MATERIAL ALLIANCE OF LIGNIN WITH NATURAL FIBRES

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ABSTRACT
With the use of common processing technologies of the synthetic industry thermoplastic wood based products from lignin, natural additives and vegetable fibres can be made. Within the scope of a joint project material properties of hot pressed structural ARBOFORM®- panels are verified and potential application areas for the building branch will be acquired.

I. INTRODUCTION

Each year over 100 million tons of polymers from fossil resources are produced and released to the atmosphere after their utilization. The incineration of these polymers causes an accumulation of CO_2 in the atmosphere and this is one reason for the greenhouse effect. Recent climate simulations suggest that the global, annual mean temperature increases by 2.5°C to 4°C at the end of the 21st century if emissions of carbon dioxide and other greenhouse gases continue to grow unabatedly (1).
The use of raw materials from renewable resources for the production of polymers offers an opportunity to reduce the increasing accumulation of CO_2 in the atmosphere and presents a new way to a sustainable future. In a first step natural fibres have been used as a substitute for glass fibres for the reinforcement of synthetic polymers in a lot of applications. The starting point for a new class of thermoplastic materials is lignin, the second most abundant natural polymer after cellulose. The macromolecular lignin is present in every wooden plant with contents between 20-40%. It shapes a three dimensional linked frame structure of phenylpropane units and essentially contributes to mechanical wood properties especially to compression strength (2).
Worldwide, up to 70 Mio. t/a of lignin and lignin derivates are accumulated by chemical pulp manufacture. Usually waste liquor lignin is used for energy and chemicals recovery by pulp production. Approximately 1.5% of the material is only utilized, for example as ligninsulfonates (approx. 500,000 t/a) or as Kraft lignin (approx. 100,000 t/a) (3). Table 1 reveals the diversity of substantial applications.

Table 1: Potential applications of lignin (3), modified

MULTI-POLARITY PRODUCTS		MATERIALS	AGRICULTURE	HIGH-PURITY VALUE APPLICATIONS
Dispersion	**Others**			
Ceramics	Complexing agents	Phenolic resins	Soil rehabilitation	Antibacterial effects
Oil well drilling	Flocculating	Polyurethanes	Slow release fertilisers	HIV inhibition
Clay bricks & tiles	Heavy metal binders	Epoxies	Artificial humus	Digestion regulation
Cement	Ion exchanging	Particle boards	Fertiliser	Antioxidants
Concrete	Water softening	Resin boards	Encapsulation	Plant immunology
Gypsum board	Protein coagulants	Rubber reinforcing	Composting aid	Growth stimulators
Dyestuffs	Destabilization of	Block copolymers	Manure treatment	Oxygen scavengers
Electrolytes	Oil emulsions	Polyesters	Humus improvement	Hydrogels
Paper sizing	Corrosion protection	Composites	Soil stabilisation	
	Anti-scaling	Polyolefins	Insecticides	
	Metal cleaners	Biodegradables	Granulation	**MISCELLANEOUS**
	Grinding aids	Carbon sieves	Pelletising	Energy production
Emulsion		Activated carbons	Chelates	Diesel fuel
Wax		Carbon fibres		Foam stabilizers
Asphalt		Heat resistance		Binders
Bitumen		Antioxidants		Tanning agent
Vitamins		Anti-inflammation		Hydrophobization
Micronutrients		Paper bounding		Absorbents

The product ARBOFORM® was developed in the Fraunhofer Institute for Chemical Technology. In 1996 an injection moulding material based on lignin, natural additives and vegetable fibres of hemp, flax or wood was

successfully manufactured for the first time (4). As raw material basis provides a well disposable and modified alkali lignin of pulp industry, modifications of material properties are possible by changing quantity, derivation as well as mixing ratio of inserted substances. Tensile strength, for example, depends linearly on the fibre ratio of injection moulding produced ARBOFORM® (5). Under the trade name ARBOFORM® (latin: arbor – the tree) this material was advanced by a spin-off of the TECNARO GmbH. Basic material components like lignin and wood fibres are by-products of pulp and wood industry, which are locally and regionally accumulated.
Granulate processing is possible by injection moulding or extrusion with conventional converting machines of synthetic industry. With 3-zone-screws applicable for processing of thermoplastics the granulate will be treated without other compounds. Cylinder temperatures constitute between 100°C and 165°C by processing. Injector temperature should remain between 155-165°C. With the above mentioned method a wood based material will be produced like a thermoplastic synthetic. Commercial applications of injection moulding based ARBOFORM® are, for example, decorative watchcases, loudspeakers, toys or golf tees. Other products are applied in the automotive engineering and the burial branch. Investigations regarding material applications in the outer sector are currently taking place.
Another opportunity presents the hot pressing of plasticized moulding material similar to curable plastic or thermoplastic composite production. Produced and investigated prototypes of ARBOFORM®- panels are within the scope of a joint project. The raw material basis constitutes Kraft lignin.

II. EXPERIMENTAL

Information about material properties of basic material is important for the evaluation of potential application areas. The tests according to the following standards are presented in Table 2.

Table 2: Applied standards for testing material properties of ARBOFORM®

Parameters	Norm
Chemical	
Resistance	DIN 13 442 (2002)
Physical	
Density	DIN EN 323 (1993)
Thickness swelling	DIN EN 317 (1993)
Mechanical	
Bending strength	DIN EN 310 (1993)
Modulus of elasticity	DIN EN 310 (1993)
Transverse tensile strength	DIN EN 319 (1993)
Thermal	
Fire behaviour	DIN 4102-1 (1998)
Net calorific value	DIN EN ISO 1716 (2002)

Ash content and pH-value were detected according to TAPPI. For determination of CHN-content the element analyzer by Heraeus (CHN-O-Rapid) was used. EDXA (Leitz-AMR 1200; Unispec System 7000) was realized with an analysis time of 200 s and an energy incitation of 15 kV.
The mechanical tests were carried out by using a hydraulic testing machine (Test 810). The air-conditioned samples (20°C/65% relative humidity) were immediately measured before testing with the Heidenheim device. For evaluation of the results the programme DIAdem (Leibnitz Computer Center, National Instruments) was used.
Fire tests took place in the combustion stage (B2) as well as in the combustion inspection chamber (B1). The determination of net calorific value was performed in the bomb calorimeter (C2000 control, IKA®-factories) as well as with the integrated computer software CalWin (Version 2.00.030, IKA®-factories).

III. RESULTS AND DISCUSSION

The investigated material featured the following element rates: 53.3% carbon, 6.3% hydrogen, 0.5% nitrogen. In addition, relatively high contents of sulphur and calcium were detected. Ash ratio represents approx. 2.4%. The pH-value constitutes approx. 5.3. ARBOFORM® features a cold-water extract content of approx. 3%. The material is resistant against acids. The material consistency regarding bases remains but discolorations appear. This reaction behaviour is due to the low acid character of the phenol groups of lignin.
The density of ARBOFORM®-panels constitutes between 1,150-1,400 kg/m³ depending on the manufacturing method. In comparison with conventional wood based panels it is a very heavy material. With respect to this parameter the material is comparable with synthetics (see Table 3). It is difficult for water molecules to permeate

Table 3: Selected material properties of ARBOFORM® in comparison with other relevant materials. The mentioned comparative values from literature usually correspond to maximum values of respective materials. Wood as well as ARBOFORM® are given as average values. Footnotes are literature citations.

Properties	Physical		Mechanical				Thermal				
Material	**Density** ρ_{12} [kg/m³]	**Thick-ness swelling** q_{24} [%]	**Transverse tensile strength** f_t [N/mm²]	**Bending strength** f_m [N/mm²]	**Modulus of elasticity** E_m [N/mm²]	**Hardness BRINELL** HB [N/mm²]	**Fire-behav-iour**	**Net calorific value** H_u [kJ/g]	**Thermal conductivity** λ [W/mK]	**Heat accumulator capacity** c [kJ/kgK]	**Linear expansion coefficient** α [10^{-6}/K)]
Wood-Based-Panels						d = 10 mm					
HDT (high density fibreboard, HB.HLA2	800[6]	12[18]	0.65[18]	38[18]	4600[6]		B2[6]	16.5[16]	0.18...0.22[6]	1.7[6]	
MDF (medium density fibreboard), HLS2	650[6]	9[19]	0.40[19]	28[19]	3700[6]		B2[6]	16.5[16]	0.14…0.16[6]	1.7[6]	
OSB/4 (oriented strand board)	550[6]	25[17]	0.5[17]	30[17]	4930[6]		B2[6]		0.12[6]	1.7[6]	
Particle board type P7	650[6]	9[20]	0.75[20]	22[20]	3500[6]	40…50[7]	B2[6]	16.5[16]	0.12…0.13[6]	2.5[6]	
Wood		rad : tang									rad : tang
Spruce (*Picea abies*)	470[8]	3.6…7.8[8]	2.7[16]	78[8]	11000[8]	12…32[8]	B2[9]	14.5[7]	0.10…0.12[10]	2.4	24…34[16]
ARBOFORM®						d = 5 mm					
Injection moulding	1300…1400			25…45	2000…7000	20…70	B2		0.38		10…50
Hot pressing	1150…1350	4.5	2.44	32	6900		B2	21.6			
Wood-Plastic Composites (WPC)											
Arbofill	1000…1300			35…50	2000…5000						
Fasalex	1300[11]	15[11]		17…25[11]	2500[11]	90[11]					
HPL (high pressure laminate) type F	1350[12]			80[12]	9000[12]		B1[12]				
Plastics						d = 5 mm					
PP-H (polypropylene heat stabilized)	907[15]			20…55[15]	1300[15]	58…80[15]		44[13]	0.22[15]	1,7[13]	160[15]
PE-HD (polyethylene of high density)	918[15]			40[15]	600[15]	60[15]		43[13]	0.35[15]		200[15]
PVC-U (unplasticized polyvinyl chloride)	1390[15]			70…110[15]	3000[15]	110…130[15]		18…26[13]	0.17[15]	0.9[13]	70…80[15]
MF (melamine formaldehyde resin), filled	1900[15]			80[15]	7500[15]			20[13]			

the panels because of the compact material. Furthermore lignin has a hydrophobic character. These facts explain the low thickness swelling of 4-5%. Concerning the moisture influence the investigated material is dimensionally stable. This aspect is important for indoor utilization and especially in outer areas.

Considering the high density transverse tensile strength also possesses very high values. Under the same aspects the bending strength with approx. 32 N/mm² features medium values. Such bending strengths are typical for wood based materials. In comparison with synthetics these values are lower than those of high pressure laminate (HPL) or unplasticized polyvinyl chloride (PVC-U). The modulus of elasticity of hot pressed panels is very high with approx. 6,900 N/mm². Only HPL or special synthetics possess higher values. When applying short fibred components only a filling effect will be obtained. Density and deformation stiffness are rising. With a higher thickness ratio of the fibres as well as positions inside the material composites the bending strength probably increases. To realize these aspects the costs are important depending on respective standards and application areas.

Fire tests on building class B2 were passed successfully. Fire behaviour of ARBOFORM® is similar to wood and wood based panels. The determined heat of combustion constitutes approx. 21.6 kJ/g. This result is much higher than the one of conventional wood based panels. A thermal waste disposal is unobjectionable.

IV. CONCLUSIONS

The wood based thermoplastic material ARBOFORM® can be manufactured with production processes of the synthetic industry. Advantages include very low swelling and very high transverse tensile strength. In contrast to conventional synthetics ARBOFORM® is heat resistant and features low thermic expansion behaviour. In future sulphur free lignin could be the raw material basis for this product. An adequate method for lignin decomposition could be the AQUASOLV®-method, developed by the Fraunhofer Institute for Chemical Technology (21).

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