Title: Durability of acetylated Radiata Pine – investigation of the resistance against brown-, white- and soft rot fungi

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Summary

Titan Wood B.V. will start production of Accoya™ in Arnhem, the Netherlands. The technology behind Accoya™ wood is based on wood acetylation of Radiata Pine. Acetylation of wood is a chemical modification process that is known to significantly improve the dimensional stability, UV-stability and durability (resistance against brown-, white- and soft rot fungi). It is known that there is a strong relation between the durability of the wood and the degree of acetylation. In this respect Radiata Pine has been acetylated to various degrees and has been investigated according to EN 113 and ENV 807 to determine its resistance against fungal decay by brown-, white-, and soft rot fungi. The resulting durability class has been determined according to EN 350-1.

The results of the study show that the minimum degree of acetylation (acetyl content) to classify acetylated Radiata Pine as durability class 1, which is the specification of Accoya™, can be determined. At this degree of acetylation the variation in fungal decay within the samples is decreased, resulting in a better reliability of Accoya™ in respect to durability compared to that of untreated Radiata Pine.

Contents

1. Assignment

Titan Wood B.V. will start production of Accoya™ in Arnhem, the Netherlands. The technology behind Accoya™ wood is based on acetylation of Radiata Pine. Acetylation of wood is a chemical modification process that is known to significantly improve the dimensional stability, UV-stability and durability (resistance against brown-, white- and soft rot fungi). Numerous publications[1, 2, 3, 4, 5, 6, 7] have shown that there is a strong relation between the durability of the wood and the degree of acetylation, which can be expressed in Weight Percent Gain or acetyl content. As a result of this relation, the quality (in respect to durability) of each individual board can be determined on basis of the degree of acetylation.

In this respect Titan Wood B.V. appointed SHR Timber Research to investigate the durability of Radiata Pine which has been acetylated to various degrees. The durability has been investigated according to EN 113 and ENV 807 in which the resistance against fungal decay by brown-, white-, and soft rot fungi is studied. The resulting durability class has been determined according to EN 350-1.

The objective of the study is to determine the minimum degree of acetylation (acetyl content) when acetylated Radiata Pine can be classified as durability class 1, which is the specification of Accoya™.

This research is part of a research scheme that has been set-up in co-operation with a Dutch certification body, SKH, and research institute, SHR Timber Research to independently prove the quality of Accoya™ wood. This scheme consists of:

1. KOMO certificate BRL 0605 “Modified Timber”. Here the emphasis is on the uniformity and reproducibility of the production process, as well as on Titan Wood’s quality system.
2. Fulfilment of the (material) requirements as listed for in use of certified Dutch joinery (SKH Publication 97-04). Emphasis is on material properties, such as durability, dimensional stability and paintability.

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[3] *Hill, C.A.S. (2006).Wood Modification. Chemical, Thermal and Other Processes. 1st edition. John Wiley & Sons. ISBN-10: 0-470-02172-1.*

[4] *Larsson-Brelid, P.; Simonson, R.; Bergman, O. (1997). Resistance of acetylated wood of biological degradation. Evaluation of field test. The International Research Group on Wood Preservation. 28th Annual Meeting, Whistler, Canada. Document No. IRG/WP 97-30139.*

[5] *Mohebby, B.; Militz, H. (2002). Soft rot decay in acetylated wood. Chemical and anatomical changes in decayed wood. The International Research Group on Wood Preservation. 33rd Annual Meeting, Cardiff, Wales. Document No. IRG/WP-02-40231.*

[6] *Rowell, R.M.; Dawson, B.S.; Hadi, Y.S.; Nicholas, D.D.; Nilsson, T.; Plackett, D.V.; Simonson, R.; Westin, M. (1997). Worldwide in-ground stake test of acetylated composite boards. The International Research Group on Wood Preservation. Document No. IRG/WP 97-40088.*

[7] *Takahashi, M.; Imamura, Y.; Tanahashi, M. (1990). Effect of acetylation on decay resistance of wood against brown-rot, white-rot and soft-rot fungi. The International Research Group on Wood Preservation. 20th Annual Meeting Congress Centre, Lappeenranta, Finland Document No. IRG/WP/3540.*

2. Execution of the test

2.1 Production of the samples

Radiata Pine (*Pinus radiata*) boards of 25 x 150 x 2000 mm (thickness x width x length), selected to meet the criteria (orientation of annual rings) expressed in the EN 113 and ENV 807, were acetylated to various degrees by Titan Wood. In total 7 batches, each batch with a different acetylation process, were performed containing 12 boards. Each board and batch was uniquely coded. After acetylation the boards were conditioned at 65 % RH and 20°C over a period of 3 weeks. In addition to the acetylated Radiata Pine, untreated Radiata Pine was provided as well.

After conditioning, the samples for the EN 113 test (dimension of 15 x 25 x 50 mm) and the ENV 807 test (5 x 10 x 100 mm) were prepared according the following method:

- The outer 50 cm length and the outer 20 mm width of both sides of a board were excluded from the sampling area. This to avoid any possible edge effects upon the results.
- This sampling area was cut into two strips of 30 mm wide (EN 113 samples) and one strip of 20 mm wide (ENV 807 samples). This was performed in such a way that the annual ring orientation complied with the requirements of EN 113 and ENV 807 respectively.
- The 30 mm wide strips were planed on both sides to a dimension of 25 mm width and 15 mm thick. Subsequently the samples were cut to a length of 50 mm, and were all uniquely coded.
- The 20 mm wide strip was planed on both sides to a dimension of 10 mm width and 5 mm thick. The samples were then cut to a length of 100 mm, and uniquely coded.

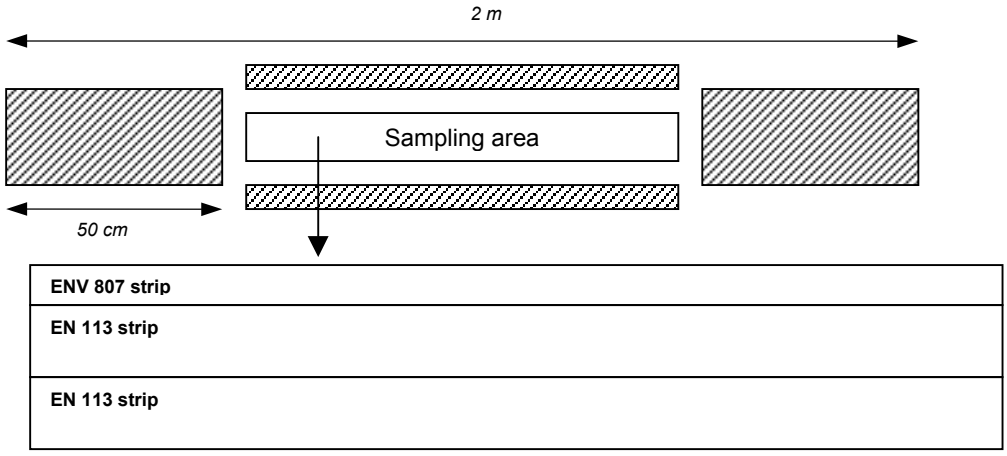

Figure 1. Preparation of strips from the (acetylated) boards.

Per board, approximately ten EN 113 samples and four ENV 807 samples were produced. One EN 113 sample was used to determine the acetyl content (degree of acetylation) as described in paragraph 2.2. The remaining samples were leached according to EN 84 (see paragraph 2.3) and used to perform the EN 113 and the ENV 807 test as described in paragraph 2.4 and 2.5 respectively.

2.2 Determination of the acetyl content

The acetyl content of one EN 113 sample of each board was determined according to the standard HPLC-method of Titan Wood. The sample was ground to wood meal and merged into water in order to convert any residual acetic anhydride into acetic acid. The sample was dried in an oven at 103 ºC for the duration of 16 hours to remove the water and any residual acetic acid. The acetyl content of the sample was hydrolysed and quantified by liquid chromatography (HPLC). The acetyl content of acetylated wood is expressed as:

[1] $$Acetyl\ Content = \frac{mass\ of\ acetyl\ groups\ in\ oven\ dry\ wood}{mass\ of\ oven\ dry\ wood} \quad [\%]$$

2.3 Leaching of the samples (EN 84)

All test samples were leached according the EN 84 leaching test. The samples were impregnated with distilled water. Subsequently the samples were exposed to a five times bigger volume of distilled water than the wood volume. The distilled water was refreshed nine times over a period of 14 days. Finally the samples were dried at 30 °C over 2 days and conditioned at 20 °C, 65% RH to equilibrium moisture content.

2.4 Laboratory test resistance against brown- and white rot fungi (EN 113)

Based on the degree of acetylation, fifty boards were selected in order to obtain an even range in acetyl content. After leaching according to EN 84 and conditioning, the samples of these boards were used to perform the EN 113 for five different fungus species. For each fungus species an adjacent sample within the board was used. In addition, five (untreated) Radiata Pine sapwood (*Pinus radiata*) samples per fungus were tested. As references, Scots Pine sapwood (*Pinus sylvestris*) samples were used. For each board (acetylated Radiata Pine, untreated Radiata Pine, reference Scots Pine), one sample was used to determine the (initial) moisture content by weighing and drying (oven of 103°C until constant weight). This moisture content was used to calculate the dry weight of all (individual) samples before the test. The samples were placed in culture vessels, which contained sterilised culture medium (agar) which was inoculated with one of the following wood destroying basidiomycetes:

- *Coniophora puteana* (cellar fungus, wet rot fungus, cellar rot fungus)
- *Coriolus versicolor* (Turkey tail fungus, shelf fungus)
- *Gloeophyllum trabeum* (conifer mazegill)
- *Poria placenta* (pore fungus)
- *Serpula lacrimans* (true dry rot fungus)

In each culture vessel two acetylated samples and one reference sample (Scots Pine sapwood) were placed. These culture vessels were placed in a culture chamber (22°C, 70% RH) for a period of 16 weeks. After the exposure period, the samples were removed from the culture vessels and weighed before and after drying at 103 °C for 24 hours.

Finally the mass loss of each individual sample due to fungal decay was calculated on the basis of the dry weight before and after the test (see equation 2). The moisture content of the samples was calculated on the basis of the weight before and after drying (see equation 3).

[2] $$ML = \frac{(m_0 - m_t)}{m_0}$$

with:

ML	*mass loss*	*[%]*
m_0	*dry weight of the sample before the test*	*[g]*
m_t	*dry weight of the sample after the test*	*[g]*

[3] $$mc = \frac{(m_{tw} - m_t)}{m_t}$$

with:

mc	*moisture content*	*[%]*
m_{tw}	*wet weight of the sample before oven drying*	*[g]*
m_t	*dry weight of the sample after oven drying*	*[g]*

2.5 Laboratory test resistance against soft rot fungi (ENV 807)

The ENV 807 method II test was performed with two samples per board of the same fifty boards that were selected for the EN 113 test. In addition 10 samples originating from 5 boards of (untreated) Radiata Pine sapwood (*Pinus radiata*) samples were tested. As references fifty samples of Scots Pine sapwood (*Pinus sylvestris*), Beech (*Fagus sylvatica*), Western Red Cedar (*Thuja plicata*) and Angelim Vermelho (*Dinizia excelsa*) were used. The (initial) moisture content that was determined for each board (see paragraph 2.4) was used to calculate the dry weight of all (individual) test samples before the test. The samples were placed in containers with specially prepared soil of known moisture content and water holding capacity. These containers were placed in a (dark) culture chamber (27°C, 95% RH). After an exposure period of 12 weeks additional Scots Pine sapwood samples (virulence control samples) indicated a more than sufficient mass loss (mass loss ≥20%) to validate the test. Half of the samples were removed from the soil containers and weighed before and after drying at 103 °C for 24 hours. The mass loss of each individual sample due to fungal decay was calculated on the basis of the dry weight before and after the test (see equation 2). The moisture content of the samples was calculated on the basis of the weight before and after drying (see equation 3). The second half of the samples was “harvested” after 20 weeks of soil exposure, and used to determine the mass loss after this exposure period.

2.6 Durability classification

The durability of the acetylated wood samples is classified according to EN 350-1, in which the mass loss of the test specimens (acetylated wood) is compared with the mass loss of the reference wood species Scots Pine sapwood (see equation 4). On the basis of the x-value the durability classification is made according to Table 1.

[4] $$x - value = \frac{average\ corrected\ mass\ loss\ of\ test\ specimens}{average\ mass\ loss\ of\ reference\ specimens}$$ [-]

Table 1. Durability classification according to EN 350-1 for laboratory tests.

Durability class	Description	x-value
1	Very durable	$x \leq 0.15$
2	Durable	$0.15 < x \leq 0.30$
3	Moderately durable	$0.30 < x \leq 0.30$
4	Slightly durable	$0.60 < x \leq 0.90$
5	Not durable	$0.90 < x$

Since the tests have been performed with various degrees of acetylated wood, the mass loss was calculated for each individual sample. This mass loss was used to determine the x-value per (individual) sample. The results (mass loss and x-value) have been plotted in relation to the acetyl content of the samples. Various mathematical regression methods have been applied to determine the best fit of the results, and to be able to calculate the minimum level of acetylation to classify Accoya™ as durability class 1 (at x-value = 0.15).

3. Results

3.1 Laboratory test resistance against brown- and white rot fungi (EN 113)

In Figure 2 the mass loss in relation to the degree of acetylation (acetyl content) is shown for the tested fungi according to EN 113. In Table 2 the average moisture content and mass loss of the reference wood species (Scots Pine sapwood) per fungus are shown. The mass loss of the reference wood species with *Coniophora puteana*, *Coriolus versicolor* and *Serpula lacrimans* is sufficient to comply with the requirements of the tests. The mass loss found with *Poria placenta* and *Gloeophyllum trabeum* is slightly to low. However, as the deviation within the results for *Poria placenta* is minimal and *Gloeophyllum trabeum* is not the decisive fungus for durability classification, the tests can be considered as valid.

Table 2. Average moisture content and mass loss of the reference wood species (Scots Pine sapwood) after 16 weeks fungal decay (EN 113). Between brackets the standard deviation is shown.

Fungal species	Moisture content [%]	Mass loss [%]	Minimum mass loss required to valid the test [%]
Coniophora puteana	65.5 *(10.7)*	40.5 *(19.8)*	20
Coriolus versicolor	52.6 *(17.2)*	28.9 *(9.4)*	15
Gloeophyllum trabeum	47.6 *(7.4)*	17.3 *(4.4)*	20
Poria placenta	67.9 *(14.5)*	19.4 *(6.2)*	20
Serpula lacrimans	53.1 *(21.9)*	31.7 *(20.0)*	20

The mass loss of untreated Radiata Pine sapwood, the x-value and the apparent durability class are shown in Table 3. The values are averages of 5 samples. In order to convert the mass loss of the samples to durability, the x-value was calculated for each sample individually. In Figure 3 these x-values are plotted in relation to the acetyl content.

Table 3. Average mass loss, the x-value, and the apparent durability class calculated from the individual fungi of untreated Radiata Pine sapwood after 16 weeks fungal decay (EN 113). Between brackets the standard deviation is shown

Fungal species	Mass loss [%]	x-value [-]	Durability class
Coniophora puteana	35.3 *(10.3)*	0.87	4
Coriolus versicolor	25.8 *(2.0)*	0.89	4
Gloeophyllum trabeum	8.7 *(4.1)*	0.50	3
Poria placenta	11.5 *(1.3)*	0.59	3
Serpula lacrimans	31.2 *(22.9)*	0.99	5
		Overall	5

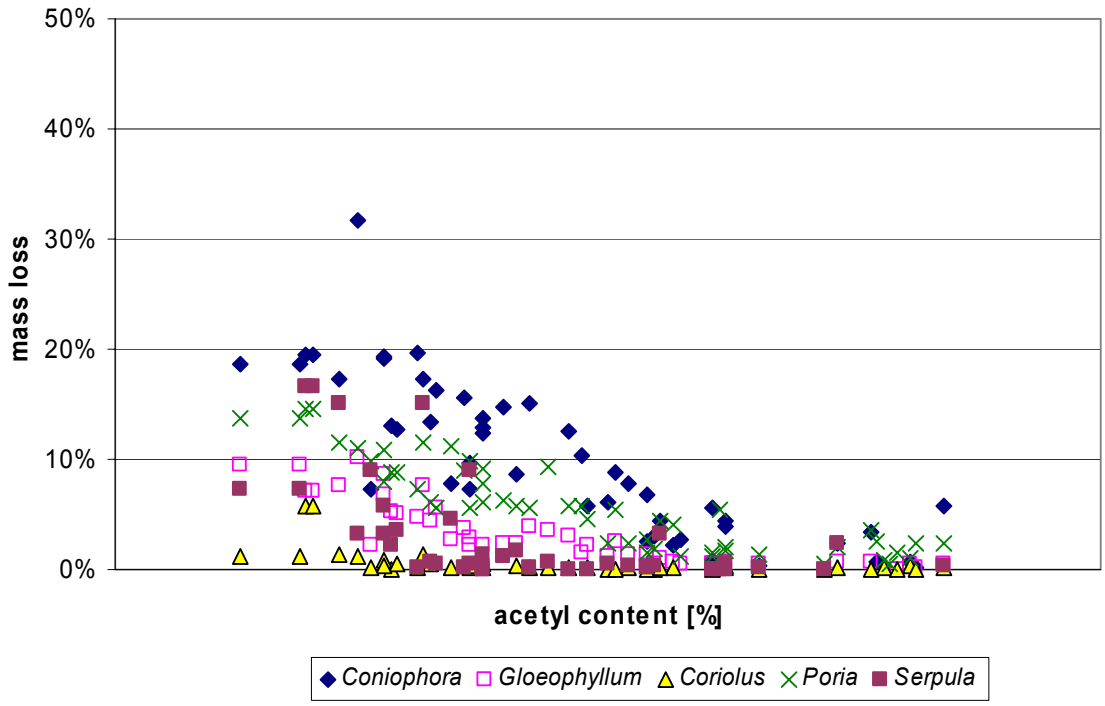

Figure 2. Mass loss of acetylated Radiata Pine caused by basidiomycetes (EN 113 test) in relation to the acetyl content.

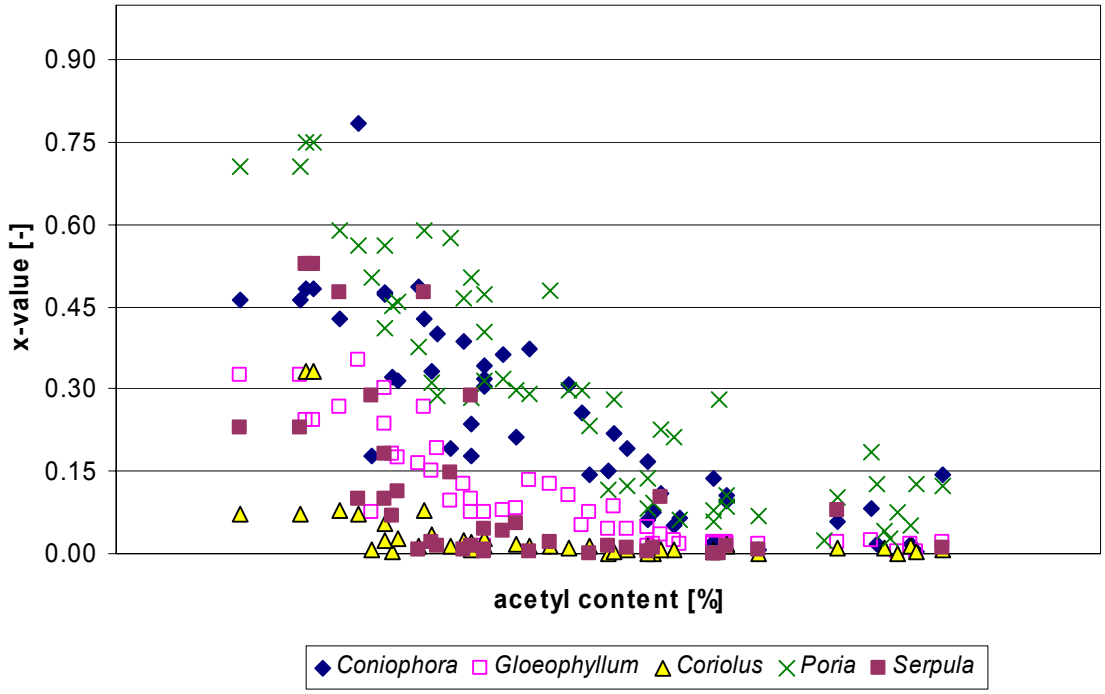

Figure 3. X-values of acetylated Radiata Pine, tested according to EN 113 in relation to the acetyl content.

3.2 Laboratory test resistance against soft rot fungi (ENV 807)

In this paragraph the results of 12 weeks soil exposure are presented. The mass loss of the reference species (Scots Pine sapwood) after this period of exposure was more than the required 20% to valid the test. Therefore these results were used to perform the durability classification.

The results after 20 weeks soil exposure show the same trends as can be seen for the 12 weeks soil exposure.

In Figure 4 the mass loss after 12 weeks of soil exposure is plotted in relation to the degree of acetylation (acetyl content). In Table 4 the average moisture content and mass loss of the reference wood species is shown. The values of Western Red Cedar, Scots Pine, Beech and Angelim Vermelho are averages of 25 samples, the values of untreated Radiata Pine are averages of 4 samples. The determined durability classes for these reference wood species correspond to the expected values. This supports the validity of the test.

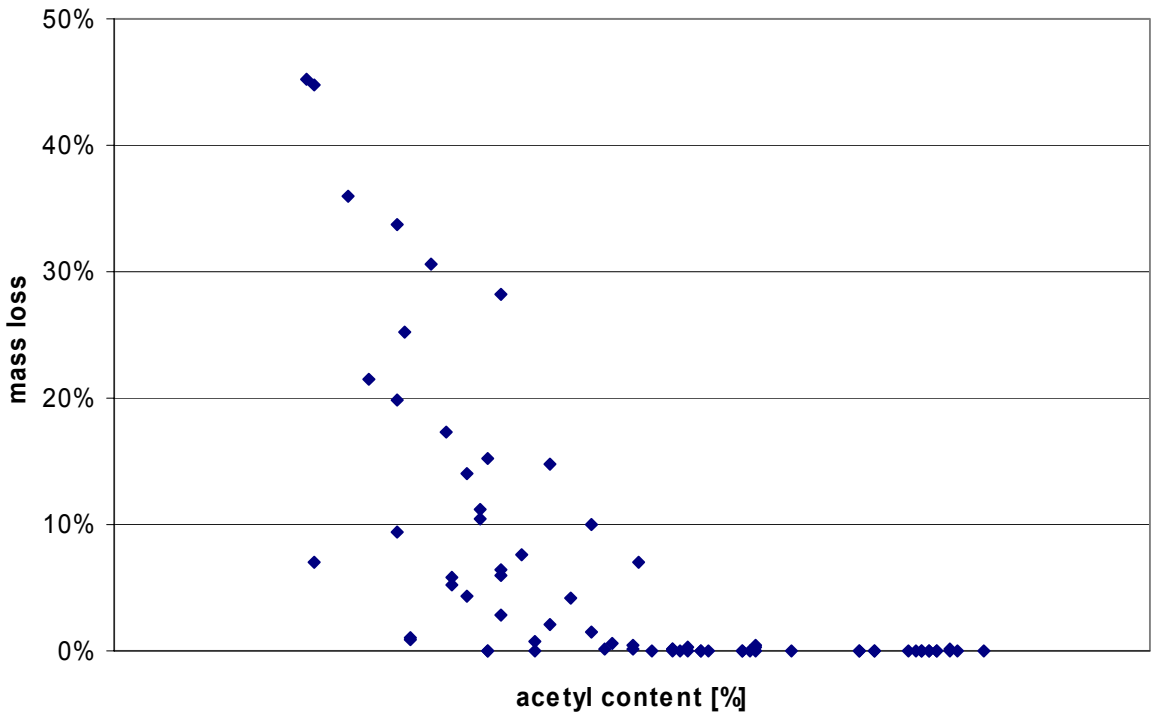

Figure 4. Mass loss of acetylated Radiata Pine caused by soft rot decay (ENV 807 test) after 12 weeks soil exposure in relation to the acetyl content.

Table 4. Average moisture content, mass loss, the x-value and durability classification of the reference wood species after 12 weeks soil exposure (ENV 807). Between brackets the standard deviation is shown.

Wood species	Moisture content [%]	Mass loss [%]	x-value [-]	Durability class
Angelim Vermelho	43.1 *(3.7)*	5.5 *(0.9)*	0.16	2
Beech	104.4 *(26.7)*	36.2 *(4.4)*	1.02	5
Western Red Cedar	42.9 *(9.2)*	2.1 *(1.0)*	0.06	1
Scots Pine sapwood	69.8 *(13.3)*	35.8 *(9.7)*	*1**	*5*
Untreated Radiata Pine	66.6 (6.8)	36.2 (13.8)	1.01	5

** The x-value of Scots Pine sapwood is 1 by definition as all samples are related to this value.*

In order to convert the mass loss of the samples to durability, the x-value was calculated for each sample individually. In Figure 5 these x-values are plotted in relation to the acetyl content.

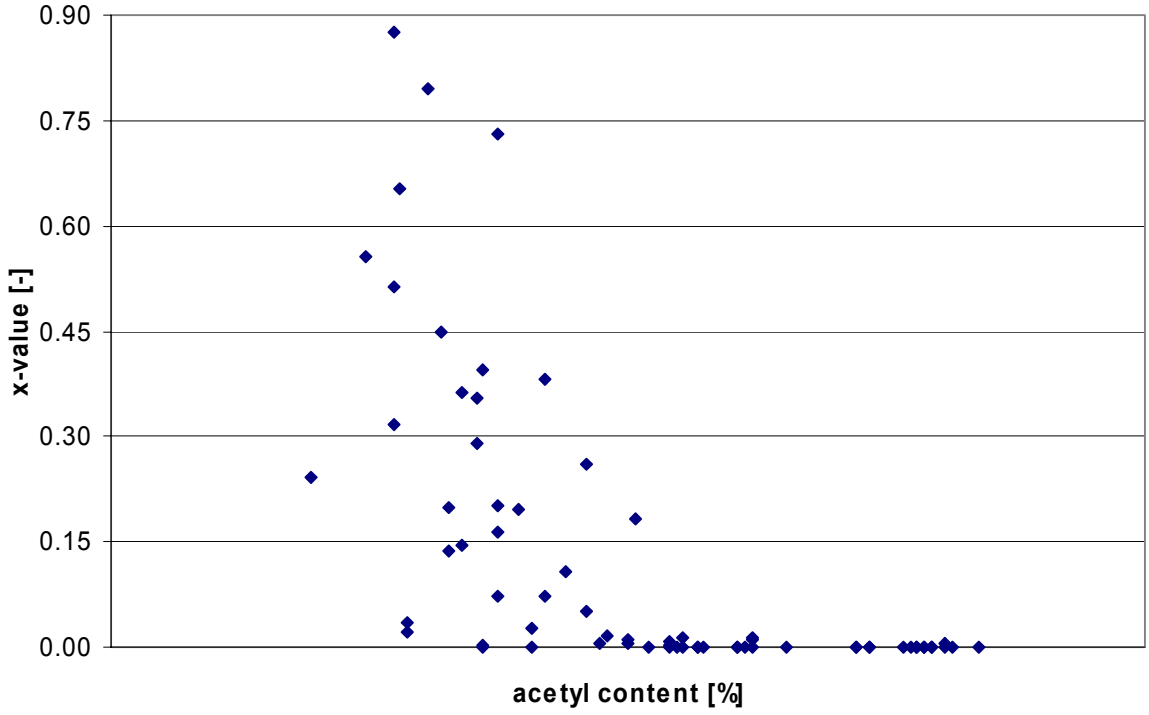

Figure 5. X-values of acetylated Radiata Pine, tested according to the ENV 807 in relation to the acetyl content.

4. Discussion and Durability classification

The results show that the most aggressive fungus for acetylated wood is the brown rot fungus *Poria placenta*. Therefore the results of this fungus are used to determine the threshold of the degree of acetylation for Accoya™ to be classified into durability class 1 (x-value ≤ 0.15).

In Figure 6 the x-value in relation to the degree of acetylation (acetyl content) is shown for *Poria placenta*. Various mathematical regression methods have been applied to determine the best fit of the results. The best fit to characterise the data was obtained with second order polynomial regression.

The variation within the results is caused by a number of factors:

- The natural variation within the wood
- The moisture content of the samples before the test was determined on a reference sample rather than the actual sample.
- The acetyl content of the samples was determined on a reference sample rather than the actual sample.
- Errors in the determination of the dimension, the weight and the acetyl content of the samples.

From the results it is evident that the variation for the untreated Radiata Pine samples is higher than those samples which are highly acetylated. In general the variation of the x-value between individual samples is decreasing with an increasing degree of acetylation (acetyl content). This illustrates that highly acetylated Radiata Pine has a more constant performance in respect to durability compared to that of untreated Radiata Pine.

Based on the fitted regression line in Figure 6 the threshold to obtain durability class 1 (x-value = 0.15) could be determined. The actual value is confidential.

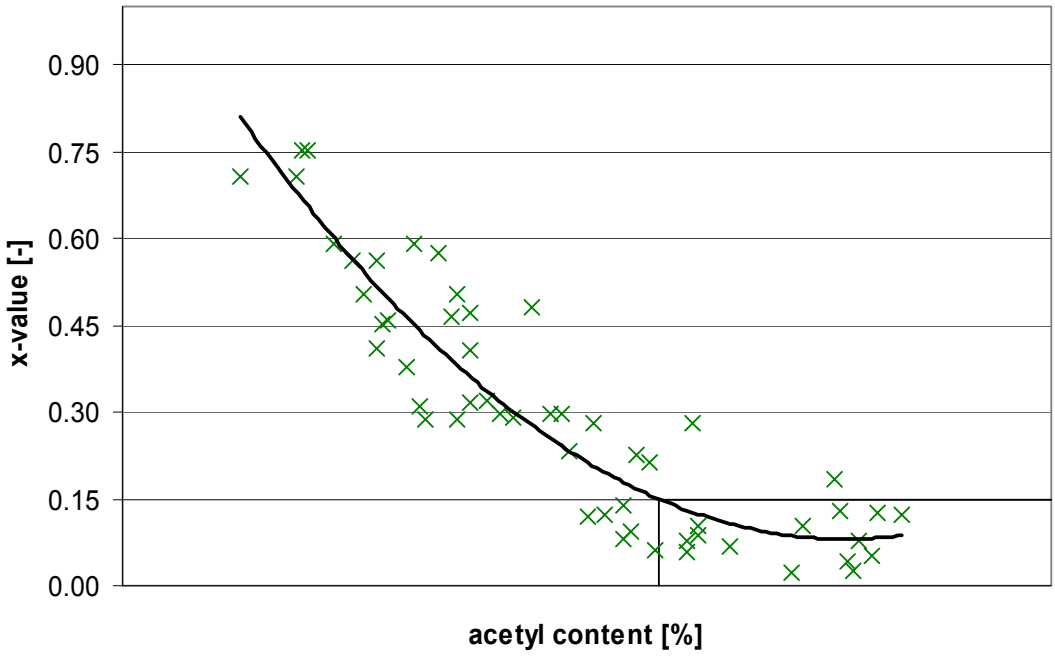

Figure 6. X-values of acetylated Radiata Pine in relation to the acetyl content, based on the EN 113 test with *Poria placenta*. The vertical line represents the mimimum acetyl content needed for durability class 1.

5. Conclusion

Acetylation can considerably increase the durability of Radiata Pine, and on the basis of the strong correlation found between the durability of the wood and the degree of acetylation, a threshold can be determined showing to which degree of modification (acetyl content) is required to classify acetylated Radiata Pine into durability class 1. At this degree of acetylation the variation in fungal decay within the samples is decreased, resulting in a better reliability of Accoya™ with respect to durability compared to that of untreated Radiata Pine.

References

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