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Composites reinforced with cellulose based fibres

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Abstract

This review article concerning natural and man-made cellulose fibre reinforced plastics, introduces possible applications of this material group. The physical properties of natural fibres are mainly determined by the chemical and physical composition, such as the structure of fibres, cellulose content, angle of fibrils, cross-section, and by the degree of polymerization. Only a few characteristic values, but especially the specific mechanical properties, can reach comparable values of traditional reinforcing fibres. This physical structure can be modified by using alkali treatment and acetylation processes. The application of natural fibres as reinforcements in composite materials requires, just as for glass-fibre reinforced composites, a strong adhesion between the fibre and the matrix, regardless of whether a traditional polymer (thermoplastics or thermosets) matrix, a biodegradable polymer matrix or cement is used. Further this article gives a survey about physical and chemical treatment methods which improve the fibre matrix adhesion, their results and effects on the physical properties of composites. These different treatments change among others the hydrophilic character of the natural fibres, so that moisture effects in the composite are reduced. To bring about hydrophobic properties to natural fibres, a special treatment, termed acetylation, can be used. The effectiveness of this method is strongly influenced by the treatment conditions used. The mechanical and other physical properties of the composite are generally dependent on the fibre content, which also determines the possible amount of coupling agents in the composite. The influence of such treatments by taking into account fibre content on the creep, quasi-static, cyclic dynamic and impact behaviour of natural fibre reinforced plastics are discussed in detail. For special performance requirements, hybrid composites made of natural and conventional fibres can be prepared with desired properties. The processing conditions play, next to the mechanical properties of natural fibres, an important role for the industrial use of these materials. The results presented in this paper show, that natural fibres can be processed with the already commonly applied methods: glass mat thermoplastic matrix (GMT), sheet moulding compound (SMC) or bulk moulding compound (BMC). For the processing of thermoplastics reinforced with natural fibres, new methods (e.g. the ‘‘EXPRESS’’ processing) are of increasing importance. Natural fibres seem to have little resistance towards environmental influences. This can be recognized in the composite and can be advantageously utilized for the development of biological degradable composites with good physical properties. © 1999 Elsevier Science Ltd. All rights reserved.

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Contents

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1. Survey of technical applications of natural fibre composites

Seventy years ago, nearly all resources for the production of commodities and many technical products, were materials derived from natural textiles. Textiles, ropes, canvas and also paper, were made of local natural fibres, such as flax and hemp. Some of these are still used today. As early as 1908, the first composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electronic purposes (paper or cotton to reinforce sheets, made of phenol- or melamine–formaldehyde resins). In 1896 for example, aeroplane seats and fuel-tanks were made of natural fibres with a small content of polymeric binders [1].

Owing to low prices and the steadily rising performance of technical and standard plastics, the application of natural fibres came to a near-halt. More recently, the critical discussion about the preservation of natural resources and recycling has led to a renewed interest concerning natural materials with the focus on renewable raw materials [2].

Compared to Western Europe, India continued to use natural fibres, mainly jute-fibres, as reinforcements for composites. Pipes, pultruded profiles, and panels with polyester matrices, were produced with these fibres [3]. The government of India promoted large projects where jute reinforced polyester resins were used for buildings, e.g. the Madras-House, 1978 [4] and grain-elevators. Natural fibres, as construction materials for buildings were known long before. For centuries, mixtures of straw and loam, dried in the sun, were employed as construction composites, e.g. in Egypt [1].

Today, a renaissance in the use of natural fibres as reinforcements in technical applications is taking place mainly in the automobile- and packaging industries (e.g. egg boxes). In the automotive industry, textile waste has been used for years to reinforce plastics used in cars, especially in the Trabant [1]. At present, a K-car-series is planned for development by Mercedes, where the ‘‘K’’ stands for ‘‘kraut’’ and ‘‘compost’’ [2]. Local European renewable fibres, such as flax and hemp, were used for these cars. Ramie-fibres are examined too, because of their specific properties [5]. To give an example, the following components were developed for the following applications [2,6,142]:

Door panels:
Moulded wood, natural fibre mouldings, laminated panels;
Car roofs:
Composites made of natural fibre-fleece—flax—with epoxy resins or polyurethane composites.

A survey regarding the possible applications of natural fibres in automobiles is published elsewhere [2]. The use of flax-fibres in car disk-breaks to replace asbestos-fibres, is another example of this type of application [7].

2. Cellulose based fibres

2.1. Technical applications of natural fibres

Natural fibres are subdivided based on their origins, coming from plants, animals or minerals. Generally, plant or vegetable fibres are used to reinforce plastics. Plant-fibres may include hairs (cotton, kapok), fibre-sheafs of dicotylic plants or vessel-sheafs of monocotylic plants, i.e. bast (flax, hemp, jute, ramie) and hard-fibres (sisal, henequen, coir).

Tanzania and Brazil are the two largest producers of sisal. Henequen is produced in Mexico, abaca and hemp in the Philippines. The largest producers of jute are India, China and Bangladesh.

The availability of large qualities of such fibres with well-defined mechanical properties is a general prerequisite for the successful use of these materials and the lack of this is one of the drawbacks at the moment. Additionally for several more technical orientated applications, the fibres have to be specially prepared or modified regarding:

- homogenization of the fibre’s properties;
- degrees of elementarization and degumming;
- degrees of polymerization and crystallization;
- good adhesion between fibre and matrix;
- moisture repellence; and
- flame retardant properties.

At present, the availability of plant fibres can only be partially assured (as shown in Table 1).

The type of fibre processing technology (e.g. microbial deterioration, steam explosion) used is one of the essential criteria of the fibre quality. The microbial deterioration of the substances begins within the fibre right after the core of the stem has dried up and continues to do so, more or less, depending on the environmental conditions. The condition reached thereby is decisive for the energy necessary for delignification and fibre separation (fibrillation) and thus also for the attainable fibre masses and, where applicable, for the fibre damages [8]. The central problem of fibre production is its procurement. In order to obtain a maximum value gain, it is important to optimally use the Nature’s facilities and synthesize. This means that the supramolecular structures of the fibres should be retained and optimally used. The traditional, microbial deterioration process is one of the most important prerequisite. In

Table 1
Production of plant-fibres compared to production of glass-fibres (1993) [87]

Fibre	Price in comparison to glass-fibres (%)	Production (1000 t)
Jute	18	3600
E-glass	100	1200
Flax	130	800
Sisal	21	500
Banana	40	100
Coir	17	100

Table 2
Mechanical properties of natural fibres as compared to conventional reinforcing fibres

Fibre	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)	References
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6	[74,131,133]
Jute	1.3	1.5–1.8	393–773	26.5	[74,76,131,134]
Flax	1.5	2.7–3.2	345–1035	27.6	[131]
Hemp	—	1.6	690	—	[135]
Ramie	—	3.6–3.8	400–938	61.4–128	[131,133]
Sisal	1.5	2.0–2.5	511–635	9.4–22.0	[74,131,136]
Coir	1.2	30.0	175	4.0–6.0	[74,136]
Viscose (cord)	—	11.4	593	11.0	[133]
Soft wood kraft	1.5	—	1000	40.0	[137]
E-glass	2.5	2.5	2000–3500	70.0	[138]
S-glass	2.5	2.8	4570	86.0	[74,138]
Aramide (normal)	1.4	3.3–3.7	3000–3150	63.0–67.0	[138]
Carbon (standard)	1.4	1.4–1.8	4000	230.0–240.0	[138]

contrast, this deterioration process can now at least be partly replaced by the newly developed chemical–physical processes. Mentioned in this context should be the tensile explosion process and the new steam explosion process, that is, the pressure process [8,9]. In this new steam explosion method, steam, and additives if necessary, under pressure and with increased temperature, penetrate the space between fibres of the fibre bundle. Because of this, the middle lamella and the fibre adherent substances are elementarized ‘‘softly’’ and made water soluble. These can be then removed by subsequent washing and rinsing.

In recent years, prices for natural fibres have not been stable, especially for flax fibres. Flax fibres show the highest values of strength, but they are about 30% more expensive than glass-fibres. Further the price depends on the extent of fibre preparation and pretreatment, e.g. size-finishing including a coupling agent and other surfactants, which are well-established for glass-fibres. For such applications, natural fibres have to be pretreated in a similar way. In most cases, the substitution of glass-fibres by natural fibres is precluded first of all by economic reasons. But, natural fibres offer several advantages over glass-fibres:

- Plant fibres are a renewable raw material and their availability is more or less unlimited.
- When natural reinforced plastics were subjected, at the end of their life cycle, to a combustion process or landfill, the released amount of CO_2 of the fibres is neutral with respect to the assimilated amount during there growth.
- The abrasive nature of natural fibres is much lower compared to that of glass-fibres, which leads to advantages with regard to technical, material recycling or process of composite materials in general.
- Natural fibre reinforced plastics by using biodegradable polymers as matrix (Section 4.3) are the most environmental friendly materials which can be composted at the end of their life cycle. Unfortunately, the overall physical properties of those composites are far away from glass-fibre reinforced thermoplastics. Further, a balance between life performance and biodegradation has to be developed.

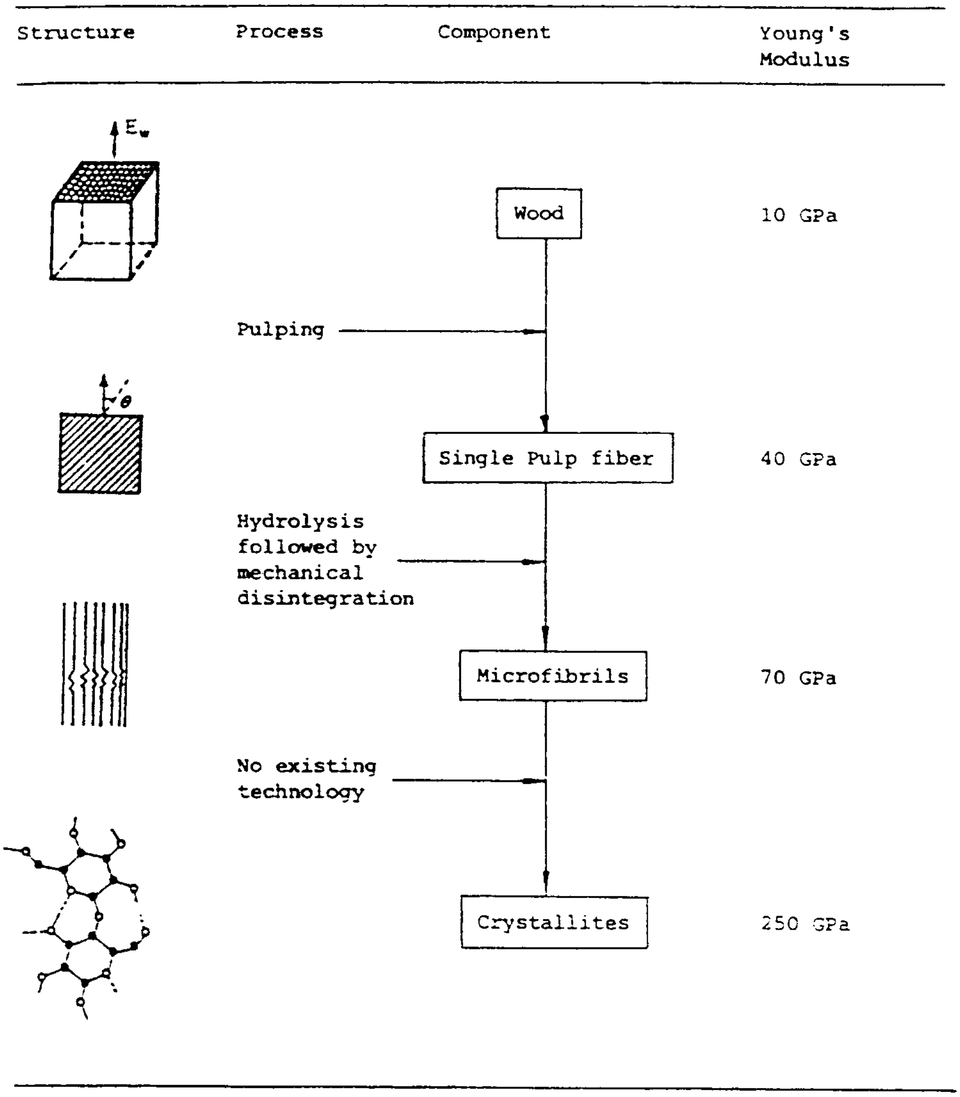
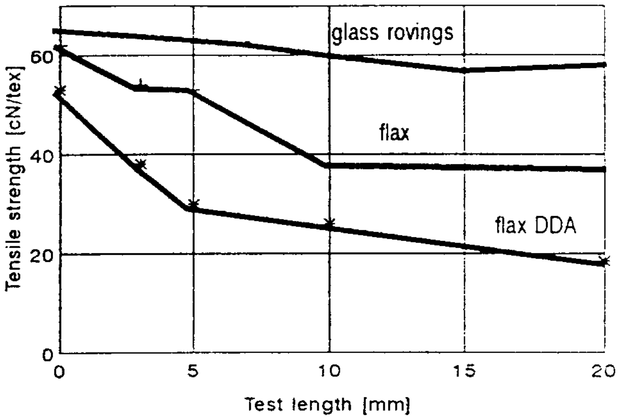


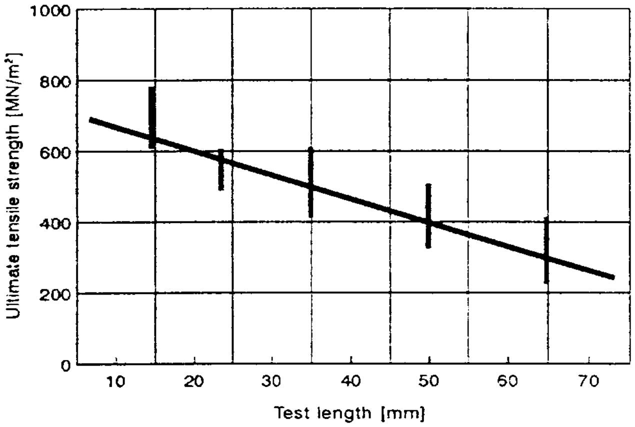
Fig. 1. Correlation between structure, who to process, resulting component, and modulus [12].

2.2. Mechanical properties of natural fibres

Natural fibres are in general suitable to reinforce plastics (thermosets as well as thermoplastics) due to their relative high strength and stiffness and low density (Table 2) [10]. The characteristic values for flax and soft-wood-kraft-fibres reach levels close to the values for glass-fibres, types E (''E'' because of their early use in electronic applications and today the most typically used glass-fibres reinforcing plastics in non-aggressive media). Nevertheless and also obvious in Table 2, the range of the characteristic values, as one of the drawbacks for all natural products, is remarkably higher than those of glass-fibres, which can be explained by differences in fibre structure due to the overall environmental conditions during



flax-/glass fibers



pineapple-fibers

Fig. 2. Dependence of tensile strength on the test length, flax-fibres [8] and pineapple-fibres [14] compared to textile glass-fibres [8].

growth. Natural fibres can be processed in different ways to yield reinforcing elements having different mechanical properties. The elements and their elastic moduli are shown in Fig. 1. The elastic modulus of bulk natural fibres such as wood is about 10 GPa. Cellulose fibre with moduli up to 40 GPa can be separated from wood, for instance, by chemical pulping processes. Such fibres can be further subdivided by hydrolysis followed by mechanical disintegration into microfibrils with an elastic modulus of 70 GPa. Theoretical calculations of the elastic moduli of cellulose chains have given values of up to 250 GPa, however, there is no technology available to separate these from microfibrils [11,12].

The fibres used currently are produced commercially by the pulp and paper industry and relate to the second level of value of elastic modulus. Discussion and future potential relate to the third and fourth levels of modulus [12].

Further as discussed previously, the fibre properties and fibre structure are influenced by several

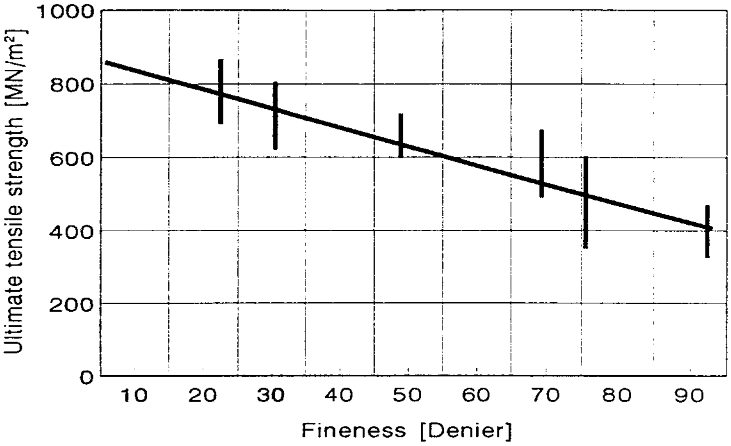


Fig. 3. Dependence of tensile strength on fibre refinement [14].

conditions and varies by area of growth, its climate and the age of the plant [144,147]. Further, the technical digestion of the fibre is another important factor which determines the structure as well as the characteristic values of the fibres.

As in the case with glass-fibres, the tensile strength of natural fibres also depends on the test length of the specimens which is of main importance regarding reinforcing efficiency. The actual tensile strength of a single fibre is typically given for a test length of zero as in the case for glass-fibres (test conditions, especially test length for the data given in Table 2 for natural fibres, were not published in the original papers. This fact can be one further reason for the differences in strength of one natural fibre type). For example, examinations dealing with that were made by Koher et al. [8], Mieck et al. [13] and Mukherjee et al. [14] on different types of flax and pineapple-fibres. Their results illustrate (Fig. 2), that the tensile strength of flax-fibres is significantly more dependent on the length of the fibre than for the case of glass-fibres. Compared to this, the tensile strength of pineapple-fibres is less dependent on the length, while the scatter of the measured values for both is located mainly in the range of the standard deviation. This

Table 3
Strength and elongation at break of dry and wet fibres [16]

Fibre	Relative tensile strength (wet) (%)	Relative elongation (wet) (%)
Cotton	105–110	110–116
Jute	100–105	100
Flax	102–106	125–133
Ramie	115–125	100
Sisal	90–120	100
Glass	75–100	100
Aramide	78–80	—
Carbon	100	100

Table 4
Composition of different cellulose based natural fibres [10]

	Cotton	Jute	Flax	Ramie	Sisal
Cellulose	82.7	64.4	64.1	68.6	65.8
Hemi-cellulose	5.7	12.0	16.7	13.1	12.0
Pektin	5.7	0.2	1.8	1.9	0.8
Lignin	—	11.8	2.0	0.6	9.9
Water soluble	1.0	1.1	3.9	5.5	1.2
Wax	0.6	0.5	1.5	0.3	0.3
Water	10.0	10.0	10.0	10.0	10.0

dependence, strength vs. test length, could be seen as degree or the homogenity or amounts of defects of a fibre or a material in general.

Further as illustrated in Fig. 3, tensile strength of the fibres is also influenced by the refinement of the fibre [14]. A decrease in fibre fineness leads to higher fibre strength.

Hydrophilic nature is a major problem for all cellulose-fibres if used as reinforcement in plastics. The moisture content of the fibres, dependent on content of non-crystalline parts and void content of the fibre, amounts up to 10 wt.% under standard conditions [15]. The hydrophilic nature of natural fibres influences the overall mechanical properties (Table 3) as well as other physical properties of the fibre itself [16]. Effect on properties of composite due to this are discussed in detail in Sections 3.3.3 and 4.2.

2.3. Natural fibres and their chemical compositions

Climatic conditions, age and the digestion process influences not only the structure of fibres but also the chemical composition. Component mean values of plant-fibres are shown in Table 4. With the exception of cotton, the components of natural fibres are cellulose, hemi-cellulose, lignin, pectin, waxes and water soluble substances, with cellulose, hemi-cellulose and lignin as the basic components with regard to the physical properties of the fibres.

2.3.1. Cellulose

Cellulose is the essential component of all plant-fibres. In 1838, Anselme Payen suggested that the cell walls of large numbers of plants consist of the same substance, to which he gave the name *cellulose*.

It is generally accepted that cellulose is a linear condensation polymer consisting of d-anhydroglucopyranose units (often abbreviated as anhydroglucose units or even as glucose units for convenience)

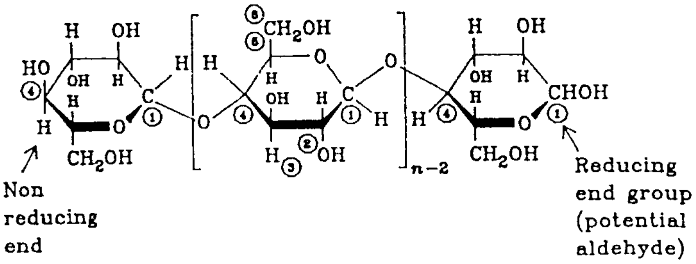
Table 5
Degrees of polymerization (P_n) of different natural fibres [129]

Fibre	P_n
Cotton	7000
Flax	8000
Ramie	6500

Table 6
Axial Young's modulus for cellulose [11]

Method	Young's modulus of cellulose (GPa) Cellulose I	Young's modulus of cellulose (GPa) Cellulose II	Material
X-ray		70–90	Fortisan
X-ray	74–103		Flax, hemp
X-ray	110		Flax
X-ray	130	90	Ramie
X-ray	120–135	106–112	Ramie
Calculated	136	89	
Calculated	168	162	

joined together by β-1,4-glycosidic bonds. It is thus a 1,4-β-d-glucan. The pyranose rings are in the $^4C_1$ conformation, which means that the $-CH_2OH$ and –OH groups, as well as the glycosidic bonds, are equatorial with respect to the mean planes of the rings [17]. The Haworth projection formula of cellulose is given by [17,18]:



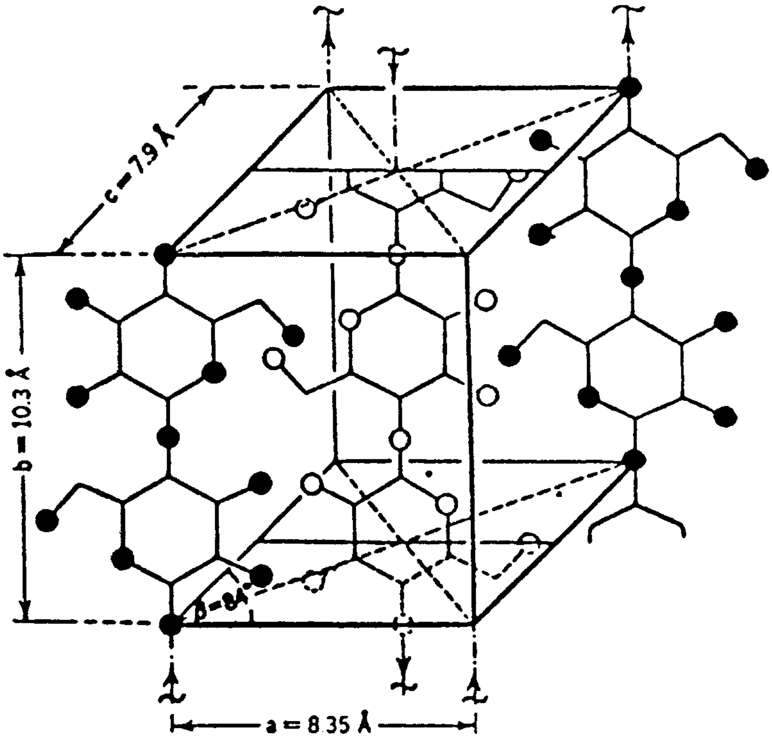
The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its chemical and physical properties. In the fully extended molecule, adjacent chain units are orientated by their mean planes at an angle of 180° to each other. Thus, the repeating unit in cellulose is the anhydrocellulobiose unit and the number of repeating units per molecule is half the DP. This may be as high as 14 000 in native cellulose, but purification procedures usually reduce it to something in the order of 2500 [17].

The degree of polymerization shows, that the length of the polymer chains varies (Table 5) depending on the type of natural fibre.

The mechanical properties of natural fibres depend on its cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties.

Fink et al. [11] related measurements according to different authors and test methods in order to compare the Young's modulus for cellulose of type I and II. Most of the authors determined higher characteristic values for type I than for type II (see Table 6).

Solid cellulose forms a microcrystalline structure with regions of high order, i.e. crystalline regions, and regions of low order, i.e. amorphous regions. Naturally occurring cellulose (cellulose I) crystallizes in monoclinic sphenodic structures. The molecular chains are orientated in fibre direction:



The geometry of the elementary cell is dependent on the type of cellulose (Table 7).

2.3.2. Further components

Hemicellulose is not a form of cellulose at all and the name is an unfortunate one. They comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The hemicellulose differs from cellulose in three important aspects. In the first place they contain several different sugar units whereas cellulose contains only 1,4-β-d-glucopyranose units. Secondly they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to one hundred times higher than that of hemicellulose.

Table 7
Lattice parameters of elementary cells in different types of cellulose [130]

Type	Source	Dimensions (nm)			β (°)
		a	*b*	*c*	
Cellulose I	Cotton	0.821	1.030	0.790	83.3
Cellulose II	Cotton, mercerized	0.802	1.036	0.903	62.8
	Cotton, viscose	0.801	1.036	0.904	62.9
Cellulose III		0.774	1.030	0.990	58.0
Cellulose IV		0.812	1.030	0.799	90.0

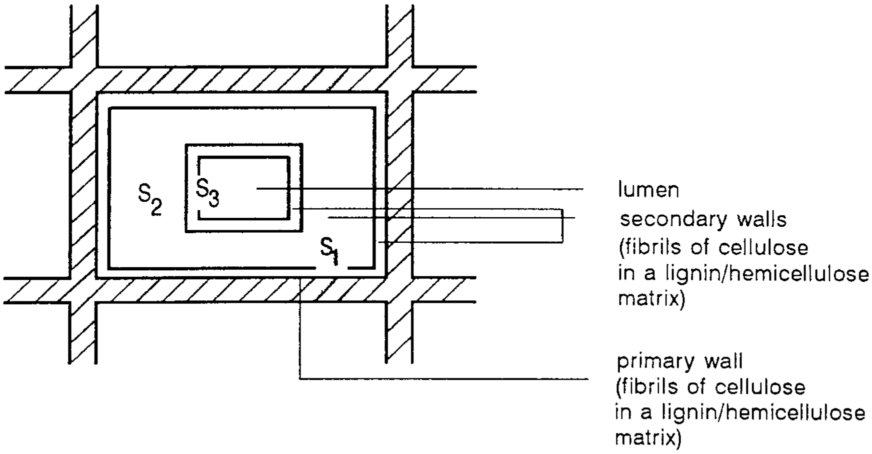
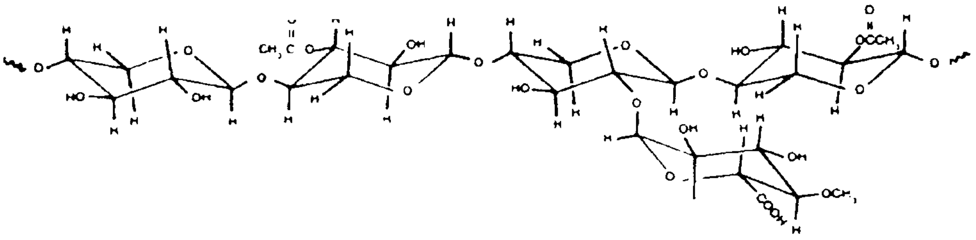
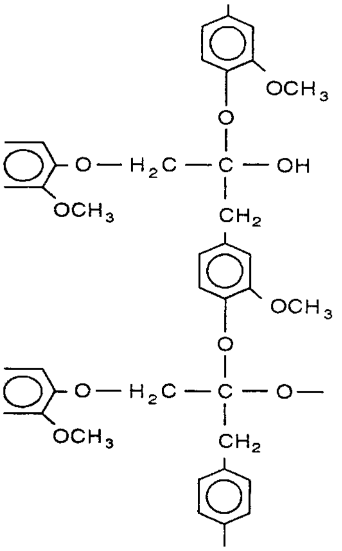


Fig. 4. Constitution of a natural fibre cell (diagramitic representation) [131].

Unlike cellulose, the constituents of hemicellulose differ from plant to plant [17]:



Lignins are complex hydrocarbon polymer with both aliphatic and aromatic constituents [17,18]:



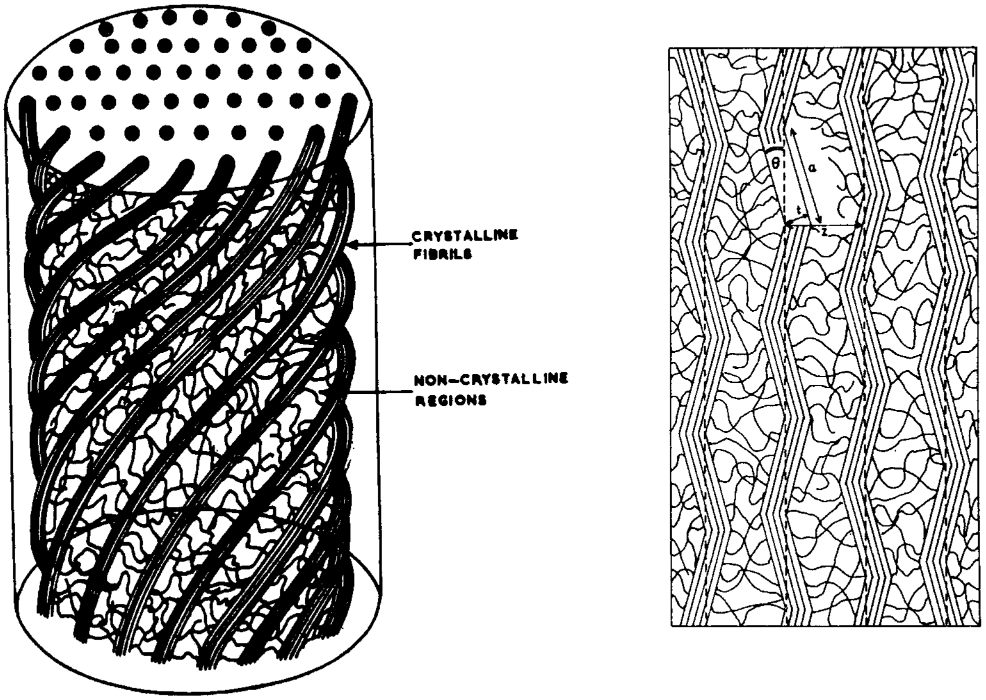


Fig. 5. Model for the description of the stiffness of the fibre [20]: (a) S_2—layers in a 3D view; (b) S_2—layers projected into a 2D view.

Their chief monomer units are various ring-substituted phenyl-propanes linked together in ways, which are still not fully understood. Structural details differ from one source to another [17].

The mechanical properties are lower than those of cellulose. At the value of 4 GPa, the mechanical properties of isotropic lignin are distinctly lower than those of cellulose [19].

Pectin is a collective name for heteropolysaccharides, which consist essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralization with alkali or ammonium hydroxide [19].

Waxes make up the part of the fibres, which can be extracted with organic solutions. These waxy materials consist of different types of alcohols, which are insoluble in water as well as in several acids (palmitic acid, oleaginous acid, stearic acid) [19].

2.4. Physical structure of natural and man-made cellulose fibres

2.4.1. Natural fibres

A single fibre of all plant based natural fibres consist of several cells. These cells are formed out of crystalline microfibrils based on cellulose, which are connected to a complete layer, by amorphous lignin and hemicellulose. Multiple of such cellulose–lignin/hemicellulose layers in one primary and three secondary cell walls stick together to a multiple-layer-composites, the cell, as shown in Fig. 4. These cell walls differ in their composition (ratio between cellulose and lignin/hemicellulose, Table 4) and in

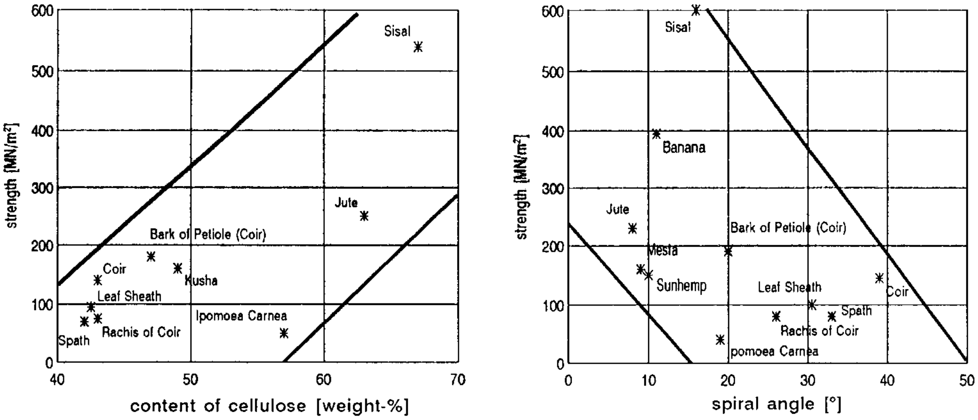


Fig. 6. Dependence of fibre strength on the content of cellulose and on the angle of fibrils [132].

the orientation (spiral angle, Table 8) of the cellulose microfibrils. The characteristic values for these structural parameters vary from one natural fibre to another as well as by physico-chemical fibre treatments such as merzerization (Section 3.5) or acetylation (Section 3.4).

The spiral angle of the fibrils and the content of cellulose, determines generally the mechanical properties of the cellulose based natural fibres. For instance, models developed by Hearle et al. [20] considers these two structure parameters to calculate the Young's modulus of the fibres. For this model, solely the S_2-layers with approximately 70% of the whole fibre were considered.

2.4.1.1. Proportion of crystalline fibrils and their orientation Till date, many authors tried to describe the mechanical characteristic values of natural fibres in consideration of their structure, e.g. Hearle in 1963 [155]. Thereafter followed models from Cowdrey and Preston (1966) [156], Page et al. (1971) [157], Brinson (1973) [158], Gordon and Jeronimides (1974) [159], Jeronimides (1976) [160] and McLaughlin and Tait (1980) [161]. All these theories consider solely two parameters: content of cellulose and spiral angle of fibrils [19].

Table 8
Structure parameters of different cellulose base natural fibres [21]

Fibre	Cellulose content (wt.%)	Spiral angle (°)	Cross-sectional area $A \times 10^{-2}$ (mm^2)	Cell-length L (mm)	L/D-ratio (D is the cell diameter (–)
Jute	61	8.0	0.12	2.3	110
Flax	71	10.0	0.12	20.0	1687
Hemp	78	6.2	0.06	23.0	960
Ramie	83	7.5	0.03	154.0	3500
Sisal	67	20.0	1.10	2.2	100
Coir	43	45.0	1.20	3.3	35

The basic idea of the model described by Hearle [20] and applied by Mukherjee et al. [21] on various natural fibres is given in Fig. 5. By taking into account different general mechanisms of deformation, three different equations for calculating fibre stiffness with respect to the fibre axis are diverted:

- The calculation of the Young's modulus of the fibre according to an equation based on an isochoric deformation.
  This equation describes well the behaviour for small spiral angles of fibrils (<45°) [20]:

  $$E_1 = [X_{1C}E_{\|,C} + (1 - X_{1C})E_{NC}]\cos^2 X_2 := E^* \cos^2 X_2 \tag{1}$$

  where $E_{\|,C}$ is the Young's modulus of cellulose in the parallel direction, E_{NC} the Young's modulus of non-crystalline parts, X_{1C} the content of the crystalline part in the fibre and X_2 the spiral angle.
- A spring-like deformation of the fibrils is the basic mechanism at spiral angles >45°. Spring-like deformation remains constant; the length of the fibrils and the Young's modulus of the fibres can be given by:

  $$E_1 = \frac{K_{NC}}{1 - X_{1C}}(1 - 2\cot^2 X_2)^2 = K(1 - 2\cot^2 X_2)^2$$

  where K_{NC} is the bulk modulus of non-crystalline parts, X_{1C} the content of the crystalline part in the fibre and X_2 the spiral angle.
- The most general formulation of the structure–modulus-relation is given by combining the already mentioned mechanisms in series. The two mechanisms will act like two springs in series, each tending to relieve the stresses in the other by an interchange of strain, and so for intermediate values of X_2 we shall have: Effective modulus due to combined factors [19], which is given as

  $$E_1 = \frac{E^* \cos^2 X_2[K(1 - \cot^2 X_2)^2]}{E^* \cos^2 X_2 + K(1 - 2\cot^2 X_2)^2}.$$

  Calculated data for the modulus by using these equations agree quite well with the experimental data for holocellulose based fibres which was discussed in detail elsewhere [22].

It is well known that in contrast to the stiffness of a material, the strength does not depend strongly on the structural arrangements like in the case of natural fibres on the cellulose content and spiral angle. Fibre strength is rather affected by their defects. Anyway, a weak correlation between strength and cellulose content and spiral angle, respectively, was found for different plant-fibres as shown in Fig. 6. In general, fibre strength increases with increasing cellulose content and decreasing spiral angle with respect to fibre axis.

An empirical structure–property relation was developed by Murkherjee et al. [21] by a proportionality between mechanical properties Y and the content of cellulose X_1, spiral angle of fibrils X_2, and the size of cells X_3. Published characteristic values for cellulose content, spiral angle, and cell size are given in Table 8.

$$Y \propto X_1^{a_1} X_2^{a_2} X_3^{a_3}.$$

Table 9
Literature reported wetting characteristics of isolated wood polymers [24]

Polymer	Water contact angle (°)	Critical surface tension (dynes/cm)	References
Cellulose	34	35.5	Luner et al. (1969) [162]
	33	—	Borgin (1959) [163]
	27.8[a]	—	Borgin (1959) [163]
Hemicellulose			Luner et al. (1969) [162]
Arabinogalactan		33	
Galactoglucomannan		36.5	
Hardwood xylan		33–36.5	
Softwood xylan		35	
Lignin			Lee et al. (1972) [26]
Hardwood kraft	60	36	
Softwood kraft	58	37	

[a] Relative humidity = 66%.

2.4.2. Man-made cellulosic fibres

There has been a large number of papers published over the years dealing with structure and properties of man-made cellulosics, particularly rayon fibres. In particular we would like to mention P.H. Hermans with his huge impact on cellulose and fibre physics [11].

Comprehensive experimental studies, particularly on viscose fibres' structure and properties, have been performed by Krässig [23]. More recent experimental investigations on the influence of structural parameters of Lenz, Schurz and coworkers involve fibres manufactured by alternative processes.

Summarizing experimental results from literature [11] it becomes clear that the mechanical properties of the man-made cellulosic depends on their structure on different levels, i.e. we have to take into account the following features:

- degree of polymerization (DP),
- crystal-structure (like type of cellulose and defects),
- supramolecular structure (e.g. degree of crystallinity),
- orientation of chains (non-crystalline and crystalline regions),
- void-structure (content of voids, specific interface, void-size), and
- fibre diameter.

Generally, the tensile strength of these fibres is strongly influenced by the length of molecules as shown for viscose and acetate type fibres. A linear correlation with a negative slope between strength and 1/DP may be modified by orientational effects, by variations of crystallite dimensions and crystallinity, by impurities and probably by pores and non-uniform cross-sections of the fibres [11]. Investigating various fibres and tire yarns, Krässig [23] found approximately linear correlations between sets of structural parameters and tensile strength, elongation at break and modulus:

$$\sigma_{\mathrm{con}} \propto (\mathrm{DP}_{\mathrm{L}}^{-1} - \mathrm{DP}^{-1})\mathrm{Cr}\ \mathrm{I}f_r^{2},$$

$$\sigma_{\mathrm{wet}} \propto (\mathrm{DP}_{\mathrm{L}}^{-1} - \mathrm{DP}^{-1})\mathrm{Cr}\ \mathrm{I}f_r^{2.5},$$

$$E_{\mathrm{wet}} \propto \mathrm{DP_L}(\mathrm{DP_L^{-1}} - \mathrm{DP}^{-1})^{-1}(1/\cos\beta - 1)^{-1}\cos\beta$$

with DP as average degree of polymerization, $\mathrm{DP_L}$ as length of the crystalline regions (level-off degree of polymerization), CrI as crystallinity index, f_r as Hermans orientation factor and $\cos\beta$ as orientational measure ($\approx f_r^{0.5}$).

2.5. Surface properties

New natural fibre or wood-based composites are being developed that could benefit from a thorough and fundamental understanding of the fibre surface. These products may require new adhesive systems to reach their full commercial potential. A better understanding of natural or wood fibre surface and adhesive bonding is necessary. The natural fibre or wood surface is a complex heterogeneous polymer composed of cellulose, hemicellulose and lignin. The surface is influenced by polymer morphology, extractive chemicals and processing conditions.

Because of the physical difficulties combined with these chemical and morphological complexity, some investigators have reported to characterize surfaces of cast films of isolated natural fibre or wood polymers (Table 9) [24].

In spite of the limited applicability of these results to the real surface of the natural fibres, the use of the isolated polymers is necessary for estimating the individual wetting characteristics of the various natural fibre components.

Toussaint et al. [25] reported about a rapid decrease of the contact angle of water with the time for cellulose films (reacted with alkyl ketone dimer), while for other test liquids such as glycerol, ethylene glycol and diiodomethane a constant contact angle was obtained after 2–5 min. Since water has a higher polarity than the other liquids, Toussaint et al. discussed the possibility that the decrease in the contact angle with the time is due to specific interactions between water and the cellulose surface allowing water to penetrate into the cellulose, causing the cellulose to swell, thus lowering the interfacial free energy and decreasing the contact angle.

For different kinds of (wood) lignin Lee et al. [26] showed decreasing contact angles of water with increasing contact time with water. A similar behaviour was detected for glycerol and formamide in contact with lignin as well as cellulose, however with only a slight contact angle decrease.

Hodgson et al. [27] successfully used the Wilhelmy technique to determine a ‘‘dynamic wettability profile’’ for wood pulp fibres. He reported about a general decrease of the (advancing) contact angle of distilled water upon repeated immersion because of the hydrophilic nature of this material. The degree to which the value decreases, however, varied significantly for the different types of wood fibres. Pure cellulose fibres exhibited a small (14°) but finite contact angle of water. In general, highly bleached, low-lignin content fibres are more hydrophilic than high yield, high-lignin content fibres.

Liu et al. [28] used dynamic contact angle analysis to characterize the surface energy of differently treated (heat treated and acetylated) rayon, cotton, and wood fibres. The investigations showed a lower surface energy for the heat treated fibres than for the untreated ones. The surface energy of acetylated wood fibres was 52 dyne/cm, which was 40% higher than that of fibres subjected to heat treatment. In the case of acetylated fibres this increase is assigned to the acetyl group polar contribution increase.

The use of different kinds of physical (i.e. corona discharge) and chemical surface treatment methods (coupling agents such as silanes) leads to changes in the surface structure of the fibres as well as to changes in the surface energy.

The treatment of rayon fibres with oxygen plasma results in increasing the total as well as in the polar part of the free surface energy with increasing treatment time, because of the increased O/C ratio. Similar results were observed by Belgacem et al. [29] for an increasing corona current level for cellulose fibres. Also Sakata et al. [30] reported on an improved wettability of wood with increasing level of corona treatment.

Felix et al. [31] used the dynamic contact angle analysis to characterize the surface energy of untreated and MAPP (= maleated polypropylene) treated cellulose fibres. As expected, the MAPP leads to a distinctly lower polar part of the free surface energy with 4.9–8.4 mJ/m^2, dependent on the molecular weight of the used MAPP. For the untreated cellulose fibres a value of about 42.2 mJ/m^2 was characteristic.

The use of silanes (A-1100, A-1120 from OSi-Specialties) as coupling agents for flax and ramie fibres showed no effects on the contact angle of water by using the capillary rise method. Typical water contact angles for the untreated flax and ramie fibres were 87° and 77°, respectively [32]. Similar to these results, Westerlind et al. [33] showed that there are no differences in the polar as well as in the dispersive part of the free surface energy of untreated or silane treated (A-174 from OSi-Specialties) cotton fibres by using the Wilhelmy technique.

3. Methods for surface modification of natural fibres

The quality of the fibre–matrix interface is significant for the application of natural fibres as reinforcement fibres for plastics. Physical and chemical methods can be used to optimize this interface. These modification methods are of different efficiency for the adhesion between matrix and fibre [34].

3.1. Physical methods

Reinforcing fibres can be modified by physical and chemical methods. Physical methods, such as stretching [35], calandering [36,37], thermotreatment [38], and the production of hybrid yarns [39,40] do not change the chemical composition of the fibres. Physical treatments change structural and surface properties of the fibre and thereby influence the mechanical bondings to polymers.

Electric discharge (corona, cold plasma) is another way of physical treatment. Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibres [41] and in case of wood surface activation increases the amount of aldehyde groups [42].

The same effects are reached by cold plasma treatment. Depending on type and nature of the used gases, a variety of surface modification could be achieved. Surface crosslinkings could be introduced, surface energy could be increased or decreased, reactive free radicals [41] and groups [43] could be produced.

Electric discharge methods are known [44] to be very effective for ‘‘non-active’’ polymer substrates as polystyrene, polyethylene, polypropylene, etc. They are successfully used for cellulose-fibre modification, to decrease the melt viscosity of cellulose–polyethylene composites [45] and improve mechanical properties of cellulose–polypropylene composites [41].

An old method of cellulose fibre modification is mercerization [17,35,46–48], it has been widely used on cotton textiles. Mercerization is an alkali treatment of cellulose-fibres, it depends on the type and concentration of the alkaline solution, its temperature, time of treatment, tension of the material as well as on the additives [17,48]. At present there is a tendency to use mercerization on natural fibres as well. Optimal conditions of mercerization ensures the improvement of the tensile properties [17,46–47] and absorption characteristics [17,46,47], which are important in the composing process (details about this method and their effects on physical properties are discussed in Section 3.5).

3.2. Chemical methods

Strongly polarized cellulose fibres [33] are inherently incompatible with hydrophobic polymers [41,50–52]. When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material, that has properties intermediate between those of the other two. There are several mechanisms [53] of coupling in materials:

- Weak boundary layers – coupling agents eliminate weak boundary layers,
- Deformable layers – coupling agents produce a tough, flexible layer,
- Restrained layers – coupling agents develop a highly crosslinked interphase region, with a modulus intermediate between that of substrate and of the polymer,
- Wettability – coupling agents improve the wetting between polymer and substrate (critical surface tension factor),
- Chemical bonding – coupling agents form covalent bonds with both materials, and
- Acid–base effect – coupling agents alter acidity of substrate surface.

The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. The main chemical bonding theory alone is not sufficient. So the consideration of other concepts appears to be necessary, which include the morphology of the interphase, the acid–base reactions at the interface, surface energy and the wetting phenomena.

3.2.1. Change of surface tension

The surface energy of fibres is closely related to the hydrophility of the fibre [33]. Some investigations are concerned with methods to decrease hydrophility. The modification of wood-cellulose fibres with stearic acid [54] hydrophobizes those fibres and improves their dispersion in polypropylene. As can be observed in jute reinforced unsaturated polyester resin composites, treatment with polyvinylacetate increases the mechanical properties [37] and moisture repellence (Section 3.3).

Silane coupling agents may contribute hydrophilic properties to the interface. Especially when amino-functional silanes, such as epoxies and urethanes silanes, are used as primers for reactive polymers. The primer may supply much more amine functionality than can possibly react with the resin at the interphase. Those amines which could not react, are hydrophilic and therefore responsible for the poor water resistance of bonds. An effective way to use hydrophilic silanes is to blend them with hydrophobic silanes such as peniltrimethoxysilane. Mixed siloxane primers also have an improved thermal stability, which is typical for aromatic silicones [53].

3.2.2. Impregnation of fibres

A better combination of fibre and polymer is achieved by impregnation [55] of the reinforcing fabrics with polymer matrixes compatible to the polymer. For this purpose polymer solutions [51,56] or dispersions [57] of low viscosity are used. For a number of interesting polymers, the lack of solvents limits the use of the method of impregnation [55]. When cellulose fibres are impregnated with a butyl benzyl phthalate plastified polyvinilchloride (PVC) dispersion, excellent partitions can be achieved in polystyrene (PS). This significantly lowers the viscosity of the compound and of the plasticator and results in co-solvent action for both PS and PVC [57].

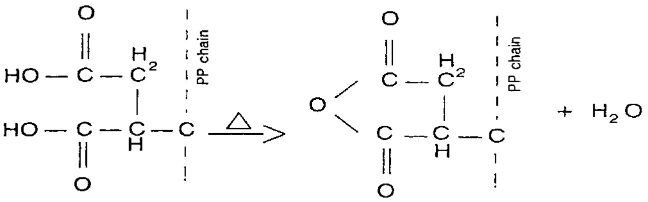
3.2.3. Chemical coupling

An important chemical modification method is the chemical coupling method, which improves the interfacial adhesion. The fibre surface is treated with a compound, that forms a bridge of chemical bonds between fibre and matrix.

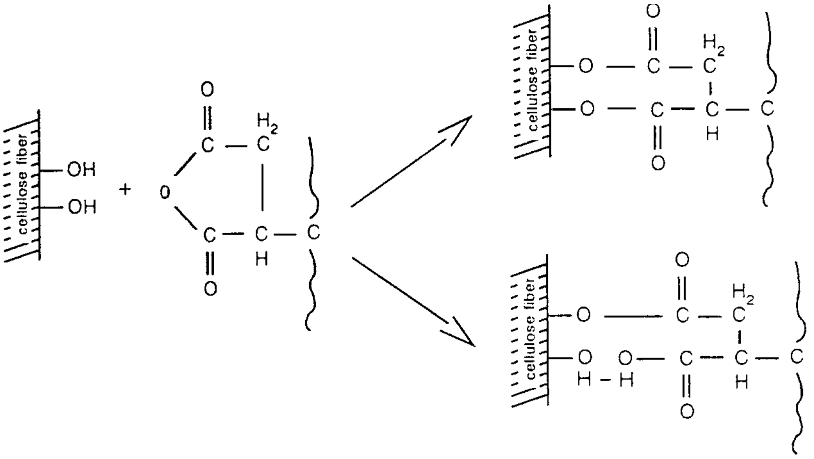
3.2.3.1. Graft copolymerization An effective method of chemical modification of natural fibres is graft copolymerization [46,47,153]. This reaction is initiated by free radicals of the cellulose molecule. The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the cellulose molecule cracks and radicals are formed. Afterwards the radical sites of the cellulose are treated with a suitable solution (compatible with the polymer matrix), for example vinyl monomer [47], acrylonitrile [46], methyl methacrylate [58], polystyrene [52]. The resulting co-polymer possesses properties characteristic of both, fibrous cellulose and grafted polymer.

For example, the treatment of cellulose fibres with hot polypropylene–maleic anhydride (MAH–PP) copolymers, provides covalent bonds across the interface [51]. The mechanism of reaction can be divided into two steps:

- activation of the copolymer by heating ($t = 170°C$) (before fibre treatment) and



- esterification of cellulose.

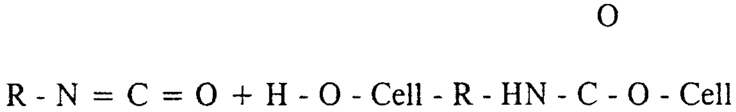


After this treatment the surface energy of the fibres is increased to a level much closer to the surface energy of the matrix. Thus, a better wettability and a higher interfacial adhesion is obtained. The polypropylene (PP) chain permits segmental crystallization and cohesive coupling between the modified fibre and the PP matrix [51]. The graft copolymerization method is effective, but complex.

3.2.3.2. Treatment with compounds which contain methanol groups Chemical compounds which contain methanol groups ($-CH_2OH$) form stable, covalent bonds with cellulose fibres. Those compounds are well known and widely used in textile chemistry. Hydrogen bonds with cellulose, can be formed in this reaction as well.

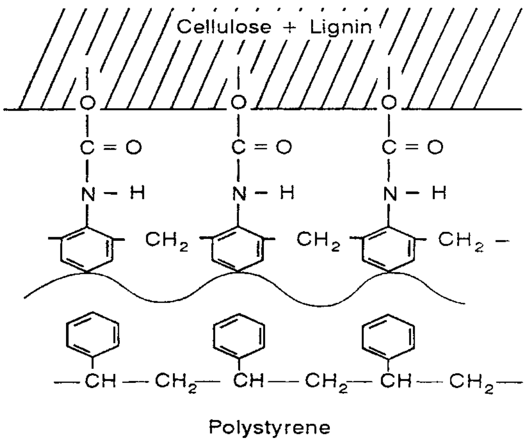
The treatment of cellulose with methanolmelamine compounds before forming cellulose unsaturated polyesters (UP) composites, decreases the moisture pick up, and increases the wet strength of reinforced plastic [59–60].

3.2.3.3. Treatment with isocyanates The mechanical properties of composites reinforced with wood-fibres and PVC or PS as resin can be improved by an isocyanate treatment of those cellulose fibres [52,61] or the polymer matrix [61]. Polymethylene–polyphenyl–isocyanate (PMPPIC) in pure state or solution in plasticizer can be used. PMPPIC is chemically linked to the cellulose matrix through strong covalent bonds:



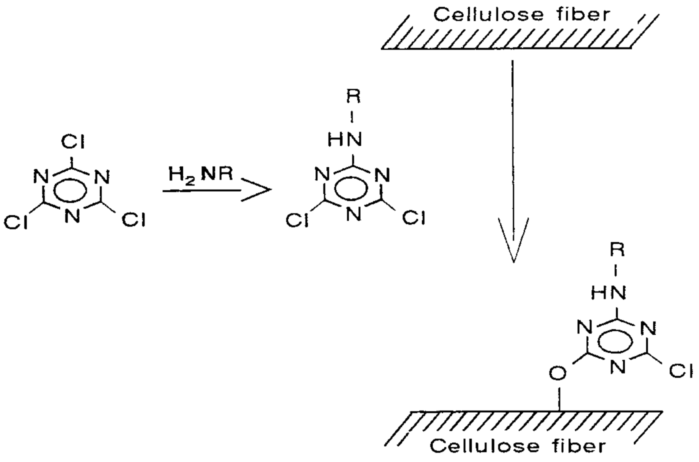
$$R - N = C = O + H - O - Cell - R - HN - \overset{O}{C} - O - Cell$$

Both PMPPIC and PS contain benzene rings, and their delocalized π electrons provide strong interactions, so that there is an adhesion between PMPPIC and PS [52]:



Comparing both methods, treatment with silanes or treatment with isocyanates, it is obvious, that the isocyanatic treatment is more effective than the treatment with silane. Equal results are obtained, when PMPPIC is used for the modification of the fibres or polymer matrix [52].

3.2.3.4. Triazine coupling agents Triazine derivatives form covalent bonds with cellulose fibres schematically:



The reduction of the moisture absorption of cellulose-fibres and their composites, treated with triazine derivatives is explained by [62,63]:

- reducing the number of cellulose hydroxyl groups, which are available for moisture pick-up,
- reducing the hydrophility of the fibre's surface, and
- restraint of the swelling of the fibre, by creating a crosslinked network due to covalent bonding, between matrix and fibre.

3.2.3.5. Organosilanes as coupling agents Organosilanes are the main group of coupling agents for glass-fibre reinforced polymers. They have been developed to couple virtually any polymer to the minerals, which are used in reinforced composites [53,140].

Table 10
Influence of coupling agents on the mechanical properties of natural fibre reinforced plastics [10]

Fibre/matrix	Coupling agent	Increase in properties (%)			
		Tensile strength	Young's modulus	Compression strength	Impact energy
Thermosets					
Jute/EP	Acrylic acid	Constant	—	—	100
Jute/UP and EP	Polyesteramid Polyol	10	10	—	—
Sisal/EP	Silane	25	—	30	—
Cellulose/UP	Dimethanolmelamine	Constant	—	—	100
Thermoplastics					
Cellulose/PS	Isocyanate	30	Constant	—	50
Cellulose/PP	Stearinic acid	30	15	—	50
	Maleinanhydride–PP-copolymer	100	Constant	—	—
Flax/PP	Silane	Constant	50	—	—
	Maleinanhydrid	50	100	—	—

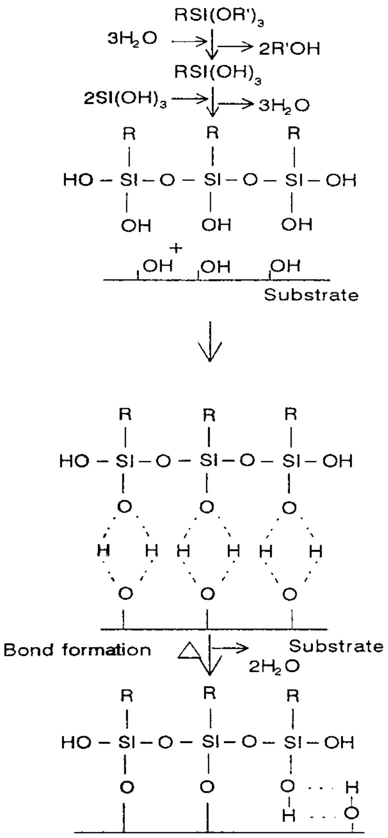
Most of the silane coupling agents can be represented by the following formula:

$R - (CH_2)_n - Si(OR')_3$

where $n = 0$–3, OR' is the hydrolyzable alkoxy group, and R the functional organic group.

The organo functional group (R) in the coupling agent causes the reaction with the polymer. This could be a co-polymerization, and/or the formation of an interpenetrating network. The curing reaction of a silane treated substrate enhances the wetting by the resin.

The general mechanism of how alkoxysilanes form bonds with the fibre surface which contains hydroxyl groups is as follows:



Alkoxysilanes undergo hydrolysis, condensation (catalysts for alkoxysilane hydrolysis are usually catalysts for condensation) and the bond formation stage, under base as well as under acid catalyzed mechanisms. In addition to this reactions of silanols with hydroxyls of the fibre surface, the formation of polysiloxane structures can take place.

Analogous to glass-fibres, silanes are used as coupling agents for natural-fibre–polymer composites. For example, the treatment of wood-fibres with methacrylate improves the dimensional stability of wood [64]. In contrast, a decrease of mechanical properties was observed for coir–unsaturated-polyester composites after a fibre modification with dichloromethylvinyl silane [65]. The treatment of mercerized

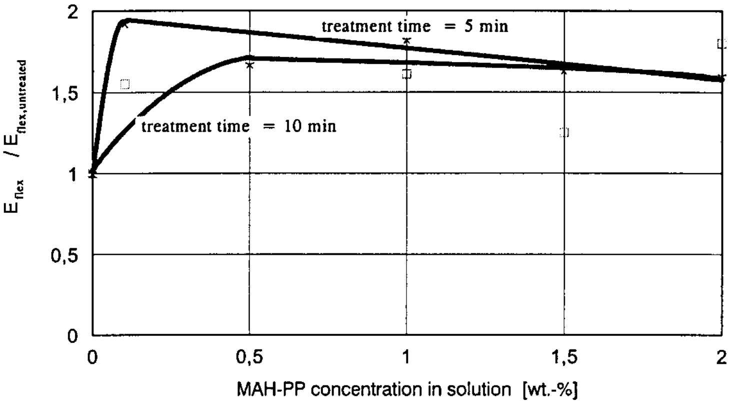


Fig. 7. Influence of MAH–PP treatment conditions on the modulus of jute-fibre reinforced polypropylene (fibre content = 30 vol.%) [67].

sisal-fibre with aminosilanes [66] before forming sisal–epoxy composites, markedly improves moisture repellence of the composite. These examples show, that theories used for the silane treatment of natural fibres are contradictory, therefore further studies are necessary.

3.3. Influence of coupling agents on the mechanical properties of composites

As shown in Table 10, the surface modifications due to coupling agents cause noticeable improvements of the characteristic values of composites, depending on the fibre, matrix, and on the type of surface treatment used.

3.3.1. Natural fibre reinforced themoplastics

Sterzynski et al. [67], used dimethylurea (in aqueous and methanol solutions) as a coupling agent for injection moulded flax–polypropylene composites. A dimethylurea concentration of 12 wt.% leads to a 25% increase in tensile strength and a 20% increase in the Young's modulus.

Other important coupling agents for polypropylenes are silanes. According to Mieck et al. [6,13,68,69], the application of alkyl-functional silanes does not lead to chemical bonds between the cellulose fibres and the polypropylene matrix. But, it seems to be realistic to assume that the long hydrocarbon chains, provided by the silane application influence the wettability of the fibres and that the chemical affinity to the polypropylene is improved.

Hydrogen bonds as well as covalent bonding mechanisms can be found in the flax–silane system. Using a methanol solution of vinyltrimethoxysilane (dibutyl dilaurate of tin was added as catalyst) Mieck et al. found a 60% increase in shear strength. The exact value depended on the silane concentration and type of catalyst.

Raj, Kokta and coworkers [52,54,61,70–72] investigated the influence of different silane types (3% by weight of the fibre) and polymethylene polyphenylisocyanate (PMPPIC, 1% by weight of polymer) on the mechanical properties of wood pulp filled polypropylene. The strength of the silane modified composites were not changed appreciably. Treatment with PMPPIC led to increased strength and

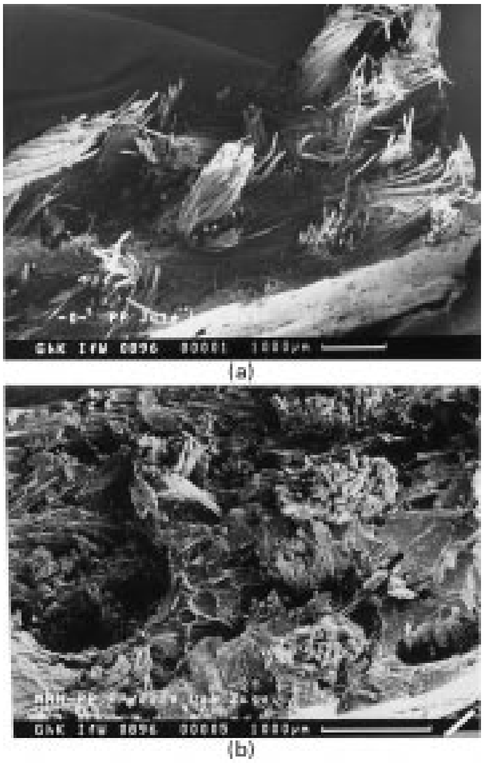


Fig. 8. SEM studies of the influence of the MAH–PP coupling agent on the fracture behaviour of jute–polypropylene composites [67]: (a) without coupling agent; (b) with coupling agent (0.1 wt.% MAH–PP in solution).

stiffness values, caused by chemical bonds between the isocyanate and the hydroxyl groups of the wood fibre surface.

Many studies were concerned with the effectiveness of maleic-anhydride–polypropylene copolymers as a coupling agent. Mieck et al. determined increased shear and tensile strengths of about 100% and 25% respectively for flax–polypropylene composites, when the coupling agent was applied to the flax fibres before the composite was processed. These values depend on the grafting rate and on the average molar mass of the graft copolymer as well as on application parameters (Fig. 7).

Similarly increased values could be obtained with a polypropylene matrix material modified with MAH. The acidic anhydride groups of the MAH coupling agent lead to hydrogen as well as chemical bonds with the hydroxyl groups of the flax fibre, anchored strongly by the coupling agent onto the fibre surface. Further, the long polypropylene chains of the MAH–PP coupling agent lead to an adaptation of the very different surface energies of matrix and reinforcement fibre, which allows a good wetting of the fibre by the viscous polymer. Again an improved wetting can increase adhesion strength by an increased work of adhesion.

Scanning Electron Microscopy (SEM) investigations on MAH–PP modified cellulose fibres (filter paper) and jute-fibres showed (Fig. 8), according to Felix et al. [51] and Gassan et al. [67], that this treatment improves wetting, resulting in better fibre–PP-matrix adhesion compared to that of unmodified

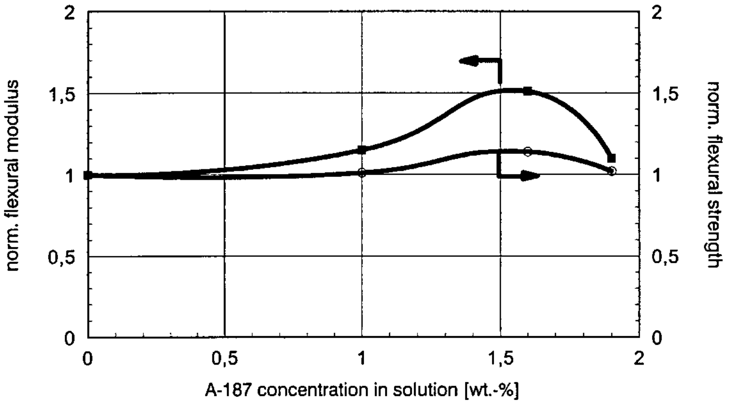


Fig. 9. Influence of silane concentration (A-187) in solution on the flexural modulus and strength of flax non-woven epoxy composites (fibre content = 15 vol.%).

fibre matrix systems. An increase in the composite strength with increasing cellulose content was achieved, similar to the results of Karmaker et al., by the covalent bonds, due to the addition of a coupling agent.

Improved mechanical properties (tensile- and impact) were determined by Avella et al. [73] for MAH-modified polypropylene composites reinforced with wheat straw fibres.

The chemical bonding between the anhydride- and the hydroxyl groups caused a better stress transfer from the matrix into the fibres, leading to a higher tensile strength.

3.3.2. Natural fibre reinforced themosets

In the materials group of natural fibre-reinforced thermosetting plastics, especially in the group of natural fibre-reinforced epoxides, there is only a little knowledge about the influence of suitable coupling agents on the parameters of composites in comparison with natural fibre and reinforced thermoplastics. Some of the most extensive examinations about the influence of silanes (γ-aminopropyltriethoxy-silane) on natural-fibre–epoxy composites were carried out by Bisanda et al. [74] and Gassan et al. [15]. Bisanda et al. used alcoholic solutions of 5% with a catalyst as well as pure silane, whereby the duration of treatment was 24 h. The water absorption of sisal–epoxy composites could be remarkably reduced by a fibre treatment with pure silane. However, the silane treatment (with a solution of 5% and catalyst) did not result in any increase in parameters at flexural strength and flexural stiffness. In contrast, the compression strength of the composites was clearly increased by the coupling agent.

Depending on the concentration of silane in the application solution (Fig. 9) as well as on the duration of treatment there was a noticeable increase in parameters, for example flexural modulus and flexural strength, published by Gassan et al.

Gliesche et al. investigated flax–EP composites and found out that there was a reduction in the flexural strength of composites, if a γ-aminopropyltriethoxy-silane was used, the flexural modulus of the composite could be increased by approximately 20%, however. The γ-aminopropyltriethoxy-silane did not result in any remarkable increase in flexural strength dealing with ramie–epoxy composites, the

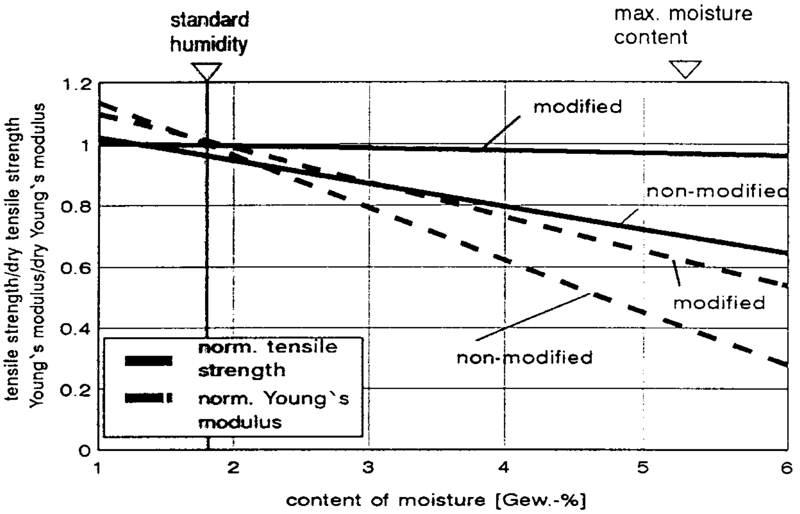


Fig. 10. Influence of silane coupling agents on the strength of jute reinforced epoxy-resin composites at different moisture contents [10].

flexural modulus was also increased by approximately 20%. Also used was a water solution of 3% silane, the fibre treatment was carried out at 80°C.

The fixing of the silanes on the surface of the natural fibres is carried out with the ligno-cellulose by chemical bonds (silanole-bonds) and hydrogen linkages, which result in an improvement of the fibre–matrix adhesion. Although, examinations about surface stresses of natural fibres as well as about the structural composition of natural fibres showed that the surface of natural fibres is essentially built of lignin and therefore the silane fixing has to be carried out with the lignin.

3.3.3. Influence of moisture

In addition to improving the mechanical properties of natural fibre reinforced composites, it is possible to minimize the moisture sensivity, by using, for example, silanes as coupling agents [139].

The investigations on unmodified jute–epoxy composites [75] regarding their moisture absorption (in distilled water at 23°C) showed [75], that the kinetic of absorption and the moisture content at equilibrium distinctly increase with increasing fibre content. This was similarly shown by Rao et al. [75] on jute–epoxy composites and by Semsazadeh [36,37] on jute–polyester resins. Semsarzadeh et al. observed an improved water repellence in jute reinforced unsaturated polyester resin composites, treated with polyvinylacetate. The increasing moisture absorption is caused among others by the higher hydrophilic nature of the jute-fibre compared to the matrix and the higher amount of interfacial area (capillary effect).

Composites with silanized jute-fibres showed about 20% lowered moisture at equilibrium [75]. After the fibre modification, the applied silane reduces the amount of hydroxyl groups which were free to bind moisture.

Due to the surface treatment with silanes, these composites showed increased (approximately 30%)

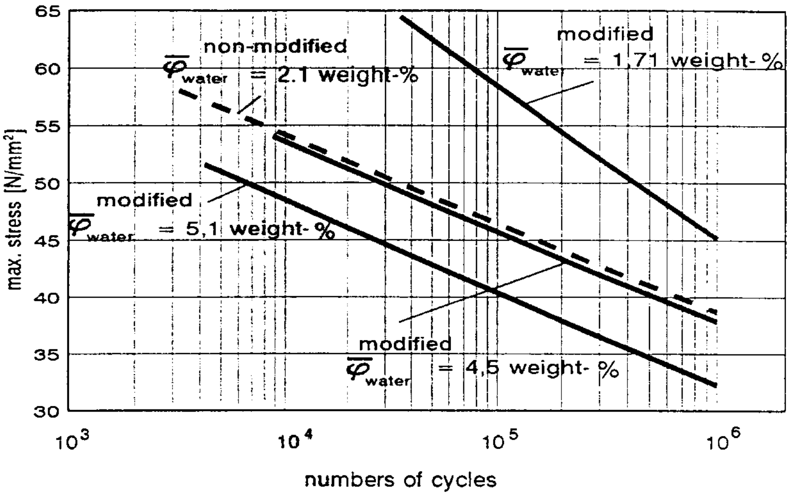


Fig. 11. Wöhler chart of silanized and unsilanized jute-reinforced-epoxy–resin at different moisture contents (stress ratio = 0.1, frequency = 10 Hz, fibre content = 40 vol.%) [10].

static characteristic values compared to unmodified composites at standard humidity (Fig. 10). Tensile strength of the silanized fibre composites is nearly independent of the moisture content of the composites. The same is known from glass-fibre reinforced plastics, where the usage of silane coupling agents reduces the dependence of the mechanical properties on moisture content. Unmodified jute–epoxy composites reach only 65% of the values of the dry-strength at the maximum moisture content of 5.2 wt.%. Shan et al. [76] already provided similar results on composites without coupling agents. He used UD–jute–epoxy (fibre content = 33 vol.%) and jute–polyester (fibre content = 22 vol.%) composites, which were stored for 2 h in boiling water. Tensile strength of these composites decreased from 10% to 16%. The decrease of Young's modulus (13–25%) is even more remarkable in Shan's investigation than for the jute–epoxy composites.

The improved moisture resistance caused by the application of the coupling agent can be explained by an improved fibre–matrix adhesion. The coupling agent build chemical bonds (silanol bonds) and hydrogen bonds, which reduces the moisture caused by fibre–matrix debonding. The Young's modulus of unmodified jute–epoxy composites follows the same trend as that for modified composites (Fig. 10), but moisture influence is distinctly lower, when the coupling agent was used. This might be explained by the decreasing Young's modulus of the jute-fibres with increasing moisture content, whereas tensile strength of the fibres does not change with changing moisture contents.

Kokta, Maldas and coworkers [52,54,61,70–72] investigated CTMP–aspen–HDPE filled materials modified with PMPPIC–isocyanate as coupling agent. These materials were stored for 4 h in boiling distilled water. Similar to the results for the jute–epoxy composites in Fig. 10, a change of tensile strength and Young's modulus were not observed. For a full comparison, results of unmodified composites are missing.

In contrast to the results of tensile test in Fig. 10, a reduced influence of humidity on flexural strength and modulus was not attained by the silane application [75]. Whereas, the decline of flexural strength of the silanized jute–epoxy composites started at a 20% higher level. This tendency, that interfacial and matrix-dominated properties are distinctly more influenced by moisture was already shown by investigations at glass-fibre reinforced epoxy resins. Add to this that the entire cross-sectional area of a material submitted to tensile stress is loaded homogeneously, while flexural loadings only afflict the marginal zone. Likewise it should be considered that natural fibres caused by their fibrillar structure, should looked at as composites (Section 2.4.1). For jute-fibres, submitted to flexural stresses, the fibrillar orientation of 8° causes a nearly transversal loading to the fibrils. So that, the hydrophilic properties of hemicellulose and lignin much more influence the properties of the composites, as they do under tensile stress.

No decrease of flexural strength was found by Bisana et al. [66] in investigations on sisal–epoxy composites (fibre content = 40 vol.%) modified with γ-aminopropyltriethoxy-silane, and stored for 72 h in water. While, strength of these unmodified composites was reduced from 15% to 20% after the same water storage. In this investigation the silane application reduced the moisture influence on the flexural modulus in the same range. Bisanda explained these effects by an improved interfacial bonding.

The fatigue tests yielded similar improvements as they were recorded at the tensile tests (Fig. 11). The surface modified composites at a moisture content of 4.5 wt.% show nearly the same curve as the unmodified composites at standard humidity (i.e. 2.1 wt.% moisture). The quality of the fibre matrix adhesion can be rated also, as published by Gassan et al. [10,75] for jute–epoxy composites, by regarding the dynamic modulus and the damping of such composites. Good adhesion between fibre and matrix led to low damping values and high values of the dynamic modulus. The damping of the modified composites was approximately two times lower than the damping of the unmodified composites, and it was nearly independent on the number of cycles. The damping of the silanized jute–epoxy composites was constant until damage initiation. The higher damping of the unmodified jute–epoxy composites was explained by the friction in the fibre–matrix interface. The increasing damping with increasing numbers of cycles was caused by this effect and by irreversible damages such as macro cracks in the matrix, delaminations, and fibre–matrix debonding. The damping of the silanized jute–epoxy composites was nearly independent on the number of cycles. But, since both types of composites were identical, the fibre modification excepted, the increased damping at the unmodified composites is caused by interfacial effects.

3.4. Acetylation of natural fibres

The unfavourable absorption of moisture by natural fibres, is, more than anything else, due to the cohesion of hydrogen by hydrogen molecules to groups of hydroxyl in cellulose in cell-wall polymers (elementary fibres, see Section 2.4.1). As already shown, reactive organic chemicals are being tied to the cell-wall hydroxyl groups of cellulose, hemicellulose and lignin.

An essential procedure thereby, is acetylation. It means that the introduction of the acetyl group into organic combinations, which contain OH–, SN–, or NH/2 groups. Normally the combinations for acetylation with acetic acid or acetylchloride are heated in the presence of a solvent, for example benzol or acetic acid. In some cases, acetylation is speeded up by using catalysts. The hydroxyl groups of the cell walls, which are to be acetylated are accessible in different ways. Without a good catalyst or co-solvent, one normally reaches only the easily accessible hydroxyl groups.

Acetylization, with acetic acid only, reaches probably no other than the easily accessible hydroxyl groups. Using this procedure, fibres of southern pine, aspin, bamboo, bagasse, jute, and water-hyacinth, were treated.

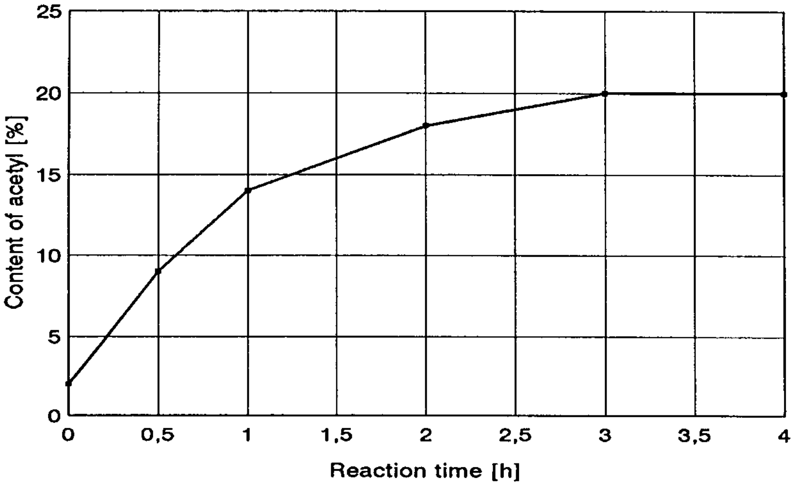


Fig. 12. Content at acetyl after acetylation, as depending on the reaction time of acetylation: (a) reaction time (h): (b) content of acetyl in % [77].

Fig. 12 shows which acetyl content the fibres attain in which time after acetylation. As of a reaction time of 2 h, the curve flattens out strongly and reaches a weight increase of 20% in 4 h. As already pointed out, the absorption of dampness is essentially due to the adhesion of hydrogen by hydrogen molecules to the hydroxyl groups in the polymers of cell walls. Hydroscopity of the cell walls will be lessened, if some hydroxyl groups are replaced at the cell wall polymers by acetyl groups.

Table 11 shows absorbed equilibrium moisture at 65% relative moisture at 27°C of different acetylated natural fibres. One recognizes that, in all fibres, the equilibrium moisture decreases with increasing acetyl content—which proves the effectiveness of the process.

Table 11
Equilibrium moisture at 65% relative moisture and 27°C in dependence of the acetyl content after acetylation, EMC = equlibrium moisture content [77]

Material	Additional weight through reaction (wt.%)	Content of acetyl (wt.%)	EMC (wt.%)
Pine	0.0	1.4	12.0
	6.0	7.0	9.2
	14.8	15.1	6.0
	21.1	20.1	4.3
Aaspen	0.0	3.9	11.1
	7.3	10.1	7.8
	14.2	16.9	5.9
	17.9	19.1	4.8
Bambus	0.0	3.2	8.9
	10.8	13.1	5.3
	14.1	16.6	4.4
	17.0	10.2	3.7
Jute	0.0	3.0	9.9
	15.6	16.5	4.8

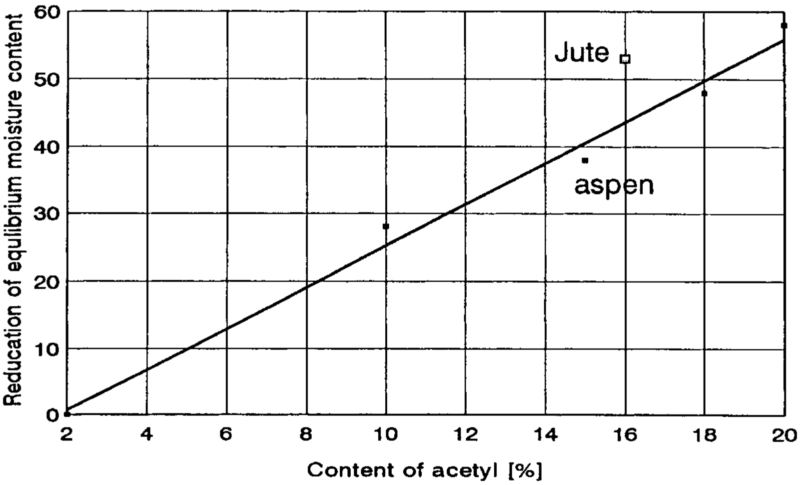


Fig. 13. Reduction of equilibrium moisture at 65% relative moisture and 27°C in dependence of the bonded acetyl content (wt.%) after acetylation [77].

If one finds the reduction of the equilibrium moisture due to acetylization and plots it above the acetyl content after acetylization, as seen in Fig. 13, the plotted values end up in a straight line, although the proportions of cellulose, hemicellulose and lignin, etc. in the fibre differs widely. The fact, that reduction of equilibrium moisture in its dependence on the coheherent acetyl content, remains the same after manipulation, indicates that the decrease of moisture absorption is engendered through a common factor [77].

3.5. Alkali treatment of natural fibres

The effects of mercerization on the suitability to mechanical treatment, notable tensile strength, of cotton fibres have been extensively studied. The standard definition of mercerization proposed by ASTM D 1965 is: the process of subjecting a vegetable fibre to an interaction with a fairly concentrated aqueous solution of a strong base, to produce great swelling with resultant changes in the fine structure, dimension, morphology and mechanical properties [78].

As discussed earlier (Section 3) cellulose forms the main structural component of vegetable natural fibres, the non-cellulosic components, e.g. lignin and hemicellulose, also play an important part in the characteristic properties of the fibres. Hemicellulose, which is thought to consist principally of xylan, polyuronide and hexosan, has shown to be very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or α-cellulose. Later studies about the alkali treatment of jute-fibres, for instance, reports about the removal of lignin and hemicellulose which affects the tensile characteristics of the fibres. When the hemicelluloses are removed, the interfibrillar region is likely to be less dense and less rigid and thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation. When natural fibres are stretched, such rearrangements amongst the fibrils would result in better load sharing by them and hence result in higher stress development in the fibre. In contrast, softening of the inter-fibrillar matrix adversely affects the stress transfer between the fibril and, thereby,

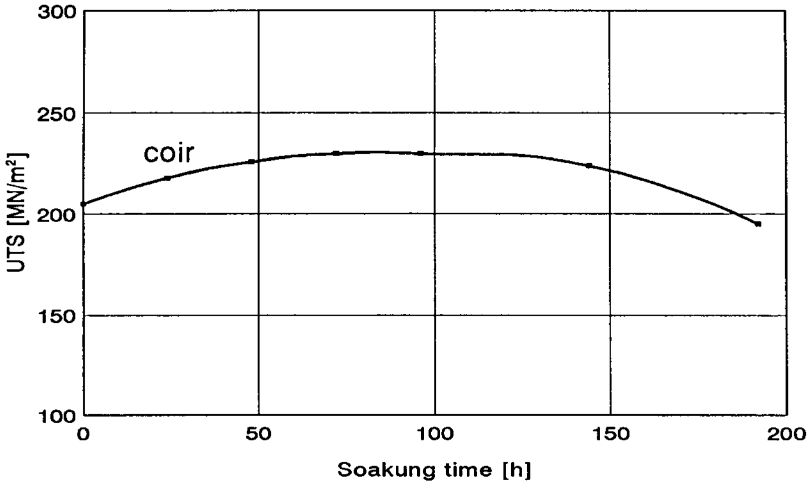


Fig. 14. Effect of soaking time on ultimate tensile strength (UTS) of coir-fibre, fibres were soaked in 5% aqueous solution of NaOH [82].

the overall stress development in the fibre under tensile deformation. As lignin is removed gradually, the middle lamella joining the ultimate cells is expected to be more plastic as well as homogeneous due to the gradual elimination of microvoids, while the ultimate cells themselves are effected only slightly.

Further, some authors reported about changes in the crystallinity through alkaline treatment on coir [79,80] and flax [81] fibres. The increase in the percentage crystallinity index of alkali treated fibres occurs because of the removal on the cementing materials, which leads to a better packing of cellulose chains [79]. Additionally, treatment with NaOH leads to a decrease in the spiral angle, i.e. closer to fibre

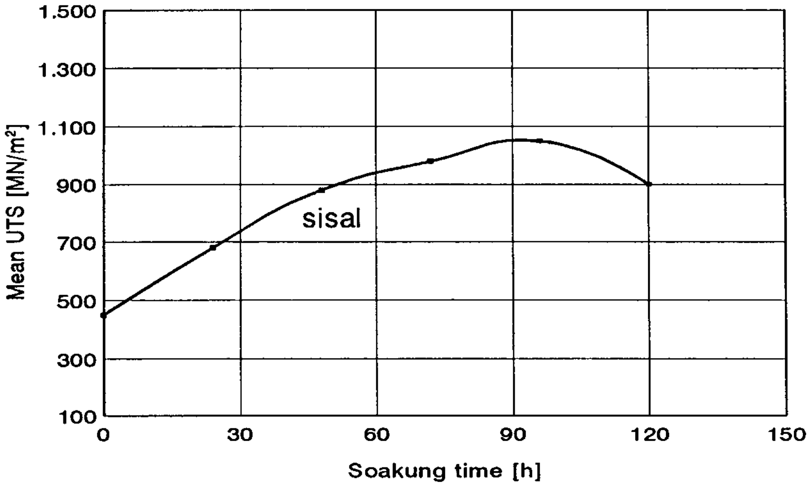


Fig. 15. Effect of soaking time on ultimate tensile strength (UTS) of sisal-fibre, fibres were soaked in 5% aqueous solution of NaOH (speed 0.02 m/min) [82].

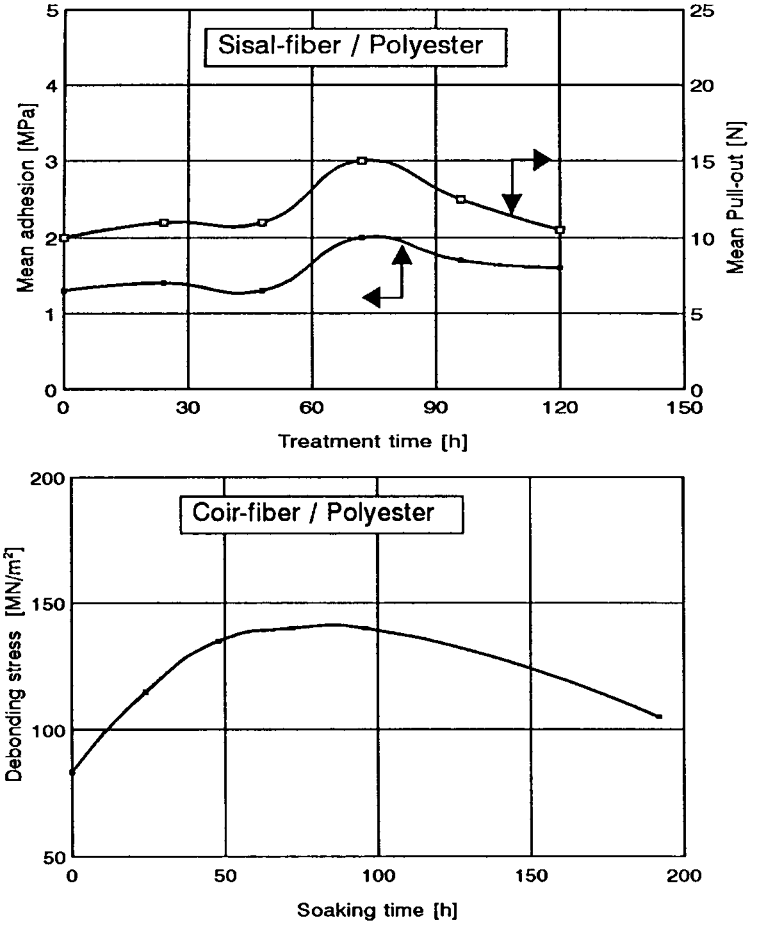


Fig. 16. Plot of adhesion and pull-out load of sisal vs. soaking time [83] and effect of soaking time on the debonding stress [82].

axis, and increase in molecular orientation. A fair amount of randomness is introduced in the orientation of the crystallites due to the removal of non-cellulosic matter [80]. The elastic moduli of fibres, for instance, are expected to increase with increasing degree of molecular orientation. Well oriented cellulosic fibres such as flax have much higher Young's modulus than fibres with medium orientation, such as cotton. In addition to the modification of orientation and the consolidation of weak points, other important factors with regard to the mechanical properties could be the crystallite length and degree of crystallinity as well as the removal of fractions of cellulose at a very low degree of polymerization.

Tests made by Prasad et al. [82] on leather fibres, and by Chaud et al. [83] on sisal fibres showed distinct index changes achieved by an alkalization process in an 8% NaOH solution. An increase of 25% in tensile strength was reached in leather fibres and of 100% in sisal fibres—also depending on the respective soaking time (Figs. 14 and 15).

Additional to the increase of the mechanical properties through alkalization [82–84], an increase of composite quality are to be expected of laminates due to the improved fibre–matrix adheshion. In the

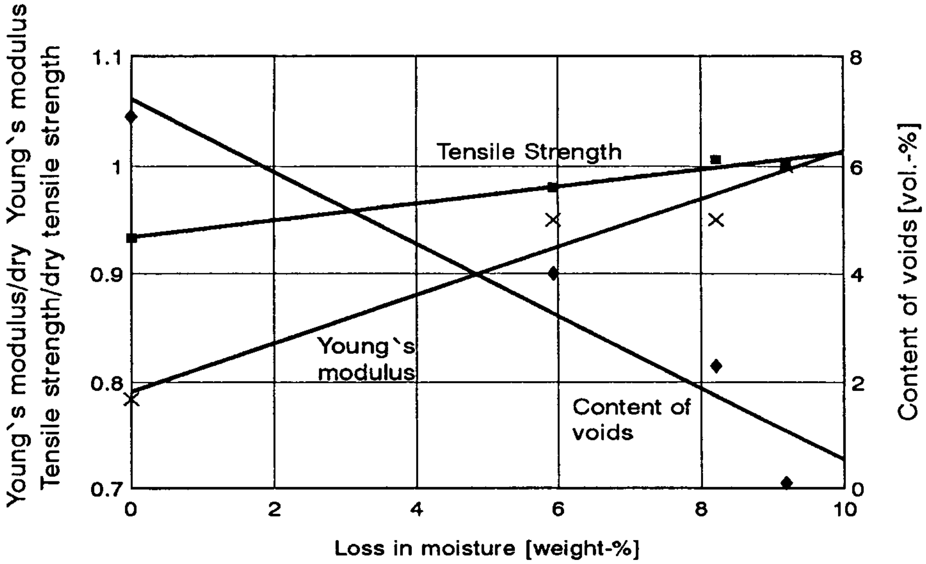


Fig. 17. Influence of fibre drying on the characteristic values of jute-reinforced-epoxy–resin composites [10].

fibre extraction (pull-out test), the cohesion of polyester resin alkalized coconut- and sisal fibres were characterized by Prasad et al. [82] and by Chaud et al. [83].

The pull-out load of alkalized sisal fibres went from 10 to 15.5 N, and the adhesion increased correspondingly (Fig. 16) up to an alkalizing time of 90 h. After that, the pull out load as well as the adhesion decreased distinctly.

A principally similar debonding stress was registered with coconut-fibre–polyester composites [82].

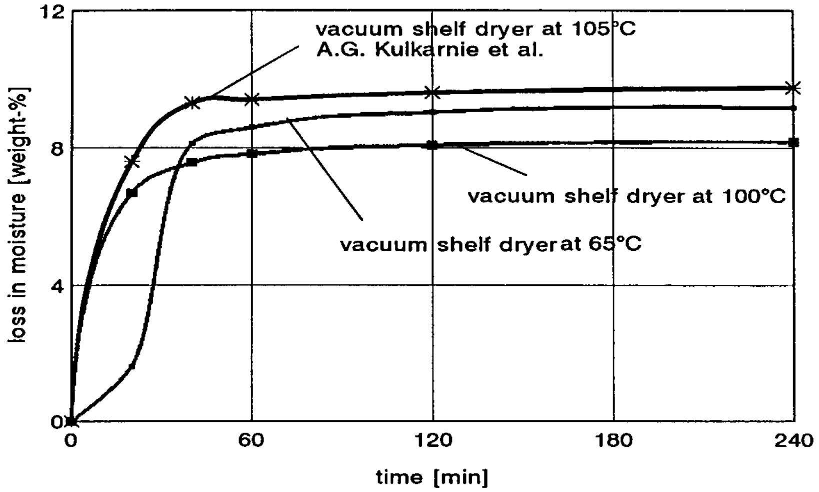


Fig. 18. Loss of humidity during drying of jute-fibres as dependent on the temperature in vacuum oven [10].

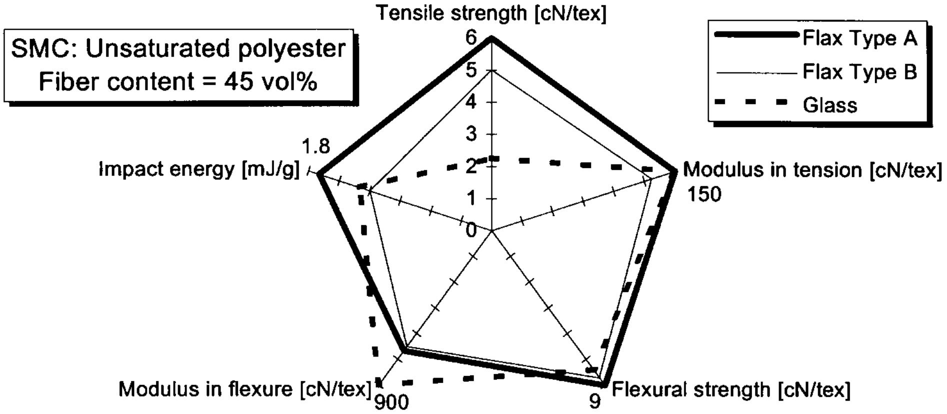


Fig. 19. Characteristic values of glass-fibre and flax-fibre SMC moulded plastics (absolute values and in reference to density) [85].

4. Processing of natural fibre reinforced plastics

4.1. Influence of humidity on the processing of natural fibre reinforced composites

Drying of fibres before processing is an important factor, because water on the fibre surface acts like a separating agent in the fibre–matrix interface. Additionally, because of the evaporation of water during the reaction process, voids appear in the matrix (most of the thermosets have a reaction temperature over 100°C, processing temperature of thermoplastics lies distinctly over the evaporation temperature of water). Both phenomena lead to a decrease of mechanical properties of natural fibre reinforced composites. For jute–epoxy composites, tensile strength of maximally pre-dried fibres (moisture content: approximately 1 wt.%) rises for about 10% compared to minimally dried fibres (moisture content: approximately 10 wt.%), the increase of stiffness with 20% is remarkably higher (Fig. 17).

Fibre drying can be done in a vacuum stove at different temperatures. This results in different degrees of loss of humidity, as shown in Fig. 18.

4.2. Natural fibre reinforced thermosets

The economically most attractive glass-fibre reinforced plastics for special technical uses, are, next to RTM (resin transfer moulding) and winding technology, etc. semiproducts made of SMC (sheet moulding compounds) and BMC (bulk moulding compounds) systems.

4.2.1. SMC

In the automobile and electronic industries, big amounts of pressed parts from SMC or BMC are used for bumpers, trunk covers and spoilers.

In Fig. 19 pressed SMC materials based on flax-fibres are compared with those made of glass-fibres. It shows, that the glass-fibre reinforced material attains higher characteristic values, except for tensile strength. However, if the measured values are regarded in reference to density, the results of the

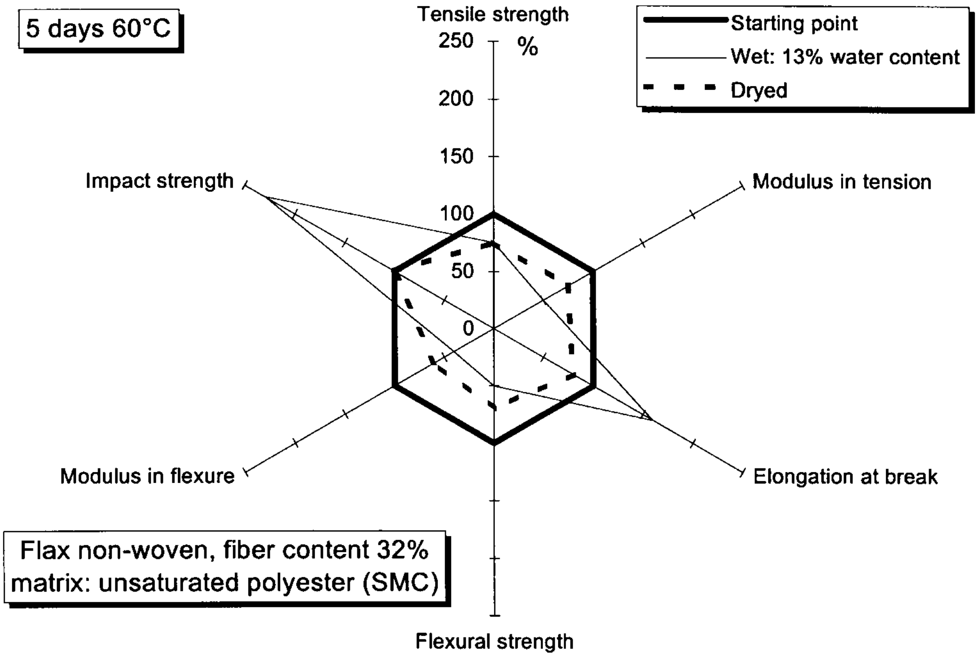


Fig. 20. Influence of humidity on the characteristic values of flax-fibre SMC moulded plastics [85].

flax-fibre based SMC moulded plastics are located in the same range as the glass-fibre SMC moulded types. As already mentioned, the characteristic values of natural fibre materials are clearly dependent on their moisture content (Fig. 20). After the fibres are dried, they reach values similar to the ones before the storage in damp stage [85].

4.2.2. BMC

In addition to SMC moulded plastics, BMC composites with natural fibres, with good mechanical properties can be produced. Owolabi et al. [86] made such composites with coir-fibres, their basic recipe is shown in Table 12.

In this examination, glass-fibres were replaced by coir-fibres. A proper treatment of the fibres improved adhesion and as a result tensile strength was increased (Fig. 21).

4.3. Natural fibre reinforced thermoplastics

In comparison to glass-fibres, the lower thermal stability of natural-fibres with up to 230°C, limits the number of thermoplastics to be considered as matrix material for natural fibre thermoplastic composites. Only those thermoplastics are useable for natural fibre reinforced composites, whose processing temperature does not exceed 230°C. These are, most of all, polyolefines, like polyethylene and polypropylene. Technical thermoplastics, like polyamides, polyesters and polycarbonates require processing temperatures >250°C and are therefore not useable for such composite procession without fibre degradation [87].

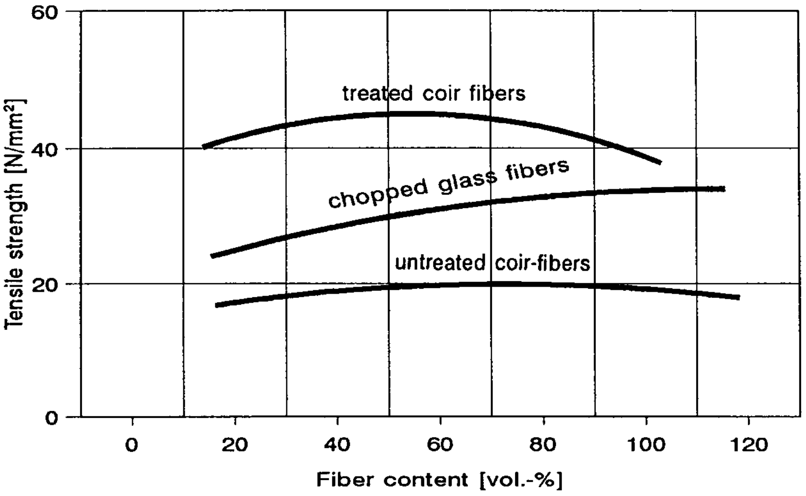


Fig. 21. Tensile strength of BMC moulded plastics as dependent on their fibre content, % fibres = g fibres/100 g UP resin [86].

Other than the processes mentioned here, natural fibres are used as structural units, by applying hybrid non-wovens, i.e. natural fibre staple-fibre-fleece [68].

4.3.1. Natural fibre mat-reinforced thermoplastics (NMT)

With the largest turn-over, glass mat thermoplastic matrix (GMT) is certainly the most important semiproduct in the group of reinforced thermoplastics. A special production process for natural fibre reinforced PP-semiproducts (NMT) has been developed by BASF AG [87]. For this process, natural fibres must be available in form of fibre-mats. Mats are produced, by stitching together layers of fibres which have been crushed before. This semiproduct, is being produced by melt-coating the fibre-mats in a double coil coating press, which is provided with a heat- and cool-press zone. In such a coil coating press, the fibre mats are brought together with the polypropylene melt between circulating steel bands.

Table 12
BMC—recipe on the basis of coir-fibres [86]

Materials	Parts by weight
Unsaturated polyester resin	100
$CaCo_3$ filler	75
MgO	3
Styrene	12
Zinc-stearate	2.5
tert-Butyl perbenzoate	1.25
Chopped fibrous reinforcement	100

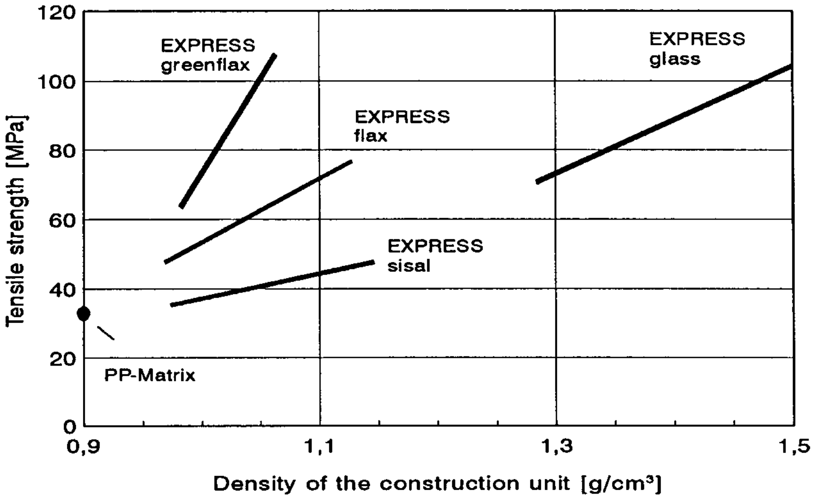


Fig. 22. Tensile strength of different types of fibre reinforced composites, produced by express-processing [88].

Wetting of the mats with the thermoplast melt takes place in the hot-press zone. Then the laminate is being cooled under pressure in the cooling-press zone.

Sisal-, flax- and glass-fibre MT can be classified by their mechanical properties, tensile strength and Young’s modulus (Table 13).

4.3.2. *‘‘Express’’-processing*

The extrusion press processing (express-processing) was developed for the production of flax-fibre reinforced PP at the research center of Daimler Benz, Ulm/Germany [88]. In this process, natural fibre non-wovens and thermoplastic melt-films are alternatively deposited and moulded in a tempered mould. The thermoplastic melt-films are laid on by a mobile extruder. If this process is optimally adapted to the element, a single passage by the extruder suffices. The structural order consists of three layers: two layers of non-wovens on the bottom and one on top, with the melt-film in between. As to density, the values for tensile strength of flax-fibres polypropylene composites exceed the characteristic values of sisal-fibre reinforced polypropylene composites (Fig. 22).

Table 13
Tensile strength and Young’s modulus of sisal, flax, and glass-fibre MTs with a fibre content of 40 wt.% [87]

Materials	Tensile strength (MPa)	Young’s modulus (MPa)
PP–wood flour	19	2500
PP–sisal non-woven	38	3600
PP–sisal non-woven with surface treatment	55	4800
PP–flax non-woven	47	5100
PP–flax non-woven with surface treatment	67	6700
PP–glass non-woven	100	6000

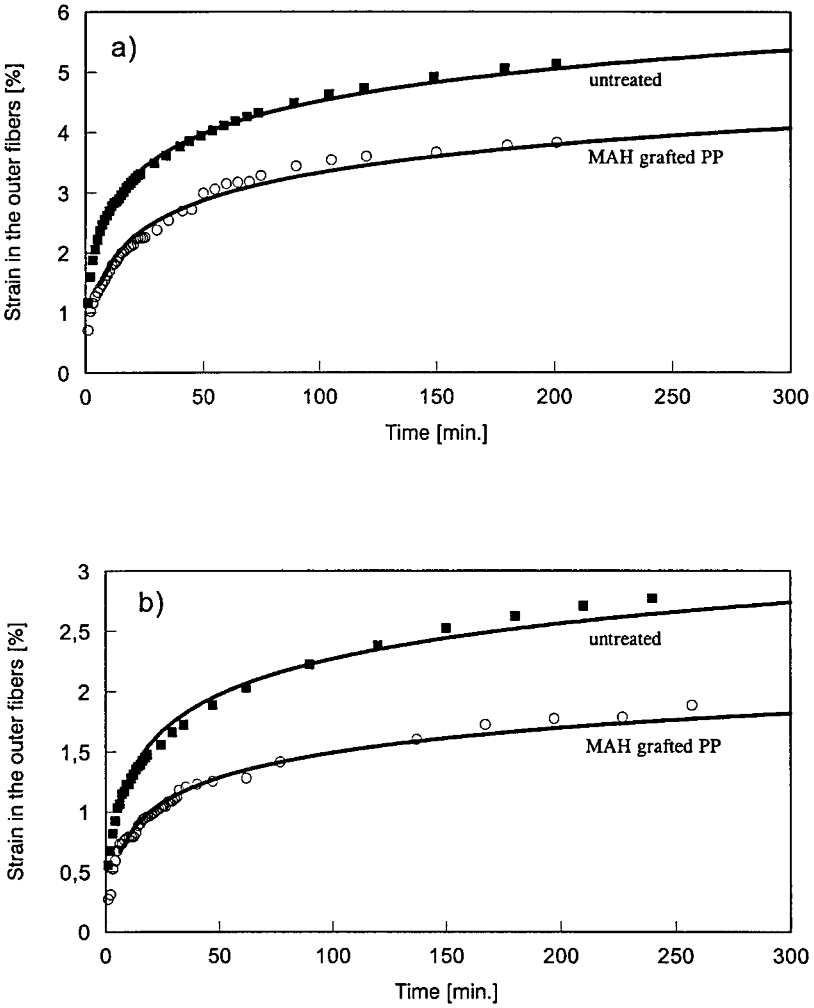


Fig. 23. Influence of the fibre treatment on the creep behaviour of jute–polypropylene composites at different fibre contents (applied flexural load = 5.1 N/mm^2): (a) fibre content = 23 vol.%; (b) fibre content = 36 vol.%.

5. Mechanical behaviour of natural fibre reinforced plastics

5.1. Creep behaviour

The creep behaviour of natural fibre reinforced plastics is still poorly investigated. The effect of coupling agents for these types of composites, perhaps except rubber matrix systems, were never systematically considered. Only Tobias [89] used thermoset composites reinforced with short abaca fibres in volume fractions of 30% and 40% to establish the influence of fibre content on the stress rupture life. His results showed that both composites fail by stress rupture. An increase in sustained constant stress reduces the life of the abaca-fibre-reinforced composite materials. In contrast, the rupture strength

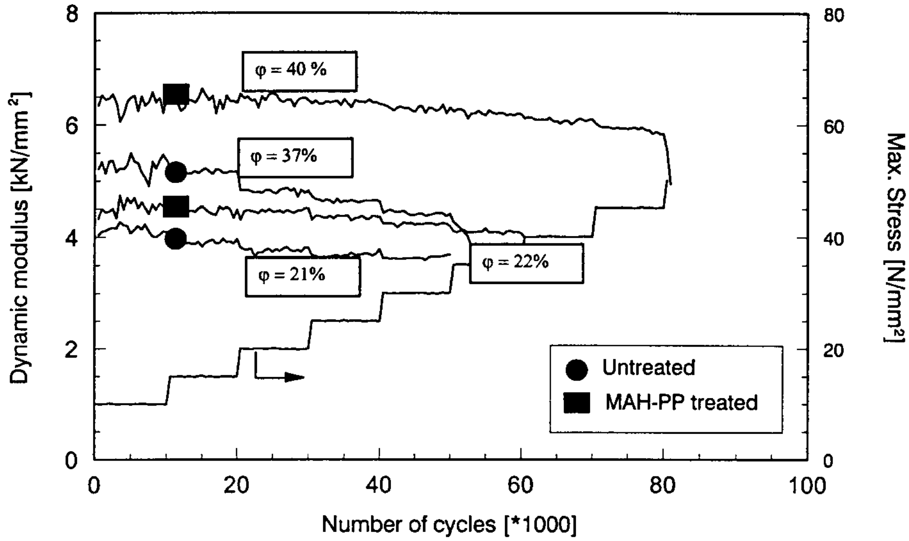


Fig. 24. Influence of the fibre treatment and fibre content on the dynamic modulus measured in load increasing test of jute–polypropylene composites (stress ratio = 0.1, frequency = 10 Hz, [fibre content] = vol.%).

of the material increases significantly as the fibre fraction increases. The rate of degradation under sustained constant stress is higher in materials with less fibre content.

Investigations about the stress relaxation in short sisal-fibre reinforced natural rubber composites demonstrate the influence of the fibre matrix adhesion [90]. For composites without a coupling agent, the rate of relaxation increased with strain level. But in the presence of a coupling agent, the relaxation rate is almost independent of the strain level because of the strong fibre-rubber interface.

Unpublished results of investigation about the influence of coupling agent (MAH grafted PP) as well as about the effect of the fibre content on the creep behaviour of jute–polypropylene composites were carried out up to a maximum time of 300 min. After this time, all samples reached the so-called secondary or steady creep state with a nearly constant creep rate. The results of these investigations for composites without coupling agent (Fig. 23) show a strain of the outer fibre of around 5% after 300 min test period for a fibre content of 23 vol.%. The experimental data were fitted by using the creep law according to Abbott. An increase of fibre content up to 36 vol.% leads to half of the strain at 300 min as well as to lower creep kinetics. As known from the creep behaviour of glass-fibre-reinforced plastics, the improved fibre–matrix adhesion reduces the creep strain distinctly because of the better matrix–fibre load transfer. In comparison to composites with untreated fibres, the strain in the outer fibre was reduced about 20–25% by the use of coupling agent. The coupling agent is necessary to get an effective stress absorption through the fibres, which is the assumption for the observed materials' behaviour.

5.2. Cyclic-dynamic behaviour

Similar to the creep behaviour, the cyclic-dynamic materials behaviour of natural fibre reinforced plastics is still poorly investigated. Investigations about this behaviour as well as the effect of couplings agents are published by Gassan et al. for thermosets [10,15] and thermoplastics [67] as matrix materials.

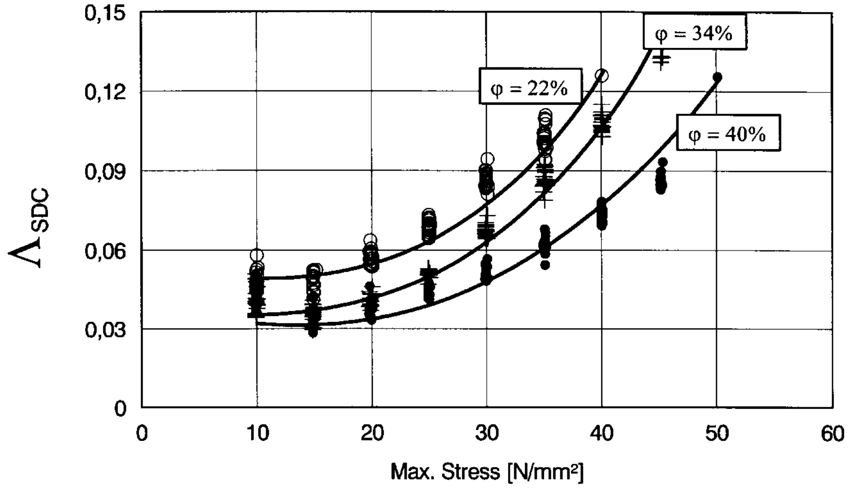


Fig. 25. Influence of the fibre content and applied max. load on the specific damping capacity (Λ_{SDC}) measured in load increasing test of jute polypropylene composites (stress ratio = 0.1, frequency = 10 Hz) [67].

An improved fibre–matrix adhesion due to a coupling agent such as MAH grafted PP leads, for these modified jute–polypropylene composites at a comparable fibre contents, to a distinctly higher dynamic strength, i.e. stress at fracture measured in the load increasing test, as for the composites with untreated jute-fibres (Fig. 24). Progress of damage for unmodified jute–polypropylene composites is nearly independent of the fibre content, which results in independent maximal stresses, due to the improved fibre–matrix adhesion, caused by the MAH grafted PP coupling agent and the thereby improved force transfer. In contrast to untreated jute–polypropylene composites, an 40% increase of dynamic strength, at comparable fibre contents (ca. 40 vol.%), is attained through the usage of the coupling agent. Fig. 25 shows, that the damage of the jute polypropylene composites (modified as well as unmodified) does not occur spontaneously, but occurs continously with the increasing stress. Whereby the limit stress, i.e. the over proportional increase of the damping (Λ_{SDC}), is moved to higher stresses (shown for jute–polypropylene composites modified with MAH grafted PP).

5.3. Impact behaviour

There are only a few studies known about the impact behaviour of natural fibre reinforced plastics compared with glass-fibre reinforced plastics. Pavithran et al. [91] determined the fracture energies for sisal-, pineapple-, banana- and coconut-fibre–polyester composites (fibre content of approximately 50 vol.%) in a Charpy-impact-test. They found out that, except the coconut-fibre–polyester composites, an increase in fracture energy was accompanied by an increasing fibre toughness (determined by the stress–strain diagram of the fibres). Natural fibre reinforced plastics with fibres which show a high spiral angle of the fibrils, indicated a higher composite-fracture-toughness than those with small spiral angles. That is why, according to Pavithran et al., composites with sisal fibres (spiral angle = 25°) show an optimum of impact properties. Pavithran et al. investigated a specific toughness of sisal–UHMPE composites, which is approximately 25% below that one of comparable glass-fibre based composites (same fibre-volume-content). By adding flax fibres Höck [92] stated an obvious increase in damaging

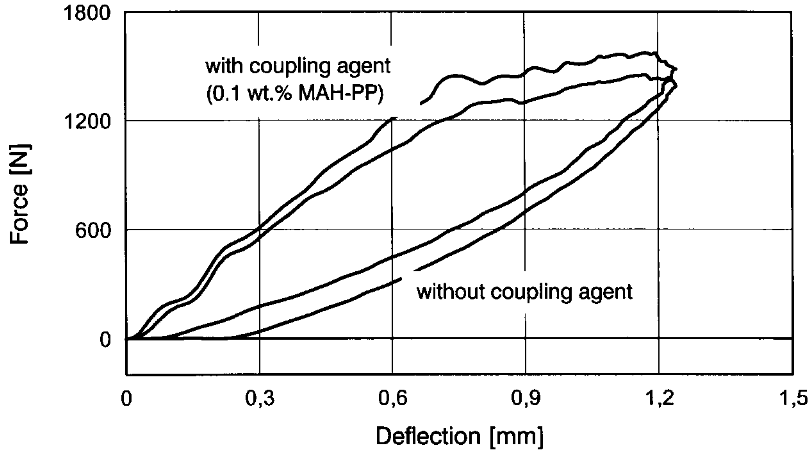


Fig. 26. Influence of fibre treatment on force-deflection behaviour of jute–polypropylene composites with untreated and MAH–PP treated fibres (impact energy = 1.5 J, fibre content = 35 vol.%, thickness of specimens = 4.4 mm).

mechanisms (determined at −40°C) compared with pure PP, a silanization of the fibres led to a reduction of this effect. During examinations about the influence of silanes as coupling agent for jute–epoxy composites, from the impact resistance only small differences could be stated by the silanes, i.e. <10% [15]. Schlößer et al. [88] determined the influence of thermal aging (storage at 100°C and 125°C) on the penetration properties of flax-fibre-reinforced polypropylene. Thereby these storages led to a remarkable decrease in maximum force.

Tobias [93] examined the influence of fibre content and fibre length from banana fibres (Abaca) epoxy composites. In this connection an increase in impact strength was stated with increasing fibre content (fibre length = 20 mm). Smaller fibre lengths led to a higher impact strength at constant fibre content. Usually at glass-fibre-reinforced PP the impact strength increases with increasing fibre length.

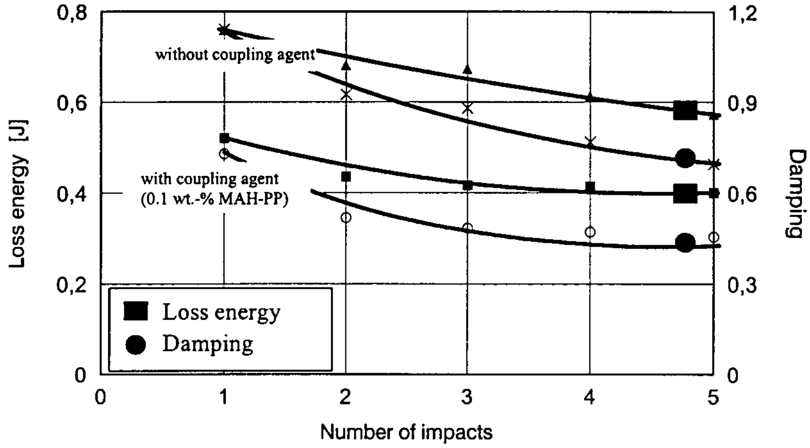


Fig. 27. Influence of multiple impact events and fibre surface treatment on the loss energy and damping of jute polypropylene composites (impact energy = 1.5 J, fibre content = 35 vol.%, thickness of specimens = 4.4 mm).

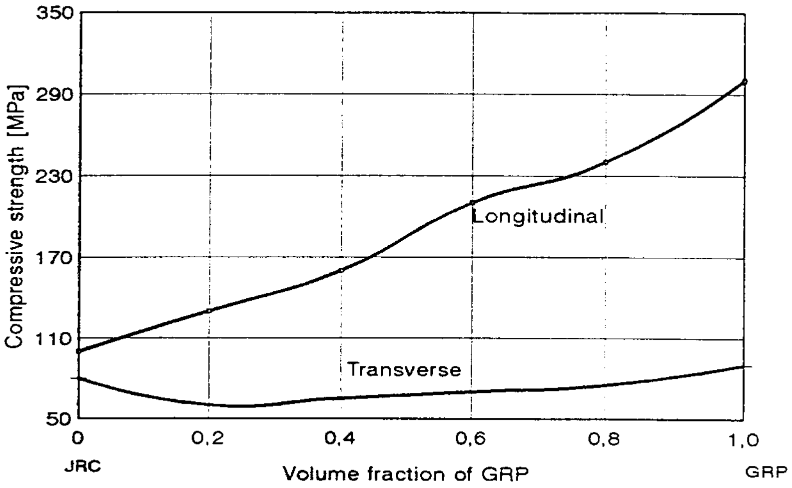


Fig. 28. Compression strength as dependent on the content of GRP in jute-fibre-reinforced–hydride composites [95].

Further, impact investigations at jute–polypropylene composites were carried out with and without coupling agent (MAH grafted PP). In that process (Fig. 26) it turned out that the damaging initiation can be shifted to higher forces with a strong fibre–matrix adhesion, as composites with a weak fibre–matrix adhesion at smaller forces break down at a load perpendicular to the fibre. For these materials it could also be shown that the dissipation factor at the composites with MAH–PP modified jute-fibres with 0.52 J is clearly smaller than those of the composites with unmodified jute-fibres with a loss-energy of 0.76 J (each at an impact energy of 1.5 J). When the composites have no coupling agent a part of the impact energy is degraded in the fibre–matrix interface, for example by debonding and friction effects. At these test conditions a multiple-impact-load, as shown in Fig. 27, leads to a decrease in loss-energy (until the third impact event), whereby, at the composites modified with MAH–PP after the third impact only slightly further damages occur, i.e. no macroscopic determinable damages. Concerning the composites without coupling agent this saturation of damage is not so pronounced.

6. Special types of composites based on natural fibres

6.1. Hybrid composites made of natural fibres and glass- or carbon-fibres

In general, the mechanical and physical properties of natural fibre reinforced plastics, only conditionally reach the characteristic values of glass-fibre reinforced systems. By using hybrid composites made of natural fibres and carbon-fibres or natural fibres and glass-fibres, the properties of natural fibre reinforced composites can be improved further [91,94–97], as shown in Fig. 28 for compression strength. For this, examinations were made by:

- Mohan et al. [95,97], Philip [98] and Clark et al. [96] on jute–glass-hybrid composites,
- Pavithran et al. [91] on coir–glass-hybrid composites, and
- Chand et al. [94,99] on sunhemp–carbon-hybrid composites.

Table 14
Mechanical properties of flax-fibre reinforced biodegradable polymers (BDG) (fibre content = 50 vol.%; linen woven, cable direction = testing direction) [100]

Fibres–BDP	Tensile strength (MPa)	Young's modulus (MPa)
Flax–Bioceta	65.7	1400
Flax–Sconacell A	106.9	8180
Flax–Mater Bi	124.3	10 580

Because of the moisture repellency of glass-fibres, the dependence of the mechanical properties on humidity is limited [97]. The moisture absorption decreases, when natural fibres are replaced by glass-fibres [91].

6.2. Biologically degradable composite materials

For ecological reasons, more activities in the area of biologically degradable composite materials, i.e. natural fibre reinforced biologically degradable polymers, ought to be recognized. For matrixes the readily available polymers as Biopol, PHB–HV copoloymer, Bioceta, Mater Bi, or Sconacell A are usually applied [100]. Tests with different flax-fibre reinforced biologically degradable polymers (Table 14), by Hanselka et al. [100], show, that tensile strength and Young's modulus of these composites, are clearly influenced by the particular matrix and the adhesion between fibre and matrix.

Tests by Gatenholm et al. [8,101,143] on PHB–HV copolymers containing cellulose fibres (for example the trade named Biopol), show, that the mechanical properties of these systems, are determined by the fibre and the fibre–matrix interface on the one hand, and by the composition of the matrix, that is, of HV proportion in the matrix, on the other hand. At an increased proportion of HV, the stiffness of the composite is reduced up to 30%, whereas elongation at break increases for about 60%. But, the processing parameters are being influenced greatly by the proportion of HV. Tests made by Avella et al. [73] on straw-fibre reinforced PHB, generally lead to good mechanical properties of such composites. The mechanical properties of extruded flax-fibre reinforced thermoplastic starch [146] (structured with water or glycerin), show clearly increased values especially for tensile strength and Young's modulus, because of the addition of green-flax-fibre rovings. Experiences mentioned in literature on this subject, suggest that, from the point of view of the mechanical properties, such bio-composites are suitable construction materials. At present, limitations must be seen where excessive environmental conditions exist. Major prospects for these material systems, are therefore, lining elements with support function, in the automobile, rail car, and furniture industries [100].

6.3. Wood filled plastics

Thermoplastics reinforced with special wood fillers are enjoying rapid growth due to a lot of advantages. Light weight, reasonable strength and stiffness are some of these advantages. The processing is flexible, economical and ecological. Since early times, wood is a preferred, aesthetically pleasing building and engineering material. Wood particles, such as chips, flakes, fibres, and wood pulps are used as reinforcement agents. Thus, previously wasted wood materials are converted into useful products, and this trend will probably accelerate in future [148,149].

The main problems of processing wood reinforced compounds are:

- variations in the quality of raw material,
- compatibility limitations because of hydrophilic wood fillers and hydrophobic matrices,
- limited thermal stability during processing, and
- shape deviation of the component caused by the swelling of wood.

Additional problems are experienced if waste wood and waste thermoplastics are used. The characteristic properties of these raw materials depend on the kind and treatment of the waste, on their origin, and on their age. In contrast, the use of waste wood and post-consumer thermoplastics will help to solve the severe environmental and recycling problems.

Despite the quantity and complexity of the influencing parameters, a lot of desired properties can be achieved by different manipulations. In this review, literature of recent years concerning the mechanical, the moisture absorption and the processing properties of thermoplastics reinforced with wood fillers are considered. Issues regarding modification of wood composites to lower the biodegradability and the flammability of wood are not discussed.

6.3.1. Properties of thermoplastics reinforced with untreated wood fillers

In any discussion regarding the properties of composites, the constituents of which the composite is made of, have to be considered first. Wood elements, used in polymer composites have a large variety of shapes and can be used alone or in combinations [102–106]. Morphic structure, mechanical properties, density and aspect ratio (average length over diameter of the fibres) change from species to species. For example, softwood fibres (spruce) are more flexible compared to fibres derived from aspen or birch (hardwoods). The basic wood elements, which are used for the production of wood–polymer composites, examined in this article are wood particles [103,107,108], flour [109–111], several types of pulp [72,112–114], and recycled wood cellulose obtained from newspaper (ONP).

Wood fibres produced from mechanical pulping still retain the most of its lignin and natural waxes—materials which can help in the fibre’s dispersion in non-polar hydrocarbon polymers [110]. The lignin content in mechanical pulps differs from 28% in softwood (spruce) to 18% (aspen) and 19% (birch) in hardwood. The length of coniferous tree fibres usually varies between 2 and 7 mm, their diameter is approximately 0.03 mm. These fibres consist of several layers of cellulosic microfibrils orientated around a lumen. Softwood fibres tend to split into ribbons during processing. Aspect ratios higher than 100 are possible [114].

The mechanical properties of wood fibres depend on the pulping process even within the same species. For fibres an average modulus of 10–80 GPa, a tensile strength of about 0.5–1.5 GPa, and an apparent density 1.5 g/cm^3, can be found [115].

The thermoplastics which are used as matrix for fibre reinforced composites are high density polyethylene (HDPE) [106,114–116,150,152], low density polyethylene (LDPE) [104,116,117,121], chlorinated (CPE) polyethylene, polypropylene (PP) [109,110,112], normal polystyrene (PS) [115,118,151,154], impact-modified PS [103,108,115,118], and polyvinylchloride (PVC) [119].

A large increase of mechanical properties of PS–wood composites can be achieved using high impact modified polystyrene by Maldas et al. New applications for synthetic polyolefines designed to be blended in all proportions with conventional wood pulps are PE and PP pulp fibres. In most cases of non-treated filler composites, tensile strength and elongation are lower compared to unfilled polymers. Both characteristic values decrease with rising filler content (elongation significantly). Nevertheless, some tests [110,114] showed that up to a critical content of filler (20–40% for PP, 30–40% for PE and 30% for PS) the strength of the composites increases in comparison to that of the polymers without fillers. Such discrepancy may be explained by the differences in fibre species, by the pretreatment, or by the processing technique.

Another critical parameter influencing the properties of these composites is the size of the fibres. Short and tiny fibres (average particle size 0.24–0.35 mm) should be preferred. They provide a higher specific surface area [112,120] and the fibres are distributed more homogeneously compared to composites with long fibres and so the compatibility of fibre and matrix is improved. With this, swelling decreases and breaks during processing are reduced. The application of wood fillers is limited mainly because of the changings in geometry due to moisture absorption and swelling. The hydroxyl groups (–OH), in the cellulose, the hemicellulose and the lignin build a large amount of hydrogen bonds between the macromolecules of the wood polymers. Submitting the wood to humidity, causes these bonds to be broken. The hydroxyl groups then form new hydrogen bonds with water molecules which induce the swelling. The swelling of wood exerts very large forces. The theoretical swelling pressure for wood is approximately 1630 atm. Such forces cause severe problems in wood composites, which are the major reason for their restricted use. Moisture absorption is increased with rising filler content in untreated wood–thermoplastic composites [110,120]. Extreme environmental conditions (soaking in boiling water for 20 h) weakens recycled PP–wood composites (50 wt.%) [110]. A 4 h soaking results leads to a significant decrease of tensile strength (35%) and elongation (48%) of wood–LDPE composites [72]. An advantage of the presence of a large amount of -OH groups in wood fibres is the possibility that different chemical groups can be connected to the surface easily.

6.3.2. Properties of thermoplastics reinforced with treated wood fillers

Chemical modification of wood involves various chemical treatments with the aim to reduce the number of –OH groups of the fillers or to introduce cross-linking by physical and chemical bonds between the wood polymer macromolecules and the matrix resin. The stability of new structures depends on the nature of the bonds. It has an important influence on mechanical and sorption properties. As long as the matrix follows the fibre during swelling or shrinking, no bonds crack during wetting or drying. Such strong interaction is possible if covalent bonds are built, e.g. when using polyisocyanates [116] and triazine based coupling agents [121]. Chemicals which are used to react with the hydroxyl groups of cell walls can be divided into two classes: those which react with the -OH group and polymerize afterwards and into those which react with a single –OH (single-site addition). Activation and change of polarity are chemical modification methods used for polymer matrices.

Use of maleated PE increases the mechanical properties and geometric stability of recycled PE reinforced with wasted cellulose [105]. Polypropylene–maleic-anhydride copolymers [121] grafted to wood fibres allows production of wood-fibre–PP composites with a high fibre dispersion, good wettability and adhesion between the two phases. Compared to untreated PP–RGP, tensile strength is three times higher, if only 2.5% MPP are added to the wood refiner ground pulp (RGP)-PP. Moisture absorption of composites with maleate-modified PP decreases remarkably [73]. A coating of wood fibres with MA in presence of initiators and PVC produce a soft, hydrophobic film on the surface of the hydrophilic fibres. As a result, the chance of debonding of the two different matrices is minimized. Only a slight increase of the mechanical properties is obtained if maleic anhydride is solely used in wood-fibre–PS composites [105,108,118].

Other important coupling agents are isocyanate and silanes, and cause an improvement of the mechanical properties. A significant improvement in strength was achieved using PMPPIC in wood–HDPE composites by Raj et al. Another group of coupling agents, used in wood composites, are silanes [105,116]. A slight improvement of tensile strength could be observed for LLDPE–wood-fibre composites, treated with silanes A-172, A-174 and A-1100 [152]. The best result was observed with 6% silane A-174 (having 30 wt.% wood filler content), where tensile strength increased from 23.8 to 28.4 MPa. The results, obtained with wood–HDPE composites, indicate that the elongation is a function of the filler concentration. Elongation is not significantly influenced by the interaction of the filler-matrix, as caused by the silane treatment.

6.3.3. Processing of wood–thermoplastic composites

The main problem in processing wood–thermoplastic composites, is the tendency of untreated wood to form large aggregates, due to a high intramolecular bonding among the fibres. Therefore, the dispersion of the fibres in the polymer matrix is small and the reinforcing ability of the fibre is reduced remarkably. The better the fibres dispersed in advance in the polymer matrix is, the better is its uniformity. The mixing time can then be shortened and thus fewer fibres break during the mechanical mixing process (by shearing) [104,106,107,111,116,122]. The dispersion of wood fibres can be improved by pretreatment with lubricants or thermoplastic polymers. An addition of 1–3% stearic acid is sufficient to achieve a maximum reduction in size and number of the wood aggregates in PP and HDPE. An impregnation or incapsulation of wood particles with chemicals, compatible to the polymer matrix [103,121] produces an insulating film of hydrophobic polymer on the surface, thus preventing agglomerization and in some cases improving the thermoplasticity of wood. Another problem is that the rate of thermal decomposition of lignocellulosics increases exponentially with an increase in temperature. At normal processing temperature (180–200°C) critical values of decomposition are realized [116]. Decomposition of the pulp components creates voids inside the composite, causing a decrease in mechanical properties. An optimization of processing temperature and time is necessary. The suggested mixing and moulding temperature for wood–PS composites is 175°C and for wood–HDPE is 170°C [120].

The fibre–matrix compatibility can be improved if suitable aids are chosen when processing. Extrusion mixing, hot-press lamination and in most cases injection moulding are the main processes for wood–thermoplastic composites, where melt-rheological properties are significant. Melt viscosity decreases with increasing shear rate and increases with higher filler content at each temperature. The properties of extruded composites are sensitive to a screw configuration and to the compounding temperature [120]. Significant improvements in the flow of birchwood-sawdust–PS mixture under moulding or extrusion conditions are reached with an addition of 1–20% plasticizer. The mechanical properties of injection moulded wood thermoplastic (virgin and recycled) composites showed that addition of cellulose fibres (CF) and old newsprints (ONP) results in a slight improvement of tensile properties. Wood flour (WF) and CF increase the impact energy of PP and decrease the impact energy of HDPE. This difference may be caused by a better compatibility of the coupling agent with PP.

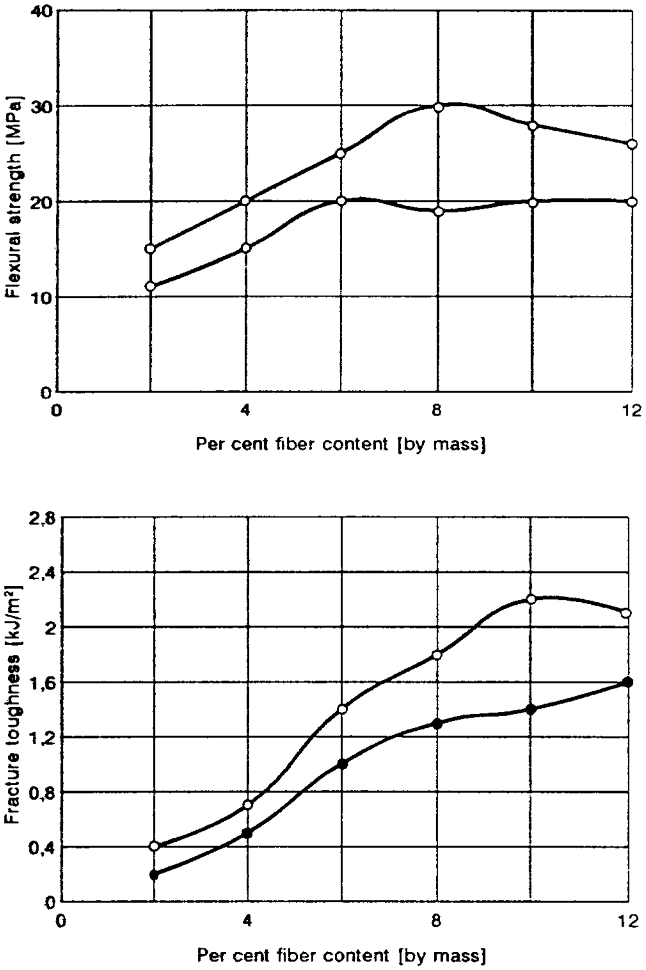


Fig. 29. Influence of fibre content on flexural strength and fracture toughness of: (○) softwood cement composites; (●) hardwood cement composites (air cured) [128].

6.4. Further applications

Plant-fibres and ''man-made'' cellulose fibres used as substitutes for asbestos-fibres in cement matrixes, show comparable characteristic values at lower costs. As with plastic composites, these values are dependent essentially on the properties of the fibre and the adhesion between fibre and matrix. Distinctly higher values of strength and stiffness of the composites can be achieved, by chemical modificatons of the fibre surface (acrylic and polystyrene treatment [124]), usually produced by the *Hatschek-process* [125–127]. Tests by Coutts and coworkers [126–128] on wood-fibre cement (soft- and hard-wood-fibres), show that even at a fibre content of 8–10% (by weight), a maximum of strengthening is achieved (Fig. 29).

Cellulose–cement composites show a similar sensibility to humidity (Table 15), as do plastic

Table 15
Influence of humidity on flexural strength and fracture toughness of cellulose-fibre reinforced cement [128] (r.h. = test samples were conditioned before testing at 50 ± 5% r.h. and 22 ± 2°C, wet = test samples were soaked in water for 48 h, dried with a cloth and then tested while wet)

Fibre content (wt.%)	Flexural strength (MPa)		Fracture toughness (kJ/m^2)	
	r.h.	Wet	r.h.	Wet
2	10.6	8.6	0.25	0.33
4	14.2	10.5	0.51	1.00
6	20.9	10.4	1.06	1.61
8	20.3	8.4	1.37	1.49
10	20.1	9.6	1.46	1.83
12	20.6	9.3	1.68	1.79

composites, that is, they show lower mechanical properties. Yet, previously reached values can again be achieved by a drying process on the composite [125].

7. Environmental effects

Whichever application of natural fibre, or natural fibre reinforced plastics, will be used, when and where, depends on the different environmental conditions, which are likely to influence ageing and degrading effects. In contrast, such effects are often desirable, as is the case with compostable materials. Natural fibres are subject to degradation in acids and in alkaline solutions, as well as under UV rays. These effects however, can be minimized by using suitable modifications. Unmodified cellulose-fibres, are normally degraded by enzymes after about 6–12 months, this can be altered through suitable treatment, so that no significant changes of mechanical properties can be noticed for two years. Within a period of 2.5 years, dry-stored fibres show only little changes in their mechanical properties. This is true especially with regard to strength and elongation at break. In this respect, sisal fibres are comparably more stable than Henequen and Abaca.

Lower temperatures, such as − 70°C, clearly result in lesser strength, but this effect can be minimized by previous drying. Higher temperatures, such as 100–130°C, lead, in the case of cotton, to a notable degradation, after 80 days. Their strength is thereby reduced to 68%, that is 10% of the original value. Depending on the temperature applied, these values are reduced to 41% and 12%, for flax-fibres, and to

Table 16
Influence of chemicals on the change of bending strength of sisal–PP composites [123]

Chemicals/time	Bending strength (MPa)	Bending modulus (GPa)
Reference samples	30	1.5
NaOH/50 h	24	1.1
NaOH/500 h	18	1.05
HCL/50 h	20	1.35
HCL/500 h	15	1.4

26% and 6%, for ramie-fibres. In composites, moisture content results in lower mechanical properties. This effect is greater when using ocean- rather than fresh water. With fresh water, it is more likely that bacteria and fungi appear on the scene. Against such influences, ramie-, jute- and kopak-fibres, are more resistant than other plant-fibres [92]. The low resistance of natural fibres, against environmental factors, decisively effects the mechanical properties of the composites (Table 16) [123].

8. Concluding remarks

As in the case of all natural products, the mechanical and physical properties of natural fibres vary considerably, These properties are determined by the chemical and structural composition, which depend on the fibre type and its growth circumstances. Cellulose, the main component of all natural fibres, varies from fibre to fibre.

The moisture sensibility is remarkable, natural fibres are easily influenced by environmental effects. Generally speaking, rising moisture content lowers the mechanical properties.

Natural fibres when used as reinforcement compete with technical-fibres, such as glass-fibres or carbon-fibres. The advantages of technical-fibres are good mechanical properties, which vary only little. Their disadvantage being difficult recycling.

The mechanical properties of composites are influenced mainly by the adhesion between matrix and fibres. As in the case of glass-fibres, the adhesion properties can be changed by pretreating the fibres. So, special processings, such as chemical and physical modification methods were developed. Moisture repellency, resistance to environmental effects, and not last, the mechanical properties are improved by these treatments. Various applications of natural fibres as reinforcement in plastics, have proved encouraging.

Several natural fibre composites reach the mechanical properties of glass-fibre composites, and they are already applied, e.g. in automobile and furniture industries. Till date, the most important natural fibres are jute, flax and coir.

Yet the development of processings and modification methods is not finished. Further improvements can be expected, so that it might become possible to substitute technical-fibres in composites quite generally.

Natural fibres are renewable raw materials and they are recyclable. In recognition of the discussion about recycling and preservation of natural resources, such a substitution seems desirable.

Reference [145] was deleted in press. The authors would like to thank the authors of Ref. [141] for the information obtained from their paper.

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