Influence of Acid Catalysts on Bending Strength of Furan Pre-polymer Modified Wood after Ageing

M.E. van der Zee[1], B.F. Tjeerdsma[1], H. Hoydonckx[2], & R. Jackson[1]

[1]SHR, Nieuwe Kanaal 9b, 6709 PA Wageningen, the Netherlands [email: m.vanderzee@shr.nl]

[2]TransFurans Chemicals, Industriepark, Leukaard 2, B-2440 Geel, Belgium [email: hans.hoydonckx@transfurans.be]

Keywords: Acid catalysts, ageing, furan pre-polymers, mechanical properties

ABSTRACT

In many modification treatments acids are formed or used as catalysts. In the past wood treated with acids, more specifically with phosphoric acid as fire retardant agent, was found to disintegrate in combination with heat and humidity. High moisture content in the wood enhances proton activity and induces hydrolytic cleavage of (hemi)cellulose. A standardised test was developed (ASTM D5664) to determine the effect of acid containing treatments on the strength properties of wood after ageing at high temperatures in a humid environment. For the work described here, wood was treated with a furan pre-polymer resin in combination with different acid catalysts. In order to determine the effect of the acid independent from the furan pre-polymer, the pure acids were also used in aqueous solutions. As reference, wood treated with phosphoric acid was used as this acid caused the structural problems in the past. Treated and untreated Scots pine sapwood and Radiata pine samples were aged at elevated temperatures and humidity for maximum 108 days. MOE and MOR were determined and changes caused by the acid under the influence of the ageing were calculated. The results of the tests show that in general the furan pre-polymer treatment increases the strength properties, irrespective of ageing or the type of acid catalyst used. When used alone, the (acid) catalyst itself has a negative effect on the strength properties with a reduction of the bending strength of 0% to over 50%. The results show the positive influence of a furan pre-polymer system, furan in counteracting any negative impact of acid on the strength properties of wood.

INTRODUCTION

Acids are present in wood in many different forms. They exist in raw material, brought into to wood for modification or treatment purposes or can be produced *in situ.* In thermal treated acetic acid and formic acid are formed (Sundqvist *et al.* 2006, Tjeerdsma and Militz 2005). In other modification treatments acids are formed in the process as well. For example during the acetylation of wood acetic acid is formed from the reaction of acetic anhydride and the cell wall hydroxyl groups. Although, the acetic acid is removed as much as possible traces will always remain within the wood. In modification processes that are based on polymerizing resins, acids are often used as catalysts as is also the case with the treatment with the furan pre-polymer resin (Van der Zee *et al.* 1998). Acids have the disadvantage that they can hydrolyse the polysaccharides in wood. Sometimes this is an desired effect, for instance in the production of ethanol from lignocellulosic materials for biofuals (Li *et al.* 2008, Iranmahbooba *et al.* 2002).

However, often structural damages are not desired. In the past constructions treated with phosphoric acid of fire retardant have been known to collapse due to strength loss of the timber. As a result present fire retardant agents used in the USA in wood for structural purposes need to pass the test described in ASTM D5664, where treated wood samples are subjected to ageing at elevated temperature an humidity. Recently experiments have been carried out to investigate the effect of phosphoric acids and other fire retardant agents on the strength properties. Lebow and Winandy (1999) showed that acidity of treated wood greatly effects the strength properties.

Although the acid concentration in this fire retardant treated timber is high as the concentration in the treatment solutions is relatively high, low concentrations can result in hydrolysis as well and thereby in strength reduction. Thermally treated wood is known to have reduced strength properties compared to the original untreated specimen (Boonstra and Tjeerdsma 2006, Sundqvist *et al.* 2006). In the ongoing investigation of the properties and possibilities of furan resin treated wood the question arose what catalyst to use. Acid catalysts were used in the earlier experiments however the choice of catalyst was still open for discussion. The current investigation has been set-up in order to screen different catalysts for their impact on the strength properties of wood in combination with a modification treatment and to investigate the impact of furan resin on the proclaimed negative effect of acid in wood in time during ageing.

MATERIALS AND METHODS

The experiments followed the ASTM standard D5664 with some exception: the number of specimen was limited to ten for each condition and the test was carried out on treated and untreated small clear samples instead of cut form larger treated boards. Scots pine sapwood (*Pinus sylvestris*) and Radiata pine (*Pinus radiate*) samples 20x20x±1400 mm were produced. These samples were cut into four paired samples of 350 mm length. Bundles of 4 times 10 samples were made each consisting of 4 times 6 Radiata pine samples and 4 times 4 Scots pine samples. The MOE of all samples was determined non-destructively. Three of the four paired bundles were treated, the fourth bundle remained untreated.

The wood was impregnated (0.5 h vacuum, 1 h 8 bar) with the chemicals shown in Table 1. A 20% (w/w) furan pre-polymer solution was used in combination with 1% (w/w) catalyst. The catalyst concentration is based on the total solution. This results in 5% catalyst based on furan pre-polymer concentration.

In order to investigate the influence of the catalysts, pure chemicals were dissolved in water in a 1% (w/w) solution. A 7% phosphoric acid concentration was included as reference as failure of this fire retardant treatment was the reason to develop the test standard ASTM D5664.

The catalyst treated samples were dried at 35 °C in a ventilated oven for 24 hours and conditioned at 20 °C, 65% RH. The furan pre-polymer treated samples were cured at 130 °C for 16 h after drying and subsequently conditioned at 20 °C, 65% RH. The MOE of all samples was determined non-destructively in a 3-point bending test before ageing.

Table 1: Concentration of chemicals used.

Catalyst		Catalyst concentration	
		+ 20% furan pre-polymer resin	
Maleic anhydride	MA	1%	1%
PTSA	PTSA	1%	1%
Acetic acid	AA	1%	1%
Phosphoric acid	PA	1%	1%
Phosphoric acid	PA 7%		1%

Treated and untreated samples were aged at 66 °C, > 50% RH for 0, 36±3, 72±3 or 108±3 days. After conditioning at 20°C, 65% RH the MOE and MOR were determined in a 3-point bending test following DIN 52 186. Changes in elasticity of the treated and untreated samples by ageing were calculated from the MOE determined after treatment but before ageing and the MOE determined after ageing.

RESULTS AND DISCUSSION

Wood treated with 20% furan pre-polymer solution becomes a deep reddish brown colour. An average weight percent gain (WPG) of the furan pre-polymer treated samples of approximately 20% was found for all treatments (Figure 1). No significant differences were found between Scots pine and Radiata pine.

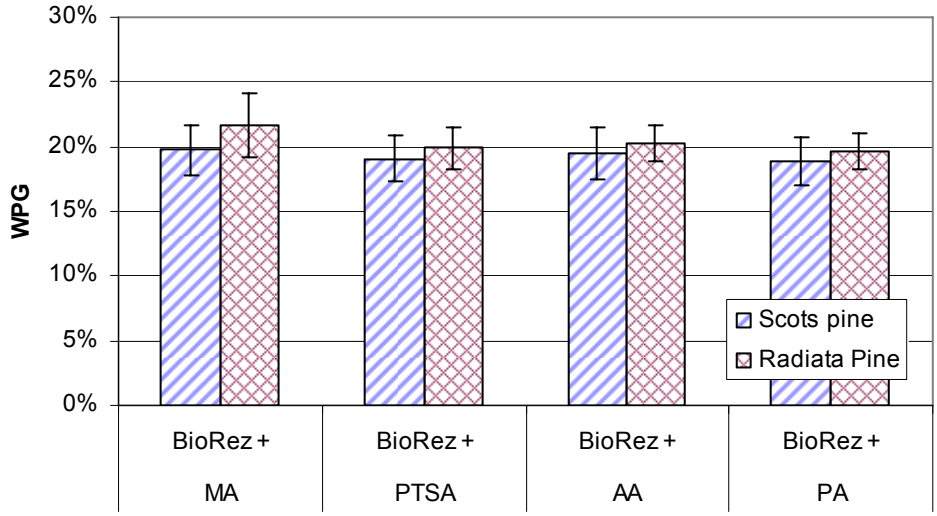

Figure 1: Average weight percent gain (WPG) of the furan pre-polymer treated samples

Modulus of Elasticity MOE

After treatment the MOE was determined non destructively before the samples were set to age. After the destined ageing time the MOE and bending strength were determined. The changes in elasticity by ageing are shown in Figures 2 (Scots pine) and 3 (Radiata pine).

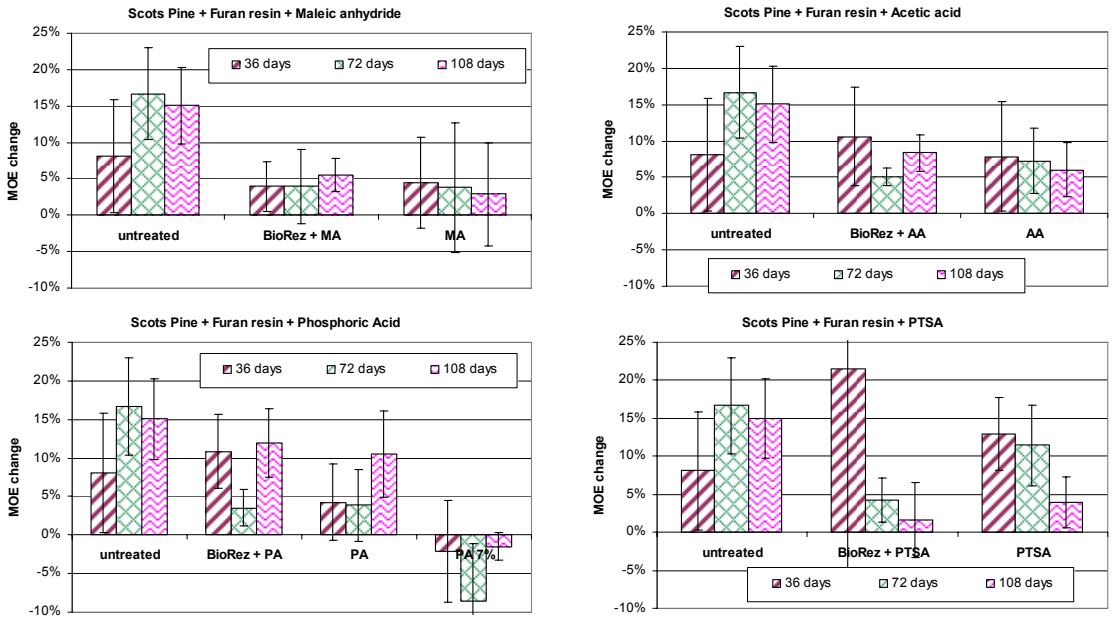

Figure 2: Changes in Elasticity (MOE) before and after ageing of treated and untreated Scots pine

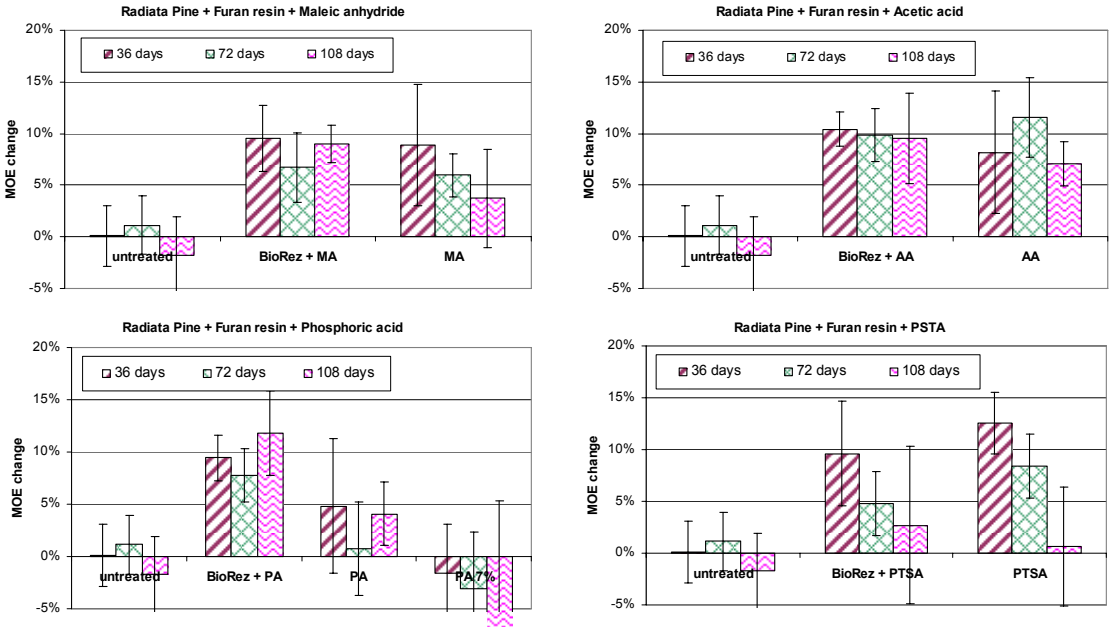

Figure 3: Changes in Elasticity (MOE) before and after ageing of treated and untreated Radiata pine

The elasticity of untreated Radiata pine was not affected by ageing. The MOE of Scots pine increased over time. Except for the wood treated with the 7% phosphoric acid solution, the MOE of the treated wood increased as well although the MOE increase of the acid treated wood diminished over time. After 108 days the MOE increase was less compared to the 36 days aged samples. Wood treated with strong acids like PTSA or with 7% phosphoric acid showed a decrease in MOE-change. Extending the ageing period is believed to result in a loss of MOE.

Bending strength, MOR

The bending strength (MOR) of treated and untreated Scots pine (Table 2) and Radiata pine (Table 3) before and after ageing is given below. The data are also graphically presented in Figures 4 and 5 respectively. For easy comparison, the untreated data are shown in all graphs.

Table 2: MOR [N/mm^2] of treated and untreated aged Scots pine samples

	start	Ageing at 66 °C, >50% RH		
		36 days	72 days	108 days
Untreated	85,2 ± 11,8	97,7 ± 9,0	99,9 ± 20,1	105,7 ± 13,3
Furan pre-polymer resin + MA	101,8 ± 12,4	92,1 ± 11,8	110,0 ± 10,1	110,2 ± 29,2
MA	83,2 ± 10,5	89,0 ± 10,4	80,8 ± 17,9	66,8 ± 35,7
Furan pre-polymer resin + AA	118,7 ± 7,5	111,9 ± 17,8	114,7 ± 16,6	123,1 ± 11,1
AA	82,4 ± 11,5	100,2 ± 12,3	106,4 ± 14,9	93,1 ± 9,4
Furan pre-polymer resin + PA	103,2 ± 13,2	99,9 ± 7,2	114,2 ± 25,6	120,9 ± 9,2
PA	80,1 ± 6,1	67,6 ± 11,0	73,2 ± 23,4	80,3 ± 29,8
PA 7%	44,4 ± 11,6	42,2 ± 14,3	47,3 ± 18,2	55,1 ± 22,8
Furan pre-polymer resin + PTSA	113,6 ± 8,5	90,3 ± 20,3	118,6 ± 20,8	121,1 ± 8,1
PTSA	78,4 ± 10,1	76,1 ± 16,7	74,8 ± 27,1	70,4 ± 18,7

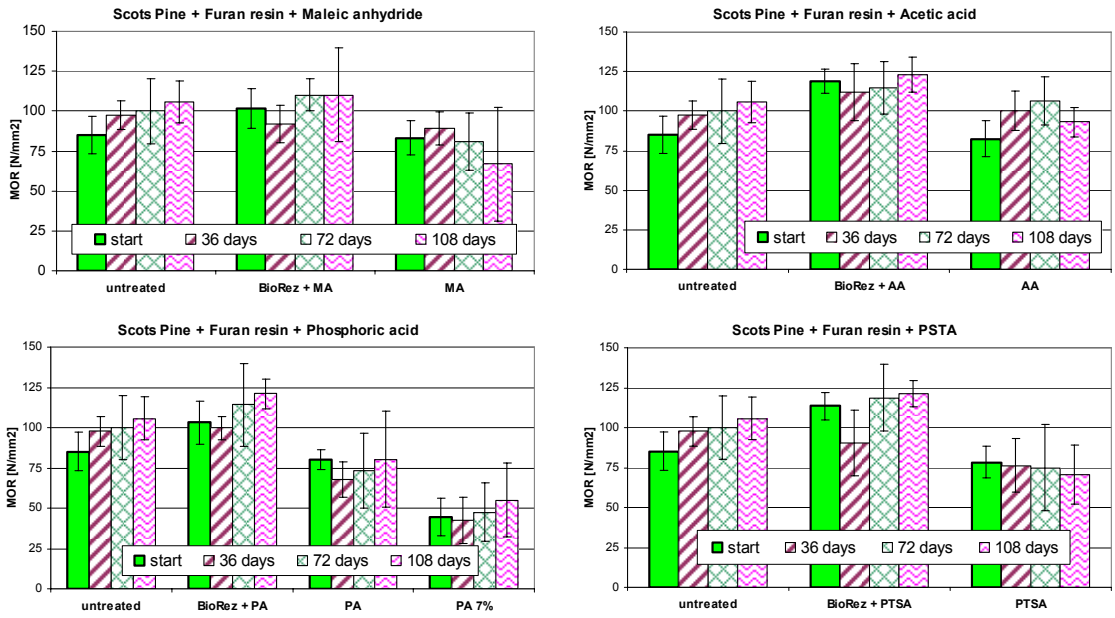

Figure 4: Bending strength of treated and untreated Scots pine after ageing

Treatment with catalysed furan pre-polymer resin increases the bending strength in Scots pine. A substantial average increase of more than 25% was found. In Radiata pine an increase was not always significantly present. The variance in the MOR in Radiata pine is believed to be caused by the wide annual rings in relation to the sample sizes (20

x 20 mm cross section). Impregnation and subsequent drying with pure catalysts solutions showed a decrease for all catalysts used. Increasing the phosphoric acid concentration to 7% (w/w), resulted in a dramatic reduction of the bending strength of ±50% in both Scots pine and radiata pine. On average, ageing has less impact on the bending strength compared to the treatment itself. In combination with catalysed furan pre-polymer resin, no significant change could be found in Scots pine as a result of ageing. In some combinations radiata pine showed a higher bending strength after 36 days. However, significant differences were not established between the treated samples before and after 108 days of ageing.

Table 3: MOR [N/mm^2] of treated and untreated aged Radiata pine samples

	start	**Ageing at 66 °C, >50% RH**		
		36 days	**72 days**	**108 days**
Untreated	94,9 ± 9,0	106,1 ± 18,7	105,3 ± 15,4	98,3 ± 16,4
Furan pre-polymer resin + MA	105,0 ± 9,7	92,9 ± 21,5	129,1 ± 19,2	106,2 ± 14,5
MA	82,8 ± 5,0	79,1 ± 16,0	71,9 ± 21,4	70,3 ± 17,6
Furan pre-polymer resin + AA	106,7 ± 10,3	133,8 ± 26,1	124,4 ± 16,6	112,4 ± 16,3
AA	84,9 ± 10,1	84,4 ± 20,1	81,5 ± 12,4	87,1 ± 16,5
Furan pre-polymer resin + PA	104,2 ± 7,1	127,0 ± 22,7	117,8 ± 17,2	98,1 ± 17,3
PA	79,4 ± 7,4	75,8 ± 20,0	67,9 ± 19,8	54,5 ± 18,1
PA 7%	44,5 ± 8,8	38,6 ± 12,3	42,3 ± 12,4	33,9 ± 13,9
Furan pre-polymer resin + PTSA	90,0 ± 35,3	124,2 ± 25,4	89,2 ± 43,5	96,8 ± 35,4
PTSA	72,4 ± 8,5	60,9 ± 16,1	49,0 ± 12,7	54,9 ± 19,1

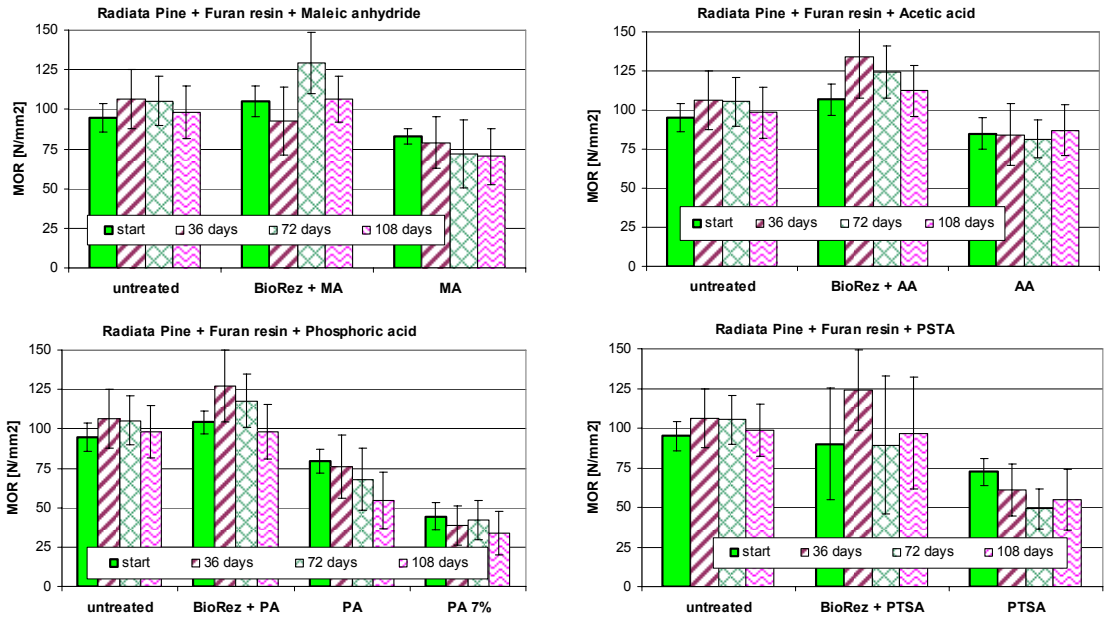

Figure 5: Bending strength of treated and untreated Radiata pine after ageing

Examples of the appearance of the wood sample after the treatement and 108 days of ageing are given in Figure 6. The furan pre-polymer treated wood on the left remained a similar colour compared to freshly treated wood. The wood treated with the catalyst solutions discoloured at elevated temperatures and humidity. The largest discoloration was found with the 7% phosphoric acid treated samples.

The acids had a negative influence on the bending strength. The strength loss already occurred after the treatment, before aging at elevated temperatures and humidity. The presence of the acids combined with drying at 35 °C already induced the strength loss. The higher the acidity the larger the strength loss. The former method to reduce flammability of wood by impregnation with pure phosphoric acid solutions as fire retardant can lead to damage of wooden structures with strength losses of 50%. In thermally treated wood, although lower in concentration, the *in situ* produced acids cause strength reduction in the processed timber (Boonstra *et al.* 2007). Remarkably, the expected decrease of the bending strength by the acid, is reversed in the presence of the furan pre-polymer resin: the bending strength increases. As biological material that polymerises within the wood structure is incorporated in the samples, higher strength properties could be expected. However, the acids added as catalysts, are also introduced into the wood. Hydrolysis of the polysaccharides could therefore occur. Still, the presence of the pre-polymer prevents this. The buffering capacity of the furan pre-polymer solution seems the most likely mechanism. As the bending strength in the cured samples does not decrease with increased aging the stabilising capacity of the polymerised furan resin is still present. The exact mechanism is not yet investigated, possibly the wood polysaccharides are shielded from the presence of the acids by the polymer.

Furan pre-polymer resin + 1% phosphoric acid | 1% phosphoric acid | 7% phosphoric acid

Figure 6 Examples of broken phosphoric catalysed samples after 108 days ageing

CONCLUSIONS

Acids in wood decrease the bending strength of wood stored at elevated temperature and humidity by hydrolysis of the polysaccarides. A decrease of 10 – 50% was found depending on type of acid and acid concentration after exposition to the warm and humid climate conditions. In a furan pre-polymer system, furan pre-polymer resin, the negative impact of the acids catalysts was found to be absent. In combination with any of the catalysts, the bending strength showed a permanent increase irrelevant of the ageing at an elevated temperature. The long-term increase in bending strength in furan

pre-polymer treated wood enhances the products possibilities. Based on the current study all four acids showed potential to be used as catalyst in a furan resin treatment of wood without the risk of unacceptable strength losses.

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