CELLULOSE CHEMISTRY AND TECHNOLOGY

BASIC CHEMICAL COMPOSITION OF WOOD AS A PARAMETER IN RAW MATERIAL SELECTION FOR BIOCOMPOSITE PRODUCTION

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In order to determine the significance of wood basic chemical composition in the selection of a raw material for biocomposite production, in this paper, the contents of ash, extractives, lignin, cellulose and alpha-cellulose of 20 temperate zone wood species have been determined. The results were discussed starting from the assumption that a biocomposite material would be produced entirely from a single wood species. More precisely, to achieve the composite material, wood cellulose would be used for the synthesis of a polymeric matrix (*e.g.* cellulose acetate), which would be then filled with various types of fillers prepared from the same wood species. As the wood used for producing such composite materials should have a specific chemical composition, the examined wood species were ranked as a function of their cellulose and alpha-cellulose contents. Thus, the species with the highest cellulose and alpha-cellulose contents, alongside the lowest lignin and extractives contents, were determined as the most suitable. The obtained results showed that white willow (*Salix alba* L.), which is a somewhat underutilized wood species, had the most favourable ratio of the determined chemical constituents, indicating that it is the most suitable for manufacturing biocomposite materials.

Keywords: wood, chemical composition, biocomposite materials, ash, extractives, lignin, cellulose, alpha-cellulose, raw material selection

INTRODUCTION

According to its structure, wood represents a complex product of different chemical reactions and, in chemical terms, it is defined as a three-dimensional biopolymer composite, composed of an interconnected network of cellulose, hemicellulose and lignin, with minor amounts of extractives and inorganic compounds.[1] Biocomposites are made entirely from raw materials that are easily renewable and available in large quantities. Such materials should have relatively long lifetime during which their physical, mechanical, thermal, aesthetic and/or insulating properties should not deteriorate. Also, at the end of their service life, they must be easy to dispose of or recycle without causing harmful effects to the environment. In order to achieve these conditions, wood can be used as raw material, but in most cases it must be chemically modified in order to fully exploit the potential of each of its individual components. Its primary component is cellulose, which can be used as a polymeric matrix for biocomposite materials in its dissolved and partially modified state (*e.g.* acetylated).[2]Dissolved cellulose (cellulose acetate, CA) can be then filled with various types of organic fillers, including unaltered wood itself or wood components, such as lignin or holocellulose.

In order to develop wood based biocomposite materials with afore-mentioned properties, it is prerequisite to combine knowledge from different scientific fields, with an emphasis on the raw materials' properties, the specifics of their utilization and the possibilities of combining them. That is so because the intrinsic properties of composite material constituents directly determine the composite materials' properties.[3] The chemical composition and structure of wood, as well as its individual components, also greatly influence the biocomposite materials' properties, especially if wood isused as filler for different types of biodegradable matrices.[4,5] Consequently, knowing the chemical composition of wood should be a prerequisite based on which the proper wood species should be selected before manufacturing the composite materials. This is especially true considering the great difference in basic chemical composition between softwoods and hardwoods, as well as between different species of the same family or genus. In general, softwood species comprise 38-50% cellulose, 25-34% lignin and 0.6-13% extractives, while hardwood species contain 40-51% cellulose, 16-30% lignin and 0.8-25% extractives.[1,6-12] However, most of the data reported in the literature on the chemical composition of wood have been collected under the conditions specific to certain experiments and basic chemical composition of wood has not been examined as a parameter in the selection of appropriate species for developing biocomposite materials. Hence, in this work, the chemical composition of 20 temperate zone wood species has been determined, including their contents of cellulose, alpha-cellulose, lignin, benzene-ethanol extractives and ash, and discussed in terms of the wood species suitability for production of biocomposites.

EXPERIMENTAL

Wood flour of 20 wood species was used for investigation (Table 1). Wood sampling was conducted in accordance with TAPPI standard T 257 cm-12,[13] and was performed during mid-June and July 2013, in various locations of the Continental Croatian region. After sampling, the obtained wood samples were transported to the laboratory and allowed to dry (without debarking) at 20±2 °C and 65±5% relative humidity until 6-10% water content was reached, as measured using a Sartorius infrared moisture analyser MA 150. The prepared samples were then debarked and milled using a Retsch SM 300 cutting mill. The obtained wood meals were screened by means of a Cisa RP.08 laboratory sieve shaking machine and particles sized between 0.5 and 1 mm were collected for further chemical analysis.

Determination of basic chemical composition consisted in isolating and calculating the contents of ash (TAPPI T 211 om-02),[14] benzene:ethanol extractives (TAPPI T 204 cm-97),[15] Klason lignin (TAPPI T 222 om-11)[16] and cellulose (Kürschner-Hoffer's method).[17]Nitric acid was used for cellulose isolation, which resulted in the preparation of slightly degraded cellulose, which still contained a small portion of hemicelluloses.[17] Therefore, alpha-cellulose contents were additionally determined in order to examine the potential of each wood species to be used as filler in the production of biocomposite materials. Alpha-cellulose contents were determined on one sample per species only, by treating2.5 g of the obtained cellulose with 17.5% (w/v) aqueous solution of sodium hydroxide, where the insoluble part that was left after filtration and drying at 103±2 °C was considered to be pure alpha-cellulose (TAPPI T 203 cm-99).[18]

RESULTS AND DISCUSSION

The results of determining the basic chemical composition for each wood species and for each individual wood component, except alpha-cellulose, are expressed as the average values of four measurements and standard deviations are provided in parenthesis (Table 1).

From the obtained results, it may be concluded that the contents of individual wood cell chemical components vary significantly as a function of the wood species. Therefore, it is almost impossible to find any relations between the variation in the content of one component and the contents of other examined wood cell chemical components. The main restrictive factor that influences these relationships lies in the fact that the contents of individual components (except ash) are more or less determined by the pretreatments that preceded their isolation. Namely, it has been proven that identical chemical treatment could have rather different effects on the examined components in different wood species.[6] Still, if one component is examined at a time and if the chemical composition of a particular wood species is compared with the data reported in the literature (Table 2), it is possible to draw certain conclusions.

Ash contents (Tables 1 and 2)vary significantly among the species, as the content of all inorganic constituents varies to a great extent with the environmental conditions under which the tree has grown.[43]The maximum content of ash was recorded for white mulberry (*Morus alba* L.),which can be explained by exposure of the tree to anthropogenic sources of inorganics, as the tree grew in a regularly fertilized plantation.[7]As for the extractives, their content is under genetic control and thus varies greatly among wood species.[44]The combined effect of the genetic control and the method and solvent used for extraction resulted in a broad range of the results. If the extractives values obtained in this investigation for all the examined wood species are compared with literature data (Table 2), it is noticeable that the values are distributed mostly within or very close to the ranges given in the literature. Both our experimental values and the literature reported ones reveal that the extractives contents are slightly higher in the case of fruit bearing tree species (*i.e.* white mulberry, common walnut, wild cherry, European (wild) pear and European plum), while coniferous tree species (*i.e.* silver fir and Norway spruce) have the lowest extractives content.

The results obtained for the lignin contents differ, in most cases, from the values reported in the literature, which can be explained by the fact that so far there is no method of isolation that does not, more or less, degrade its structure.[45,46] Other than that and regardless the fact that all the wood species were sampled following the same principle, age difference among the sampled trees and as a consequence their different morphology also influenced the results. This is supported by the fact that, so far as it is known, the content of lignin and its structure differ depending on the region of the woody xylem.[22]

Table 1
Results of wood analysis

Species	Ash (%)	Extractives (benzene:ethanol)(%)	Lignin (%)	Cellulose (%)	Cellulose I* (%)
Black locust	0.36	4.31	21.89	53.26	45.00
(*Robinia pseudoacacia* L.)	(0.01)	(0.37)	(0.96)	(0.69)	
Common beech	0.81	1.31	22.43	45.39	42.98
(*Fagus sylvatica* L.)	(0.07)	(0.17)	(1.58)	(0.74)	
Turkish oak	0.12	1.53	24.34	48.33	50.90
(*Quercus cerris* L.)	(0.02)	(0.21)	(4.53)	(0.73)	
Sessile oak	0.16	3.03	23.08	49.24	42.41
(*Quercus petraea* [Matt.] Liebl.)	(0.01)	(0.70)	(1.50)	(0.85)	
Pedunculate oak	0.17	2.22	25.10	49.04	42.19
(*Quercus robur* L.)	(0.03)	(0.27)	(1.29)	(0.73)	
Common hornbeam	0.48	1.35	16.58	47.93	68.21
(*Carpinus betulus*L.)	(0.02)	(0.17)	(2.59)	(3.78)	
Silver fir	0.16	0.84	27.47	54.47	44.68
(*Abies alba* Mill.)	(0.04)	(0.09)	(1.55)	(2.23)	
Norway spruce	0.31	2.30	27.43	50.69	47.74
(*Picea abies*[L.] H. Karst.)	(0.02)	(0.01)	(3.01)	(1.99)	
White poplar	0.26	4.11	20.21	50.76	44.95
(*Populus alba* L.)	(0.04)	(0.19)	(1.35)	(0.54)	
Black poplar	0.38	5.78	27.04	53.97	49.91
(*Populus nigra* L.)	(0.05)	(0.23)	(1.21)	(0.95)	
Black alder	0.38	4.95	21.81	50.94	56.47
(*Alnus glutinosa* [L.] Gaertn.)	(0.03)	(0.06)	(1.55)	(1.01)	
White willow	0.35	2.05	26.35	54.06	50.78
(*Salix alba* L.)	(0.04)	(0.16)	(3.94)	(0.72)	
Small-leaved lime	0.39	6.05	17.76	55.33	40.06
(*Tilia cordata* Mill.)	(0.06)	(0.17)	(1.04)	(1.19)	
Field maple	0.43	1.48	26.46	50.90	36.49
(*Acer campestre* L.)	(0.02)	(0.14)	(1.51)	(0.54)	
Silver birch	0.28	2.40	22.82	54.97	30.55
(*Betula pendula* Roth.)	(0.11)	(0.19)	(4.02)	(0.49)	
White mulberry	1.39	11.96	23.17	47.20	47.01
(*Morus alba* L.)	(0.08)	(0.30)	(0.45)	(0.49)	
Common walnut	0.48	3.14	26.25	49.79	44.56
(*Juglans regia* L.)	(0.02)	(0.12)	(0.93)	(0.35)	
Wild cherry	0.44	9.98	26.16	44.57	37.38
(*Prunusavium*[L.] L.)	(0.02)	(0.19)	(1.52)	(0.88)	
European wild pear	0.57	1.37	33.99	41.01	38.49
(*Pyrus pyraster* [L.] Burgsd.)	(0.04)	(0.05)	(0.75)	(1.79)	
European plum	0.02	13.42	32.40	43.53	41.73
(*Prunus domestica* L.)	(0.02)	(0.12)	(0.70)	(0.48)	

*Alpha-cellulose contents are expressed with regard to total cellulose content

Table 2
Literature data on chemical composition of examined wood species

Species	Ash (%)	Extractives* (%)	Lignin (%)	Cellulose (%)
Black locust[6,11,19,20]	0.3	2.8-8.1	17.5-20.6	40.7-50.1
Common beech[6,10,21-23]	0.3-1.4	0.8-2.1	17.0-31.3	39.4-49.1
Turkish oak[24]	N/A	5.0	25.8	N/A
Sessile oak[6,25]	0.3	3.0-5.9	24.0-24.9	37.5-44.0
Pedunculate oak[6,10,26,27]	0.3-1.3	0.4-2.3	23.7-29.6	41.1-45.1
Common hornbeam[6,10,11,28]	0.4-0.6	1.0-4.4	17.6-19.3	44.9-46.4
Silver fir[6,29-31]	0.8	0.9-2.3	28.9-32.9	40.7-42.3
Norway spruce[6,11,22,32,33]	0.18-0.2	1.0-2.0	27.3-29.0	41.7-54.0
White poplar[6,34,35]	0.2-1.0	1.6-3.8	17.7-25.2	43.1-49.3
Black poplar[6,11]	0.4	5.0	19.0	48.0
Black alder[6]	0.5	3.8	23.9	43.4
White willow[10,11,35-37]	0.3-0.9	2.0-2.4	20.3-28.0	38.4-50.6
Small-leaved lime[10,11]	0.6-0.8	2.0	18.0-24.4	50.0-51.0
Field maple[10,38]	0.7	3.1**	22.0-24.3	36.7-49.9
Silver birch[6,22,32,39,40]	0.3	2.6-3.8	19.4-21.8	41.0-48.5
White mulberry[11,41]	1.1	12.0	24.6	57.4
Common walnut[6,11]	0.5-0.8	4.4-5.0	22.0-29.1	40.8-49.0
Wild cherry[10,11]	0.3-0.41	7.0	18.0-18.3	45.0-46.6
European pear[11]**	0.4	1.0	24.0	44.0
European plum[42]	N/A	2.8	32.3	51.6

Note: Amounts are given as mean values or as minimum-maximum range
*Extracted using various solvents or solvent mixtures (*e.g.* ethanol, benzene:ethanol, toluene:ethanol or acetone:ethanol mixtures); **Hot water extractives; ***Data given for European (common) pear (*Pyrus communis* L.)

Still, it is noteworthy that small-leaved lime (*Tilia cordata* Mill.) had the lowest lignin content and the highest cellulose content among all the examined wood species.

This can be explained by the fact that lignin is associated with hemicelluloses so that lignin-carbohydrate complexes, which are resistant to hydrolysis, are formed.[47]

As in commercially prepared lignin, there are 2-8% (by weight) of carbohydrates, it is easy to conclude why the relationship between the lignin and cellulose contents for small-leaved lime is as shown in Table 1.[48] As for the carbohydrate portion of wood, the obtained cellulose contents are mostly higher than those reported in the literature (Table 2). This can be associated with the fact that Kürschner–Hoffer's method of cellulose isolation leads to obtaining slightly degraded cellulose, which still contains small portions of hemicelluloses.[17] The presence of hemicelluloses, their type and varied degrees of water solubility are most likely the reasons for the significant differences between the amounts of cellulose estimated in the present study and those reported in the literature for black alder (*Alnus glutinosa* [L.] Gaertn.), white mulberry (*Morus alba* L.) and European plum (*Prunus domestica* L.).[49]

Considering that the results in Table 1do not allow judging about the suitability of certain wood species for developing biocomposite materials, all the results were analysed individually and an additional selection was performed. The main goal of this selection was to separate the species with cellulose contents above 50%, as further experiments on species with less cellulose would not be economical. The species in this group were ranked as a function of their cellulose and alpha-cellulose contents, and the species with the highest cellulose content was considered as the most appropriate as a raw material for biocomposites (Table 3). Similarly, the wood species were ranked as a function of their amounts of extractives and lignin, however, the species with the lowest amounts was considered as the most appropriate. This is so because the extractives and the lignin should be removed if, for instance, only the extracted wood or the carbohydrate part of the wood (*e.g.* alpha-cellulose) is to be used as filler for biocomposite materials. Such filler has beneficial effects, as the removal of extractives and lignin improves the interfacial bonds between the polymer matrix and the filler. Consequently, composite materials with favourable physical, mechanical and thermal properties can be produced.[50-52] As a result, the suitability of the wood species for producing biocomposite materials was determined by summing up the rankings, regarding the contents of individual wood cell chemical components, excluding ash. The species with the lowest sum was regarded as the most appropriate. As the ash content seldom exceeds 1% of dry wood weight and as its contents vary widely both within and between wood species,[53] the amount of ash should have a low impact on the species suitability for biocomposite production and therefore the ash contents were excluded from this additional analysis.

Table 3
Selection and ranking of wood species regarding their chemical composition

Species	Cellulose (>50%)	Cellulose I (%)	Extractives (benzene:ethanol)(%)	Lignin (%)	Sum
Small-leaved lime (*Tilia cordata* Mill.)	1	8	10	1	20
Silver birch (*Betula pendula* Roth.)	2	10	4	5	21
Silver fir (*Abies alba* Mill.)	3	7	1	10	21
White willow (*Salix alba* L.)	4	2	3	6	15
Black poplar (*Populus nigra* L.)	5	3	9	8	25
Black locust (*Robiniapseudoacacia*L.)	6	5	7	4	22
Black alder (*Alnus glutinosa* [L.] Gaertn.)	7	1	8	3	19
Field maple (*Acer campestre* L.)	8	9	2	7	26
White poplar (*Populus alba* L.)	9	6	6	2	23
Norway spruce (*Picea abies* [L.] H. Karst.)	10	4	5	9	28

The results of the additional selection are presented in Table 3 and they reveal that, from the viewpoint of producing biocomposite materials entirely from a single wood species, white willow (*Salix alba* L.) is the most appropriate. This is supported by its cellulose content above 50% and its more favourable content ratio of alpha-cellulose, extractives and lignin, compared to the corresponding values of the other wood species.

CONCLUSION

It is suggested that chemical composition of wood is an important parameter for raw material selection if considering the production of biocomposite materials entirely from the same wood species. Due to its chemical composition, white willow has been found to be the most suitable for developing such materials. This is supported by the chemical composition of white willow, primarily its cellulose and alpha-cellulose contents, which is more favourable for this objective discussed here than the composition of the other examined species. As white willow is mainly used for energetic purposes or as raw material for paper and particleboard production, the finding of this study could lead to broadening the range of its industrial utilization.

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