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Citric acid crosslinking of paper products for improved high-humidity performance

Petri Widsten*, Nicola Dooley, Robin Parr, Jaworski Capricho, Ian Suckling

Scion, Te Papa Tipu Innovation Park, 49 Sala Street, Private Bag 3020, Rotorua, New Zealand

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ABSTRACT

Fibre crosslinking with polycarboxylic acids can be used to improve certain properties of paper products, including wet tensile and compressive strength. In the present work it was proposed that citric acid (CA) crosslinks the cellulosic fibres of linerboard by self-catalysed esterification of cellulosic hydroxyl groups, which makes an additional catalyst unnecessary. An increase in CA dose or curing temperature increased linerboard compressive strength. In CA-treated corrugated board most of the applied CA was esterified with fibres while some CA thermolysis products were also present. A significant portion of the applied CA was unaccounted for. The deficit was attributed to thermolysis to give volatile anhydrides of unsaturated acids. Under cyclic humidity and static compressive loading, CA-treated corrugated boxes showed a greater than three-fold increase in resistance to compressive creep, showing that CA treatment can be used to extend the lifetime of corrugated boxes used for horticultural produce storage.

1. Introduction

Corrugated cardboard boxes used for packaging perishable horticultural produce such as apples for export are usually stacked and stored under varying humidity conditions in coolstores. The lifetime of the boxes under these conditions is limited due to compressive creep and buckling of the corrugated board side panels which ultimately causes box failure. An effective strategy of combating compressive creep is to reduce moisture ingress by adding wax to the board. This method, however, renders boxes difficult to recycle which is why it is not allowed in many countries. Crosslinking may reduce box creep by decreasing fibre moisture uptake and the ensuing disruption of fibre-to-fibre hydrogen bonds. Other methods such as formaldehyde crosslinking for reducing box creep may work but are not practicable due to health and safety concerns or other reasons. One potentially suitable crosslinking method is the use of polycarboxylic acids (PCA) crosslinkers.

Cellulose crosslinking with PCAs such as butanetetracarboxylic acid (BTCA) and citric acid (CA) (Fig. 1) has been investigated in the textile industry as a means for imparting easy care properties to cotton fabrics (Schramm & Rinderer, 1999; Welch & Kottes Andrews, 1989; Welch, 1988). PCA crosslinking has also been used for improving the wet strength properties of paper (Caulfield, 1994; Yang & Xu, 1998; Zhou, Luner, Caluwe, & Tekin, 1993), decreasing the water solubility of cellulose derivative films (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003), producing crosslinked fibres for absorbent applications (Herron & Cooper, 1993), crosslinking of flax fibres (Surina & Andrassy, 2013) and for improving the dimensional stability of wood (Vukusic et al., 2010).

The above-cited research was conducted using PCA crosslinking catalysts such as sodium hypophosphite (SHP). Herron and Cooper (1993) suggested that SHP reacts with polycarboxylic acids to give acylphosphinates which then react with cellulose hydroxyls to form the ester bonds. Yang and Wang (1998) and Xiaohong and Yang (2000) found evidence for the formation of 5-membered cyclic anhydride structures from BTCA during cross-linking reactions. In the study of Yang and Wang (1998), the anhydride band assigned to CA was weak and overlapped, unlike those ascribed to BTCA and *cis*-1,2,3,4,-cyclopentanetetracarboxylic acid. Xiaohong and Yang (2000) also reported that strong intramolecular hydrogen bonding between the carboxyl groups in crystalline BTCA prevents anhydride formation at temperatures much below its melting point (196 °C). According to these authors, SHP and similar phosphorus-based catalysts lower the temperature required for anhydride formation by reducing the hydrogen bonding and making BTCA more amorphous. It has also been suggested that catalysts such as SHP might act as buffers, shifting the pH to values low enough to promote acid-catalysed for esterification (Herron & Cooper, 1993; Xiaohong & Yang, 2000). Whatever the catalytic mechanism of SHP

* Corresponding author. Tel.: +64 7 343 5899; fax: +64 7 348 0952.
E-mail addresses: petri.widsten@scionresearch.com (P. Widsten), nicola.dooley@scionresearch.com (N. Dooley), robin.parr@scionresearch.com (R. Parr), jaworski.capricho@scionresearch.com (J. Capricho), ian.suckling@scionresearch.com (I. Suckling).

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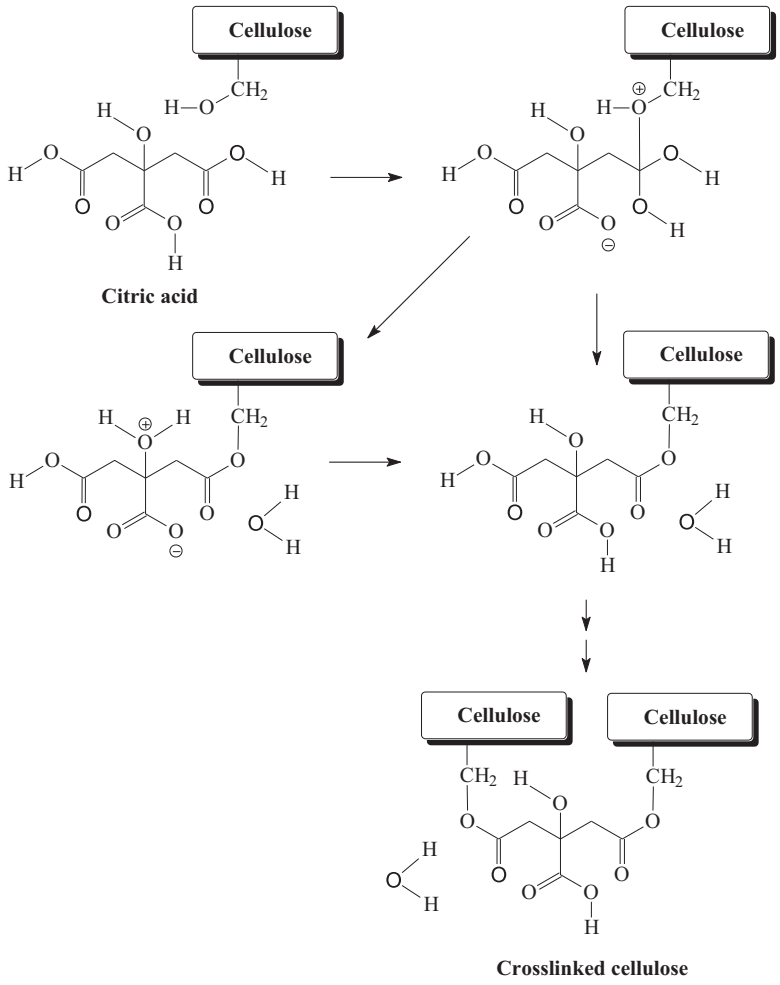

Fig. 1. Proposed main mechanism for the CA-crosslinking of cellulose.

and related compounds may be, a catalyst was considered essential in the majority of published investigations on PCA crosslinking of cellulosic or lignocellulosic materials. For economical reasons, however, it would be advantageous to effect crosslinking without a catalyst. Phosphorus-based catalysts will also produce toxic decomposition gases such as phosphine if heated to their decomposition point, as may happen in high-temperature curing. Other things being equal, it is preferable to use CA rather than BTCA for industrial cross-linking applications. In particular, CA is a relatively inexpensive bulk chemical derived from natural sources, whereas BTCA is synthetic and relatively expensive. Unlike BTCA, citric acid is also a food ingredient with GRAS (Generally Regarded As Safe) status in the US, which makes it more attractive for food packaging applications.

Not all PCA crosslinking studies have found the use of a catalyst important. In a patent by Herron and Cooper (1993) dealing with preparation of individualised PCA crosslinked fibres (i.e. fibres with mainly intrafibre crosslinking) catalysts were not deemed necessary for achieving significant crosslinking reaction rates with CA, BTCA or other PCAs as long as the pH was maintained within an optimal range (2.0–3.5). Coma et al. (2003) did not find a catalyst (NaH_2PO_4) to have any significant effect on the properties of CA-crosslinked cellulose derivatives. In the work of Pantze, Westermark, and Karlsson (2008), esterification occurred when cellulose (filter paper) was heated with certain types of monocarboxylic acids, in the absence of a catalyst; the crucial structural feature in terms of esterification with butyric acid derivatives was a hydroxyl or keto group *alpha* to the carboxyl group. Acids lacking such an *alpha* substituent or an aromatic unit at the *alpha* position produced no esters. While BTCA lacks *alpha* hydroxyl or ketone groups, CA has a carboxylic acid group with an α-hydroxyl group, accounting for the relatively low p*K*a (3.1) of citric acid.

While BTCA melts at 196 °C in the absence of a catalyst, anhydrous CA, sometimes known as "CA anhydride," melts at 161 °C (Wyrzykowski, Hebanowska, Nowak-Wiczk, Makowski, & Chmurzyński, 2011). The lower melting point gives CA an advantage over BTCA as a cross-linking agent. The low p*K*a of the carboxylic group on C-3 facilitates donation of a proton to one of the other carboxylic groups, as shown in Fig. 1. This donor effect catalyses esterification to cellulose. The proton might return via the α-hydroxyl group, as shown, or directly to the carboxylate anion. The proton might then be donated to the second carboxylic group, creating a second linkage to cellulose.

CA undergoes thermolysis decomposing at >161 °C to form cyclic anhydrides of unsaturated di- and tricarboxylic acids (UAs) and 3-hydroxyglutaric acid (Fig. 2) (Fischer, Merwin, & Nissan, 1995; Shriner, Ford, & Roll, 1931a, 1931b; Wyrzykowski et al., 2011). The low p*K*a value of 2.8 and three carboxylic groups of aconitic acid indicate a potential for cross-linking that might exceed that of citric acid. Aconitic anhydride might also show potential for cross-linking. Neither itaconic nor citraconic anhydride are able to donate protons for acid-catalysed esterification, but either structure might participate in cross-linking if the reaction is catalysed by neighbouring acid molecules. However, the

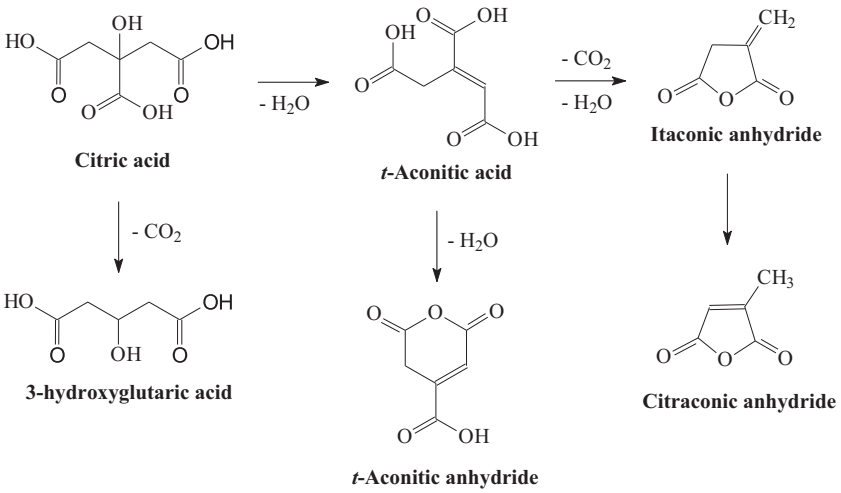

Fig. 2. Thermolysis of citric acid (Fischer et al., 1995; Shriner et al., 1931a, 1931b; Wyrzykowski et al., 2011).

reactivity of the UAs and their anhydrides may be reduced by the lack of freedom of rotation due to their planar molecular structures. Itaconic and citraconic anhydrides distill over the ranges 175–190 °C and 200–215 °C, respectively (Shriner et al., 1931a, 1931b), so the potential for cross-linking will be lost if the curing temperature is raised far above the melting point of anhydrous citric acid. Fischer et al detected 3-hydroxyglutaric acid among the CA thermolysis products but no compelling evidence for the anhydride that would be formed from 3-hydroxyglutaric acid by loss of two water molecules. 3-Hydroxyglutaric (p*K*a 3.52) is expected to be a weaker esterification agent than CA.

The objectives of this paper were to: (1) elucidate the crosslinking mechanism of CA with cellulosic fibres, (2) study the effects of catalyst and process parameters (dose, curing time and curing temperature) on compression strength of CA-treated linerboard and (3) find out whether the compressive creep performance of CA-treated cardboard boxes under cycling humidity conditions is able to be improved.

2. Experimental

2.1. Chemicals

The CA monohydrate used in this work came from The British Drug Houses Ltd. *t*-Aconitic and itaconic acids and SHP were from Sigma–Aldrich and citraconic acid from Fluka. All chemicals were used as received.

2.2. Linerboard treatment and curing

Commercial linerboard samples (basis weight 160 g m^{-2} or 180 g m^{-2}), three per experimental point and measuring 300 mm × 300 mm, were clamped between two aluminium frames. Clamping is required to minimise expansion and contraction of board during wetting and drying conditions to reduce buckling. Clamping is required to minimise expansion and contraction of board during wetting and drying conditions to reduce buckling. Clamping is required to minimise expansion and contraction of board during wetting and drying conditions to reduce buckling. Only the board edges were covered by the frames. Both sides of the boards were treated with an aqueous CA solution (16.6 wt.%) in a track sprayer booth calibrated to deliver a known dose of CA onto the spray area. When the catalyst was used (5 g m^{-2} of SHP), it was dissolved in the CA solution. For the study on the effect of pH, 1 M NaOH solution was used to adjust the starting pH (1.6) to the desired level. The spraying was performed from above while the linerboards were horizontal and, to avoid runoff, the initially sprayed sides were allowed to dry before the other side was sprayed. The treated linerboards were cured in a forced-air Contherm oven at target temperature ±2 °C. After curing the frames were transferred to a conditioning room maintained at 23 °C and 50% relative humidity (rh) for re-conditioning. The frames were loosened to allow boards to be re-conditioned without tension. For infrared spectroscopic studies, the linerboard was treated with 10 g m^{-2} CA (applied by pipetting); the boards where then cured for 5 min at 190 °C. The cured boards were treated by soaking in 10 ml of dilute acid (0.5 M HCl) and base (0.1 M NaOH) solutions, respectively, with 48 h of air-drying after each treatment. After infrared analysis, the samples were placed into a Thermoline conditioning cabinet at 90% rh and 4 °C for one month before further infrared analyses.

2.3. Linerboard compression strength testing

Linerboard samples conditioned at 50% rh and 23 °C were cut into ten strips (1.5 cm × 12.0 cm) in the machine direction (MD) and ten in the cross-direction (CD). Testing of in-plane short-span compression strength (SCT) at 50% rh was carried out according to AS/NZS 1301.450rp:2006 (compression test of paper and board-short) using a Lorenzen and Wettre SCT tester. SCT testing at 90% rh was performed inside a Thermoline conditioning cabinet using an SCT machine adapted for high humidity conditions and the Buchel van der Korbut recording programme using test strips conditioned at 90% rh and 4 °C. Pre-conditioning and conditioning were carried out per an internal standard high humidity method of 1 d at 4 °C/90% rh, 1 d at 23 °C/50% rh then 5 d at 4 °C/90% rh. Testing took place on the sixth day. Moisture uptakes of the SCT samples were calculated after testing an overnight 105 °C oven dry conditioning.

2.4. Corrugated box treatment and curing

Regular slotted container (RSC) blanks of the simplest form, from standard industrial production, measuring 358 mm × 255 mm × 315 mm when assembled and with a liner weight of 145 g m^{-2}, were sprayed using the track sprayer also used for linerboard treatment. The inner liner was sprayed first then dried with a 2-bar IR heater mounted 100 mm above the sample on a wheeled frame which was slowly pulled over the board as drying was observed. The outer liner was then

similarly treated and dried. The blanks were then cured in the Contherm oven at target temperature ±2 °C and re-conditioned at 50% rh and 23 °C for at least 24 h before made into cartons for compressive creep testing. Cartons were formed by hot-melt glueing the tab to the opposite side and pressing with weights for 3 min, folding the base flaps and taping with packaging tape, inserting a Friday tray to the centre of the carton (to act as contents in the carton), then folding and taping the top flaps.

2.5. Corrugated box testing

Corrugated boxes were tested in presses under a constant load of 35 kg and a diurnal humidity cycle (50–90% rh). The temperature was not controlled and so varied with the changing humidity in the range 9–19 °C.

2.6. Corrugated board treatment for high-pressure liquid chromatography (HPLC) analysis

Corrugated board squares (10 cm × 10 cm) cut from corrugated boxes with a liner weight of 145 g m^{-2} were treated with CA solution (10 g m^{-2}) by depositing the solution onto the board (10 cm × 10 cm) using a pipette. Curing was effected at 190 ± 2 °C in a Contherm oven for 10 min and the treated samples conditioned at 50% and 23 °C prior to HPLC analysis.

2.7. Determination of acids by HPLC

Two types of analyses were carried out: (1) unbound acids were analysed by cutting the samples into squares and extracting them with water (25 ml) at 70 °C (5 min) in a 50 ml round-bottomed flask, then filtering and washing the squares with water (3 × 50 ml). These conditions were chosen as likely to convert anhydrides to acids for HPLC analysis. (2) Bound acids were analysed by adding NaOH (25 ml, 1 M) to the residues from the first analysis, and refluxed for 10 min. These conditions were chosen as likely to hydrolyse ester linkages. The solution was filtered with a cotton plug and collected into a 100 ml volumetric flask and the plug washed with water. The filtrate was neutralised with 1 M sulphuric acid and the volumetric flask topped up with water. Before HPLC analysis, the samples were filtered through 0.45 μm nylon mesh. The HPLC analyses were run on an HPLC Agilent 1290 Infinity system equipped with a UV detector (detection at 210 nm). The column was Phenomenex ROA Organic Acid (300 mm × 7.8 mm). Calibration curves for CA and UAs were constructed using the corresponding standard compounds. The eluent was 0.005 M sulphuric acid, the flow rate 0.6 ml/min, the column temperature 80 °C and the injection volume 10 μL.

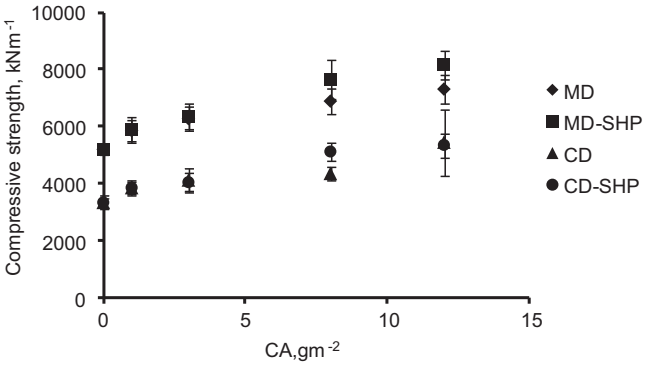

Fig. 3. Effect of CA dose and catalyst (SHP) on the in-plane compressive strength of 160 g m^{-2} linerboard at 50% rh cured at 190 °C. MD = machine direction, CD = cross direction.

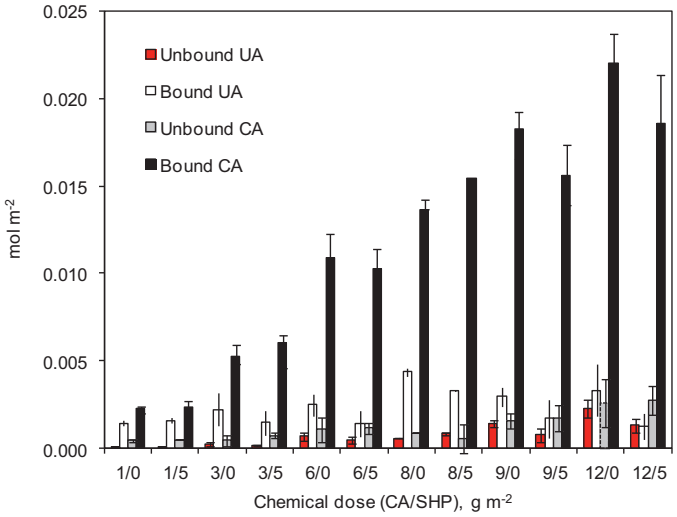

Fig. 4. Amount of unbound and bound (esterified) CA and UA in CA-treated and cured corrugated board by HPLC. The first and second numbers in the *x*-axis value labels denote CA and SHP doses, respectively.

2.8. FTIR-ATR analysis of linerboard

Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) spectra of air-dry linerboard samples were collected with a Bruker IRscope II IR microscope. For each sample, absorbance spectra of the scan range 4000–600 cm^{-1} (128 scans) were recorded at three locations and averaged. The average spectra were baseline corrected and normalised to the cellulose CH-band at 1373 cm^{-1}. The peak ratio 1730 cm^{-1}/1373 cm^{-1} (carboxyl/cellulose) was measured first after acid treatment and base treatments, respectively. Samples stored at 90% rh for one month were analysed similarly.

3. Results and discussion

3.1. Effects of CA dose and catalyst on linerboard compressive strength

As shown in Fig. 3, the compressive strength of linerboard at 50% rh increased with an increase in CA dose both in the presence and absence of the catalyst, SHP. Although the increases were mostly greater at the highest two doses when SHP was present, the results show that substantial increases in compression strength can also be obtained without a catalyst.

The CA present on the linerboards after curing can occur as unbound or bound (esterified) CA or UAs, or as UA anhydrides. The CA molecule can in principle be connected to cellulose by just one ester bond (no crosslink) or two ester bonds (an intra- or interfibre crosslink), as shown in Fig. 1. The analytical method used in the present study cannot distinguish between one and two ester bonds per CA molecule. The amounts of CA and UAs in linerboard treated with different CA doses with and without the SHP catalyst are shown in Fig. 4. Esterified CA was the only, and by far the most prominent, component that increased significantly with an increase in CA dose, regardless of whether the catalyst was present. The fact that there was generally more esterified CA in the samples treated without the catalyst suggests that esterification occurred according to the self-catalysed esterification mechanism illustrated in Fig. 1 rather than by a mechanism involving cyclic anhydride intermediates. Citraconic acid comprised almost all of the unbound

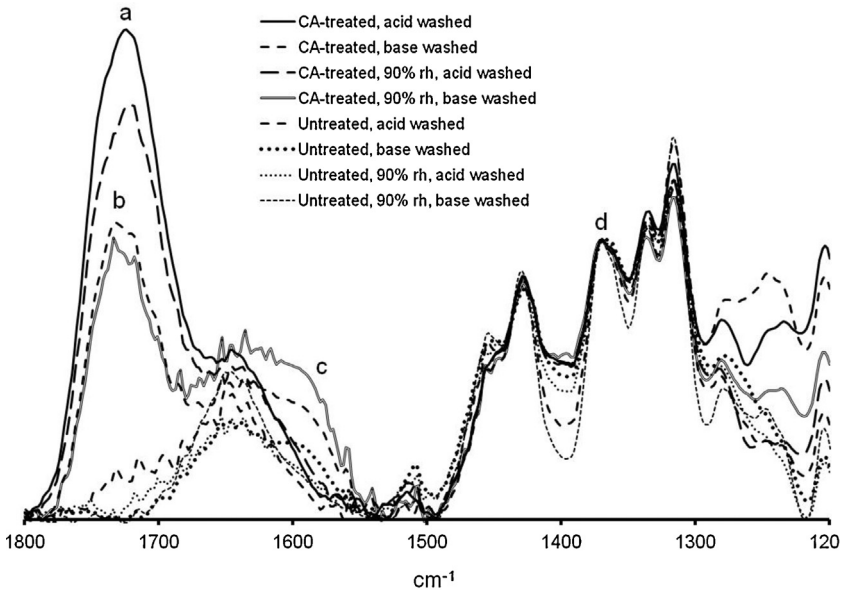

Fig. 5. Partial FTIR-ATR spectra of linerboard after various treatments and before and after one month storage at 90% rh. Selected band assignments: (a) (1720 cm^{-1}): free and esterified carboxyl groups of CA and UAs; (b) (1730 cm^{-1}): esterified carboxyl groups of CA and UAs; (c) (band area centred at ca. 1575 cm^{-1}): carboxyl anions from CA and UAs; d) (1373 cm^{-1}): CH bending in cellulose. The spectra are normalised to peak *d*. The carboxyl bands have a minor contribution from lignocellulosic carboxyl groups.

UAs, while among the bound UAs the three UAs were present in variable relative proportions with none of the three clearly dominating. However, the total bound UAs were low compared to bound CA, implying that so the crosslinking should be mostly due to CA. The total amount of acids detected as a molar percentage of the applied dose remained rather constant at 50 ± 5% at all doses except at 1 g m^{-2} where it was 90–95%. The balance may have been converted into UA anhydrides (Shriner et al., 1931a, 1931b; Wyrzykowski et al., 2011), volatile under the high curing temperatures applied, but may also have been bound to fibres in a way such that neither water nor NaOH extraction was able to remove it. For example, the α-β-conjugated UAs might react by radical crosslinking with heat-generated radicals present in fibres. An increase in the curing temperature lowered the percentage yield of recovered acids when SHP was applied but only a minor trend in this direction was observed without the catalyst.

The FTIR-ATR spectra of untreated and CA-treated and cured linerboard (Fig. 5) corroborate the above HPLC data. The boards were at first treated with 0.5 M HCl to ensure protonation of all unbound carboxyl groups and to wash off any unattached CA and UAs. The resulting spectrum of the treated board shows a prominent band centred at 1720 cm^{-1} from free and esterified carboxyl groups from CA and UAs. Upon treatment with 0.1 M NaOH the free carboxyl group component of this band is shifted to a broad band centred at ca. 1575 cm^{-1} (carboxyl anion) while the remaining band at 1730 cm^{-1} proves the existence of bound (esterified) CA and UAs (Morris, Catalano, & Kottes Andrews, 1995). As the signal from the carboxyl anion was shifted, the peak ratio 1720–1730 cm^{-1}/1373 cm^{-1} (unbound + bound carboxyl/cellulose) changed from 1.69 in the acid treated board to 1.09 (bound carboxyl/cellulose) after base treatment. The untreated board shows only minor carboxyl peaks, which are attributed to hemicellulose and lignin.

3.2. *Effect of curing time and temperature on linerboard compressive strength and moisture uptake*

The effects of curing time and temperature on linerboard compression strength and moisture uptake at 90% rh were investigated at a CA dose of 10 g m^{-2} in the absence of SHP. As seen from Fig. 6a, there was approximately a tenfold decrease in the curing time required to achieve maximum MD compression strength in going from 190 °C to 300 °C. The maximum SCT strengths reached at 225–300 °C were also greater than that obtained at 190 °C. Results in CD (not shown) followed the same trends, the absolute values being somewhat lower than the MD values. The moisture uptakes of

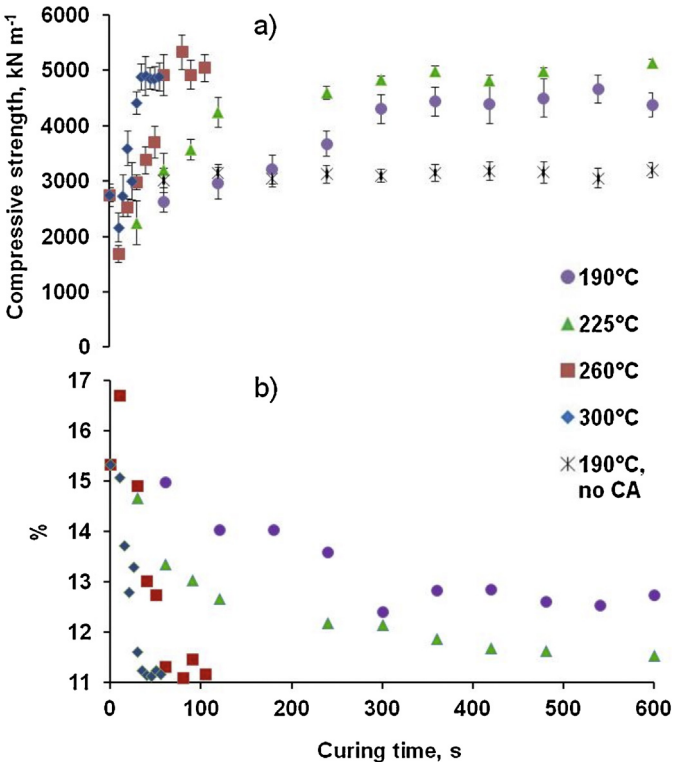

Fig. 6. Effect of curing temperature and time on (a) MD compressive strength and (b) moisture content at 90% rh of 180 g m^{-2} linerboard treated with 10 g m^{-2} CA. The zero-time value is from untreated board.

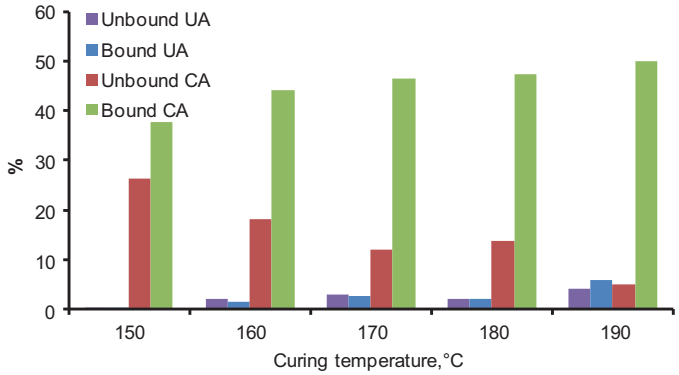

Fig. 7. Effect of curing temperature on the percentage yield of UA and CA recovered (molar basis on a dose of 10 g m^{-2}) from corrugated board treated with CA without a catalyst (mean values of two samples).

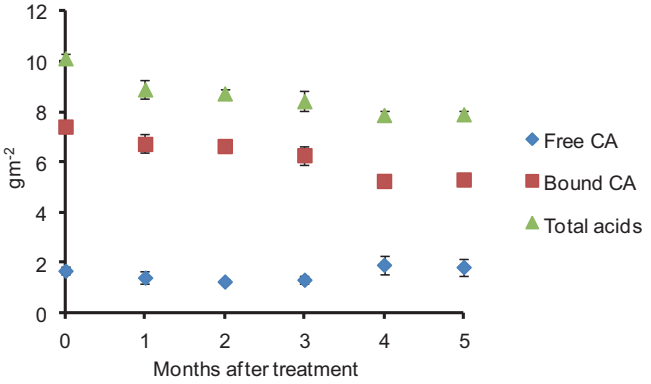

Fig. 8. Long-term survival of ester bonds in CA-treated corrugated board upon storage at 90% rh by extraction and HPLC analysis.

the cured linerboards (Fig. 6b) were lower than those of untreated board, probably as a result of there being less space available for absorbed water in the more crosslinked boards. In fact, compression strength and moisture uptake at a given curing time were highly and linearly correlated with r^2 (Pearson coefficient of correlation) values ranging from 0.94 to 0.98, depending on the temperature. As the curing temperature increased, the boards acquired a progressively darker shade of brown. This was probably due to a greater extent of CA decomposition into chromophoric UAs and acid degradation of polysaccharides. These results clearly show that no additional catalyst is required for linerboard esterification/crosslinking.

Curing temperatures of 150–180 °C resulted in linerboard with lower SCT strength than that cured at higher temperatures; moreover, its moisture uptake often exceeded that of untreated board (no data shown). As seen from Fig. 7, this is probably due to its larger content of hydrophilic unbound acids and lower crosslinking (less esterification). Both of these factors may increase water absorption and fibre swelling, resulting in a decrease in SCT strength due to disruption of hydrogen bonding.

As shown in Fig. 6a, the compressive strength of linerboard improved somewhat with heat treatment at 190 °C compared to untreated linerboard. Prolonged heat treatments (no CA) at 180 °C for 5–30 min all gave similar compressive strength (no data shown). Heat treatment has been reported to improve the wet tensile strength of paper products by generating acetal and hemiacetal crosslinks between the fibres (Back, 1967; Morgan, 1998). Compression strength at 50% rh is not much affected because of the strong hydrogen bonding in the sheets but in wet paper the hydrogen bonding is so weak that the covalent crosslinks created improve its compression strength.

3.3. Effect of pH of CA solution on linerboard compressive strength

Herron and Cooper (1993) found the pH of the PCA treatment solution to be important factor for fibre crosslinking with an optimum pH of between 2.0 and 3.5, while Pantze et al. (2008) found a pH of <2 to strongly favour esterification of cellulose by 2-hydroxybutyric and other monocarboxylic acids at 180 °C. In the present investigation, the pH of the CA solution (1.6–3.0) at a CA dose of 10 g m^{-2} without SHP and curing at 190 °C did not affect the SCT strength of linerboard (no data shown). This suggests that esterification may have been self-catalysed (Fig. 1).

3.4. Longevity of crosslinking

The long-term survival of ester crosslinks is important for box performance. The longevity of ester crosslinks in corrugated board treated with CA (10 g m^{-2}) and cured at 190 °C for 10 min was studied by determining unbound and bound UAs and CA in the board over 1–5 months of storage at 90% rh by HPLC (Fig. 8). The amount of UAs was very low and did not change during storage (no data shown) but the amount of bound CA declined steadily by about 30% during the first four months (Fig. 8). However, analysis shows there was no corresponding increase in the amount of unbound CA,

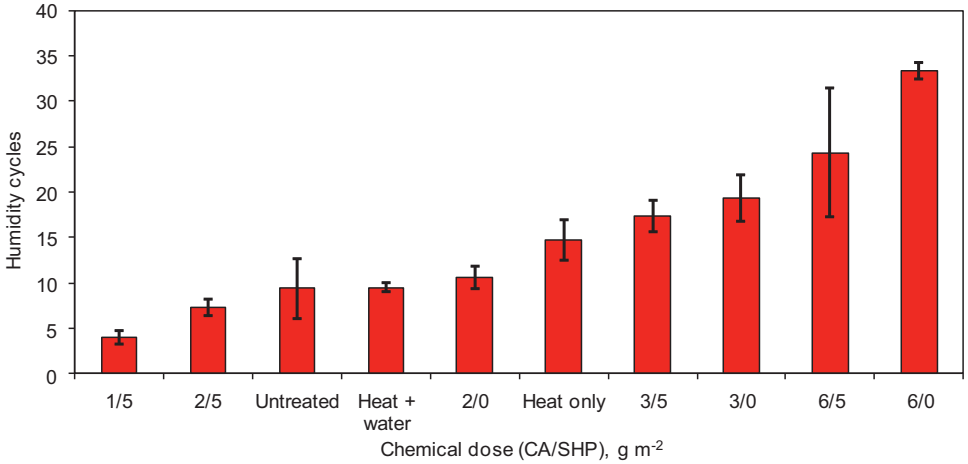

Fig. 9. Compressive creep performance of untreated and treated corrugated boxes. The first and second numbers in the *x*-axis value labels denote CA and SHP doses, respectively.

as one would have expected. The fate of this CA fraction remains unclear; unknown side reactions, e.g., with board additives, offer a potential explanation. The results of FTIR-ATR analysis (Fig. 5) of the linerboard are in line with the HPLC data, the latter showing a 12% reduction in total acids after one month. In the CA-treated board, the ratio of the carboxyl peak at ~1730 cm^{-1} to the cellulose peak at ~1373 cm^{-1} was also reduced by 12% during one month of storage at 90% rh. According to the HPLC results, the bound CA decreased by 9% during one month of storage at 90% rh, in good agreement with the FTIR spectra of the corresponding base treated samples before and after storage at 90% rh. These spectra showed a 6% reduction in the ester to cellulose peak ratio (1730 cm^{-1}/1373 cm^{-1}) at 90% rh as the peak from the unbound carboxyl groups was shifted away from this region to a broad band at centred at ca. 1575 cm^{-1} (carboxyl anion).

3.5. *Effect of CA dose and curing catalyst on compressive creep of corrugated boxes*

The creep performance of corrugated boxes treated with CA under cycling humidity conditions and a constant load was investigated under typical storage conditions of high and variable humidity. As shown in Fig. 9, box performance in terms of humidity cycles survived increased with an increase in CA dose, likely due to an increase in crosslinking as suggested by the linerboard investigations. The spraying of water only (same amount as in the application of CA) resulted in reduced box lifetime, i.e., boxes lasted fewer humidity cycles before failure. However, a subsequent application of heat seemed to cancel out this negative effect. Treatments in the presence of the catalyst gave shorter box lifetimes than the treatments with the equivalent dose of CA without the catalyst. A possible explanation is that the catalyst itself might have attracted more moisture into the boxes while providing no benefit in terms of catalysing esterification. Overall, results show that boxes with more crosslinked linerboards and a lower moisture uptake survived longer before failing due to less compressive creep occurring in their load-bearing side panels.

4. Conclusions

Treatment of linerboard with CA followed by thermal curing can markedly increase its compressive strength at high humidity via increased inter- and intrafibre crosslinking and associated reduced moisture uptake. An additional curing catalyst is not required for effective crosslinking which is ascribed to self-catalysed esterification of cellulosic fibres by CA. Higher curing temperatures tend to promote crosslinking, as estimated by linerboard SCT strength, and reduce the curing time required to obtain maximum SCT strength. The lifetime of corrugated boxes under cycling humidity conditions and a constant load can be more than tripled by CA treatment without an added curing catalyst.

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