

Chapter 2

Processing and Characterization of Natural Polymers

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2.1 Introduction

Polymer processing involves two main aspects, processing of polymers into forms for further processing as powders and pellets and processing of polymers into finished products of desired geometry such as scaffolds, microneedles, and films for food packaging. The former involves techniques such as extrusion and blending, while the latter could involve processes such as injection molding or film casting. Such will be discussed in this chapter. Furthermore to determine the usefulness and for quality assurance and safety, it is necessary to characterize polymers to determine properties such as mechanical strength, thermal conductivity, microstructure, and density. For such purpose techniques such as Fourier transform infrared spectroscopy, transmission electron microscopy, differential scanning calorimetry, and thermogravimetry analysis have been developed and are widely applied in characterization of polymers.

Many processing techniques applied for the industrial synthetic polymers are applicable to natural polymers, however, in several cases certain limitations exist which limit the applicability of some of the conventional polymer processing techniques to natural polymers. Measures have been taken by researchers to address such limitations and/or modify the polymer processing technique to suit natural polymers. For example, starch is plasticized to form thermoplastic starch (Nafchi et al. 2013) which can be processed using extrusion molding, a process typically applied to thermoplastics.

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Proper characterization aids in the selection of polymers for specific application such that the best suited polymer or combination of polymers can be selected. It is desired that the typical processes used in industry for processing of synthetic polymers to be adoptable for natural polymers in order to save costs and for convenience. In this chapter we also look at processing of natural polymers into composites and blend. This extends to combination of natural and synthetic polymers. We look at the role of natural polymers in composites containing either natural or synthetic polymers as matrices. Typical characterization methods which are applied in industry and how they are applied for characterization of natural polymers are discussed.

2.2 Blends and Composites

Blends and composites are a good means of obtaining broader usability from polymers either as matrix or fillers. Composites have been defined as a combination of two or more elements with distinct identity and properties bonded to form a multiphase multicomponent system, while the component elements maintain their physical and chemical identities. A composite is made up of a polymer as a matrix and a filler, where the filler could be a fiber, flake, or a woven fabric which could be a ceramic, metal, or polymer element. Polymers can therefore play the role of a filler or matrix in composites. The need for such systems is in the desire for physical and/or physicochemical parameters which cannot be met by other simple mono-component synthetic or natural materials (Cazacu and Popa 2005).

Composites can be made up of both synthetic and natural polymers. The blending of both natural and synthetic polymers yields a new breed of materials with more varied properties for broader applications. Composites based on natural polymers have gained increasing attention as over the years largely due to the fact that the production of synthetic polymers, albeit involving advantages such as consistency of product and ease of production, have raised environmental concerns due to their nonbiodegradability and potential toxicity.

Blends are formed when two or more polymers are physically mixed either in the molten state or dissolved in appropriate solvent. Polymer blends obtained from mixing of polymers can be of various forms such as miscible one phase, miscible separated phase, compatible, incompatible, alloys, interpenetrating and semi-interpenetration polymer networks, or molecular composites. The two main classifications of polymer blends are either as compatible or incompatible blends.

Incompatible blends are immiscible blends where the separate phases are well defined. These blends generally have poor mechanical properties. Compatible blends are those blends which form a single phase where different components cannot be separately identified morphologically. These types of polymer blends are more likely to attain superior mechanical properties than the component polymers. Incompatible blends are more common than compatible polymer blends.

Composites exist in nature in the form of wood and bones. Wood, for example, is a good representation of polymer composite. The hemicellulose and lignin act as the polymer matrix component, while the cellulose fibers act as the filler components (Freudenberg 1932; Lee et al. 2014). The interactions between the hydrophobic lignin and hydrophilic cellulose components are thought to be due to one ester and one ether linkage forming a lignin cellulose complex (LCC) (Rozmarin 1984), which acts as a compatibilization agent thought to be responsible for the peculiar structural stability of wood (Takase et al. 1989). Understanding of naturally existing composites has contributed to the development of novel composites with improved properties.

Man-made composites have been in existence since 500 BC where pitch was used by the middle easterners as binders, papyrus, and reeds in building boats. The Europeans, Asians, and Americans are also reported to have used laminated wood veneers as decorations as far back as first century AD. Shellac resin-based laminates have also been used by the Indians for over 300 years, while evidence of laminated wood is seen in Thebes dating as far back as 1500 BC (Cazacu and Popa 2005; Lee 1989).

Methods employed in formation of blends and composites include hand lay-up, low-pressure injection molding, compression, molding, extrusion, centrifugal casting, spray-up, reinforced reaction injection rolling, filament winding and pultrusion methods (Cazacu and Popa 2005; Kulshreshtha 2002).

2.2.1 *Compatibilization*

The compatibility of polymer blends can be significantly improved by the presence of specific interactions such as hydrogen bonding (Cao et al. 1989) electron-donor and electron-acceptor complexation (Simmons and Eisenberg 1986) and ion-ion pairing (Simmons and Eisenberg 1986; Cazacu and Popa 2005). The properties of a polymer blend are dependent of the properties of individual components. These properties can be improved by modifying the interfacial and superficial properties of the components. This process is referred to as compatibilization.

Compatibilization can be achieved by the use of additives known as compatibilizing agents. Compatibilization is also done by using a graft copolymer of the natural polymer which is miscible with each of the components of the polymer blend. This is reactive compatibilization and is chemically formed during mixing. Chemically modifying the natural or synthetic polymers such that certain functional groups are formed on the polymers, thus improving interactions between the components of the polymer blends. Copolymerization, i.e., forming polymers from more than one monomer unit, is also a method of compatibilization as the different monomer units result in interactions which may improve miscibility.

Silanes such as amino silanes, aminopropyltriethoxysilane, glycidoxypopyltrimethoxysilane (Tran et al. 2014) and methacrylopropyltrimethoxysilane (Salon et al. 2005), and isocyanates can also be used alongside or in place of MAPP.

The mechanism of compatibilization involves a silanol group (Si–OH) forming between the silane and the water molecule on the cellulose. This then forms a covalent or hydrogen bond with the cellulose (Xie et al. 2010). Silane has also been used as compatibilizer in cellulose/low-density polyethylene (LDPE) composites. Pre-impregnated cellulose fibers in LDPE dissolved in xylene solution yielded composites which show up to 50 % increase in mechanical strength (Herrera-Franco and Aguilar-Vega 1997).

In one innovative approach degraded LDPE is used as a compatibilizer for LDPE–wood composites (Ndlovu et al. 2013). As the LDPE degrades they form functional groups which make them applicable as compatibilizers. Although the degraded LDPE does not increase the thermal stability, significant improvement in the mechanical and viscoelastic properties of the LDPE–wood composite can be achieved using the degraded LDPE as compatibilizer. Such processing techniques allow for utilization of partially degraded LDPE which could be in the form of recycled LDPE contributing toward waste recycling. Some detailed examples of compatibilizers used for producing composites of synthetic and natural polymers can be found in (Cazacu and Popa 2005). Some of which are listed in Table 2.1.

2.2.2 Blending of Natural Polymers with Synthetic Polymers

The mixing of natural and synthetic polymers allows for the combination of the desirable high-performance mechanical properties, consistency, and water resistance property of synthetic properties with the low cost, biodegradability, multifunctionality, and biocompatibility of natural polymers. This leads to achieving new materials with more varied physical and physicochemical properties for broader applications. The main aims of mixing natural and synthetic polymers are either to reduce cost, improve performance, or tune specific properties such as biodegradability.

Blending of polymers allows the possibility of mixing inexpensive and relatively abundant polymers with expensive ones using low-cost mixing methods, thus reducing the cost of the polymer while still attaining high performance required. The presence of natural polymers within synthetic polymer systems also speed up the process of biodegradation. The degradation of the blend or composite begins with the degradation of the natural polymer component within the material which results in increasing the surface area available for water, photo, chemical, and microbial action. This is due to the degradation of the natural polymer within the material leaving behind spaces between the fragments of the material making it more susceptible to degradation (Cazacu and Popa 2005). Figure 2.1 shows a sketch of possible route for degradation of natural polymer composites.

Lignocellulose-based biomass is used in combination with synthetic polymers as they are widely available. Lignocellulose deposited to the biosphere annually is reported to be about 200 billion tons. This includes lignocellulose from wood waste, e.g., furniture and construction industry, agro wastes of plants, waste from

Table 2.1 Natural/synthetic composites and compatibilizers

Synthetic polymer	Natural polymer	Compatibilizer	Processing technique	Reference
Polypropylene	Sawdust	Maleic anhydride	Extrusion	Cazacu and Popa (2005)
Polypropylene	Wood fibers	Ethylene-propylene or ethylene-propylidene copolymer Maleate polypropylene Calcium stearate	Injection forming	Cazacu and Popa (2005)
Low density polyethylene	Lignocellulosic fibers Sawdust	Ionomer polyethylene Maleate polypropylene Low molecular weight polypropylene Maleic anhydride	Extrusion Injection	Cazacu and Popa (2005)
Polyurethane	Mechanical pulp	Isocyanates	Pressing	Cazacu and Popa (2005)
Phenol formaldehyde	Lignocellulose	Chemical modified fibers	Pressing	Cazacu and Popa (2005)
Polyester + PE + PP	Wood fibers	Phenol resins	Pressing	Cazacu and Popa (2005)
Carboxylated Nitrile Rubber	Natural Rubber	Maleic anhydride grafted polyisoprene epoxy resin	Roll milling	Onyeagoro (2013)
Chlorinated Polyethylene	Natural Rubber	Maleic anhydride grafted ethylene propylene diene rubber EPDM-g-MA	Thermal mixing followed by roll milling	Sirisinha et al. (2004)
Carboxylated nitrile rubber	Natural rubber	Bis(disopropyl) thiophosphoryl polysulphides	Thermal mixing followed by roll milling	Naskar et al. (2001)
Poly(lactic acid)	Natural rubber	Poly(lactic acid)-natural rubber tri block copolymer		Chumeka et al. (2014)

pulp and paper industries (Cazacu and Popa 2005). This is even more than the quantity of synthetic polymers produced every year which is estimated at 150 million tons per year.

The main challenges in blending natural polymers such as lignocellulose with synthetic polymers lie in the hydrophilic nature of natural polymers such as polysaccharides and the hydrophobic nature of synthetic polymers such as

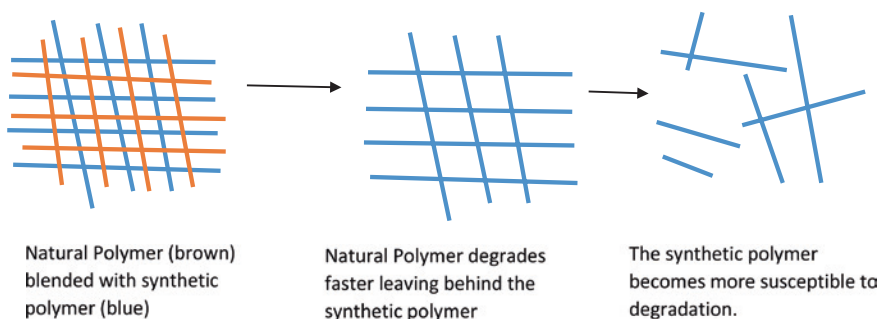


Fig. 2.1 Degradation of natural and synthetic polymers

polyethylene. The polarity leading to intermolecular attraction between the natural polymer but poor adhesion between the natural polymer and the synthetic polymer leading to poor wettability and dispersion. An advantage of natural polymers is the presence of many functional groups such as hydroxyl, ester, and carbonyl groups (Rozmarin 1984). This makes it possible for them to be modified for desired functionality and to improve compatibility with synthetic polymers, thus forming blends and composites of high performance.

Natural polymers can be blended with synthetic polymers either as fillers, reinforcement fibers, mixing components, or grafted copolymers for compatibility. Figure 2.2 shows some materials obtainable from mixing of natural and synthetic polymers and some example applications summarized from various texts (Yeh 1995; Garg and Jana 2007; Cazacu and Popa 2005).

Incorporation of natural polymers within synthetic polymer matrices can be done through impregnation of the natural polymer component within the monomer units such as styrene, vinyl chloride or methyl acrylate, resins such as epoxy or polystyrene or within polymer–monomer systems such as styrene–polyester resin or methyl methacrylate–polyester resin–styrene systems, followed by polymerization. This impregnation allows for strong interaction between the functional groups and components of the natural polymer and the impregnation agent.

Another means of incorporating natural polymers with synthetic polymers is through compounding. This involves mechanical mixing of the natural polymer with the synthetic polymer either in the melt state followed by extrusion and thermoforming or at room temperature. Polypropylene, polystyrene, and polyethylene are the most common synthetic polymers blended with natural polymers.

TPS blended with LDPE and linear low-density polyethylene (LLDPE) are formed in a twin screw extruder using PE-grafted maleic anhydride as compatibilizer. Despite the reduction in tensile strength and elongation from 18 to 10.5 MPa and 340–200 % as the TPS content increased from 5 to 20 % (Sabetzadeh et al. 2015), the composites had sufficient thermoplastic property to be processed into films using the conventional blowing process used for commonly used polymers in industry. The films also had the required standard mechanical properties suitable for packaging application according to ASTM standards.

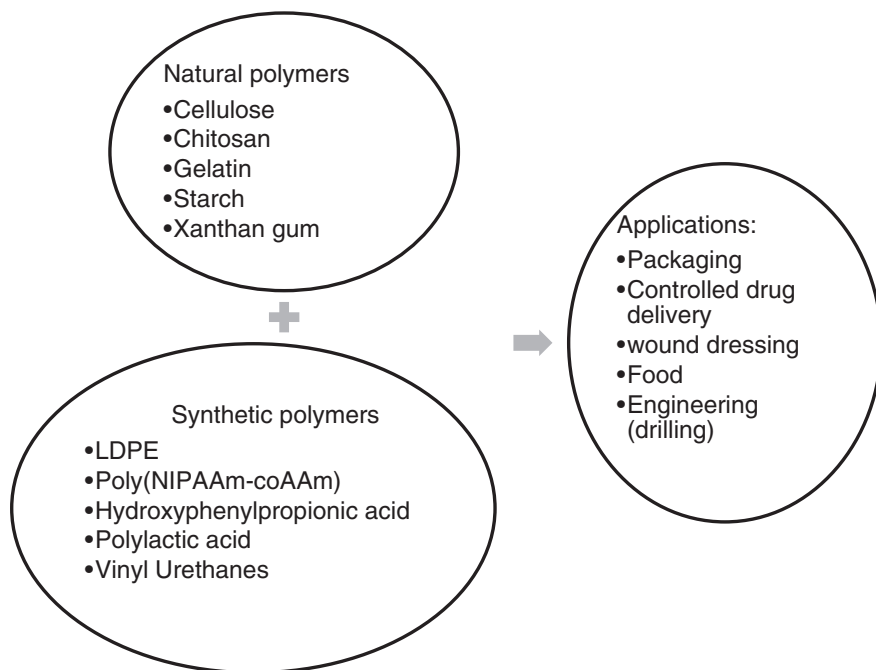


Fig. 2.2 Blends of natural and synthetic polymers with example applications (arranged in order of correspondence)

It is important to be able to process biopolymers using the common industrial processes as this makes them more adoptable industrially without the need for specialized equipment which could increase cost of production. It must therefore be considered that a trade-off between the optimum performance property of the material and the environmental friendliness should be carefully considered, while selecting natural- and synthetic-based polymers for any industrial application.

Natural polymers are also blended with other natural polymers. This allows a combination of their properties to obtain a fully biodegradable material with improved properties. For example, a combination of chitosan with cellulose combines the film-forming properties of chitosan with the structural strength of cellulose. Such blends of natural polymers tend to be more compatible due to the similarity in structure and hydrophilic nature.

Energy of mixing for blends and composites

It is not enough to simply mix components to obtain a composite with the expectation that it would result in a new material with desired properties. It is important to study the particular properties of each component, the interactions between the component, compatibility or incompatibility of the components, and the long-term stability of the produced composite. The structural and molecular characterization of the composites is therefore of importance.

Detailed understanding of the structural and morphological properties of components makes it possible to pre-evaluate the miscibility of components to form composites thus making for easier selection processes. Such did not become possible until 1995 (Cazacu and Popa 2005). It is established that the miscibility of two or more polymers is dependent on the free energy of mixing (ΔG_{mix}).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} < 0 \quad (2.1)$$

ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy variations and T is temperature. To form a miscible blend, the ΔG_{mix} must be negative (Cazacu and Popa 2005).

2.2.3 Natural Polymers as Matrix in Composites

Natural polymers are used as matrices for composites either alone or in combination with synthetic or other natural polymers. Natural polymers such as rubber, starch, cellulose, chitosan, and gelatin are used as composite matrix in various applications such as construction and biomedical. This could be either in their modified form, refined form, partially isolated form, or in their raw complex form. Although natural polymers have disadvantages such as poor consistency, high moisture absorbance, low resistance to UV, chemical and microbial activity, they possess advantages such as low cost, biodegradability, lightweight, versatility (due to the fact that they can be modified into different forms based on their functional groups) and availability, for example, lignocellulose-based waste estimated to up to 200 billion tons annually).

Starch is a good candidate for polymer matrix, however, starch is prone to destruction and polymerization during processing into the melt state (Bergthaller et al. 1999). This challenge is addressed by adopting the right processing conditions, using a twin screw extruder or a corotating twin screw extruder. The application of plasticizers such as glycerol, sorbitol, urea, polyethylene glycol, poly vinyl alcohol, and sucrose also improves the processibility of starch (Roper and Koch 1990). This results in a thermoplastic, flexible, biodegradable, hydrophilic starch form referred to as thermoplastic starch (TPS). TPS has better thermoplasticity, film forming, and molding properties (Cazacu and Popa 2005).

TPS starch composites incorporating natural and synthetic polymers can be formed using industrial thermoforming methods such as extrusion and injection molding. In particular, example compounding TPS from cassava source with synthetic polymer, LDPE significantly improves the thermal and mechanical properties of TPS. Further improvement in the mechanical properties is observed by modification into composites using cotton fibers as reinforcement and carrageenan as gelling agent. The composite was processed using an internal melt mixer followed by injection molding without damaging effects on the TPS (Prachayawarakorn and Pombage 2014).

Composites of glycerol-plasticized TPS from rice starch with either cotton or LDPE as reinforcing agents show improved tensile strength and Young's modulus

with the incorporation of cotton or LDPE compared to TPS only. The compatibility between TPS and LDPE is improved using either maleic anhydride polyethylene or vinyltrimethoxysilane as compatibilizing agents. The water absorption property which is important in maintaining the stability of the material is reduced by the inclusion of cotton and LDPE in the TPS matrix (Prachayawarakorn et al. 2010). In this case the synthetic polymer is also acting as a filler rather than a matrix in the composite, while the natural polymer TPS acts as the matrix component.

2.2.4 Natural Polymers as Fillers and Reinforcements

Natural polymers in their modified, refined, or complex raw form can also be incorporated into natural or synthetic polymer matrixes. In Table 2.2 we summarize some natural polymers used as filler in composites of natural and synthetic polymers. Most of the natural fibers used as reinforcement in polymer composites are cellulose, lignocellulose, or pectin based. They derived from sources such as wood, cereal straw, bagasse, cotton bark, rice husks, pulp, and vegetables such as jute, flax, sisal, hemp, and ramie (Cerqueira et al. 2011).

Cellulose is commonly used as reinforcement or fillers in natural and synthetic polymer matrices as fibers, viscose, and powders or in modified forms as esters, ethers, or grafted onto the polymer. Other than being the most abundant polymer in nature, it offers advantages such as low cost, low density, mechanical strength, ease of processing and biodegradability (Cazacu and Popa 2005). Cellulose also tends to form better bonds with polymers, a property thought to be due to the interaction between the $-OH$ groups in cellulose's anhydroglucose unit

Table 2.2 Natural polymer as matrices in composites

Natural polymer matrix	Filler/reinforcement	Compatibilizer	Processing method	Reference
Natural rubber	Jute fiber	–	Roll milling followed by hot compression	Pantamanatsopa et al. (2014)
Wheat starch	Cotton fiber	–	Hand layup	Komuraiah et al. (2013)
Natural rubber	Organophilic layered clay (organoclay)	Epoxidized natural rubber	Internal mixer followed by vulcanization using conventional sulphuric system	Teh et al. (2004)
Natural rubber/LLDPE blend	White rice husk ash	Poly(propylene–ethylene–acrylic acid) (PPEAA)	Internal mixer	Ismail et al. (2001)
Rice starch	Cotton fiber	–	Hand layup	Komuraiah et al. (2013)

and the functional groups present in the synthetic polymers. Cellulose has three –OH groups which have different polarity and regioselectivity which attribute to the peculiar physical properties of cellulose and its ability to form various derivatives. The versatility of cellulose makes it possible to modify for various composite systems.

The poor solubility in organic solvent, low thermal stability, hydrophilicity, and polarity of cellulose poses some challenges in application as fillers in composites. This leads to poor dispersion in melted polymer, weak interaction between the cellulose fiber and matrix and difficulty in thermal processing. These challenges can, however, be met by using a compatibilizer, chemical modification of the cellulose, or by dissolving cellulose in a suitable solvent prior to dispersing in non-solvent for better dispersion (Cazacu and Popa 2005).

As an example we look at natural fiber jute reinforced natural rubber. In this case natural polymers are being used as matrix and reinforcement. Compatibilization is achieved through coating of the jute fiber with natural rubber using immersion technique. The fibers are treated with sulphuric acid to delignify prior to coating. The impact of treatment of the jute fiber is compared with untreated jute fibers and natural rubber in Fig. 2.3. In Table 2.2 we list some composite systems which use natural polymers as matrices. While Table 2.3 gives some examples of natural polymers as fillers in synthetic and natural matrices.

Polypropylene is one of the common synthetic polymers for producing cellulose-reinforced composites. For this purpose maleic anhydride-grafted polypropylene (MAPP) is the preferred compatibilizing agent. MAPP can be bonded covalently through esterification to the cellulose functional groups. The effectiveness of the bonding depends on the PP chain length in the MAPP. Where short

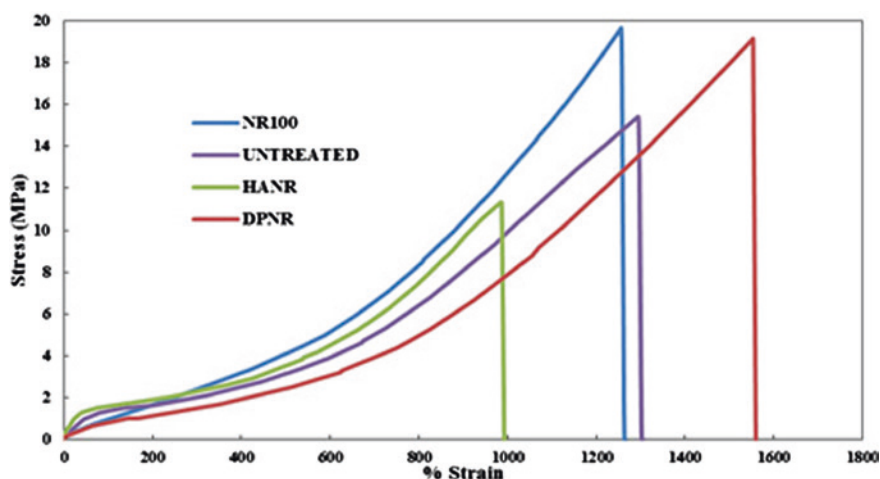


Fig. 2.3 Stress-strain graph of HANR and DPNR-treated jute composite compared with untreated jute composite and natural rubber (Pantamanatsopa et al. 2014) (creative commons license)

Table 2.3 Some examples of natural polymer fillers in synthetic and natural matrices

Natural polymer filler	Polymer matrix	Compatibilizer	Processing method	Reference
Cotton fiber	Rice starch Wheat starch Urea formal dehyde Plaster of paris		Hand layup	Komuraiah et al. (2013)
Sugarcane bagasse fiber	Polypropylene		10 % Sulfuric acid, delignification and compounding in a thermokinetic mixer	Cerqueira et al. (2011)
Sisal fiber	Poly lactide (PLLA)	Bacteria nanocellulose coating	Solvent casting followed by injection molding	Lee et al. (2012)
Cellulose	Fish gelatin	—	Solvent casting	Santos et al. (2014)

chains facilitate coupling between polar groups on cellulose and nonpolar groups of the synthetic plastic. While longer PP chains cause steric hinderance which limits the attraction between the cellulose and polymer to the superficial layer (Felix and Gatenholm 1991; Cazacu and Popa 2005).

Composites of natural polymer blends can be produced by dissolving the fiber and matrix material, mixing the dissolved form followed by film casting and drying. This can be achieved by either dissolving the fiber and matrix in the same solvent, coagulating in a nonsolvent or coagulation in a vinyl solvent prior to polymerization of the resulting gel (Nishio 1994; Cazacu and Popa 2005).

2.3 Processing Techniques

The method of processing of polymer composites depends on the factors such as the nature of the polymer and fiber, the targeted application which could be biomedical applications such as wound healing and scaffold or for construction or producing vehicle car parts. In this section we will look at some specific examples where natural polymer has been processed into composites for various applications. In so doing we will discuss the processing techniques used to produce the natural polymer being discussed. The processing techniques discussed here vary from those used for engineering applications such as composites used for aircrafts to those used in biomedical applications such as scaffolds for tissue replacement and transdermal films for wound healing.

2.3.1 Extrusion Molding

Extrusion molding is generally used for polymers with thermoplastic properties. The process involves melting polymers under heat and shear to achieve uniformity of the polymer with or without other polymers and additives to form blends or composites. Processing of polymers as matrixes for applications such as pharmaceutical or engineering often require processing the polymer in its melt state to attain uniformity and desired shape. Extrusion molding is mostly based on flow of a molten polymer in a screw, while injection molding in addition to this involves flow of the molten polymer into a cavity and cooling of the polymer within the cavity. The polymer is usually introduced into the system through the hopper in the pellet or granular form, this then forced through a screw and barrel which melts and mixes it and then through a die where it forms into desired shape. There usually exists a breaker plate and screen between the barrel and die to filter out unwanted particles and achieve uniformity. This is followed by sizing and cooling where the extruded polymer is formed into final size and cooled. The conditions (such as temperature, pressure, speed, time) in an injection or extrusion molding system depend on the type of polymer and other constituents of the blends (fillers, additives, etc.). Extrusion is a very versatile process of much industrial relevance. Typically, extrusion process is used widely in plastics industries to achieve end products such as pipes, tubing, straws, and films for packaging. Further reading on extrusion can be found in Seymour and Carraher (1992) and Ebewele (2000). Figure 2.4 is a representative sketch of an extruder.

This method has been applied in various industries such as pharmaceutical (Vervae et al. 2008). In the pharmaceutical application, for example, where the incorporation of drug within a polymer is required as a matrix carrier for drug component and other additives. A hot melt extrusion process is used to achieve a uniform blend of the drug formulation. In such applications there are usually temperature restriction to prevent denaturing of the active drug ingredient such that hot melt extrusion of pharmaceutical agents employ polymers which can be thermoformed at relatively low temperature which will not damage the drug ingredient. Hot melt extrusion is often preferred over other methods such as compression molding or casting due to its continuity which makes automation more possible as all processes (mixing, melting, and shaping) can be completed in a single equipment (Repka et al. 2007; Crowley et al. 2007).

Hot melt extrusion is also preferred due to the homogeneity attainable from the process. Examples of natural polymers which can be processed using hot melt

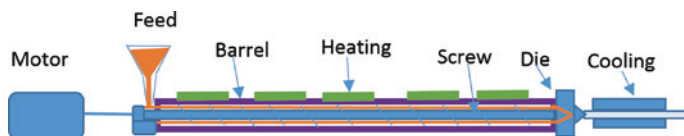


Fig. 2.4 Illustrative sketch of an extruder

process include gelatin (Andreuccetti et al. 2012), starch, waxes, lipids, and derivatives of cellulose such as ethyl cellulose (Vervae et al. 2008). Often plasticizers are used to improve the thermoplastic properties of the polymer for better thermal processing.

Here we use an example of the preparation of gelatin-based films containing *Yucca schidigera* extract using glycerol as plasticizer where extrusion molding is applied in preparing the films (Andreuccetti et al. 2012). Glycerol concentration varies between 0.25 and 8.75 g per 100 g of protein. When extrusion, blown extrusion and casting method are compared, the processing technique does affect the properties of final film formed. The films produced by extrusion showed higher flexibility than the blown or casted films. While the solubility of the films is not affected by the processing method, the extrusion blown films had lower water permeability. It is also necessary to add water up to a moisture content of 35 % to the gelatin-based film to further aid the extrusion process. Prior to extrusion the samples are allowed to equilibrate at 5 C and 60 % humidity for 24 h. The temperature in the feeding zone of the extruder was 65, 100 C in the intermediate zone and 75 C at the die while the screw rotated at a speed of 47.2 rpm.

In one novel approach, conditions in an extrusion process provided the right conditions (temperature and pressure) for wood to exhibit flow properties which results in more compatible blending with engineering plastics to form better wood plastic composites. Here the wood was first modified using phenol formaldehyde. Under these conditions the polymers in wood, mainly lignin and carbohydrate serve as plasticizers and binders, to give wood its thermoplastic properties making it possible for wood to be heat extruded like other engineering plastics (Miki et al. 2014).

Multilayer extrusion is also possible. This is of particular importance for moisture-sensitive polymers such as starch and proteins. In this case a layer of water-resistant polymer or other material can be coated unto the moisture-sensitive polymer forming multiple layers of controlled thickness (Yu et al. 2006; Martin et al. 2001; Van Tuil et al. 2000; Wang et al. 2000).

2.3.2 Injection Molding

Injection molding is also a fairly versatile process of industrial significance. It involves conversion of thermoplastic and thermosetting polymers in the molten or viscous state into solid finished materials. It is typically used for achieving finished products such as forks, spoons, and parts for electronics. The process generally involves heating of the polymer which is introduced in the form of pellets of powder, followed by injection within a heated barrel and screw and then injecting into a mold cavity and cooled under pressure to minimize shrinkage. The resulting cooled polymer is then ejected from the unit.

Injection molding has been shown to be applicable in the biomedical area for producing, for instance, 3D scaffolds. Scaffolds developed from cornstarch-based polymers have been introduced using hydroxyapatite as reinforcement and

carboxylic acid-based blowing agent (Gomes et al. 2001). It is possible to achieve 3D scaffolds with complex structures and porosity, while maintaining significant mechanical strength. Producing scaffolds using conventional injection molding offers the possibility of achieving a reproducible method for producing biodegradable polymer-based scaffolds for load-bearing tissues. A review of injection molding and its applications in drug delivery contains some natural polymer-based polymer products of injection molding (Zema et al. 2012).

A biocomposite consisting of crayfish powder with 60 % protein and polycaprolactone has been used to prepare biocomposite using injection molding (Felix et al. 2015). The plasticity of the protein was enhanced using glycerol as plasticizer. The injection molding conditions such as temperature and speed were optimized by rheometry and thermal analysis. The mechanical properties of the crayfish powder protein were significantly enhanced to yield a composite material with suitable mechanical properties for injection molding.

2.3.3 Solvent Casting

This is a processing method commonly used for forming polymer films. The ability of polymers to form films is important for various applications such as packaging, transdermal drug delivery, and wound healing. Films may also be used as coatings. Uniformity is key characteristics of films for any application. To achieve consistency in film formation either from neat polymers or blends certain procedures are followed. Methods for film forming include self-absorption of monolayers (SAM), spin coating, thermal spraying, solvent casting, floating technique, and Langmuir–Blodgett film forming. Most common techniques being solvent casting and spin coating.

Here we take a case study of nanocellulose as a reinforcement in polymer composite focusing on the processing techniques applied in developing such composite. Gelatin from fish skin is acting as the polymer matrix, while cellulose whiskers from cotton linter are used as the reinforcement component (Santos et al. 2014).

First water at 24 °C was used to hydrate the gelatin and glycerol using 25 wt% glycerol concentration. The suspension was heated to 50 °C and stirred for 15 min at this temperature. This was followed by slowly adding the cellulose whiskers, while homogenizing at 10,000 rpm for 10 min. After the first 2 min the cellulose was completely added. The homogenization is a mechanical method of preventing aggregation of the cellulose in the gelatin mixture. To eliminate gas bubbles, some of which might have been formed during the homogenizing, the gelatin/cellulose mixture was vacuum degassed using a V-700 vacuum pump at 30 mbar for an hour. The films were formed by pouring on a glass plate and allowed to dry at room temperature for 24 h, after which dry films are formed. The films are detached from the glass plate and can be stored in a desiccator to maintain a constant humidity (Santos et al. 2014).

2.3.4 Spin Coating

Spin coating is a well-established technique widely used in polymer industry to produce thin films on substrates. The typical setup includes a dispenser unit and a spinning unit as illustrated in Fig. 2.5. The dispenser deposits a small amount of the material which could be in the form of a neat polymer, a polymer composite or a resin, onto the center of the substrate attached to the spinning unit. The spinning unit then spins at a set speed which is usually between 1500 and 6000 rpm depending on the requirement. This spinning motion induces a centripetal force, which results in the material spreading to form a thin film. Excess film is spun off the substrate. A film in the micrometer range is classified as a thin film.

The film thickness can be controlled by varying parameters such as spinning speed, spinning time, and the fluid viscosity. This process has been employed for coating thin films of natural polymers such as chitosan (Mironenko et al. 2014), hyaluronic acid (Ding et al. 2012), and cellulose (Da Roz et al. 2010) for various applications. An example is the coating of thin films of chitosan in application as planar optical waveguides (Mironenko et al. 2014).

2.3.5 Self-assemble of Monolayers (SAM)

Although more applied to synthetic polymers, the SAM method has been used to process cellulose into biofunctional interfaces (Yokota et al. 2008). The cellulose maintained its biological functionality after processing by the SAM method. This was evident by good cell proliferation and adhesion. This method involves modifying the surface of a material in order to impose certain functionalities to improve properties such as adhesion, biosensing, friction, and wetting (Chaudhury 1995). The mechanical properties of the material such as stiffness and flexibility may be

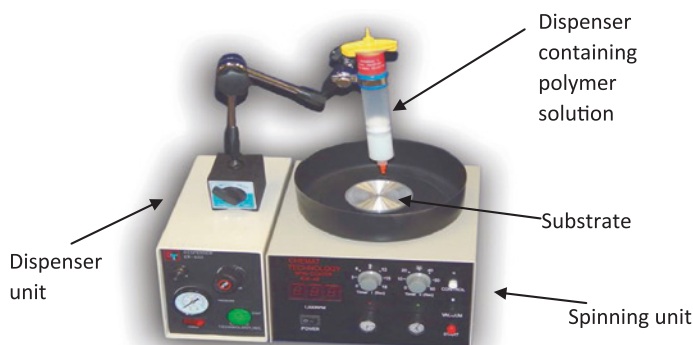


Fig. 2.5 A commercially available spin coater Chemat precision spin from Sigma Aldrich (image publicly available at www.sigmaaldrich.com)

desired, however, the surface properties might limit its applicability for particular functions. Self-assembly of monolayers is applied to alter the surface properties, while retaining the mechanical properties of the material. For instance in applications for scaffold, a polymer material may possess the required mechanical properties, however, the surface properties could limit cell adhesion and proliferation.

2.3.6 *Natural Polymer Microneedles*

The field of micromanufacturing has been fast expanding in the past decades. The ability to make micron-sized devices with precision and mass reproducible techniques is of much industrial significance. This is key to designing more effective tools for applications in biomedical, engineering, and pharmaceutical industries for example. Natural polymers are particularly attractive for micromanufacturing due to their relative low cost and ease of processing. In this section particular focus is placed on microneedle production as example of micromanufacturing-based devices used in biomedical applications for drug and vaccine delivery.

Microfabrication of microneedles from natural polymer generally requires obtaining the dissolved form of the polymer such that the polymer is molded using centrifugal micromolding followed by drying to allow the solvent evaporate leaving behind a polymer which takes the shape of the mold. Silk fibroins from the *Bombyx mori* silkworm have been used to fabricate fast-dissolving microneedles using the centrifuge casting method (Kaplan et al. 2013; You et al. 2011). In a typical process the silk is extracted from the *Bombyx mori* silkworm by boiling for 30 min in aqueous solution of sodium carbonate (Na_2CO_3) followed by thorough rinsing with deionized water to extract the sticky sericin proteins. This was followed by overnight drying of the extracted fibroin. Dissolving the dried fibroin in 9.3 M Lithium Bromide (LiBr) solution at room temperature yielded a 20 wt% solution. The LiBr was then removed from the solution through the dialysis process in water for 48 h. To remove particulates and contaminants the silk fibroin was centrifugated and microfilters yielding 8–10 wt% fibroin. Dry fibroin is obtained through evaporation to remove water. Microneedles are fabricated from the silk fibroin using the typical micromolding process as illustrated in Fig. 2.6, similar methods for polymer microneedle production have been presented in other studies (Olatunji et al. 2014). The polymer in the dissolved form is poured over a PDMS (Polydimethyl siloxane) mold which has been prepared by either reverse micromolding or laser drilling, under applied centrifugal force of about 2500 rpm for 15 min, the polymer takes the shape on the PDMS as illustrated in Fig. 2.6. The polymer is then left to dry in the mold, after which it is separated from the mold.

Likewise fish scale biopolymers have been microfabricated into microneedles using centrifuge molding (Olatunji et al. 2014). Biopolymer was extracted from fish scale using thermal hydrolysis. The polymer was then used to produce microneedles which were shown to have sufficient strength to penetrate into the

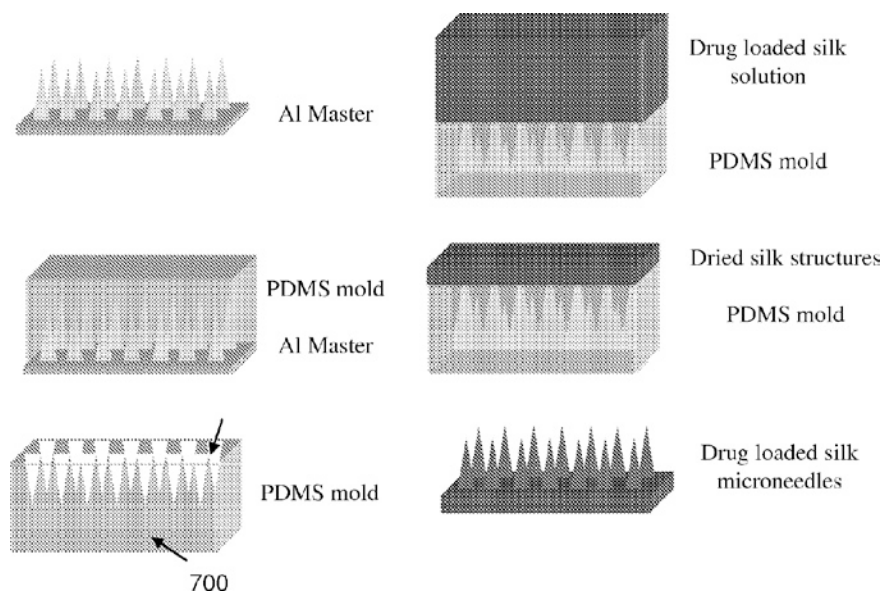


Fig. 2.6 Schematics of micromolding process for silk fibroin microneedles (Kaplan et al. 2013). Reproduced with permission License number 3623650472538

skin. Figure 2.7 shows the microneedle gradually dissolving in the skin. Such microneedles take advantage of the fact that when in the dry form these polymers form hard glassy material but when in contact with moisture in the skin they dissolve to release the active ingredients embedded within the structure.

More recently, compression molding at low temperature of about 50 °C has been introduced for micromolding of fish scale polymer-based microneedles with cellulose nanocomposites. The study showed that the compression molding method can be used to obtain microneedles with sharp tip by optimizing the operating conditions for particular fish scale/nanocellulose compositions. As the polymer films of fish scale/nanocellulose blend do not easily redissolve in water,

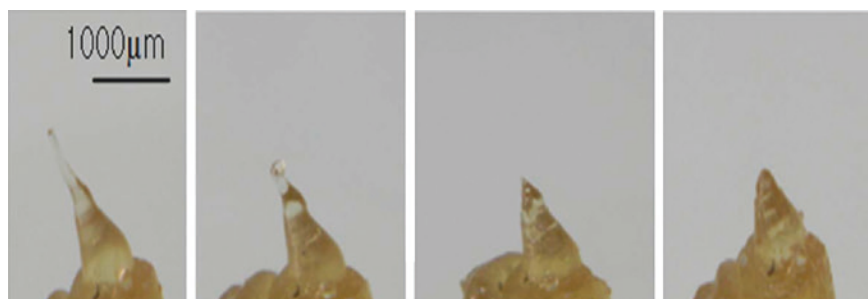
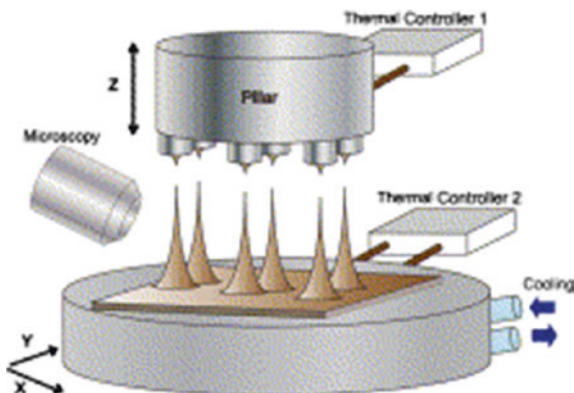


Fig. 2.7 Fish scale microneedles gradually dissolving in the skin (Olatunji et al. 2014)

Fig. 2.8 Spatially discrete thermal drawing of biodegradable polymer microneedles (Choi et al. 2013) with permission from Elsevier License number 3632190774292



this method offers a more ideal microfabrication to achieve microneedles from the fish scale nanocellulose blends and similarly for other polymer blends which do not easily dissolve in water but have limited thermoplasticity. Other novel methods for processing biodegradable polymer microneedles make use of spatially discrete thermal drawing (Choi et al. 2013). In this process the polymer is dispensed on a tray followed by application of another tray such that the polymer lies between the two plates. The plates are heated to a certain temperature depending on the melting and transition point of the polymer. The upper plate is then moved upward such that the polymer is pooled at a controlled speed while cooling this is illustrated in Fig. 2.8. The pulling results in formation of microneedles with sharp tips. Microneedles produced from glass albeit limited to experimental applications are produced using thermal drawing of glass micropipettes over Bunsen burner or using a pipette puller to form glass microneedles (Olatunji et al. 2014).

2.3.7 Cellulose Nanoparticles

Reduction of particle size to the micro or nano scale could improve the functionality of the polymer significantly. Many research efforts are currently being placed on nanocellulose for production of high-performance composites. Nanocellulose is sourced from the bottom-up approach through biosynthesis by some bacteria such as bacteria of the *Acetobacter* species. Alternatively, they can be sourced from plants through the top-down approach by disintegration of the plant matter (Turbak et al. 1983; Herrick et al. 1983). Nanocellulose is also sourced from Algae (Preston and Nicolai 1948) and tunicate (Belton et al. 1989; Lee et al. 2014). Figures 2.9 and 2.10 show example of a plant and bacterial cellulose.

Magnetic decoration of cellulose nanoparticles have been used to achieve tough membranes suitable for application in speakers' production. Using the magnetic decoration method, well-dispersed nanomagnets in cellulose fiber network can be achieved leading to tough structures. Figure 2.11 shows steps in the preparation of

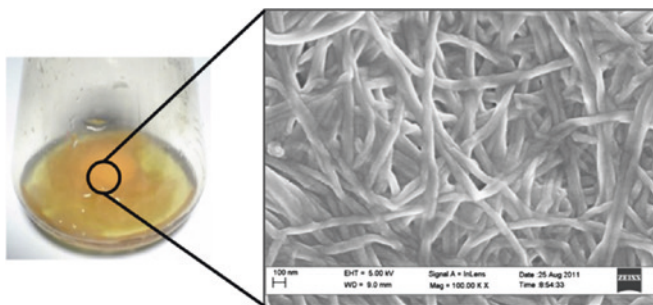


Fig. 2.9 Image showing a 3-day-old culture of *Acetobacter xylinum*. The gel-like pellicle can be seen in the culture. Under SEM, the pellicle appears to be made of a nanofibrillar network of cellulose. Obtained from Lee et al. (2014). Reproduced under creative commons license

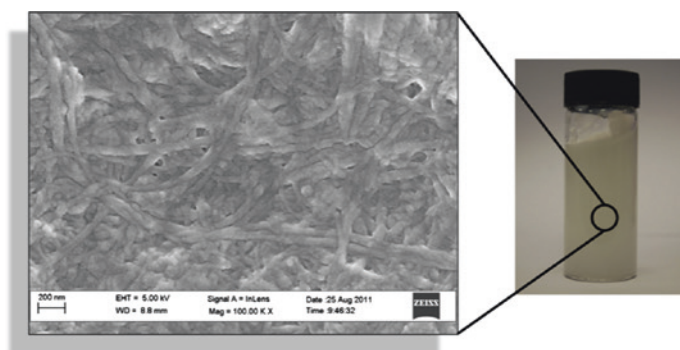


Fig. 2.10 Image showing the nanometre scale of a 1 wt% NFC suspension in water (Lee et al. 2014). Figures taken from Lee et al. (2012a, b). Reproduced under creative commons license

magnetic nanocomposites from decorated cellulose nanofibrils (NFC). (a) shows structure of a softwood tissue; this is processed using high shear microfluidization to obtain nanofibrils from the cell wall; AFM image of the cellulose nanofibrils. (b) Magnetic decorated nanofibrils are obtained by in situ precipitation of magnetic ferrite nanoparticles onto the nanofibrils from metal salt solutions; SEM image of a decorated nanofibril. (c) Further drying results in formation of magnetic nanocomposite hydrogel, overnight drying, and rotation on a Teflon surface resulted in formation of hard permanently magnetized spherical beads—this is followed by vacuum filtration of the magnetic decorated nanofibril suspension to obtain large magnetic membranes (20 cm diameter); the image next to it shows adaption of hybrid magnetic membranes in a thin prototype loudspeaker without external magnet. The consecutive processing steps are indicated by the numbering in Fig. 2.11.

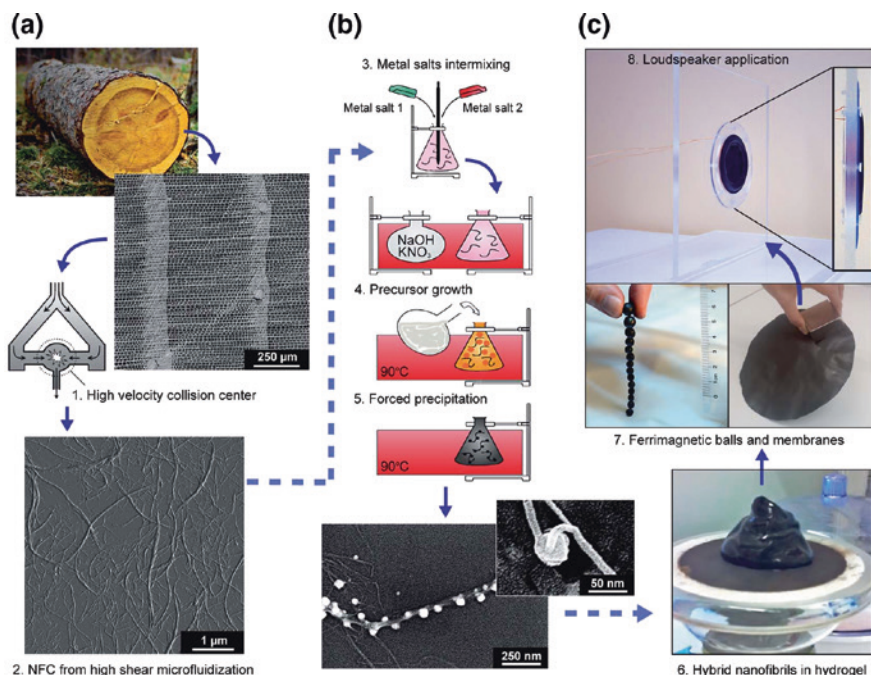


Fig. 2.11 It shows steps in the preparation of magnetic nanocomposites from decorated cellulose nanofibrils (NFC). **a** Shows structure of a softwood tissue; AFM image of the cellulose nanofibrils. **b** Magnetic decorated nanofibril; SEM image of a decorated nanofibril. **c** Magnetic nanocomposite hydrogel, hard permanently magnetized spherical beads—large magnetic membranes (20 cm diameter); adaption of hybrid magnetic membranes in a thin prototype loudspeaker without external magnet. Reproduced under creative commons attributed license

2.3.8 Electrospinning, Melt Spinning, and Wet Spinning

Production of microfibers from composite materials with good dispersion and mechanical properties in a reproducible manner can be achieved using electrospinning, melt spinning, and wet spinning. Figure 2.12 is a schematics of the working principles of electrospinning and melt spinning.

A typical electrospinning process consists of a syringe attached to a syringe pump with a pump controller, a high voltage supply, and a collector plate. The metallic tip of the needle of the syringe is connected to the high voltage supply. The pump pushes the polymer out of the syringe while the high voltage causes a spinning of the polymer resulting in fibers in the nano or micro range forming on the collector plate. The nature of the electrospun fiber obtained depends on operating conditions such as voltage, fluid properties of the polymer, nature of collector plate, flow rate, distance from collector plate, and dimensions of the needle tip (Rojas et al. 2009). Here we use an example of electrospun nanowhiskers with

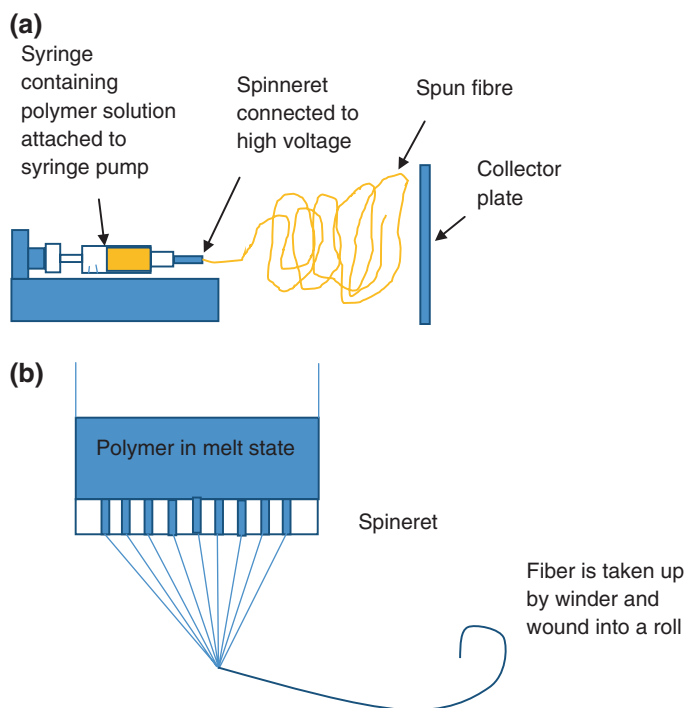


Fig. 2.12 Schematics of **a** electrospinning process, **b** melt spinning process

polystyrene shown in Fig. 2.13. Electrospinning has been applied for processing of natural polymers such as silk fibroin (Cho et al. 2012), Chitosan (Wan et al. 2008).

Melt spinning process generally involves passing a polymer in the melt state through multiple spinnerettes and into a series of rolls and finally winder where it is wound up into fiber bundles (Fig. 2.12b). The main challenge in this process for application in the processing of natural polymers lies in the thermal sensitivity of natural polymers compared to synthetic thermoplastic polymers. Nonetheless melt spinning has been applied to a variety of natural polymer-based materials. For example, smooth defect-free nanocomposite fibers based on cellulose nanocrystals have been achieved using melt spinning process with the inclusion of cellulose acetate butyrate and triethylacetate. The spinning was done with a twin screw micro-compounder and it was observed that increasing the cellulose nanocrystal volume in the composite resulted in a fiber with better mechanical properties (Hooshmand et al. 2014).

Additionally, shell-core structured carbon fibers containing pyrolyzed fuel oil and natural polymer, lignin from wood have achieved using melt spinning. The blend was spun into fibers following dissolving in tetrahydrofuran as solvent. The blends were spun at 280 °C. The fibers showed both crystalline and amorphous regions due to the presence of lignin, however, they possessed good mechanical properties (modulus = 100 GPa) (Kim et al. 2015). In other studies PLA/bacteria

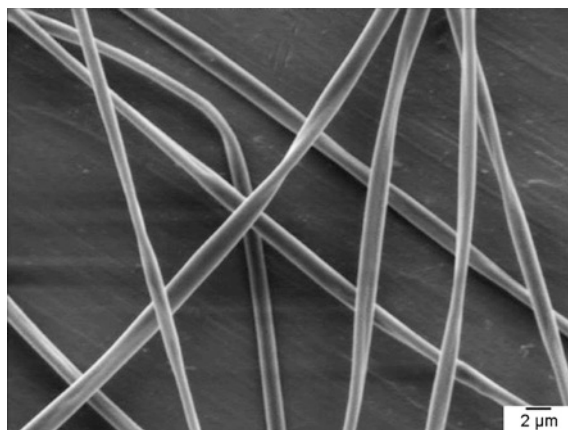


Fig. 2.13 SEM of electrospun PS microfibers filled with 6 % cellulose nanowhiskers in the presence of nonionic surfactant (PS:CNW:S ratio of 94:6:6) showing ribbon-shaped structures. The operating conditions were 20 % PS in THF, $Q = 0.2$ mL/min, 40 kV, distance = 16 cm. Reproduced with permission from Rojas et al. (2009). License number 3632200995714. Original Publisher John Wiley and Sons

cellulose blends reinforced with PDLA (poly(D, L) lactide) were achieved using melt spinning (Blaker et al. 2015).

The wet spinning process similarly involves passing molten polymer through a spinnerette using a pump. The exiting fiber from the spinnerette in this case is passed to a spin bath containing solvent which allows coagulation to occur. This is then followed by further stretching, washing and drying, all in continuous stages on a series of rolls. The fiber is finally passed into a winder where it is wound up into a bundle. Collagen fibers have been processed using the wet spinning process and showed better mechanical properties than thermally spun collagen (Meyer et al. 2010).

2.4 Characterization

The structural characterization to determine the conformation of polymers such as polysaccharides is based on understanding the characteristic energy release for specific types of linkages which is measured by the angle of rotation about the linkage. This is particularly effective for compounds with well-established conformations such as polysaccharides and oligosaccharides. For instance by having information on the dihedral angles of rotation about the monosaccharide linkages in a polysaccharide or oligosaccharide chain, a detailed geometry of compound can be obtained (Kijawara and Miyamoto 2007). A random conformation is assumed, for example, for a polysaccharide showing independent rotations at each

monosaccharide link. Interactions between and within chains limit the likelihood of a random conformation as this allows less room for independent rotation.

Conformation is important in the functionality of the polymer. Taking a case of cellulose and amylose, polysaccharides both made up of the same monomer units and are both poly-D-glucans with (1→4)-α-D-Linkages. However, that of amylose results in a wobbled helix while cellulose has a stretched zig-zag chain conformation. This difference in conformation results in edible and soluble amylose while cellulose is inedible and water insoluble. Characterization of polymers also help determine the crystalline or amorphous nature of a polymer. Crystalline compounds tend to form much stronger structure. Polysaccharides rarely form crystal structures while proteins maintain their crystal structures even in solution (Kijawara and Miyamoto 2007).

In this section techniques such as small-angle X-ray scattering, X-ray diffraction, Fourier transform infrared spectrometry and magnetic resonance are employed.

2.4.1 Small-Angle X-ray Scattering (SAXS)

This is an X-ray-based method that is characterized by a small angle. SAXS can produce rapid analysis of polymers such as proteins (Putnam et al. 2014) and polysaccharides (Kijawara and Miyamoto 2007) in solution. This process is based on the principles of reciprocal law which relates the distance r in a real space with the scattering vector q in a scattering space also known as the Fourier space (Kijawara and Miyamoto 2007).

As presented by Glatter and Kratky, the electron density distribution within the object can be determined from the scattering intensity $I(q)$. This is done by expressing $I(q)$ as the Fourier transformation of the scattering angle (Eq. 2.2) (Glatter and Kratky 1982).

$$I(q) = V \int_0^{\infty} 4\pi r^2 \gamma(r) \cdot \exp(-iq \cdot r) dr \quad (2.2)$$

where $\gamma(r)$ represents averaged product of two electron density fluctuations as a distance r . The scattering vector is expressed as a function of the wavelength θ and the scattering angle λ given as:

$$V = (4\pi/\lambda) \sin(\theta/2) \quad (2.3)$$

The shape of the scattering object $p(r)$ is characterized by the distance distribution which is defined as:

$$p(r) = Vr^2 \cdot \gamma(r) \quad (2.4)$$

The number of electrons in the object is represented by the scattered intensity. Maximum scattered intensity is at zero scattering angle and relates to the number

of electrons in the object. The set of relationships can then be solved by various mathematical models presented in literature (Putnam et al. 2014; Kijawara and Miyamoto 2007; Takeda et al. 1977). The data are then matched with existing models of conformations to establish the true conformation of the polymer being analyzed.

SAXS provides rapid but low-resolution structural characterization of polymers; it is also used in combination with other methods. As the properties of the X-ray being used is known, the other parameters can be calculated from the various mathematical models that exist for SAXS profile (Putnam et al. 2014). As an advantage SAXS is not limited to crystallized samples only and can be used to study macromolecules in solution. This is of particular advantage for natural polymers which do not easily crystallize. The reader is referred to other texts (Burchard and Meuser 1993; Glatter and Kratky 1982; Kijawara and Miyamoto 2007; Putnam et al. 2014) for more details on SAXS method.

2.4.2 Nuclear Magnetic Resonance (NMR)

The assignment of specific protons or carbons to specific linkages and determination of conformation of these linkages provides more detailed information about a material. This can be done using NMR. This is a noninvasive spectroscopic method used for the structural analysis and conformational dynamics of polymers. A NMR spectrometer typically consists of a magnet, a radio frequency (RF) transmitter (Oscillator), and an RF detector. A sample placed between the magnets is subjected to an RF at a known frequency. The material absorbs the RF and the detector picks up the absorption of the RF at a particular frequency and the magnetic field strength. The absorption of the RF is called resonance. A plot of the oscillator frequency against the magnetic strength at the particular frequency provides information on the chemical property of the material (Roberts 1959).

Despite its limitation to polymers which are mostly noncrystalline, it is relatively robust as it can be used to obtain data on the conformation, stereoregularity, primary and secondary structure of proteins, polysaccharides and synthetic polymers in liquid, solid, or gel forms. NMR spectroscopy is specific, the analysis can be directed at functional groups, main chain and side chains at specific sites. Information on the time-dependent structure of the polymer as well as molecular motion can be obtained. When compared to other methods such as X-ray scattering, NMR has a better sensitivity to microscopic structure within a short-range order, however, on a long-range and higher order information is not well retained and may be lost. NMR does not accurately determine spatial position of atomic groups. NMR also takes a considerable amount of time to run compared to other more rapid methods such as SAXS (Kijawara and Miyamoto 2007). A number of NMR techniques exist, these include one-dimensional pulse NMR which can be used for determining relaxation times and primary structures of carbohydrates and sugars in solution, solid-state high-resolution NMR is applied to determine the

structure of polymers in viscose solution, gel and solid forms while two-dimensional and tree-dimensional NMR techniques provide information on the primary and secondary structures and conformation of polymers (Kijawara and Miyamoto 2007). The technique chose therefore depends on the nature of the polymer to be analyzed and the information required.

Analysis of polymers using the NMR technique is based on the chemical shifts and relaxation times recorded from an NMR spectrometer. Reading of ^1H NMR signal peaks at specific regions of the spectrum between 2 and 6 ppm provides information of the polymer being analyzed such that proper translation of the presence of particular peaks at certain points of the NMR spectra provides information on the presence of certain structures in the object being analyzed. Table 2.4 summarizes ^1H NMR chemical shifts for identifying monomer units of polysaccharides.

The relaxation time relates to the local tumbling motion and conformational changes of polymers under NMR. The time-dependent structure and dynamics of a polymer such as hydration structure, helix–coil transition, amorphous and crystal-line structures, sol–gel transition, and the structure-dependent molecular motion

Table 2.4 Chemical shifts (ppm) of monosaccharides from acetone at 2.225 ppm in D_2 at 22.27 °C (Kijawara and Miyamoto 2007)

Monosaccharide ^a	Protons								
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	CH ₃	NA _c
α -D-Glc-(1→	5.1	3.56	3.72	3.42	3.77	3.77	3.87	–	–
B-D-Glc-(1→	4.4	3.31	3.51	3.41	3.45	3.74	3.92	–	–
α -D-Man-(1	1.9	3.98	3.83	3.70	3.70	3.78	3.89	–	–
β -D-Man-(1	4.7	4.04	3.63	3.58	3.37	3.76	3.93	–	–
α -D-Gal-(1→	5.2	3.84	3.90	4.02	4.34	3.69	3.71	–	–
β -D-Gal-(1→	4.5	3.52	3.67	3.92	3.71	3.78	3.75	–	–
β -D-GlcNAc-(1→	4.7	3.75	3.56	3.48	3.45	3.90	3.67	–	2.04
α -D-GalNAc-(1→	5.2	4.24	3.92	4.00	4.07	3.79	3.68	–	2.04
β -D-GalNAc-(1→	4.7	3.96	3.87	3.92	3.65	3.80	3.75	1.23	2.01
α -L-Fuc-(1→	5.1	3.69	3.90	3.79	4.1–4.9 ^b	–	–	1.28	–
α -L-Rha-(1→	4.9	4.06	3.80	3.46	3.74	–	–	–	–
β -D-Xyl-(1→	4.5	3.27	3.43	3.61	^c	–	–	1.32	–
3- θ -Me- α -L-Fuc-(1→	4.8	3.70	3.40	–	3.89	–	–	1.32	–
3- θ -Me- α -L-Rha-(1→	5.0	4.24	3.59	3.52	3.77	–	–	1.32	–
2,3-di- θ -Me- α -L-Rha-(1→	5.1	3.94	3.52	3.41	3.73	–	–	–	–
3,6-di- θ -Me- β -D-Glc-(1→	4.7	3.34	3.31	3.51	3.51	3.66	3.78		–

^aThese are average values for nonreducing terminal sugars linked by a glycosidic linkage to the adjacent monosaccharides. Signals for protons at the ring carbons are shifted downfield when linked by another monosaccharide at the hydroxyl group of that carbon

^bThese are signals which are considerably vary more than other signals due to conformational features

^cH5ax 3.29; H5eq 3.93

can be obtained from the relaxation times. This involves the spin–lattice relaxation time (T_1) and the spin–spin relaxation time (T_2).

T_1 can be measured using repeated pulse sequence of π – τ – 2π radio frequency through the inversion recovery method using the following equation:

$$\ln(A_\infty - A_\tau) = \ln 2A_\infty - \tau/T_1 \quad (2.5)$$

A_τ and A_∞ represent the magnitude of the recovering vector of magnetization evolved the pulse at time $t = \infty$ and $t = \tau$. A plot of $\ln(A_\infty - A_\tau)$ against τ . T_1 also relates to viscosity η and temperature T (Bovey 1972).

$$\frac{1}{T_1} = \left(\frac{128\pi^3}{h^2} \right) \left(\frac{\mu^4 a^3}{r^6} \right) \left(\frac{\eta}{kT} \right) \quad (2.6)$$

where μ denotes a nuclear moment, a is the effective radius of a spherical molecule, and r is the distance from the observed nucleus to its magnetic neighbor. T_1 decreases in proportion to η/T and a^3 increases with r^6 . The effective volume a^3 is replaced with the molar volume in the case of oligosaccharides and polysaccharides in solution. T_1 as a function of the correlation time indicated the degree of molecular motion, and T_1 takes a minimum at the temperature when the relaxation occurs according to the dipole–dipole interaction,

The correlation time is given by:

$$\tau_c = 4\pi^3 a^3 \eta / 3kT \quad (2.7)$$

The spin–spin relaxation time T_2 is used in extreme situations of low viscosity and fast motion. T_2 is derived using the Carr–Purcell method or the Meiboom Gill (CPMG) method (Carr and Purcell 1954; Meiboom and Gill 1958). In the case of spin–spin relaxation time pulse sequence $(\pi/2) - \tau - \pi\gamma - 2\tau - \pi\gamma - 2\tau - \pi\gamma - \rho \dots$ at τ pulse intervals.

2.4.3 X-ray Diffraction

The extent of crystallinity, crystalline microstructure, occurrence of amorphous structure and the phases present in a polymeric material can be determined using X-ray diffraction. The working principles of X-ray diffraction are based on the diffraction and interference of X-ray beams as they leave a crystal. XRD can also provide other information about a material such as the orientation of the filler within the polymer or the orientation of the polymer itself. Example, biaxially orientated polypropylene properties vary significantly from that of polypropylene with other orientations.

The crystallization of a polymer sample can also be measured in situ while the process is ongoing. This can allow for controlling parameters during processing.

Sample for XRD must be well crystallized and well oriented in order to achieve good quality readings. There are a variety of methods for preparing samples for

XRD analysis, for example, starch powders and films can be pretreated by drying and conditioning in a desiccator prior to XRD analysis (Detduangchan et al. 2014).

For a diffraction to occur Bragg's law must be obeyed

$$n\lambda = 2d \sin \theta \quad (2.8)$$

where $n = 1, 2, 3, \dots$, d is the spacing between adjacent plane, λ is the wavelength of the X-ray, and the diffraction angle is 2θ kl.

Here we look at some XRD processing methods that have been used for natural polymers (Polnaya et al. 2013). The starch sample was dried into powdered form and tightly packed in a sample holder of the X-ray diffractometer. X-ray beam at 30 kV and 30 mA was passed through the sample scanning at a diffraction angle of $2\theta = 5^\circ$ to 5° at 0.40 intervals with a rotary speed of 30 min^{-1} and a count time of 1 s. The degree of crystallinity was obtained by identifying an amorphous region and a crystalline region by plotting a smooth curve on the diffractogram. This is illustrated in Fig. 2.14.

Crystallinity is calculated using the following equation:

$$\text{Crystallinity (\%)} = A_c / (A_c + A_m) \times 100 \quad (2.9)$$

where A_c and A_m are the area of the crystalline and amorphous regions respectively.

Figure 2.15 shows the X-ray diffraction curves, which is a plot of X-ray intensity against diffraction angle, for native sago starch (NSS) (a) and sago starch

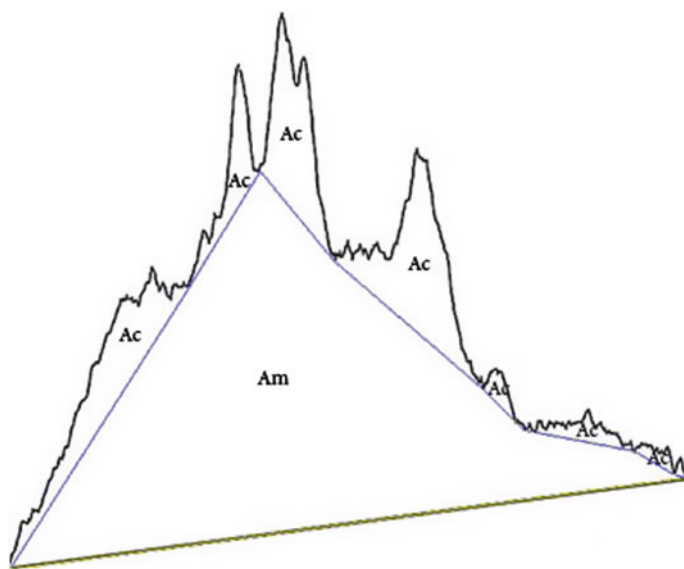
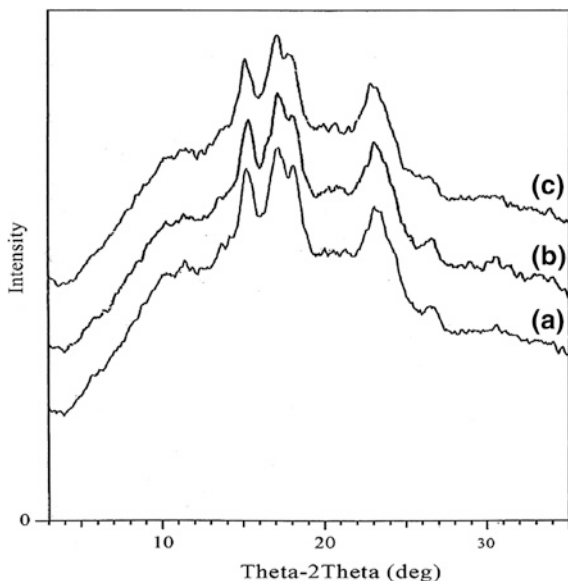


Fig. 2.14 Smooth curve on diffractogram showing amorphous and crystalline portions of a starch sample. Reproduced from Polnaya et al. (2013) under IFRJ open access stated terms

Fig. 2.15 Intensities for native sago starch (a) and sago starch treated by phosphorylation with 5 % sodium tripolyphosphate STPP (b) and cross-linking with 4 % phosphorous oxychloride (POCl₃) (cN) (Polnaya et al. 2013). Reproduced from Polnaya et al. (2013) under IFRJ open access stated terms



treated by phosphorylation with 5 % sodium tripolyphosphate STPP (b) and cross-linking with 4 % phosphorous oxychloride (POCl₃) (c).

The plot shows that native starch shows a C-type crystalline pattern which is suggested by the weak diffraction pattern at a diffraction angle of 5.67° and broad peaks at 15.3°, 17.12°, 18.08°, and 23.46°. These crystalline patterns are typical of native sago starch as it has been observed in other studies on native sago starch where similar peaks were exhibited (Leong et al. 2007). The nature of crystallinity shown by the material, in this case starch is indicative of the composition. In this case starch with relatively high amylose content is reported to display such XRD peaks (Polnaya et al. 2013; Ahmad et al. 1999). Further study of the X-ray diffraction graphs shows that the phosphorylation and the cross-linking had no effect on the crystallinity of the starch. Although the peaks at 18° disappeared and new peaks were formed at 17.88° and 17.84° for cross-linked and phosphorylated sago starch, the degree of crystallinity was not much affected.

2.4.4 Thermogravimetry

Thermal characterization of polymers to determine the behavior of the polymer under different temperature conditions is usually carried out using DSC or TGA. Thermogravimetry analysis involves monitoring the changes in the mass of a substance with respect to temperature over a given time under controlled atmospheric conditions. The setup typically consists of a sensitive weighing balance, a pan connected to the weighing balance, and a high temperature furnace with an inlet and purge for inert gas (which could be helium, nitrogen, or argon). The change in

mass over the duration of heating is indicative of the degradation property of the material at different temperatures.

2.4.5 Differential Scanning Calorimetry

The differential scanning calorimeter typically consists of two heating pans connected to heating plates and a temperature reader connected to a computer. This is illustrated in Fig. 2.16. The process involves placing the polymer sample on one of the heating pans while the other pan acts as a reference pan. Heat is then applied at a constant heat flow rate. The temperature readings of both pans are recorded at different times and heat flow.

Here we look at examples where the thermal properties of nanocellulose-coated sisal fiber-reinforced PLLA is obtained using DSC (Lee et al. 2012a, b). 20 mg of the nanocomposite sample is placed on the heating pan. This particular process involves a heating period where the sample was heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$, followed by a cooling period where the sample is cooled at a rate of $50\text{ }^{\circ}\text{C min}^{-1}$, and then another heating period where the sample is reheated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ to a temperature of $210\text{ }^{\circ}\text{C}$. The heating curves are then plotted for each heating and cooling cycle. The crystallinity of the composite after thermal processing is calculated from the Eq. 2.10. The properties obtained for each sample are shown in Table 2.5.

$$x_c = \frac{\Delta H_m - \Delta H_c}{(1-f)\Delta H_m^0} \times 100\% \quad (2.10)$$

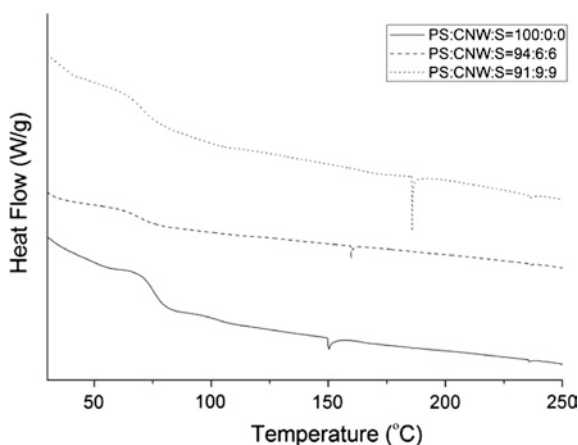


Fig. 2.16 DSC thermograms of electrospun polystyrene microfibers showing neat polystyrene PS (100:0:0) and polystyrene loaded with 6 and 9 % cellulose whiskers (CNW) using an equivalent amount of nonionic surfactant (S). Reproduced with permission from Rojas et al. (2009). License number 3632200995714. Original Publisher John Wiley and Sons

Table 2.5 Crystallization and melt behavior of neat PLLA and its fiber/BC reinforced hierarchical composites T_g , T_c , T_m and x_c are glass transition temperature, crystallization, temperature, melt temperature and crystallinity of the composites based on the 1st heating curve, respectively (Lee et al. 2012b)

Sample	Heating	T_g (°C)	T_c (°C)	T_m (°C)	X_c (%)
PLLA	1st	63	113	171	18 ± 2
	2nd	61	110	169	
PLLA–sisal	1st	57	100	168	21 ± 3
	2nd	59	103	168	
PLLA–DCNS	1st	57	88	168	20 ± 3
	2nd	62	93	169	
PLLA–HNSF	1st	57	94	166	18 ± 2
	2nd	57	94	166	
PLLA–sisal–BC	1st	55	83	165	23 ± 4
	2nd	–	–	168	
PLLA–DCNS–BC	1st	56	85	163	18 ± 3
	2nd	–	–	166	
PLLA–HNSF–BC	1st	54	81	165	24 ± 4
	2nd	–	–	167	

where x_c is the crystallinity of the composite H_m , H_c , f , and H_m^0 are the melting enthalpy and cold crystallization enthalpy determined from DSC curves, weight fraction of the reinforcing phase (20 wt%) and the melting enthalpy of pure crystalline PLLA (75.57 Jg^{-1}) respectively.

The transition temperature can also be obtained from dynamic mechanical analysis, this is discussed in the next subsection. Differential scanning calorimetry for thermal characterization of natural polymer-based materials include electrospun polystyrene cellulose nanofibers (Rojas et al. 2009). In this case the glass transition temperature for electrospun polystyrene with varying amount of cellulose nanowhiskers were compared (Fig. 2.16). The said fibers were electrospun at 20 % PS in THF, Q $\frac{1}{4}$ 0.2 mL/min, 40 kV, distance $\frac{1}{4}$ 16 cm. Electrospun microfibers of cellulose nanowhiskers showed lower glass transition temperature of 78 °C compared to film casted polystyrene films with the same amount of cellulose nanowhiskers which had a glass transition temperature of 93 °C (Rojas et al. 2009). This is attributed to high voltage used in the electrospinning process causing some structural modifications in the polystyrene nanocellulose fiber. The difference in glass transition temperature of electrospun fibers compared to film casted fibers with the same contents indicated that the processing method has an effect on the structural properties of the material.

2.4.6 Mechanical Characterization

Tensile Strength Test

The tensile test is most commonly applied to polymer materials to establish the amount of work input required to cause the material to yield or fail. Properties such as stress at break, elongation at break, Young’s modulus, and work of failure can be obtained from a static strength test on a polymer material. The standard

procedure for natural polymer materials is the same for other synthetic materials. This generally involves placing a strip of known dimension, i.e., width thickness and length, between two grips of a tensile testing machine. At a set speed the strip is pulled apart as the force applied varies with the displacement/elongation of the polymer strip (Singh et al. 2009).

A typical tensile testing machine consists of a station and a static crosshead, grips, load sensor, and a monitor or computer which records and displays the force displacement profile for the test.

The tensile properties can be calculated from the following equations (Belton et al. 1989):

$$t = \frac{L_{\max}}{A_i} \quad (2.11)$$

$$\varepsilon = \frac{\Delta l_b}{l_i} \times 100 \quad (2.12)$$

$$YM = dL/dm/A_i \quad (2.13)$$

$$w = AUC \times \frac{\delta}{A_i} \quad (2.14)$$

where L_{\max} is the maximum load, A_i is the initial cross-sectional area of the sample, l_i is the initial gauge length, Δl_b is the increase in the length at the breaking point, dL/dm is the slope of the linear portion of the elastic deformation, w is a function of the work done in the breaking of a film specimen and representative of film toughness. AUC refers to the area under the curve (Singh et al. 2009). The results obtained are dependent on humidity and temperature, therefore these parameters should be noted and kept constant as much as possible.

The tensile properties of biopolymers derived from fish (Olatunji et al. 2014; Santos et al. 2014), jute/natural rubber composite (Pantamanatsopa et al. 2014) have been reported. Table 2.6 lists Young's modulus, elongation at break and stress at peak for some natural polymer-based materials.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis refers to the study of a material's behavior under sinusoidal applied force applied at a frequency f Hz and an angular frequency of ω . A phase lag δ usually exists between the stress and strain of a viscoelastic body. Such that the dynamic stress σ and strain ε can be expressed as:

$$\varepsilon = \varepsilon_o \sin(\omega t) \quad (2.13)$$

$$\sigma = \sigma_o \sin(\omega t + \delta) \quad (2.14)$$

Table 2.6 Mechanical properties of some natural polymer materials

Material	Elongation (%)	Stress at break (N/mm ²)	Young modulus (N/mm ²)	Reference
Fish scale biopolymer	393.45	1.8105	0.2324	Olatunji et al. (2014)
Gelatin + glycerol	71.66	1.040	1.452	Jadhav et al. (2010)
Wheat starch + cotton	0.94	15.2175	154.27	Komuraiah et al. (2013)
Rice starch + cotton	1.28	12.828	119.57	Komuraiah et al. (2013)
Fish gelatin + nano-cellulose	18	17	650	Santos et al. (2014)

The stress can be divided into real and imaginary parts. The real part refers to the ability of the material to store energy and release this energy when deformed while the imaginary part represents the energy lost as heat during deformation. Including the in-phase and out-of-phase components the stress can be expressed as:

$$\sigma = \sigma_o \sin(\omega t) \cos \delta + \sigma_o \cos(\omega t) \sin \delta \quad (2.15)$$

where $(\sigma_o \cos \delta)$ is the in-phase component and $(\sigma_o \sin \delta)$ is the out-of-phase component. These define the real and imaginary moduli E' and E'' respectively as follows:

$$\sigma = \varepsilon_o E' \sin(\omega t) + \varepsilon_o E'' \cos(\omega t) \quad (2.16)$$

$$E' = \frac{\sigma_o}{\varepsilon_o} \cos \delta \quad (2.17)$$

$$E'' = \frac{\sigma_o}{\varepsilon_o} \sin \delta \quad (2.18)$$

$$\varepsilon = \varepsilon_o \exp(i\omega t) \quad (2.19)$$

$$\sigma = \sigma_o \exp(\omega t + \delta)i \quad (2.20)$$

$$E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_o}{\varepsilon_o} e^{i\delta} = \frac{\sigma_o}{\varepsilon_o} (\cos \delta + i \sin \delta) = E' + iE'' \quad (2.21)$$

Such a relationship between the shear modulus G^* and storage modulus G' and the loss modulus G'' can be expressed as:

$$G^* = G' + iG'' \quad (2.22)$$

Or in terms of phase angle as:

$$\tan \delta = \frac{G''}{G'} \quad (2.23)$$

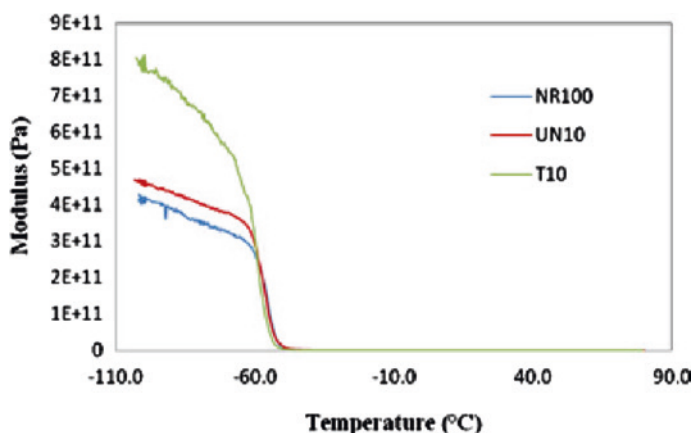


Fig. 2.17 Modulus of elasticity for natural neat natural rubber (NR), unmodified jute fiber in natural rubber matrix (UN) and treated jute fiber with natural polymer matrix (Pantamanatsopa et al. 2014)

While the storage modulus relates to the stiffness of the material or Young's modulus, the loss modulus relates to the internal friction of the material. Factors such as motions at the molecular level, transitions, relaxation, and morphology affect the loss modulus.

The glass transition temperature is also obtainable from dynamic mechanical analysis. The glass transition temperature of -60°C was obtained for natural rubber matrix using the DMA (Pantamanatsopa et al. 2014). As shown in Fig. 2.17, the sharp drop in the modulus beyond 60°C corresponds to a glass transition state of the material. Where NR100 indicates a neat natural rubber polymer, UN10 indicates a natural rubber polymer matrix with untreated jute fiber reinforcement and T10 indicates natural rubber matrix containing treated jute fiber as reinforcement.

2.4.7 Microscopy

Most commonly used microscopy method for characterization of natural polymers is scanning electron microscope (SEM) and transmission electron microscope (TEM). Scanning electron microscopy is often used to obtain microphotographs of fibers and composites in the micro- and nanoscale in order to study the morphology of the material. In an example the morphology of electrospun cellulose nanowhiskers were obtained using a Hitachi S-3200N variable pressure SEM (Fig. 2.13). The process required collecting of the electrospun nanowhiskers on aluminum foils, shadowing with an approximately 150 \AA thick layer of gold-palladium. The prepared sample was observed at a working distance of 3 and 60 mm and accelerating voltage of between 0.3 and 30 kV. Scanning electron microscopy gives good information about the dispersion of the fiber within the composite and compatibility between the polymers. It has been widely applied in studying natural

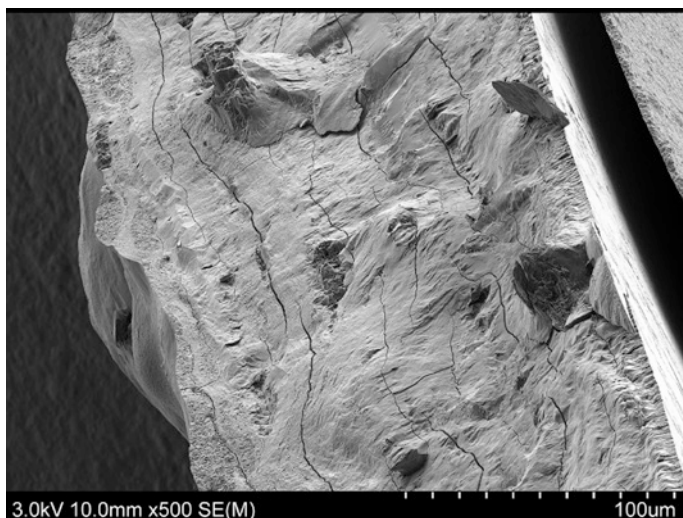


Fig. 2.18 TEM images of fish scale gelatin with cellulose nanocrystals as reinforcement (Olatunji and Olsson 2015)

polymers used as fillers, fibers, or matrix in films and composite. Figure 2.18 shows scanning electron micrographs of fish scale gelatin with cellulose nanocrystals from wood (Olatunji and Olsson 2015).

Through the micrographs issues such as aggregation or beading can be observed. For example, Rojas et al. (2009) observed using SEM that the beading in electrospun polystyrene–cellulose nanowhiskers was significantly reduced with the use of nonionic surfactant by comparing micrographs of the electrospun fibers with and without surfactant. The diameters of the fibers formed were also observed using SEM.

TEM is often used for more detailed analysis of polymer morphology. Figure 2.19 shows the TEM images of electrospun polystyrene–cellulose nanowhiskers. For this purpose a Hitachi HF-2000 TEM using a cold field emission electron source at a 200 kV voltage was employed. TEM grids which are made up of 3-mm copper mesh were placed on the collector plate during electrospinning to collect the electrospun samples on the TEM grids. Figure 2.18a shows TEM of neat electrospun polystyrene films without cellulose nanowhiskers, these had smoother surface while those of electrospun polystyrene with cellulose nanowhiskers shown in Fig. 2.18b were rougher and darker. Figure 2.18c shows the cellulose containing fibers at a higher magnification to show the surface roughness.

2.4.8 Fourier Transform Infrared (FTIR) Spectrometry

FTIR is commonly used to analyze polymers with the aim of identifying the chemical bonds which exist within a sample. FTIR could also be a measure of

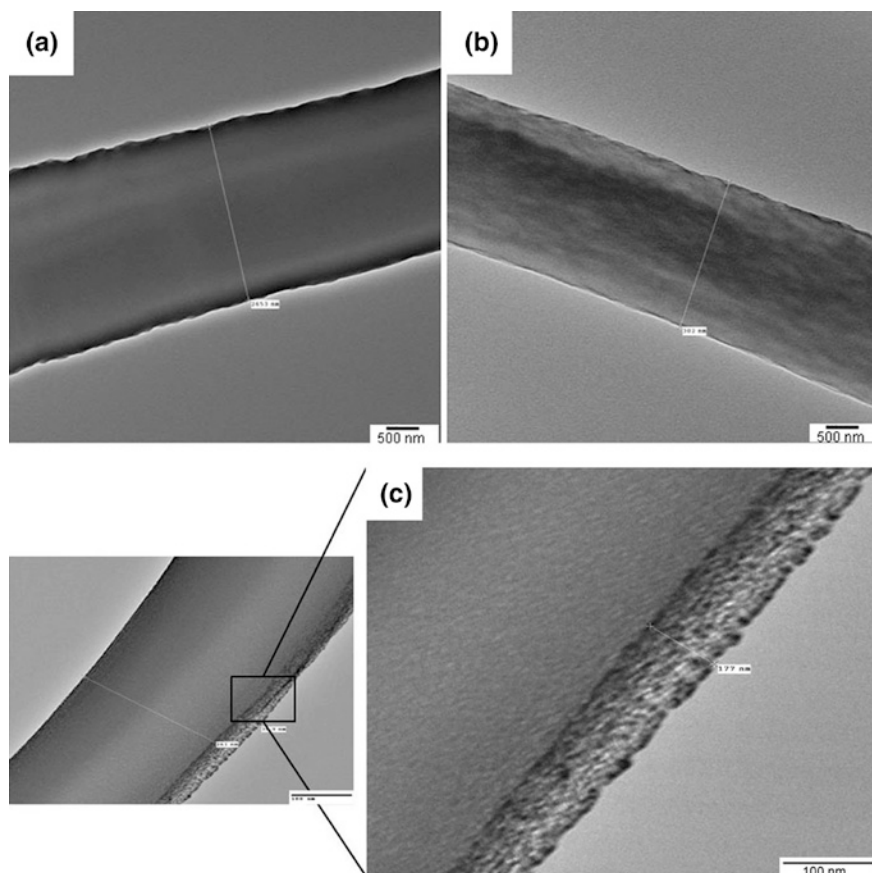


Fig. 2.19 TEM of electrospun microfibers from neat polystyrene (a) and from polystyrene filled with 9 % cellulose nanowhiskers in the presence of equivalent amount of nonionic surfactant (b, c). Operating conditions: 20 % PS in THF. $Q = 0.2$ mL/min, 40 kV, distance = 16 cm. Reproduced with permission from Rojas et al. (2009). License number 3632200995714. Original Publisher John Wiley and Sons

compatibility between polymers. Figure 2.20 shows FTIR of lignin, cellulose, and hemicellulose obtained from biomass.

The main functional groups represented by the peaks in Fig. 2.20 for the three components, lignin, cellulose, and hemicellulose are shown in Table 2.7. Using FTIR the observation of the peaks translate to the presence of specific bonds which can be used to determine the chemical components of a sample. In the particular study by Yan et al. (2007), the FTIR was used to identify the components of biomass from plants prior to pyrolysis. The pyrolysis of biomass is of importance in the industries for energy generation from biomass from waste plant product as an alternative to fossil fuel which is fast depleting (Yan et al. 2007).

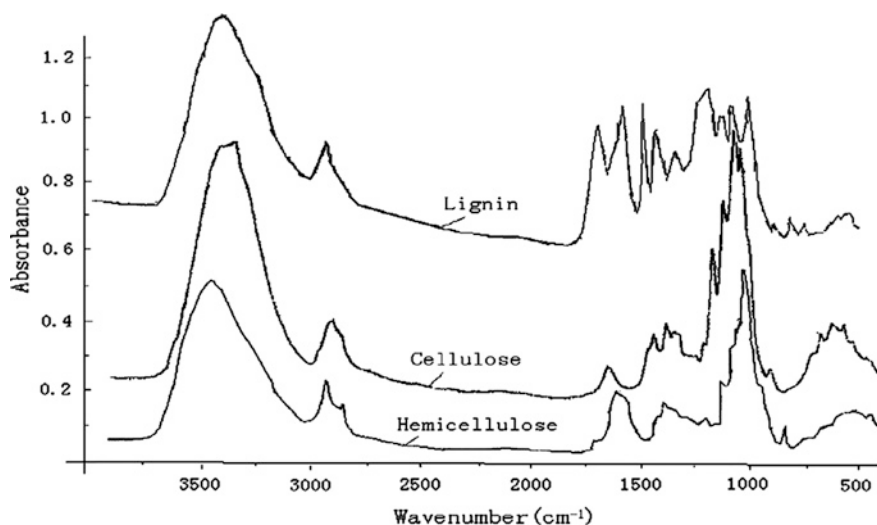


Fig. 2.20 FTIR of lignin, cellulose, and hemicellulose (image obtained from Yan et al. 2007 with permission from Elsevier, license number 3633510294045)

Table 2.7 The main functional groups in lignin, cellulose, and hemicellulose from FTIR

Wave number (cm^{-1}) ^a	Functional groups	Compounds
3600–3000 (s)	OH stretching	Acid, methanol
2860–2970 (m)	C–H _n stretching	Alkyl, aliphatic, aromatic
1700–1730 (m), 1510–1560 (m)	C=O stretching	Ketone and carbonyl
1632 (m)	C=C	Benzene stretching ring
1613 (w), 1450 (w)	C=C stretching	Aromatic skeletal mode
1470–1430 (s)	O–CH ₃	Methoxyl–O–CH ₃
1440–1400 (s)	OH bending	Acid
1402 (m)	CH bending	
1232 (s)	C–O–C stretching	Aryl–alkyl ether linkage
1215 (s)	C–O stretching	Phenol
1170 (s), 1082 (s)	C–O–C stretching vibration	Pyranose ring skeletal
1108 (m)	OH association	C–OH
1060 (m)	C–O stretching and C–O deformation	C–OH (ethanol)
700–900 (m)	C–H	Aromatic hydrogen
700–400 (w)	C–C stretching	

^as strong, *m* middle, *w* weak

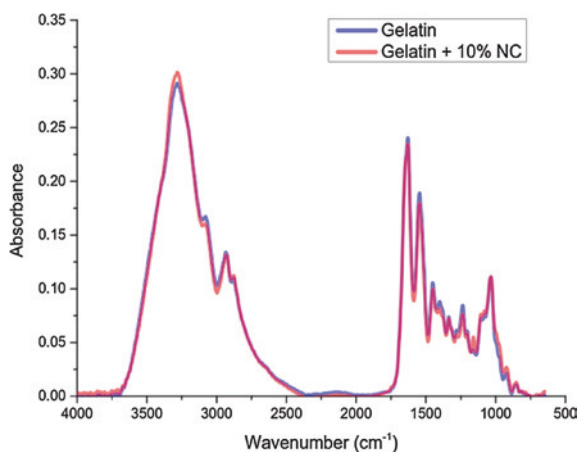


Fig. 2.21 FTIR of fish gelatin with and without cellulose nanowhiskers (obtained from Santos et al. 2014 with permission from Elsevier, License number 3633491129379)

In another example Santos et al. (2014) obtained the FTIR analysis of gelatin with and without nanocellulose blended (Fig. 2.21). This was carried out using a Varian 660-IR spectrophotometer equipped with an attenuated total reflectance (ATR) sampling accessory scanning at a wavelength between 4000 and 6500 cm⁻¹. The samples showed similar peaks for both samples with a slight increase in intensity at 3280 cm⁻¹, representative of the amide A functional group, for the nanocellulose-blended sample (Gelatin + 10 %NC). There is also a decreased intensity at the amide I, II, and III group seen at 1361, 1542, and 1238 cm⁻¹ wavelength respectively. These are attributed to the protein dilution effect and/or the cellulose gelatin interactions (Santos et al. 2014).

More recent approach to FTIR makes use of nondestructive methods in which the samples require no pretreatment. As a further example the FTIR analysis of nanocellulose is carried out and shown in Fig. 2.22. To obtain FTIR peaks for the

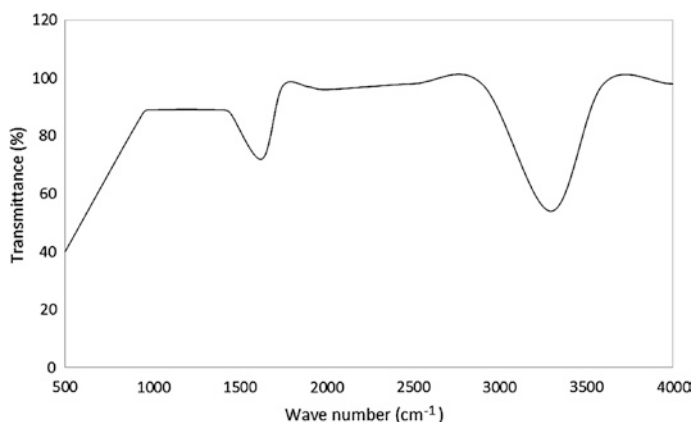


Fig. 2.22 FTIR of nanocellulose extracted from wood

nanocellulose gel, a diamond ATR spectrometer accessory attached to the Agilent Cary 630 FTIR using a diamond crystal at a wavelength ranging between 63,000 and 350 cm^{-1} is employed. The sample of nanocellulose gel is placed on the sample window and the press closed to allow contact. The sample is then scanned to obtain the absorbance plot (Fig. 2.22). The main peaks obtained occur at about 3600 cm^{-1} which is indicative of the presence of OH group due to intramolecular hydrogen bonding. The other major peak occurs at about 1600, which is indicative of absorbed water. Similar peaks for nanocellulose have been reported by (Zain et al. 2014) using a Perkin Elmer type FTIR.

2.5 Conclusion

Processing of natural polymers into blends and composites consisting of natural polymers as fillers or as matrices in combination with other polymers can significantly alter the properties and applicability of the polymer. Further processing techniques common to industry such as extrusion, electrospinning, and microneedle production can be used to form products from natural polymers for different applications. Natural polymers can be characterized using methods such as XRD, TEM, DMA, and TGA. Although a variety of other methods exist and others are yet to emerge the techniques discussed here are those with known applications in natural polymers. In each case, examples of reported applications of these processing and characterization techniques to natural polymers are provided. Some characterization techniques presently applicable to synthetic polymers are not applicable to natural polymers due to limitations in their physical or mechanical properties. Modifications of these properties have extended some of the methods previously limited to only synthetic materials to natural polymers.

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