Durability of carbon fibre reinforced polymer laminates used to reinforced concrete structures

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Abstract

Due to their excellent mechanical properties and easy application carbon fibre reinforced polymers (CFRP) are being successfully used to repair and renew old and damaged civil engineering infrastructures. In particular, the method of strengthening concrete members with externally bonding of CFRP laminates has become increasingly popular. In fact, extensive research has shown that this technique can lead to a substantial improvement in the flexural and shear strength capacities of the member repaired. In such applications, materials involved will be exposed to outdoor environmental conditions, including humidity, water from rain, saline-water, ground water and high alkalinity solutions due to chemical composition of the concrete itself, as well as solar ultraviolet (UV) radiation. Thus, it is of great relevancy to study the durability of the materials involved, namely epoxy adhesives and CFRP laminates, as well as, the integrity of the entire system, when subjected to those environmental factors. This work is part of a much larger research study to predict the long-term behaviour of several commercial CFRP laminate/adhesive systems used in the rehabilitation of concrete structures. In the whole project it is recognised that the durability of these solutions depends not only on the durability of the composite materials but also on the performance of the systems used to bond them to the concrete. This present document provides details about the durability of CFRP laminates and the study carried out to investigate the environmental and accelerated ageing effects on three types of commercially available CFRP laminates. The changes in CFRP laminates properties after exposure up to 18 months under different environmental conditions – immersion in demineralised water, saline and alkaline solutions at room temperature, 40°C and 60°C, as well as under constant humidity condensation atmosphere at 40°C – are reported and discussed. The results of tests performed in accelerated weathering chambers – with UV radiation – are also included. Results obtained offer valuable information about the progression of material degradation under different ageing conditions (some of them accelerated), which can be used, not only to characterise the behaviour of CFRP laminates, but also for a better understanding of the degradation mechanisms involved, which is a base for the design of service life-prediction models.

Keywords: carbon fibre reinforced polymer; concrete structures; durability; rehabilitation.

1. Introduction

The repair and strengthening of deteriorated, damaged and old infrastructures has become an important civil engineering challenge worldwide [1]. One of the most popular techniques used to rehabilitate concrete structures is the external bonding of carbon fiber reinforced polymer (CFRP) laminates to them. Epoxy resins are usually selected as structural bonding adhesives. The use of CFRP laminates in these applications is based on their excellent attributes, such as lightweight, high stiffness and strength-to-weight ratios, easy field installation, lower maintenance costs and potentially high overall durability [2]. The much larger use of such repairing solutions enhanced the elaboration of new application guidelines and codes [3, 4], as well as standards and specifications nowadays [5, 6].

However, since composite materials still are relatively unknown to engineers great concerns subsist about their overall durability, especially related to the ability of these materials to sustain performance under harsh and changing environmental conditions [7, 8]. In fact, civil engineering structures are often highly contaminated by different environmental agents like rain, saline water, ground water and high alkalinity solutions generated by the concrete chemical compositions itself [9]. The durability of concrete structures reinforced with externally bonded FRP composites shall be analysed at two levels: (i) the durability of FRP material itself and (ii) the durability of the bond between the FRP material and the lf and the durability of the bond between the FRP material and the concrete substrate. Intrinsically the latter includes the durability of the resin/adhesive layer at the interface between the FRP composite and the concrete substrate.

The work described in this paper is part of a research study that is being made to predict the long-term behaviour of several commercial CFRP laminate/adhesive systems used in concrete structures rehabilitation. In the whole project it is recognised that the durability of this rehabilitation scheme depends, not only on the durability of the materials involved but also the performance of the bonding between concrete and the reinforcement system. The present document provides details about the part of the investigation concerning the durability of CFRP laminates.

2. Materials and methods

2.1. Materials

Three commercial CFRP laminates used to reinforce externally concrete structures by adhesive bonding were selected to be studied in the present work. Along this document, the letters A, B and C will designate each one of the laminates chosen. Specimens cut in the longitudinal direction of the original laminates were submitted to the different tests made, after ageing.

2.2. Methods

2.2.1. Accelerated ageing schedule In order to investigate the environmental effects on CFRP laminates, it was performed an ageing schedule described in Table 1.

2.2.2. Material characterisations before and after aging After exposure to different ageing conditions presented in Table 1, test CFRP laminates were subjected to the following tests:

1. Mass changes: Control specimens, were removed periodically from exposure to evaluate the mass changes.
2. Flexural testing (Instron 4483, Norwood, MA, USA): Three point bending flexural tests were conducted according to ISO 14125 [12] in CFRP laminates specimens using a span-to-depth ratio of 40. The loading rate was 2 mm/min. At least five replicates were tested for each material and aging conditions.
3. Dynamic Mechanical Analysis (DMA) (TA Instrument DMA Q800, New Castle, DE, USA): DMA has been used to analyse the viscoelastic response of laminates and to assess the glass transition temperature (T_g), in accordance with ISO 6721 [13]. Single cantilever type clamp specimens were tested at the constant frequency of 1 Hz and strain amplitude of 10 μm. The analysis was carried out from room temperature to 200°C, at a rate of 2°C/min.

Two replicates were tested for each material and aging condition.

4. Fourier transform infrared spectroscopy (FTIR) (Nicolet–ThermoFisher Scientific, Magna 550 series II, Watertown, CT, USA): Infrared spectra of laminates, before and after ageing exposure, were studied in the 450 cm⁻¹ and 4000 cm⁻¹ region by using an Infrared Spectrometer. For these measurements, powder samples scraped from the surfaces of test specimens, were mixed with dry spectroscopic grade potassium bromide and pressed into pellets. Thirty-two scans were collected and averaged at a spectral resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Mass change

Figure 1 illustrated the mass variation measured during different immersion ageing (in water – IW; in saline solution – IS and in alkaline solution – IL) and temperature conditions (23°C, 40°C and 60°C) for the three laminates (A, B and C).

As may be seen, all laminates seem to reach a quasi-equilibrium state after immersion in water and saline solution at room temperature, 40°C and 60°C. At those temperatures the overall mass variation observed is always smaller than 1% for the three laminates. The rate of approach to equilibrium is more rapid at the highest immersion temperatures, as expected in a diffusion controlled process. Those results are consistent with others described for different types of polymeric composites [14].

For laminate C, the alkaline solutions caused fairly higher variation of mass, than the other immersion liquids, at the same temperature.

The immersion in alkaline solutions shows a complete different scenario for laminates A and B. Laminate A shows a drastic initial mass increasing at higher immersion

Table 1 Aging schedule.

| Type of exposure and durations	Duration	Conditions and duration
Continuous condensation (CC-40)	18 months	• Temperature: 40(±2)°C • Relative humidity: 100%
Immersion in demineralised water (IW-23), (IW-40), (IW-60)		• Temperatures: 23(±2)°C, 40(±1)°C and 60(±1)°C
Immersion in salt-water (IS-23), (IS-40), (IS-60)		• Composition: 35 g/l NaCl • Temperatures: 23(±2)°C, 40(±1)°C and 60(±1)°C
Immersion in alkaline solution (IL-23), (IL-40), (IL-60)		• Composition: 118 g/l Ca(OH)$_2$; 4 g/l KOH, 0.9 g/l NaOH • Temperatures: 23(±2)°C, 40(±1)°C and 60(±1)°C
UV radiation and humidity (QUV and xenon)	2000 hours	• Fluorescent lamps – cycles of light and moisture continuously produced by condensation of water under controlled conditions according ISO 4892-part 3 [10] • Cycles: 4 h of permanent exposure to UV radiation at 60°C+4 h of exposure to moisture caused by constant condensation of de-ionised water at 50°C • Xenon-arc lamp – continuous irradiation with intermittent cycles of water spray under controlled conditions, according ISO 4892 – part 2 [11] • Cycles: 18 min of wet cycle (water spray)+102 min of dry cycle (65°C of black standard temperature and 65% of relative humidity)
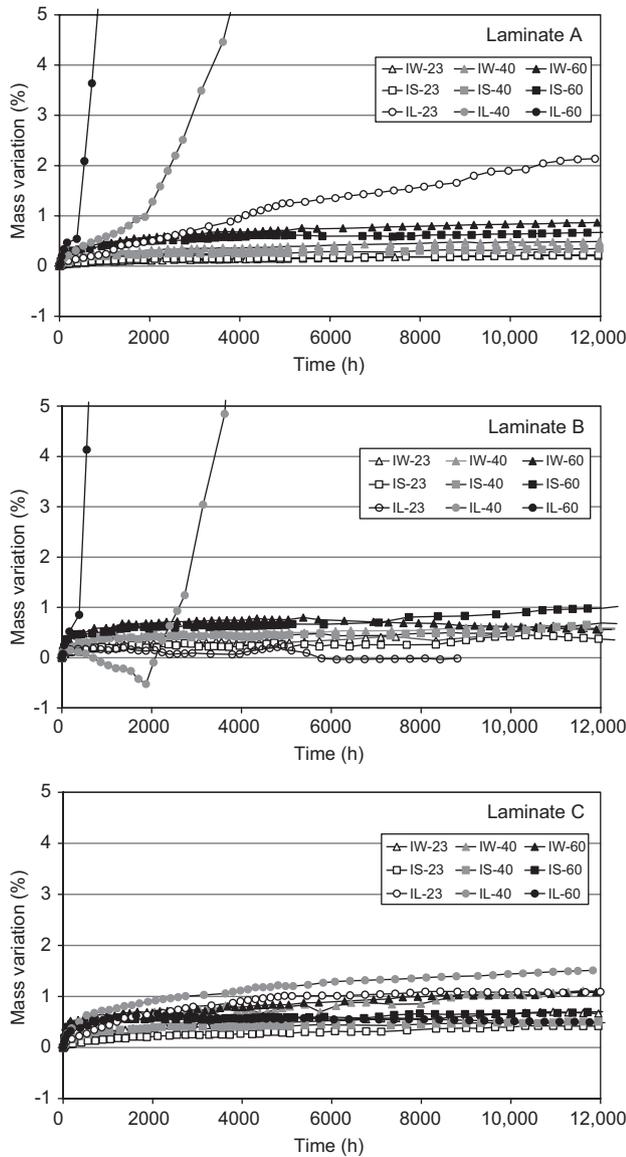
Figure 1 Mass variation of laminates during different immersion conditions.

temperatures and less expressive mass variations at room temperature. Laminate B shows insignificant mass variation at room temperature. This laminate immersed in the alkaline solution at 40°C shows an initially mass loss, followed by an unexpected rapid increasing. At 60°C the mass variations are very sharp. Those test specimens showed an important swelling during the increment of their mass.

In general, the performance of the laminates is much well distinguished at higher temperature in the alkaline solution and laminate C has shown to be the most performing one.

3.2. Flexural properties

All laminates exhibited a quite linear behaviour prior to failure and quite similar load-displacement experimental curve. The flexural properties (mean value±standard deviation)

determined in the laminates after different ageing conditions are plotted in Figure 2. The flexural strength (in MPa) and flexural modulus (in GPa) are represented in those plots by bars and single squares, respectively. Laminates A and B were attacked by the alkaline solution, with the extraction of the polymeric matrix. For this reason, in some conditions it was impossible to perform the flexural tests.

An overall decrease in flexural properties was observed for every immersion liquid's conditions, for all laminates. Furthermore, higher temperature caused further degradation. In fact, water absorption seems to have had a noticeable influence on the reduction of flexural strength and this effect was increased by temperature.
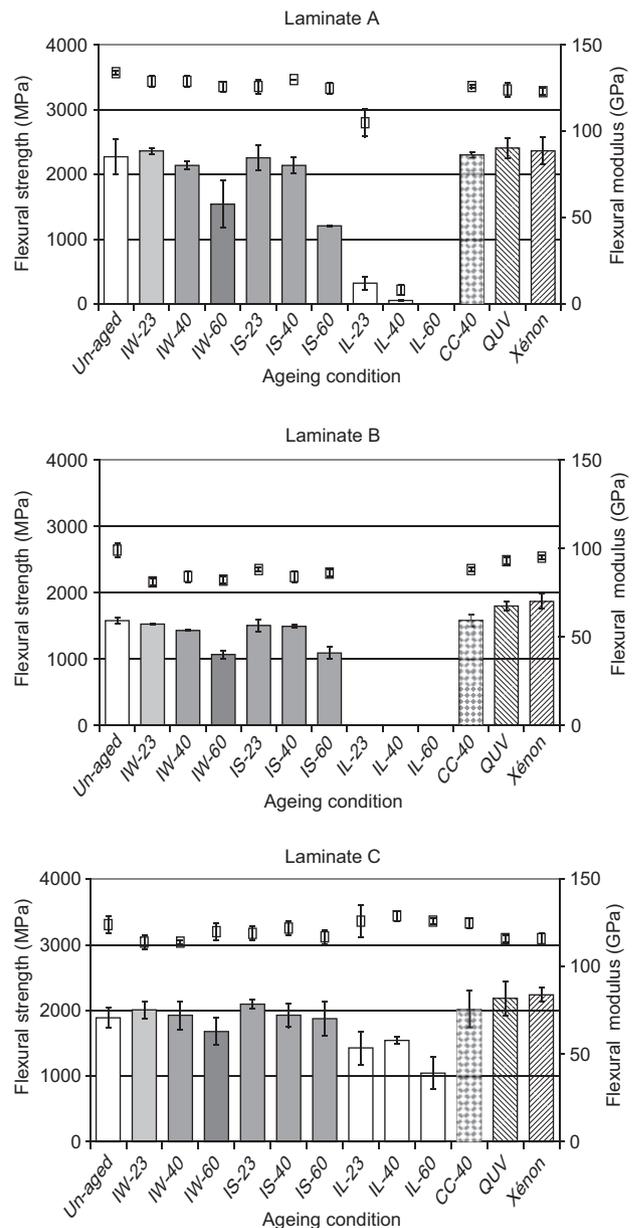

Figure 2 Flexural properties for laminates A, B and C before and after different ageing conditions.

Laminates A and B presented a clear decreasing of the flexural strength after immersion in water and saline solution, while the flexural modulus was less affected. At 60°C, the laminate A presented flexural strength retentions of 68% and 53% after immersion in water and saline solution, respectively. For laminate B, the flexural strength retention was 68% and 69% for immersion in water and saline solution, respectively. The flexural strength of laminate C was less affected by those types of immersions, with retention of 89% (in water) and 99% (in saline solution), at 60°C.

The large flexural strength reductions observed in laminate A after immersion in alkaline solution at 23°C and 40°C is a clear indicator of its degradation. The same type of behaviour was observed for laminate B at the three testing temperatures. In fact, as can be seen in Figure 3, test specimens of laminates A and B after the immersion in alkaline solutions at different temperatures have shown separation of carbon fibres accompanied by the polymeric matrix release.

The hygrothermal ageing of laminates by continuous condensation at 40°C promotes an increase in flexural strength, besides the little decrease observed on modulus. All types of laminates aged in QUV and xenon chambers increased the flexural strength and decreased the modulus. This behaviour seems to be a direct result of postcuring of the epoxy matrix due to exposure to temperature and ultraviolet radiation (UV) radiation.

3.3. Dynamic mechanical analysis

Figures 4–6, show experimental dynamic mechanical curves for laminates A, B and C, respectively, after submission to the different ageing conditions (for each condition, only one curve corresponding to a typical tested specimens is shown). At the left, plots show changes in dynamic storage modulus (E') with temperature, for the different exposure conditions; the corresponding $tan\ \delta$ curves are shown at the right.

Changes in the storage modulus behaviour reflect changes in the polymer matrix (and/or fiber-matrix interface) because the carbon fibre modulus does not change in the temperature region studied. In measuring storage modulus by DMA, using cantilever geometry the measured properties are sensitive to changes in the matrix.

In general, the immersion in water and saline solution generated a slight reduction in the storage modulus, as well as in the T_g value. For laminates A and C, the maximum T_g decreasing was observed at the higher immersion temperatures (up to 8% for laminate A and 10% for laminate C). These results show substantial evidence of plasticisation.
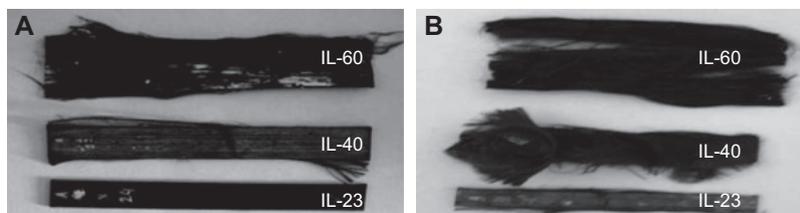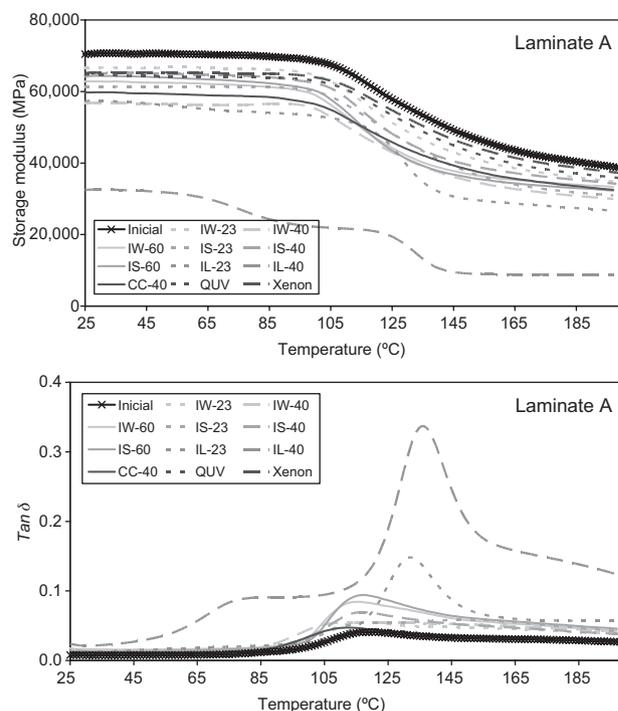

Figure 4   DMA experimental curves for laminate A after different ageing conditions.

Laminate B presented the same trend, with different $tan\ \delta$ peak sharp. In this case, it is interesting to note that an additional peak was exhibited at higher temperatures in all experimental curves. The occurrence of two $tan\ \delta$ peaks may be attributed to the different mobility of two kinds of segments in the polymeric matrix, due to their different extension of plasticisation. A similar behaviour was found in the hygrothermal ageing of epoxy resins [15, 16].

For all laminates, the samples exposed to UV radiation ageing have shown stiffness and T_g, increases, probably due to a polymeric matrix post-cure, as it was already mentioned in the flexural testing discussion.

3.4. FTIR analysis

Figures 7–9 show infrared spectra determined on the laminates (A, B and C, respectively) after submission to the different ageing conditions.
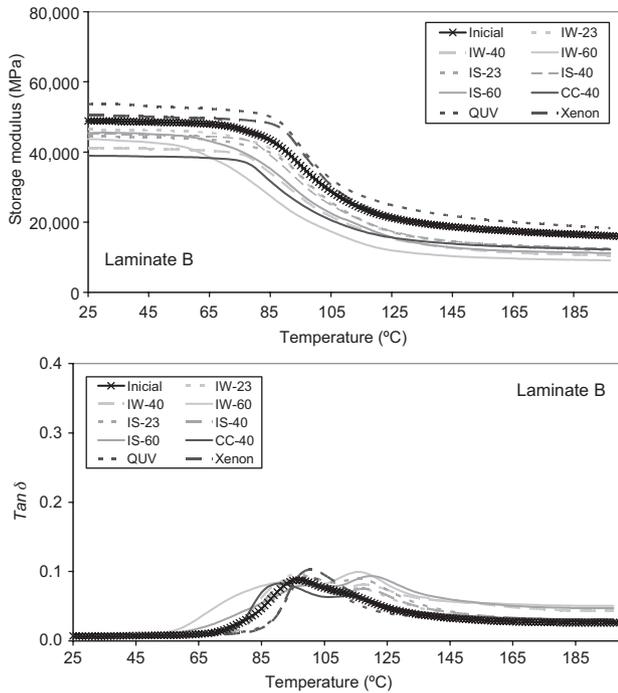

Figure 3   Test specimens of laminates A and B after immersion in alkaline solution at different temperatures.

Figure 5 DMA experimental curves for laminate B after different ageing conditions.

Relative to the unaged spectrum, very few changes were observed in the infrared spectra of laminates after immersion in water and saline solution. This fact gives important evidences that the degradation mechanisms are physical, but not chemical, in nature. After immersion in alkaline solutions,
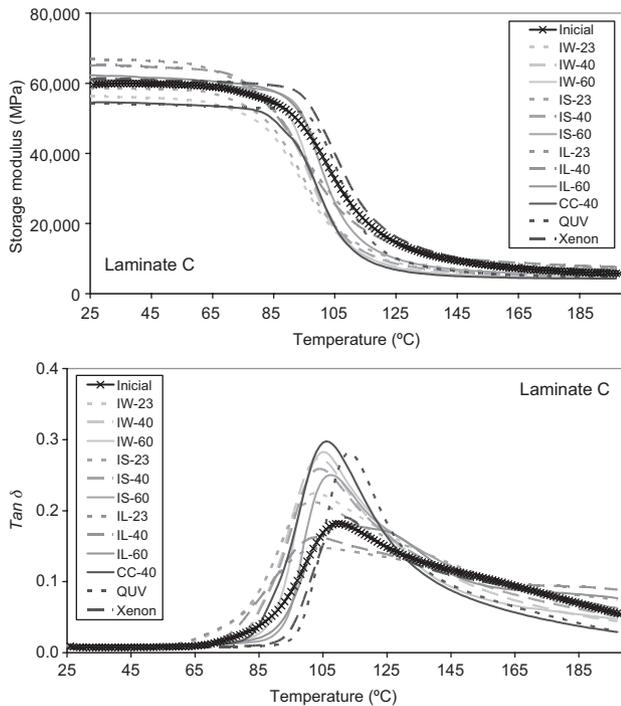

Figure 6 DMA experimental curves for laminate C after different ageing conditions.

spectra show little changes for laminate A and C, but clear evidences signs of chemical degradation in the case of laminate B, where important infrared absorption peaks presented different position and intensity.

Exposition to UV radiation in the xenon chambers exhibited the greatest change in band position and intensity. These spectral changes are consistent with chemical degradation observed in the surface layer of composites. Previous studies on the UV degradation of epoxies have showed that both crosslinking and chain scission mechanisms operate in a competing manner during the degradation process [17].

4. Conclusions

Based on the results of the present work, the following conclusions may be taken:

1. Immersion in water and saline solution may had a noticeable effect on the flexural strength of CFRP, but the degree of the retention after ageing depends on the type of laminate. Nevertheless, the degradation is mainly due to physical phenomena, such as plasticisation of the polymeric matrix, since no appreciable chemical degradation was revealed by FTIR.
2. Alkaline solution caused the most severe degradation in all laminates, but was particularly harsh for laminate B which undergoes degradation even at room temperature.
3. The hygrothermal ageing during continuous condensation caused the same effects of water immersion at the same temperature, for all laminates.
4. Besides the chemical degradation that was detected in the FTIR experiments, the ageing conditions which involved UV radiation (QUV and xenon) have been shown to not affect the flexural properties. These results confirm that the degradation is confined to the top of the surface of laminates, having limited influence on their mechanical behaviour.

The presence of alkaline salts in aqueous solution has shown to cause higher levels of deterioration (in the case of laminate C) and/or total deterioration (for the other types of laminates) than the other two immersion solutions. The higher level of degradation of laminates caused by the alkaline ambient is one of the most important conclusions of this work. In fact, similar commercial CFRP laminates could have very different environmental resistance, particularly, in alkaline aqueous ambient.

For each type of immersion, the temperature increase always has caused the intensification of the degree of degradation, because it increases the rate of diffusion. It can be concluded that temperature may be used as a good accelerator factor in order to predict long-term performance in durability studies.

Clearly, the influence of different conditions in the neighbourhood of the materials could result in distinct consequences on the performance of each type of laminate, as
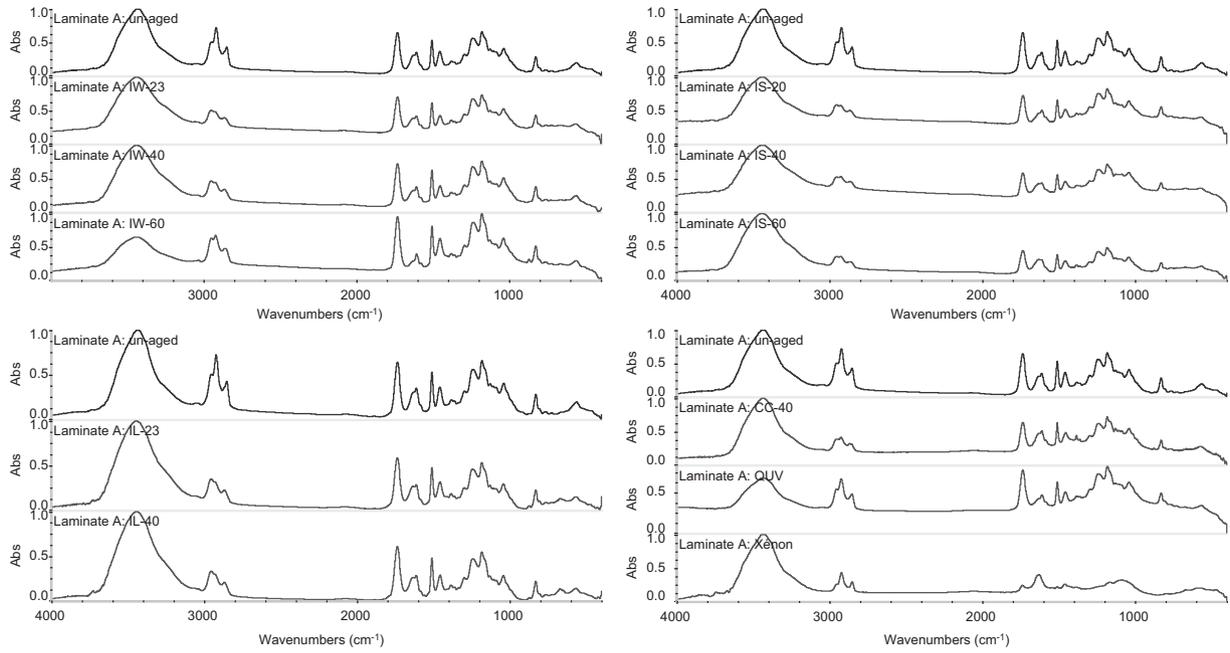
Figure 7   Infrared spectra for laminate A after different ageing conditions.

demonstrated in the present work. Generalisation of these results for other materials and environmental conditions is not straightforward without a complete understanding of the degradation mechanisms involved.

In fact, the durability and long-term performance of CFRP materials have been subjected to much research; however this investigation remains in progress. Furthermore, long-field data are not yet available, and is still difficult to predict accurately the performance of laminates and strengthening systems used in civil engineering. Many issues regarding bonding of the CFRP system to the substrate also remain the focus of a great deal of research.
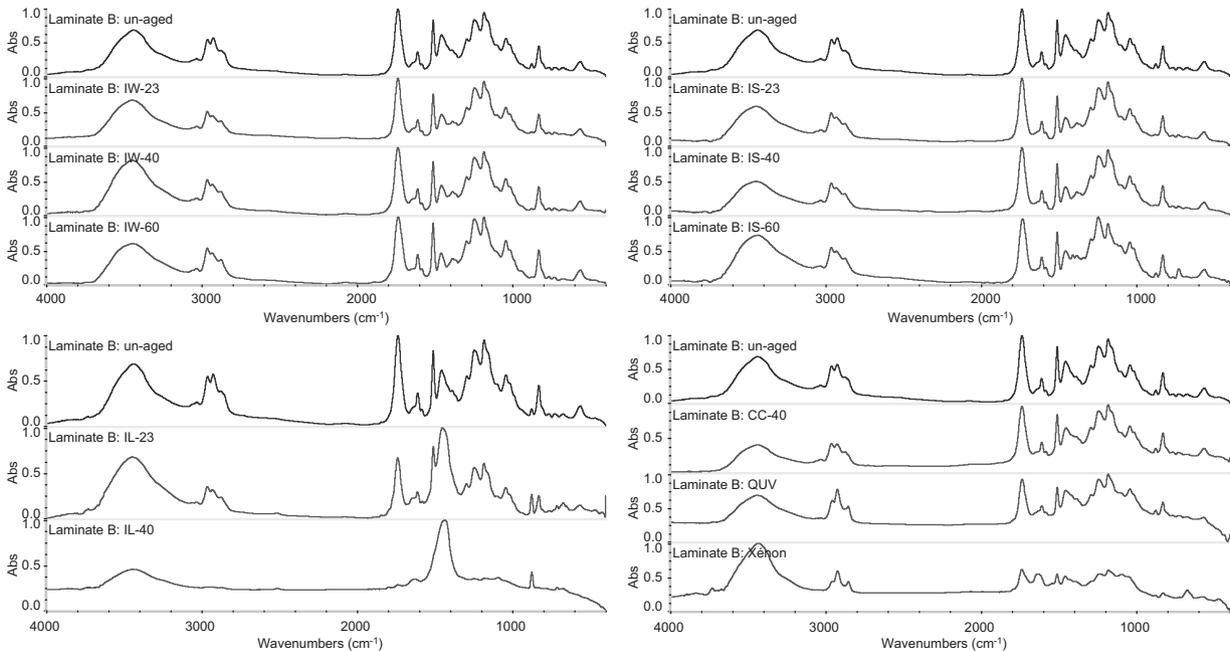

Figure 8   Infrared spectra for laminate B after different ageing conditions.
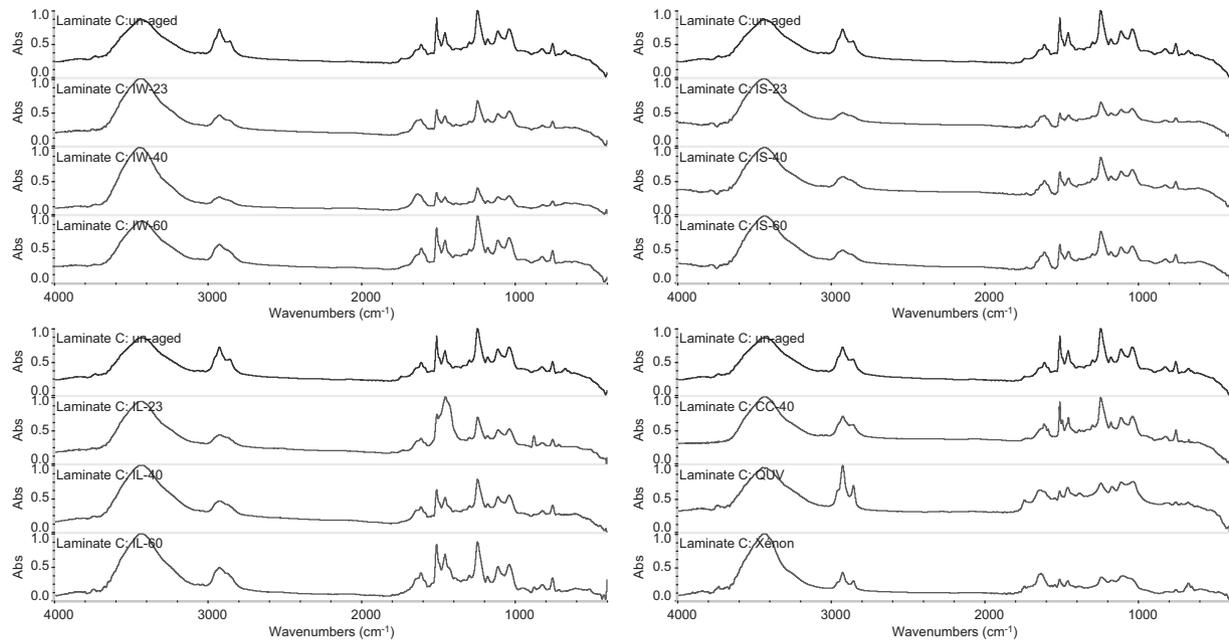
Figure 9   Infrared spectra for laminate C after different ageing conditions.

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