Review Article

Radiation-induced modifications in natural fibres and their biocomposites: Opportunities for controlled physico-chemical modification pathways?

Nicolas Le Moigne[a,*], Rodolphe Sonnier[a,*], Roland El Hage[a,1], Sophie Rouif[b]

[a] *Centre des Matériaux des Mines d'Alès (C2MA), Ecole des mines d'Alès, 6 avenue de Clavières, 30319 Alès Cedex, France[2]*
[b] *Ionisos SAS, Parc Dombes Côtière Activités, 01120 Dagneux, France*

ABSTRACT

Active research is currently being done on the development of efficient surface modifications and functionalization of natural fibres aiming to improve biocomposites performances. Electron beam and gamma (γ) radiation treatments have been widely used to treat various lignocellulosic biomass with the aim of improving their accessibility to solvents and reagents for their subsequent chemical modification and processing, or for enhancing cellulose enzymatic hydrolysis for the production of ethanol and 2nd generation biofuels. The relevance of ionizing radiation treatments for the modification of natural fibres and their biocomposites is addressed in this review. They can indeed generate radicals or functional groups available for grafting functionalized molecules of interest on natural fibres. The effect of ionizing radiations on the structure of lignocellulosic substrates, and more particularly natural fibres, is discussed. The impact of composite and fibre irradiation on biocomposites properties is detailed. The last part of the review presents insights on advantages of radiation-grafting as an innovative strategy to functionalize natural fibres and improve functional properties of biocomposites. The industrial feasibility and costs of radiation induced modifications are also discussed. Based on literature, it appears that ionizing radiation methods used in suitable and controlled conditions are relevant over other physical and chemical methods developed for the surface modification and functionalization of bio-reinforcements in composite applications.

1. Introduction

Nowadays, natural fibres are considered as a promising alternative to synthetic fibres, such as glass, in composite applications (Deyholos and Potter, 2014; Faruk et al., 2012). Biocomposites reinforced with lignocellulosic or protein fibres have some advantages over glass fibre based composites, thanks to their biobased and renewable origin and biodegradability, low cost, low density, low abrasiveness and good damping performances. Natural fibres also exhibit high specific mechanical properties (i.e. mechanical properties to fibre density ratio), even if their ultimate performances still remain lower than those of glass fibres. Besides, the low thermal stability of natural fibres limits their use in composite applications to polymer matrices having low processing temperatures.

In particular, mechanical properties of biocomposites suffer from the low mechanical interlocks and physico-chemical interactions at the fibre/matrix interface. The quality of the interfacial adhesion is primarily related to the differences in surface energy and polarity between

matrix and fibres, the fibre surface topography, as well as the availability of reactive functional groups at the fibre surface and the possible presence of weakly bonded components on the fibres. Other parameters can be considered as the presence of moisture into natural fibres or their intrinsic porosity which may act as weak points within their microstructure or at the fibre/matrix interface. In this respect, glass fibre-based composites, for which fibre sizing intended to improve fibre/matrix adhesion was widely developed over the last decades, generally exhibit much higher mechanical performances.

Strategies to improve the adhesion between natural fibres and matrix are focused in particular to the surface modification of natural fibres. Because the nature of lignocellulosic substrates is totally different from that of glass fibres, the sizing formulations used for the latter cannot be directly applied for the former. Thereby, active research is currently being done on the development of efficient surface modifications and functionalization of natural fibres aiming to improve the performances of biocomposites. Hydrophobic treatments are also considered to control the water uptake of these fibres in composite and

---

textile applications. Among many other chemical and physical treatment methods (Belgacem and Gandini, 2005; Faruk et al., 2012; Kalia et al., 2009), electron beam (e-beam) and gamma (γ) radiation treatments have been widely used to treat various lignocellulosic biomass with the aim of improving their accessibility to solvents and reagents for their subsequent chemical modification and processing, or for enhancing cellulose enzymatic hydrolysis for the production of ethanol and 2nd generation biofuel (Arthur, 1971; Driscoll et al., 2009; Fischer et al., 1985; Klemm et al., 1998; Loow et al., 2016). Irradiation can also be used to modify natural fibres, and generate radicals or functional groups available for grafting functionalized molecules of interest. Nevertheless, it is well known since several decades that ionizing radiations can degrade cellulosic substrates, at relatively low ionizing doses. Therefore, the relevance of these ionizing radiation methods for the modification of natural fibres is questionable (Belgacem and Gandini, 2005).

In this review, we recall briefly the main molecular and microstructural features of natural fibres. The influence of ionizing radiations on lignocellulosic substrates, and more particularly on natural fibres at the different scales of their structure, is discussed according to the main characteristics and influencing parameters (dose, atmosphere, moisture…) of both e-beam and γ-radiations. Then, the impact of pre-irradiation of fibres or matrix and of post-irradiation of biocomposites is also detailed. Indeed, it is important to identify the effective role of fibre irradiation when radiation-induced changes or radiation-grafting are considered to improve the interfacial interactions between natural fibres and matrices. Insights on advantages of radiation-grafting as an innovative strategy to functionalize natural fibres and improve fibre/matrix interactions in biocomposites are exposed. The last part of the review propose a discussion on the industrial feasibility and costs of radiation induced modifications.

2. Molecular and cell wall structure of natural fibres

Natural fibres usually refer to lignocellulosic biomass such as wood fibres and other plant cells from fruit, grass, leaf, seed, and stem. Their chemical composition varies within the different parts of the plant, from one plant to another, according to soil and climate conditions, and maturity of the cells. When considering the dry matter, the predominant chemical components are carbohydrates (sugar-based polymers: holocellulose « cellulose and hemicelluloses » and pectins) in combination with a complex polymer of aromatic alcohols named lignin, and in lower amounts, extractives (e.g. fatty acids, fatty alcohols, free sterols, ferulic acid esters, waxes, sterol, and other aromatic compounds), starch, proteins and inorganic components (e.g. silicon, calcium, potassium, zinc, iron, aluminum, boron, etc.) (Bismarck et al., 2002; Brosse et al., 2012; Gutierrez et al., 2008; Misra et al., 1993; Yan et al., 2014). Cellulose is the most abundant biopolymer on the planet, representing more than half of the Earth's biomass. It is indeed estimated that nature produces between 10^{10} and 10^{11} tons of cellulose annually, which constitutes at least 50% of the plant mass (Hon, 1994). Cellulose is a linear homopolymer of chemical formula $C_6H_{10}O_5$. The macromolecular chains are composed of anhydroglucose units (AGU) linked together by β-(1,4)-glycosidic bonds, and are associated through intra and inter-molecular hydrogen bonds and organized in crystalline elementary fibrils of about 3.5 nm in diameter and microfibrils of 4–35 nm in diameter according to cellulose sources (Klemm et al., 2005). Degree of polymerization (DP) of native cellulose from various origins varies from 1000 to 30,000 with a large polydispersity, and from 200 to 3000 after extraction (Heinze et al., 2012; Klemm et al., 1998; Krässig, 1993). Cellulose substrates may contain as much as 70% of highly ordered crystalline regions (Atchison, 1983; O'Sullivan, 1997), whose main lattice forms are either type I for native cellulose or type II for regenerated cellulose. Thanks to its well-organized structure, cellulose provides strength, stiffness and structural stability to natural fibres. The hemicellulose fraction of natural fibres consists in branched

heteropolysaccharides, mainly xylans, mannans and xyloglucans, containing 5 ($C_5H_{10}O_5$) and 6 ($C_6H_{12}O_6$) carbon sugars: D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amounts of other sugars. Hemicelluloses, in their native state, are low molecular weight branched polymers which are non-crystallizable but still contribute to the structural organization of the plant cells as a matrix component (Pettersen, 1984). Pectins are complex high-molecular-weight acidic polysaccharides whose chain backbone is rich in galacturonic acid with different degree of methyl esterification. The most common pectic polysaccharides present in natural fibres are linear homogalacturonans and branched rhamnogalacturonans (RG type I, RG type II). They act as adhesives in the middle lamellae between plant cells and contribute to the mechanical strength of the cell walls (Jarvis, 1984; Morvan et al., 2003). Non-wood fibres (e.g. bast fibres) have significant amount of pectins in their structure. Lignin is a three-dimensional phenylpropanoid heterogeneous, amorphous and highly cross-linked macromolecule that represents the second most abundant natural polymeric material on earth. Despite extensive investigations, the complex and irregular structure of lignin is not completely understood (Argyropoulos and Menachem, 1998; El Hage et al., 2010a,b; Fengel and Wegener, 1989). Lignin structure varies within different plant species and is usually composed of three basic building blocks of guaiacyl, syringyl, and p–hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants (Sjöström, 1981). Lignin is considered as a cell wall adhesive that also acts as an encrusting component between cellulose microfibrils, like the matrix constituents mainly composed of hemicelluloses and pectins (Morvan et al., 2003). Chemical compositions of some selected natural fibres are given in Table 1.

In general, the cell wall morphology of natural fibres (Fig. 1) is made of an outer layer, the primary (P) wall (0.1–0.5 μm thick), and concentric inner layers constituting the secondary (S1) and (S2) walls (0.1–0.3 μm and 1–10 μm thick, respectively), where the different chemical components detailed above are distributed and organized, thereby forming a complex, tri-dimensional bio-assembly (Klemm et al., 1998; Klemm et al., 2005; Krässig, 1993). In these different layers and walls, cellulose microfibrils are oriented along the fibre axis and holded together due to cooperative function of hemicelluloses, lignin and pectins that act as matrix and adhesive components (Sjöström, 1981). These fibrillar cells, also called elementary fibres, are gathered in fibre bundles into wood and grass, and within the stem, fruit or leaf of annual plants, or can be eventually already individualized as is in the case of cotton fibres. A combined method using visible photomicrograph, associated with a 3-D mid-infrared transmission, allowed to localize the distribution of the different cellulosic and non-cellulosic components across flax stem sections (Morvan et al., 2003), and showed that stem surface (epidermal region) is composed mainly of pectins and waxes. Underneath the epidermis, the internal zone rich in bast fibres, where cellulose is predominant, showed substantial amounts of pectins and acetylated non-cellulosic polysaccharides accumulated in the primary wall and cell junction that act as adhesives in the cohesion of flax fibre bundles. Aromatic components (e.g. lignins) and non-cellulosic polysaccharides appeared to be more concentrated in the core tissues of flax stems. These observations thus show that natural fibres can undergo wide variations in biochemical composition according to their localization within higher plants.

Bismarck et al. (2002) proved that surface characteristics of natural fibres vary according to fibre extraction and separation processes. As observed by scanning electron microscopy (SEM), BET-adsorption and ξ-potential measurements, extraction processes affect the surface morphology and the specific surface area of fibres as well as their surface physical chemistry. In particular, the hydrophilic character of natural fibres is related to the amount of waxes on their surface. Lower waxes content leads to higher hydrophilicity and to higher water sorption (Kuehn et al., 1986). Furthermore, the content and the nature of surface