Spectroscopic Characterization of Multilayered Functional Protective Polymers via Surface Modification with Organic Polymers against Highly Toxic Chemicals

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Additional information is available at the end of the chapter

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Abstract

Recent advances in biopolymers, including functional biomaterials for the manufacture of personal protective garments (PPGs) or equipment (PPE) have dramatically improved their efficiency and performance. Good and acceptable permeation characteristics, mechanical strength and durability are common attributes of these materials simultaneously without compromise for their cost-effectiveness and manufacturability. The comprehensive characterization of these materials and specimens' three-dimensionality with the endeavor to obtain the highest resistance to highly toxic agents such as nuclear, chemical and biological warfare agents is the must fulfilling aim in today's global interest in continuous development in this area.

Because energy absorption component seems to be important in considering quality the requirements related to the application of most protective materials (e.g. clothing), spectroscopy would seem to be the cornerstone to be considered for most analytical purposes to supplement the qualitative and quantitative assessment of polymeric materials. The major techniques worth mentioning include: scanning electron microscopy coupled to X-ray dispersive spectroscopy (SEM/EDS), atomic force microscopy (AFM), scattering-type near-field optical microscopy, scanning tunneling microscopy (STM), attenuated total reflectance Fourier transform spectroscopy (ATR-FT-IR), infrared spectroscopic ellipsometry, nano-FTIR absorption spectroscopy, near-field optical microscopy, and infrared vibrational nano-spectrosocopy. This chapter will discuss the importance of a particularly important natural polymer (cellulose) containing acetyl groups to form modifiable biopolymers (e.g. cellulose acetate polymers), doped to yield multi-layered functional protective materials (MFPMs) or composites (MFPCs). The ultimate aim seeks to provide critical insights into understanding the enhancement of their permeation characteristics against exposure to toxic industrial chemicals, including chlorine which is currently being used as a chemical warfare agent of choice in the Syrian conflict. MFPMs or MFPCs are a group of materials made from a combination of fiber or polymers together with varying amounts of additives possessing tailored physical and mechanical properties. Many of these materials should not only be durable but also must provide cost-competi-

tive products in the manufacturability of personal protective garments (PPGs). The key advantages and disadvantages of available protective materials manufactured with synthetic polymers compared to biopolymeric ones based on the objective of achieving the highest quality, maximum protection, or both are presented. The chapter will also explain the fundamental differences of each material- and how biopolymers can potentially affect their design and the outcome of use. The challenges related to the cost and characterization for the purpose of facilitating correlation of different physical properties and morphological heterogeneities will be presented. The need for advanced characterization and analytical tools (such as spectroscopy and microscopy) shall be dealt with. This should pave the way in the critical understanding of how better permeation studies can be achieved from suitable biopolymer--based personal protective garments (PPGs). The reutilization of waste materials in the production of multilayered functional protective materials (MFPMs) or composites (MFPCs) have advantages to the economy, environment, and technology. The synthesis of targeted multi-layered metal-organic doped polymers via surface modification can be achieved in well planned experiments to yield products of acceptable permeation studies for industry use in the manufacture of PPGs and hence boost the third generation economy. The simple biopolymer preparation yet robust with intuitive practical applications in the industry will explore a strong scientific elucidation of mechanisms to explain or achieve the desired properties while overcoming the boundary of expensive needs for the development of the industry.

Keywords: Polymers, cellulose, functionalization, multilayer, personal protective garments, toxic chemicals, characterization, spectroscopy , microscopy

1. Introduction

According to Wang et al. [1], it has been documented that a fast depletion rate of non-renewable energy and environmental pollution caused by synthetic or petroleum-based polymers has motivated the utilization of naturally occurring polymers leading to the creation of a wide range of new materials with interesting physicochemical, mechanical and morphological characteristics. Cellulose [2] forms the structural component of the cell walls of plants and is by far the most abundant natural polymer (polysaccharide) on earth. Cellulose provides many manufactured products, including paper and paper products, rayon, linen, and cellulose nitrate (a constituent of nail polish). This natural abundance offers cellulose an attractive attention due to its renewability, wide availability, low cost, biocompatibility and biodegradability [1]. Cellulose acetate and rayon are known examples with many day-to-day applications ranging from thin-films to regenerated cellulose for particular usage such in packaging materials, e.g. cellophane. Rayon is the most important regenerated natural fiber [3], produced from cellulose derived from wood pulp. Cellulose acetate [4] has been widely produced from processed wood pulp (Figure 1) dictating the current market source with intense research focused on various other renewable materials as feedstock [5-7].

Cellulose can also be degraded with NaOH followed by carbon disulfide reaction to form cellulose xanthate and regenerated through precipitation in an acid medium- and then cold drawn to form spinnerette fibers for specific usage. Regenerated cellulose materials endowed with different functions and properties have been designed and fabricated in different forms,
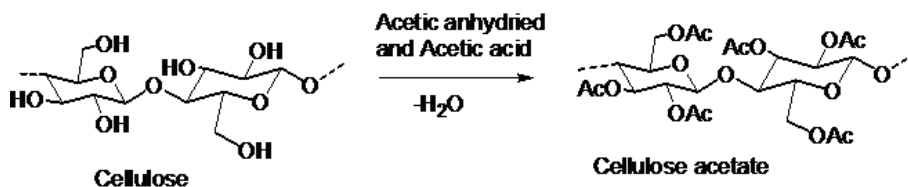
Figure 1. Reaction scheme for the synthesis of cellulose acetate - a modified natural polymer [8].

such as filaments, films/membranes, microspheres/beads, hydrogels/aerogels and bioplastics, for various applications and use in day-to-day demands. In this regard, the process of regeneration follows a physical process resulting in a number of novel regenerated cellulose materials employed for wide applications in textiles, packaging, biomedicine, water treatment, optical/electrical devices and agriculture and food materials. The 'ease-of-car' properties such as crease resistance can be imparted to cellulose by various cross—linking agents [3]. The most common are di-(N-hydroxymethyl) ureas. In the presence of Lewis acid, these reagents bridge hydroxy groups on adjacent polycellulose chains as shown in reaction scheme 1.
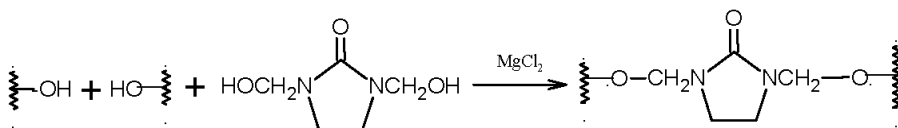
Scheme 1. Bridging of hydroxy groups on adjacent polycellulose chains [3].

However, many processes have been developed to improve the fiber characteristics of cellulose. For example, treatment with strong aqueous NaOH (mercerization) alters the strength, surface character, and dyebility of cellulose during manufacturing.

Another interesting research area that expands its scope of development mainly in the fields of tissue engineering for many years is in the processing of organic-inorganic hybrids and photoactive polymer nanocomposites. In this area, processing strategies with very strong scientific interest and several applications in the nanocomposites field are based on the development of interpenetrating networks and sol–gel processed materials [9-16]. Other processing strategies of polymer nanocomposites that should be mentioned here include the microwave-assisted processes [17, 18], frontal polymerization [19-24] and processing of foams [25, 26] and aerogels [27-29]. In all these processes, the presence of nanofillers and the inter-action with the matrix represent again relevant factors for the processing behavior and the final properties of the nanocomposites obtained, which can be exploited in the manufacture of protective polymeric materials such as personal protective garments (PPGs).

Amidst all these recent advances in biopolymers, including functional biomaterials, their usage for the manufacture of personal protective garments (PPGs) or equipment (PPE) have dramatically improved their efficiency and performance. Thus from the research point of view,

generating wide impact and benefits of the regenerated cellulose materials to the society. Good and acceptable permeation characteristics, mechanical strength, and durability are common attributes of these materials simultaneously without compromise for their cost-effectiveness and manufacturability. The comprehensive characterization of these materials and specimens three-dimensionality with the endeavor to obtain highest resistance to highly toxic agents such as nuclear, chemical and biological warfare agents is the must fulfilling aim in today's global interest in the continuous development in this area.

The reutilization of waste materials in the production of multilayered functional protective materials (MFPMs) or composites (MFPCs) has advantages to the economy, environment, and technology. The synthesis of targeted multi-layered metal-organic doped polymers via surface modification can be achieved in well planned experiments to yield products of acceptable permeation studies for industry use in the manufacture of PPGs and hence boost the third generation economy. The simple biopolymer preparation yet robust with intuitive practical applications in the industry will explore a strong scientific elucidation of mechanisms to explain or achieve the desired properties while overcoming the boundary of expensive needs for the development of the industry. Apart from the 'green' methodologies of material processing and the resultant properties and functions, with emphasis on the regenerated cellulose materials and the composite materials, this chapter also emphasizes other composite blending procedures. Wang et al. [1] reported that the latter processes followed new intensive developments resulting in environment-friendly biopolymerization steps. This avoided consuming chemicals because most of the agents (solvents, coagulants, etc.) may be recycled and reused, with no accompanying chemical reaction. These authors pointed out that regenerated cellulose varies in different shapes, such as powder, fibers, films, hydrogels, and spheres, especially the applications of 'green' cellulose solvents in dissolution and regeneration, leading to sustainable development, environmental preservation and energy conservations.

Although new polymers have been developed from complex polymeric blends, generally through multilayered linkages, for the purpose of improving their surface function and performance, their molecular self-assembly has proportionately led to very complex organic and inorganic molecular interactions at even nanoscales [30]. Hence, the understanding and control of such materials during the manufacturability of protective equipment, including personal protective garments (PPGs) have been impeded by difficulties in their characterization using conventional analytical techniques [31]. Various state-of-the-art spectroscopic and hyphenated techniques are currently available for both qualitative and qualitative characterizations of polymeric protective materials (PPMs) to directly resolve nanoscale morphology and associated intermolecular interactions for the systematic control of functionality in multicomponent systems and manufacturability. These include, but not limited to techniques such as:

1. Scanning electron microscopy coupled to X-ray dispersive spectroscopy (SEM/EDS) for surface imaging [32-35] and structural elucidation.

2. Atomic force microscopy (AFM) [36] and scattering-type near-field optical microscopy [37, 38] for nanoscale morphology and nanoscale-resolved subsurface imaging.

3. Scanning tunneling microscopy (STM) [39] for associated intermolecular interactions.

4. Attenuated total reflectance Fourier transform spectroscopy (ATR-FT-IR) [40, 41].

5. Infrared spectroscopic ellipsometry [42] and nano-FTIR absorption spectroscopy [43, 44] for apertureless near-field optical microscopy [45, 46], and infrared vibrational nanospectrosocopy [47].

This chapter fundamentally addresses these challenges by first overviewing the chemistry of an important natural polymer, cellulose, critically discussing the potential of its use to form modifiable biopolymers (e.g. cellulose acetate polymers), doped to yield multi-layered functional protective materials (MFPMs) or composites (MFPCs). The mention of regenerated cellulose processing is being made. The ultimate aim of the chapter seeks to provide critical insights into understanding the acetylation mechanisms for the enhancement of their permeation characteristics against exposure to toxic industrial chemicals, including chlorine which is currently being used as a chemical warfare agent of choice in the Syrian conflict. MFPMs or MFPCs are a group of materials made from a combination of fibers or polymers together with varying amounts of additives possessing tailored physical and mechanical properties. Many of these materials should not only be durable but must provide cost-competitive products in the manufacturability of personal protective garments (PPGs). The key advantages and disadvantages of available protective materials manufactured with synthetic polymers compared to biopolymeric ones based on the objective of achieving the highest quality, maximum protection, or both are presented. The chapter will also explain the fundamental differences of each material and how biopolymers can potentially affect their design and the outcome of use. The challenges related to the cost and characterization for the purpose of facilitating correlation of different physical properties and morphological heterogeneities are presented. This should pave the way in the critical understanding of how better permeation studies can be achieved from suitable cellulosic biopolymer--based personal protective garments (PPGs).

2. Overview of natural polymer chemistry

2.1. Natural polymers

Polymers are large molecules constructed by the repetitive bonding of many smaller molecules called monomers (or monomer residues) [48]. Although synthetic polymers appear in many forms that are familiar to the consumer, biopolymers constitute all living organisms [7]. Biopolymers are responsible for the structural and functional chemistry of all plants and animals. The polymeric sugars, known as polysaccharides, are an important component of the cell membranes of plants. The chemical formula of this type of sugar is illustrated in Figure 2b.

Wool is a fibrous insoluble animal protein known as keratin. In its natural form, it has an α-keratin structure and is a classic example of the protein α-helix. A variety of groups that make up a polypeptide provide many possibilities for inter- and intramolecular interactions. Hydrogen bonding, steric repulsions, van der Waals attraction, and solvation contribute to the
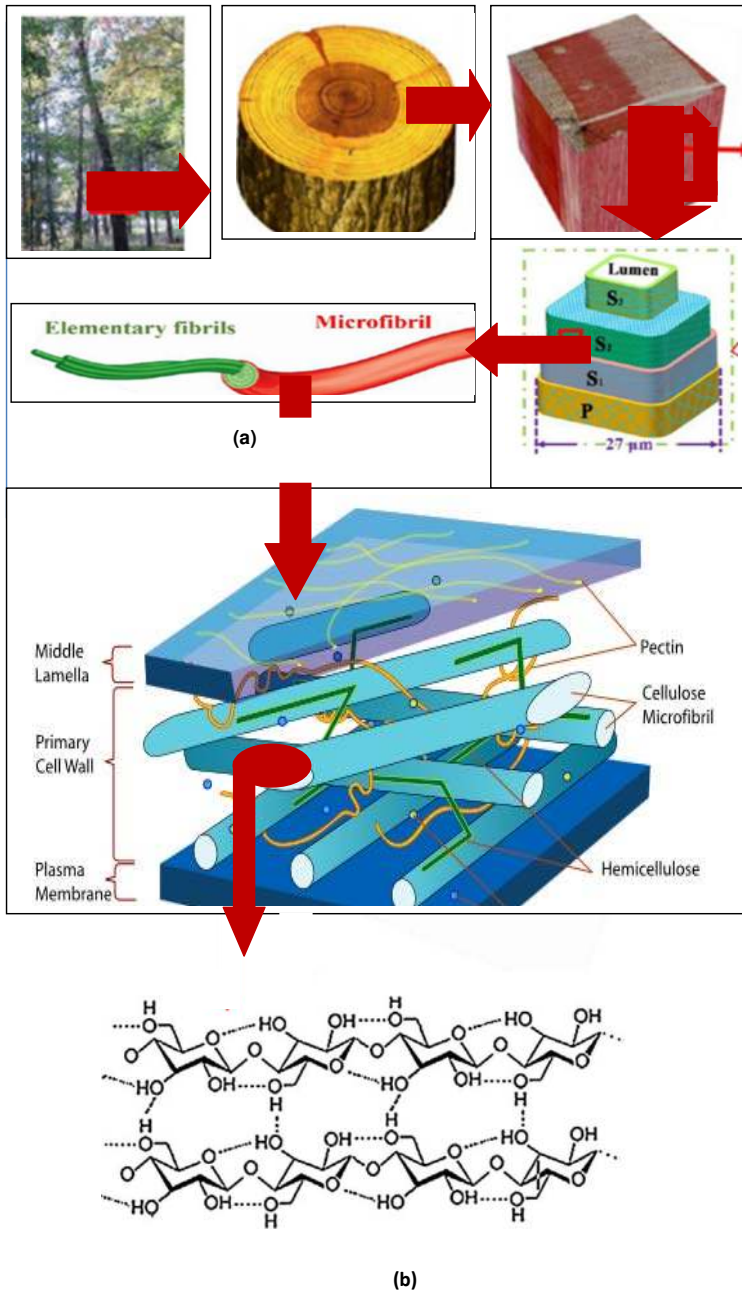
Figure 2. (a) Hierarchical structure from plant to cellulose chains, Adapted from Peponi et al. (2014). (b) A strand of cellulose (Nelson and Cox, 2013).

three-dimensional conformations of these types of proteins. The peptide bond (C-H) is the major factor in determining peptide conformation (Figure 3). Rotations are most important at the single bonds connected to the α-carbon atoms.
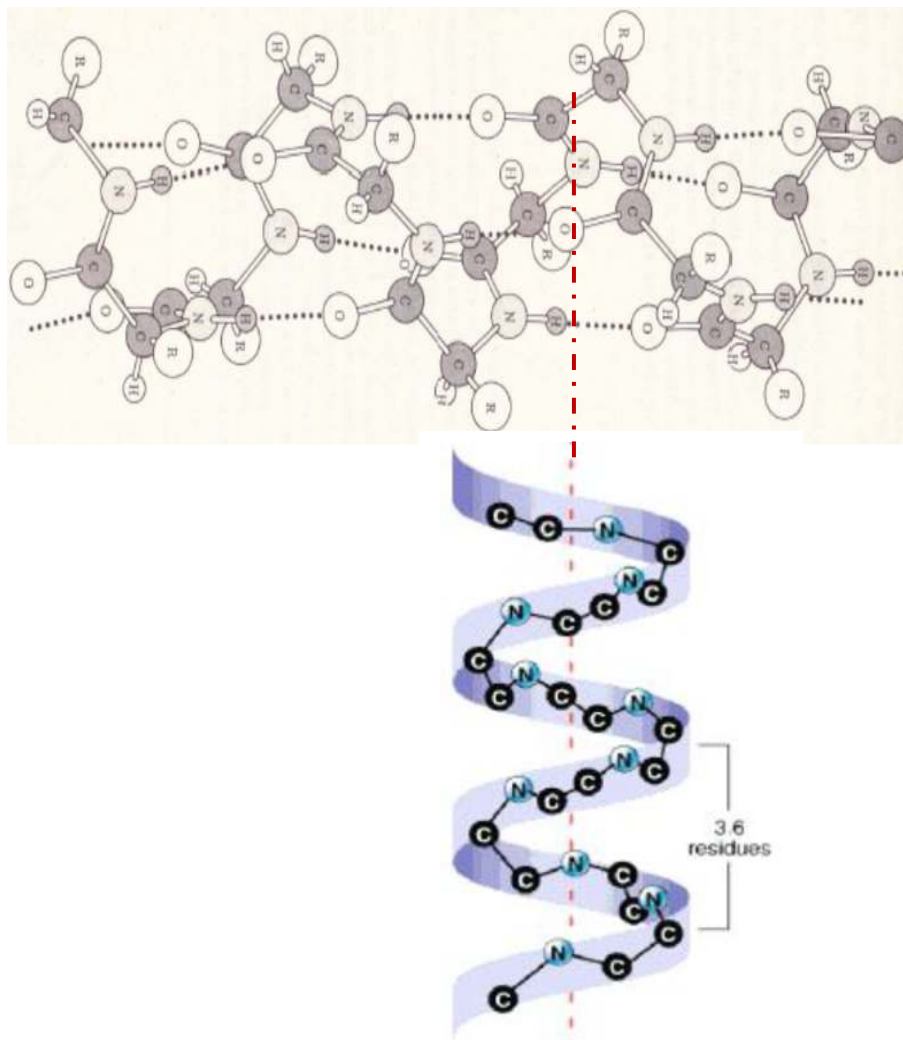

Figure 3. A schematic representation of a protein α-helix showing possibility of rotations at the single bonds connected to the α-carbon atoms, Adapted from [3, 51].

The reshaping of wool fibers usually involves the reductive cleavage of the disulfide bonds and the formation of new cross-links involving disulfides or other groups. These cross-linking modifications are used to impart permanent press to wool fabric (Scheme 2).
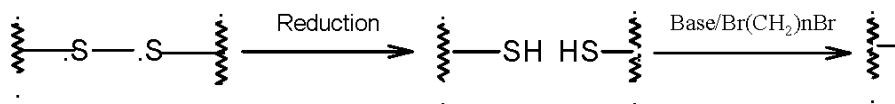
Scheme 2. Cross-linking modifications to impart pressability to wool fabric.

The flexible protein structure of wool leads to fabric with excellent handling qualities. When exposed to moisture and heat, the tendency to shrink creates a problem. However, blends of wool and synthetic fibers are currently the most effective approach to shrink-resistant "wool" fabrics.

Pure pulp from cotton (Figure 4), with the scientific name as *Gossypium herbaceum spp.* [52] is widely available in the arid regions of the world, particularly Africa. This natural polymer is very rich in α-cellulose consisting of 95 – 98% [53]. Cellulose is the most widely available biopolymer in this class (cotton) and accounts for approximately 50 % of total linear β-1,4-polyglucoside exhibiting a strong fibre structure that is quite versatile [54]. Cotton fibers are also cross-linked for crease resistance by using epichlorohydrin (3-chloropropylene oxide) or the diepoxide of butadiene. Cotton fabrics retain their strength whether wet or dry. They have excellent wearability and are pleasing in appearance and to the touch. However, the resistance of these fibers against toxic chemicals can be possibly improved through surface modifications.

Figure 4. A photograph of fiber from the *G. herbaceum* species represents the purest natural form of cellulose, containing more than 90% of this polysaccharide [55].

Cellulosic fibers from natural protein (silk) are most widely spread out in southern Africa, and elsewhere [56]. Silk is a fibrous protein produced by insects, including those from sources such as the common *Bombyx mori* or the wild *Antheraea pernyi* and *Antheraea assama*. The "pleated sheet" structure of silk fibroin (Figure 5) has a repeating sequence of glycine at every other position with alanine or serine in between. The sheet sections interact through dispersion forces.
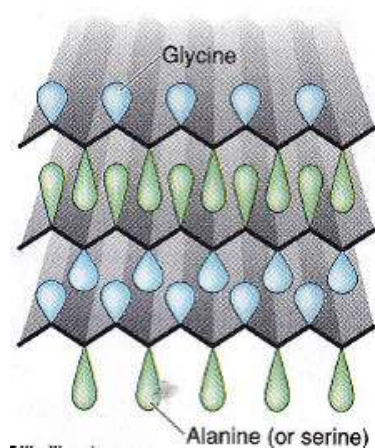

Figure 5. A schematic representation of silk fibroin, Adapted from [57].

The polymer chains tightly pack together in pleated sheet conformations that result in a strong fiber. Interestingly, silk fabric does not have good wear resistance, and because of its high price it is luxury fabric. All these fibrous materials can be very good basic raw biomaterials for manufacturing cellulose acetate biopolymers. The cocoons of various silkworms (moth larvae), after appropriate chemical treatment, provide the fibroin used for most silk fabric. More than 70 % of the average composition of fibroin is due to the small amino acids glycine, alanine, and serine.

Cotton is not the only source of cellulose polymers but just one of the available sources. Non-wood bioresources has always constituted an enormous supply potential for cellulosic biopolymers for centuries [58] and would continue to be potentially so [59] should exploitation follow sustainable principles. A polymeric form of glucosamine known as chitin is a major component of the exoskeleton (shell) of many insects [3].

2.2. Cellulosic biomaterials

Cellulose, $(C_6H_{10}O_5)$n is an organic compound (polysaccharide) with the chemical structure presented in Figures 6A and B. This molecule is the major chemical component of the cell wall fiber, contributing to 40 % - 45 % of the wood's dry weight [60]. This polysaccharide is composed of linear chains of β(1 → 4) D-glucose units held together by ß-1,4-glycosidic bonds

(Figure 7). In bleached kraft pulps prepared from native wood, there is possibly a degree of polymerization from 10,000 to 1,000 units [61]. The D-anhydroglucopyranose unit is endowed with hydroxyl (-OH) groups at positions C_2, C_3, and C_6. These groups are capable of undergoing the typical reactions known for primary and secondary alcohols [62].
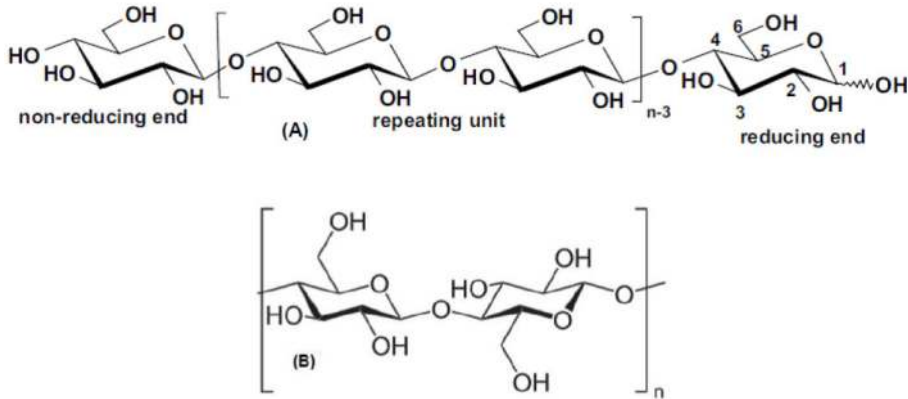

Figure 6. Molecular structure of cellulose (A): Chain of several hundred to more than 10,000 β(1 → 4) linked D-glucose units [60, 63], (B): polymeric polysaccharide [54].

On one hand, cellulose exhibits a strong tendency to form intra- and inter-molecular hydrogen bonds via the hydroxyl groups as shown in Figure 7. On the other hand, the linear cellulose chains tend to stiffen the entire straight chain, thus, promoting aggregation into a crystalline structure that gives the cellulose molecule a multitude of partially crystalline fiber structures and morphologies [60].
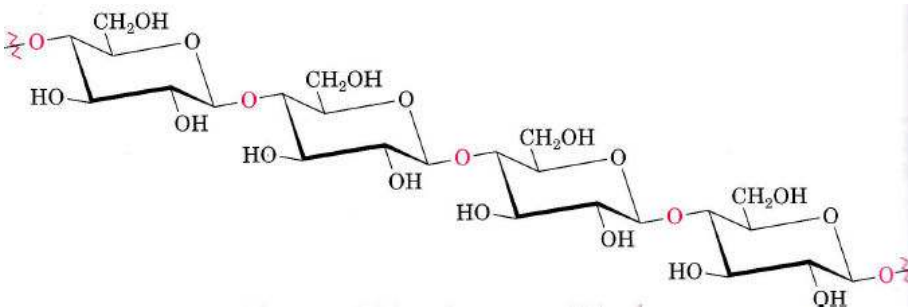

Figure 7. Cellulose, a 1,4′-O-(β-D-glucopyranoside) polymer, Adapted from [2, 48].

A schematic representation of a strand of cellulose (conformation I_α) showing the hydrogen bonds (thin lines) within and between cellulose molecules [50] is illustrated in Figure 8.
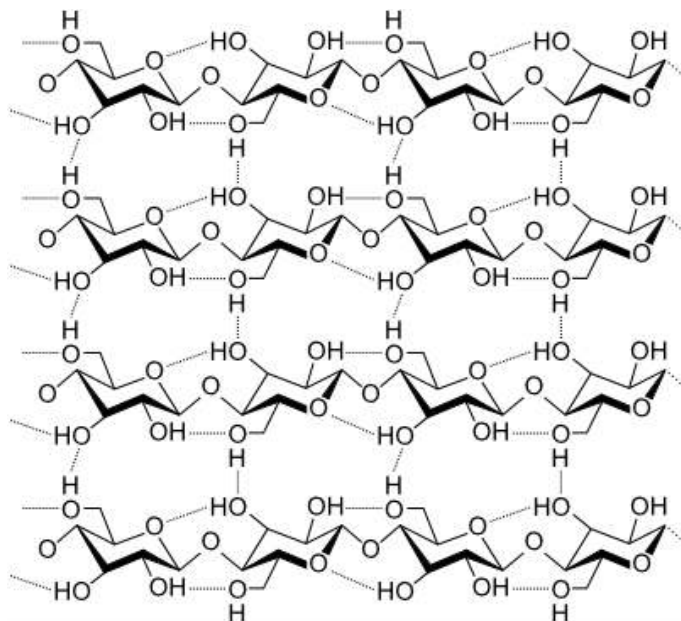
Figure 8. A schematic representation of a strand of cellulose (conformation I_α) showing the hydrogen bonds (thin lines) within and between cellulose molecules [50].

This readily bioavailable resource thus offers a great potential for continuously applied polymer research because, as already mentioned, it is the most abundant organic chemical on earth. It is reported in the literature [64] that more than 50% of the carbon in plant occurs in the cellulose support structure of stems and leaves; wood is largely cellulose, and cotton is more than 90% cellulose. It is worth mentioning that the great strength of wood is due largely to the H bonds between cellulose chains [57]. Cellulose is composed of long unbranched chains from 100 to 10,000 glucose molecules. Groups of these chains, held together by the hydrogen bonding between – OH groups on adjacent chains, are twisted into rope-like structures that make cellulose tough and fibrous [64]. Note that the absorbent properties of cotton and paper towels are due to capillary action and formation of hydrogen bonds between water molecules and –OH groups on cellulose chains.

2.3. Cellulose polymers

Cellulose acetate (Figure 9) is one of the oldest man-made macromolecules used extensively in the textile and polymer industries [63]. It has an inherent advantage in that the starting material, cellulose (Figure 7), is a renewable natural resource [66] widely produced from processed wood pulp (Figure 2a) dictating the current market source with intense research focused on various other renewable materials as feedstock [5-7].
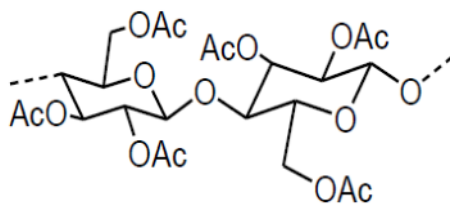
Figure 9. Cellulose acetate molecule [4].

Cellulose acetate is currently being used in fiber or film processing; however, it has been reported [67] to have high glass transition temperature which limits its thermal processing. Current applications of cellulose acetate include textiles, cigarette tow, lacquers, cellulose films, and in food packaging [68, 69]. Because it is nontoxic, it possesses a great potential to be used in new blends for the manufacture of a variety of biomaterials with very high potential eco-friendly characteristics. An example of such application(s) is in the manufacture of protective materials, e.g. personal protective garments. Cellulose acetate is broadly classified into two types:- cellulose diacetate and cellulose triacetate with acetyl values of approximately 55% (degree of substitution: 2.4) and 61% (degree of substitution: 2.9), respectively [67]. This type of biopolymer, sourced from a variety of renewable materials could undoubtedly revolutionize the polymer industry in just the near future owing to its versatility in chemical modification for better physicochemical qualities.

Cellulose acetate gives fabrics a silk-like appearance [8] (Figure 8) and it can be blended easily with fibers from other materials, providing room for the manipulation of the physico-chemical properties for improvement via surface modification with organic polymers and/or metal-organic supramolecules. Its texture is soft and cool against the skin, is naturally absorptive and breathable, has good drape and is excellent at combating static cling [70]. Cellulose acetate is also frequently used for linings in suits or coats, for formal wear including wedding gowns [71].

Two conventional acetylation techniques have successfully been employed in the fibrous and solution processes [65] to fully acetylate purified plant-derived cellulose-based mechanical pulp. The reaction media for acetylating pulp by the fibrous process consist of xylenes, acetic anhydride, and H_2SO_4. Xylene acts as a non-solvent, diluent. Cellulose acetate is isolated from the remainder of the acetylated components by differential solubility in dichloromethane/methanol (9:1,v/v) [65].

Through this approach, it is possible to modify cellulosic fiber using raw materials that contain acetyl groups capable of forming cellulose acetate polymers. Such raw materials used in the manufacture of these types of biopolymers are usually acetic acid and acetic anhydride. Acetic acid is one of the simplest organic acids; a main component of vinegar can be prepared naturally or synthetically from chemical processes. Acetic anhydride is produced by combining two acetic acid molecules with the removal of a water molecule. Thereafter, it follows a comprehensive evaluation by measuring key physicochemical parameters characterizing the polymer and some chemical/instrumental analyses are also conducted to complement the physicochemical measurements in the evaluation protocol.

Thus, the biopolymer preparation protocol is simple (Fig. 10) and entails that cellulosic fibre, acetic acid, and acetic anhydride should be mixed together and reacted to form cellulose acetate polymers. This process is aided by the addition of a small amount of H_2SO_4 which is subsequently neutralized during processing. The unique properties [8, 72] of the biopolymer (cellulose acetate) enable a great variety of end-use applications to be investigated in a number of permeation studies against selected Industrial toxic material, nuclear, biological and chemical agents.
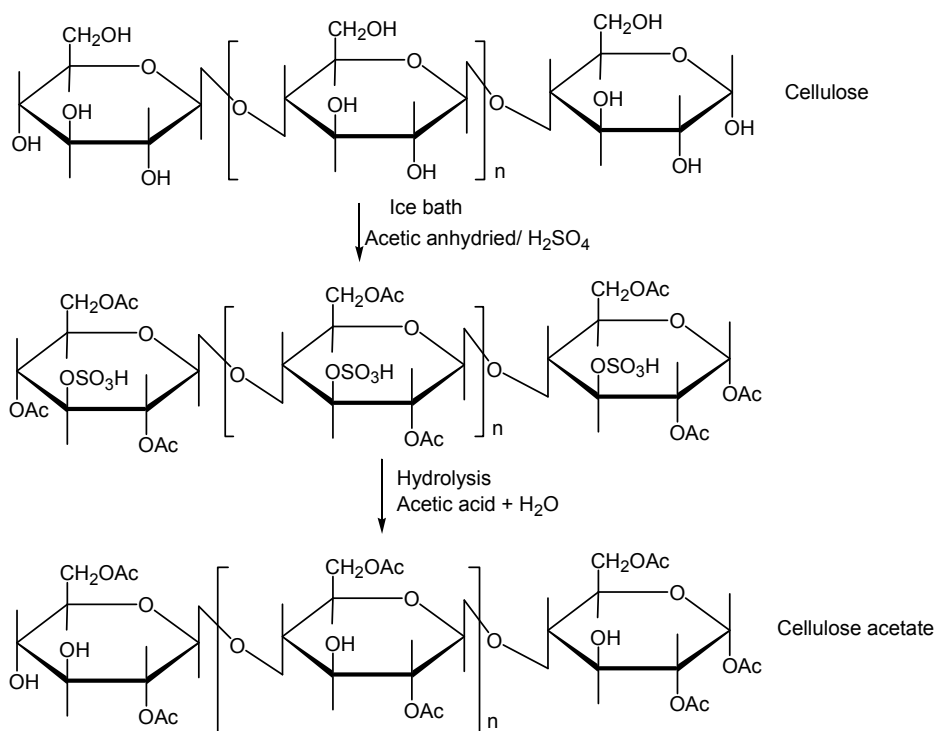

Figure 10. A simple preparation protocol of cellulose acetate polymer [73].

2.4. Biopolymers and crystallinity

A particular polymer is not made up of a single molecular species but is a mixture of macromolecules with similar structures and molecular weights that exhibit some average characteristic properties. The monomer-polymer term has probably been erred since time immemorial before humans employed it to such an advantage today. Biological macromolecules are nothing more than condensation polymers created by nature's reaction chemistry and improved through evolution [57]. Remarkably, these molecules are today's greatest proof of the versatility of carbon and its kingdom of atomic partners. Polymers, therefore, do not

crystallize in exactly the same way that "pure" compounds do. The packing of identical molecules required to form precise crystal structures is only partially attained. Yet some polymers have many of the physical characteristics of crystals said to be crystalline. For example, long segments of linear polymer chains are oriented in a regular manner with respect to another. Such crystalline regions of a polymer are referred to as crystallites [74]. Structurally, amorphous and noncrystalline regions lie between the crystallites and constitute defects in the crystalline structure [72].

Biopolymers that have polar functional groups show considerable tendency to be crystalline. This would seem a positive character that favors surface modification to meet specific demands, for example, to create "creuse" blends with considerable resistance to nuclear, chemical and biological warfare agents. During processing and manufacturability, orientation can be aided by alignment of dipoles on different chains. Another good example is proteins, constituting a group of the many natural polymers that can crystallize because of their regular helical structure. In this regard, the order imposed by hydrogen bonds is further inducement to malleable crystallinity. Because polar groups are not, however, a necessary prerequisite to crystallization, crystalline polyethylene and polypropylene can be prepared interlayered with biopolymer to yield a desired strength and wearability. The van der Waals interactions between the long hydrocarbon chains provide sufficient total attractive energy to account for the high degree of regularity within the polymers. Sight should not be lost, though, that irregularities such as branch points, comonomer units, and cross-links lead to amorphous polymers. In other words, crystalline polymers usually are relatively strong and nonelastic and have characteristic melting points, such as synthetic fibers (e.g. nylon and Dacron). Because amorphous polymers do not have true melting points but instead have glass transition temperatures at which the rigid and glasslike material becomes a viscous liquid as the temperature is raised, multilayered surface modifications via organic or biopolymers can be envisaged to enhance the functional protective properties.

Each type of protein has its own amino acid composition, specific number and proportion of the different amino acids. The forces responsible for protein shapes (varying from long rods to undulating sheets, baskets with deep crevices to Y-shaped blobs) are the same bonding and intermolecular forces that operate for all molecules in nature. The –SH ends of two cysteine R groups often form an –S-S- bond, a covalent disulfide bridge that brings distant parts of the chain together as clearly illustrated in Figure 11 [57].

Polar and ionic R groups usually protrude into the aqueous fluid, interacting with water through ionic-dipole forces and H bonds: sometimes securing the chain's bends through an acid (-COO$^-$) R group lying near a basic (-NH$_3^+$) one to form an electrostatic salt bridge. This allows for an enormous potential for multilayer intercalation with other functional organic biomaterials to obtain desirable characteristics and qualities. The helical and sheet-like segments, thus, arise from H H bonds between the C=O of one peptide bond and the N-H of another. Other H bonds act to keep distant portions of the chain near each other. Nonpolar R groups usually congregate through dispersion forces within the protein interior. As such, fibrous proteins have relatively simple amino acid compositions and structures shaped like
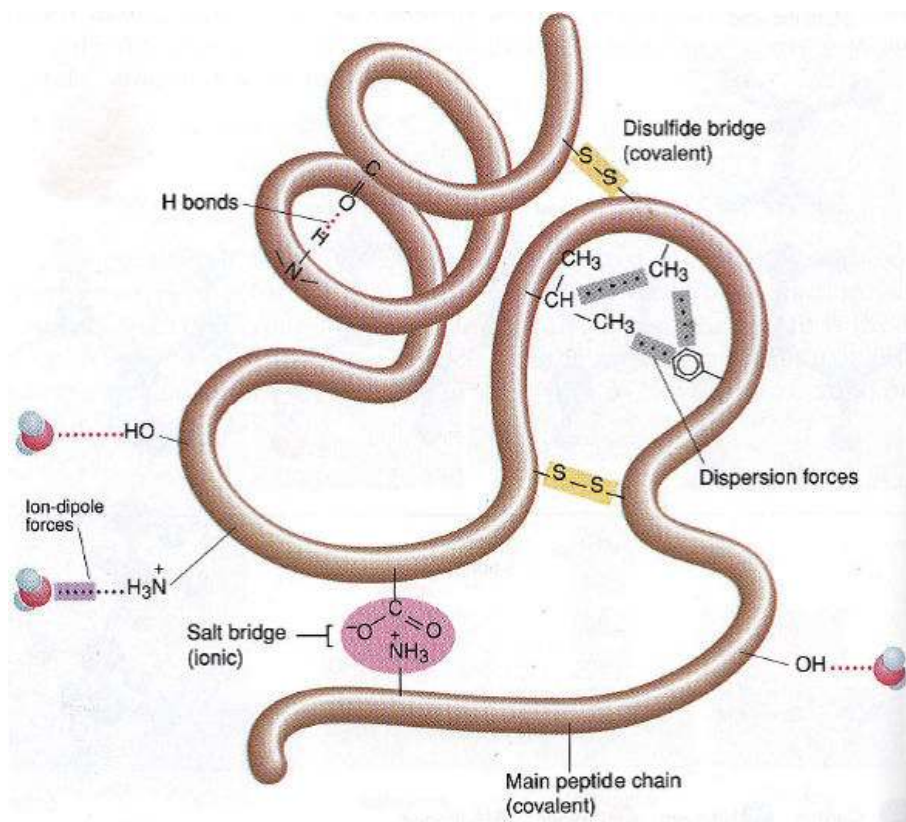
Figure 11. Schematic depiction of the forces operating in many fibrous proteins, Adapted from [57].

extended helices or sheets. These are key components of hair, wool, skin, and connective tissue materials that require strength and flexibility.

Finally but not the least, spatial configurations (Scheme 3(a)) of polymer molecules have a critical effect upon the physical properties of the polymer. The structure of natural rubber is an example to illustrate this. In this case, three spatial arrangements can result from polymerization process:

1. Atactic, in which the configurations are random along the polymer chain.

2. Isotactic, in which the configurations at each chiral center are identical.

3. Syndiotactic, in which the configurations at each chiral center alternate.

If the polypropylene stereoisomers have been prepared, the regular structures of the isotactic and syndiotactic polymers lead to hard crystalline materials. The random repeating configurations along the atactic polymer chain result in soft, amorphous, elastic material.
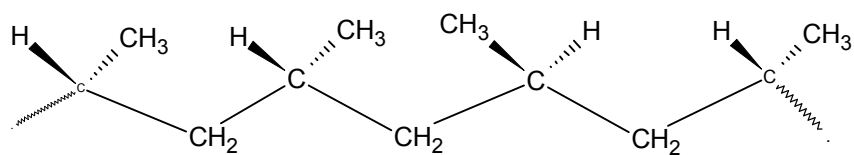
(a) Atactic
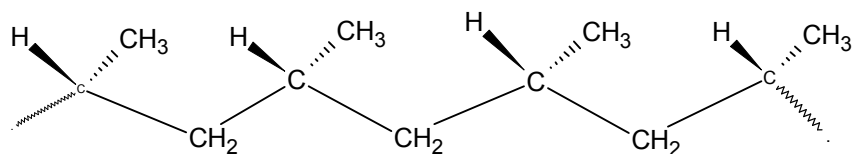
(b) Isotactic
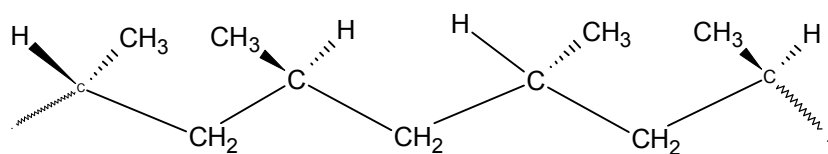
(c) Syndiotactic

Scheme 3. Configurations of polypropylene: (a): atactic, (b): isotactic, and (c): syndiotactic [3].

Further processing using biopolymer copolymerization under well- monitored conditions could further improve not only the resistance of such polymers against both toxic industrial and chemical agents but also may not create great wearability and manufacturability.

3. Polyelectrolytic polymers

3.1. Polymeric Ionic Liquids (PILs)

Polyelectrolytes constitute a class of polymers with repeating units bearing an electrolyte group. The main moieties of polyelectrolytes are polycations and polyanions. In an aqueous medium, these groups are susceptible to dissociate yielding charged polymers. As such,

polyelectrolyte properties are similar to both electrolytes in the form of salts and usual high molecular weight polymeric compounds. Thus, polyelectrolytes are sometimes called poly-salts (Figure 12). However, theoretical approaches [75-77] to describing the statistical proper-ties of these charged macromolecules differ profoundly from those of both their electrically neutral and synthetic counterparts [78], while technological and industrial fields exploit their unique properties for a wide range of applications.
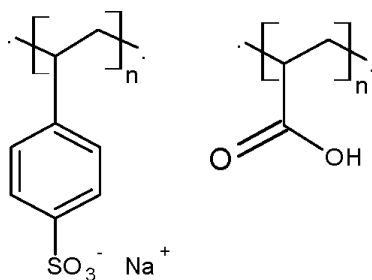

Figure 12. Example of a polyelectrolyte molecule, a molecule in which a substantial portion of the constitutional units has ionizable or ionic groups, or both [77]. The chemical structures of two synthetic polyelectrolytes: To the left is poly(sodium styrene sulfonate) (PSS), and to the right is polyacrylic acid (PAA).

As illustrated in Figure 12, PSS is a 'strong' polyelectrolyte (fully charged in solution), whereas PAA is a 'weak' polyelectrolyte (partially charged). Like polymers, their solutions are often viscous. Charged molecular chains, commonly present in soft matter systems, play a funda-mental role in determining the structure, stability and the interactions of various molecular assemblies. Both natural and synthetic polyelectrolytes are used in a variety of industries. The good examples to be discussed in this chapter are those of natural polyelectrolytes (e.g. liquid cellulose). For instance, polypeptides (already discussed in Section 2.4), glycosaminoglycans, and DNA are good examples of natural polyelectrolytes.

The main factor strongly affecting the physical properties of polyelectrolyte solutions is the degree of charging. The dissociation of polyelectrolytes would release counter-ions directly affecting the solution's ionic strength and the Debye length. Consequentially, other properties such as electrical conductivity are affected.

If a polyelectrolyte completely dissociates in solution with reasonable pH values yields, it is referred to as very 'strong'. In contrast, polyelectrolytes that partially dissociate at immediate pH with a dissociation constant (*pKa or pKb*) in the range of ~2 to ~10 are termed 'weak'. Electrochemically, it can be seen that, weak polyelectrolytes are not always fully charged in solution. Moreover, their fractional charge can be modified by changing the solution *pH*, counterion concentration, or the ionic strength. These properties have been exploited in several industrial applications. The introduction of new ionic moieties, cations and anions, extend the properties and classical applications of the polyelectrolytes. Ndibewu et al. [79] used two locally available ionic polyelectrolytes (PP1 and PP2) to study the polymeric cementation mechanistic types on two South African subgrade soils (black cotton soil: BCS and reddish

chert soil: RCS) during soil composite pavement compaction processes. The compositional physicochemical properties (*pH* and electrical conductivity, mS) of the two polyelectrolytes measured by preparing a 0.03% (v/v) solution at ambient temperature are presented for illustration in Table 1.

Ionic-lignosulfonate based polyelectrolytes (Stabilizers)	pH	Conductivity (mS)	Turbidity (NTU)	Total Dissolved Solutes (TDS in mg/L)
PP1	4.31±0.02	1.016±0.017	0.58±0.03	0.51±0.03
PP2	3.85±0.01	0.400±0.052	1.57±0.03	0.21±0.01

Table 1. Compositional chemical-physical properties of the enzyme-based formulations measured by preparing a 0.03% (v/v) solution at ambient temperature

In this study, the authors were able to access (via infrared synchrotron light spectroscopy and micro-imaging spectroscopy) the strength enhancement properties (plasticity index) affected by the use of the polyelectrolytes. Although, it wasn't possible for them to describe the exact mechanisms through which polyelectrolytes achieved this kind of polyelectrolytic polymeric-enhanced surface networking, new molecular and complex bonding rearrangements were prominent in more performing microcrystalline formations (Figure 13), demonstrating the polymer character of this important group of natural polyelectrolytes.

PILs have many applications, mostly related to modifying flow and stability properties of aqueous solutions and gels. For instance, they can be used to destabilize a colloidal suspension and to initiate flocculation (precipitation). These properties, if so well desirably monitored, can yield very interesting sought properties obtained from blends with their synthetic counter-parts.

Mecerreyes [78] in his review article has discussed the two main approaches for synthesizing ionic liquids (Figure 14) or polyelectrolytes, named polymeric ionic liquids (PILs) in analogy to their monomeric constituents. This author listed a few examples herein included: cations such as imidazolium, pyridinium, and pyrrolidonium and anions such as hexafluorophos-phate, triflates, and amidotriflates. These new liquid macromolecules are now giving rise to a new family of functional polymers with particular properties and new applications. The first part of this chapter has focused on the renewable sources of these PILs while synthetic aspects of PILs and the main aspects related to their physico-chemical properties are being discussed. There are a few technological applications of these polymers, namely: polymer electrolytes used in electrochemical devices, use as building blocks in materials science, nanocomposites, gas membranes, innovative anion-sensitive materials and smart surfaces. There are also a countless set of applications in different fields such as energy, environment, optoelectronics, analytical chemistry, biotechnology and catalysis. It would be interesting to explore other possibilities targeting their synthesis and blends in the manufacture of personal protective materials.
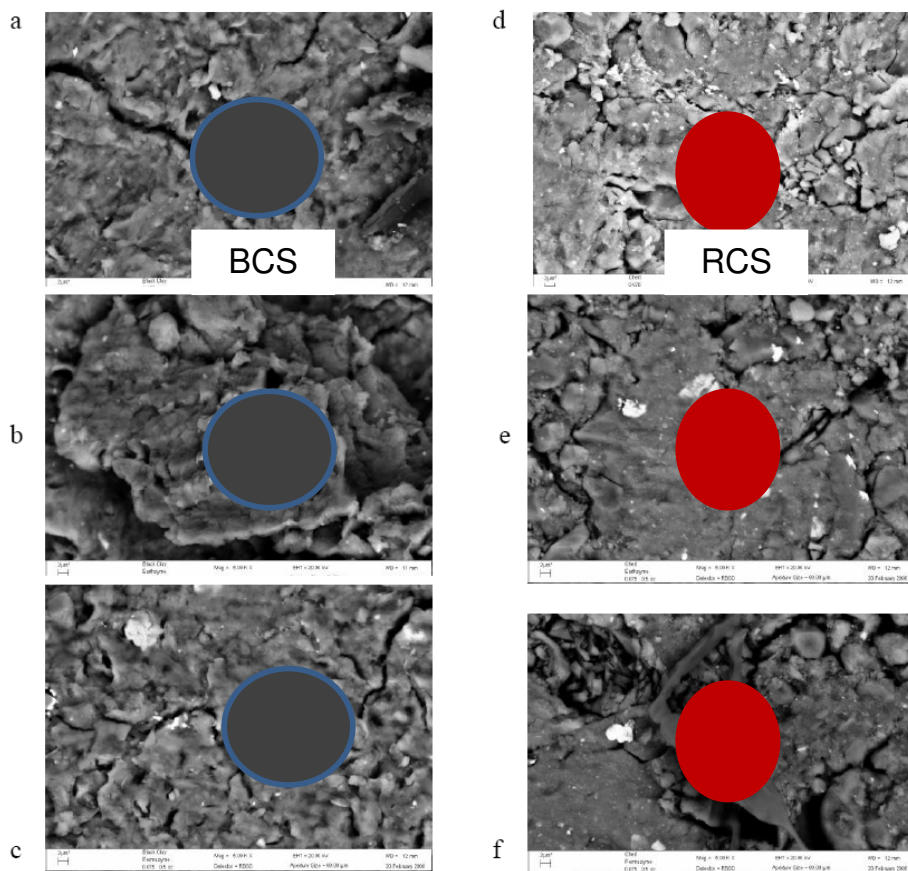
Figure 13. SEM micrographs of (a) black soil composite specimen (BCS), (b) stabilized with PP1 (BCS-PP1) or (c) stabilized with PP2 (BCS-PP2) and (d) red chert soil composite specimen (RCS), (e) stabilized with PP2 (RCS-PP1) or (f) stabilized with PP2 (RCS-PP2) [79].

The potential use of PILs in blends or complex composites of new clothing with high resistance against nuclear, chemical and biological agents is because PILs can potentially impart a surface charge to neutral particles, enabling them to be dispersed in aqueous solution or mixtures (superplasticizer). Elsewhere, they are often used as thickeners, emulsifiers, conditioners, clarifying agents, and even drag reducers. They are used in water treatment and for oil recovery. Many soaps, shampoos, and cosmetics incorporate polyelectrolytes. Some of the polyelectrolytes that appear on food labels are pectin, carrageenan, alginates, and carboxymethyl cellulose. All but the last are of natural origin. Finally, they are used in a variety of protective or surface coating components, e.g. cement.

PILS are also being investigated for biochemical and medical applications exploiting the high solubility characteristics. For example, much research currently focuses on using biocompat-
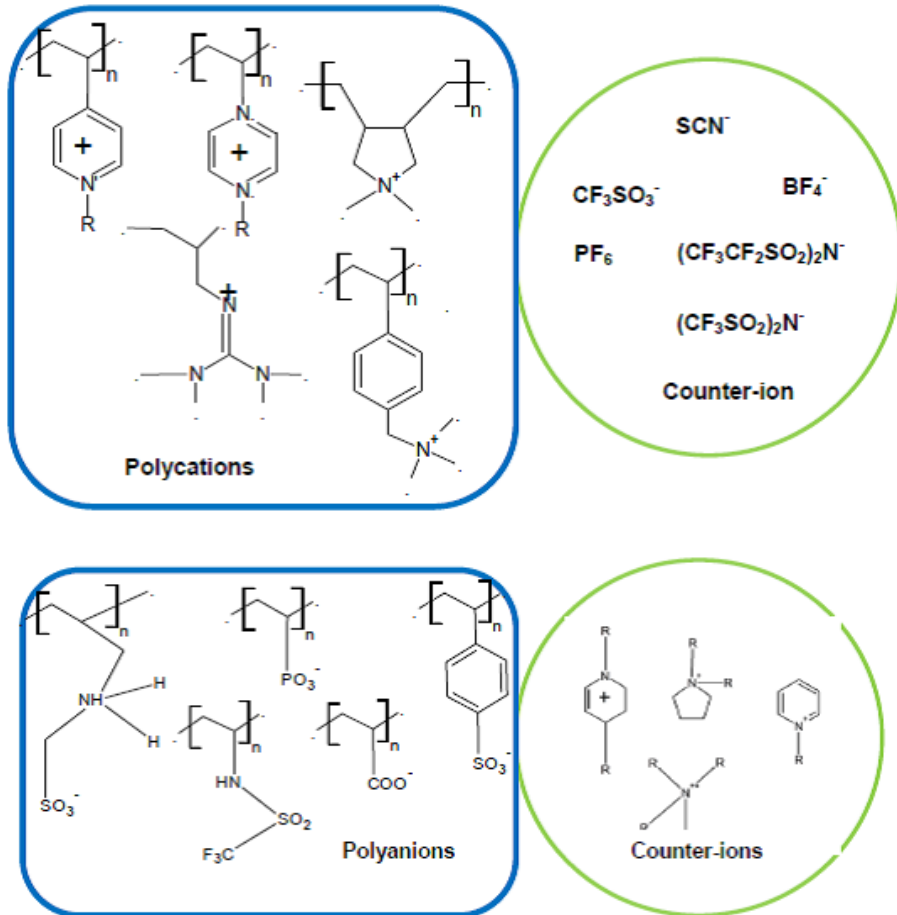
Figure 14. Typical chemical structures of polymeric ionic liquids [80].

ible polyelectrolytes for applications in: implant coatings, controlled-drug release, and many other applications. Recently, the biocompatibility and biodegradability of macroporous materials composed of polyelectrolyte complexes have been described in which the material is presented to exhibit excellent proliferation of mammalian cells [81]. Perhaps, the approach to incorporate PILs into synthetic polymer blends for desired properties and characteristics could exploit the recent processing strategies of polyelectrolyte multilayers (PEMs) utilized in the formation of new types of materials for fuel cells. These thin films are prepared using a technique known as the layer-by-layer (LbL) deposition. In the technique, a suitable charged growth substrate is dipped back and forth between dilute polyelectrolyte solution baths that are positively and negatively charged. The mechanism of polyelectrolyte deposition during which the surface are reversibly charged is adsorption. This allows for a gradual but controlled

build-up of electrostatically cross-linked films of polycation-polyanion layers. This procedure sounds feasible in creating intercalated layers in cellulose-based polymeric protective garments of any controlled thickness to stop the penetration of toxic or chemical agents. The advantage is that thickness control of such films down to single-nanometer scale maybe possible. LbL films can also be constructed by substituting charged species such as nanoparticles or clay platelets [82] in place of or in addition to one of the polyelectrolytes. LbL deposition has also been accomplished using hydrogen bonding instead of electrostatics. Another interesting avenue to explore in this regard could be polyelectrolyte adsorption.

The main benefits of using water-based processes in PILs-cellulose-based garment manufacturing would be reasonably less costs, the utilization of particular chemical properties of the film for further modification, such as the synthesis of inner surface metal-organic, nanoparticles, or porosity phase transitions to create anti-reflective coatings, chemical shutters, and superhydrophobic surface coatings with environmental benefits to biodegrade.

As illustrated in Figure 14, Mecerreyes [80] has also reported that PILs present some of the unique properties of ILs (ionic conductivity, thermal stability, tuneable solution properties and chemical stability) together with the intrinsic polymer properties that are unique. This uniqueness is premised on the ground that most PILs are not soluble in water but in polar organic solvents. This is in contrary to classic polyelectrolytes, usually water soluble while dissociating in aqueous solutions and making the polymers charged to form polysalts. This is due to the hydrophobic character of the counter-ion and the reduced columbic interactions.

Thus, the preparation of inorganic–organic nanocomposites/polymeric blends offer a potential route for producing functional materials that combine the best features of inorganics (e.g. improved mechanical strength, thermal stability) with the properties of PILs.

4. Functional protective materials

4.1. Functional polymers

Because the relatively high persistence length of the cellulose molecular chain conformation and their close packing through numerous hydrogen bonds have made the dissolution of cellulose - a difficult process, the development of new polymeric compounds (e.g. regenerated cellulose) using environment-friendly low-cost solvents for cellulose regeneration is essential for the successful utilization of the cellulose as a component of polymeric materials with a wide applications including the use in the manufacture of protective materials such as PPGs.

Regenerated celluloses have drawn attention owing to their ease to be fabricated. Also, they are biocompatible and biodegradable while thermal and chemically stable.

It should be noticed, though that there is still some persistence difficulty in dissolving this natural polymer thus widening the field of current research into using them in preparing "green" solvents for further polymerization processes.

The different solvents used in the preparation of regenerated cellulose confer to the regenerated newer functional properties (physicochemical and mechanical). These solvents have been extensively discussed elsewhere by Wang et al. [1]. It is worth mentioning a few of these solvents here including: N-methylmorpholine-N-oxide (NMMO), LiCl/N, N-dimethylacetamide (LiCl/DMAc), NaOH aqueous solution, alkali/urea, NaOH/thiourea aqueous solution, and tetra butyl ammonium fluoride/dimethyl sulfoxide system.

5. Toxic industrial chemicals and their potential use by terrorists

5.1. Toxic industrial chemicals

The industrial revolution brought prosperity and improved quality of humankind, along with it the use of chemicals and complex technologies. As a result, industrial chemicals are produced in large quantities, transported and stored for making petroleum, textiles, plastics, fertilizers, pesticides, herbicides and other products for peaceful use [84]. Some of these chemicals such phosgene are utilized for making isocyanates, perfumes and fumigants; cyanogen chloride for making herbicides, dyes and vitamins; and hydrogen cyanide for making plastics, pesticides and sanitizers. Phosgene and cyanogen chloride were used during World War II as chemical weapons. These served to illustrate that some of these industrial chemicals are toxic. According to some researchers [84-86], a substance is toxic if it has a median lethal concentration (LC_{50}) in air of more than 200 parts per million (ppm) but not more than 20 mg/L of mist, fume or dust when administered by continuous inhalation for 1 hour (or less, if death occurs within 1 hour) to rats weighing between 200 and 300 g. It should be noted that the toxic effects of chemical, biological, radiological, nuclear, explosive and other toxic industrial chemicals (TICs) are dose dependent and depends on the mode of exposure such as inhalation through the lungs, ingestion, injection through puncture and absorption through skin.

Interestingly, a substantial use of chemicals is essential to meet the social and economic goals of the world community,, and today's best practice demonstrates that chemicals are used widely in a cost-effective manner and with a certain degree of safety. However, past events such as the 1984 accidental release of methyl isocyanate in Bhopal, India, resulted in 3 000 deaths [87] and according to Sohrabji [88], it contaminated underground water within a 3.5 km radius around the affected industrial buildings. The recent Tianjin hazardous chemical storage facility explosions [89] on the 23 August 2015 resulted in 123 people confirmed to have died and another 50 reported to be missing and most of them being fire fighters. This incident has demonstrated that more work need to be done, to ensure the environmentally sound management of toxic chemicals within the principles of sustainable development. According to the United Nations Environment Programme (UNEP) Agenda 21 [90], there are two challenges, particularly in developing countries, which are: (a) a lack of sufficient scientific information for the assessment of risks associated with the use and storage of a large number of chemicals, and (b) a lack of resources for the assessment of chemicals for which data are available. However, countries such as Germany, Switzerland and China [91], in partnership with the International Co-operation and Assistance Division of the Organisation for the

Prohibition of Chemical Weapon Convention (OPCW) are addressing some of these challenges. They are developing and implementing program such as 'Promoting Chemical Safety Management Training' [92] and the internship program in organic chemistry, respectively, which are aimed at developing skills of personnel from developing countries.

In the current political situation, many governments of the world are afraid that if some of these toxic industrial chemicals fall on the hands of terrorist, or deliberately released, they may have some serious effects on the exposed individuals. A detailed list of toxic industrial chemicals was compiled by International Task Force 25: 1998 Industrial Chemicals Final Report 1998 [93]. As an example, chlorine is commonly used in water treatment facilities, and paper and cloth manufacturing industries and it is often transported by road. According to the United Nations Security Council, Report No. S/2007/314, insurgents in Iraqi have increasingly used chlorine in improvised devices for the purpose of harming unprotected people. Historically, chlorine was used by Germans in 1915 [94, 95] against the British forces, and it was released against the military in Iraq in 2007. Furthermore, chlorine has attracted some attention in both the Syria and Iraqi conflicts, where the parties involved are accusing each other of using chlorine gas as a chemical weapon [94].

5.2. Chemical and biological warfare agents

Chemical warfare agents (CWAs) are chemical substances, whether gaseous, liquid or solid, which are used because of their direct toxic effects on humans, animals or plants. In military operations, CWAs are intended to kill, seriously injure, or incapacitate the victims and are particularly effective because of their extremely high toxicity [85, 97]. They have been classified into nerve, blister or vesicants, choking or lachrymators, blood, tear, vomiting and incapacitating agents [98] based on mode of their effect on humans [99].

Dr Gerhard Schrader of I.G Farben in Germany discovered the nerve agents in the 1936 [100]. The first nerve agent to be discovered was Tabun, followed by Sarin and Soman, their chemical structures are shown in figure 15.

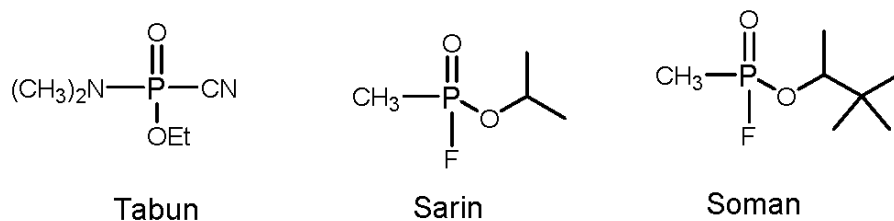**Figure 15.** Selected nerve chemical warfare agents.

More ominously, governments such as those of Germany, Britain, the United States, the former U.S.S.R and Japan invested in the development of delivery system technology comprising artillery shells, unguided gas rockets and the Mark 116 'Weteye' air- dropped gas bombs [101]. The Chemical Weapon Convention (CWC) prohibits the development, production, stockpil-

ing, and use of chemical weapons, except for the purpose not prohibited by the CWC such as industrial, agricultural, pharmaceutical and other peaceful purpose [102].

The most widely published chemical terror incident involving nerve agent Sarin occurred in Japan [103]. A Japanese religious doomsday sect used Sarin against unprotected people in Matsumoto resulting in the death of seven people [104]. Sarin was again used in terror attack by the same religious sect on 20 March 1995 Tokyo subway resulting in approximately 5 500 people seeking medical attention [105, 106]. Unfortunately, the first responders also become victims. Seemingly, the terror attack with CWAs seems to be an on-going activity in Syria, where multiple incidents involving Sarin gas were reported and some investigated by the OPCW [107-109]. The most disturbing threat according to Almemar [96] is the increasing amount of evidence of chlorine gas attacks, by the Islamic State of Iraq and Syria (ISIS) in Iraq and Syria against Kurdish Peshmerga.

Biological warfare agents refer to the military or terrorist employment of microbial or other biological agents such as bacteria, viruses, fungi and toxins to intend or inflict death, temporary incapacitation or permanent harm in humans, animals and plants [110]. This is important in case of filoviruses, Marburg and Ebola; both these agents pose a serious threat as lethal pathogens and their use by terrorist will results in fear and panic [111]. Contemporary biological warfare has its roots in World War I and the post-war era. According to Guillemin [110], the German military spy agents mounted an international sabotage by infecting horses and mules that were being shipped to Britain and France with glanders and anthrax from neutral nations such as the United States, Norway, Spain and Romania. This resulted in entire shiploads of animals being sick and killed. After the tragic terror events of 11 September 2001 in the United States, an unknown perpetrator mailed four letters containing Anthrax spores to unsuspecting victims in Florida, New York and two senators in Washington DC [112]. As a result, 5 of the victims eventually died of inhalation of anthrax wheras 17 others who contracted a cutaneous form of the diseases were successfully treated [112].

Similar to chemical agents, governments around the world are worried that if some of the biological agents, such as anthrax, small pox, plague, tularemia, Ebola, Marburg and others, may find their way into the hands of terrorists, such attack may cause a huge economic loss [113]. According to Aken and Hammond [114], the members of the Japanese cult, Aum Shinrikyo reportedly tried unsuccessfully to get their hands on Ebola virus during an outbreak of the diseases in the Democratic Republic of Congo (formally known as Zaire) in the early 1990s. They attempted using a complex published method for cultivating polio; however, only highly trained experts would be able to master the technique [114]. Thus, with the current developments in biotechnology, there is a possibility that in the near future, such groups or interested states could theoretically, cultivate viruses in the laboratory [115].

In conclusion, perhaps the human suffering and economic impacts resulting from biological agents were recently illustrated in West African countries (Guinea, Liberia, Sierra Leone, Senegal and Nigeria) with the outbreak of Ebola in March 2014. As of 2 October 2014, according to the World Health Organisation (WHO) [116], 7157 of Ebola infections and 3330 deaths were suspected, with only 3953 infections that were positively confirmed by laboratory results.

5.3. Protection against biochemical warfare agents

The two incidents namely: terror attack in Tokyo subway and the Ebola outbreak in West African countries have demonstrated the importance of protecting the first responders and health workers. In the Tokyo subway incident, it was reported [117] that the first group of responders and health-care workers involved in the initial response were not wearing proper personal protective equipment (PPE), and surely not knowing that a highly toxic nerve agent was released to unsuspecting passengers. As a result, 135 of the 1364 fire department personnel who responded to the incident experienced secondary exposure while transporting victims to emergency facilities [118]. Lastly, some the first firefighting responders in the Tianjin series of chemical explosions were also reported to be the victims of the secondary explosions [89].

According to Bray [111], in Africa, Ebola outbreaks resulted in a large number of infections among health practitioners, such as doctors and nurses, mainly because of the inability to employ proper infection control measures, such as proper use of gloves, gowns and masks. Furthermore, people handling the deceased, conducting funerals, traditional healers, mid-wives, mothers, humanitarian and aid workers may also become the victims [119, 120], which may illustrate the importance of training the above groups in the techniques of using personal protective garments correctly.

According to DuPont [121], safe and reliable protective clothing is essential to prevent spreading infection and protect against chemicals. They have recommended different over-the-counter garments that are tailor-made to offer protection against biological contaminated liquids and dust that first responders should consider.

5.4. Personal protective garments against industrial toxic chemicals

For any operation, proper protective clothing is required. However, it comes with numerous variables to be considered such as weight, comfort, level of protection, and duration of protection. Furthermore, it is dependent on the nature of the challenges to be encountered, for example, CWAs or TICs. The commonly used chemical protective clothing are carbon-based hooded suits (one- or two-piece), worn together with gloves and boots and some even wear the carbon-based undergarments [122, 123]. Tugara et al. [124] reported that the elimination of one or more of the ensemble components will reduce and improve weight, logistic concerns, and cost reduction while increasing comfort. More researchers are considering alternative materials such as membranes in the form of films, electro-spun nanofibers, super-hydrophobic materials, fabrics and others [125, 124]. When evaluating the membranes relative to protective clothing, the main properties to be considered for some applications, for instance, the military would include the following: high strength, antiballistic performance, fire-retardant characteristics, vapor absorption and liquid barrier characteristics [124]. So far, the spun-bond and melt blown non-woven materials used for protective clothing offer low cost, improved barrier properties, impermeability to particulate matter, medium strength and comfort [124, 126, 127].

There are different types of materials used as personal protective garments (PPGs). Mostly they are found as multilayers to provide multiple functions. The classic types of the multilayered PPGs consist of the following: (a) air-permeable materials that usually consist of a woven

shell fabric, a layer of sorptive material (for example, activated carbon-impregnated foam or a carbon-loaded non-woven felt), and a liner fabric. At low hydrostatic pressures, liquids can easily penetrate permeable materials; hence the shell fabrics are usually coated with Quarpel and other fluoro-polymers to improve liquid repellency [124, 126]; (b) semi-permeable materials that consist of two types of membranes, the porous as well as the solution-diffusion membranes; and (c) impermeable materials that provide better protection against TICs and CWAs. However, because they prohibit transmission of sweat from the body to the environment, they should be cautiously used with the appropriate microclimate cooling/heating system (Rao, 2006; SANS 5101, 2004). Some examples of the impermeable PPGs are: 4H by the Safety 4 Company, Tychem by DuPont [121], and CPF3 by Kappler [126,127].

Types of fibres	Composition	Commercial products	Protection from mechanical hazards (stab, ballistic, puncture, chainsaw, etc.)	Protection from flame, fire and thermal hazards	Protection from chemical and biological hazards
Aramid fibres	p-aramid (poly-para-phenylene terephthalamide)	Kevlar (DuPont), Twaron (Acordis), and Technora (Teijin)	++ Tenacity: 194.3~229.6 cN/tex Modulus: 4061.8~9713 cN/tex	++ LOI: 25~28 T*: 190°C	+
	m-aramid (poly(meta-phenyleneisophthalamide))	Nomex, Kermel and Corex	++ Tenacity: 33.6~63.6 cN/tex Modulus: 106.0~123.6 cN/tex	+ LOI: 30 T*: 205°C	+
Polyamide imide (PAI) fibre and Polyimide	Polyimide (PI)	Torlon (Solvay) P-84® (Evonik)⁸	+ Tenacity: 37.1 cN/tex	++ LOI: 38 T*: 260°C	+ Poor in alkali
PBI fibres	Polybenzimidazole	PBI (Celanese)	++ Tenacity: 23.8 cN/tex Modulus: 282.6 cN/tex	++ LOI 41 T*: 250°C	+
PEN, PBO and PIPD fibres	PEN (polyethylene-2,6-naphthalate) PBO (p-phenylene-2,6−benzobisoxazole)	Zylon (Toyobo), M5 (Akzo Nobel) Novel yarn	++ (excellent abrasion) Tenacity: 370.9 cN/tex Modulus: 11479 cN/tex	++ LOI: 68 T*: 288~315°C	++ Fair in acid
UHMW-PE fibres⁹,¹⁰	Ultra-high Molecule Weight Polyethylene, Gel spun	Dyneema (DSM), Spectra (Honeywell), Tekmilon (Mitsui)	++ abrasion Tenacity: 264.9 cN/tex Modulus: 12362 cN/tex	− LOI 41 T*: 121°C	++
LCP fibre¹¹	Polyarylate, liquid crystal polymer fibre	Vectran (Kuraray)	++ (excellent abrasion) Tenacity: 247.2~256.1 cN/tex modulus: 61.8~88.3 cN/tex	++ LOI 37 T*: >392°C	++ Good in solvent
PPS fibres	Polyphenylene sulphide, Crystalline thermoplastic fibre	Ryton® (Amoco), Procon® (Evonik), Toray PPS® (Toray)	+ Tenacity: 30.9~39.7 cN/tex modulus: 61.8~88.3 cN/tex	+ LOI: 34 T*: 288~315°C	++
PEEK fibre	Polyetheretherketone, Semi-crystalline thermoplastic fibre	ZYEX, ZEUS	++ Tenacity: 12.7 cN/tex modulus: 70.6 cN/tex	++ LOI: 95 T*: 260°C	++

Table 2. Properties of high-performance fibres used for protective clothing [128]

There has been an extensive research work conducted to improve the properties of the materials while trying not to compromise the protection capacity. The material industry has expanded and adventured into many alternatives that are available to meet the individual's requirements. There are selectively permeable materials (SPMs) that have the combined properties of the impermeable and semipermeable materials; they are extremely thin, and lightweight, and consist of flexible protective barrier materials offering resistance to CWAs and selected TICs. Their protection mechanism is based on selective solution/diffusion process instead of adsorption process that is used by the activated carbon materials [126, 129]. Other material types consist of self-detoxification abilities in which the agent-reactive catalysts are incorporated to reduce the hazard by either hydrolyzing the chemical or trapping it [124, 126].

In general, the list of different types of PPG materials does not end here; there are many more technologies that are also focusing on improving the protection of the PPGs. Some of these technologies include super-repellency functions and electronic fabrics with sensors, for example to monitor physiological parameters [125, 127]. It all depends on what functions one chooses to focus on, ultimately for each requirement, there will be a suitable technology.

Mao [128] recently reviewed the properties of high-performance textile materials available in the form of fiber, film, membrane and liquid (herein presented in Table 2), used for protective clothing. These materials are reported to have exceptional mechanical, fire resistance and chemical resistance.

6. Spectroscopy and permeation tests

6.1. Permeation tests for evaluation of chemical protective materials

Several tests for the evaluation of chemical protective materials have been evaluated [130-135]. This includes that of the mustard gas and a matrix thereof has been compiled, especially in the textile industry [136]. However, most of the materials tested either are expensive or need further improvement. The matrix of materials evaluated will automatically increase the chance of developing readily available ones, also for use by civilians. The challenge remains though in the sampling and detection systems developed so far. A variety of sampling and detection systems have been used to meet the analytical needs of a particular testing scenario described in detail by other authors [137, 138]. Test cell designs prescribed by standard methods have remained basically fixed for over two decades [130, 131]. This has led to the continuous questioning of the analytical reliability for these standard cell designs [139- 141] noticeably with the desire for further improvement. In this regard, some authors [142] have extensively discussed the efforts to improve current nerve guide conduits (NGCs). Their article focuses on research to improve material selection, geometric structures, and incorporation of cells and chemical cues. In this report, they suggested that the advanced NGC model suggested by Hudson and Evans [143] is considered the most widely accepted based on which model the above six major components need to be considered and integrated in an advanced NGC.

Despite all these developments, there is still a general consensus that a comprehensive description of performance criteria for permeation test cells is lacking [144] in the literature. This suggests that there is an urgent need to define scientifically acceptable procedures and criteria addressing a test cell design with minimum attributes that ensure its reliability for the evaluation of chemical protective materials. In this line of thinking, Verwolf et al. [144] emphasized the vapor challenges as one of the more problematic than liquid permeates. These authors state that flowing vapor streams exiting the feed side require precision in its generation and proper monitoring of standard atmospheres of the test chemical(s). This operation is often not an easy task. This can result in large volumes of contaminated air to be disposed of. Furthermore, there would be the requirement of decontamination of the vapor flow path and vent stream upon the completion of a test run. As a practical example, highly toxic compounds such as chemical weapon agents (CWAs) could make this approach practically and economi-

cally not feasible or even prohibitive. Finally, the delivery of a standard vapor to the feed side of the test material may not be taken for granted, because the transfer conduit and connectors could interact with the analyte via sorption phenomena or via a chemical reaction, and/or undesirable partitioning in stagnant regions.

6.2. Resistance of protective materials and spectroscopic characterization

The quality of chemical protective materials is generally judged by the breakthrough time [145- 149]. This parameter describes the time from the beginning of the exposure until the chemical appears on the inside of the glove [148]. As an example, the time range is from 15 minutes to more than 24 hours for different pesticides through different types of glove material [150, 151] Furthermore, the resistance against penetration of a given toxic chemicals through a protective material will depend on chemical-specific physico-chemical properties [128]. This parameter is very important during manufacturability and testing or decontamination exercise. It could be thoroughly evaluated using permeation studies [152] for various toxic chemicals against the protective materials or personal protective garments used for this purpose.

From most of the literature reports and published results [128], the overall outcome is that composite materials and hybrid structures used in protective clothing and personal protection equipment (helmet, knee protection panel, gloves, protection curtains, protection tent and shield, etc.) would be those with unique properties, and should be highly resistant to toxic chemicals. Continuous research should focus on the development of composite materials and hybrid structures usually employed to provide multiple functions in addition to resistance requirements. The results on stress–strain relationship and deformation characteristics during development and manufacturability can no longer be over-emphasized here. This then also places lots of emphasis on simultaneous analytical capabilities and techniques to accompany efforts in the development of traditional protective equipment to highly desired ones such as in the decontamination after any chemical spillage. Because the energy absorption component seems to be important in considering the quality requirements related to the application of most protective materials (e.g. clothing), spectroscopy would seem to be the cornerstone to be considered for most analytical purpose. This is because qualities (aesthetic properties, clothing comfort and human mobility) of protective materials can successfully be assessed or quantitatively evaluated employing many already discussed spectroscopic techniques in the introduction of this chapter such as scanning electron microscopy coupled to X-ray dispersive spectroscopy (SEM/EDS) for surface imaging and structural elucidation; atomic force microscopy (AFM) and scanning tunnelling microscopy for both morphology, and surface-resolved property or associated intermolecular interactions; scattering-type near-field optical microscopy for nanoscale morphology and nanoscale-resolved subsurface imaging, attenuated total reflectance Fourier transform spectroscopy (ATR-FT-IR) for functionalized surface identifications, infrared spectroscopic ellipsometry and nano-FTIR absorption spectroscopy for apertureless near-field optical microscopy, and infrared vibrational nanospectrosocopy for nanoscale composite network formations.

7. General conclusion

7.1. General outlook

The general outlook is a peaceful world, free from not only hunger and poverty but wars and natural disasters. Perhaps amongst the challenges that man must tackle to create a safer environment is not only the need to develop new products to suit specific needs using more sustainable technologies is his ability to solve both yesterday's pollution that include toxic chemicals dumps into the environment and quickly act to stop further chemical accidental spillages. Since man is at the center of protection against nuclear and chemical attack whether conscious or unconscious, his safety is critically important. These projects continue research into the future focusing on developing far more performance protective materials, e.g. polymeric materials of various composite blends with required both mechanical strength and chemical resistance for common use and in the manufacture of personal protective equipment. To realize this sustainable world, we are facing the emerging challenges in agriculture, forestry, academia, government and industry. Thus, stakeholders (governments and researchers) should find the need here to work together for the common goal. From the 'green' perspective, cellulose is the most abundant natural and renewable resource, and is a prime candidate for replacing the petroleum-based products to expand to new applications without polluting the earth. We, as well as have indicated the inherent advantages of safety, biocompatibility and biodegradability of cellulose owing to the fact that cellulose is intrinsically a part of plants and animals (tunicates), and thus, a renewable biomaterial. Co-workers in their works have demonstrated the versatility of the cellulose natural polymer. The abundance of the OH groups endows cellulose with the affinity to inorganic/organic substances, leading to the preparation of hybrid materials, and expanding the potential application of cellulose as a functional material. This chapter has further expanded on the diversity and richness of regenerated cellulose materials fabricated via physical dissolution. Numerous citations have been exploited in putting this chapter together pointing out how in the last decades, regeneration have been astonishing, demonstrating promising potentials in textiles, packaging, biomedicine, water treatment, optical/electrical devices, agriculture and food fields. From one of the literature source, the general agreement is that physical dissolution and regeneration process are environmentally friendly by avoiding the consumption of chemicals because most of the agents can be recycled and reused, and the nature of cellulose is retained. As a result, no chemical reaction occurs, promising to bring another Green Revolution to the comprehensive utilization of cellulose-like natural resources. Therefore, we herein agree to it that cellulose-polymeric focused research impact and benefits are truly fascinating to society. This considers the physical processes in the preparation of new materials via environment-friendly technologies as substitution to the petroleum-based materials.

The overall outlook of functional polymers against toxic chemicals broadly discussed in this chapter can be coined in the following problem statement 'Explorations in cellulose (natural polymer) as a renewable resource may improve the world to be greener and more sustainable in the future, particularly in terms of functional polymers processing (e.g. usage in PPGs and PPE against toxic chemicals) if current efforts encourage further investigations of cellulose-

based materials; that will increase a deeper understanding of the new mechanisms involved in the cellulose dissolution, regeneration and blends tunable with various applications owing to improved mechanical strength and physicochemical properties'. To achieve these goals, a spectroscopic and microscopic approach that combines newly developed simple to advanced hyphenated techniques will surely provide an efficient tool to supplement the existing ones for the assessment of structural integrity and durability of polymeric materials; and to determine differences between designs and manufacture deficiencies towards improvement. Sample preparation may affect the quality of results and their interpretation thus, higher-quality results and reliability will depend on the quality and appropriate sample preparation techniques. An understanding of the impact of sample preparation on the results is vital.

7.2. Conclusion and future perspectives

This chapter started with an overview of natural polymer chemistry with focus on cellulose and cellulose acetate. Polyelectrolytic materials, a typical class of polymeric ionic liquids (PILs), have been discussed to stimulate interest in the cellulose polymers and regenerated cellulose. It is herein shown how modified/functionalized cellulose employing 'green' procedures and strategies owe a great potential in producing new polymeric materials with improved mechanical strength and physicochemical properties against toxic chemical penetration. A subsection has dealt with toxic industrial chemicals and their potential treat in terrorism or bioterrorism. In this section, emphasis has been placed on the resistance of current protective materials to deal with this dreadful threat to world peace and development. Before providing an overview of the authors' outlook on the cellulose polymers and future research perspectives; key analytical features to supplement the understanding of both structural and morphological integrity and the mechanisms imparting enhanced manufacturability/wearability are briefly discussed.

With no intention to claim for any exhaustive review, the chapter has attempted to provide a broad vision on the importance of natural polymers (e.g. cellulose), their regeneration via 'green' routes, processing, blends via multilayering strategies that have been accomplished to date, to stimulate the increasing interests in cellulose research and development. Advantages and disadvantages co-exist, no matter what technologies one invents; however, it is worth noting that the novel "green" cellulose solvents as well as the physical dissolution/regeneration techniques open up a completely new avenue to create novel enticing materials with desired properties and functions. The current challenge to effectively deal with any incident of toxic chemical spillage while protecting the recue agents, as well as preventing environmental disasters constituted the backbone of motivations to undertake this project of writing this chapter.

In view of the literature sources reviewed in this chapter, further explorations in cellulose-based polymeric research could give a full perspective view of the preparation of the environment-friendly cellulose materials and their potential use in personal protective garments (PPGs) against nuclear and chemical agents. New cellulose functionalized materials or regenerated solvents modified for specific properties could also add hope to decontamination

exercises when dealing with cases of usage of chemical war agents'. On a final note, informa-tion provided in this chapter is far from being conclusive, but simply a calling for more research interest and creativity into making the world a more peaceful environment if the clean-up of toxic chemicals or decontamination of nuclear and chemical agents were dealt with effectively using appropriate protective materials and clothing.

7.3. Recommendations

This chapter has limitations, and we apologize for any during readership. We humbly realize that not all that the audiences would expect could be provided in such a short chapter. The first conclusive recommendation would be further readership through the exhaustive list of references and citations. Second, research should continue to provide in the nearest future a validated permeation test cell(s) for many known toxic industrial chemicals and/or specific nuclear and chemical agents of immediate treats to mankind. Moreover, research is encour-aged in the creation of new cellulose-based polymeric materials modified with organic/synthetic counterparts to acquire the most desired characteristics for a wider use in protective materials in general, and for use in the manufacture of personal protective garments (PPGs) against toxic chemicals in particular. Testing of current materials should be done in ambient temperatures to assess the impact of environmental factors such as humidity and air velocity on their permeation breakthrough rates, as well as penetration resistance for specific chemicals.

Experimental challenges during permeation studies lie in the difficulty to determine exactly the start of the chemical breakthrough. This is because of factors such as variations in the temperature settings, the evaporation of the agent exposed and the chemical bonding and interlocking within the material that interferes with the detection of breakthrough [136]. In some types of materials, the permeation time is directly proportional to the material thickness, whereas in some, the permeation time depends on the composition of the material. For example: aluminum foil and activated carbon cloth are materials that can be used for the manufacture of personal protective clothing and whose permeation time would depend much on their chemical or physical composition. In view of the above, it is highly recommended to use non-toxic chemicals for initial testing and experiments before an attempt to simulate 'real' situation experimental designs. Of interest would be a need to compile a world compendium of existing polymers prepared and tested or investigated under set conditions to serve future research purpose. A deeper understanding of the new or old mechanisms involved in the cellulose dissolution and regeneration/processing will not only make the regenerated cellulose materials more functional, but also more reproducible in view of their particular applications in this particular example.

The development of new analytical capabilities, as well as new method development is encouraged to explore the nano- and macrostructure of polymer integrity and durability. This could be specific, starting with cellulose-based polymers or regenerated solvents. There should be an increasing interest for investigations of the renewable resources with 'limit-less' abundance or which can be non-competitively produced. Nanostructured polymers and nanocomposites have been gaining popularity in the last two decades due to their exciting

bulk and surface properties. Indeed, nanocomposites based on polymeric matrices could yield new properties of particular interest. A number of new nanoparticles with extraordinary properties have encouraged the enlargement of the polymer markets. To name a few, carbon nanotubes, graphenes, as well as nanoclays, nanocellulose, metals and ceramics have created new and exciting possibilities. Unfortunately, the successful development of these new materials would strongly depend on the scale-up of reliable processing technologies. Organic–inorganic hybrids are also an interesting research area since many years mainly in the fields of tissue engineering and photoactive polymer nanocomposites. This area can be explored for the development of new interpenetrating networks through sol–gel processes.

Current industry trends in the processing of polymers focus on traditional synthetic polymers with only targeted composite blends or nanocomposites using some particular techniques and approaches, proprietary to industries. The modernization of processing infrastructures at transformation companies must be encouraged to involve research, including fundamental research, as well as collaborative research between industry-based research and development (R & D). Technical efforts are dedicated to the modification and updating of the current equipment and real innovations in new polymer creation and processing strategies are relevant in conquering most challenges raised in this chapter and elsewhere.

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