Study Report

SR476 [2022]

Durability of polyurethane-based structural adhesives and bonded interfaces

Catherine Nicholson

Funded from the
Building Research Levy

1222 Moonshine Rd, RD1, Porirua 5381
Private Bag 50 908, Porirua 5240
New Zealand
branz.nz

ISSN: 1179-6197

Acknowledgements

The work related to the laminated samples formed the basis of a PhD study undertaken at the University of Auckland by Dr Zubin Karami, supervised by Dr Gary Raftery. Thanks also to Roger Stanford for sample preparation for FTIR spectroscopy.

Much of the data and figures related to the laminated samples in section 2.2 and 4 are reproduced from the published PhD thesis (Karami, 2020), except where previously unpublished work is indicated.

The contribution of materials to this research from industry is gratefully acknowledged.

Durability of polyurethane-based structural adhesives and bonded interfaces

BRANZ Study Report SR476

Author

Catherine Nicholson

Reference

Nicholson, C. (2022). *Durability of polyurethane-based structural adhesives and bonded interfaces*. BRANZ Study Report SR476. Judgeford, New Zealand: BRANZ Ltd.

Abstract

This project was initiated in response to a need for more technical information on the durability performance of polyurethane (PUR) adhesives and preservative-treated radiata pine products bonded with PUR adhesives subjected to the environmental conditions relevant to New Zealand’s climate. Testing was comprised of accelerated ageing under a range of temperature and humidity conditions. Fourier transform infrared (FTIR) spectroscopy was used to investigate the performance of the adhesives by detecting structural changes indicative of chemical degradation and provided chemical information complementing the mechanical test data. Bond performance was evaluated using a range of tests, including conventional delamination, shear strength testing and fracture energy investigation. Scanning electron microscopy (SEM) was used to assess adhesive penetration into the wood. The effects of temperature and moisture on the adhesive bonds were investigated through a comprehensive experimental programme comprising both accelerated and natural ageing of samples as well as ambient and wet testing. There is no evidence from this study that would raise concerns around the use of PUR adhesives for service class 3 bonding radiata pine preservative treated with CCA or MCA to hazard class H3.2. Further work would be required to assess the performance of bonding preservative-treated timber with higher retention levels and when exposed to in-ground conditions.

Keywords

Engineered wood products; structural adhesives; polyurethanes; preservative-treated timber; durability.

Contents

Figures

Tables

Executive summary

Structural adhesives are critical for maintaining the structural performance of engineered wood products (EWPs) over their minimum expected lifetime of 50 years. With increasing interest in the use of polyurethane (PUR) adhesives in EWPs such as glulam and cross-laminated timber (CLT) manufactured or used in New Zealand, the long-term durability of laminated structural timber elements under local conditions needs to be well established.

This report summarises the results of a study investigating the durability performance of PUR adhesives and preservative-treated radiata pine products bonded with PUR adhesives subjected to the environmental conditions typical of New Zealand's climate. This study took the approach of studying both PUR adhesive films and laminated samples on the basis that their complementary advantages would together enhance an overall understanding of structure-durability relationships.

Testing of PUR adhesives has provided data that can contribute to answering questions typically asked as part of a BRANZ technical assessment for a new material or product. Testing comprised accelerated ageing of adhesives under a range of temperature and humidity conditions for up to 3 years. Performance was investigated spectroscopically by detecting structural changes indicative of chemical degradation. Accelerated testing at constant elevated temperature and humidity followed by a spectroscopic structural integrity check could provide a basic initial screening test for new adhesives that are anticipated to be used in laminated structural timber.

Testing of the laminated samples showed that both untreated and preservative-treated samples met the delamination requirements of AS/NZS 1328.1:1998 *Glued laminated structural timber – Performance requirements and minimum production requirements*. Testing also concluded there was no evidence from this research that would raise concerns around the use of the two commercially available PUR adhesives investigated in this study for service class 3 bonding radiata pine preservative treated with CCA or MCA to hazard class H3.2. However, it was noted that further work was required to assess the performance of bonding preservative-treated timber more fully as well as with higher retention levels of preservative and with products exposed to in-ground conditions.

This report concludes with the following recommendations for taking the work forward in terms of practical steps for manufacturers, suppliers and users of PUR-bonded EWPs and the further research that is required for verifying long-term durability performance:

- Explore how PUR adhesives can begin to be formally recognised in New Zealand standards, including options such as incorporation into revised existing standards.
- Increase accessibility of existing New Zealand EWP performance and durability data to provide a New Zealand equivalent of European case studies focusing on evidence of long-term durability.
- More research on durability aspects of preservative-treated EWPs, with consideration of both new and emerging treatments.
- More research on durability for in-ground contact applications, for which little data is currently available.
- Development of predictive service life models, which remain a high priority for research in this area.

1. Introduction

Engineered wood products (EWPs) are laminated structural timber elements and include laminated veneer lumber (LVL), cross-laminated timber (CLT) and glulam. They have been successfully used by the construction industry overseas for several decades and have been gaining increasing market share in New Zealand in recent years.

EWPs rely on adhesive bonds for their structural performance. These bonds are provided by structural adhesives. During its lifetime, every adhesively bonded wood product will be subjected to specific service conditions. These conditions can adversely affect the performance of the bond. In particular, recurring changes in temperature and relative humidity lead to changes in the physical dimensions and chemical behaviour of the wood and adhesive. Consequently, the bond may be subjected to considerable hygrothermal stresses and degradation, ultimately leading to premature failure in a worst-case scenario.

Use of EWPs is becoming more widespread in New Zealand, and their use is likely to continue to trend upwards. From the results of recent industry surveys on perspectives on the use of structural EWPs and adhesives in New Zealand (Nicholson & Walsh, 2019) and their uptake (Carradine, 2020), EWPs were generally viewed positively by the building sector, but more technical information provided by product manufacturers about their long-term performance and durability was found likely to assist with further increasing practitioner understanding and confidence in these products.

In New Zealand, formaldehyde, phenolic or resorcinol-based adhesives have a long history of use in the industrial production of loadbearing timber structures and are known to perform well over many decades. However, the polyurethane-based (PUR) adhesives that are used widely throughout Europe and North America (Lehringer & Gabriel, 2014) are gaining increasing industry interest due to perceived health and environmental benefits and the potential production advantages associated with PURs.

The diversity of the chemical structures of polyurethanes makes it possible to develop specific formulations to satisfy the requirements of intended service conditions with either one-component (1C) or two-component polyurethane adhesives. The curing of 1C-PUR adhesives takes place in the presence of water, which is generally provided by the wood moisture content. 1C-PURs are therefore also known as moisture-cure polyurethanes and provide practical advantages such as good abrasion and chemical resistance, thermal stability, low spread rate and glue usage, fast curing at room temperature, clear bond lines and good resistance to humidity. Single packaging is simple and convenient for users since application is easier without the requirement to mix in exact proportions.

In Europe, PUR adhesives are used extensively for exterior structural applications, with the associated performance requirements included in European standards such as BS EN 15425:2017 *Adhesives – One component polyurethane (PUR) for loadbearing timber structures – Classification and performance requirements*. In New Zealand, there is no simple prescriptive compliance path for PUR adhesives within the current standards.

Unlike other parts of the world, the New Zealand Building Code requires evidence of a minimum durability of 50 years for all structural building elements. Without a sufficiently long history of use or long-term durability data available for PUR bonding performance to be evaluated in products, it is difficult to demonstrate that structural building elements containing PUR adhesives will meet the minimum 50-year durability clause.

In response to this difficulty with demonstrating durability, the work described in this report was initiated to provide the industry with technical information relevant to the timber products and service conditions commonly encountered in New Zealand. EWPs manufactured locally are predominantly produced using radiata pine (*Pinus radiata*) that has been preservative treated. Chromated copper arsenate (CCA) is widely used as a timber treatment, with micronised copper azole (MCA) being a newer alternative on the market. This study therefore focused on the durability of PUR adhesives and preservative-treated radiata pine products bonded with commercially available PUR adhesives subjected to the environmental conditions typical of New Zealand's climate.

It is important to highlight that the specific adhesive formulation, wood species, timber preservative treatment and typical in-service climate conditions are all key parameters to take into consideration with respect to durability. All of these factors have an influence on the mechanical properties of laminated materials. For this reason, simple extrapolation of overseas performance and durability data cannot be assumed to be appropriate when determining the suitability of EWPs for use in New Zealand even when similar products have been successfully used elsewhere. Specifically, the radiata pine predominantly used in timber products in New Zealand is not a wood species commonly used elsewhere in the world. Durability studies using one species cannot simply be extrapolated to another species even if the same adhesives are being used for bonding.

Because of the 50-year durability performance that is required of structural timber elements, it is impractical to rely solely on natural ageing tests for evaluation by outdoor weathering. There is, therefore, a continuing need for the development of standard test methods for the service life prediction of materials for specific applications such as these (Lee et al., 2008; Marston et al., 2011). Accelerated ageing is commonly used in these types of studies.

The majority of experimental studies in this field have focused on the mechanical performance of the timber-adhesive bond in laminated specimens, reflecting the emphasis in other countries on structural performance rather than long-term durability of EWPs. However, two notable studies by Ren and Frazier (2013a, 2013b) and van Langenberg (2010) recognised that, by studying the adhesive itself as an integral component of the overall laminate, important additional knowledge could be added to an overall understanding of the adhesive-timber composite material.

This project took the same dual approach of investigating both adhesive films and composite samples on the basis that the complementary advantages of both would enhance an overall understanding of structure-durability relationships in PUR adhesives used for timber bonding. Given the wide range of PUR compositions available and that structure-property relationships are critical to many aspects of materials chemistry, the rationale for this part of the study was to better understand the long-term behaviour of polyurethane films subjected to accelerated ageing without the added complexity of the timber in composite laminated samples.

The methodology used to examine the adhesive films aimed to enhance our fundamental understanding of PUR materials chemistry by subjecting adhesive films to various environmental conditions and monitoring structural changes over time using Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy has been widely used in the analysis of construction materials (Shaw & Marston, 2016; Pellizzi et al., 2014; Zhang et al., 2013; Mitchell et al., 2013; Jelle et al., 2012) and polyurethanes (Bockel et al., 2018; Clerc et al., 2017; Ren & Frazier, 2013a, 2013b; Sterley et al., 2012). It is a rapid, non-destructive analytical technique that can also be used for in situ testing. Chemical changes in the structure of the PUR adhesive due to ageing and accelerated weathering can be monitored to predict likely degradation mechanisms, durability characteristics and expected service life.

The methodology used to examine the laminated specimens aimed to produce technical information on the performance of PUR adhesives used to bond preservative-treated radiata pine. This involved subjecting test samples to various environmental conditions followed by assessment of mechanical characteristics including shear strength, delamination resistance and bond fracture energy. The performance of polyurethane-bonded joints was compared to a conventional formaldehyde-based formulation. Natural ageing based on outdoor exposure testing was used for evaluating results from the accelerated ageing tests with the objective of developing a model for predicting long-term durability.

A separate report on polyurethane adhesives (Li, 2016) informed the work on the adhesive films prior to the experimental methodology being developed. A comprehensive literature review was undertaken by Karami (2020) as part of a PhD study on the laminated samples.

Conclusions and recommendations from this research incorporate the findings of an industry survey of perspectives on the use of structural engineered wood products and adhesives in New Zealand (Nicholson & Walsh 2019).

2. Experimental methodology

The experimental methodology is divided into two parts. Section 2.1 details the methods related to adhesive films while section 2.2 outlines the methods related to the laminated specimens.

For the adhesive films described in section 2.1, previously published work can be found in Nicholson, Shaw and Marston (2017) and Nicholson (2020).

For the laminated samples described in section 2.2, a detailed description of the experimental methodology and full details of testing, results and data relating to these laminated specimens is given in Karami (2020), apart from the freeze-thaw accelerated ageing test methodology (section 2.2.2.2), which has not been previously published.

2.1 Adhesive films

The objective of studying the adhesive films was to assess their response to hygrothermal stress in the absence of the timber substrate. This would allow insight into the chemistry of the PUR adhesives.

It is important to note that these tests were not intended to be an investigation of individual material or product performance. For instance, the PUR adhesives used in this study were not formulated to withstand exposure to UV light. This did, however, present a problem when attempting to correlate accelerated ageing mechanisms with natural ageing. With rapid destruction of PUR films by UV, outdoor exposure tests had limited value, and as a result, these are not further discussed in this report.

2.1.1 Adhesives

Five commercially available one-component PUR-based adhesives were selected to undergo accelerated ageing tests (PUR 1–5). Adhesives were cast onto wooden sticks and clamped to minimise the effect of foaming due to release of CO_2 during curing. All samples were allowed to cure for at least the minimum time recommended by the manufacturer under normal laboratory conditions (approximately 22°C, 55% RH) before undergoing FTIR analysis after ageing at intervals of up to 3 years. Control samples were stored in a constant climate laboratory at 20°C and 50% RH in an enclosed cupboard to minimise light exposure.

2.1.2 Accelerated ageing

The adhesive samples were exposed to a range of temperature and humidity conditions (Table 1). A complete Cycle A was 1 day in length, a complete Cycle B was 1 week in length and Cycle C represented constant exposure to elevated temperature and humidity. Controls were sampled at the same time intervals as the exposed samples.

Table 1. Accelerated ageing cycles for adhesive films.

Cycle A	Cycle B	Cycle C
6 hours @ 30°C, 95% RH	5 days @ 70°C, 90% RH	Constant 65°C, 100% RH
6 hours @ 60°C, 75% RH	1 day @ -20°C	
6 hours @ 10°C, 50% RH	1 day @ 80°C, < 15% RH	
6 hours @ -10°C		

2.1.3 ATR FTIR spectroscopy

Attenuated total reflection (ATR) FTIR spectroscopy was performed with an Agilent Technologies 4300 instrument. Spectra were collected using MicroLab PC software and a diamond ATR sampling interface over the spectral range 650–4000 cm^{-1}. A background of 16 scans was recorded before each spectrum of 64 scans with a resolution of 4 cm^{-1} was acquired. Spectra were analysed using GRAMS IQ (version 9.1) software. Figure 1 shows a representative spectrum of a PUR adhesive, and Table 2 shows the spectral regions of interest relevant to the PUR structure.

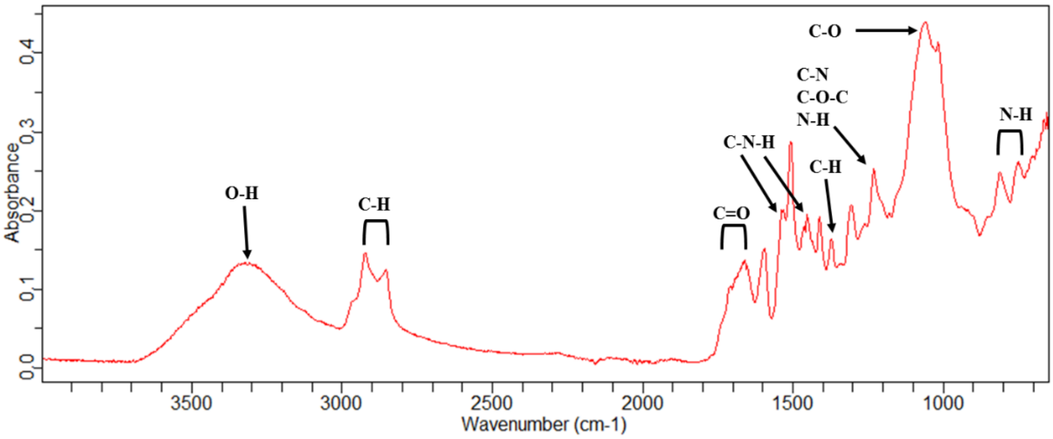

Figure 1. Representative ATR FTIR spectrum of PUR adhesive.

Table 2. Spectral band assignments for regions relevant to PUR structure in ATR FTIR spectra (modified from Delpech & Miranda, 2012).

Wavenumber (cm^{-1})	Band assignment	Vibrational mode
800–400	N-H	Bend
1075	C-O (urethane and ether)	Stretch
1250–1240	C-O-C (ether) N-H C-N	Asymmetric stretch Bend Stretch
1374	C-H (methyl)	Symmetrical bend
1450	C-N-H (urea)	C-N stretch N-H symmetrical bend
1560–1530	C-N-H (urethane)	C-N stretch N-H symmetrical bend
1715–1630	C=O (urethane and urea)	Stretch
2250–2275	O=C=N (free isocyanate)	Stretch
2970–2850	C-H (methyl and methylene)	Stretch
3335–3320	N-H (urethane and urea)	Stretch

2.1.4 Predictive models

ATR FTIR spectra were used to attempt development of preliminary predictive models to assess correlation between changes in spectral features and exposure time. GRAMS IQ (v 9.1) software was used with PLS-1 (partial least squares) calibration and cross-validation to assess the quality of the models. Three spectra from each of the five PUR adhesives at 15 sampling intervals for Cycle C (constant high temperature and humidity) were used to generate the predictive models. The 'Grams Predict' function was then used to predict the equivalent Cycle C exposure time represented by spectra from control samples that had been stored under normal laboratory conditions.

Once the predictive model was generated, cross-validation was used to test the validity of the model. To do this, spectra that were used to create the predictive model were subsequently used as new inputs into the model to create a cross-validation plot. A perfect model has a correlation coefficient (R^2) of 1.00. The greater the deviation of the model from ideality, the lower the value of R^2.

2.1.5 In situ monitoring of the adhesive bondline

ATR FTIR spectroscopic measurement of the bondline requires destructive sampling of the specimen where the sample is broken apart at the bondline to be able to analyse the adhesive. The objective of exploring in situ monitoring was to assess how adhesives performed in laminated specimens during accelerated ageing with a novel sampling methodology that was non-destructive and allowed real-time data to be collected. Proof of concept was required with adhesive films before use in laminated samples.

The method consisted of an in situ spectroscopic technique using fibre optics embedded in the adhesive layer. Preliminary validation work to identify the spectral response of one PUR adhesive of interest was conducted to establish the underlying feasibility of the concept. Monitoring of spectral changes in adhesives using fibre optics was then assessed through reflection, transmission or absorption techniques.

Samples of PUR 3 adhesive ~200 μm thick for absorbance measurements were obtained by applying the adhesive to a parafilm or Teflon surface and allowing to cure overnight. Thicker samples were made for reflection.

Absorbance/transmission measurements were made using a Lambda 1050 Perkin Elmer instrument in the wavelength region 300–2700 nm and a Bruker Tensor II FTIR in ATR mode in the wavenumber region 4000–800 cm^{-1}. Reflection measurements were made using an Avantes Avaspec 2048L in the wavelength region 300–1100 nm and an NIRLine in the wavelength region 1100–1700 nm. Diffuse and specular reflection measurements were made using reflection probes and attachments and a reflection standard. For the purposes of this study, five spectral regions of interest were defined spanning the UV to mid-IR regions (Table 3).

Table 3. Spectral regions of interest for in situ spectroscopy

Spectral region	Approximate wavelength	Comments	Availability of optical fibre systems
Ultraviolet	< 400 nm (potentially down to 200 nm)	High energy photons – most polymers/adhesives have a strong absorbance step below 400 nm (of limited use)	Moderate – glass is poor transmitter at shorter wavelengths
Visible	400–700 nm	Broad spectral features – could be of limited use	Excellent – glass transmits very well; sensitive equipment available
Near infrared (near-IR)	700–1700 nm	Some overtones of chemical signatures – tend to be spectrally broad	Excellent due to telecoms industry; equipment not as cost effective < 1100 nm due to silicon cut-off

Spectral region	Approximate wavelength	Comments	Availability of optical fibre systems
Short-wave infrared	1700–2500 nm	Not a well-utilised region – some strong water absorptions	Limited but possible to do measurements; optical fibres start to become specialised (non-standard glass)
Mid-infrared (mid-IR)	2500–12000 nm	Well used in chemical identification (FTIR) – vibrational modes of molecules very strong	Moderate and improving for 2500–5000 nm; very challenging for 5–10 microns

The aim of this investigation was to examine the spectral characteristics of PUR 3 using a combination of spectrometers from UV to mid-IR.

Table 4 shows the combination of measurements and spectral regions targeted.

Table 4. Spectral regions and measurements for in situ spectroscopy.

	Reflection	Transmission/absorbance
Ultraviolet	Diffuse and specular reflection measurements (300–400 nm)	Potentially down to 190 nm, however adhesives are likely to be strongly absorbing at < 350 nm
Visible	Diffuse and specular reflection measurements (400–700 nm)	400–700 nm measurements (on thin films)
Near-IR	Diffuse and specular reflection measurements (700–1700 nm)	700–1700 nm measurements (on thin films)
Short-wave infrared	Challenging – would require further investigation	1700–2500 nm (on thin films)
Mid-IR	FTIR (already in use for characterising the PUR adhesives)	FTIR (already in use for characterising the PUR adhesives)

2.2 Laminated samples

The objective of studying the laminated samples was to investigate the durability of preservative-treated radiata pine bonded with one-component PUR adhesives. This would assess the performance of the adhesive bondline when subjected to environmental conditions typically encountered in New Zealand.

Bond performance was evaluated using a range of tests including conventional delamination and shear strength testing. ATR FTIR spectroscopy provided chemical information complementing the mechanical test data, while scanning electron microscopy (SEM) was used to assess adhesive penetration into the wood.

The effects of temperature and moisture on the adhesive bonds were investigated through a comprehensive experimental programme comprising both accelerated and natural ageing of samples as well as ambient and wet testing (Table 5).

Table 5. Summary of experimental test conditions and ageing methods.

Conditions	Description	Duration
Ambient	20°C, 65% RH	-
Wet	Submerging in water, 30 min 75 kPa vacuum, 2 hr 540 kPa pressure	-
Natural ageing	12 months full exposure to outdoor environment (service class 3)	3, 6, 9, 12 months
Vacuum-pressure soak-drying cycle (Cycle A)	Submerging in water, 5 min 75 kPa vacuum, 1 hr 600 kPa pressure – x 2, 21 hr drying 65 ± 5°C, < 15% RH	2, 4, 8, 16 cycles
Freeze-thaw (Cycle B)	5 days @ 70°C, 90% RH 1 day @ -20°C 1 day @ 80°C, < 15% RH	8 weeks
Constant long-term high temperature and humidity (Cycle C)	Constant 65°C, 100% RH	3, 6, 9 months

2.2.1 Sample fabrication

New Zealand-grown radiata pine was used for the test samples. Samples were either untreated or preservative treated with chromated copper arsenate (CCA) or micronised copper azole (MCA). Samples were fabricated to ensure variations in wood density were taken into account.

Two PUR adhesives were included in the study with a resorcinol-formaldehyde (RF) adhesive as a control.

Test specimens bonded with different PUR adhesives were compared to samples bonded with traditional resorcinol-formaldehyde (RF) adhesive. Solid timber samples were also included in the study to provide a performance reference for the adhesively bonded samples.

2.2.2 Accelerated ageing

The adhesive samples were exposed to a range of temperature and humidity conditions represented by Cycles A, B and C (Table 6). Cycle A consisted of vacuum-pressure soak-drying for 2, 4, 8 and 16 cycles. Cycle B represented freeze-thaw high-temperature ageing with each cycle being 1 week in length. Cycle C represented constant exposure to elevated temperature and humidity. Controls were sampled at the same time intervals as the samples exposed to accelerated ageing.

Samples subjected to accelerated ageing were compared to ambient controls. Some testing was also carried out on wet samples to provide a comparison between samples under wet and dry conditions.

Table 6. Accelerated ageing cycles for laminated samples.

Cycle A	Cycle B	Cycle C
Vacuum-pressure soak-drying for 2, 4, 8 and 16 cycles	5 days @ 70°C, 90% RH 1 day @ -20°C 1 day @ 80°C, < 15% RH	Constant 65°C, 100% RH

2.2.2.1 Vacuum-pressure soak-drying

This test is based on AS/NZS 1328.1:1998, which assesses delamination of Type 1 adhesives. Test blocks were submerged in water in a pressure vessel. A vacuum was applied for 5 minutes followed by pressure for 1 hour and the cycle repeated.

2.2.2.2 Freeze-thaw

This test subjects samples to extremes of temperature and humidity over a cycle duration of 1 week. It represents a severe test method and is based on ECCS/CIB 257 *European recommendations for sandwich panels* (Joint Committee, 2020). This test was not published in the thesis by Karami (2020) and so it is reported here.

2.2.2.3 Constant high temperature and humidity

Samples are subjected to a constant high temperature, high humidity environment. The test represents another severe test method and is based on BS EN 14509:2013 *Self-supporting double skin metal faced insulating panels. Factory made products. Specifications.*

2.2.3 Natural ageing

Samples were fully exposed to the outdoor environment (service class 3) for 12 months in Newmarket, Auckland. Natural ageing was carried out on 40 samples that were exposed to the outdoor environment.

2.2.4 Delamination

Delamination tests were carried out on specimens cut from commercially sourced laminated timber beams. The test methodology followed AS/NZS 1328.1:1998. Two delamination cycles were tested as per the standard, and extra readings were taken to look at earlywood delamination and latewood percentage adjacent to the bondlines.

2.2.5 Shear strength

Specimens for shear strength testing were fabricated to maximise moisture stress on the bondlines through alternation of annular ring orientation (Figure 2a). A limited number of samples were prepared to deliberately reduce moisture stress for comparison (Figure 2b).

Figure 2. Annular ring arrangements: (a) alternating annular ring orientation with pith side of outermost laminations facing inwards; (b) limited alternation in annular ring orientation with pith side the outermost laminations facing outwards.

Step-stair shear test specimens were fabricated by cutting laminated blocks using a CNC machine (Figure 3).

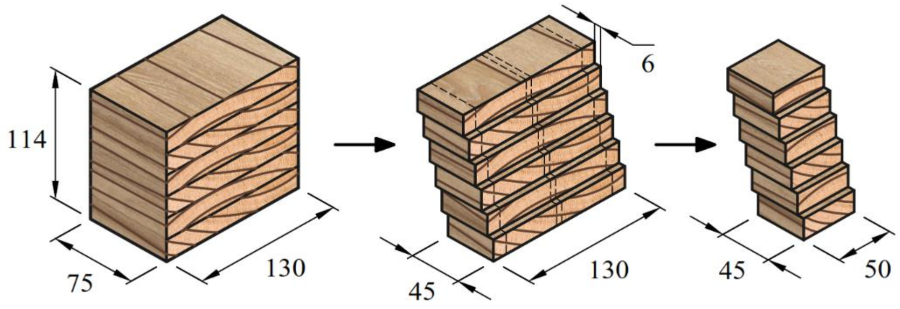

Figure 3. Fabrication of step-stair shear test specimens.

Shear testing was carried out using a universal material test machine with a 100 kN load cell and a constant loading rate to target a failure time of 60 ± 30 s on samples fabricated following an adaptation of ASTM D2559-12a(2018) *Standard specification for adhesives for bonded structural wood products for use under exterior exposure conditions*. Afterwards, the bonded interface was visually inspected and the wood failure percentage estimated.

2.2.6 Fracture energy

Preparation of the fracture energy specimens (Figure 4) and subsequent testing was adopted from ISO 25217:2009 *Adhesives – Determination of the mode 1 adhesive fracture energy of structural adhesive joints using double cantilever beam and taped double cantilever beam specimens*. As with the shear tests, afterwards the wood failure percentage was estimated by visual inspection.

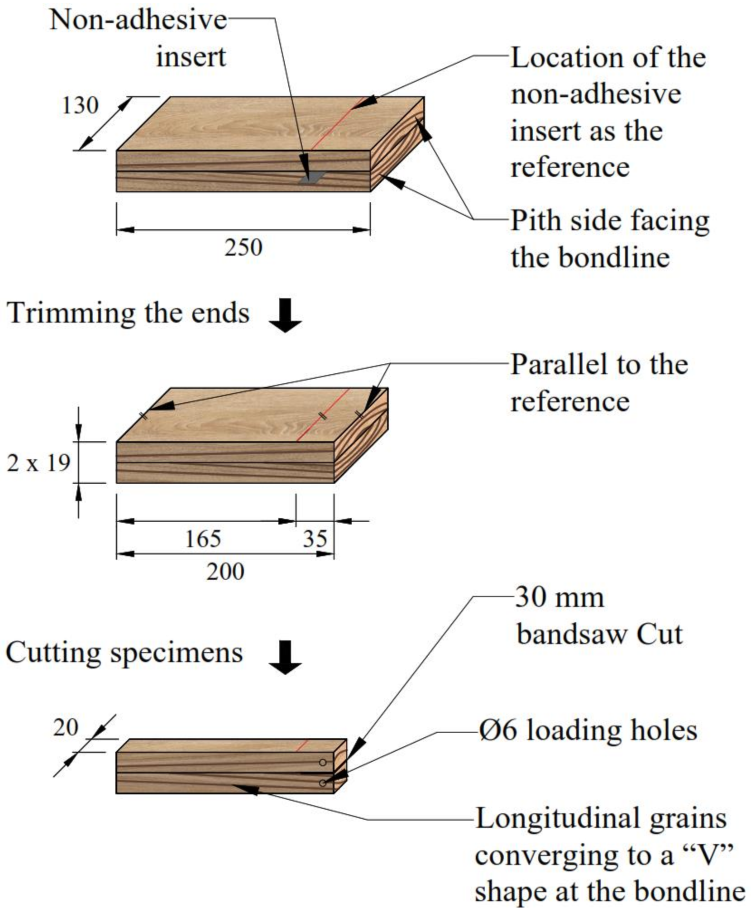

Figure 4. Preparation of fracture energy test specimens.

2.2.7 SEM

SEM was used to visualise the bond line microstructure and estimate the penetration of the adhesive.

2.2.8 ATR FTIR spectroscopy

ATR FTIR spectroscopy was used in the same way as for the adhesive films (section 2.1.3). For the laminated samples, analysis was also carried out on the wood substrate (Figure 5 and Table 7) as well as the adhesive film (Figure 1 and Table 2).

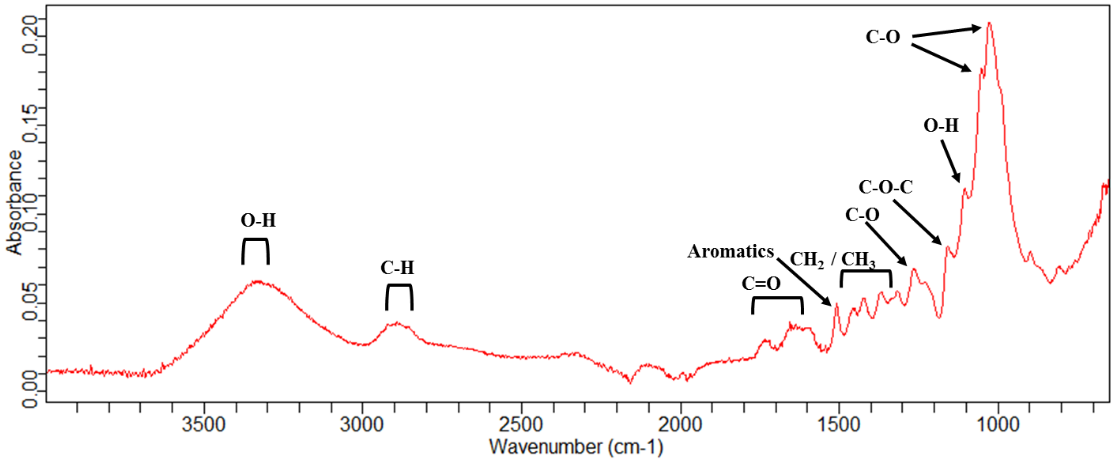

Figure 5. Representative ATR FTIR spectrum of wood substrate.

Table 7. Spectral band assignments for regions relevant to wood structure in ATR FTIR spectra (modified from Fahey et al., 2017).

Wavenumber (cm^{-1})	Band assignment	Vibrational mode
1026	C-O (cellulose/hemicellulose)	Stretch
1053	C-O (polysaccharides)	Stretch
1105	O-H (polysaccharides)	Association band
1157	C-O-C (polysaccharides and cellulose/hemicellulose)	Antisymmetrical stretch
1265	C-O (lignin)	Stretch
1440–1315	CH_2/CH_3 (cellulose, lignin and polysaccharides)	Various
1507	Aromatics (lignin)	Various
1730–1660	C=O (lignan and xylans)	Stretch
2970–2850	C-H (cellulose/hemicellulose)	Stretch
3600–3100	O-H (cellulose/hemicellulose)	Stretch

3. Adhesive film test results

3.1 ATR FTIR

All five adhesives had broadly similar composition as determined by ATR FTIR (Figure 6).

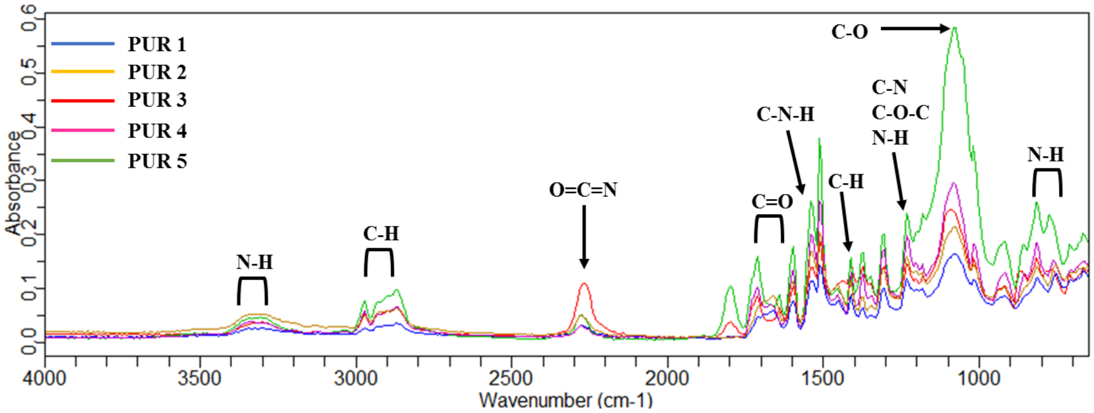

Figure 6. ATR FTIR spectra of freshly cured adhesive samples.

The adhesives were affected by the three exposure cycles (Table 1) in different ways. In general, PUR 1 and PUR 2 exhibited little discernible difference between the control and aged specimens. This is illustrated in Figure 7, which shows sample PUR 1 after exposure to Cycle A for 18 months, Figure 8, which shows sample PUR 2 after exposure to Cycle B for 18 months, and Figure 9, which shows sample PUR 1 after exposure to Cycle C for 3 years. Considerable colour changes were observed for both PUR 1 and PUR 2. Originally, both were cream coloured. They turned light yellow during Cycle A, orange/brown during Cycle B and dark brown during Cycle C. Control samples did not change colour when stored under laboratory conditions for the same periods.

Structural changes in the FTIR spectra of PUR 3 were minimal after exposure to Cycle A (Figure 10) but clearly evident during Cycles B (Figure 11) and C (Figure 12) when compared to controls. These differences were observed throughout multiple regions of interest. Colour changes were also observed for these specimens. Originally beige, as ageing progressed, they remained beige during Cycle A, turned white and powdery during Cycle B and became chocolate brown during Cycle C. Control samples did not change colour when stored under laboratory conditions for the same periods.

PUR 4 and PUR 5 behaved in a similar manner to each other. Some differences were observed in spectra when compared with the controls during all three exposure cycles, but their behaviour was closer to that of PUR 1 and PUR 2 rather than PUR 3. This is illustrated in Figure 13, which shows PUR 5 after exposure to Cycle A for 18 months, Figure 14, which shows PUR 4 after exposure to Cycle B for 18 months, and Figure 15, which shows PUR 4 after exposure to Cycle C for 3 years. Both PUR 4 and PUR 5 darkened significantly in colour during ageing in Cycles B and C but not Cycle A.

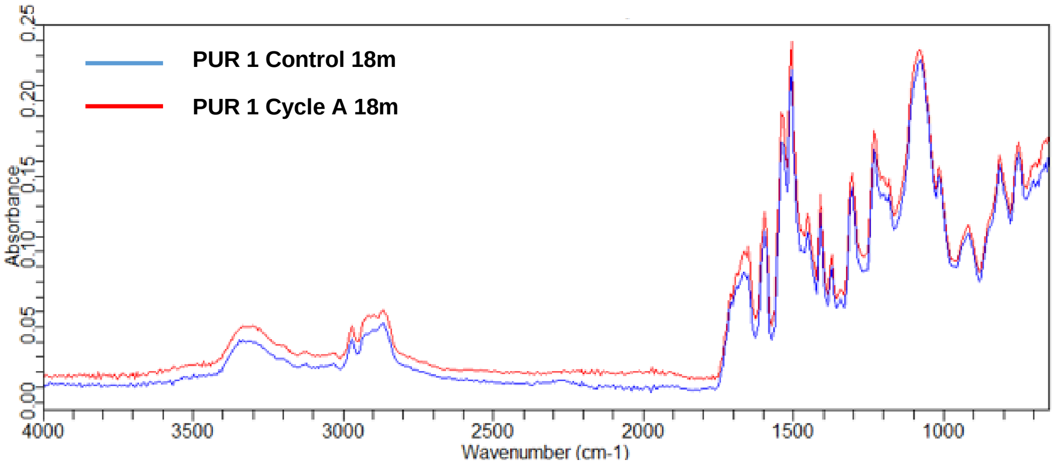

Figure 7. ATR FTIR spectra of sample PUR 1 and control after 18 months of exposure to Cycle A.

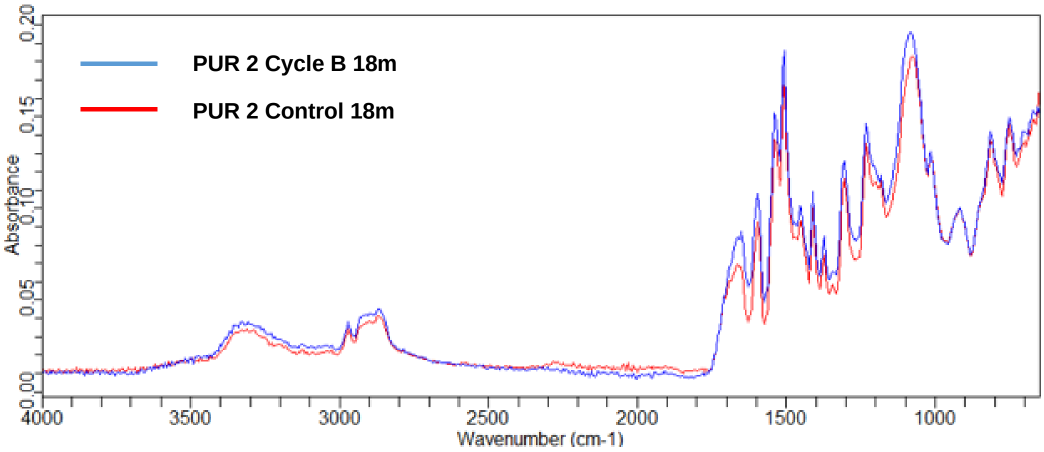

Figure 8. ATR FTIR spectra of sample PUR 2 and control after 18 months of exposure to Cycle B.

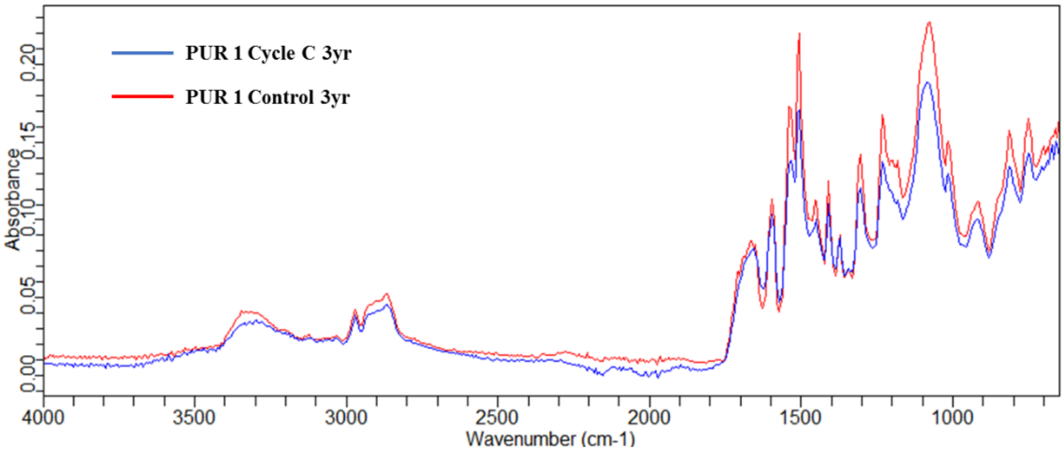

Figure 9. ATR FTIR spectra of sample PUR 1 and control after 3 years of exposure to Cycle C.

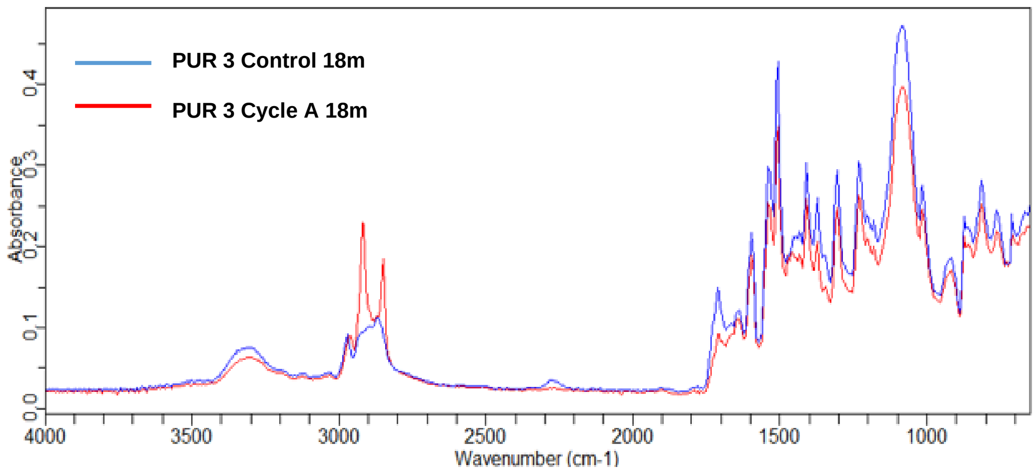

Figure 10. ATR FTIR spectra of sample PUR 3 and control after 18 months of exposure to Cycle A.

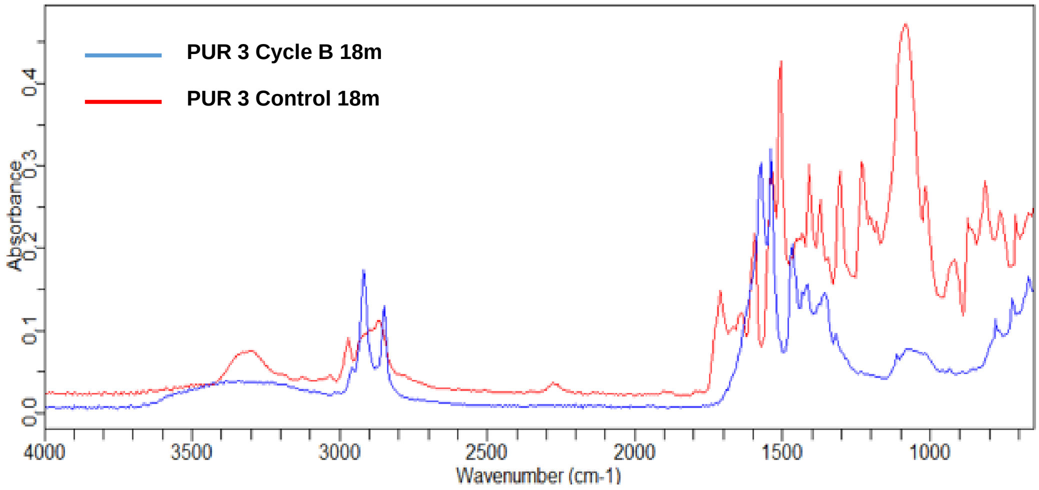

Figure 11. ATR FTIR spectra of sample PUR 3 and control after 18 months of exposure to Cycle B.

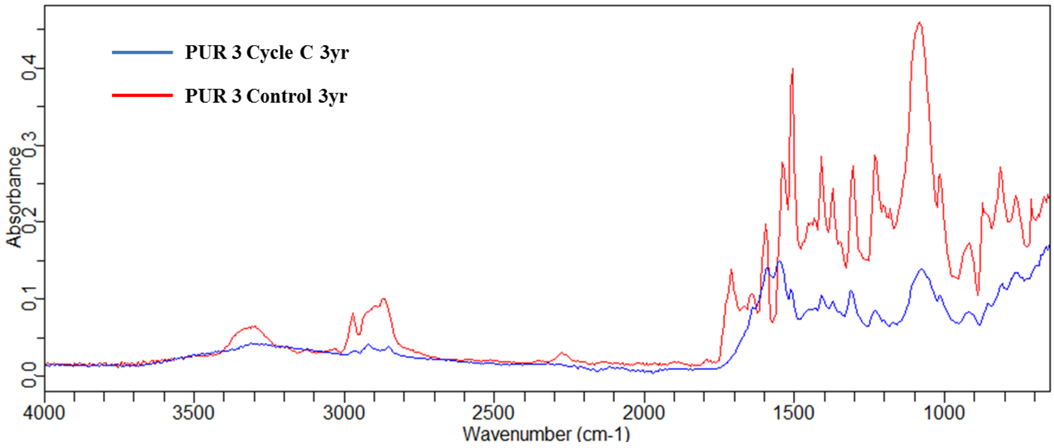

Figure 12. ATR FTIR spectra of sample PUR 3 and control after 3 years of exposure to Cycle C.

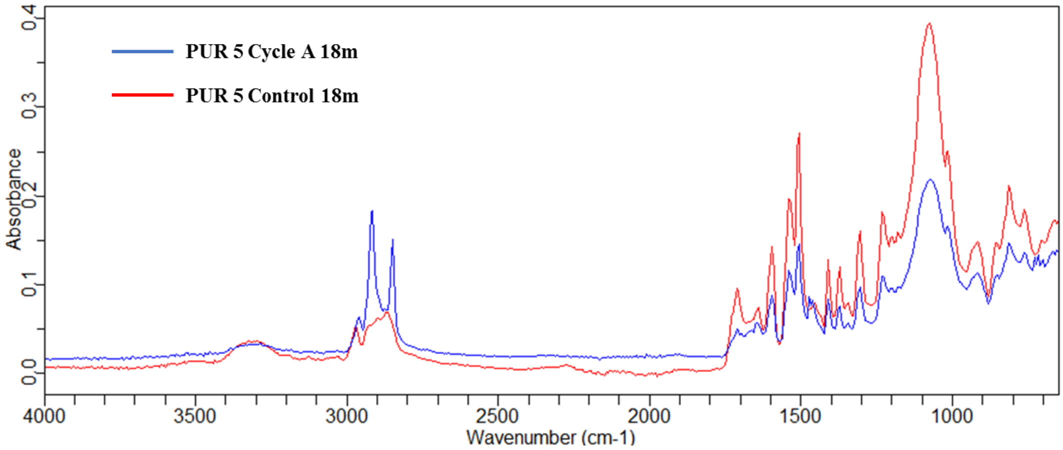

Figure 13. ATR FTIR spectra of sample PUR 5 and control after 18 months of exposure to Cycle A.

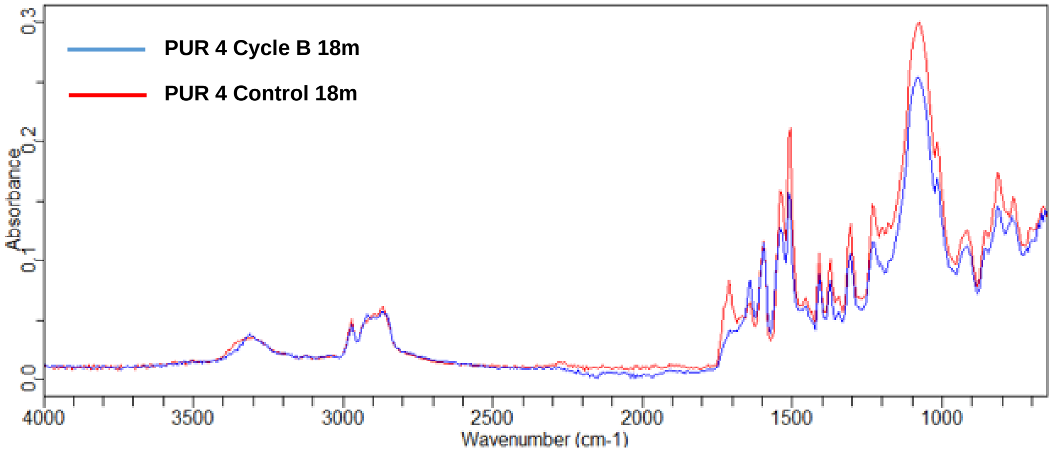

Figure 14. ATR FTIR spectra of sample PUR 4 and control after 18 months of exposure to Cycle B.

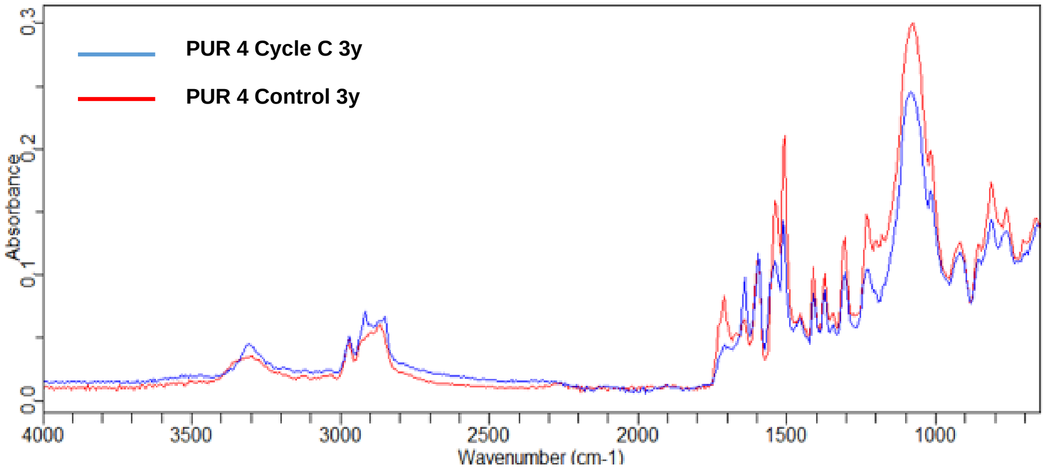

Figure 15. ATR FTIR spectra of sample PUR 4 and control after 3 years of exposure to Cycle C.

3.2 Predictive models

Validation results for predictive models of each adhesive sample and accelerated ageing condition were variable, ranging from unusable through to potentially useful. The most promising model was from PUR 1 subjected to Cycle C for up to 3 years with a coefficient of determination (R^2) of 0.91. The cross-validation plot for this predictive model is shown in Figure 16.

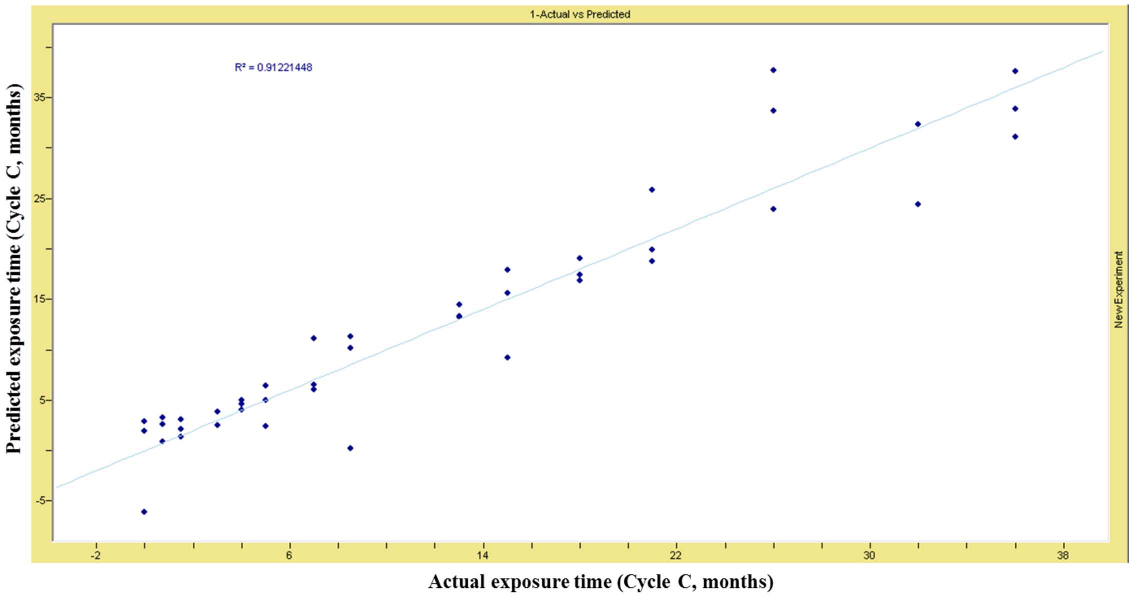

Figure 16. Cross-validation plot for the predictive model based on PUR 1 subjected to Cycle C for 18 months (R^2 = 0.91).

Predictive models are only useful where the degradation mechanisms of the accelerated ageing method and control are similar, the control usually being a sample subjected to natural outdoor ageing.

In this case, outdoor samples could not be used as the control samples since their degradation due to UV exposure was rapid (within several weeks) and not reflective of in-service conditions where the adhesive would not be subjected to light. Rather, the controls were samples that had been stored in the dark under laboratory conditions.

While the correlation coefficient for PUR 1 under Cycle C was good, there was still a problem with developing predictive models since, over the 3-year timeframe of the experimental work, PUR 1 and 2 showed virtually no degradation.

3.3 In situ monitoring of the adhesive bondline

Figures 17–19 show the absorption spectra obtained for the PUR 3 films in different spectral regions of interest.

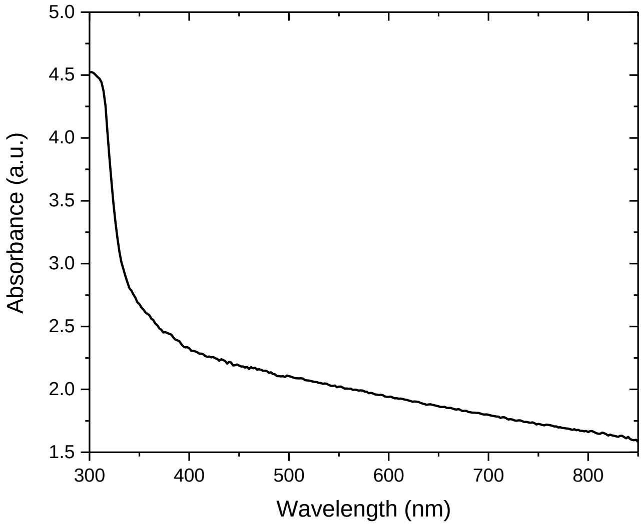

Figure 17. UV/visible absorption spectrum of PUR 3.

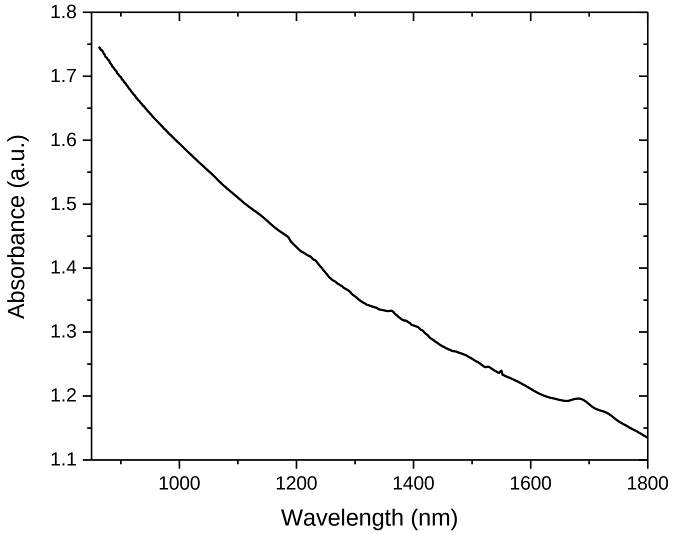

Figure 18. Near infrared absorption spectrum of PUR 3.

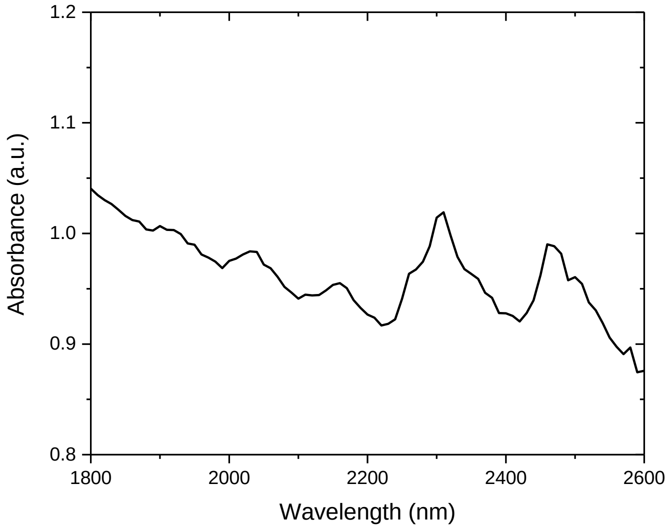

Figure 19. Short-wave infrared absorption spectrum of PUR 3.

Figure 20 shows the absorption spectrum in the mid-infrared region, analogous to the ATR FTIR spectra displayed in section 3.1. Absorbance is shown for consistency, where the following conversion from transmission was used:

A = 2 – log (%T) [where A = absorbance, T = transmission]

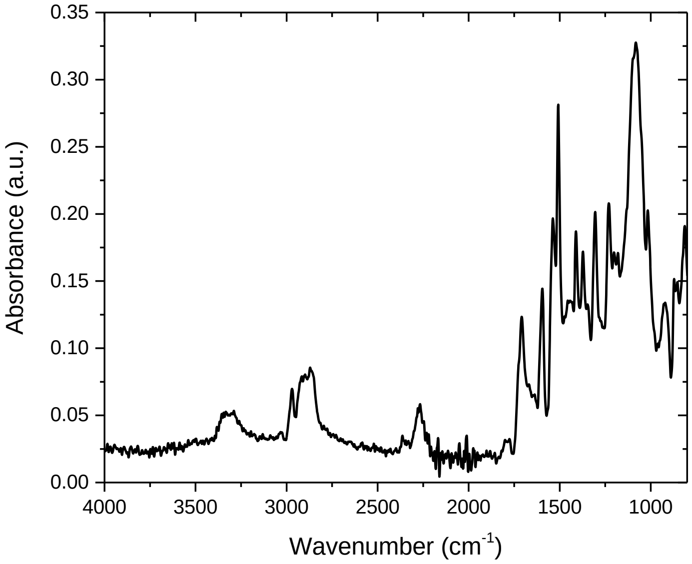

Figure 20. Mid-infrared absorption spectrum of PUR 3.

The absorption spectra of PUR 3 did not show significant features in the region encompassing the UV to about 2500 nm. In contrast, absorbance in the infrared region had distinct characteristics that could be identified, including features at around 3300, 2900 and 2300 cm^{-1} and an onset of multiple peaks from around 1750–800 cm^{-1}, consistent with the ATR FTIR spectra in section 3.1.

The diffuse and specular reflection spectra obtained for the PUR 3 film across the entire spectral region of interest were generally consistent in features but without prominent defining features.

Overall, the most prominent features for PUR 3 were absorbance features in the infrared, as used for the ATR FTIR measurements previously discussed.

On the basis of these results, the likely required fibre optic material was a chalcogenide glass. This is a glass containing sulfur, selenium or tellurium. With no off-the-shelf solutions available, some work was required to connect the fibre to the FTIR to get the light out and back into the detector. Initial trials with mid-IR fibre resulted in very little transmission being observed. A slightly different configuration with some small IR sources and spectral detectors already available was explored. This resulted in some light being observed through the delivery fibre, but this was ultimately too weak for practical purposes.

It was concluded that additional materials and equipment would need to be purchased, along with some method development activities to achieve a functional system for the successful in situ chemical measurement of adhesives. While this was believed to be technically achievable across the entire wavelength range of ~ 1000–5000 cm^{-1}, encompassing all of the spectral features of interest for PUR adhesives, this work fell outside the scope of the project and was not continued.

3.4 Discussion

When BRANZ is requested to undertake a technical assessment of a new material or product, there is a series of typical questions that are initially asked. For a new adhesive, these would include:

- What is the service history for the adhesive?
- Has testing been completed to characterise the chemical degradation that occurs in the adhesive during in-service conditions?
- What accelerated testing has been completed and how can this be used to predict expected New Zealand service life?
- Does chemical analysis indicate that the degradation pathway in accelerated tests mirrors that found in service?
- What is the expected failure mechanism of the adhesive?

The data from this study of PUR adhesives can contribute to answering these questions and providing an evidence base for their use while also identifying some remaining knowledge gaps.

The accelerated ageing cycles were chosen according to the likelihood that PURs would be subjected to hygrothermal stress under in-service conditions. It is known that, under conditions of elevated temperature and moisture, the constituent polyol and urethane chemical entities may be hydrolysed (Dubelley et al., 2018). The susceptibility to and extent of degradation of individual PURs is highly dependent on composition.

Photolysis induced by UV exposure is usually an important factor to consider. Photolysis results are not presented in this report because the adhesive films used in this study were not formulated to withstand UV exposure and were severely degraded within only days or weeks of accelerated and outdoor ageing, respectively.

Although the five PUR adhesive samples had similar compositions, differences in spectra between control and aged samples were observed during accelerated ageing. These differences ranged from subtle to pronounced but indicate that structural changes had occurred.

PUR 1 and PUR 2 exhibited no obvious structural changes during any of the three ageing cycles (Figures 7–9). The only difference noted was the reduction in intensity and eventual disappearance of the peak at around 2275 cm^{-1}. This peak is associated with free isocyanate, and its disappearance would be expected as the adhesive cured. This is confirmed by the control sample, which exhibited identical behaviour. On the basis of the spectroscopy data, these adhesives both appear to be highly resistant to hydrolysis. However, colour changes were noted, suggesting some structural changes occurred that were not immediately apparent by spectroscopy.

In contrast, PUR 3 showed evidence of significant hydrolytic degradation during cycles B and C (Figures 11 and 12). There was an overall reduction in peak intensity compared with the control and complete loss of structure in the region 1000–650 cm^{-1}, this being associated with N-H bonds. In addition, reduction in peak intensity was observed over 3400–1800 cm^{-1}, this also being associated with N-H as well as C-H bonds (Table 2). Pronounced reduction in the peak at 1538 cm^{-1} associated with C-N-H bonding is indicative of loss of the urethane structure and accounts for the observed discolouration of the samples. The disappearance of the peaks between 1750–1650 cm^{-1} further supports degradation of the urethane structure, this being associated with the C=O bonds in urethane.

PUR 4 and PUR 5 showed evidence of subtle structural changes around 1700 cm^{-1} associated with the C=O and C-N-H bonds in urethane and more obvious changes between 3000–2800 cm^{-1} associated with C-H bonding (Figures 13–15).

While the three exposure cycles were designed to be severe, they are not extreme relative to the New Zealand climate. Conditions experienced by building materials may well reach or even exceed 70°C and 80% humidity in the north of the North Island in summer and drop to -20°C in the south and central South Island in winter. However, it is the continuous nature of exposure under these conditions that would not be expected in service.

Producing a reliable method to accurately predict the correlation between natural and accelerated ageing of a material has long been a significant challenge for this field of research with few successful examples (Marston, Jones & Shaw 2014). Most studies of this kind have focused on a comparison of mechanical properties between naturally aged samples and those after accelerated ageing. Development of reliable models for durability prediction was not achieved, and there continues to be a need for such models to be developed, tested and validated. A large global study to survey a very wide range of wood species offers future potential for improved service life prediction (Brischke et al. 2021a, 2021b).

Non-destructive investigation of adhesives that could be applied to direct, in situ testing of the bondline in a laminated sample was ultimately not completed and would require further investigation. However, this appears to be technically feasible and is potentially an exciting and fruitful line of enquiry for future work.

4. Laminated sample test results

Detailed test results are available in Karami (2020), with the main points being reproduced here. The exception to this is the ATR FTIR results from samples subjected to Cycle B and related observations during Cycle C summarised in section 4.6, which have not been previously published.

4.1 Delamination

Standard delamination test results showed that CCA and MCA preservative-treated samples met the delamination requirements of AS/NZS 1328.1:1998 for type 1 adhesives for use in service class 3. Delamination was associated with latewood areas at the bondline (Figure 21). CCA-treated samples showed higher delamination compared to untreated and MCA-treated samples, mainly in the latewood. Decreasing the moisture stress through modification of the annular ring orientation (Figure 2) increased delamination resistance.

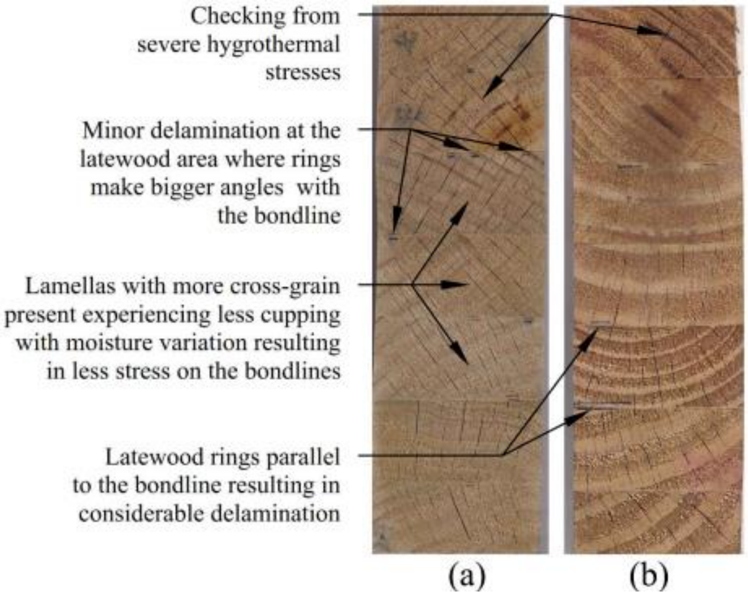

Figure 21. Aged samples from commercial beams: (a) CCA-treated; (b) MCA-treated.

While it is recognised that delamination is an accepted industry performance measure for laminated products, it should be noted that the delamination testing carried out as part of this project was only one of a suite of testing methods used for durability assessment. It is acknowledged that these delamination tests were not comprehensive as the reported results are from a very limited number of samples using only two commercial beams and one PUR adhesive. Delamination testing of samples to AS/NZS 1328.1:1998 went beyond the required number of standard cycles to assess performance at greater levels of stress. The delamination results should be viewed in the context of a research study, providing information complementary to other durability test methods, and not as an industry quality control exercise.

4.2 Shear strength

Under wet conditions, all samples had significantly reduced shear strength (Figures 22–24).

CCA and MCA-treated samples had a statistically significant greater strength reduction than RF samples, but the mean strengths of all samples fell within a narrow range. The wood failure percentage of PUR samples was lower than RF samples, particularly for the CCA-treated wood.

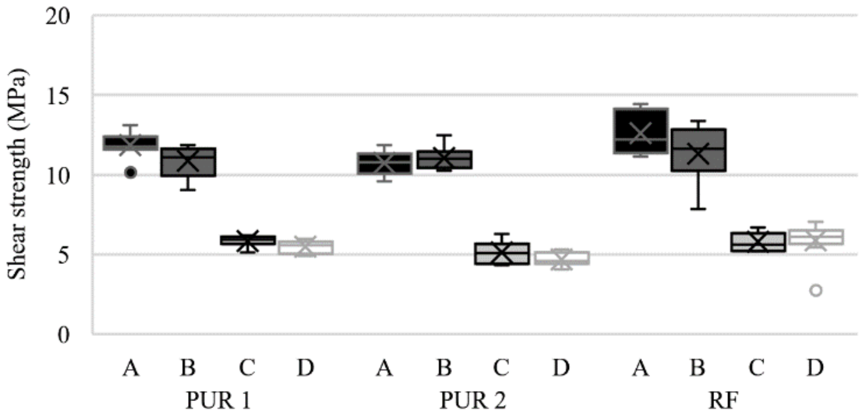

Figure 22. Shear strength of bonded and solid untreated specimens in the ambient and wet conditions: A = solid, ambient; B = bonded, ambient; C = solid, wet; D = bonded, wet.

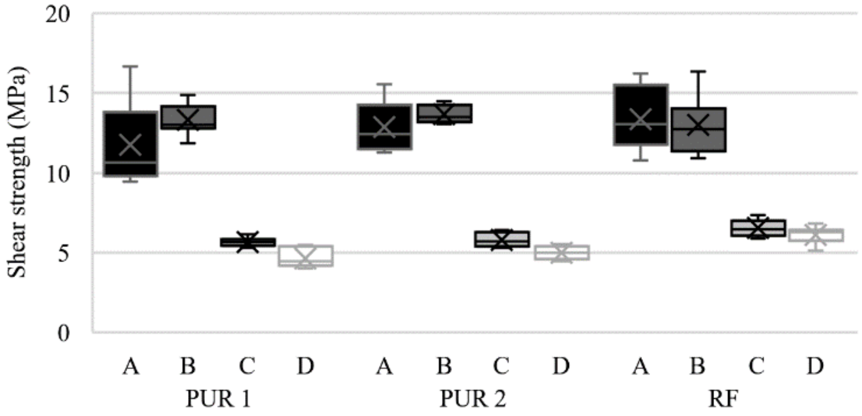

Figure 23. Shear strength of bonded and solid CCA-treated specimens in the ambient and wet conditions: A = solid, ambient; B = bonded, ambient; C = solid, wet; D = bonded, wet.

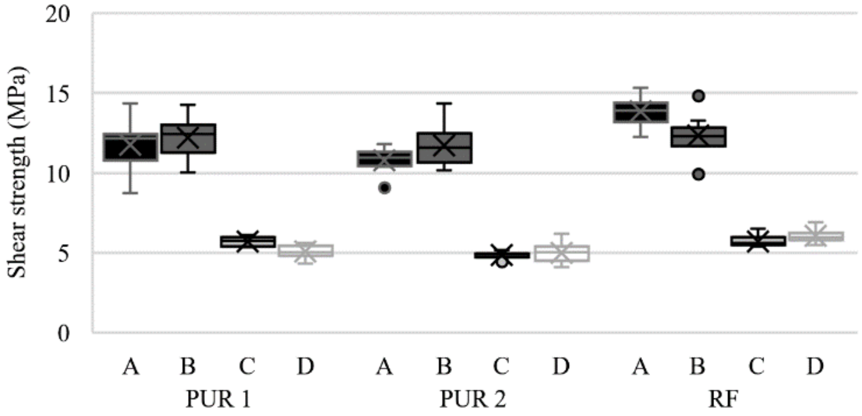

Figure 24. Shear strength of bonded and solid MCA-treated specimens in the ambient and wet conditions: A = solid, ambient; B = bonded, ambient; C = solid, wet; D = bonded, wet.

After natural ageing, untreated samples did not show any significant reduction in shear strength regardless of adhesive type (Figure 25). There was more of a strength decrease observed for the CCA-treated samples for both PUR and RF adhesives (Figure 26). MCA-treated samples showed comparable performance (Figure 27).

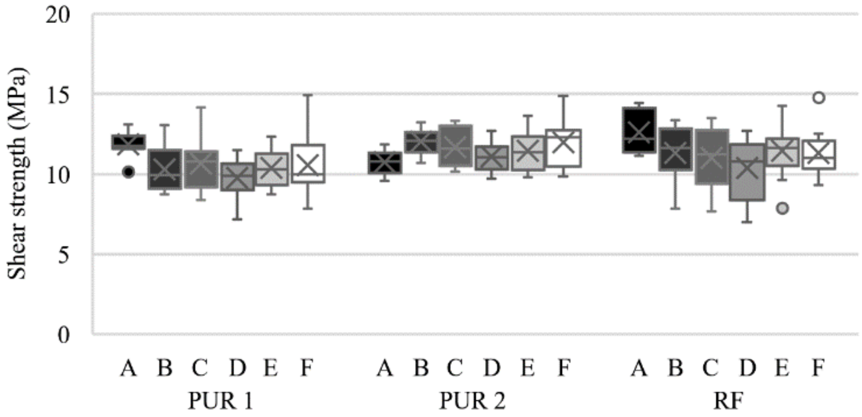

Figure 25. Shear strength of untreated specimens after natural ageing: A = solid; B = unaged; C = 3 months; D= 6 months; E = 9 months; F = 12 months.

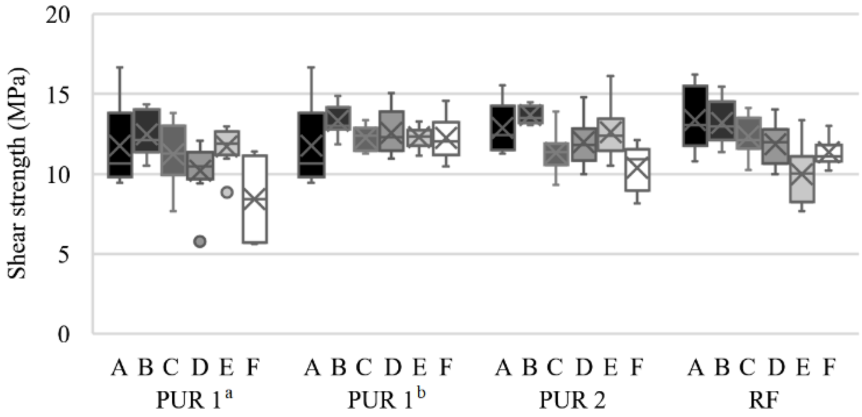

Figure 26. Shear strength of CCA-treated specimens after natural ageing: A = solid; B = unaged; C = 3 months; D= 6 months; E = 9 months; F = 12 months; a = ring arrangement in Figure 2a; b = ring arrangement in Figure 2b.

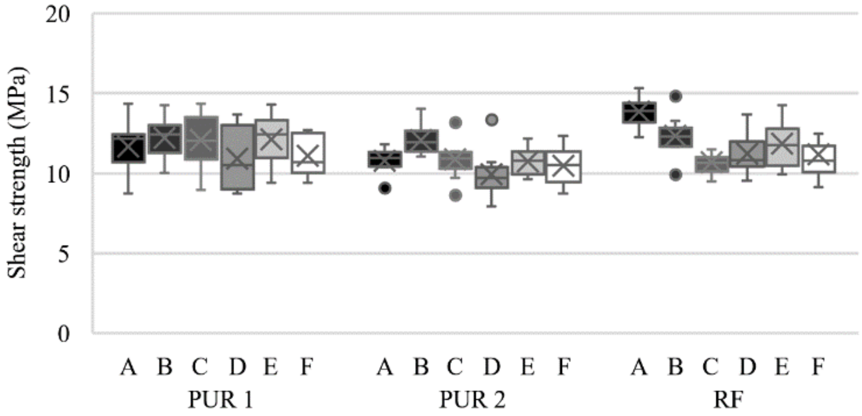

Figure 27. Shear strength of MCA-treated specimens after natural ageing: A = solid; B = unaged; C = 3 months; D= 6 months; E = 9 months; F = 12 months.

After vacuum-pressure soak-drying cycles, shear strength was comparable amongst adhesives (Figures 28–30). Statistically insignificant strength reductions were seen for the CCA-treated samples with all adhesives. MCA-treated samples showed similar strengths with all adhesives.

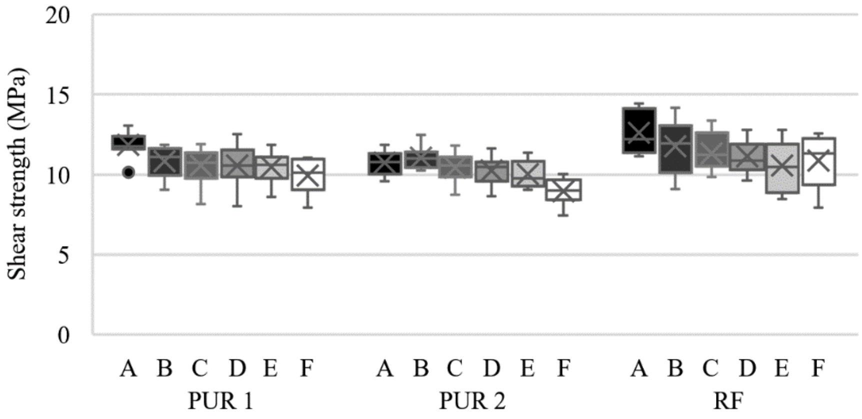

Figure 28. Shear strength of untreated specimens after vacuum-pressure soak-drying ageing: A = solid; B = unaged; C = 2 cycles; D = 4 cycles; E = 8 cycles; F = 16 cycles.

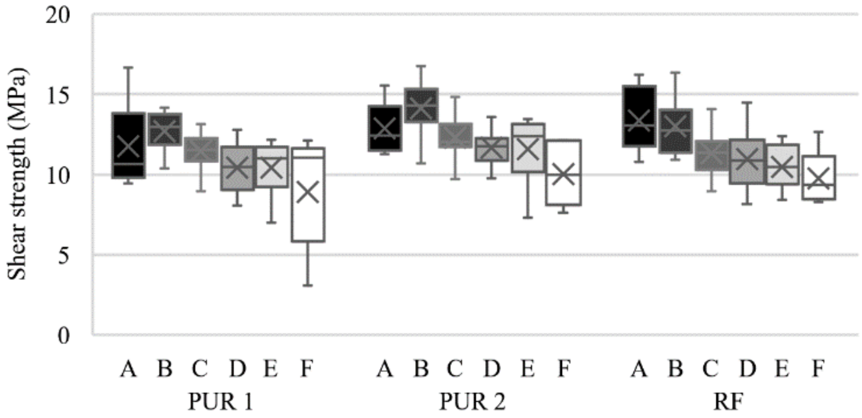

Figure 29. Shear strength of CCA-treated specimens after vacuum-pressure soak-drying ageing: A = solid; B = unaged; C = 2 cycles; D = 4 cycles; E = 8 cycles; F = 16 cycles.

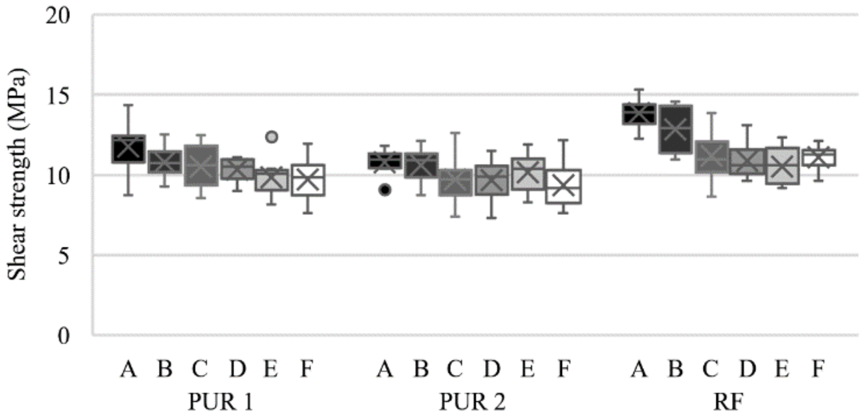

Figure 30. Shear strength of MCA-treated specimens after vacuum-pressure soak-drying ageing: A = solid; B = unaged; C = 2 cycles; D = 4 cycles; E = 8 cycles; F = 16 cycles.

After ageing at constant high temperature and humidity, the shear strength of all specimens was reduced (Figures 31–32). A statistically significant strength reduction was recorded for CCA-treated samples bonded with RF adhesive. All adhesives performed comparably for the MCA-treated samples.

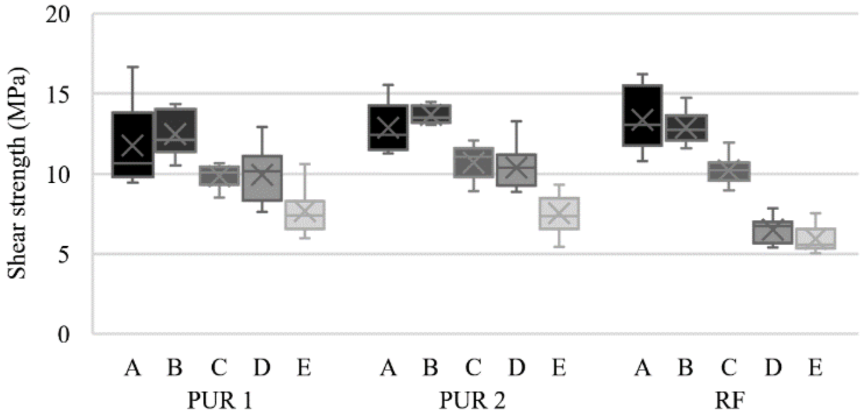

Figure 31. Shear strength of CCA-treated specimens after high temperature and humidity ageing: A = solid; B = unaged; C = 3 months; D= 6 months; E = 9 months.

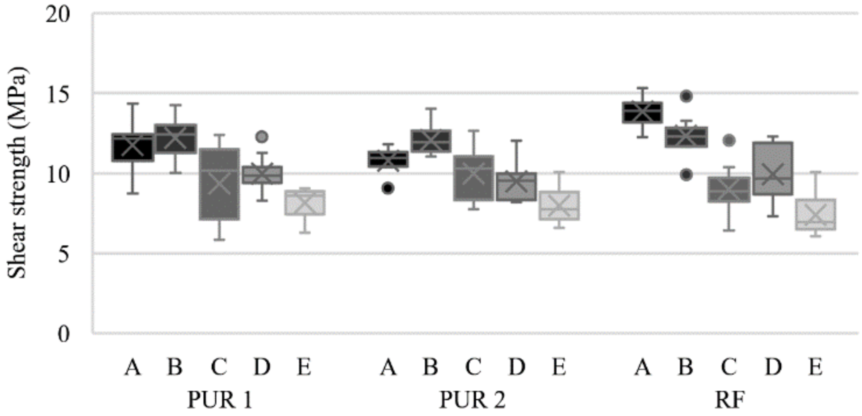

Figure 32. Shear strength of MCA-treated specimens after high temperature and humidity ageing: A = solid; B = unaged; C = 3 months; D= 6 months; E = 9 months.

4.3 Fracture energy

Results of fracture energy tests under ambient and wet conditions for solid and bonded specimens are shown in Figures 33–35.

Under ambient conditions, the adhesive fracture energy[1] of the bonded samples was generally higher than the solid samples.

Under wet conditions, the energy release rate of the PUR adhesives varied depending on the adhesive and preservative treatment but it compared well with solid specimens under dry conditions for both treated and untreated wood.

In contrast, the energy release rate for RF bonded samples significantly increased with both untreated and treated wood in a similar manner to solid specimens.

---

[1] The term ‘adhesive fracture energy’ is used in this report in preference to ‘energy release rate’, the latter being used throughout the original PhD thesis from which the reported data has been extracted (Karami, 2020).

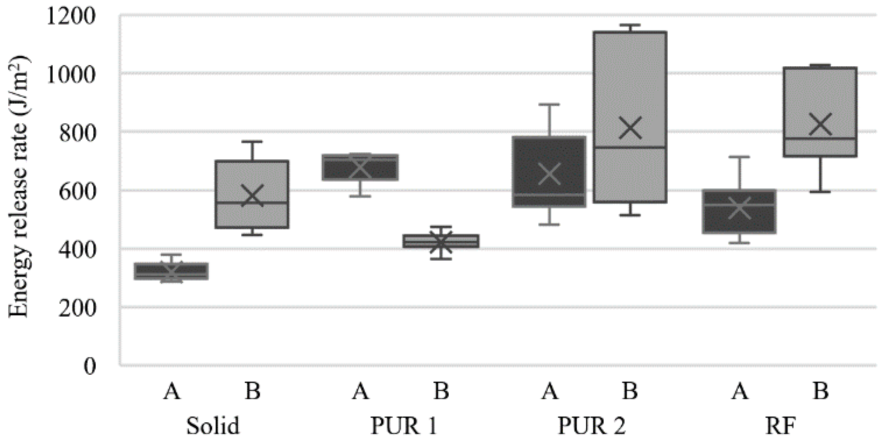

Figure 33. Adhesive fracture energy of solid and bonded untreated specimens under ambient and wet conditions: A = ambient; B = wet.

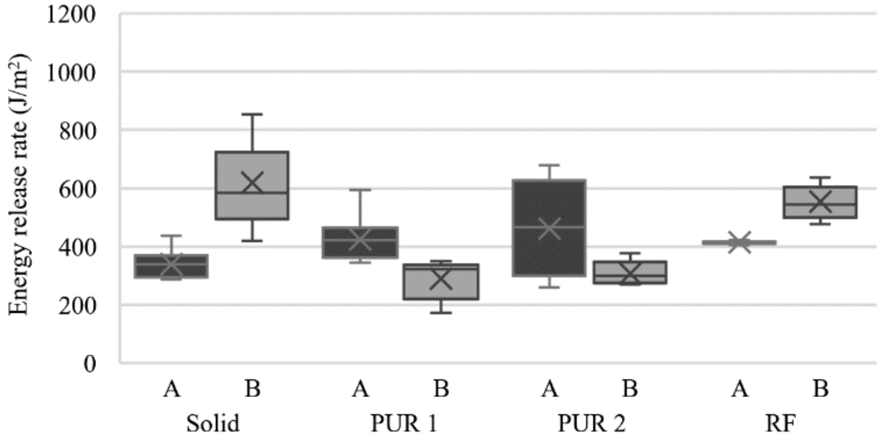

Figure 34. Adhesive fracture energy of solid and bonded CCA-treated specimens under ambient and wet conditions: A = ambient; B = wet.

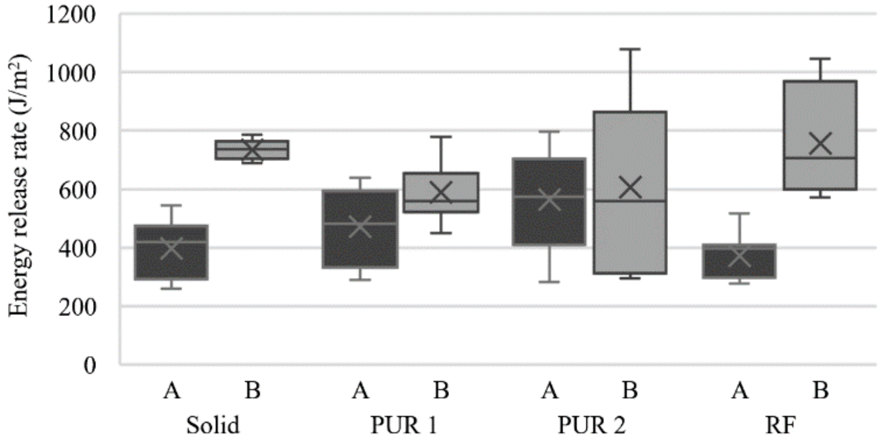

Figure 35. Adhesive fracture energy of solid and bonded MCA-treated specimens under ambient and wet conditions: A = ambient; B = wet.

After 12 months of natural ageing, solid specimens and samples bonded with different adhesives performed comparably (Figures 36–38).

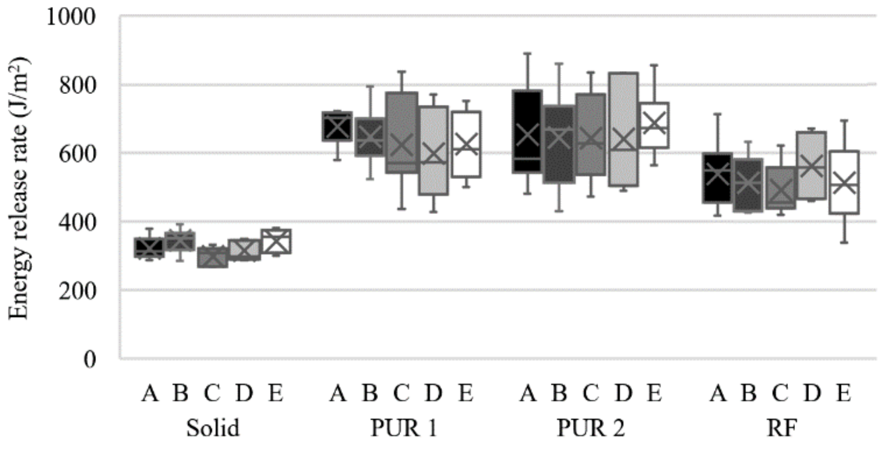

Figure 36. Adhesive fracture energy of untreated specimens after natural ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months; E = 12 months.

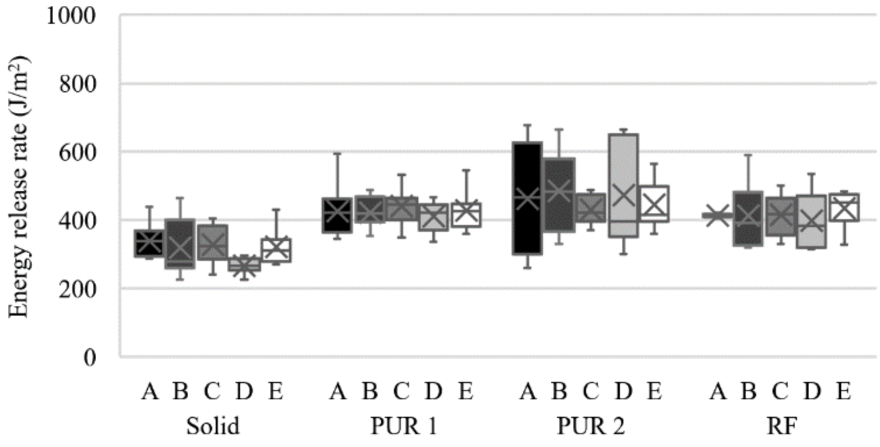

Figure 37. Adhesive fracture energy of CCA-treated specimens after natural ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months; E = 12 months.

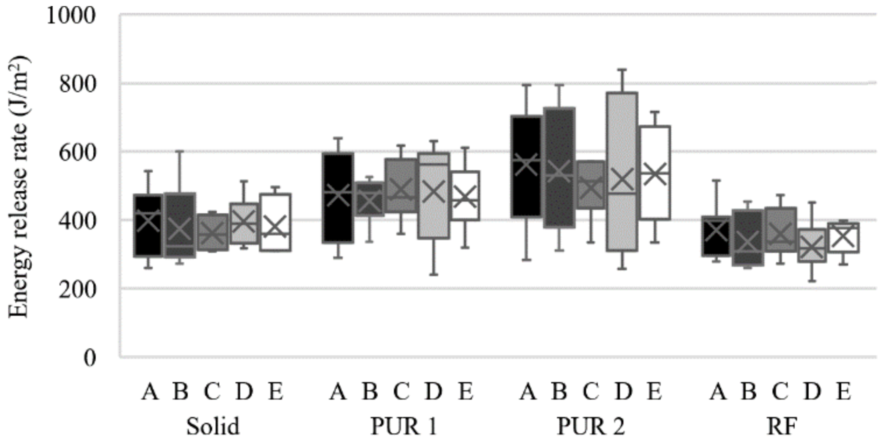

Figure 38. Adhesive fracture energy of MCA-treated specimens after natural ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months; E = 12 months.

Visual inspection of the naturally aged fracture test blocks revealed similar findings to the laminated test blocks in that delamination in PUR-bonded untreated and MCA-treated samples was lower than CCA-treated blocks and that delamination occurred mainly in latewood areas (Figure 39).

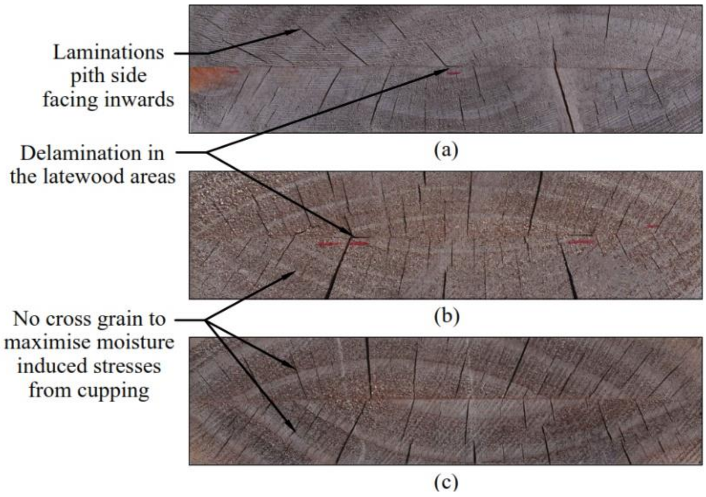

Figure 39. PUR 1 bonded fracture energy test blocks subjected to natural ageing: (a) untreated; (b) CCA-treated; (c) MCA-treated.

After vacuum-pressure soak-drying, the adhesive fracture energy of both PUR and RF samples was also comparable for the untreated and preservative-treated samples (Figures 40–42).

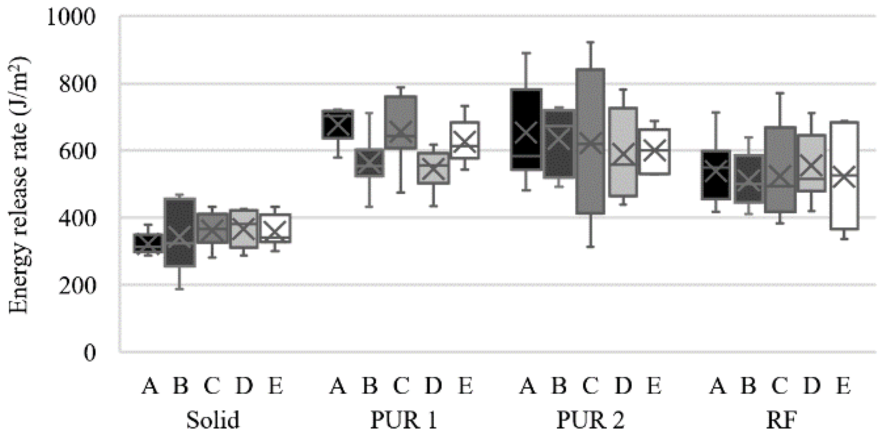

Figure 40. Adhesive fracture energy of untreated specimens after vacuum-pressure soak-drying ageing: A = unaged; B = 2 cycles; C= 4 cycles; D = 8 cycles; E = 16 cycles.

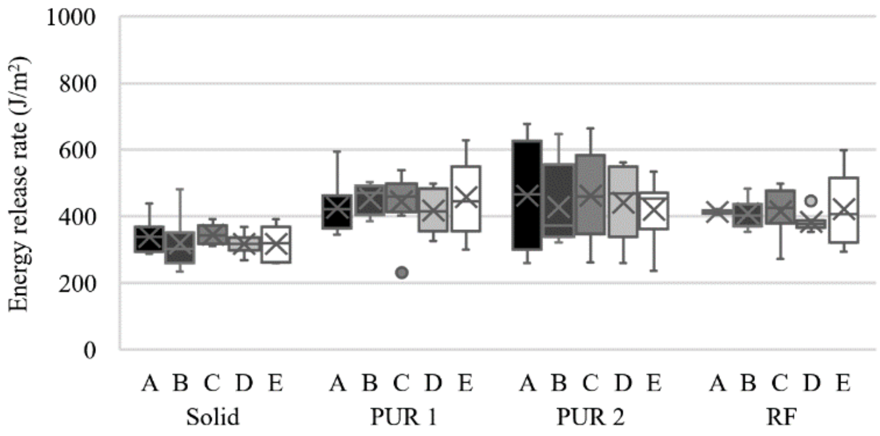

Figure 41. Adhesive fracture energy of CCA-treated specimens after vacuum-pressure soak-drying ageing: A = unaged; B = 2 cycles; C= 4 cycles; D = 8 cycles; E = 16 cycles.

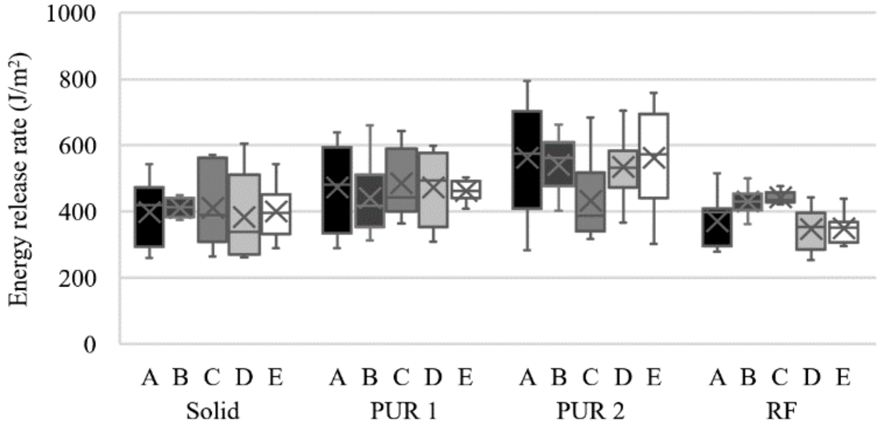

Figure 42. Adhesive fracture energy of MCA-treated specimens after vacuum-pressure soak-drying ageing: A = unaged; B = 2 cycles; C= 4 cycles; D = 8 cycles; E = 16 cycles.

Exposure to constant high-temperature, high-humidity conditions substantially reduced the adhesive fracture energy of all specimens (Figures 43–45). For untreated and MCA-treated wood, the reduction shown by different adhesives was not significantly different. For CCA-treated wood, the reduction for RF samples was significantly greater than for the PUR samples.

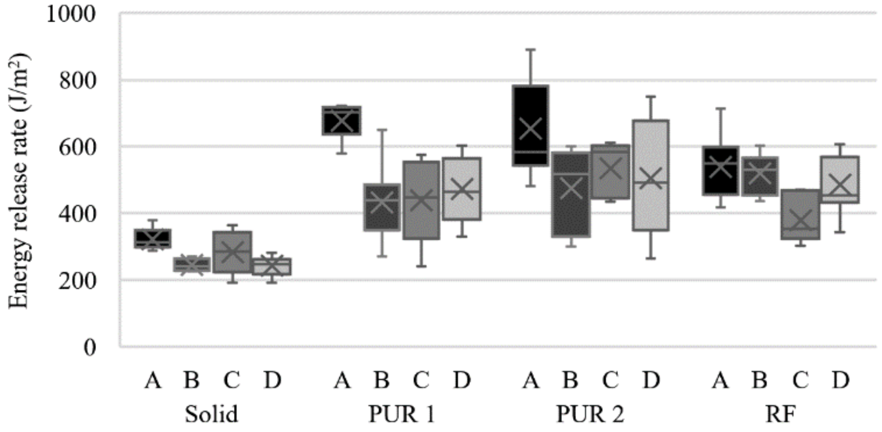

Figure 43. Adhesive fracture energy of untreated specimens after constant high temperature and humidity ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months.

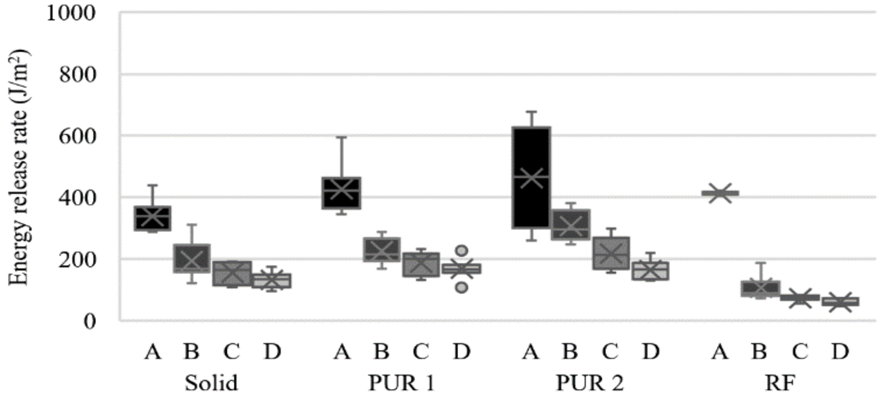

Figure 44. Adhesive fracture energy of CCA-treated specimens after constant high temperature and humidity ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months.

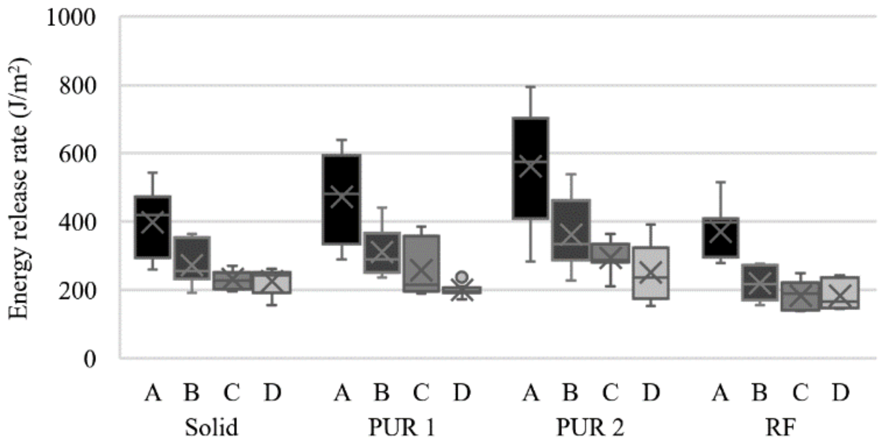

Figure 45. Adhesive fracture energy of MCA-treated specimens after constant high temperature and humidity ageing: A = unaged; B = 3 months; C= 6 months; D = 9 months.

4.4 Ageing models

To evaluate the effect of the ageing intensity on different adhesive-wood combinations subjected to different ageing methods and also find a correlation between these methods, ageing models were obtained by fitting a regression equation to the results. The logarithmic regression model used for the shear strength results is shown in Eq. 1:

$$y = -A \times \ln(x) + B \qquad \text{(Eq. 1)}$$

where:

y = strength retention
x = ageing intensity
A = degradation rate
B = intercept

For the naturally aged specimens subjected to variable weather conditions, the decay hazard at different ageing intervals, rather than ageing duration, was used to determine ageing intensity. The decay hazard was calculated using Scheffer's climate index (Scheffer, 1971), shown in Eq. 2:

$$Climate\ index = \frac{\sum[(T-2)(D-3)]}{16.7} \qquad \text{(Eq. 2)}$$

where:

T = average monthly temperature (°C)
D = number of days with precipitation ≥ 0.25 mm in the month

For vacuum-pressure soak-drying and constant high-temperature, high-humidity ageing, ageing intensity was represented by the number of cycles and test duration respectively.

Based on the shear strength results, ageing models are shown for natural ageing (Figure 46), vacuum-pressure soak-drying (Figure 47) and constant high temperature/humidity (Figure 48). The degradation rate of CCA-treated samples was greater than MCA-treated and untreated samples. However, a reliable correlation could not be predicted from these relationships.

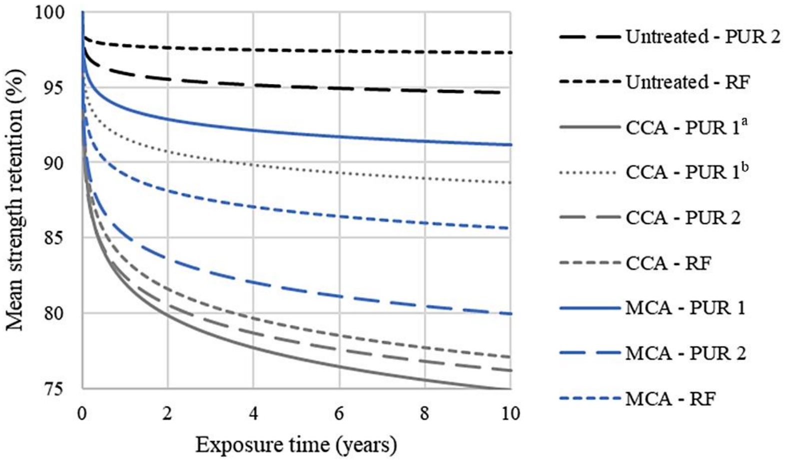

Figure 46. Relationship between mean shear strength retention and ageing intensity for natural ageing (extrapolated trend for 10 years based on 12-month testing): a = ring arrangement in Figure 2a; b = ring arrangement in Figure 2b.

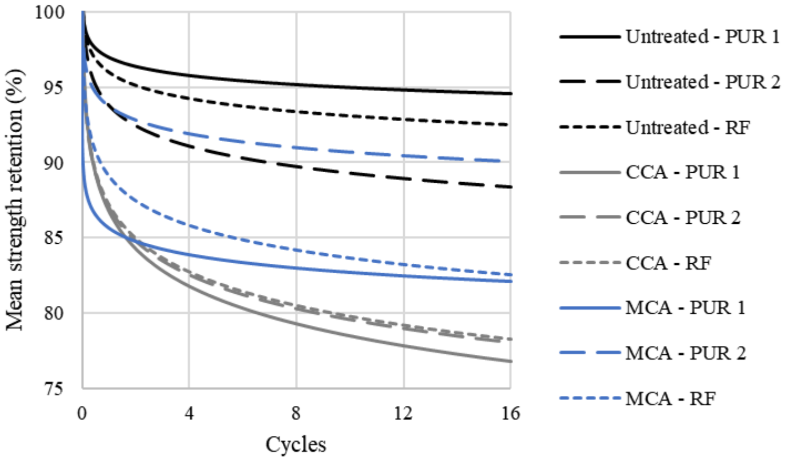

Figure 47. Relationship between mean shear strength retention and ageing intensity for vacuum-pressure soak-drying ageing.

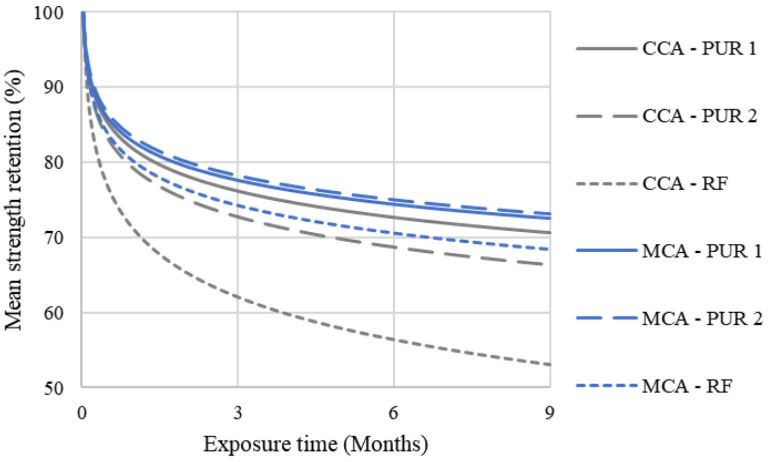

Figure 48. Relationship between mean shear strength retention and ageing intensity for constant high-temperature, high-humidity ageing.

Based on the adhesive fracture energy results, ageing models are shown for natural ageing (Figure 49), vacuum-pressure soak-drying (Figure 50) and constant high temperature/humidity (Figure 51). The CCA-treated samples had the greatest degradation rate under constant high temperature and humidity conditions but not under other ageing conditions. Due to the high variability of the overall results, a reliable correlation could not be predicted from these relationships.

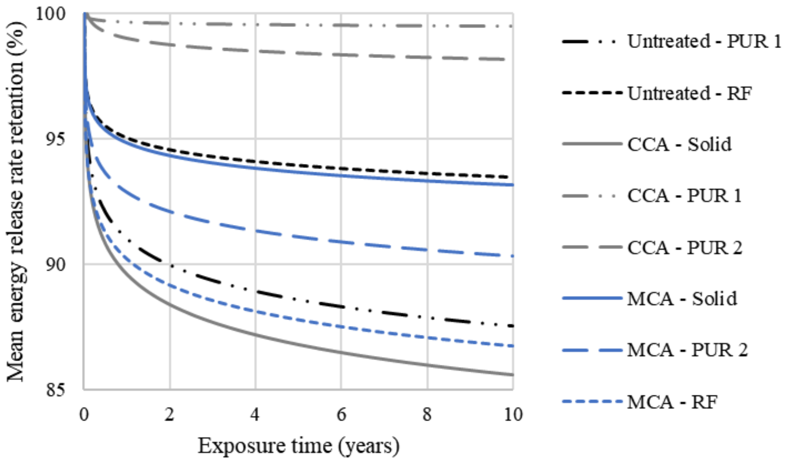

Figure 49. Relationship between mean adhesive fracture energy retention and ageing intensity for natural ageing (extrapolated trend for 10 years based on 12-month testing).

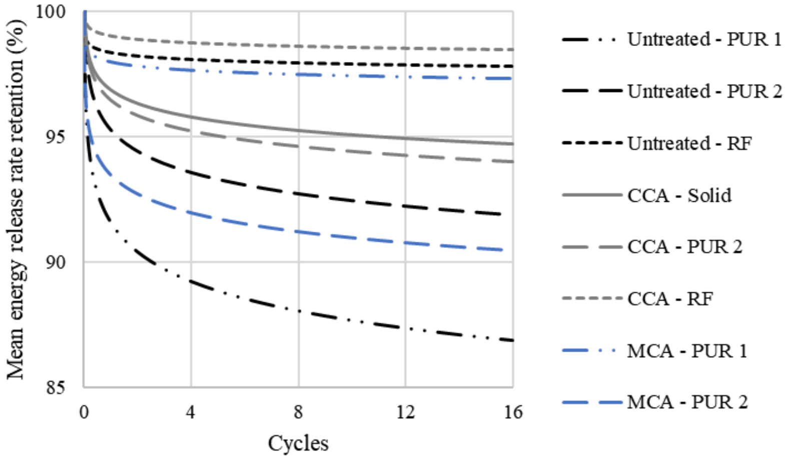

Figure 50. Relationship between mean adhesive fracture energy retention and ageing intensity for vacuum-pressure soak-drying ageing.

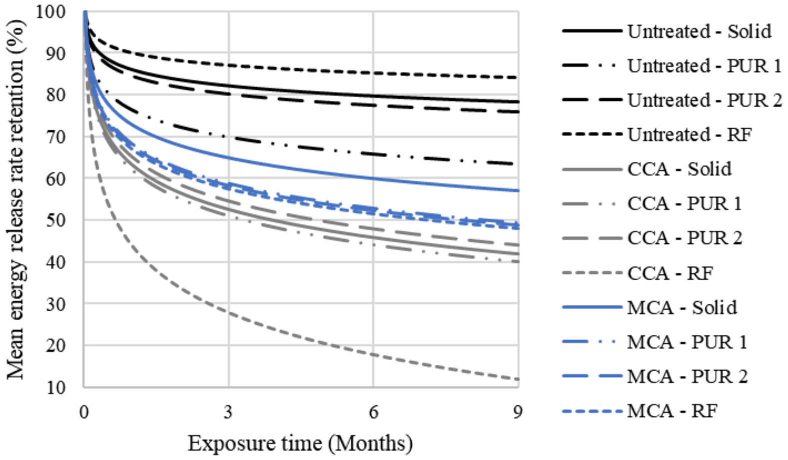

Figure 51. Relationship between mean adhesive fracture energy retention and ageing intensity for constant high-temperature, high-humidity ageing.

4.5 SEM

BSE SEM images are shown for untreated, CCA-treated and MCA-treated samples in Figures 52–54.

PUR bondlines were observed to have clear boundaries and were generally thicker than RF bondlines. The boundaries of the RF bondlines were difficult to visualise. Preservative treatments did not appear to affect adhesive penetration of the wood. Adhesive penetration was observed to be significantly lower in the latewood area of the annular rings for all adhesives and preservative treatments.

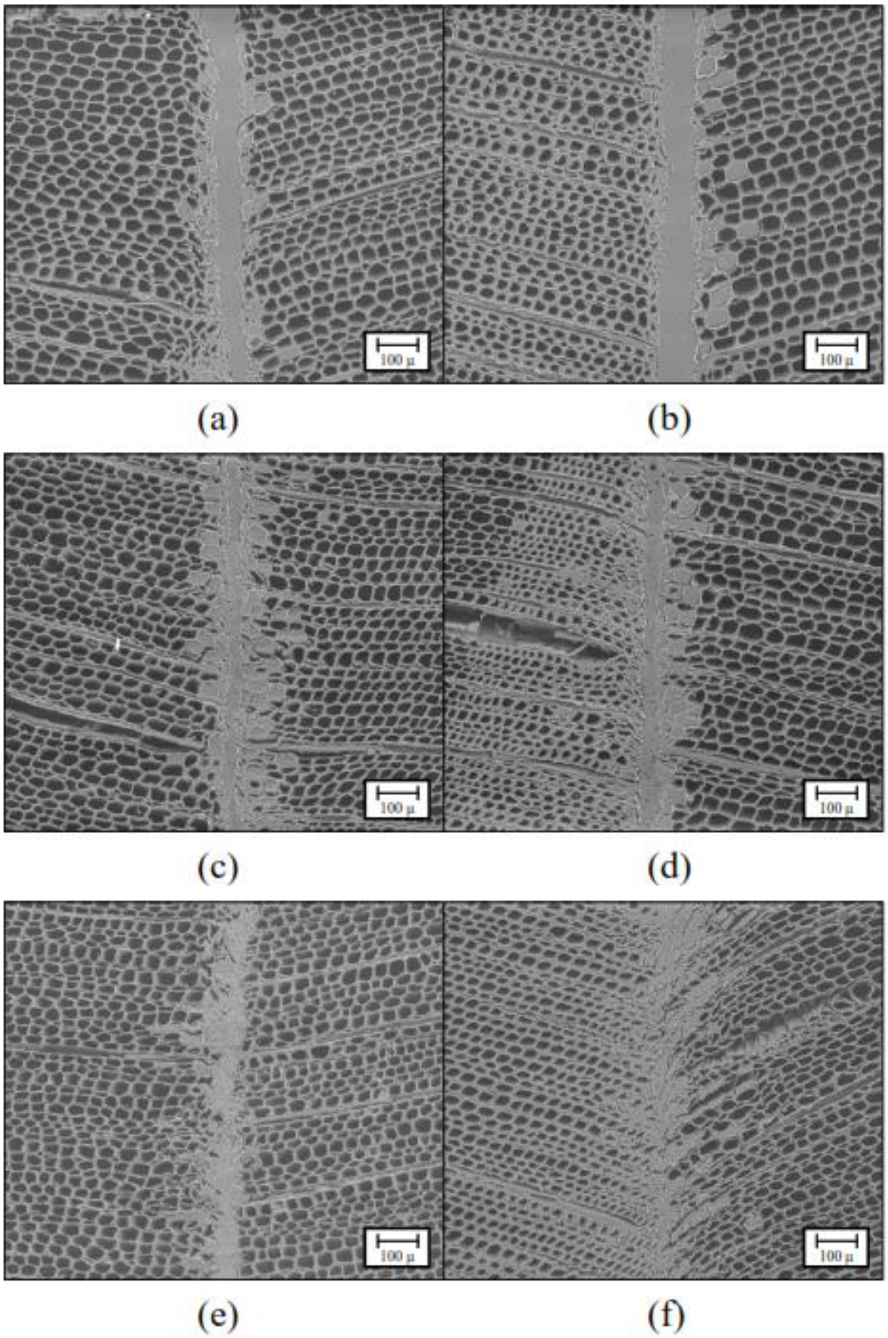

Figure 52. SEM BSE micrographs of untreated samples: (a) PUR 1 earlywood-earlywood; (b) PUR 1 latewood-earlywood; (c) PUR 2 earlywood-earlywood; (d) PUR 2 latewood-earlywood; (e) RF earlywood-earlywood; (f) RF latewood-earlywood.

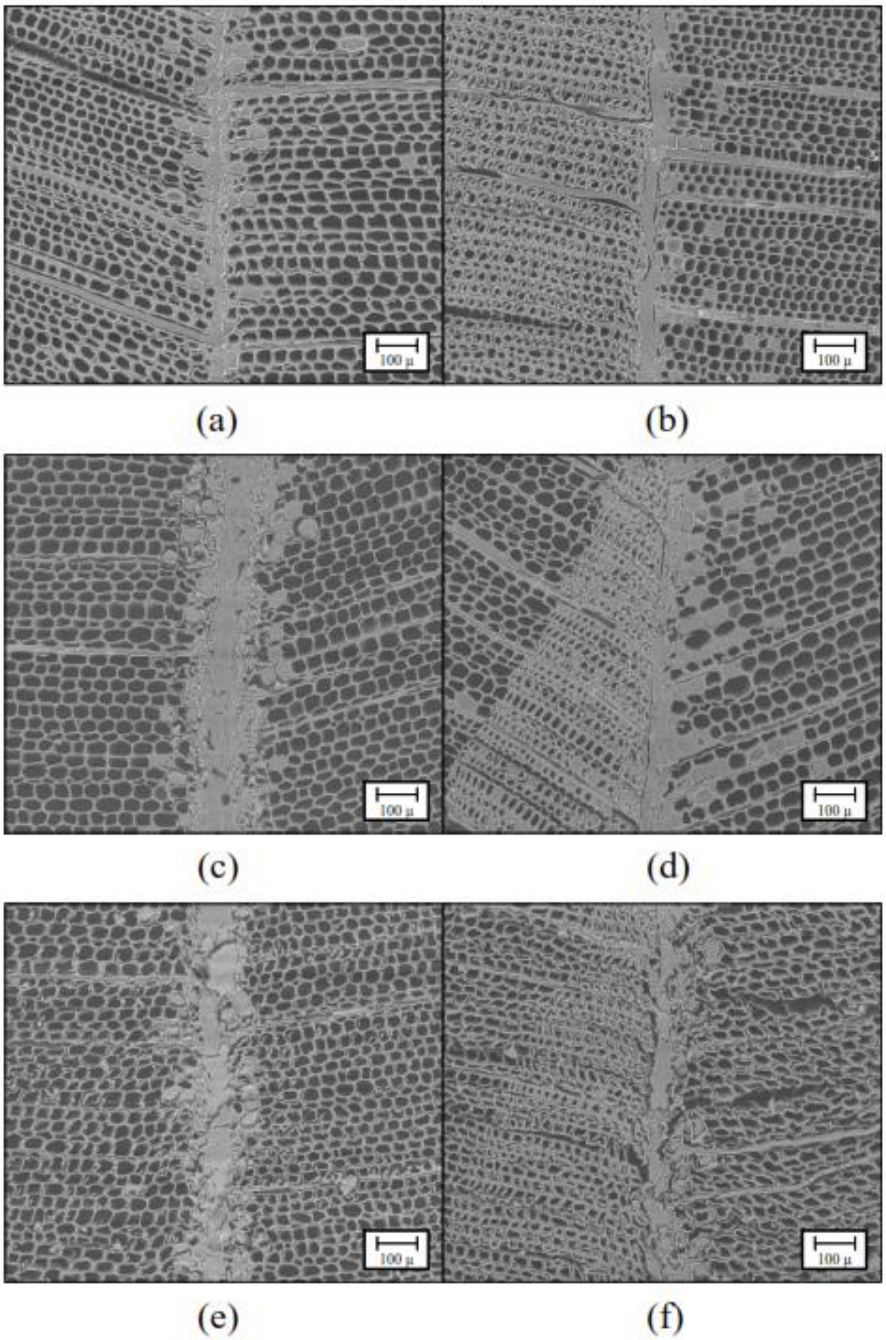

Figure 53. SEM BSE micrographs of CCA-treated samples: (a) PUR 1 earlywood-earlywood; (b) PUR 1 latewood-earlywood; (c) PUR 2 earlywood-earlywood; (d) PUR 2 latewood-earlywood; (e) RF earlywood-earlywood; (f) RF latewood-earlywood.

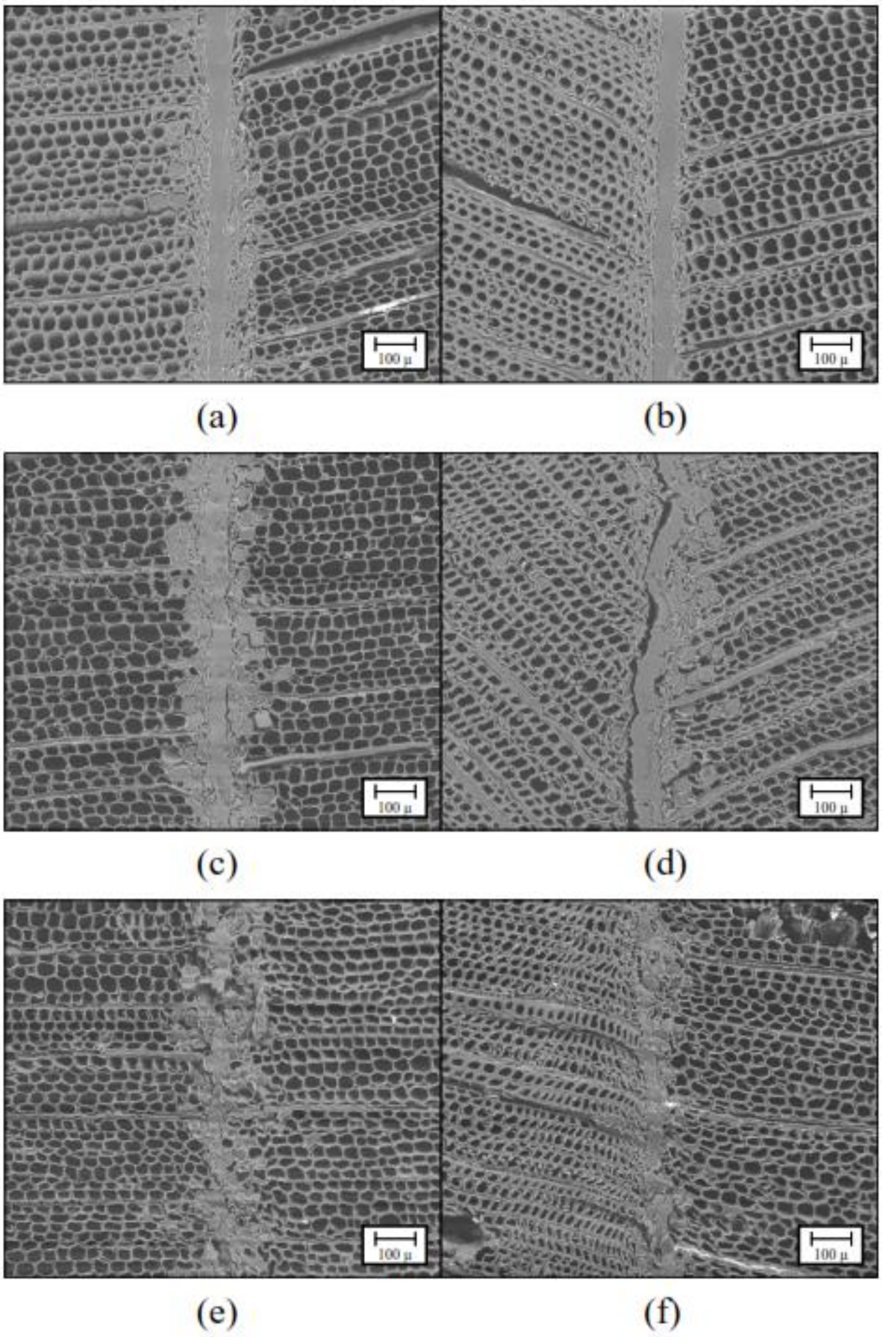

Figure 54. SEM BSE micrographs of MCA-treated samples: (a) PUR 1 earlywood-earlywood; (b) PUR 1 latewood-earlywood; (c) PUR 2 earlywood-earlywood; (d) PUR 2 latewood-earlywood; (e) RF earlywood-earlywood; (f) RF latewood-earlywood.

4.6 FTIR

In general, FTIR did not reveal any notable changes in structure after natural or accelerated ageing, suggesting that the accelerated conditions did not have an appreciable impact on the laminated samples. There was also little to suggest any detrimental effect of preservative on the samples. An example is shown in Figure 55 for both the adhesive and the wood substrate.

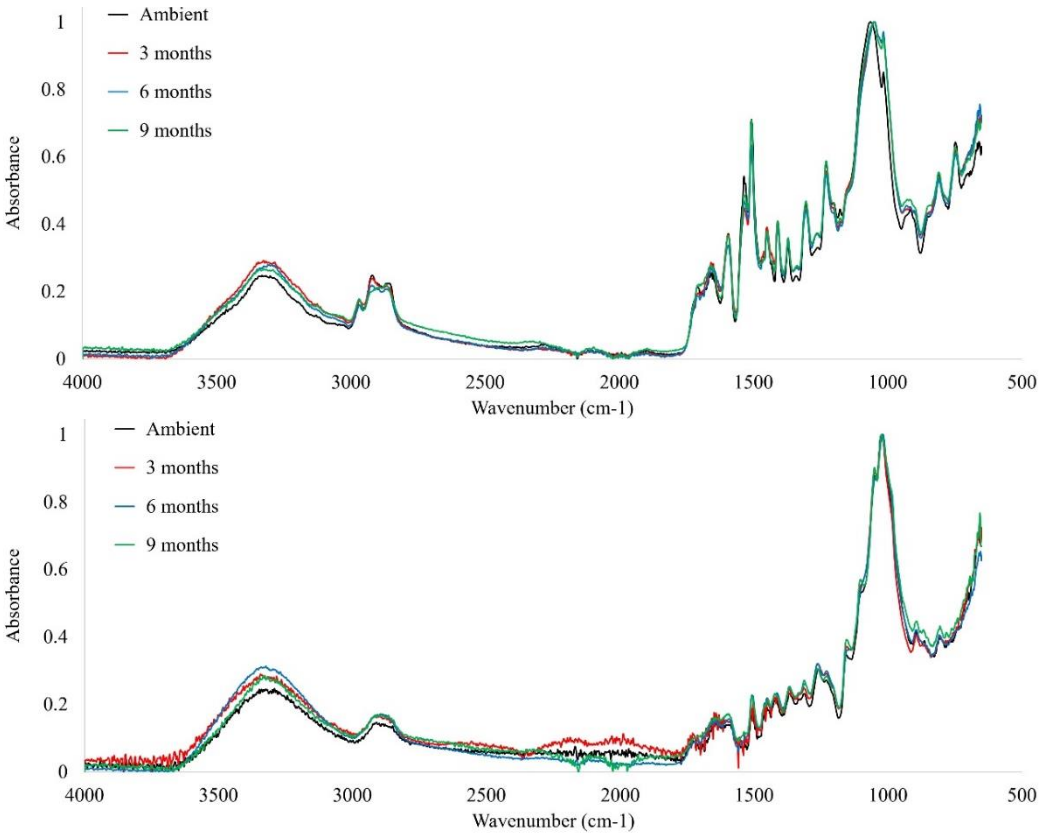

Figure 55. Similar FTIR spectra of (top) PUR adhesive and (bottom) wood after ageing at 65°C and 100% RH (Cycle C) indicate no significant degradation after 9 months.

4.6.1 Cycle B

The results of Cycle B tests were not included in the published thesis and so they are presented here. Note that, for these tests, an extra PUR adhesive sample (PUR 3) was included in the testing. Again, in general, ATR FTIR did not reveal any notable structural changes in the adhesives after 8 weeks of testing (Figure 56), suggesting that the accelerated conditions did not have an appreciable impact on the laminated samples. Some minor changes were noted in the spectra with CCA-treated samples (Figure 57) and MCA-treated samples (Figure 58).

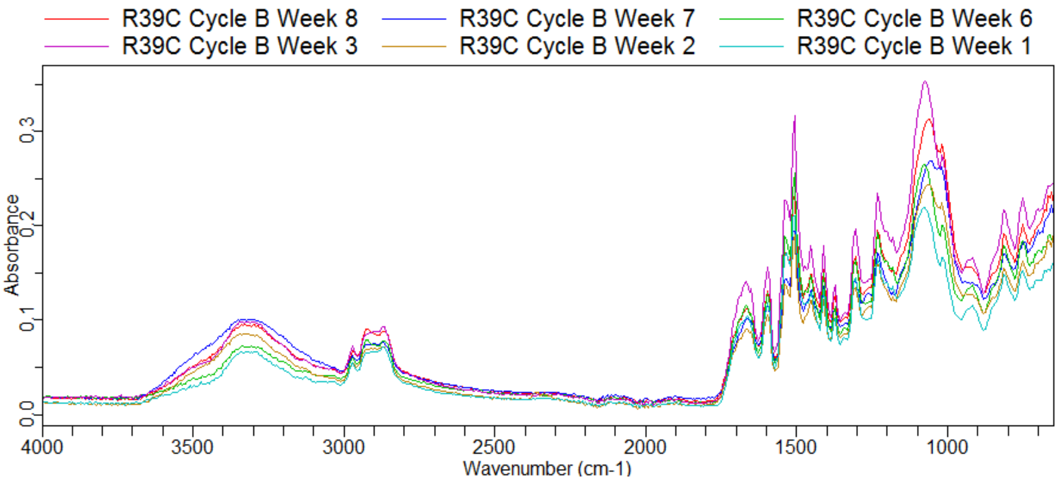

Figure 56. ATR FTIR spectra of PUR 1 bonded untreated wood for Cycle B.

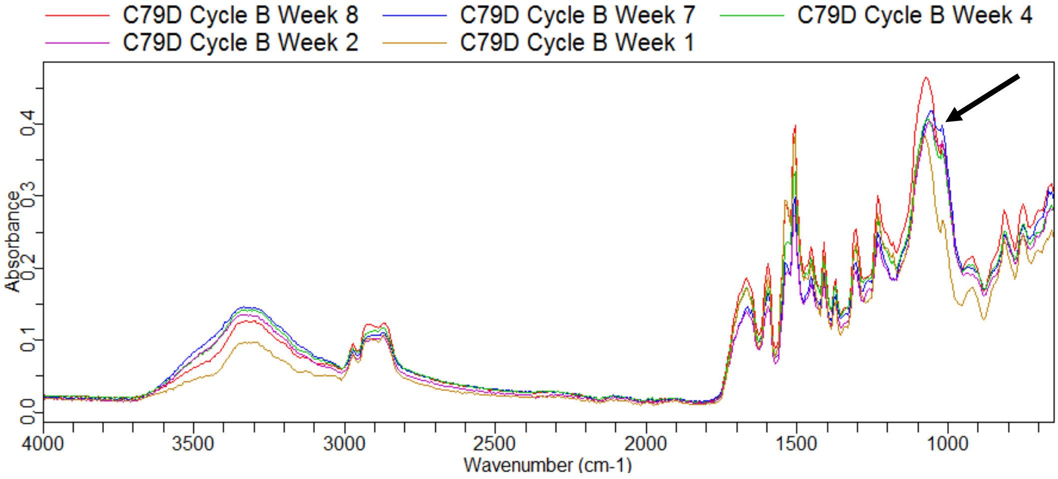

Figure 57. ATR FTIR spectra of PUR 2 bonded CCA-treated wood for Cycle B.

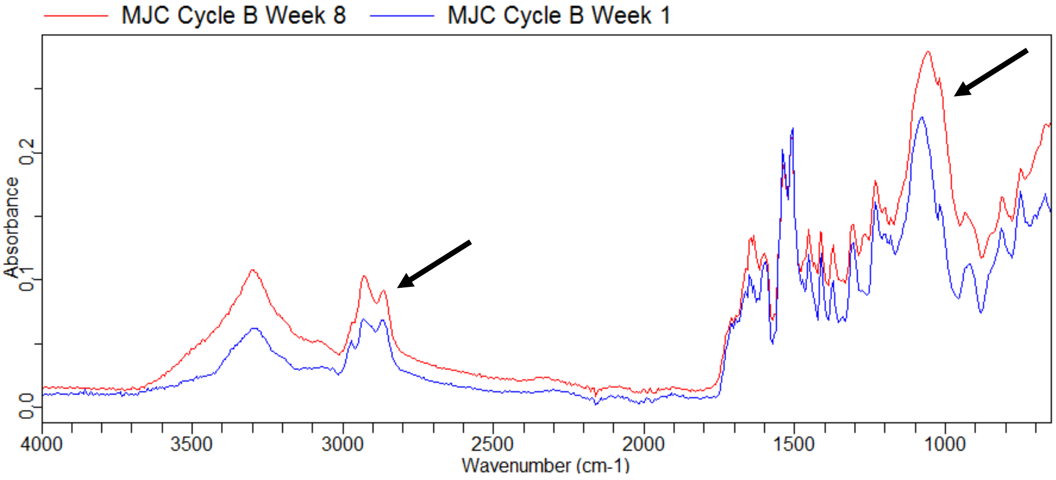

Figure 58. ATR FTIR spectra of PUR 3 bonded MCA-treated wood for weeks 1 and 8 of Cycle B.

No structural changes of note were observed for the wood substrate of untreated or treated samples (Figures 59–61).

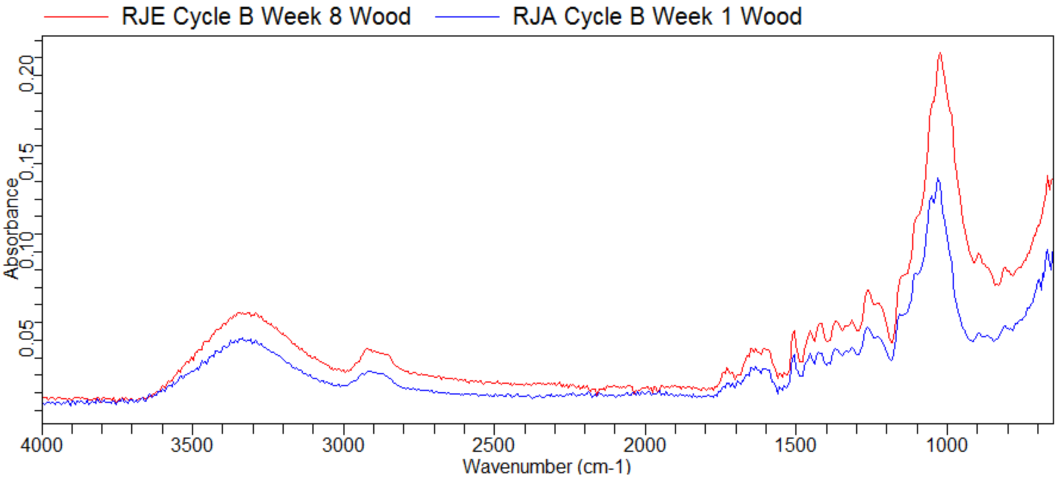

Figure 59. ATR FTIR spectra of PUR 3 bonded untreated wood for weeks 1 and 8 of Cycle B.

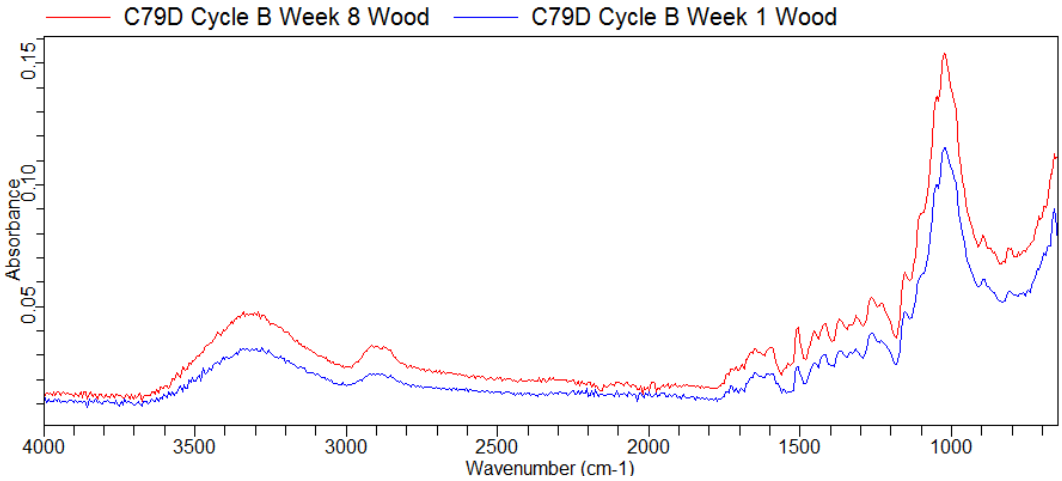

Figure 60. ATR FTIR spectra of PUR 2 bonded CCA-treated wood for weeks 1 and 8 of Cycle B.

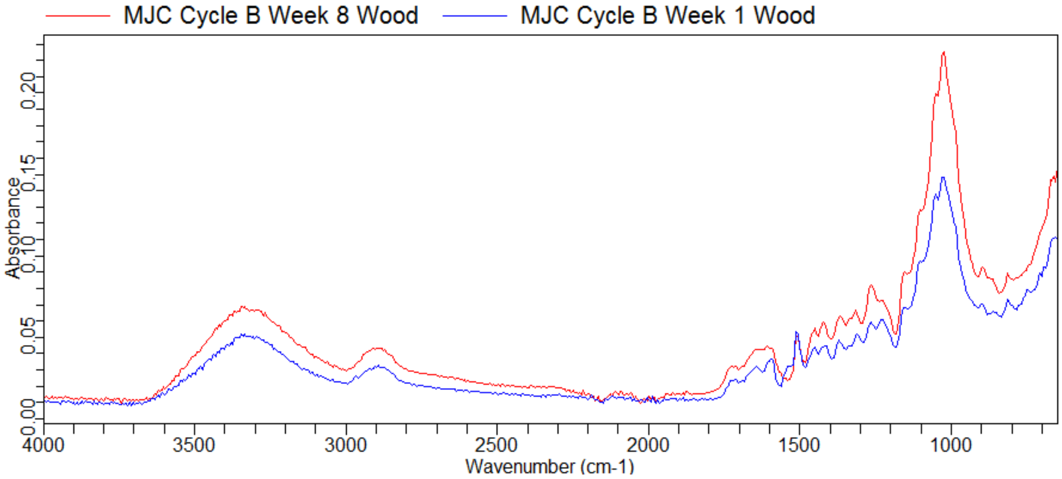

Figure 61. ATR FTIR spectra of PUR 3 bonded MCA-treated wood for weeks 1 and 8 of Cycle B.

A noteworthy observation from Cycle B testing is of as yet unknown significance and concerns the apparent offgassing from some of the samples that subsequently caused serious corrosion and the ultimate failure of the environmental chamber used to perform the tests.

The environmental chamber used for the Cycle B testing suddenly and unexpectedly stopped working. It was subsequently returned to the supplier who found that corrosive chloride ions had attacked the evaporator and caused the failure. The only source of chloride that could be identified was from the MCA-treated timber samples that were in the chamber for the 8-week period comprising Cycle B.

This was a virtually new chamber that had been commissioned only a few months prior to this testing and had not been used for any samples with chloride as a known component. It is believed that the timber outgassed corrosive species and the corrosion was exacerbated by the small size of the chamber through concentration effects. We have had no experience of this happening before at BRANZ. To the best of our knowledge, outgassing of corrosive species from preservative-treated timber has not been previously reported.

Potential offgassing of corrosive species from treated timber was unanticipated, and this raises questions around the prevalence, significance and effect of similar events in timber building elements used in construction. At this stage, it is unknown whether what we have seen is simply a one-off anomaly or if this is a new finding. The limited number of samples and lack of ability to repeat the experiments means that no firm conclusions can be drawn regarding these results.

Nevertheless, this unexpected finding, in combination with a significant decrease in shear strength of both the CCA-treated and MCA-treated samples after being subjected to Cycle B testing (unpublished results), is believed to be worthy of further attention.

Visual inspection of the samples revealed that the colour of the wood and adhesive had turned noticeably darker compared to controls. The failure interface was also found to have different characteristics, namely the wood failure patterns that appeared were dissimilar to controls with respect to shallower wood failure. That said, all samples achieved almost 100% wood failure (unpublished results).

While no or negligible delamination was observed in the untreated and MCA-treated samples respectively, PUR 1 bonded CCA-treated samples showed 7.6% delamination, most of which was in the latewood area (unpublished results).

As a result of these observations, further work in a separate project is under way to investigate the potential for preservative-treated timber offgassing under a range of temperature and humidity conditions. The aim of the new work is to shed light on whether these were aberrant results or if this is something that needs to be investigated more fully.

4.6.2 Cycle C

Following failure of the environmental chamber after the laminated samples had been subjected to Cycle B for up to 8 weeks, deposits of a whiteish powder were observed on the fan blades of the large environmental chamber used for the samples subjected to Cycle C for up to 9 months. Subsequent analysis of this powder by X-ray diffraction (XRD) and SEM/energy dispersive X-ray analysis (EDX) confirmed the presence of chloride salts.

Given that this environmental chamber has been used for many years for many different materials, the chloride found cannot be definitively linked to the laminated samples in this study. However, these chloride-containing deposits have not been previously observed, and the presence of chloride in the smaller chamber used for Cycle B may not be coincidental.

ATR FTIR spectra are shown for the PUR adhesives (Figures 62–64) and the wood substrate (Figures 65–67) illustrating no or minimal structural changes after ageing for untreated and preservative-treated samples subjected to constant elevated temperature and humidity under Cycle C for up to 9 months.

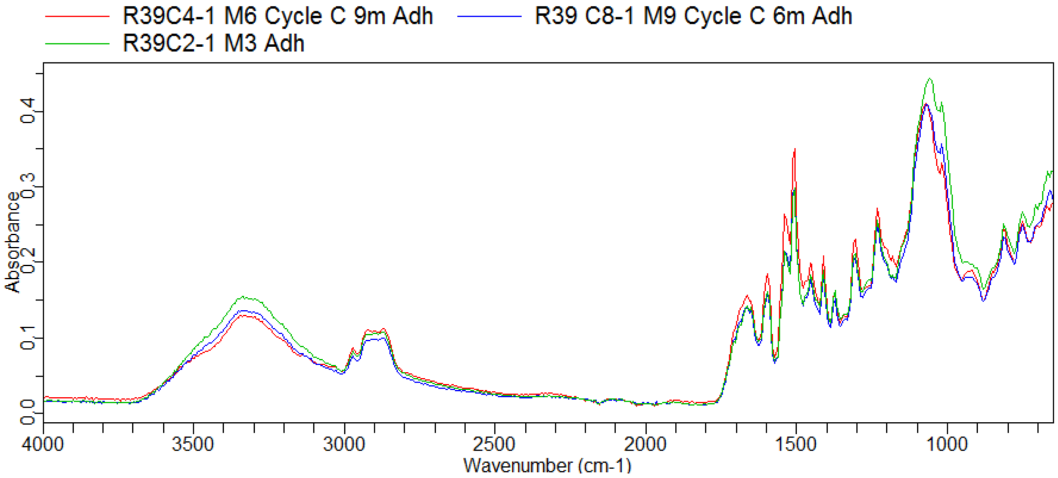

Figure 62. ATR FTIR spectra of PUR 1 bonded untreated wood aged for 3, 6 and 9 months under Cycle C.

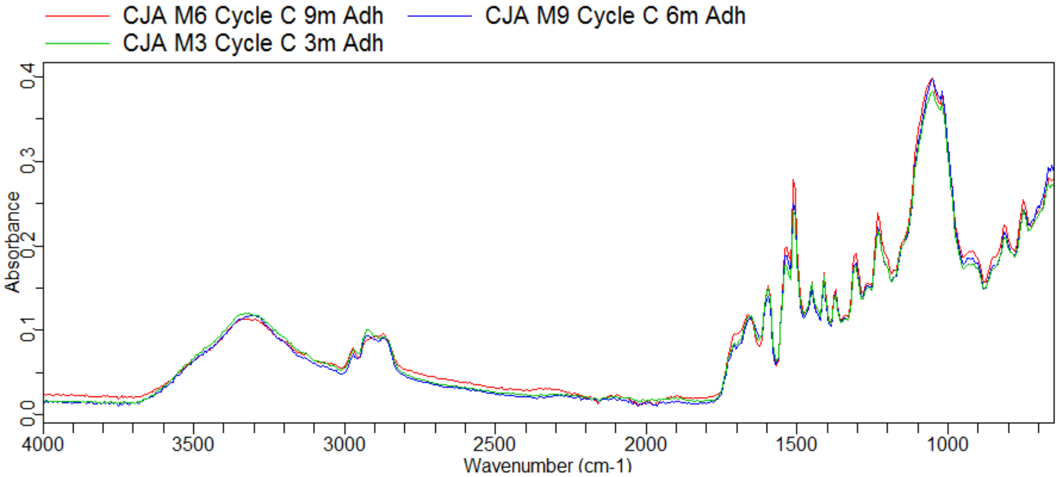

Figure 63. ATR FTIR spectra of PUR 3 bonded CCA-treated wood aged for 3, 6 and 9 months under Cycle C.

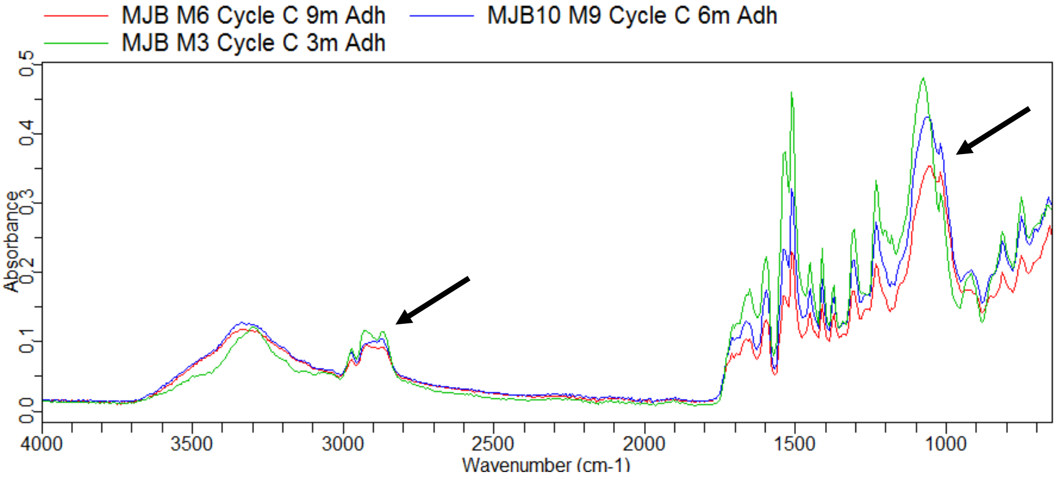

Figure 64. ATR FTIR spectra of PUR 3 bonded MCA-treated wood aged for 3, 6 and 9 months under Cycle C.

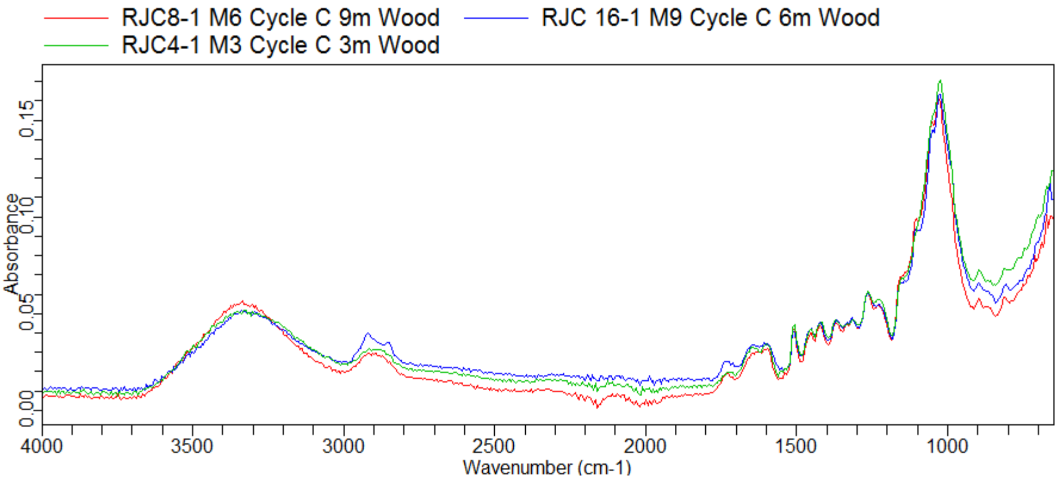

Figure 65. ATR FTIR spectra of PUR 3 bonded untreated wood aged for 3, 6 and 9 months under Cycle C.

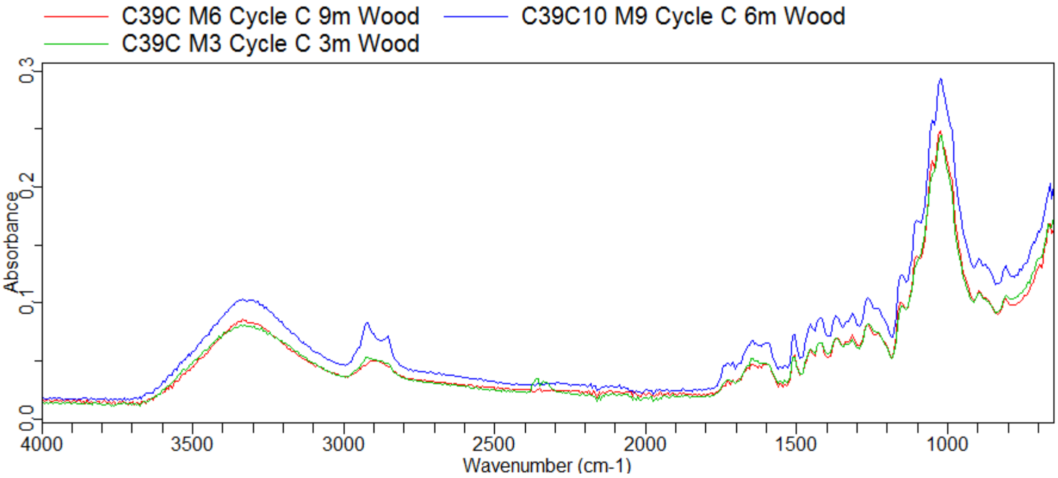

Figure 66. ATR FTIR spectra of PUR 1 bonded CCA-treated wood aged for 3, 6 and 9 months under Cycle C.

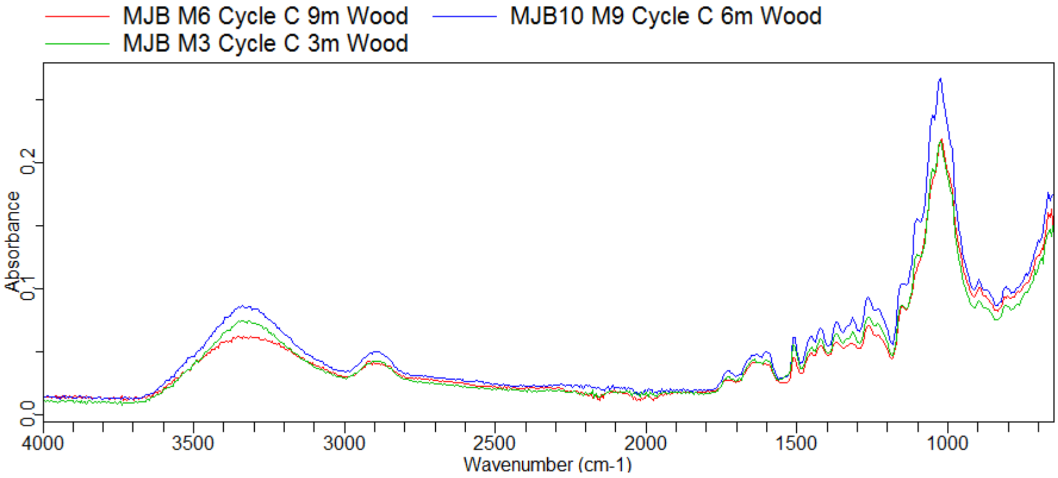

Figure 67. ATR FTIR spectra of PUR 3 bonded MCA-treated wood aged for 3, 6 and 9 months under Cycle C.

4.7 Discussion

Testing of the suitability of one-component PUR adhesives for use in structural timber applications began in Switzerland in the early 1970s. By the 1980s, they had also caught attention and growing interest in Germany, prompting a requirement for rigorous testing to determine their suitability for this purpose. Since the early 1990s, significant numbers of buildings have been constructed with PUR-bonded EWPs, including CLT, providing a 30-year in-service history for service class 3.

An important aspect of the testing programme was establishing the long-term performance of these adhesives, including the placement of samples under permanent load and different environmental conditions – 3-year tensile tests and 10-year bending tests, both under permanent load, were carried out with satisfactory results.

The vast majority of CLT in Europe and virtually all CLT in North America uses one-component PURs. In these parts of the world, delamination and shear tests are used to assess compliance with relevant standards. In this study, the delamination tests showed interesting differences between areas of earlywood and latewood. While minor delamination was associated with RF bondlines and PUR bondlines in earlywood areas, more delamination was observed with PUR bondlines in latewood areas (Karami & Nicholson, 2021). Greater delamination appeared to be related to less adhesive penetration into the timber and when there was a higher percentage of latewood adjacent to the bondline. The orientation of the annular growth rings was also found to be important. Samples with alternating growth ring orientation and outer laminations with the pith side facing inwards showed more delamination.

Controlling the angle of growth rings is likely to be difficult to achieve in practice for sawmills since this is constrained by cutting logs for maximum yield. Adjusting ring orientation is included in BS EN 14080:2013 *Timber structures – Glued laminated timber and glued solid timber – Requirements*, but it is not a production requirement in New Zealand. It also presents a problem for timber manufacturers during fabrication, especially when the timber boards are cut down into smaller pieces to remove any defects before finger-jointing. Despite the challenges, developing an automated process that optimises growth ring angle and orientation may be worth considering in the context of delivering improved product performance.

Previous studies have indicated that mode I fracture is a decisive factor affecting delamination resistance and durability. While the adhesive fracture energy of samples under ambient conditions or subjected to accelerated ageing were similar for both PUR and RF adhesives, the different types of adhesives were differentiated under wet conditions.

The spectroscopy results indicated that there was little to distinguish the spectra visually before and after accelerated ageing for any of the cycles investigated or after natural ageing outdoors. Similarly, there was little to suggest that the preservative treatment, with either CCA or MCA, had any significant influence on the adhesive or wood substrate when compared to the untreated samples. There was, therefore, no clear spectroscopic evidence to suggest that any significant structural changes had occurred during natural or accelerated ageing processes. This suggests that the polyurethane adhesives, as well as the wood itself, are highly resistant to hygrothermal stress. Any small differences in the wood spectra are likely to be attributable to natural wood variability.

However, there were some individual spectra that did show subtle signs of structural changes in some preservative-treated specimens including CCA-treated samples (Figure 20) and MCA-treated samples (Figure 21) subjected to Cycle B and an MCA-treated sample subjected to Cycle C (Figure 27), but their significance is currently unknown. Discolouration of adhesives and wood in Cycle B was also noted and is another potential indicator of chemical changes that could have an impact on structural properties. This merits further investigation.

There was reason to believe that chloride ions were released from some samples during this cycle, most likely from the chloride-containing fungicide tebuconazole in the MCA-treated specimens. The significance of this is being further investigated in a separate study.

Because only discrete areas of the adhesive bondline and wood substrate were sampled, it is possible that, if localised changes occur during ageing, these might be missed during spectroscopic analysis. Another possible explanation for the subtle structural changes is that changes were only beginning to become apparent and that longer ageing times would have been required to see clear evidence of structural changes.

Another consideration is that FTIR spectroscopy may not be sensitive enough to pick up structural changes induced under the experimental conditions. However, the results described in section 3.1 have shown clear evidence that ATR FTIR can be used to detect structural changes resulting from exposure to accelerated ageing for polyurethane-based adhesives that are not resistant to hygrothermal attack. Such changes were not observed in the experiments with the laminated samples that had been bonded with commercially available PUR adhesives formulated for structural applications.

Overall, the mechanical testing results have revealed that the PUR adhesives examined in this study show acceptable performance in laminated structural timber elements and are suitable for use under local conditions. Due to the high variability of results, reliable ageing models could not be developed.

5. Conclusions

As with all research studies, it is recognised that the research findings must be interpreted within the limitations of the study scope. The most significant of these constraints include the limited number of samples examined in some tests (for example, delamination) and the limited number of PUR adhesives used to fabricate the laminated specimens.

Taking a dual approach of investigating individual PUR adhesives and PUR-bonded laminated samples, this study provides the New Zealand industry with previously unavailable durability data specific to EWPs manufactured and used under New Zealand conditions.

It is clear that PURs cannot be treated as a generic class of adhesives that will behave identically. The properties of a PUR-based adhesive, including its likely durability, are strongly related to its composition and structure. Even apparently similar PURs can exhibit pronounced differences in behaviour when subjected to hygrothermal stress. In addition, the same adhesive may not always exhibit the same structural changes when subjected to different ageing cycles. This suggests that a generic durability test for all PUR-based structural adhesives is unlikely to be feasible. It is more likely that new PUR adhesives will need to be tested individually to assess performance or at least as individual product lines with minor differences in chemical composition that only affect properties such as open time.

However, spectral changes indicative of structural degradation were observed to have a relatively early onset within weeks or a few months of exposure to the test cycle. The results from this work suggest that a relatively simple accelerated ageing test based on Cycle C – performed at elevated temperature and humidity over a period of several months – could give an indication of the durability of a PUR adhesive to hygrothermal stress.

Structural adhesives are formulated to provide a bondline that outperforms the strength of the timber substrate in service. On the basis of the spectroscopy results, and assuming heterogeneity is not a significant feature of the adhesive samples, it would be predicted that failure would be more likely to occur in the wood substrate or at the adhesive-wood interface rather than as a direct result of failure of the adhesive itself.

While spectroscopy alone cannot determine long-term durability, this technique can contribute important chemical information and complement more-conventional mechanical testing methodologies currently used as the basis for several relevant standards. Development of predictive models may further enhance the value of spectroscopic analysis. The inability to reliably evaluate the long-term performance of engineered timber products within a limited timeframe has also highlighted an urgent need for the development of appropriate accelerated ageing methods that can be accurately correlated with the behaviour of materials and products during natural ageing.

With the laminated specimens, ageing of the samples led to a reduction in strength, but this was found to be generally comparable across all adhesives. FTIR spectroscopy of the PUR adhesives before and after ageing did not reveal any notable changes in their chemical structure, suggesting that the PUR adhesives were resistant to degradation under the test conditions. However, deterioration due to the effect of heat or moisture over a longer timeframe cannot be excluded. Shear and fracture test results after ageing were also found to be comparable, despite the difference in the observed delamination of the RF and PUR bondlines.

Under wet conditions, the shear strength for all bonded and solid specimens dropped significantly, although they were all still within a comparable range. Wet samples had a moisture content of 120–150% when tested. Shear strength reduction when wet was greatest for the PUR bonded samples. Resistance to moisture (and UV radiation) are extremely important considerations for PURs being used in exterior situations. Other studies have shown that the performance of some PURs under wet conditions is poorer than when dry and that some PURs are susceptible to UV degradation, with our own testing results in agreement with this.

Further investigation is still required to definitively establish the effect of preservative treatments on PUR bond performance in radiata pine EWPs. A general comparison of the data suggested that CCA-treated timber was more challenging to bond. Based on an ageing model fitted to the results, the CCA-treated and untreated specimens had the highest and lowest degradation rates, respectively, for shear strength retention. However, preservative treatment was not found to affect the penetration behaviour of the adhesives observed by SEM, nor did FTIR spectroscopy definitively indicate any detrimental effect of preservatives on the bondline.

It is important to also note that most EWPs in Europe and North America are not preservative treated as they are used internally (Leggate, 2018). For external applications, improved durability focuses on appropriate design, construction and maintenance but it is also noteworthy that mandated preservative treatment is being actively discussed as an additional safety measure.

There is an increasing global push towards reducing the use of known or potentially toxic chemicals used in preservative treatments. In Europe, development of new preservative treatments is moving away from toxic chemicals and biocides towards wood modification – for example, thermal treatments, acetylation, furfurylation and dimethyloldihydroxyethelenurea (DMDHEU).

Wood decay hazards are also expected to increase due to climate change, further increasing the importance of wood preservative treatments in the future. MCA is widely used throughout Europe. Europe also undertakes extensive testing of wood product durability and efficacy trials of wood preservatives, including leaching experiments with wood preservatives.

From previous survey results (Nicholson & Walsh, 2019), more technical information from manufacturers around the long-term performance of EWPs and adhesives would assist with increasing confidence in these products. Instances of product failures, while representing a small percentage of product, present an opportunity for manufacturers to collect data in order to better understand why failure may occur. This data would also assist in ensuring that products are used within the stated scope and that they are fit for their intended purpose. There is currently insufficient data to comprehensively track usage and trends of EWPs in New Zealand. Given the increasing importance of EWPs as construction materials, this is an area that would benefit from improved data collection.

5.1 Recommendations

Several recommendations are made for how the results of this research could be used by the industry in the near term along with suggestions for further work required to ensure that PUR-based structural adhesives can continue to be used successfully in the future.

Explore how PUR adhesives can begin to be formally recognised in New Zealand standards

There is already widespread use of PUR adhesives in EWPs throughout New Zealand, and this is likely to continue on an upwards trajectory. For this reason, there needs to be specific recognition of PUR adhesives in more New Zealand standards either through incorporation into revised existing standards or as a new standard, including consideration as a joint Australia/New Zealand standard. The approach taken to gain their approval could be similar to that taken for phenolics in the past, prior to their establishing a long history of use, with findings from this research and technical data held by manufacturers used to help inform an evidence-based approach. Given that some properties such as creep and stiffness may vary between different EWPs under the same conditions, consideration should be given to how specific or generic any new standards should be.

Increase accessibility of existing New Zealand EWP performance and durability data

Industry representatives have indicated that they are carrying out ongoing monitoring of existing structures and newly constructed buildings, providing a New Zealand equivalent of European case studies on long-term durability. Making this information publicly available would assist with independent performance evaluation and allow users to have increased confidence in these products.

More research on durability aspects of preservative-treated EWPs

This work has highlighted substantial gaps in our knowledge of the long-term performance of EWPs treated with CCA and MCA. In addition, as new preservative methods are developed and begin to be used due to the likely phasing out of some current treatments such as CCA, similar research should be prioritised to ensure there are no impacts on the long-term durability of any products.

More research on durability for in-ground contact applications

Much more data is needed in this area. Microbial degradation of adhesives is not well understood. In relation to exposure conditions, there are also important questions to answer around the effect of freshwater versus saltwater in a marine environment and situations where groundwater levels rise due to sea-level rise.

Development of predictive service life models

Reliable working models for prediction of service life remain a high priority to develop. An international research effort currently under way to model a wide range of wood species may provide much-needed improved service life prediction capability in the future.

Bibliography

Bockel, S., Mayer, I., Konnerth, J., Niemz, P., Swaboda, C., Beyer, M., Harling, S., Weiland, G., Bieri, N. & Pichelin, F. (2018). Influence of wood extractives on two-component polyurethane adhesive for structural hardwood bonding. *The Journal of Adhesion*, *94* (10), 829–845.

Brischke, C., Alfredsen, G., Humar, M. et al. (2021a). Modelling the material resistance of wood – Part 2: Validation and optimization of the Meyer-Veltrup model. *Forests*, *12*(5), 576–589.

Brischke, C., Alfredsen, G., Humar, M. et al. (2021b). Modelling the material resistance of wood – Relative resistance in above- and in-ground situations – Results of a global survey. *Forests, 12(5),* 590–604.

Carradine, D. (2020). *Usage and uptake of engineered wood products in New Zealand*. BRANZ Study Report SR453. Judgeford, New Zealand: BRANZ Ltd.

Clerc, G., Brulisauer, M., Affilter, S., Volkmer, T., Pichelin, F. & Niemz, P. (2017). Characterization of the ageing process of one-component polyurethane moisture curing wood adhesive. *International Journal of Adhesion and Adhesives*, *72*, 130–138.

Delpech, M. C. & Miranda, G. G. (2012). Waterborne polyurethanes: Influence of chain extender in FTIR spectra profiles. *Central European Journal of Engineering*, *2*(2), 231–238.

Dubelley, F., Bas, C., Planes, E., Pons, E., Yrieix, B. & Flandin, L. (2018). Durability of polymer metal multilayer: Focus on the adhesive chemical degradation. *Frontiers in Chemistry*, *6*, Article 459.

Fahey, L. M., Nieuwoudt, M. K. & Harris, P. J. (2017). Predicting the cell-wall compositions of *Pinus radiata* (Radiata pine) wood using ATR and transmission FTIR spectroscopies. *Cellulose, 24*(12), 5275–5293.

Jelle, B. P., Nilsen, T. -N., Hovde, P. J. & Gustavsen, A. (2012). Accelerated climate ageing of building materials and their characterization by Fourier transform infrared radiation analysis. *Journal of Building Physics*, *36*, 99–112.

Joint Committee. (2000). *European recommendations for sandwich panels*. ECCS/CIB Report 257. Ottawa, Canada: International Council for Research and Innovation in Building and Construction.

Karami, Z. (2020). *Durability assessment of preservative-treated wood bonded using one-component polyurethane adhesives* (PhD thesis). University of Auckland, Auckland, New Zealand. https://researchspace.auckland.ac.nz/bitstream/handle/2292/55001/Karami-2020-thesis.pdf?sequence=4&isAllowed=y

Karami, Z. & Nicholson, C. L. (2021). Durability of treated PUR-bonded wood. *Build*, *185*, 80–82.

Karami, Z., Raftery, G., Lim, J. & Nicholson, C. L. (2018). *Bond quality of one-component polyurethane bonded laminated timber exposed to wet climatic* *conditions.* Paper presented at the World Congress on Timber Engineering, Seoul, Korea, 20–23 August.

Leggate, W. (2018). *Improving the durability performance of engineered wood products: A study tour of Europe and North America*. Montreal, Canada: Forest Product Innovations

Lehringer, C. & Gabriel, J. (2014). Review of recent research activities on one-component PUR-adhesives for engineered wood products. In S. Aicher, H. Reinhardt & H. Garrecht (Eds.), *Materials and joints in timber structures* (pp. 405–420). Dordrecht, Netherlands: Springer.

Lee, N. P., Bennett, J. M., Jones, M. S., Marston, N. J. & Kear, G. (2008). *A durability assessment tool for the New Zealand Building Code*. Paper presented at the 11th International Conference on Durability of Building Materials and Components, Istanbul, Turkey, 11–14 May.

Li, Z. (2016). *Literature review report – structural adhesives*. Unpublished BRANZ report.

Marston, N. J., Jones, M. S. & Vohora, S. R. (2011). *A residual service life assessment tool for New Zealand*. Paper presented at the 12th International Conference on Durability of Building Materials and Components, Porto, Portugal, 12–15 April.

Marston, N. J., Jones, M. S. & Shaw, P. (2014). *Building resilience.* Paper presented at Building a Better New Zealand Conference, Auckland, New Zealand, 3–5 September.

Mitchell, G., France, F., Nordon, A., Tang, P. L. & Gibson, L. T. (2013). Assessment of historical polymers using attenuated total reflectance-Fourier transform infra-red spectroscopy with principal component analysis. *Heritage Science*, *1*, 28.

Nicholson, C. L., Shaw, P. & Marston, N. (2017). *Preliminary investigation of the durability of structural adhesives using FTIR spectroscopy and chemometrics*. Paper presented at the 14th International Conference on Durability of Building Materials and Components*,* Ghent, Belgium, 29–31 May

Nicholson, C.L. (2020). *Durability studies of polyurethane-based structural adhesives used in engineered wood products in New Zealand*. Paper presented at the 15th International Conference on Durability of Building Materials and Components, Barcelona, Spain, 20–23 October.

Nicholson, C. L. & Walsh, A. (2019). *Perspectives on the use of structural engineered wood products and adhesives in New Zealand: Results of an industry survey*. BRANZ Study Report SR438. Judgeford, New Zealand: BRANZ Ltd

Pellizzi, E., Lattuati-Derieux, A., Lavedrine, B. & Cheradame, H. (2014). Degradation of polyurethane ester foam artifacts: Chemical properties, mechanical properties and comparison between accelerated and natural degradation. *Polymer Degradation and Stability*, *107*, 255–261.

Ren, D. & Frazier, C. E. (2013a). Structure/durability relationships in polyurethane wood adhesives: Neat films or wood/polyurethane composite specimens? *International Journal of Adhesion and Adhesives*, *45*, 77–83.

Ren, D. & Frazier, C.E. (2013b). Structure-property behavior of moisture-cure polyurethane wood adhesives: Influence of hard segment content. *International Journal of Adhesion and Adhesives*, *45*, 118–124.

Scheffer, T. C. (1971). Climate index for estimating potential for decay in wood structures above ground. *Forest Products Journal*, *21*(10), 25–31.

Shaw, P. & Marston, N. (2016). Reliable durability prediction of polymeric materials. *Chemistry in New Zealand*, *80*, 137–142.

Sterley, M., Trey, S., Lundevall, A. & Olsson, S. (2012). Influence of cure conditions on the properties of a one-component moisture-cured polyurethane adhesive in the context of green gluing of wood. *Journal of Applied Polymer Science*, *126*, E296–E303.

van Langenberg, K., Warden, P., Adam, C. & Milner, H. R. (2010). *The durability of isocyanate-based adhesives under service in Australian conditions. The results from a 3 year exposure study and accelerated testing regime*. Melbourne, Australia: Forest & Wood Products Australia.

Verification Method B2/VM1 and Acceptable Solution B2/AS1: For New Zealand Building Code clause B2 Durability (2nd Edition, Amendment 12) 2019. https://www.building.govt.nz/assets/Uploads/building-code-compliance/b-stability/b2-durability/asvm/b2-durability-2nd-edition-amendment-12.pdf

Zhang, Y., Maxted, J., Barber, A., Lowe, C. & Smith, R. (2013). The durability of clear polyurethane coil coatings studied by FTIR peak fitting. *Polymer Degradation and Stability*, *98*, 527–534.

Standards

AS/NZS 1328.1:1998 *Glued laminated structural timber – Performance requirements and minimum production requirements.*

AS/NZS 4364:2010 *Timber – Bond performance of structural adhesives*.

ASTM D2559-12a(2018) *Standard specification for adhesives for bonded structural wood products for use under exterior exposure conditions*.

ASTM D4502-92(2019) *Standard test method for heat and moisture resistance of wood-adhesive joints*.

BS EN 14080:2013 *Timber structures – Glued laminated timber and glued solid timber – Requirements.*

BS EN 14509:2013 *Self-supporting double skin metal faced insulating panels. Factory made products. Specifications.*

BS EN 15425:2017 *Adhesives – One component polyurethane (PUR) for load-bearing timber structures – Classification and performance requirements.*

ISO 25217:2009 *Adhesives – Determination of the mode 1 adhesive fracture energy of structural adhesive joints using double cantilever beam and tapered double cantilever beam specimens*.