

Fully Green Elastomer Composites

Daniel Pasquini

Abstract In this chapter we will discuss the preparation of fully green elastomer composites. First we will define the term green and when we can classify a material as a green. Then we will discuss the alternatives for the replacement of major components of composite materials, viz. filler and matrix, which are usually derived from non-renewable and synthetic materials, with materials from renewable sources. Finally we will describe some work in which fully green elastomer composites were studied.

1 The Green Concept

The concept of “green”, actually employed to describe the concept of sustainability and environmental friendliness, is not new. What is new is the use of this word, because the word green is a modern term used to describe the environmentalism movement that began in the nineteenth century and that was characterized as using, preserving and renewing the available resources. Briefly, a definition of environmentalism is the sustainable management of resources and the stewardship of the environment.

In our days, the concept of what makes a product green is still evolving. There is no exact definition of the term green; on the contrary, there is some consideration of the benefit that the product brings to the environment. If a product improves the environment it can be considered a product with a degree of greenness. More specifically, a product is green if the impact on the environment is direct, measurable and intrinsic to the product. We can list some common criteria for classifying products as green:

D. Pasquini (✉)

Instituto de Química, Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Campus Santa Mônica, Bloco-1D, Uberlândia MG, CEP: 38400-902, Brazil
e-mail: pasquini@iqufu.ufu.br; danielpasquini2005@yahoo.com.br

1. Products that have no toxic emissions;
2. Products that save energy;
3. Products made from recycled materials;
4. Products made from industrial and agroforestry residues;
5. Products that are biodegradable;
6. Products made from renewable resources.

Despite the fact that many products that have no toxic emissions are not properly green, these products can usually be considered as green products because they generally replace a hazardous material. In the same way, products that save energy are also considered green. Although they are not intrinsically green, they have a positive impact on the environment.

Nowadays, everyone knows what recycled products are and what their benefits are. Recycled materials have two direct impacts on the environment: (i) they reduce the emissions of residues and (ii) they also reduce the resource demand. As a consequence of these benefits, they can be classified as green materials.

A product made from industrial and agroforestry residues reduces the resource demand. These residues include sugar cane bagasse, sugar cane straw, wood chips, sawdust, cereal shells, corn husks, rice hulls and similar materials. They have many different applications and their use reduces the resource demand.

For a product to be considered biodegradable, it needs to be degraded in a short period of time. However, as yet there is no standard that defines the exact amount of time that qualifies a product as biodegradable. In general, the products considered as green are those that are biodegradable in a short period of time, and this time can be interpreted in different ways.

Finally, products made from renewable resources are intrinsically green. Here we can classify them in two groups of renewable resources: the first group, the rapidly renewable resources, consists of those that can typically be regenerated in a growing season in a year and the second group is the renewable resources that take more than a season to grow and to regenerate.

The use of green materials is expanding and undergoing constant growth at same time that the use of materials that are not bio based, biodegradable or recyclable is being restricted by new legislation. In this chapter the use of renewable resources will focus on the production of fully green elastomer composites. If there is a commitment of society to preserving the environment, focusing on the rational use of renewable resources, the development of new materials, particularly elastomers, has its place in our industry.

2 Composite Materials

The basic definition of composite materials is materials made from two or more constituents with significantly different mechanical properties, which remain separate and distinct within the finished structure [1]. The two main constituents of

a composite are: matrix and filler (or reinforcement). The matrix surrounds and supports the filler by maintaining its relative position. The filler is responsible for the improvement of the physical and mechanical properties of the matrix. Due to the wide variety of matrices and fillers available, the association of different fillers and matrices can produce a large amount of composite materials with variable properties and with potential application in many areas.

The most common commercially available composites, polymers, are employed as matrices. The fillers are often fibres but also commonly ground minerals. Strong fibres such as fibreglass, quartz, Kevlar or carbon fibres give the composite its tensile strength, while the matrix binds the fibres together, transferring the load from broken fibres to unbroken ones and between fibres that are not oriented along the tension lines. The fillers can be divided into two main categories, macro- and microscopic fillers. In the last case, we refer to nanoparticles.

Among the options for the polymers and fillers used to form a composite, we can see that these components do not always come from renewable sources. The focus of this chapter is the production of green elastomeric composites, which have as their main components materials from renewable resources. Thus, we discuss below the options for matrices and fillers from renewable resources that could serve as substitutes for the resources that are not renewable.

2.1 Fillers from Renewable Resources

Regarding fillers from renewable sources, the subject obviously leads us to the use of plant and animal resources. Plants are the main source of potential substitutes for fillers from non-renewable resources. The use of plant components, for example sawdust, fibres and nanoparticles, as reinforcement in polymer matrices is well known and widely studied [2–8]. There are many advantages of using fillers from plant sources as reinforcement in polymer matrices, e.g. low density, low cost and low energy consumption, high specific strength, renewability and biodegradability, abundant availability in a variety of forms throughout the world, flexibility, non-abrasive nature to processing equipment, non-toxicity, ease of handling, reactive surface, organic nature and the economic development opportunity for non-food farm products in rural areas [9].

The properties of natural fibres are strongly influenced by many factors, particularly chemical composition, internal fibre structure, microfibrillar angle, cell dimensions and defects, which differ between different parts of a plant as well as between different plants. The mechanical properties of plant fibres are in general much lower when compared with those of the most widely used reinforcing glass fibres (Table 1). However, because of their low density, the specific properties, which are property-to-density ratio dependent, viz. strength and stiffness, are comparable with those of glass fibres.

Carbon fibres can be produced from vegetal macromolecules as an alternative to the conventional non-renewable polymer used for this purpose. An example is

Table 1 Physical properties of various natural fibres and their comparison with some synthetic organic and inorganic fibres [9–11]

Fibre	Density ($\text{g}\cdot\text{cm}^{-3}$)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Abaca	1.5	12	400	3–10
Alfa	0.89	22	350	5.8
Bagasse	1.25	17	290	–
Bamboo	0.6–1.1	11–17	140–230	–
Banana	1.35	12	500	5.9
Coir	1.2	4–6	175	30
Cotton	1.5–1.6	5.5–12.6	287–597	7–8
Curaua	1.4	11.8	500–1,150	3.7–4.3
Date palm	1–1.2	2.5–5.4	97–196	2–4.5
Flax	1.5	27.6	345–1,035	2.7–3.2
Hemp	1.48	70	690	1.6
Henequen	1.2	10.1–16.3	430–570	3.7–4.9
Isora	1.2–1.3	–	500–600	5–6
Jute	1.3	26.5	393–773	1.5–1.8
Kenaf	–	53	930	1.6
Nettle	–	38	650	1.7
Oil palm	0.7–1.55	3.2	248	25
Piassava	1.4	1.07–4.59	134–143	7.8–21.9
Pineapple	0.8–1.6	400–627	1.44	14.5
Ramie	1.5	24.5	560	2.5
Sisal	1.5	9.4–22	511–635	2.0–2.5
Viscose	–	11	593	11.4
Soft wood kraft	1.5	40	1,000	–
E-glass	2.5	70	2,000–3,500	2.5
S-glass	2.5	86	4,570	2.8
Aramide	1.4	63–67	3,000–3,150	3.3–3.7
Carbon	1.4	230–240	4,000	1.4–1.8

the production of carbon fibres from lignin, which has been extensively studied. Lignin is one of the most abundant natural polymers. It is produced in the chemical pulping industry as a by-product, and is used for energy generation and the recovery of pulping chemicals. In previous studies, lignin preparations were converted into fibrous materials by simple thermal treatment and/or polymer blending methods followed by thermal spinning [12, 13]. These lignin fibres were transformed into carbon fibres using a thermal conversion process similar to that found in industry. The mechanical properties of these carbon fibres were comparable with industrial general performance grade carbon fibres prepared from conventional polymers.

A special class of filler from renewable resources is nanofillers. In this group we can include whiskers [6, 9] (obtained from vegetal cellulose fibres and from animal sources) and starch nanocrystals [14]. Cellulose nanocrystals, known as whiskers

or nanowhiskers, occur in the form of rod-like nanoparticles with lengths ranging from 200 to 2,000 nm and diameters ranging from 4 to 15 nm depending on the source [9]. Starch nanocrystals occur in the form of platelet-like nanoparticles with lengths ranging between 20 and 40 nm, widths between 15 and 30 nm and thicknesses between 5 and 7 nm for waxy maize starch [14]. Their nanoscale dimensions and impressive mechanical properties make nanoparticles, particularly when occurring as a high-aspect ratio, ideal candidates for improving the mechanical properties of the host material when compared with macroscopic fillers. The physical incorporation of these nanocrystals into a polymeric matrix leads to nanocomposites with outstanding properties.

However, despite their attractive properties, vegetal fibres are used only to a limited extent in industrial practice due to the difficulties associated with surface interactions. The primary drawback of agro-based fibres is associated with their inherent polar and hydrophilic nature and the non-polar characteristics of most thermoplastics. These result in difficulties in compounding the filler and the matrix, and therefore in achieving acceptable dispersion levels, which yield composites with low performances.

This hydrogen bonding phenomenon is best exemplified in paper, where these secondary interactions provide the basis for its mechanical strength. It also results in high moisture absorption and swelling of the fibres. A poor fibre–matrix interface induces a decrease in mechanical properties.

Moreover, the processing temperature of composites is restricted to about 200 °C, because of the possible degradation and/or the emissions of volatile compounds that could affect the composite properties. Higher temperatures could be used if the processing time is short. This limits the type of thermoplastics that can be used with polysaccharide fillers to commodity plastics such as polyethylene, polypropylene, polyvinyl chloride and polystyrene. However, it is worth noting that these cheap plastics constitute about 70 % of the total thermoplastic-based products consumed by the plastics industry.

Several strategies have been suggested in the literature to improve the compatibility of lignocellulosic fibres with thermoplastic polymers, by surface modifications that include (i) physical treatments, such as solvent extraction; (ii) physico-chemical treatments, like the use of corona and plasma discharges or laser, γ -ray and UV bombardment; and (iii) chemical modifications, both by direct condensation of the coupling agents onto the cellulose surface and by grafting by free-radical or ionic polymerizations [15, 16].

The different modifications of lignocellulosic materials are generally located on the surface materials. The main purpose of the modifications is to improve the compatibility of these materials with the polymer matrix. The strength of interaction depends on the type of modification performed, since only physical changes will result in weaker interactions than those from chemical modifications. Chemical modifications are more efficient because they act by changing the values of surface energy and leading to greater adhesion between the filler and the polymer matrix. Besides the reduction of surface energy values of lignocellulosic materials, another important factor is the reduction in the values of the surface

polar character, which is observed by the reduction in the values of the polar contribution of surface energy. As a general rule, materials with similar values of surface energy tend to have a better affinity. Additionally, compounds with similar chemical characteristics, i.e. polar and non-polar similar characters, also tend to have a higher affinity. As a consequence, there will be better adhesion between these materials. Table 2 exhibits some values of surface energy for conventional polymers and for some lignocellulosic materials before and after surface chemical modifications.

Many papers describe chemical modifications related to the modification of natural polysaccharides, namely their hydrophobization [16, 21, 22]. A weak point in chemical modification is the fact that changes must be performed under mild conditions to prevent the degradation of the lignocellulosic materials, otherwise it would result in a loss of mechanical properties of these materials and the resulting composite, due to the lignocellulosic materials' degradation [23].

Table 2 Surface energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) contributions, for conventional polymers and some lignocellulosic materials before and after surface chemical modifications

Sample	Chemical modification	Surface energy ($\text{mJ}\cdot\text{m}^{-2}$)			References
		γ_s	γ_s^p	γ_s^d	
Avicell cellulose (AV)	–	55.7	23.9	31.8	[17]
Whatman paper cellulose (WP)	–	52.3	20.2	32.1	
TFPS-treated AV	Grafting with trifluoropropyl trimethoxysilane (TFPS)	28.9	1.1	27.8	
TFPS-treated WP		26.7	0.6	26.1	
PFOS-treated AV	Grafting with 1H, 1H, 2H, 2H-perfluorooctyl trimethoxysilane (PFOS)	20.8	0.5	20.3	
PFOS-treated WP		19.9	0.1	19.8	
Bleached kraft cellulose (KC)	–	51.9	34.2	17.8	[18]
Bleached organosolv cellulose (ORC)	–	51.6	35.7	15.9	
DC-treated KC	Grafting with dodecanoyl chloride (DC)	31.3	7.0	24.3	
DC-treated ORC		33.1	4.4	28.7	
OC-treated KC	Grafting with octadecanoyl chloride (OC)	30.2	6.5	23.6	
OC-treated ORC		33.1	1.8	31.3	
Polyethylene-linear (PE)	–	35.7	0	35.7	[19, 20]
Polypropylene-isotactic (PP)	–	30.1	0	30.1	
Polystyrene (PS)	–	40.7	6.1	34.5	
Polymethylmethacrylate (PMMA)	–	41.1	11.5	29.6	
Polyethyleneterephthalate (PET)	–	44.6	9	35.6	
Polycarbonate (PC)	–	34.2	6.5	27.7	
Polyisobutylene (PIB)	–	33.6	0	33.6	

Although there are many works that aim at the surface modification of ligno-cellulosic materials, these are still mostly limited to materials with macroscopic dimensions, i.e. fibres, sawdust, starch, etc. Few works are found in the literature where changes are made to starch, chitin and cellulose nanoparticles [24–27]. The incorporation of nanocrystals of cellulose and starch into polymer matrices is of great interest, but their modification for compatibility with polar polymers has been little explored, and it is a challenge for the coming year.

In short, we can verify that there are many alternative types of filler from renewable resources that can be used to replace fillers that are not from renewable resources in polymeric matrices. The use of fillers from renewable sources produces materials with varying physical and mechanical properties, and choosing the correct type of filler obtains composites with similar properties to the composites using fillers that are not from renewable resources.

2.2 *Elastomer Polymers*

An elastomer is a polymer with the property of viscoelasticity, generally having a notably low Young's modulus (E') and high yield strain compared with other materials. The predominant property of elastomers is their elastic behaviour after deformation by compression or tension. Elastomers are macromolecular materials that quickly recover their initial shape and dimensions after ceasing the application of pressure. Not all amorphous polymers are elastomers. Some are thermoplastics, depending on the classification of the glass transition temperature, T_g , defined as the temperature above which a polymer becomes soft and ductile and below which it becomes hard and brittle, like glass. We can say as a general rule applicable only to amorphous polymers that an amorphous polymer with a T_g below ambient temperature is an elastomer, while an amorphous polymer with a T_g higher than room temperature is a thermoplastic [28]. Table 3 displays a list of the major elastomers that are currently available and their abbreviations according to ISO standard 1629 (1987), as well as their T_g values.

The term, which is derived from elastic polymer, is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanizates. Elastomers are usually thermosets (requiring vulcanization) but may also be thermoplastic. At ambient temperatures rubbers are thus relatively soft ($E' \sim 3$ MPa) and deformable.

The main difference between thermoset elastomers and thermoplastic elastomers (TPE) is the type of crosslinking bond in their structures. In fact, crosslinking is a critical structural factor that contributes to imparting high elastic properties. The crosslink in thermoset polymers is a covalent bond created during the vulcanization process. On the other hand the crosslink in thermoplastic elastomer polymers is a weaker dipole or hydrogen bond or takes place in one of the phases of the material.

Table 3 Tg values of the major elastomers currently available

Elastomer	Abbreviation	Tg (°C)	
Polyacrylate rubber	ACM	-22 to -40	
Polyesterurethane	AU	-35	
Bromobutyl rubber	BIIR	-66	
Polybutadiene	BR	-112	
Chlorobutyl	CIIR	-66	
Chlorinated polyethylene	CM	-25	
Epichlorohydrin (homopolymer)	CO	-26	
Polychloroprene	CR	-45	
Chlorosulfonated polyethylene	CSM	-25	
Ethylene and methyl acrylate copolymer	EAM	-40	
Epichlorohydrin and ethylene oxide copolymer	ECO	-45	
Terpolymer ethylene (propylene) sulfur cured	EPDM, S	-55	
Terpolymer ethylene (propylene) peroxide cured	EPDM, P	-55	
Polyetherurethane	EU	-55	
Ethylene and vinyl acetate copolymer	EVM or EVA	-30	
Fluorocarbon elastomer (co or terpolymers)	FKM or FPM	-18 to -50	
Fluorinated silicone	FVMQ	-70	
Butadiene and acrylonitrile hydrogenated copolymer	H-NBR	-30	
Butyl rubber (isoprene and isobutylene copolymer)	IIR	-66	
Butadiene and acrylonitrile copolymer	Low content of acrylonitrile	NBR	-45
	Medium content of acrylonitrile		-34
	High content of acrylonitrile		-20
Natural rubber (or polyisoprene)	NR (IR)	-72	
Polyglycol ether	OT	-50	
Polydichlorophosphazene fluorinated	PNF	-66	
Styrene and butadiene copolymer	SBR	-50	
Vinyl-silicone	VMO	-120	
Carboxylated nitrile rubber	XNBR	-30	

In most cases the polymer's elasticity is due to covalent crosslinks, but it can be due to thermodynamic reasons. The individual segment of the chain must be flexible to take Brownian motion at room temperature. Thus, the molecules assume any statistically ordered conformation when subjected to tensile stresses. Once this tension is removed, they return to their random conformation (state of maximum entropy); the deformation process can be described thermodynamically, considering that under ideal conditions the internal energy is unchanged.

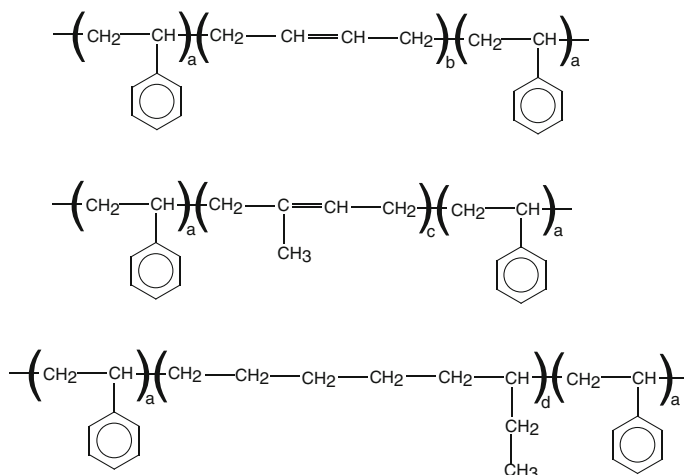


Fig. 1 Chemical structures of three common styrenic block copolymers: **a** styrene (50–80 units), **b** polybutadiene (20–100 units), **c** polyisoprene (20–100 units) and **d** polyethylenebutylene (20–100 units) segments

The TPEs may be classified on the basis of their chemistry and morphology. All of them have two polymeric phases: a soft rubbery one and a hard thermoplastic one. The TPEs' compositions can be formed by (i) block copolymers with alternating soft and hard segments, (ii) blends of a rubbery polymer and thermoplastic or (iii) rubbery polymer–thermoplastic compositions in which the former is highly vulcanized and finely dispersed in the latter.

There are six generic classes of TPEs generally considered to exist commercially. They are styrenic block copolymers, polyolefin blends, elastomeric alloys, thermoplastic polyurethanes, thermoplastic copolyesters and thermoplastic polyamides [29].

Styrenic block copolymers, commonly referred to as styrenics, are copolymers with the S-D-S structure, where S is a hard segment of polymerized styrene or styrene derivative and D is a soft central segment of polymerized diene or hydrogenated diene units. Figure 1 shows the chemical structures of three common styrenic block copolymers with the most commonly used soft diene segments: polybutadiene, polyisoprene and polyethylenebutylene.

The characteristics of these TPEs depend on the relative proportions of the polymerized styrene and diene units as well as the chemical nature of the monomers. At low styrene levels, the TPEs will be soft and rubbery with relatively low tensile properties. With increasing styrene content, the TPE progressively becomes like a harder rubber.

Copolyesters are polymers with the –A-B-A-B- structure, where A and B are alternating hard and soft polymeric segments connected by ester linkages, such as the structure of a commercial copolyester shown in Fig. 2. These block

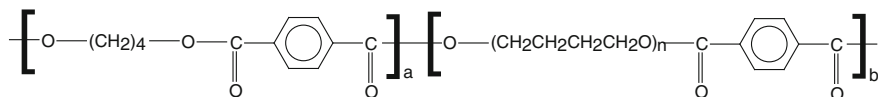


Fig. 2 Structure of a commercial copolyester: **a** hard segment (16–40 units), **b** soft segment (16–40 segments), (n) 10–50

copolymers differ from simple polyester thermoplastics, which are typically hard and crystalline polymers of organic dibasic acids and diols.

The copolyester polymers perform as TPEs if the structures of A and B are chosen to give rubbery properties to the copolymer over a useful temperature range. The structure of the soft segment provides the flexibility and mobility needed for elastomeric performance.

Thermoplastic polyurethanes are TPEs that have the same block copolymer morphology as the styrenic and copolyester polymers. Their general structure is –A-B-A-B–, where A represents a hard crystalline block derived by chain extension of a diisocyanate with a glycol. The soft block is represented by B and can be derived from either a polyester or a polyether. Figure 3 shows the typical thermoplastic polyurethane structures.

The urethane linkages in the blocks are capable of a high degree of inter- and intramolecular hydrogen bonding, and consequently increasing of the crystallinity of the hard phase, and can influence the mechanical properties of the thermoplastic polyurethanes, i.e. hardness, modulus and tear strength. As with other block copolymers, the nature of the soft segments determines the elastic behaviour and low-temperature performance of the resulting material.

The elastomeric polyamides are a class of TPEs in which amide linkages connect the hard and soft segments and the soft segment may consist of polyester, polyether or polyetherester chains. As in other block copolymer TPEs, the structure of the hard and soft blocks also contributes to the performance characteristics of the elastomeric polyamides. The nature of the hard segments determines the melting point of the elastomeric polyamides and their performance at elevated temperatures.

Thermoplastic elastomeric olefins are simple blends of a rubbery polymer, such as natural rubber (NR) or terpolymer ethylene (propylene) (EPDM), with a

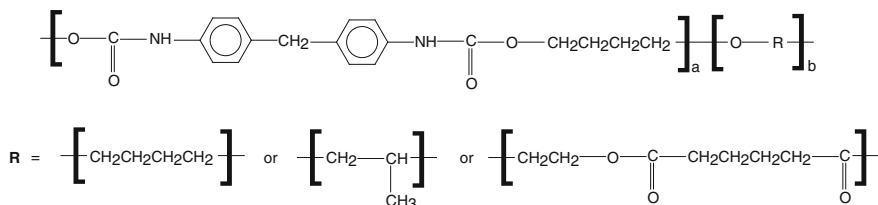


Fig. 3 Typical thermoplastic polyurethane structures: **a** hard block (30–120 units), **b** soft block (8–50 units)

thermoplastic polymer, such as polypropylene (PP) or polyvinyl chloride (PVC). Each polymer will have its own phase, and the rubber phase will have little or no crosslinking. The polymer present in a larger amount will usually be the continuous phase, with the thermoplastic being favoured due to its lower viscosity. The discontinuous phase should have a small particle size for the best properties of the thermoplastic elastomeric olefin. Reasonable compatibility of the two polymers requires their solubility parameters and polarities to be similar.

Thermoplastic vulcanizates elastomers (or elastomeric alloys) differ from thermoplastic elastomeric olefin in that the rubber phase is highly vulcanized (cross-linked). As a result, the properties and performance of a TPV are much closer to those of a conventional thermoset rubber. This difference will reflect in the final properties of the thermoplastic vulcanizates elastomers, when compared with the thermoplastic elastomeric olefin, which for a given elastomer–thermoplastic system are (i) resistance to plastic deformation, (ii) great resistance to fluids, (iii) good retention of properties at an elevated temperature relative to those at an ambient temperature and (iv) low creep and stress relaxation.

Until now we have provided a description of the common elastomers, their chemical compositions and their properties. However, within this class of polymers only natural rubber fits the criteria for classification as “green”, as discussed earlier in this book chapter, because it is from a renewable source. Composite materials made from natural rubber, which serves as the polymer matrix, and reinforcing agents from plant sources have been studied and will be discussed later in this and other chapter of this book.

2.3 Polymers from Renewable Resources

The objective of including the discussion on elastomeric polymers was to provide an opportunity to compare the polymers produced from renewable sources that could serve as possible substitutes for polymers that compose the major known elastomers and that are not renewable. In nature, more specifically plant and animal sources, we can find many chemical compounds whose molecules can act as monomers or macromonomers in polymerization processes, which may be a possible replacement for fossil monomers.

Among the molecules from renewable sources that have the potential to produce new polymers, and several studies are underway in this direction, we can highlight cellulose, hemicellulose, lignin, chitin, proteins, vegetable oils, polyhydroxyalkanoate, terpenes, tannins, starch and polylactic acid. A recently published book by Belgacem and Gandini [30] describes the various recent studies concerning the use of these molecules and others, from renewable sources, in the production of polymers, monomers and composite materials. However, in this current book chapter we will emphasize the work that resulted in elastomeric polymers or blends.

Most of the polymers produced from the molecules described above are thermoplastic polymers and do not show the characteristic properties of elastomers. In the case of the thermoplastic materials obtained, the solution to using them in elastomeric composite matrices would employ them in the production of blends in the same manner as the thermoplastic elastomeric olefins described above. Another alternative is to use these polymers, which are mostly polyether, polyester or polyols, as substitutes for the corresponding polymers used in the preparation of TPEs, for example, as described above, by copolymerization.

Several works were carried out employing vegetable oils as precursors for the synthesis of vegetable oil-based polymers, in which the resulting polymers had elastomeric or rubbery properties [31–39]. In these works the vegetable oils such as linseed, tung, soybean, corn, castor oils and others, or the modified vegetable oils, were crosslinked by vinyl monomers, such as styrene, α -methyl styrene, divinyl benzene, cyclopentadiene and others. The resulting copolymers were characterized by dynamic and thermal mechanical analysis (DMA and TMA), thermogravimetry (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The gelation time in these very different systems varied from a few minutes to a few days. The Tg values and the moduli of the prepared copolymer varied from -60 to 105 °C and from 0.1 to $2,000$ MPa, respectively. These values are comparable with those of commercial rubbers synthesized from petroleum-based monomers.

The use of starch in the production of new polymers has been studied extensively. Blending is one of the most promising alternatives to make starch useful as a polymer in the replacement of other plastics, and the fast progress occurring in this field is attested by several reviews published recently [40–43]. Most polymers produced by blending starch and other polymers are thermoplastic polymers, but some of them are elastomeric or rubbery polymers. Arvanitoyannis et al. [44] studied blends of starch with 1,4-transpolyisoprene (gutta percha) with and without plasticizers by melt processing and observed that they were biodegradable because of the presence of starch. The plasticizers increased the percentage elongation considerably whereas they decreased the tensile strength, glass transition and melting points of the composite matrix. The Tg values varied from -56 to 12 °C depending on the amount of starch and 1,4-transpolyisoprene. For the mixture of starch and 1,4-transpolyisoprene 1:1 (w:w), varying the content of plasticizer glycerol, the elongation and tensile modulus varied from 6 to 40 % and from 2 to 12 MPa, respectively. Rouilly et al. [45] also prepared blends of starch and unmodified and modified natural rubber by casting mixtures of aqueous starch with glycerol and latex. The natural rubber was modified by grafting with dimethyl-aminoethyl methacrylate (DMAEMA) to form a latex with cationic water-soluble polymeric “hairs” of polyDMAEMA, which should form hydrogen bonds with starch. The unmodified latex acted only as a filler in the starch films, but with modified natural rubber, the mechanical properties of the films were significantly altered. The elastic modulus was greatly decreased and the strain at break greatly increased. The glass transition temperature increased from -48 to -32 °C, suggesting significant compatibilization. Carvalho et al. [46] blended native starch

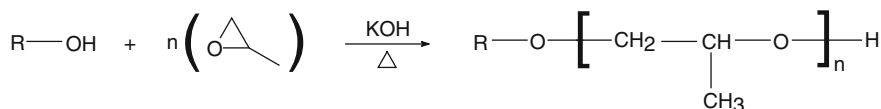
granules and a natural rubber latex by melt processing calling upon water as a plasticizer for starch. The blends were prepared in an intensive batch mixer at 150 °C, with natural rubber content varying from 2.5 to 20 %. The blends were characterized by mechanical analysis (stress–strain) and by scanning electron microscopy. The stable dispersion and the good adhesion between the two natural polymers were attributed in part to the natural non-rubber constituents present in the latex. The results revealed a reduction in the modulus and in tensile strength, the blends becoming less brittle than thermoplastic starch alone. Phase separation was observed in some compositions and was dependent on rubber and on the plasticizer content (glycerol). Increasing the plasticizer content made possible the addition of higher amounts of rubber. The addition of rubber was, however, limited by phase separation, the appearance of which depended on the glycerol content. Scanning electron microscopy showed good dispersion of the natural rubber in the continuous phase of thermoplastic starch matrix.

Poly(lactic acid) (PLA) and poly(hydroxyalkanoates) (PHAs) are polymers that have their origin in bacteria. In the case of PLA, the precursor of this polymer is lactic acid (LA). Lactic acid is mainly prepared in large quantities by the bacterial fermentation of carbohydrates. PLA is produced by the condensation polymerization of the LA monomer, but it is difficult to obtain high molecular weights. In order to obtain high molecular weights it is necessary to use coupling or esterification-promoting agents [47, 48]. The molecular weights of PLA before and after the increase in chain length are $M_w = 1,000\text{--}5,000$ and $M_w > 100,000$. In the case of PHAs, they are produced directly by various bacteria in many grades, differing in composition, molecular weight and other parameters. The formation of a particular material, either homo- or copolymer, depends on the type of bacteria, but even more important are the conditions of polymer formation, mainly the substrate used for feeding the bacteria and the conditions of their growth. The two main PHAs, with commercial interest, are poly(hydroxybutyrate) (PHB) and its copolymer with valerate, poly(hydroxybutyrate-valerate) (PHBV) [49]. It is important to highlight that PHAs can also be produced by chemical synthesis from the relevant substituted propiolactones [50]. The typical PLA glass transition temperature (T_g) ranges from 50 to 80 °C, whereas its melting temperature (T_m) ranges from 130 to 180 °C. For instance, enantiomerically pure PLA is a semi-crystalline polymer with a T_g of 55 °C and a T_m of 180 °C. The mechanical properties of PLA-related polymers were recently reviewed by Sodergard and Stolt [48]. The mechanical properties of PLA can vary to a large extent, ranging from soft and elastic materials to stiff and high strength materials, according to different parameters, such as crystallinity, polymer structure and molecular weight, material formulation (plasticizers, blend, composites, etc.) and processing (e.g. orientation). For instance, commercial PLA has a modulus of 2.1 GPa and an elongation at break of 9 %. After plasticization, its Young's modulus decreases to 0.7 MPa and the elongation at break rises to 200 %, with a corresponding T_g shift from 58 to 18 °C [51]. With regard to the basic poly(hydroxyalkanoates) (PHAs), PHB and PHBV, their T_g values are 4 and 5 °C, their moduli are 3.5 and 900 MPa and their elongations at break are 5 and 15 %, respectively. However, their properties can change when copolymerized with other

PHAs. Some examples are the copolymers PHB-co-20 mol% hydroxyvalerate and PHB-co-3 mol% 3-hydroxydecanoate/3 mol% 3-hydroxydodecanoate, the final T_g values of which, in comparison with PHB, decrease to -1 and -8 °C, the moduli decrease to 0.8 and 0.2 MPa and the elongations at break rise to 50 and 680 %, respectively [52]. Interesting materials have been developed based on copolymers of PHAs and caprolactone. It was verified that with rising caprolactone, a decrease in T_g is observed from 2 to -42 °C, for caprolactone contents of 0 and 72 %, respectively [53].

Proteins are natural macromolecules consisting of different amino acid residues arranged in a three-dimensional structure. Amino acids have two functional groups, namely an amino group ($-NH_2$) and a carboxyl group ($-COOH$). The main proteins with potential applications in materials are soy protein, zein, wheat protein and casein, the first three being from plant sources and the last one from animal sources [54, 55]. In the same way as the other macromolecules described above, the properties of proteins can be modified by blending or by the addition of plasticizers [56–58]. For example, there are two glass transitions (T_{g1} and T_{g2}) in the soy protein plasticized with glycerol, corresponding to glycerol-rich and protein-rich domains, respectively. The T_{g1} of the plasticized protein decreases from -28.5 to -65.2 °C with an increase in glycerol content from 25 to 50 wt%, whereas the T_{g2} is almost invariable at about 44 °C [59]. Blends of soy protein and biodegradable polyesters have been prepared using glycerol as a compatibilizing agent. Good miscibility was obtained only when the soy protein was initially combined with glycerol under high shear at elevated temperatures in an extruder. Under these conditions, partial denaturing of the soy protein led to specific interactions between the functional groups of the protein and the glycerol. Screws with large kneading blocks that produced high shear mixing were preferred and led to thermoplastic blends with high elongation and tensile strength [60].

The main constituents of plants are cellulose, hemicelluloses and lignin. These molecules have been extensively studied in many applications, using them in natural form or as derivatives. As mentioned previously, the polymers derived from these molecules and also for chitin and chitosan can be used in the production of blends with elastomeric polymers, particularly with polyurethanes and NBR polymers, in order to obtain as a result an elastomeric polymer [61–67]. These elastomeric materials can be used as a polymeric matrix in elastomer composites. Alternatively, in another approach, these molecules can be used in copolymers, in which these molecules are copolymerized with elastomeric polymers. In the latter case, we highlight the production of polyols from these and other molecules separately or lignocellulosic material containing a mixture of these molecules, by oxypropylation [68–77]. This process is employed in the polyurethane industry for the preparation of low-cost polyols from abundant and renewable biomass resources. Simple sugars and other polyols such as glycerol are commonly oxypropylated for that purpose. Following this trend, several types of polymeric substrates arising from renewable resources have been subjected to oxypropylation and the resulting macromonomer (polyol) can be used in polyurethane, polyether or polyester formulations. The oxypropylation of natural polymers and other



R = cellulose, lignin, hemicelluloses, etc.

Fig. 4 Schematic view of the oxypropylation reaction

complex substrates from biomass is a method whose objective is to increase the OH functionality of the starting material by moving the hydroxyl groups to the chain end by growing a polypropylene oxide chain on the original molecule, making them much more accessible for further reaction. A scheme of reaction can be seen in Fig. 4.

The oxypropylation of natural polymeric substrates has been attracting considerable attention recently, mainly in response to the economic and environmental aspects, because this process does not require the removal of any solvent or other component, nor does it require any separation or purification procedure for the recovery of the final polyol mixture [68]. The oxypropylation can be total or partial, and in this last case a thermoplastic sleeve is formed on the material surface, and the resulting material is a composite. This process will be discussed later in this book chapter.

Finally, a promising alternative for the production of elastomeric polymers is the use of furanic molecules such as furfural and hydroxymethylfurfural. Furfural and hydroxymethylfurfural are produced from the pentose and hexose sugars, respectively. These sugars are derived from hemicelluloses, cellulose and starch. From these two compounds, furfural and hydroxymethylfurfural, many monomers can be produced through their functionalization. So, these monomers can be polymerized and the resulting polymers may have thermoplastic properties and even rubbery properties. Figures 5 and 6 show the structure of furfural and hydroxymethylfurfural as well as some monomers produced from them and their synthetic homologues monomers, respectively.

Furfural is a typical precursor to furan monomers bearing a moiety that can be polymerized by chain reaction mechanisms, and hydroxymethylfurfural, on the other hand, is ideally suited as a precursor to bifunctional furan monomers to be used in step growth reactions. All the monomers derived from furfural and hydroxymethylfurfural, shown in Figs. 5 and 6, and others not shown here, were synthesized and polymerized. These studies are described in many reviews in the literature where the synthesis route and the resulting polymer properties are described [78–82]. These monomers were employed in the preparation of polyesters, polyamides, polyurethanes and others, and their resulting properties, in many cases, were not studied. Although these properties have not been fully studied, it is believed that these properties are similar to the polymers produced with their homologous synthetic monomers. So, these monomers can be used in copolymerization with other monomers to give elastomeric polymers, or they can be used to produce polymers and for blending with elastomeric polymers. From

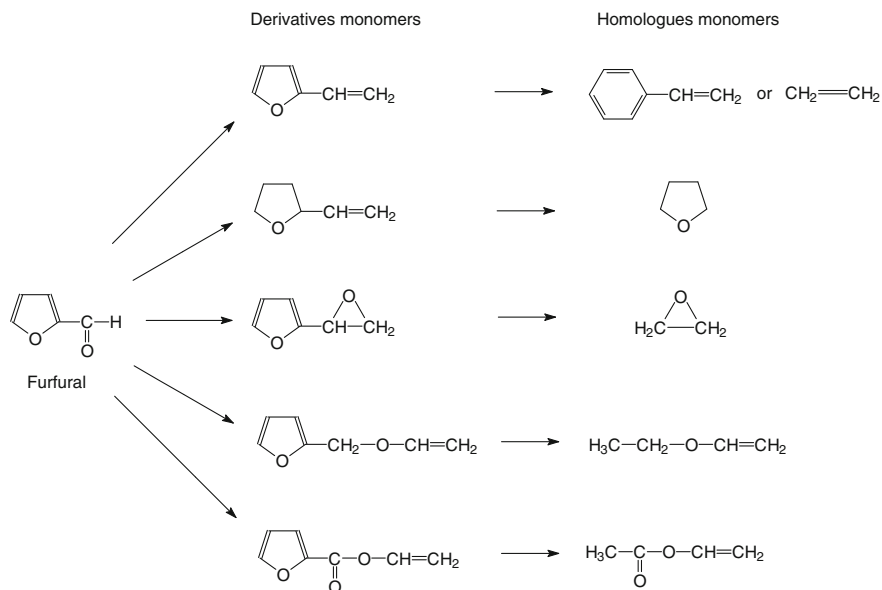


Fig. 5 Structure of furfural, some monomers produced from it and their synthetic homologues monomers

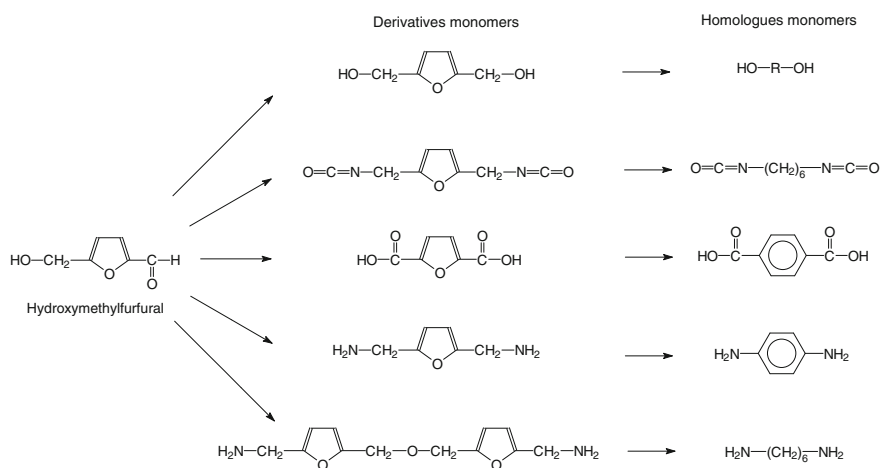


Fig. 6 Structure of hydroxymethylfurfural, some monomers produced from it and their synthetic homologues monomers

studies conducted with monomers derived from furfural and hydroxymethylfurfural, we highlight the production of polyesters [83] and polyurethanes [84, 85] by copolymerization of these furanic monomers with synthetic monomers, in which the resulting copolymer showed characteristics of elastomers. In the case of

polyesters, they were semi-crystalline materials with glass transition temperatures of -51 to -62 °C and were stable up to 225 °C. In the case of the polyurethanes, thermoplastic elastomers based on furanic-aliphatic, furanic-aromatic, fully furanic moieties and other monomers such as 1,4-butanediol or 2,5-bis(hydroxymethyl)-furan as diols, methylene diphenyl diisocyanate as diisocyanate and polytetramethylene oxide glycol, poly(caprolactone) or poly(butadiene)glycol as flexible macrodiols were prepared, and the resulting T_g values of the soft segments were around -60 °C and the melting point of the rigid counterparts ranged from 150 to 190 °C.

As a partial conclusion of this topic, we can verify that, except for natural rubber, all other molecules from renewable sources by themselves or in a polymerized form do not exhibit the characteristics of elastomers. The polymers produced from these molecules are mostly thermoplastic, and to provide elastomeric characteristics they need to be modified by grafting, copolymerization or blending. For the production of fully green elastomer composites, the biggest challenge is the production of elastomeric polymers from molecules from renewable sources, which will be used as a matrix in these composites. This is an area in which there are still many possibilities to explore and the production of new elastomeric polymers will be the source of many research works.

3 Green Elastomer Composites

Few works are found in the literature describing the preparation and study of fully green elastomer composites. This is mainly due to the fact that, with the exception of natural rubber, there are a few polymers derived from renewable sources that show the characteristics of elastomers. In this section we will present some studies found in the literature in which the resulting composite can be classified as a fully green elastomer composite, and we will discuss initially the composites where the polymer matrix is natural rubber and the charges were macroscopic vegetable fibres and in some cases nanoparticles. Finally, we will describe other works in which the polymeric matrix was an elastomeric polymer other than natural rubber.

The reinforcement with many kinds of macroscopic vegetal fibres in natural rubber has been extensively studied. Among the types of fibres used in these works, we can mention: coir [86, 87], sisal [88, 89], grass [90, 91], pineapple [92, 93], jute [94], isora [95], oil palm [89, 96], waste paper [97], woven sisal fabric [98], a combination of sisal and oil palm fibres [99, 100] and a combination of carbon fibre and kenaf [101]. The effects observed in these studies due to the fibre reinforcement on the mechanical properties of natural rubber composites include increased modulus, increased strength with good bonding at high fibre concentrations, decreased elongation at failure, greatly improved creep resistance over particulate-filled rubber, increased hardness and a substantial improvement in cut, tear and puncture resistance.

The uses of nanoparticles as a reinforcement agent in natural rubber-based nanocomposites have also been extensively studied. In this case, these nanoparticles were extracted from different sources. The nanoparticles from cellulose sources and chitin are called whiskers, and those from starch are called starch nanocrystals. The difference between them was discussed earlier in this chapter. So, the studies found in the literature were carried out employing nanoparticles as a reinforcing agent in natural rubber-based nanocomposites, from different sources such as cassava bagasse [102], sugar cane bagasse [103], rachis of palm tree [104–106], Crab shell chitin [107–109] and *Syngonanthus nitens* (Capim Dourado) [110]. The effects of nanoparticles' loading on tensile properties, thermal properties, moisture sorption, water vapour permeation and soil biodegradation were studied. Significant improvements in Young's modulus and the tensile strength were observed as a result of the addition of nanoparticles to the rubber matrix, especially at high nanoparticle loadings. Dynamic mechanical thermal analysis (DMA) and differential scanning calorimetry (DSC) results showed that in most of the cases there was no significant change in the glass transition temperature (T_g) of the rubber matrix upon the addition of nanoparticles but at the softening of rubber, nanoparticles have a reinforcing effect on the rubber. The presence of nanoparticles resulted in an increase in moisture sorption of rubber films with a low content while at higher nanoparticle loadings the moisture sorption tended to decrease. The barrier properties to water vapour decreased with a low content of nanoparticles, but increased with a further increase in the nanoparticle loading.

The use of regenerated cellulose as a filler in natural rubber vulcanizates composites was also studied [111]. These composites showed an unexpected reinforcement effect, with maximum tensile properties at 15 phr of cellulose. The swelling behaviour of these compounds was studied and the density of crosslinks was determined in heptane and benzene. The crosslink density is higher in vulcanizates containing regenerated cellulose than in vulcanizates containing carbon black. It is also higher when the swelling is carried out in heptane than when it is carried out in benzene. The crosslink density increases when the amount of filler increases for the experimental conditions.

The use of lignin acting as a reinforcing filler in natural rubber-based composites was also studied [112]. This new type of composite elastomer material was prepared by the addition of lignin biopolymer to styrene-butadiene rubber. The effect of lignin on the processing and mechanical properties of the prepared composites was examined. It was verified that the addition of lignin in an amount up to 30 wt% to rubber blends improved the mechanical properties of vulcanizates.

The production, characterization and properties of the natural rubber-based composites and nanocomposites will be explored more deeply in other chapters of this book.

Elastomer composites employing proteins and other carbohydrates were studied. The aqueous dispersion of defatted soy flour containing soy protein, soy carbohydrate and soy whey was blended with a styrene-butadiene latex to form elastomer composites [113]. The inclusion of soy carbohydrate increased the tensile stress in the small strain region, but reduced the elongation at break.

The inclusion of soy carbohydrate and soy whey also improved the recovery behaviour in the non-linear region. At small strain, the shear elastic modulus of 30 % filled composites at 140 °C is about 500 times higher than that of the unfilled elastomer, indicating a significant reinforcement effect generated by defatted soy flour. Compared with soy protein isolate, the stress softening effect and recovery behaviour under dynamic strain indicated that the addition of soy carbohydrate and soy whey had enhanced the filler–rubber interactions.

A novel series of protein composites has been prepared from 30 to 50 wt% polyurethane prepolymer with soy dreg (a by-product from the isolation process of soy protein), soy whole flour and soy protein isolate, by a compression-moulding process at 120 °C, without the addition of any plasticizers [114]. The toughness, thermal stability and water resistivity of these composites was significantly improved. By increasing the polyurethane prepolymer content, elastomeric materials could be obtained. With an increase in the cellulose content in the system, the tensile strength and water resistivity of the ensuing composites increased. The tensile strength, elongation at break and water resistivity were 6.9 MPa, 100 % and 0.55 for soy dreg with 50 wt% polyurethane prepolymer, and 4.8 MPa, 140 % and 0.50 for soy protein isolate with 50 wt% polyurethane prepolymer, respectively.

Composites with an elastomeric character were prepared from wheat gluten, which acts as a matrix, and methylcellulose microfibrils, which act as a filler [115]. These environmentally friendly green composites were prepared by the conventional blending of wheat gluten, methylcellulose microfibrils and glycerol as a plasticizer, followed by compression moulding of the mixture at 127 °C to crosslink the matrix. Their thermal and mechanical properties were evaluated in relation to their methylcellulose microfibril content. It was found that the addition of methylcellulose microfibrils can significantly improve the Young's modulus and tensile strength of the composite, which is accompanied by rises in the glass transition temperatures of the wheat gluten matrix. The influences of the methylcellulose microfibril content on the thermal decomposition and gluten solubility in water are also discussed. The presence of methylcellulose microfibrils can accelerate the moisture desorption of the composites during TGA testing. However, the addition of methylcellulose microfibrils with content above 33.3 wt% can delay the thermal decomposition of the composites. Because both methylcellulose microfibrils and glycerol are water soluble, the composites might be used as a kind of biodegradable material in low relative humidity conditions.

The combination of elastomeric polymers and filler from renewable resources to produce a fully green elastomer composite has seldom been explored when the elastomeric polymer matrix is a material other than natural rubber. This is an area to be explored, which is still deficient in publications. As previously mentioned, the difficulty is the production of elastomeric polymers from renewable sources.

4 Self-Reinforced Composites Obtained by Partial Oxypropylation

A new class of composites was prepared by the partial oxypropylation of different kinds of cellulose samples viz. regenerated cellulose Rayon, filter paper, microcrystalline cellulose Avicell, Eucalyptus bleached Kraft pulp and starch [116–119]. The oxypropylation reaction scheme can be seen in Fig. 4. The difference between total and partial oxypropylation is that, in the last case, the oxypropylation is only on the surface of the material. As a result we have a new biphasic material consisting of a low glass transition temperature component surrounding the inner core (cellulose samples or starch granules), which could be hot pressed to form films of the filler dispersed into a thermoplastic matrix. Figure 7 displays SEM micrographs of the filter paper cellulose fibres before and after partial oxypropylation.

The SEM micrographs of the filter paper fibres (Fig. 7) show the presence of a thermoplastic sleeve around the modified fibres. It was observed that, after hot pressing, these materials showed a high interfacial adhesion giving rise to a continuous morphology, unachievable with the unmodified material. The DSC tracings of the oxypropylated products showed systematically a glass transition at ca. $-50\text{ }^{\circ}\text{C}$ (albeit with different ΔC_p , depending on the extent of oxypropylation), absent from the corresponding pristine substrates, which was assigned to the modified portion of the cellulose samples or starch granules, in tune with the T_g of commercial hydroxypropylcelluloses, which ranges from -60 to $-70\text{ }^{\circ}\text{C}$. Polysaccharides grafted with oligoether chains only display the glass transition of the grafts, which explains the constant value of T_g in the present context.

Self-reinforced composites in which the oxypropylated outer sleeve of substrate generates the matrix upon hot pressing, leaving their inner core to act as reinforcing elements, were shown to be readily prepared using a variety of substrates. The interest of this process resides not only in the novel exploitation of renewable resources, but also in its green connotation, since it requires neither the use of solvents nor the application of any processing operations, given the fact that the

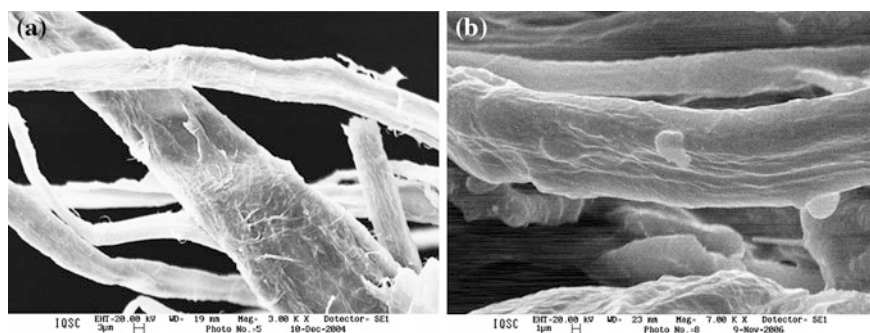


Fig. 7 SEM micrographs of the filter paper cellulose fibres **a** before (magnification 3,000X) and **b** after (magnification 7,000X) partial oxypropylation

final product is ready for further exploitation as it is removed from the reactor. There is no information about the mechanical properties of these novel materials, but they can be blended in association with other elastomeric polymers, in order to produce as a resulting material an elastomer composite.

5 Conclusions

We can conclude that the production and study of fully green elastomer composites has been largely unexplored. This is because of the difficulty in preparing an elastomeric polymer employing molecules from renewable sources. We found that the fillers from renewable sources are largely available and varied, and range from macroscopic particles to nanosized particles, and these fillers have varied reinforcement properties and can be readily employed as a substitute for fillers that are not renewable. The production of elastomeric polymers from renewable sources is a challenge and at the same time a big problem to be solved. Research efforts must be concentrated on solving this problem and thus opening new opportunities in the preparation of fully green elastomer composites and generating new applications for them as replacements for conventional elastomer composites.

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