Compreg-type of Products by Furfurylation during Hot-pressing

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ABSTRACT

Compreg™, phenolic resin impregnated veneers cured under high pressure, was developed in the US during the early 1940s and immediately found use as replacement for stainless steel in specific niche applications, *e.g.* for pitch propellers and connector plates in the WW2 allied air fleet. Similar material is still produced here in Europe under the trade name *PanzerHolz* which is used for *e.g.* joinery products for official German buildings (bullet-proof windows etc.). This paper presents two materials, similar to Compreg, developed within an EU-project (Ecobinders). Veneers were impregnated either with furfuryl alcohol (FA) or water-borne furan prepolymer resin with dissolved catalyst and thereafter dried/pre-cured in an oven. The impregnated veneers were cross-wise glued with FA/lignin or pre-polymer/lignin adhesive between the plies, and cured in a hot-press under high pressure. The result was in both cases highly densified modified wood products. The products had a hardness higher than any known wood species, high dimensional stability and decay resistance. The properties were generally better for the material modified with monomeric FA compared to the material modified with the prepolymer, which, however, had lower WPGs. Kitchen counter top and flooring board prototypes were manufactured by laminating MDF or cork boards with the FA-compregs. Trials with direct-laminating the impregnated veneers on HDF boards were also made. The prototypes, without additional coating, were tested for surface resistance to scratching and chemicals and the results fulfilled the criteria for coated kitchen bench tops.

INTRODUCTION

Compreg (Stamm and Seborg 1941, Stamm 1942, Winslow 1942) was developed in the United States at the Forest Products Laboratory during the 2nd world war. Compreg is made by impregnating wood veneers with water-soluble phenol formaldehyde resin, drying the veneers at low temperature, stacking them in piles and curing them at approximately 150 ºC under 7-10 MPa pressure. To obtain the maximum dimensional stability and mechanical properties, a resin content of about 30 percent and a specific gravity of 1.3 to 1.4 are desired (Seborg *et al*. 1962). However, Compreg is nowadays often produced at 4-5 MPa pressure during curing leading to specific gravities of around 1.2 (what Stamm called semi-compreg). The increase in strength properties of Compreg, except for impact strength, is proportional to the increase in specific gravity. Compreg has rather high dimensional stability, very high hardness and high biological durability, *e.g*. compreg stakes put out in ground field 1940 were perfectly sound in 1962 whereas the controls had an average service life of 2 years due to decay and termite attack (Blew 1962, MacLean 1959, Stamm 1946). Similar resin-treated compressed wood products were developed in Germany already before the 2nd world war under the trade name *Panzerholz* (Thum and Jacobi 1938) or simply *Kunstharzschichtholz* (Kollenen 1936, Kollmann *et al.* 1975). The early applications of both Panzerholz and Compreg was for aircraft parts, gears, pulleys, shuttles, bobbins and picker sticks for looms, instrument bases and cases, electrical insulators, and musical instruments. (Stamm 1964, Stamm and Seborg 1944). Both Panzerholz and Compreg are still being produced, although the term Compreg has lately been used also for compressed melamine resin treated wood veneers made in China. Panzerholz is currently being produced by companies belonging to the Delignit AG group and used in *e.g.* bullet proof joinery in Germany and UK. Compreg is currently produced in Poland and several Asian countries. Furfuryl alcohol modified wood, furfurylated wood, exhibits high durability and dimensional stability (Lande *et al*. 2004). Since furfuryl alcohol resins are technically similar to phenolic resins, the objective of the study presented in this paper was to produce compreg-type materials using furfuryl alcohol or furan prepolymer resins.

MATERIALS AND METHODS

Wood Materials

Veneers of birch (*Betula pubescens* L.) and spruce (*Picea abies* L.) were mainly used for the trials. The thickness of the birch veneers was 1.4 mm and of the spruce veneers 1.6 mm. For control plywood boards 400x400mm plies were cut and for most of the compregs 250x250 mm plies were cut.

Impregnation solutions

Solution A (monomeric furfuryl alcohol solution) composition: 95% furfuryl alcohol (FA), 1% maleic anhydride (MA), 2% citric acid (CA) and 2% water by weight. Solution A was prepared by first dissolving the MA in the FA and then slowly adding CA dissolved in water under stirring. Solution B (furan prepolymer solution) composition: 97.1% BioRez 91 MEAM (40% prepolymer and 60% water) and 2.9% MA.

Bond-line forming adhesive

Adhesive used for monomer FA-compregs consisted of: 60% solution A and 40% lignin (Protobind 3000 from Granit SA). Adhesive for prepolymer furan compregs (*i.e.* BioRez-Compreg) consisted of: 77.1% BioRez 050915-A (90% solid content), 2.9% MA and 20% lignin (Protobind 3000). The lignin, Protobind 3000, is a purified biproduct from solda-pulping of sarkanda grass. It was used as filler for improvement of bond strength and gap-filling properties.

Board preparation

The reference boards, ordinary plywood boards, were produced from 7 plies each, following the recommendations from the resin manufacturer (Casco Adhesives). The resin used for the reference boards was a phenolic resin (PF 1550) with the hardener H7101 added. The compreg-type boards were manufactured according to figure 1, where Step 1 (impregnation) meant dipping for a short period in solution A or dipping for 1h during warming-up in BioRez solution (solution B). The second step (pre-curing) was 15-20min at 100 ºC for solution A impregnated veneers and slightly longer for BioRez impregnated veneers. Step 3 (filler addition) comprised application of adhesive which was single-spread with 100 g/m² in the case of the FA/lignin adhesive and with 150 g/m² in the case of the BioRez/lignin adhesive. Step 4 (Hot-pressing) was pressing at 140 ºC during a pressure ramp (2-6 MPa) for 90 min for the FA-compregs and 60 min for the BioRez-compregs. Step 5 (Post curing) was only applied for the FA-compregs at 100 ºC in an oven over night.

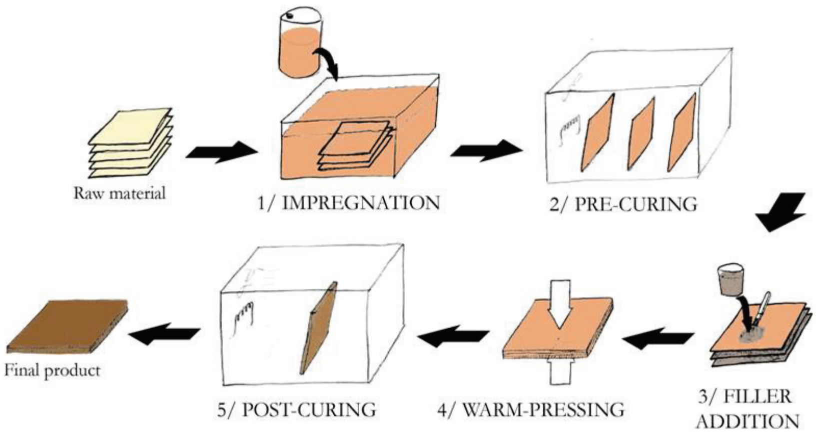

Figure 1: Scheme for manufacturing of FA-compregs

Test of bondline shear strength and bending strength of board

The shear strength of the bond line was determined according to EN 314-1 Plywood – bonding quality: Part 1. Tests were performed in dry state and in wet state after two pre-treatments:

- 24 hour immersion in water at 20 ^{o}C (interior use)
- 2h boiling

The bending strength test was carried out according to EN 789 (for plywood).

Test of dimensional stability and moisture resistance

After oven-drying for 24 hours at 100 ºC, the weight, length, width and thickness of the specimens were measured. Then, the specimens were conditioned in a climate chamber at 27 ºC and 90% RH until they reached equilibrium (around 21% moisture content (MC) in unmodified wood, as reference) Measurements of dimensions and weight were repeated. The EMC (equilibrium moisture content) for 90% RH at 27 ºC was calculated as well as swelling in plane and thickness. Furthermore the MC could be calculated and plotted against conditioning time. After this the specimens were soaked in water for five days and measured once more so that the swelling from oven-dry state to water saturated state could be calculated.

Test of surface hardness and resistance to wear

Resistance to indentation (Brinell hardness) was determined according to standard EN 1534 (2000) Wood and parquet flooring – Determination of resistance to indentation (Brinell) – test method. Resistance to wear was tested according to EN 14 354 Wood-based panels - Wood veneer floor covering.

Test of surface resistance (Furniture testing) and small scale reaction to fire

Methods for testing surface resistance used in this trial are based on several standards. Reference to these standards is given in Table 5. Small scale reaction to fire was determined in the Cone calorimeter according to ISO 5660, at heat flux level 50 kW/m².

Analysis of VOC emissions

Analyses of VOC emissions were performed by GC-MS and HPLC after sampling with absorbent tubes from FLEC (Field and Laboratory Emission Cell) on 3 and 28 days old compreg surfaces, respectively. The procedures followed ISO 16000 standard methods (parts 3, 6 and 10).

Test of biological durability

Tests were done according to an expanded version of ENV 807, where three test soils were used – a neutral compost soil with soft rot and tunnelling bacterial decay type, a sandy soil with dominating brown rot decay type and a mixed forest soil with dominating white rot decay type. The duration of the test was 32 weeks after which the mass loss due to decay was calculated.

RESULTS AND DISCUSSION

Shear strength and bending strength

Results for shear strength are shown in Table 1. The reference plywoods loose 55% (birch, from 4.26 to 1.93 MPa) and 40% (spruce, from 2.39 to 1.43 MPa), respectively, in wet condition after 2 h boil test. FA-compreg, on the other hand more or less retains its shear strength after water soaking and boiling.

Table 1: Results from shear test

Board type	**Shear strength (MPa)**		
	Conditioned in 20°C, 65%RH	**After 24h in water**	**After 2 h boiling**
Reference spruce plywood	2.39 ± 0.11	1.53 ± 0.08	1.43 ± 0.09
FA-compreg, spruce (WPG=31)	2.16 ± 0.20	2,33 ± 0.13	1.89 ± 0.04
Reference birch plywood	4.26 ± 0.15	2.44 ± 0.16	1.93 ± 0.14
FA-compreg, birch (WPG=33)	2.53 ± 0.06	2.96 ± 0.13	3.05 ± 0.18
BioRez-compreg, birch (WPG=23)	2.80 ± 0.80	4.00 [a] ± 0.90	2.90[b] ± 0.80

[a] 6 specimens had mainly bond-line failure whereas the other 6 had 100% wood failure

[b] 4 (out of 16) specimens delaminated during boiling and were not included in the average

The BioRez (WPG=23) compreg boards had the highest remaining shear strength after 24h water immersion (64% higher than the reference plywood). FA-compreg birch boards had the highest remaining shear strength after 2h boiling in water (58% higher than the reference plywood).

The bending strength of FA-compreg was almost 200 MPa parallel to the grain of the outer veneers which is 2.5 times higher than the reference plywood (80 MPa). The bending strength of BioRez-compreg (105 MPa) was 30% higher than the reference.

Dimensional stability and moisture resistance

Compreg swelling results are shown in tables 2 and 3.

Table 2: Swelling of 3-ply birch compregs between oven-dry state and tropical climate (27°C, 90%RH)

Board type	Swelling (%) from OD state to 27°C, 90%RH		
	In grain direction of top and bottom veneers	In grain direction of the centre veneer	In thickness
Reference birch plywood	n.a.	n.a.	21.00 ± 0.50
FA-compreg, birch (WPG=26)	0.17 ± 0.10	0.36 ± 0.11	2.01 ± 1.48
BioRez-compreg, birch (WPG=23)	0.24 ± 0.10	0.48 ± 0.12	8.31 ± 3.68

The thickness swelling (spring-back or recovery of set) of the BioRez-compreg between OD state and tropical climate is approximately four times larger than that of the FA-compreg. This corresponds to an ASE (anti-swelling efficiency) of 60% for BioRez-compreg compared to 90% for FA-compreg since the control plywood had much higher swelling. However, in-plane swelling of BioRez-compreg was only 33% higher than the in-plane swelling of FA-compreg.

Table 3: Swelling of 3-ply birch compregs between oven-dry state and water saturated state

	Swelling from OD state to water saturated state	
	(%)	Std dev. (%)
In thickness for FA-compreg	5.70	2.23
In thickness for BioRez-compreg	20.64	6.55

The thickness swelling between oven-dry and water-saturated state for the BioRez-compreg (20.64%) is almost four times larger than the swelling of the FA-compreg (5.70%).

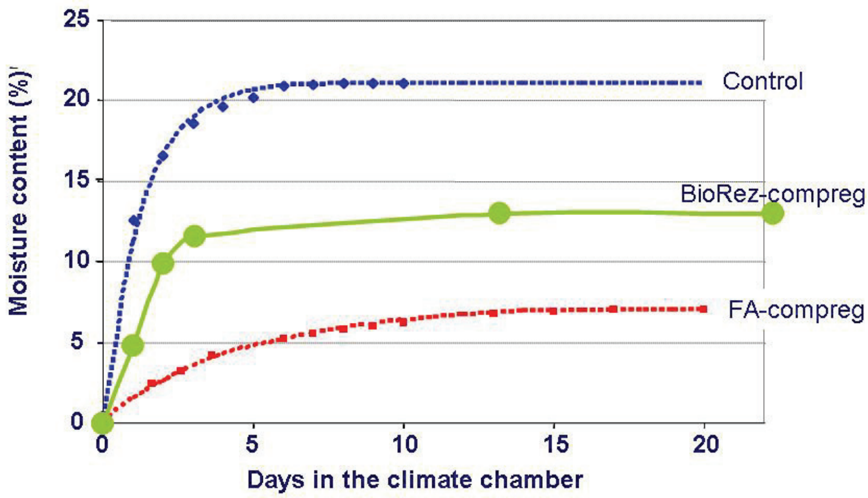

Figure 2: Moisture content in tropical climate chamber when starting from oven-dry state

The moisture content (MC) curve for BioRez-compreg is steeper during the first days compared to the FA-compreg and the final MC (EMC) when the curve has levelled out (13.5%) is approximately double the EMC of FA-compreg which is 1/3 of the EMC for the control plywood (with an EMC of 21%).

Surface hardness and resistance to wear

The Brinell hardness of the FA-compreg (HB 10.3) was 5 times higher than the reference plywood (see Table 4), reaching hardness levels similar to high-pressure paper laminates. The hardness of the BioRez compreg was almost 3 times the reference plywood hardness. The hardness of the BioRez-compreg is approximately the same as for the hard tropical timber ipe and the FA-compreg has 31% higher Brinell hardness than ipe (Table 4).

Table 4: Brinell hardness for compreg compared to very hard tropical timber

	Brinell hardness	Standard deviation
Reference birch plywood	2,1	0,1
FA-compreg, birch (WPG=26)	10,4	0,4
BioRez-compreg, birch (WPG=23)	7,5	1,2
IPE	7,9	0,4

In the test of resistance to wear the amount of removed material after 100 revolutions was 7.0 mg for both FA-compreg and BioRez-compreg. As a comparison, it can be noticed that for iroko the value is 16.5 and for beech 15.9 mg/100rev.

Surface resistance (Furniture testing) and small scale reaction to fire

Results from the set of tests are shown in Table 5. The FA-compreg shows excellent results (approved) in all tests. The BioRez-compreg, on the other hand was not approved in the cup test of water over 24 h, nor with slightly acidic water for 1 h, which is more concerning.

Table 5: Surface resistance

Staining/scratch Test		Test standard	Results (rating figure[a] – overall rating)	
			FA-compreg	**BioRez-compreg**
Water	- 6h	EN 12720	**4** – Approved	**4** – Approved
	- 16h	EN 12720	**4** – Approved	**4** – Approved
	- 24h	EN 12720	**4** – Approved	**3** – Not approved
	- acidic, 1h, pH 5.5	ISO 105-E4	**5** – Approved	**3** – Not approved
	- alkaline, 1h, pH 8	ISO 105-E4	**5** – Approved	**5** – Approved
Paraffin oil, 24h				
	- without scratch	EN 12702	**4** – Approved	**5** – Approved
	- after scratch, 3N	SS 83 91 22	**5** – Approved	**5** – Approved
	- after scratch, 6N	SS 83 91 22	**5** – Approved	**5** – Approved
Ethanol	48% (aq.)	EN 12720	**5** – Approved	**5** – Approved
Coffee		EN 12720	**5** – Approved	**5** – Approved
Scratch resistance				
	- 3N	SS 83 91 17	**<0.5** mm – Appr.	**<0.5** mm – Appr.
	- 6N	SS 83 91 17	**<0.5** mm – Appr.	**<0.5** mm – Appr.

[a] 1 – severely damaged surface; 2 – damaged surface; 3 – visible spot; 4 – barely visible spot; 5 – no visible change

Test results from fire testing with the Cone calorimeter ISO 5660 at heat flux level 50 kW/m2 shows that the time to ignition is low for all board types, and is in general lower for spruce samples than for beech samples. Furthermore, both FA Compregs and BioRez-compregs had much higher RHRpeak (Rate of Heat Release per exposed area, peak value) than reference plywood boards. SEA (Specific smoke Extinction Area per mass loss, average during burning period) was low as expected for wood products. Based on results from the cone calorimeter test, both FA-compreg and BioRez-compreg can be classified as Euroclass D (the same as for unmodified plywood).

Analysis of VOC emissions

The emissions from Biorez-compreg samples exhibited minimal emissions (a sum of around 10 µg/m²h) already at the first measurement. This low emission rate is so low that only very few building materials for indoor use can match these. The emissions from the FA-compreg samples were dominated by a few furan compounds and summed up to over 10 time higher emission than for the Biorez-compreg. However, the emissions after 28 days of conditioning had decreased substantially (33-35 µg/m²h in total). However, the FA-compreg boards had not been post-cured before emission test.

Decay resistance

Results from the decay resistance testing are presented in Table 6. The decay resistance of FA-compreg boards was very high – all compreg test specimens were completely sound after the test, whereas the beech and pine wood controls were severely decayed. Birch and spruce reference plywood performed as bad as the solid wood specimens and even the tropical timber, iroko, performed badly although it is usually classified as durable to very durable.

Table 6: Corrected mass loss due to decay in three different soils according to ENV 807

Wood specie	Type of wood or board	Mass loss (in %) after 32 weeks in EN 807 test		
		Compost soil (soft rot and bact.)	**Brown rot soil** (Simlångsdalen)	**White rot soil** (Forest soil)
Beech	Solid wood control	39.7	55.4	14.4
Birch	Reference plywood	31.4	60.7	15.4
Birch	FA-compreg (WPG=33)	1.1	0.0	0.0
S. y. pine	Solid sapwood control	23.9	38.0	7.3
Spruce	Reference plywood	18.9	27.6	9.1
Spruce	FA-compreg (WPG=31)	1.6	1.5	1.9
Iroko	Tropical hardwood reference	23.1	19.7	9.7

CONCLUSIONS

The results listed below are valid for FA-compreg:

- High decay resistance
- Highly increased hardness
- High dimensional stability
- Acceptable tensile shear strength (bond line of good quality)
- Surface resistance to staining is acceptable
- High resistance to wear and scratching
- The same European reaction to fire class as untreated wood and plywood products
- Emissions of VOC slightly too high, but acceptable after post-curing step

The properties for BioRez-compreg is generally slightly poorer but this is probably mainly due to the lower WPG. However, at higher WPG levels other problems (mainly of esthetical character) occurred with the BioRez-compreg.

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