an adhesive and was difficult to remove [42]. Methylcellulose mixed with PVA (50-50) was recommended to be used for most work on book covers [57].

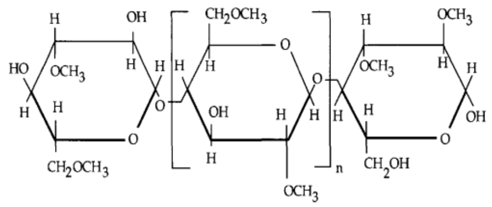

Fig. 4. Chemical structure of Methylcellulose [54]

Hydroxy propyl cellulose: Hydroxy propyl cellulose (HPC) is a non-ionic cellulose ether (Fig. 5), the trade name is (Klucel G) It is used as consolidation and adhesive for paper, bookbindings, pigments, and inks [53, 58].

It is also used in the treatment of red rot of leather, [50] it can soluble in isopropyl, methyl, or ethyl alcohol [59] and has been used successfully in water/alcohol solutions. Klucel G is a weak adhesive and can use as a size with lining to improve the adherence of the lining paper [60]. Ludwick [61]

(2012) said the disadvantages of Hydroxy propyl cellulose include breaking down when exposed to sulphuric acid, becoming rigid with time, and cracking if put under stress. Mohamed and Ali [58] (2017) said that Klucel G (3%) caused a significant change in cellulose crystallinity after artificial aging. Klucel G does not cause obvious discoloration of the treated area but sometimes can be darkened in the case of extremely degraded areas with the use of Klucel solutions in ethanol, isopropanol, and acetone. Therefore, it should test a small area with any consolidant prior to use.

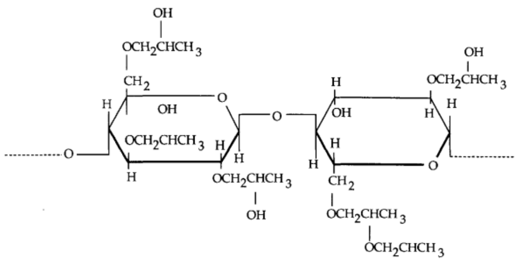

Fig. 5. Chemical structure of hydroxypropyl cellulose [54]

Sodium carboxy methyl cellulose: Sodium carboxy methyl cellulose (CMC) is anionic cellulose ether containing sodium compound (Fig. 6.). It was used as an adhesive, Consolidant, size for paper, and cleaner [53, 54] It is also considered the most wide material used in current practice in paper conservation [55]. It is soluble either in cold or hot water. CMC is a polar adhesive that makes a good bond between papers. At low concentrations such as .5%, it can enhance the fiber-to-fiber bonding which makes the paper more durable. It causes the yellowing of the paper with 2.5% concentration under artificial humid aging conditions [56]. Zaja [62] (2021) evaluated CMC loaded with Magnesium oxide in nano size to treat paper, and the results showed that papers retain a neutral pH value when it was exposed to an acidic atmosphere. It improved the tensile properties of the paper after impregnation. Darwish et al. [63] (2020) said that 0.3% of titanium oxide in nano size with 2% CMC can give an acceptable total color difference even after accelerating aging of paper. While 0.1% of zinc oxide with 2% CMC can give a great total color change for paper. CMC is used to adhere Japanese paper on torn paper [21]. It is also used with paper pulp to fill the missing parts of the leather [51].

Cellulose acetate: Cellulose acetate is a synthetic adhesive. It is the acetate ester of cellulose (Fig. 7) it was used as a Consolidant, adhesive, and coating. It is soluble in acetone, ethyl acetate, and methyl ethyl ketone. A solution of 1-2 % can improve the mechanical properties, decrease the color change resulting from accelerated aging, and increase the Crystallinity of the paper before and after the heat aging cycle. A higher concentration than 2% should be rejected because it caused changes in papers [1]. It was also used to fixing of inks or colors soluble in water. Cellulose acetate oxidizes at room temperature, and it becomes weaker and more brittle. Traces of acid catalysts from the manufacturing process make degradation increased considerably [56].

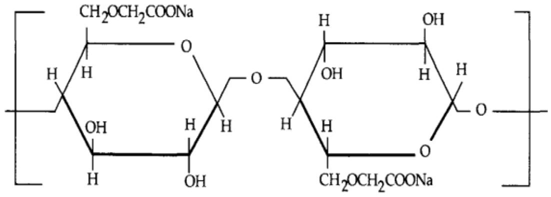

Fig. 6. Chemical structure of Carboxymethylcellulose [54]

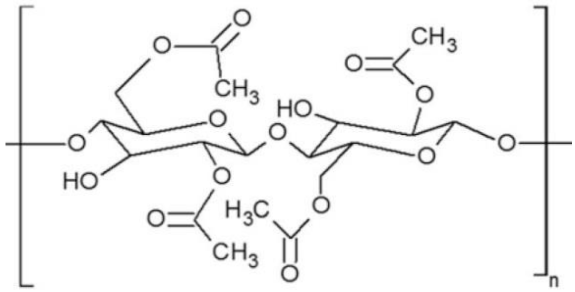

Fig. 7. Chemical structure of Cellulose acetate [65]

Ethyl hydroxyethyl cellulose (Ethulose): Ethyl hydroxyethyl cellulose (Ethulose) is non-ionic cellulose ether; it was used as an adhesive. Ethulose is soluble in water and can be diluted with an equal volume of pure ethyl alcohol. It has a matte appearance and suitable flexibility. Applying Ethulose needs to humidify the manuscript before consolidation to help penetration of the consolidant [56].

Starch: Starch is a complex polysaccharide (Fig.8) that occurs naturally in plants such as corn, wheat, and potato. The starch composition includes two basic components: amylose and amylopectin. [66]. Starch is used in the conservation of paper and leather as an adhesive [59; [64, 67].Starch dissolves in water by heating, Abdel-Maksoud and Khattab [68] (2021) said that using starch in Nano size and starch nanoparticles dissolved in water blended with CMC dissolved in water for paper improves the properties of paper. the disadvantages of starch are that applying it too thickly or dryly can stiffen the paper too much, sometimes difficult to reverse, and shrink upon drying and over time lose moisture and shrink further under conditions of low relative humidity. It could avoid this problem through preparation and use of the paste, it can determine the appropriate viscosity during the cooking process, and not dilute after that with water, as the added water would then not be fully absorbed into the starch [47].

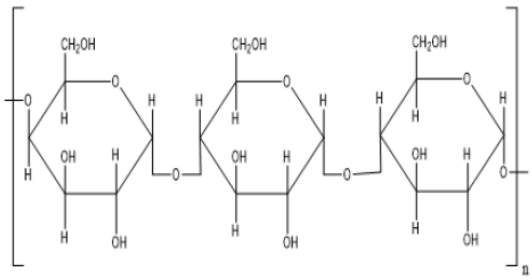

Fig.8. Chemical structure of Starch [69]

Agarose: Agarose is a neutral polysaccharide (Fig.9) that is the prime component of Agar which is derived from a species of red algae. It was used for the cleaning of superficial dirt and soiled material from paper and manuscripts, as a water-based cleaning system. This gel belongs to the category of physical gels [70]. It is readily soluble in hot water, stable in a relatively extended pH range, safe, and non-toxic [71]. Passaretti [72] (2021) said that the use of gels has become necessary when cleaning manuscripts, for which the conventional procedure of immersion in water solution was not ideal. It was also used as a solvent gel in ethanol, 1:1 acetone: ethanol, and ethyl acetate to remove pressure-sensitive labels from paper. It was also used to remove moisture-sensitive adhesives on paper artifacts. When it is used as a water-based cleaning system, it can be loaded with enzymes and surfactant solutions [73]. The gel cleaning system requires further washing with organic solvents in a free form, because the gel may leave gel residues on the surface after cleaning [70].

Carrageenans: Carrageenans are a family of sulfated galactans (Fig.10) extracted from different species of red seaweeds [74]. It was used as a consolidation for paper. Noshy et al [75] (2021) said that the three concentrations 0.5, 1, and 1.5% of carrageenan improved the mechanical properties of paper, especially the concentrations 5.0%, and referred to the improvement of mechanical properties depending on the paper type, in addition to protecting the paper from oxidation, decomposition and gave a slight color change after accelerated aging.

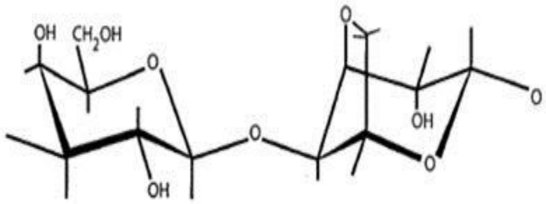

Fig. 9. Chemical structure of Agarose [73]

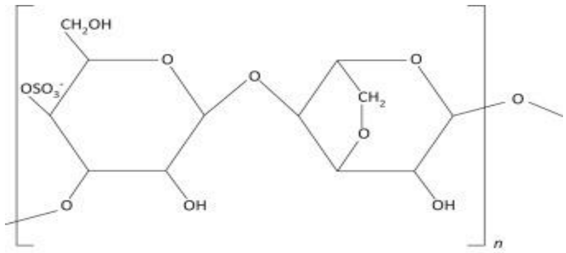

Fig.10. Chemical structure of Carrageenans [67]

Funori: Funori is a polysaccharide (Fig.11a) extracted from seaweed mucilage products of marine algae. It is a weak adhesive and was used as a consolidation for paper and pigments. It is used in aqueous solutions. The mucilage is extracted with hot water and the residual material is filtered off [64]. The use of the Funori has broadened to other circumstances as well, including cleaning, stain removal, the reduction of distortion, flattening, and successful treatments on paper and maps (Fig.11 b, c) [77]. It has a very low viscosity and can be applied repeatedly without giving bulk. It is also used as a weak adhesive in mending and facing. Its advantages as a consolidant are that it has a very low viscosity and can be applied repeatedly without giving bulk to the treated pigment and or paper, and it appears matte and is more flexible [60, 78].

- **Essential oils**

Essential oils are one of the natural products of plants and they are complex volatile compounds extracted from roots, branches, twigs, leaves, flowers, fruits, buds, and seeds [79]. The most common essential oils used as antimicrobials on the surfaces of the paper are tea tree, lavender, and thyme oils [80].

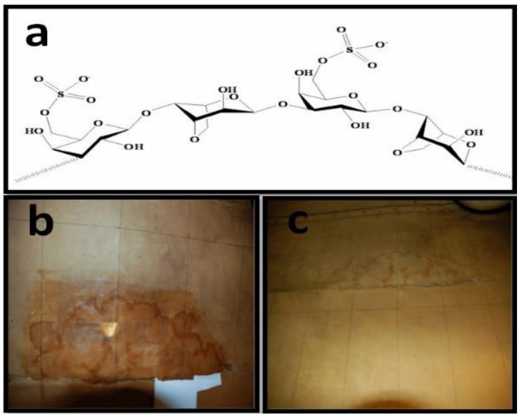

Fig.11 Chemical structure of Funori (a), reducing water stain in a map using funori before treatment (b) and after treatment (c). [77].

Tea tree oil at a low concentration (0.25%) is the most effective in inhibiting the growth of all fungi and bacteria with a slight color difference of paper, followed by lavender oil and thymus oil, which was only effective at higher concentrations of 0.5% and 1.0% with giving a color difference of paper. The tea tree oil was also added to the pulp in the leaf-casting machine to manufacture paper sheets that use to fill the missing parts in the paper of historical manuscripts. [52].

Thymol (2-Isopropyl-5-methyl phenol) is a natural product found in the essential oils of aromatic plants like thyme, oregano, or savory. It is used as an important phytochemical component against fungal activity for paper and leather. It is used mainly in its crystalline form. It can be applied by fumigation technique with amounts ranging from 1 to 90 g m3, and the time of exposure from 24 h to 3 weeks. It can also be applied directly to the paper in a 10% solution in denatured ethanol [81]. It was used with different concentrations (0.3%, 0.5%, and 0.7%) in an experimental study on paper. the fungal activity was much less with a concentration of (0.7%), while in concentrations of 0.3%, and 0.5% appear the presence of fungal activity. A mixture of 5 ml eugenol with 5 ml thymol was used for the Manufacturing of sterilized pulp sheets by adding the mixture to the tank of the leaf-casting machine which contains 40 liters of water, then adding (2 ml) eugenol and (2 ml) thymol to 10 liters of pulp solution for making pulp sheets. It is also added to the consolidation materials of paper and leather because these materials should be sterilized to avoid any fungal and bacterial infection [82]. There are some studies that referred to changes in the physical-chemical characteristics of filter paper samples treated with thymol, while polymerization degree and pH) remained alike and there was practically no yellowing. On the other side, Thymol vapors caused the yellowing of paper prints [81].

Linseed oil is used in the treatment of historical leathers. Hassan [83] (2016) evaluated the effect of linseed oil and glycerine emulsion for the surface treatment of archaeological leather samples, which were taken from a historical leather book cover. the emulsion of a linseed oil composed of (20 ml linseed oil, 7 g glycerine, 5 g cetyl alcohol, 5 g stearic acid, 100 ml distilled water) and said that the emulsion led to improvements in pH values by reducing the acidity of the treated leather, also improving mechanical properties.

2.2. Biopolymer materials from Microorganisms and their applications

Levan (Hlevan): Levan is a fructose-based homo polysaccharide, a fructan that is mainly composed of β-D-fructofuranose residues linked by β-(2-6) glycosidic bonds (Fig.12). Levan is produced by miscellaneous microorganisms such as Acetobacter, Bacillus, Erwinia, Gluconobacter, and Microbacterium, [84]. It was used as an adhesive and consolidation for paper; it dissolves in water and has a unique combination of properties such as strong adhesiveness, very low intrinsic viscosity, and high biocompatibility. Saglam et al [34] (2020) evaluated 7% and 10% (w/v) of levan solutions in distilled water and compared them with starch; Adhesive-applied samples were initially prepared by the application of different historical recipes of sizing and ink. Then, they underwent accelerated thermal aging. They said that results showed that there is a color change for all samples after aging, but it is more pronounced for some samples with Hlevan. Hlevan is slightly less acidic than starch in all cases and acted as a plasticizer for a kind of sizing material.

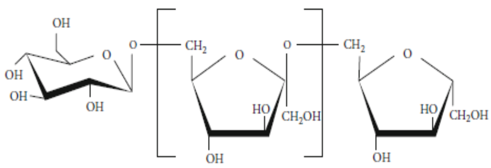

Fig.12.Chemical structure of levan [34]

Bacterial cellulose: Cellulose as mentioned above is a polysaccharide extracted traditionally from the plant, there is also bacterial cellulose which is produced by certain bacterial species by fermentation, and it is a very pure cellulose product with unique properties. Bacterial cellulose is a water-insoluble material [38]. It was used as a reinforcing or lining for damaged papers such as Japanese paper [85]. Santos et al. [48] (2015) studied the use of bacterial cellulose as reinforcing or lining for damaged papers and said that it can improve the mechanical properties of paper, and the legibility of the texts is much better when papers are lined with bacterial cellulose (Fig.13) compared with Japanese paper, the legibility of the texts is very important with the documents to restore their high historical value. Bacterial cellulose provides adequate protection for the paper to avoid the effects of possible degradation agents and protect the documents from the most important agents in paper degradation, which are humidity and atmospheric pollutants [48].

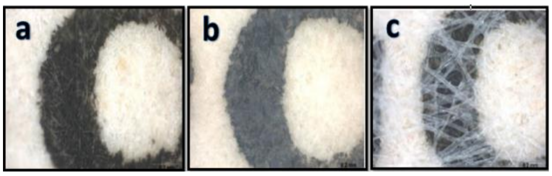

Fig. 13. Unlined and lined book paper with bacterial cellulose and Japanese paper: (a) Unlined book paper, (b) linked book paper with bacterial cellulose, (c) Linked book paper with Japanese paper under an optical microscope [48]

Gellan gum: Gellan gum is a linear anionic heteropolysaccharide produced by Pseudomonas elodea, it is biodegradable, and its structure is based on a tetrasaccharide repeating unit composed of (1-3)-β D-glucose, (1-4)-β-D-glucuronic acid, (1-4)-β-D-glucose, and (1-4)-α-L-rhamnose as the backbone (Fig.14) [73]. Gellan gum was used for cleaning superficial dirt, soiled materials, degradation products, and dust from manuscripts [41, 86], in addition to bleaching, or deacidification of paper. [73]. It also belongs to the category of physical cleaning gels. Gellan hydrogel-immobilized α-amylases were used for removing starch paste from ancient paper documents [87]. It was used with antifungals such as titanium dioxide nanoparticles to remove the foxing and mold stains. It is also used with enzymes to remove some adhesives. It was used as a solvent gel with an organic solvent such as methanol, or ethanol [73, 86]. The use of gelan gum sometimes leaves gel residues on the surface of the paper after cleaning; therefore it is requiring further washing of paper with organic solvents in a free form [70].

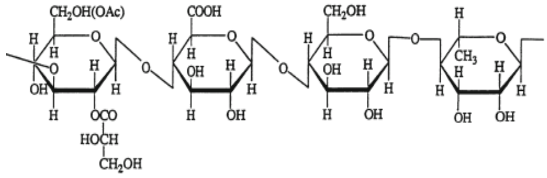

Fig. 14 Chemical structure of gellan gum [45]

2.3. Biopolymers materials from animals and their applications

Chitosan: Chitosan is a linear structure composed of randomly distributed β-(1,4)-linked d-glucosamine and N-acetyl-d-glucosamine monomers [39] (Fig. 15). Chitosan which is naturally available in noncommercial quantities from insect exoskeletons is derived from the base-catalyzed chemical deacetylation of chitin [88]. Chitosan had been used to improve the fungal resistance of paper but decreased the paper's strength, whiteness, and pH values [55, 89]. Abdel-Maksoud and Al-Saad [1] (2009) evaluated chitosan with different concentrations (0.5, 1, 1.5, 2%) to treat paper and they said that the best concentration was 1%, it can improve the properties of paper such as the crystallinity of cellulose fibers, mechanical properties. They also said that the 1.5 and 2% concentrations should be rejected for the treatment of paper. Ardelean [21] (2009) evaluated carboxymethyl-chitosan as a consolidation for a fragile paper and said that it improves the tensile, and bursting strength and maintains the same water suction capacity, and acted as an antifungal. Ciolacu [55] (2017) evaluated three water-soluble chitosan derivatives; carboxymethyl- chitosan (CCh), alkyl-chitosan (ACh), and quaternary-chitosan (QCh) as a coating for paper conservation. The results showed strength improvement for the CCh/QCh coatings, the ACh had little effect on the strength but developed an effective barrier to water. CCh or QCh with ACh provided the best relationship between the strength and barrier properties and proved their effectiveness as strengthening/protective materials in the treatment of naturally aged paper.

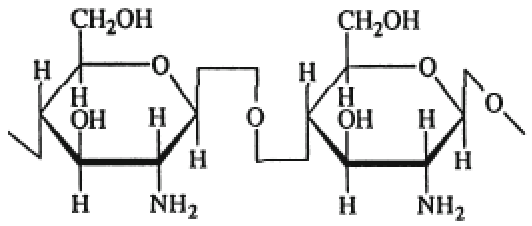

Fig. 15 Chemical structure of chitosan [45]

Animal Glue: Animal glue is a protein, which was used for centuries by bookbinders and restorers as an adhesive, and it can be reversed with water. The glue comes in cake or granular form; it is diluted with water and then heated in an electric pot. The glue must be heated on a regular basis and water added from time to time to maintain the right consistency to avoid mold and decay and it must not be allowed to burn. Now because of the characteristics related to their preparation, it is no longer used as an adhesive for bookbinding in most libraries [44].

Gelatin: Gelatin is a protein that contains 18 amino acids (fig16) obtained from animal skin [90]. In the past, papers were sized with gelatin which coats the paper and also penetrates into the sheets. It was also used in conservation as a consolidant. It was used and dissolved in warm water with percentages as low as 0.5 or 1%. It can be diluted successfully with isopropyl alcohol up to percentages of 75:25 alcohol: water. It can be effective in setting down flakes of leather to reattach or softening the flake prior to reattachment [50]. It was used as a binder with filler mixed with cellulose powder, acacia arabica, and clay nanoparticles to fill small holes in the bookbindings [91]. It was used as re-sizing on iron gall ink corrosion on a fiber that was previously gelatin-sized, gelatin delays the degradation of cellulose as Iron is chelated by gelatin that forms a gel during cooling and retaining iron, thus the concentration of iron inside the fiber is lowered [12]. There are some disadvantages to gelatin when it is used for consolidation such as: supporting microorganism growth in high relative humidity, attractive to insects, becoming brittle under excessively dry conditions and it is degraded by ultra-violet light and yellows with age, additionally, the low grades of gelatin contain metallic salts and other impurities ([44]. onally, the low grades of gelatin contain metallic salts and other impurities.

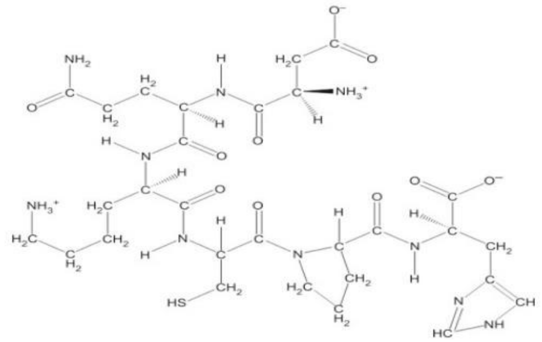

Fig.16. Chemical structure of gelatin polypeptide [89]

Skin and parchment glues: Skin and parchment glues are protein materials primarily composed of collagen derived from cattle and sheep skins depending on the material from which they are made; they may contain contaminants from skin preservatives or tanning agents. The skin and parchment glues have the highest strength of animal glues. Acid hydrolysis or alkaline hydrolysis can be the method employed to break down or denature the collagen molecules and allow the protein to be brought into a colloidal suspension. Glue is soluble in a few solvents at room temperature but will swell in cold water to form a gel and can be diluted using water and isopropyl alcohol which goes in more slowly, penetrates more deeply, takes longer to evaporate, and allows more of the glue to be absorbed before it sets. The pH of hide glue is 6.0-7.5. Skin and parchment glues are used in the manufacture of bookbinding, and gummed tapes [50] and can be quite effective in consolidating flaking or powdery pigments in historical manuscripts.

Bone glue: Bone glues are derived from the bones, sinew, and cartilage of animals such as cattle. Bone glues are considered inferior to skin and parchment glues [92]. Typically the pH is 5.8 - 6.3. Bone glues are commercially used as cartons and box adhesives [50]. Bone glues are produced and sold as coarse powders, pearls, cubes, and cakes or plates [93].

Fish glue: Fish glue is a protein material extracted from fish. There are two types of fish glue; the first type is known as isinglass which is made almost entirely from the swim bladders of fish and considers the highest quality such as sturgeon glue, which is extracted from the swim bladders of the sturgeon (*Acipenseridae sp.*). The second type of fish glue is extracted from heads, skins, and skeletal waste from different types of fish, and considers a much less expensive product. Fish glues were used as a size for parchment and as a medium or binder for painting materials. It was used in restoration as an adhesive and consolidate for manuscripts [93, 50]. Sturgeon glue (Isinglass) dissolves in hot water and then can be diluted with isopropyl alcohol when cooled to room temperature. The disadvantage of Sturgeon glue is that it is very responsive to moisture and can become dry and embrittled in conditions of storage with low relative humidity [56].

Lanolin and Beeswax: Lanolin is shelf Neats foot oil and a pale yellow fatty oil extracted from raw wool, (Lanolin) and made by boiling the skin, the feet (excluding hooves), and shinbones from cattle [94]. It is the most common component of dressing material for leather binding; it is useful for its emulsifying properties, and penetrating power. Beeswax or vegetable wax was sometimes added to boost the body of the lanolin. It can lubricate the fibers of the leather and seal them against atmospheric pollutants, in addition to preventing it from drying up and cracking [95]. Beeswax is a long-chain fatty acid and long-chain monovalent alcohol extracted from Bees. The beeswax acts as a polish, it also prevents air pollutants to enter the leather as shown in (Fig. 17) [31], on the downside it disturbs the moisture balance, risking drying because it closes off the pores of the leather [94]. The most common dressing mixture is Pliantine dressing (British Museum Leather Dressing, BML) consists of lanolin, beeswax, cedarwood oil, and diethyl ether or hexane, the beeswax is sometimes omitted, and the cedar wood oil acts as a fungicide. It should be used in dressings sparingly to obtain satisfactory results because it can considerably darken the leather, and over-applying leaves the surface tacky [61].

Enzymes: Enzymes are proteins produced by living cells composed mainly of the twenty amino acids [96] alpha-amylase, protease, and lipase, are the common types of enzymes used in the conservation of works on paper to assist in the breakdown of adhesive residues from previous restorations or to facilitate the removal of secondary supports such as linings or mounts, and stain removal [7]. The principal advantages of these enzymes are their specificity and efficiency in catalyzing hydrolytic cleavage of polymers such as proteins, polysaccharides, and lipids [97]. Therefore, fragile documents would be separated easily with less physical damage. Their speed of action and their potential for use depend, however, on two factors that may not be well-defined. These are the activity of the enzyme and the precise composition of the manuscript. Performance is highly dependent on pH and temperature and is different for each enzyme. Amylases are used for starch adhesives and proteases for protein-based adhesives. Animal glues, fish glues, bone glues, and casein glue are all protein-based adhesives that can be broken down by the use of enzymes [98, 99].

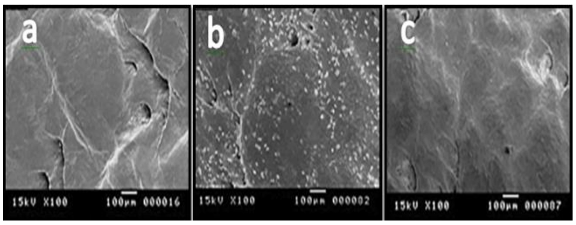

Fig. 17. The surface morphology by SEM for: (a) Untreated leather, (b) Aged untreated leather, (c) Treated sample with a mixture of beeswax and paraffin wax after 5 weeks at 50 ºC, 85% relative humidity, and a sulfur dioxide at a concentration of 500 ppm. [31]

2.4. Biopolymers based on Synthetic materials and their applications

Polyurethane: Polyurethanes (PU) are prepared by the polycondensation reaction of disocyanates with alcohols and/or amines [100] (fig 18). It was used as a retannage material for leather [101], and as a consolidated material for paper [102]. PU can endow treated leather with excellent comprehensive properties. It was used as a retannage material for leather. Because its molecular chains are similar to those of the leather collagen peptide chain. it can endow the treated leather with excellent comprehensive properties such as enhancing the thermal stability of the treated leather fibers, in addition, to improving the physical and mechanical properties of the treated final leather fiber[101]. PU can protect the leather from air pollution gases because it acts as a coating film on the surface of the leather preventing the leather from absorbing gases such as sulfur dioxide.

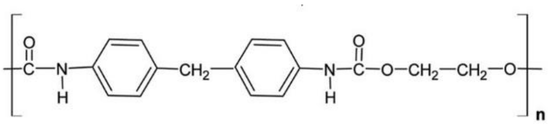

Fig.18. Chemical structure of Polyurethanes [100]

3. Conclusion

Sometimes, historical manuscripts and leather bindings in museums, libraries, archives, and storehouses suffer from deterioration caused by improper environmental conditions. Accordingly, some aspects of deterioration appeared such as darkness, stains derived from different sources, missed parts, weakness, and fragility. The use of biopolymers in the field of conservation has become vital, especially in the field of manuscripts and leather binding conservation. This is due to the multiple purposes of using these polymers in the conservation field. It can be added that the unique and varied properties of biopolymers such as biocompatibility, reversibility, and similarity in chemical properties with paper and leather offer significant benefits that increase their use in the applications of preservation of historical manuscripts. Recent research has demonstrated that using natural biopolymers only or in combination with synthetic biopolymers can make great development in this field.

It is observed that among biopolymers polysaccharides-based materials are considered the most appropriate consolidants and compatible materials in their physiochemical properties with paper manuscripts. Polysaccharides are extracted from different sources such as plants, seaweeds, microorganisms, etc.

Essential plant oils such as tea tree and lavender oils are the most common biopolymers used as antimicrobials. Chitosan from animal sources also has antifungal properties. fatty oils and fatty acids from animal sources such as lanolin and beeswax are the most common biopolymer materials used as dressing materials for leather bindings.

Japanese papers from cellulose fibbers and bacterial cellulose are the most appropriate for completing the missing parts of the paper and leather. Agarose derivative from red algae and gellan gum derivative from Microorganisms were used as physical cleaning gels for cleaning superficial dirt, soiled materials, degradation products, and dust from manuscripts. Alpha-amylase, protease, and lipase are the common types of enzymes used to assist in the breakdown of adhesive residues from previous restorations. Polyurethanes, as a synthetic biomaterial, were used as a coating to protect the leather from gas pollution.

Referances

1. Abdel-Maksoud, G., Al-Saad, Z., Evaluation of cellulose acetate and chitosan used for the treatment of historical papers, Mediterr. Archaeol. Ar-chaeom, 9 (1), 2009: 69-87.
2. Fouda, A., Abdel-Nasser, M., Eid, A. M., Hassan, S., Abdel-Nasser, A., Alharbi, N. K., AlRokban, A. H., Abdel-Maksoud, G., An Eco-friendly approach utilizing green synthesized titanium dioxide nanoparticles for leather conservation against a fungal strain, Penicillium expansum AL1, involved in the biodeterioration of a historical manuscript, Biology, 12 (1025), 2023: 1-26.
3. Abdel-Maksoud, G., Analytical techniques used for the evaluation of a 19th century quranic manuscript conditions, Measurement, 44(9), 2011: 1606-1617.
4. Odabas, Z.Y., Odabaş, H., Polat, C., The Ottoman Manuscripts and the Projects of Digitizing the Manuscripts in Turkey, Globalization and the Management of Information Recources, Sofia, Bulgaria, 2008:1-10.
5. Hassan, R. R. A., Behavior of Archeological Paper after Cleaning by Organic Solvents Under Heat Accelerated Ageing, Mediterranean Archaeology and Archaeometry, 15(3), 2015:141–50.
6. Kouchakzaei, A., Mehrabad, M., Evaluation of iron on structural deterioration of chrome leather in buried conditions, based on degradation indices in FTIR spectra, Journal of Research on Archaeometry, 5(2), 2019: 91-104.
7. Abdel-Nasser, M., Abdel-Maksoud, G., , Abdel-Aziz, M. S., Darwish, S. S., Hamed, A. A., Youssef, A.M., Evaluation of the efficiency of nanoparticles for increasing α-amylase enzyme activity for removing starch stain from paper artifacts, Journal of Cultural Heritage,. 53C, 2022: 14-23.
8. Abdel-Nasser; M., Abdel-Maksoud, G., Eid, A. M., Hassan, S., Abdel-Nasser, A. Alharbi, M., Elkelish, A., Fouda, A., Antifungal activity of cell-free filtrate of probiotic bacteria Lactobacillus rhamnosus ATCC-7469 against fungal strains isolated from a historical manuscript, Microorganisms 11, 1104, 2023 : 1-23.
9. Duran A, Perez-Rodriguez JL, Espejo T, Franquelo ML, Castaing J, Walter P. Characterization of illuminated manuscripts by laboratory-made portable XRD and micro-XRD systems. Anal Bioanal Chem, 395(7), 2009: 1997-2004.
10. Salim, E., Abdel-Hamied, M., Salim, S., Gamal, S., Mohamed, S., Galal, F., Tarek, F. Hassan, R. A., Ali, H., Reduction of borax/agar-based gel residues used to neutralize acidity of a historical manuscript with use of different paper barriers: artificial ageing results, Bioresources, 15 (3), 2020: 6576-6599.
11. Abdel-Maksoud, G., Nasr, H., Samaha, S.H. and Kassem, M.S.E., Analytical methods for evaluating the state of preservation of a historical manuscript dating back to the 15th century AD in Al-Azhar Library-Egypt", Pigment & Resin Technology, Vol.

ahead-of-print No. ahead-of-print. https://doi.org/10.1108/PRT-02-2023-0018.
12. Gimat, A., Schoeder, S., Thoury, M., Dupont. A, Impact of the Paper Degradation State and Constituents on Its Behavior During and After X-ray Exposure, 2021:1-34
13. Vyskočilova, G., Carşote, C., Ševčik, R. and et al, Burial-induced deterioration in leather: a FTIR-ATR, DSC, TG/DTG, MHT and SEM study, Heritage Science, 10 (7), 2022: 1-14.
14. Abdel-Maksoud, G., Marcinkowska, E., Effect of artificial heat ageing on the humidity sorption of parchment and leathers compared with archae-ological samples, J. Soc. Leather Technol. Chem. 84 (5), 2000: 219-222.
15. Gandhi, I.R., Ponnavaikko, V., A Study towards Ancient and Modern Preservation Techniques of Historical Manuscripts against Deterioration, International Journal of Emerging Trends & Technology in Computer Science (IJETTCS), 6 (4), 2017: 8-10.
16. Saada, N. S., Abdel-Maksoud, G., Abd El-Aziz, M. S., Youssef, A. M., Evaluation and utilization of lemongrass oil nanoemulsion for disinfection of documentary heritage based on parchment, Biocatalysis and Agricultural Biotechnology, 29, 2020 101839.
17. Abdel-Maksoud, G., Abdel-Hamied,, M., El-Shemy,H. A., Analytical techniques used for condition assessment of a late period mummy, Journal of Cultural Heritage, 48, 2021: 83-92.
18. Abdel-Maksoud, G., Awad, H., Rashed, U. M., Elnagar, Kh., Preliminary study for the evaluation of a pulsed coaxial plasma gun for removal of iron rust stain from bone artifacts, Journal of Cultural Heritage, 55, 2022: 128-137.
19. Fouda, A., Abdel-Nasser, M., Khalil, A. M. A., 1 , Hassan, S. E., Abdel-Maksoud, G., Investigate the role of fungal communities associated with a historical manuscript from the 17th century in biodegradation, npj Materials Degradation, 88, 2022: 1-13.
20. Ismail, M., Abdel-Maksoud, G., The restoration of mummies in Ancient Egypt, Egyptian Journal of Chemistry, Vol. 66, No. 11, 2023, pp. 163 – 175.
21. Ardelean, R., Nicu, R., Asandei,D., Bobu, E., Carboxymethyl-chitosan as consolidation agent for old documents on paper support, European journal of science and theology, 5(4), 2009: 67-75.
22. Abdel-Maksoud, G., Abdel-Nasser, M., Hassan, S. EEid, A. M., Abdel-Nasser, A., Fouda, A., Biosynthesis of titanium dioxide nanoparticles using probiotic bacterial strain, Lactobacillus rhamnosus, and evaluate of their biocompatibility and antifungal activity, Biomass Conversion and Biorefnery, 2023, pp. 1-23.
23. Abdel-Maksoud, G., Abdel-Nasser; M., Hassan, S., ; Eid, A. M., Abdel-Nasser, A., Fouda, A., Green synthesis of magnesium oxide nanoparticles using probiotic strain Lactobacillus gasseri and their activity against fungal strains isolated from historical manuscripts, Egyptian Journal of Chemistry, Vol. 66, No. 10, 2023, pp. 179 – 189.
24. Fistos, T., Fierascu, I., Fierascu, R.C., Recent Developments in the Application of Inorganic Nanomaterials and Nanosystems for the Protection of Cultural Heritage Organic Artifacts, Nanomaterials, *12*(2), 2022: 207.
25. Abdel-Maksoud, G., Evaluation of wax or oil/fungicide formulations for preservation of vegetable-tanned leather artifacts, Journal of the Society of Leather Technologists and Chemists, 90, (2), 2006: 58-67.
26. Abdel-Maksoud, G., Study of cleaning materials and methods for stains on parchment, Journal of the Society of Leather Technologists and Chemists (JSLTC), 90(4), 2006: 146-154.
27. Abdel-Maksoud, G., Al-Shazly, E.E.A., El-Amin, A., Damage caused by insects during mummification process: An experimental study, Archaeological and Anthropological Sciences, 3(3), 2011: 291-308.
28. Abdel-Maksoud, G., El-Sayed, A., Analysis of archaeological bones from different sites in Egypt by a multiple techniques (XRD, EDX, FTIR), Mediterranean Archaeology and Archaeometry, 16(2), 2016: 149-158.
29. Operamolla, A., Mazzuca, C., Capodieci, L., Benedetto, F., Severini, L., Titubante, M., Martinelli, A., Castelvetro,V., Micheli, L., Toward a Reversible Consolidation of Paper Materials Using Cellulose Nanocrystals, ACS Appl. Mater. Interfaces, 13(37), 2021: 44972–44982.
30. Abdel-Maksoud, G., Ghozy, H., Ezzat, R., Helmy, M., Elsaka, M., Gamal, M., Mohamed, W. S., Evaluation of the efficiency of sodium alginate for the consolidation of archeological bones, Egyptian Journal of Chemistry, 66(2), 2023: 357-366.
31. Abdel-Maksoud, G., El-Nagar, K. Kassem, M.SE., Evaluation of Different Coatings in Protecting Leather Artifacts in Museums and Libraries from Air Pollution. MAPAN (2023). https://doi.org/10.1007/s12647-023-00658-6.

32. Abdel-Maksoud, G., Abdel-Hamied, M., Abdel-hafez, A.A.M, Evaluation of the condition of a Mamluk illuminated paper manuscript at Al-Azhar Library, Egypt, Pigment & Resin Technology, 52 (1), 2023: 49-59.
33. Șendrea, C., Miu, L., Crudu, M Badea, E., the influence of new preservation products on vegetable tanned leather for heritage object restoration, Leather and Footwear Journal, 17 (1), 2017:9 -16. 32
34. Saglam. R.O., Genc. S., Oner. E.T., Evaluation of the Potential Use of Levan Polysaccharide in Paper Conservation, Advances in Polymer Technology, (2020) 2020. 33
35. Olivia. M., Jingga. H., Toni. N., Wibisono. G, Biopolymers to improve physical properties and leaching characteristics of mortar and concrete: A review, *IOP Conf. Ser.: Mater. Sci. Eng,* 345, 2018: 012028. 34
36. Hassan. M. E., Bai. J., Dou. D., Biopolymers; Definition, Classification and Applications, Egyptian Journal of Chemistry, 62(9), 2019: 1725 -1737.
37. Niaounakis. M., biopolymers: reuse, recycling, and disposal, handbook series, plastics design library (PDL), United States of America, 1st Edition, 2013.
38. U.S. Congress, Office of Technology Assessment, Biopolymers: Making Materials Nature’s Way-Background Paper, OTA-BP-E-102,Washington, DC: U.S. Government Printing Office, 1993.
39. Kee. Y., Lee. D., Biopolymer Micro particles Prepared by Microfluidics for Biomedical Applications, Nano-Micro Small Journal, 16(9) 2020: e1903736.
40. Gilbert, R. D.. Kadla, J. F., Polysaccharides – Cellulose, Chapter 3, Biopolymers from Renewable Resources, D. L. Kaplan (Ed.) Springer-Verlag Berlin Heidelberg New York, 1998: 47-95.
41. Zidan, Y., El-Shafei. A., Noshy. N., Salim. E., A Comparative Study To Evaluate Conventional And Nonconventional Cleaning Treatments Of Cellulosic Paper Supports, Mediterranean Archaeology and Archaeometry, 17(3), 2017: 337-353.
42. O'Hern, R., Pearlstein. E, Label removal from deteriorated leather-bound books, Journal of the Institute of Conservation, 36 (2), 2013: 109-124.
43. Jia, M., Zhang, X., Weng, J., Zhang, J., Zhang, M., Protective Coating of PaperWorks: ZnO/Cellulose Nanocrystal Composites and Analytical Characterization. J. Cult. Herit, 38, 2019: 64-74.
44. Kathpalia, y. p., Conservation and restoration of archive materials, Documentation, libraries and archives: studies and research, Enesco, Paris, 1973: 48-78.
45. Kaplan, D. L., Introduction to Biopolymers from Renewable Resources, CHAPTER 1 Chapter 3, Biopolymers from Renewable Resources, D. L. Kaplan (Ed.) Springer-Verlag Berlin Heidelberg New York 1998: 1-26.
46. Prestowitz, B., katayama, Y., Washi: Understanding Japanese Paper as a Material of Culture and Conservation, The Book and Paper Group Annual, 37, 2018: 77-91.
47. Anderson, P., , J. S., primanis, O., john, k., Use of Adhesives on Leather Discussion, The Book and Paper Group 22, 2003: 99-104.
48. Santos, S.M., Carbajo, J.M., Gómez, Quintana, E., Ladero, M., Villar, J., Use of bacterial cellulose in degraded paper restoration. Part II: application on real samples. J Mater Sci, 51, 2016:1553–1561.
49. Takahashi, K, "Japanese Paper and Paper Conservation, Honor’s College Freeman Research Journal, 17, 2019.
50. Kite, M., Thomson, R., Conservation of Leather and Related Materials. 1st ed. Jordan Hill: Taylor & Francis Group, Elsevier Ltd, 2006: 1-363.
51. Hsieh, P., Sleem E., Aish. S., Merva Zaki. M., Abdel- Hamied, M., Rushdy A., ET AL Conservation methods of a full leather-covered medieval rare book collected in Ain Shams University Central Library entitled, Bulletin of the Center Papyrological Studies 37 (1), 2020: 431-460.
52. Noshy, W., Osman, E. and Mansour, M., An investigation of the biological fungicidal activity of some essential oils used as preservatives for a 19th century Egyptian Coptic cellulosic manuscript”, International Journal of Conservation Science, 7 (1), 2016: 41-56.
53. Steger. S., Eggert. G., Horn. W., Krekel. C., Are cellulose ethers safe for the conservation of artwork? New insights in their VOC activity by means of Oddy testing, Heritage Science 10(53) (2022).
54. Feller, R., Wilt, M., Evaluation of cellulose ethers for conservation, Paul Getty Trust, Getty Conservation Institute, United States of America, Second printing, 1993.
55. Ciolacu, F., Nicu, R., Balan, T., Bobu, E., Chitosan Derivatives as Bio-based Materials for Paper Heritage Conservation, Bio Resources, 12(1) 2017: 735-747.
56. Bertalan, S., Craddock, A., Clement, D., Dwan, A., Eirk, K., Goldman,J., Hamburg, D.,

Hartwell, D., Herrenschmidt, F., Zieske, F., Consolidation, fixing, facing, Paper conservation catalog category, 23 (5),1988: pp.1-20. Rodgers .
57. Balloffet, N., Hille, J., preservation conservation for libraries and archives, American library association, Chicago, 2009.
58. Mohamed, M., Ali, M., A Comparative Study to Evaluate Consolidation of Paper Manuscripts Using Cellulose Derivatives, Al-kgizanah journal, 1(2), 2017.
59. Jhon, K., Survey of Current Methods and Materials Used for the Conservation of Leather Bookbindings, The Book and Paper Group Annual 19, 2000: 131-140.
60. Messager, M., Rouchon. V., Damaged Blue Papers : Optimising Consolidation while Preserving Original Color, Journal of Paper Conservation, 14 (2), 2013: 8-19.
61. Ludwick, L., "A comparative study on surface treatments in conservation of dry leather with focus on silicone oil" University of Gothenburg, Department of Conservation, Sweden, 2012, 1-35.
62. Zaja˛c, I.; Szulc, J.; Gutarowska, B.The Effect of Ethylene Oxide and Silver Nanoparticles on Photographic Models in the Context of Disinfection of Photo Albums.J.Cult. Herit, 51, 2021:59-70.
63. Darwish, S, S., Hassan, R. R. A., b, Abdel Hakim, A. A., Lado, M . J., Evaluation the Effectiveness of CMC and Klucel-E Modified with TiO2 and ZnO Nanoparticles Used for Consolidation the Damaged Paper Maps, International Journal of Sciences: Basic and Applied Research, 52(2) 2020: 217-232.
64. Webber, p., the use of Asian paper conservation techniques in Western collections, Adapt & Evolve, East Asian Materials and Techniques in Western Conservation, Proceedings from the International Conference of the Icon Book & Paper Group, 2015 (London, the Institute of Conservation: 2017), 12–27.
65. Ribba, L.G., Cimadoro, J.D., D'Accorso, N.B., Goyanes, S.N., Removal of Pollutants Using Electrospun Nanofiber Membranes. In: Goyanes, S., D'Accorso, N. (eds) Industrial Applications of Renewable Biomass Products. Springer, Cham, 2017: 301–324. https://doi.org/10.1007/978-3-319-61288-1-12.
66. Gadhave, R.V.I., Gadhave, C.R., Adhesives for the Paper Packaging Industry: An Overview, Open Journal of Polymer Chemistry , 12, 2022, 55-79.
67. Liu, J.; Xing, H.; Zhou, Y. Chao, X.; Li, Y.; Hu, D, An Essential Role of Polymeric Adhesives in the Reinforcement of Acidified Paper Relics. Polymers, 14(1), 2022: 207.
68. Abdel-Maksoud, G., Khattab, R.,Evaluation of traditional, starch nanoparticle and its hybrid composite for the consolidation of tracing paper, Egyptian Journal of Chemistry, 64(11), 2021: 6251 – 6268.
69. Baranwal, J., Barse, B., Fais, A., Delogu, G.L., Kumar, A., Biopolymer: A Sustainable Material for Food and Medical Applications, Polymers, 14(5), 2022: 983. https:// doi.org/10.3390/polym14050983.
70. Prati, S., Volpi, F., Fontana, R., Galletti, P., Giorgini, L., Mazzeo, R., Mazzocchetti,L., Samorì,C., Sciutto, G., Tagliavini, E., Sustainability in art conservation: a novel bio-based organogel for the cleaning of water sensitive works of art." Pure and Applied Chemistry, 90, 2017: 239 - 251.
71. Ali, M. A., "The evaluation of Agarose-based gel systems for surface cleaning albumen prints vs. the conventional water treatment", Egyptian Journal of Archaeological and Restoration Studies, 12 (1), 2022: 7-27.
72. Passaretti, A.; Cuvillier, L.; Sciutto, G.; Guilminot, E.; Joseph, E. Biologically Derived Gels for the Cleaning of Historical and Artistic Metal Heritage. Appl. Sci, 11, 2021: 3405.
73. Wahba W.N., Shoshah N.M., Nasr H.E., Abdel-Maksoud G, The Use of Different Techniques for Removal of Pressure-Sensitive Tapes from Historical Paper Documents: A Review Egyptian Journal of Chemistry, 65 (13), 2022: 1019-1031.
74. P.A. Williams, G.O. Phillips, GUMS | Properties of Individual Gums, Editor(s): Benjamin Caballero, Encyclopedia of Food Sciences and Nutrition (Second Edition),Academic Press, 2003: 2992-3001.
75. Noshy, W., R. R. A. Hassan, and Mohammed, N., Using biopolymers to strengthen the historical printed paper: mechanical and optical characters", Pigment & Resin Technology. 51(2) 2022: 212-226.
76. Vitthal S., Shaw, C., Use of Polymers and Thickeners in Semisolid and Liquid Formulations, Chapter 5, Essential Chemistry for Formulators of Semisolid and Liquid Dosages, Academic Press, 2016: 43-69.
77. Jillian, H., Wyszomirska-Noga, S., Funori: The use of a traditional Japanese adhesive in the preservation and conservation treatment of Western objects, the International Conference

of the Icon Book & Paper Group, London, 2015:69-79.

78. Bettina, G.F., Giambra, B., Cavallaro, G., Lazzara, G., Megna, B., Fakhrullin, R., Akhatova, F., Fakhrullin, R. Restoration of a XVIICentury's predella reliquary: From Physico-Chemical Characterization to the Conservation Process, Forests, 12(345), 2021: 1-11.
79. Yasin, M., Younis, A., Javed, T. Akram, A., Ahsan, M., Shabbir, R., Ali, M.M., Tahir, A., El-Ballat, E.M., Sheteiwy, M.S., River Tea Tree Oil: Composition, Antimicrobial and Antioxidant Activities, and Potential Applications in Agriculture. Plants, 10(10), 2021: 2105.
80. Khazova, S., Velikova, T., Lisitskaia, T., Influence of various oiling compositions used in conservation on the physical and mechanical parameters of binding leather, E3S Web of Conferences 215(3), 2020: 1-10.
81. Sequeira, S., Cabrita, E, J., Macedo, M. F., Antifungals on paper conservation: An overview, International Bio deterioration & Biodegradation, 74, 2012: 67- 86.
82. Azab, N., new method of sterilization and restoration in conservation, proceeding of international conference on conservation of cultural heritage, Florence, October 19, 2009, Editor: Mahmoud Salem printed at 2013:213-222.
83. Hassan, R.R.A., A Preliminary Study on Using Linseed Oil Emulsion in Dressing Archaeological Leather, Journal of Cultural Heritage, 21(2), 2016: 786-795.
84. Feng, Y., Gu, Y., Recruiting a new strategy to improve levan production in Bacillus amyloliquefaciens," Scientific Reports, 5(1), 2015, 13814.
85. Fornari, A.; Rossi, M.; Rocco, D.; Mattiello, L. A Review of Applications of Nanocellulose to Preserve and Protect Cultural Heritage Wood, Paintings, and Historical Papers. Appl. Sci, 12, 2022: 12846.
86. Napoli, B., Franco, S., Severini, L., Tumiati, M., Buratti, E., Titubante, M., Nigro,V., Gnan, N., Micheli, L., Ruzicka, B., Mazzuca, C., Angelini, R., Missori, M., Zaccarelli, E., Gellan Gum microgels as Effective Agents for a Rapid Cleaning of Paper, ACS Applied Polymer Materials, 2 (7), 2020 :2791-2801.
87. Mazzuca, C., Micheli, L., Marini, F. et al. Rheoreversible hydrogels in paper restoration processes: a versatile tool. Chemistry Central Journal, 8(10), 2014:1-11.
88. Campos, M., Melo, M. O., Junior, F., Effects of Polysaccharide-Based Formulations on human Skin, Polysaccharides Bioactivity and Biotechnology Kishan Gopal Ramawat. Editors: Jean-Michel Me´rillon, Springer International Publishing Switzerland 2015: 2046-2060.
89. Rushdy, A., Wahba, W.N., Abd-aziz, M.S., Samahy, M., Kamel, S., A comparative study of consolidation materials for paper conservation, 8, (3), 2017: 441-452.
90. Alihosseini, F., Plant-based compounds for antimicrobial textiles, Editor(s): Gang Sun, In Woodhead Publishing Series in Textiles, Antimicrobial Textiles, Woodhead Publishing, 2016: 155-195.
91. Hassan, R. R A., The restoration of two historic leather bindings according to a new strategy, Journal of the Institute of Conservation, 42(3), 2019: 210-225.
92. Ntasi, G., Sbriglia, S., Pitocchi, R., Vinciguerra, R., Melchiorre, C., Ioio, L., Fatigati G., Crisci, E., Bonaduce, I., Carpentieri, A., Marino, G., Birolo, L.. Proteomic Characterization of Collagen-Based Animal Glues for Restoration. J Proteome Res, 21 (9), 2022:2173-2184.
93. Haghighi, z., Molecular Characterization of Animal Glues for the Purpose of Restoration Treatments, master Thesis, Universidade de Évora, 2019: 1-121.
94. Brewer, T., SC6000 and Other Surface Coatings for Leather: Chemical Composition and Effectiveness, Technology and Structure of Records Materials, 2004:.1-8.
95. Herro H, Nolley S, Cowan W, Wright K. Oil on Paper: A Collaborative Conservation Challenge. Book Pap Group Annu, 36, 2017: 18-27.
96. Decoux, S., Enzymes Used for Adhesive Removal in Paper Conservation: A literature review, Journal of the Society of Archivists, 23(2), 2002:187-195.
97. Van-Dyke, Y.., (2012). Practical Applications of Protease Enzymes in Paper Conservation, the Book and Paper Group Annual 23, 2004: 93-107.
98. Petherbridge, G., Conservation of library and archive materials and the graphic arts, The Institute of Paper Conservation and the Society of Archivists, Butterworths, 1987: 1-304.
99. Xiaoxia, H., Application of Enzymes in Paper Documents Restoration, Libraly Journal, 41(2), 2022: 128-134.
100. Akindoyo, J.O., Beg, M.D., Ghazali, S., Islam, M.R., Jeyaratnam, N., & Yuvaraj, A.R. Polyurethane types, synthesis and applications

– a review. RSC Advances, 6, 2016: 114453-114482.

101. Xu, w., Chai, X., Zhao, G., Li, J., Wang, X., Preparation of reactive amphoteric polyurethane with multialdehyde groups and its use as a retanning agent for chrome-free tanned leather, Appl. Polym. Sci, 136(37) , 2019: 47940.
102. Abed-Maksoud G., Artificial Accelerated Ageing and Investigation Method used for the evaluation of the effectiveness of polyurethane Applied for consolidation paper, Journal of The faculty of Archaeology, Cairo University Press 14, 2010.