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Morphological, Chemical and Crystalline Features of Urea-Formaldehyde Resin Cured in Contact with Wood

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ABSTRACT

The issue whether urea-formaldehyde (UF) resins possess crystallinity when cured in contact with wood has not been clearly resolved, although according to some published work low mole UF resins do not exhibit crystallinity in contact with wood. Here we provide evidence using field emission scanning electron microscopy (FE-SEM), Fourier transform infrared (FTIR) spectroscopy and wide angle X-ray diffraction (WAXD) that UF resin with a low formaldehyde/urea (F/U) mole ratio does crystallize when cured in contact with wood and show that crystals have various morphologies and sizes and thus can be regarded as polycrystals. Morphological characterization by FE-SEM revealed the presence of globular/nodular particles and crystalline structures. The particles occurred in two distinct populations with respect to their size, and the fractured faces of particles and their associated plate-like structures revealed presence of sub-particles of extremely small size (26.3~56.1 nm size range). Some crystalline regions of the resin contained expanded fan-shaped crystals, representing mature crystals. Other crystalline regions displayed features suggestive of emergence of crystals from globular particles. Transmission electron microscopy (TEM) made it possible to obtain electron diffraction (ED) pattern by analyzing directly the resin contained within cell lumens, which also suggested resin crystallization into polycrystals. The micromorphological information presented, particularly on nano-substructures and crystalline features, is novel and provides greater understanding of the architecture and crystalline characteristics of UF resin cured in contact with wood. Furthermore, information included provides evidence of a close relationship of emerging crystals with globular particles. FTIR spectra demonstrated that a quantitative calculation of the methylene linkages formed by cross-linking of UF resins in contact with wood has been advanced in its cure and crystalline structures formed in the cured UF resin. WAXD results also confirmed a polycrystalline nature of UF resin cured in contact with wood. These results corroborate that a low formaldehyde thermosetting UF resin cured in the presence of wood possesses distinct crystalline structures, an aspect of UF resin behavior that remained poorly understood and needed clarification. However, presence of crystallinity, albeit not widespread, may negatively impact cohesive strength of the resin, leading to a poor adhesion performance.

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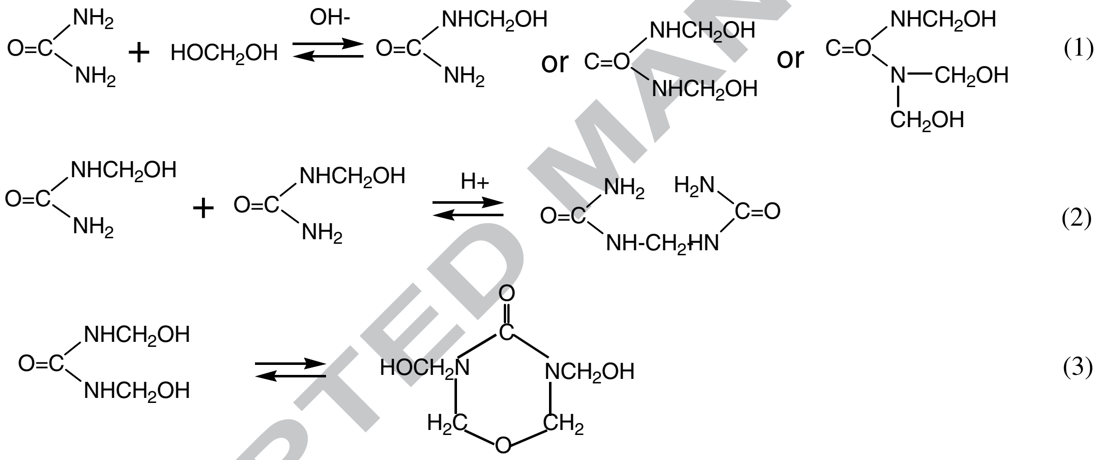
KEYWORDS: thermoset, urea-formaldehyde resin, crystalline feature, nano substructure, cross-linking, electron diffraction, wood

1. Introduction

Urea-formaldehyde (UF) resin is an aminoplastic thermosetting resin that has been widely used as an adhesive in the manufacture of wood-based products, such as plywood, particleboard and medium density fiberboard. The UF resin cures fast and has high gluing strength and a clear appearance in manufactured products. Also, the cost of purchase and application of this resin is relatively low. However, because of hydrolytic sensitivity of the resin [1] formaldehyde emission from UF resin adhesive bonded wood products in service is of concern from health and environmental perspectives, particularly when products are used in built environments. Over the last several years, research on UF resin has focused on reducing formaldehyde emission, and among the various approaches considered, developing formulations with lower formaldehyde to urea (F/U) mole ratio in the UF resin is an attractive but challenging approach to tackle the problem [2-9].This is because during curing cross linking in the resins of low F/U mole ratios is lower compared to high mole ratio resins, which are also considered superior in performance. In this regard, a thorough understanding of the structural and chemical characteristics of low mole UF resins in the liquid state as well as during curing (polymerization) processes would be helpful in fine tuning resin formulations and the processes and factors related to resin curing, such as the length and temperature of resin curing and the level and type of hardener used.

UF resin production involves two reactions, methylolation and condensation (Scheme 1). The methylolation in alkaline condition proceeds with the addition of up to three (four in theory) molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methylolated ureas (reaction 1). The produced molecular species from the methylolation include mono-, di-, and tri-methylolureas. It is known that tetra-methylolurea has never been isolated [10]. Low temperature and weak acidic pH favors the formation of di-methylene ether bridges (–

CH_2OCH_2–) over methylolation [10]. Each methylolation step has its own rate constant (*k*), with different *k* values for the forward and backward reactions. The reversibility of this reaction is one of the most important aspects of UF resins. This feature is responsible for both the low resistance against hydrolysis and the subsequent formaldehyde emission. The presence of some of these species was detected in many other studies [10-12]. The condensation reaction in acidic condition refers to the reaction of methylolated ureas into methylene ureas with water as a by-product (reaction2). An acid condition for UF resin synthesis is known to produce a variety of uronic derivatives (reaction 3) [10].



Scheme 1. Chemical reactions in UF resins

The information available on low mole UF resins is still limited. One common feature of liquid UF resins appears to be its colloidal nature [13]. During aging colloidal particles undergo clustering to form larger and complex aggregates. The architecture of cured UF resins consists of particles which have been variously described as nodular, globular and spherical structures [1,14-16]. Particles are larger in size and more abundant in low mole UF resins [1,13,15], which also exhibit crystallinity [14, 17-21]. Improved hydrolytic stability of low mole UF resins has been attributed in part to their crystalline nature [22]. Whether the entire UF resin is crystalline or the crystallinity is confined to certain components of the resin, such as nodular/globular structures, awaits clarification.

Structural and chemical characteristics influence the quality and performance of UF resins as wood adhesives, and improved understanding of the features of low mole UF resins can accelerate developments for a more environmentally acceptable UF resin based adhesion technology. An important area of gap in our knowledge is whether wood has an influence on UF resins when cured in contact with wood tissues. Indications are that UF resins are amorphous when cured in the presence of wood, even those of a low F/U mole ratio which is considered to favor crystallinity [19,23]. Morphological demonstration of the presence of crystals in low mole UF resins will substantiate X-ray analytical data; however, the presence of morphologically well-defined crystals has rarely been recorded [1]. Using FE-SEM with plasma sputtered osmium [24], which essentially produces structure-less film and thus enables high resolution imaging with SEM [25], we demonstrate presence of nanometer size substructures within nodular structures and morphologically distinct crystalline structures as part of the architecture of 1.0 F/U mole UF resin that had been cured in contact with radiata pine (*Pinus radiata*) wood veneers using 0.1% ammonium chloride (NH_4Cl) hardener. Furthermore, FE-SEM images from some crystalline regions showed a close relationship of what appeared to be forming crystals with globular particles, an aspect of UF resin behavior not investigated before. Use of TEM coupled with electron diffraction, FTIR spectroscopy and WAXD confirmed that the UF reins cured in contact with wood possessed a crystalline feature and that the resin crystallized into polycrystals.

2. Experimental

2.1. Materials

Technical grade urea granules (99%) and formalin (37%) were used for the synthesis of UF resins. Aqueous solutions of both formic acid (20%) and sodium hydroxide (20%) were used to adjust the pH level during the UF resin synthesis. An aqueous solution (20%) of ammonium chloride (NH_4Cl) used as hardener was added into the resin on the basis of the non-volatile resin solids of UF resins prepared.

2.2. Experimental methods

2.2.1. Preparation of UF resin

Liquid UF resin of 1.0 F/U (formaldehyde/urea) mole ratio was prepared in the laboratory following conventional alkaline-acid two-step reaction by adding the 2nd urea. Formaldehyde (37 %) was placed in the glass cooking reactor with the mantle heater. Then, the 1st urea was placed into the reactor, and stirrer speed was kept constant until temperature increases to 40°C. Aqueous solutions of sodium hydroxide (20 wt%) and formic acid (20 wt%) were used to adjust pH at 7.8~8.0 for addition reaction and to control pH at 4.6for condensation reaction. The mixture was heated to 90 °C for 60 min to allow the addition reaction. The temperature was then adjusted to 80 °C. When the temperature reached 80 °C, the pH had to be controlled to 4.6, and the condensation reactions were carried out until it reached a target viscosity of JK, which was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). When the condition was reached, the 2nd urea was added to the reactor using funnel. After all of the urea dissolved, the UF resin was cooled to room temperature, and the pH was subsequently adjusted to 8.0.

2.2.2. *Preparation of bond-line samples*

Ammonium chloride (0.1%) was added as a hardener and mixed with the UF resin prior to gluing veneers. Commercially sourced radiata pine (*Pinus radiata*) veneers were glued in pairs with UF resin adhesive, keeping the orientation of the wood grain of the two veneers parallel. The liquid UF resin (quantity three times the normal industrial application of 177 g/m^2) was spread thinly over one face of a veneer, and then the other veneer of the pair was placed over it (in contact with the resin). The paired veneer was pressed at room temperature with a weight applied (240 kg/m^2) for 24 hours for the resin to penetrate into wood tissues from the bond line. The paired veneer was then placed in an oven, with a same weight applied, for the resin to cure at 60ºC for 24 hours.

2.2.3. *Imaging with FE-SEM*

Paired veneer was sectioned (70 μm thickness) on a sliding microtome, which enabled fractured and un-fractured regions of the UF resin adhesive to be examined in the same section. Both transverse and longitudinal sections were obtained, however, for FE-SEM of resin architecture, longitudinal sections were used, as they provided much larger fractured surfaces of the resin adhesive contained within cell lumens. In addition, glued veneers were longitudinally split with a single edge razor blade to fracture the resin contained within cell lumens.

Sections were mounted on SEM stubs using carbon adhesive tape, coated with osmium [25] in a Plasma Coater (HPC-1SW, Vacuum Device Inc.) for 5 seconds and the adhesive structure was imaged with S-4800 Hitachi FE-SEM (Korea Basic Science Institute, Daegu) at 5 kV. The size measurements of UF resin particles were undertaken on 20 particles for each sample using IMT (Image and Microscope Technology) i-solution software (Vancouver, Canada).

2.2.4. Imaging with TEM

The sections were infiltrated with and embedded in the spurr's resin, according to the method described elsewhere in detail [26]. Ultrathin sections obtained on an ultramicrotome using a diamond knife were stained for 7 minutes with 2% aqueous uranyl acetate solution. The sections were viewed with H-7100 Hitachi TEM operating at 75 kV. Electron diffraction (ED) was undertaken on the resin contained within cell lumens with JEM-2100F TEM (Jeol, Japan), operating at 150 kV.

2.2.5. FTIR spectroscopy.

The paired plywood samples prepared were split along the bond line to scrape out the cured UF resin from the exposed bond line. Resin was then sieved to 200 micron size particles. A KBr pellet mixed with the cured UF resin (0.5% concentration) was used to obtain infrared spectra by FTIR spectroscopy (Nicolet 520P, Nicolet Instrument). Although 1.0 F/U mole ratio resin cured using 0.1% NH_4Cl was the focus of characterization work, FTIR analysis was undertaken on resins cured using two different levels (0.1 and 3%) of NH_4Cl hardener. This was done to compare quantitatively chemical changes to confirm that the resin in contact with wood had been cured.

2.2.6. Wide angle X-ray diffraction (WAXD)

About 2 grams of the resin obtained from the exposed bond line were scanned with an X-ray diffractometer (D/Max-2500 Rigaku, Tokyo, Japan) to investigate the crystallinity of the resin. Neat UF resin (without the hardener and wood) was also prepared using the same curing condition as the bond-line resin. Both resins were milled, powdered and analyzed at ambient temperature using a CuKα X-ray source with a wavelength (λ) of 1.5405 Å. The angle of incidence was varied from 10°to 60° by a step of 0.02°/min.

3. Results

Morphological features of cured UF resins in contact with wood is based on FE-SEM observations of fractured regions of UF resin present in the lumens of tracheids that were in contact with or in vicinity to the adhesive line and were impregnated with the resin adhesive (Fig. 1). Both sectioning on the sliding microtome and splitting of glued paired veneers longitudinally caused fracturing of parts of the resin, and the images illustrated were prepared from both types of preparation. In describing results, no distinction is made between these sample sources as architectural features of fractured resin were similar. In the description relating to the texture of the non-crystalline part of the resin, the terminologies used here to describe particulate structures are ‘globular’ and ‘nodular’ depending upon particle morphology, state of particle coalescence and their association with platy structures. Additionally, the terms ‘structures’ and ‘particles’ are used interchangeably as appropriate.

In the FE-SEM image presented in Fig. 2 unfractured regions of UF resin appear smooth, whereas fractured regions appear ‘finely granular’ or ‘coarsely granular’. As shown in Fig.2, the finely granular region appears to have a particulate texture, whereas coarser texture of the coarsely granular region is due to the presence largely of what appear to be needle-shaped crystals. However, as shown in the inset of Fig.2, a highly magnified view of the boxed region of cell ‘B’, crystals are not actually needle-shaped, but more like fan-shaped or plate-like formations, as illustrated further and described in greater detail later on.

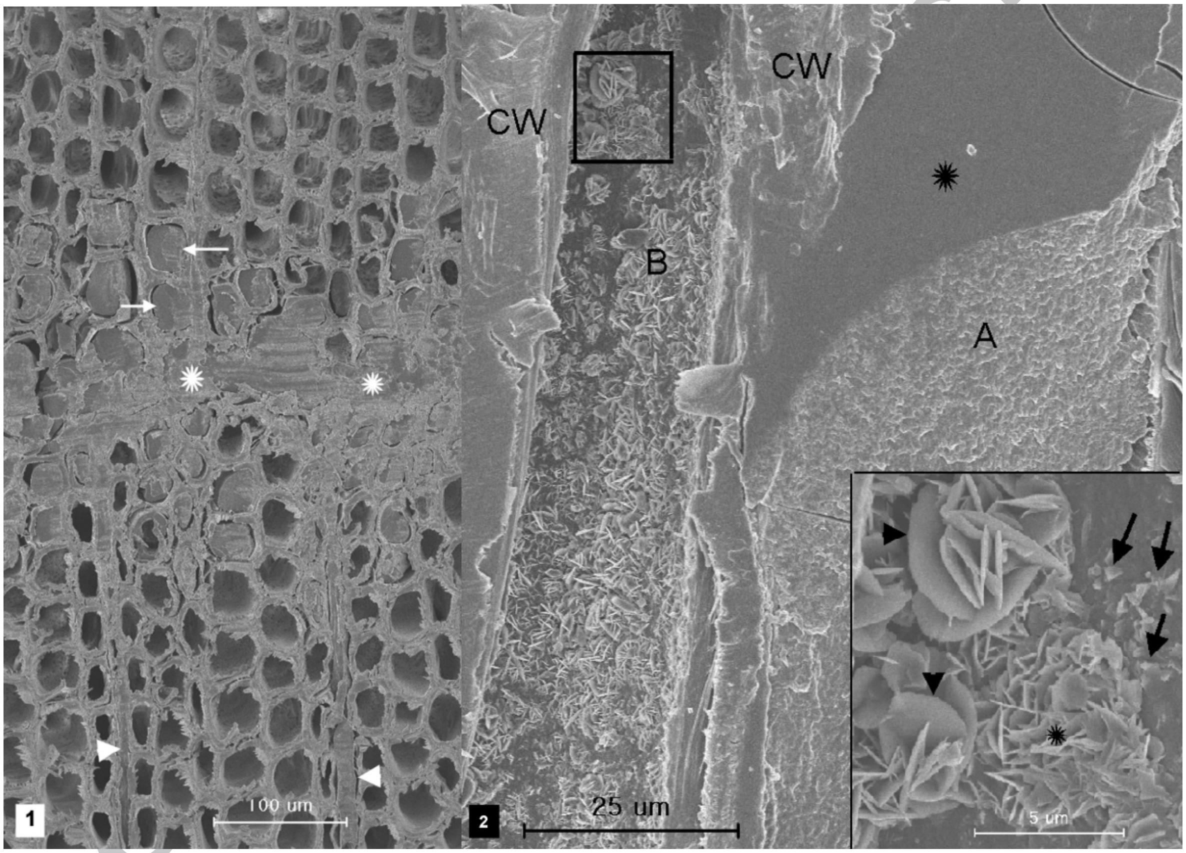


Fig.1. Transverse section through glued paired radiata pine veneers showing UF resin- adhesive bond line (asterisks) and resin filled tracheids (arrows) and rays (arrowheads). The resin contained in the lumens of tracheids, located in the vicinity to and contact with the bond line, was closely examined with FE-SEM in longitudinally sectioned or fractured veneer strips.

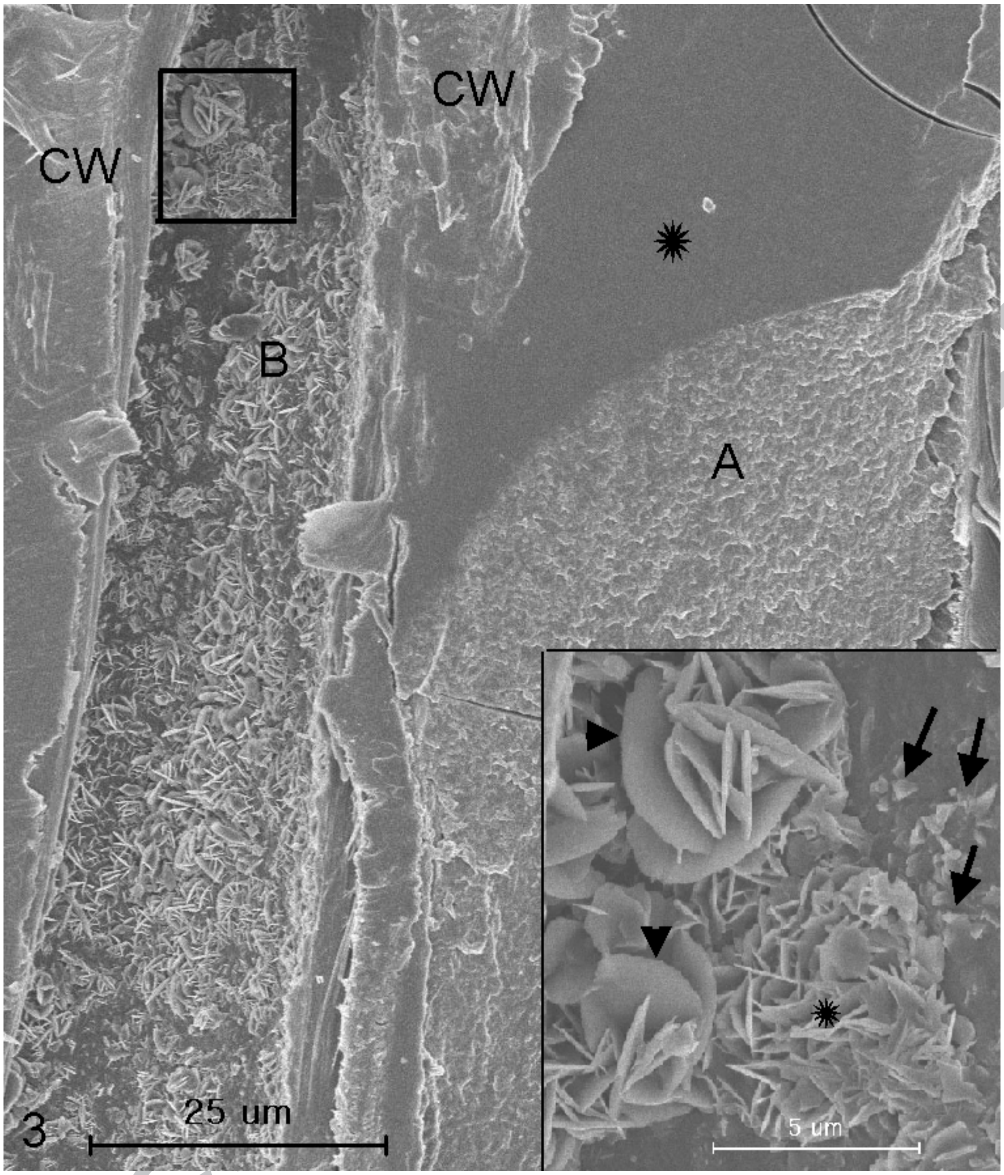


Fig.2. Low magnification view of UF resin filled tracheids (longitudinal direction). Unfractured region of the resin appears smooth (asterisk). Fine granularity of the fractured region of the resin is due to the presence of particulate structures (A) and coarse granularity is due largely to the presence of crystalline structures (B). CW: cell wall. Inset: High magnification view of the boxed region in upper left corner of the micrograph. Crystalline aggregates consist of a range of

differently shaped crystals, identifiable as fan-shaped (arrowheads), platy (asterisk) and small emerging (arrows) crystals.

High magnification imaging of finely granular regions revealed the presence of globular (Fig. 3) and nodular structures (Figs. 4 & 5). In Fig. 3 two distinctly different populations of particulate structures are present; one population consists of large size particles (1453.9~2581.5 nm), which appear to be globular in shape. Large globular particles appear to be coalescing, judging by fused appearance for the majority of these particles as differently shaped formations, including beaded and platy structures. Only occasional particles can be seen as secrete individual entities; majority appear to be a part of above shaped formations, being physically confluent with them. Smaller size particles (378.8~546.6 nm) in Fig. 3 appear to be partly embedded in a matrix, protruding from it, and in this respect and in their size the particles may share commonality with those illustrated in Fig.4. The architecture of a finely granular part of the resin, shown in Fig. 4, is a complex of similar size particles (420.1~604.5 nm), which appear to be connected to and confluent with platy formations. Particles appear to protrude from the surfaces and margins of platy structures, and thus we define them as being nodular in form. Fig. 5 includes a finely granular part of UF resin, containing nodular particles connected to platy formations. Whereas surfaces of both nodular particles and platy formations appear smooth, their fractured regions reveal presence of nanometer size substructures/sub-particles. The linear arrangement of the substructures visible in places points to existence of an order at a very fine level of organization of the architecture of nodular and lamellar structures. High magnification view of the boxed region in Fig. 5, displayed in Fig. 6, confirms linear alignment of sub-particles in some parts. High magnification images, such as the image in Fig.6, were also useful in size measurement of sub-particles (26.3~56.1 nm).

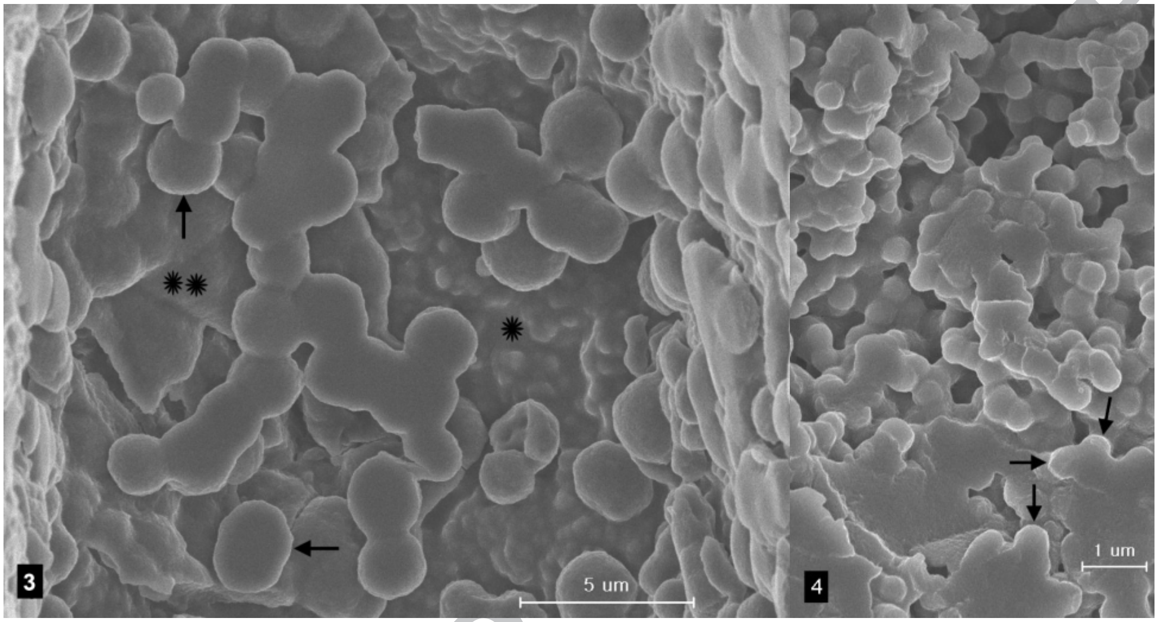


Fig. 3. A finely granular region of UF resin revealing the presence of two distinctly different populations of particles, comprised of large (arrows) and small (asterisk) size particles within the same region of the resin. Large particles appear to be coalescing, resulting into beaded and other types of formations. A plate-like structure, with protrusions resembling large particles, is marked by paired asterisks.

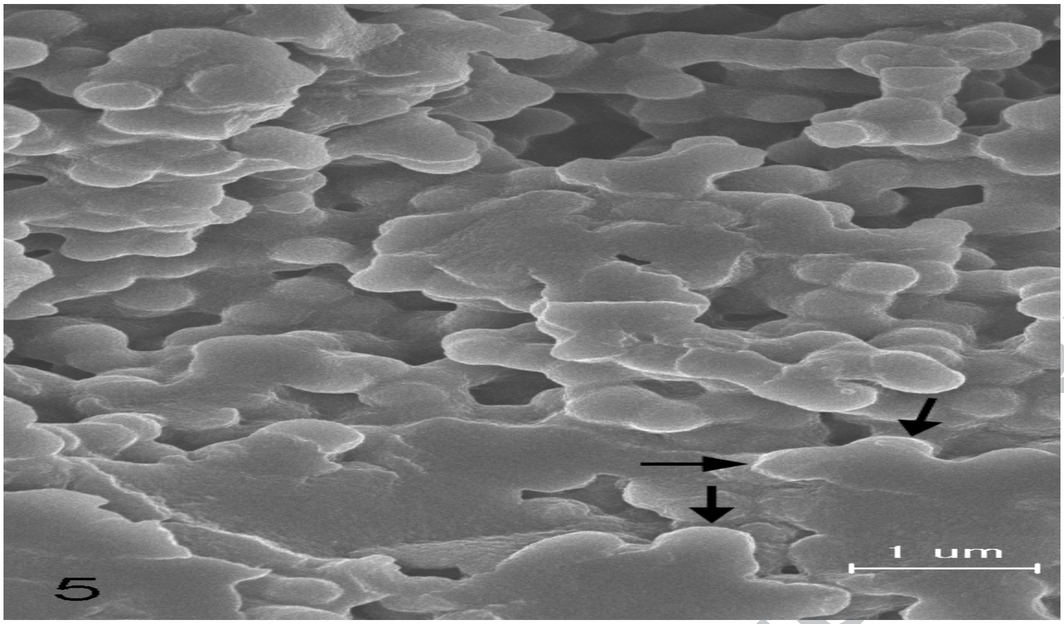


Fig. 4. A finely granular region of UF resin contains similar size particles, which have coalesced resulting in a range of morphologically different formations, some of which appear flattened plate-like structures, with nodular surface protrusions (arrows).

A part of the coarsely granular region of UF resin, illustrated in Fig. 7 and Fig.S1, contains both globular/nodular particles and crystalline structures, as crystal aggregations and small developing crystals. Where observable as small single crystals, crystals are associated with globular/nodular particles and appear to be emerging from them. The impression obtained is that particles may be transforming into crystals, judging by the relationship observable between the extent of distortion in particle shape and crystal size. In this context, particles of globular forms are associated with the smaller size crystals and those of distorted forms with larger size crystals. Small emerging crystals are not visible within inter-particle regions of the resin architecture, which appears relatively smooth. Crystals present in aggregations, perhaps representing more advanced states of their growth, appear as curved plates, some plates being highly convoluted.

Fig. 8 displays fan-shaped expanded crystals, some with finely serrated edges. This shape may represent an advanced or fully grown form of crystals. Superficially, some crystals appear needle-shaped, but a closer observation suggests that the needle-like appearance stems from a particular orientation of crystals, where only the edges of crystals are visible. Whether there is a developmental relationship of fan-shaped crystals with platy crystals can only be a conjectural judgment. It is, however, tempting to speculate that fan-shaped crystals have arisen from unfolding of convoluted platy crystals.

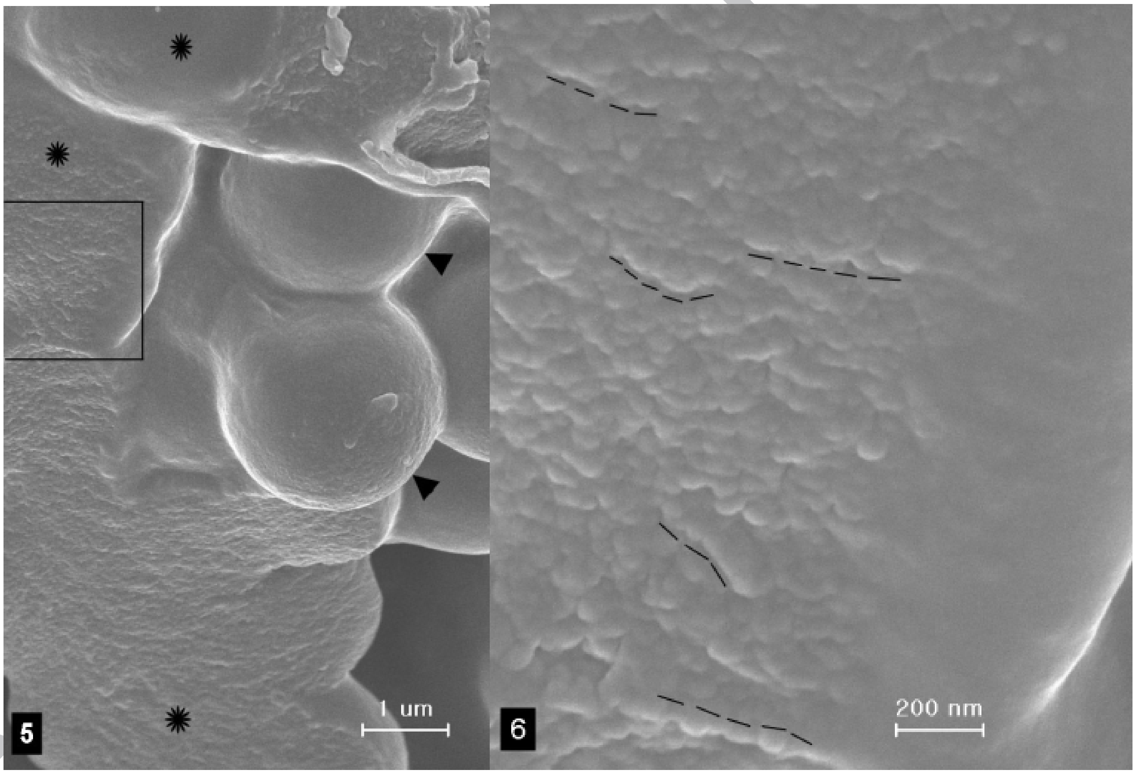


Fig. 5. A finely granular region of UF resin with large nodular particles (arrowheads) and platy structures (asterisks). Fractures through parts of the resin reveal the presence of

substructures/particles within the platy structures and nodular surface protrusions. The boxed region is shown at high magnification in Fig. 6.

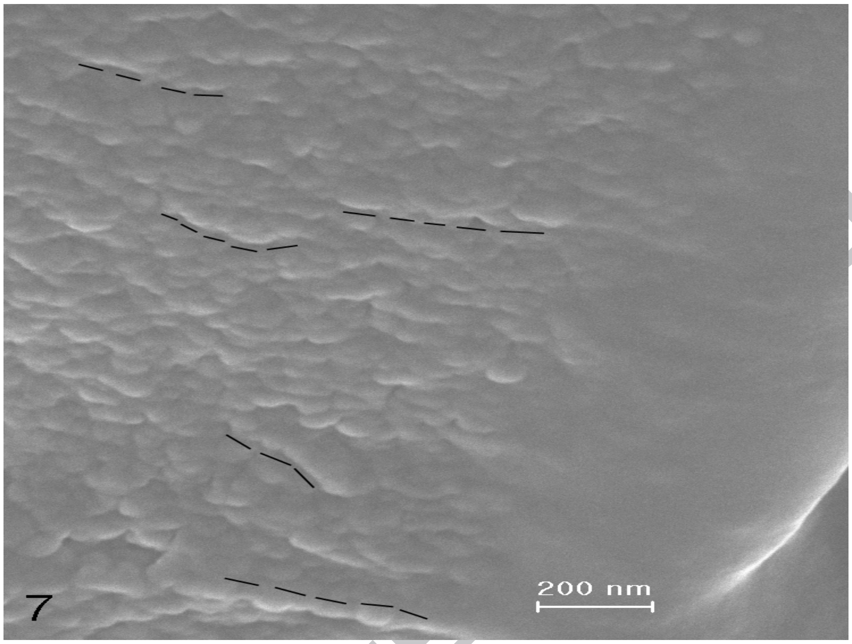
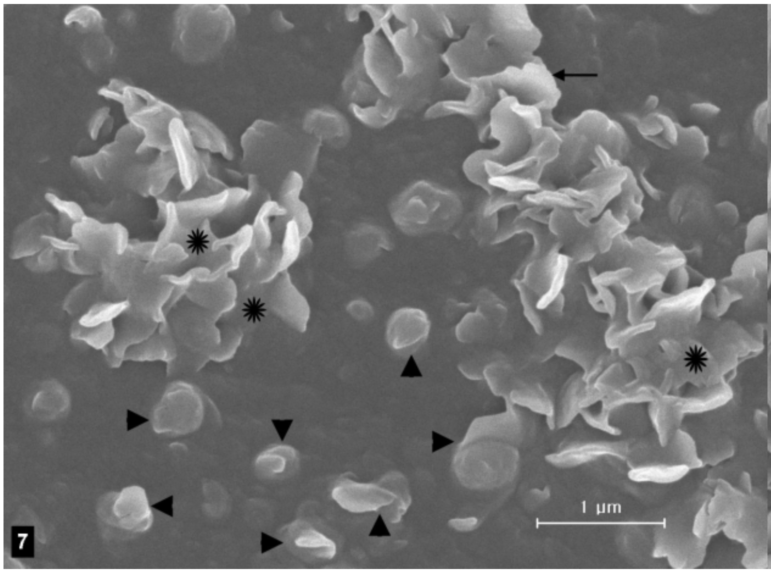


Fig. 6. High magnification view of the boxed region in Fig. 5 showing the morphology and distribution of substructures as nano-size particles. In places, short linear arrays of particles are visible (stippled lines). Particles vary in their size.



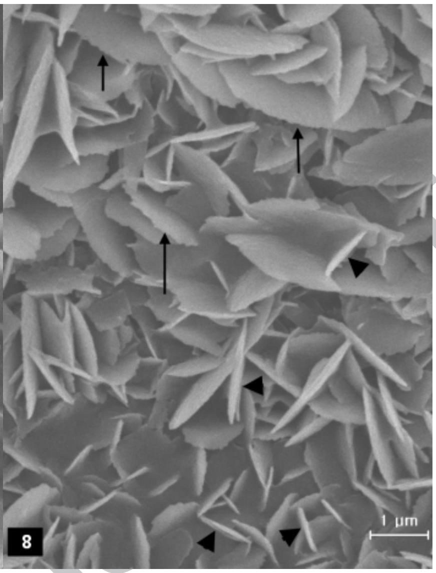


Fig. 7. High magnification view of a region of UF resin containing both globular/nodular particles and crystalline structures. Crystals appear to have curved plate-like forms (asterisks), with some displaying highly convoluted forms (arrow). Where crystals are visible as single bright structures, a close physical association between a crystal and a globular particle is visible (arrowheads).

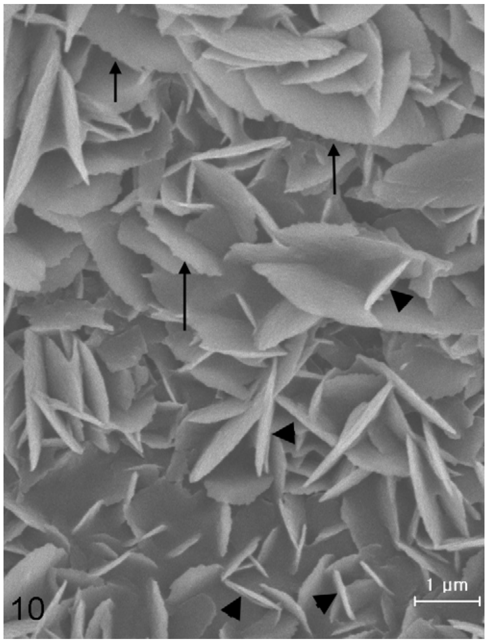


Fig. 8. Crystalline region of UF resin containing expanded fan-shaped crystals. Crystals with only their edges exposed appear needle-shaped (arrowheads). Crystal edges appear serrated (arrows).

TEM observation also revealed the presence of spherical particles as the dominant component of the architecture of UF resin adhesive contained within cell lumens (Fig. 9, a), thus confirming FE-SEM observation. These spherical structures are considered to be globular/nodular particles transversely cut in the process of ultrathin-section preparation. TEM was also useful in undertaking electron diffraction (ED) work at high resolution on the particles contained within the cell lumen in ultrathin sections, in order to obtain further evidence of crystalline nature of 1.0 mole UF resin cured in contact with wood. The ED pattern, shown in Fig. 9 (b), appears as multiple concentric rings (about 4 rings), which suggest presence of isotropic polycrystals, with no significant preferential orientation relative to the incident electron beam. The radii and spacing of the rings are governed by the inter-planar spacing, the electron wavelength, and the camera constant of ED. Thus, these results indicate that cured UF resins in contact with wood are poly-crystalline structures with different orientations of crystals.

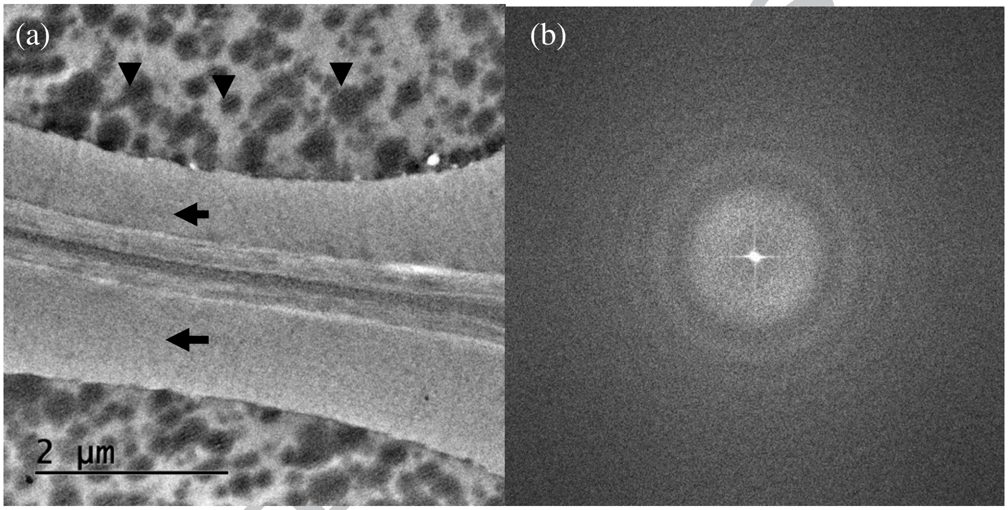


Fig.9. Images of TEM and ED result from cured UF resin at the bond-line. (a) TEM image of cured UF resin particles in the lumen of wood cells (resin particles: arrowheads; wood cell wall: arrows); (b) ED pattern of resin particles.

FTIR spectroscopy was also used to compare chemical features of cured UF resins removed from the bond line (Fig. 10, a). Although 1.0 F/U mole UF resin with 0.1 % NH_4Cl hardener, was the primary focus of our characterization work, FTIR was run using two levels (0.1 and 3%) of this hardener to confirm that the resin in contact with wood had been cured by comparing chemical changes quantitatively.

FTIR spectra of neat UF resin with no NH_4Cl, 0.1% NH_4Cl and 3% NH_4Cl are quite similar to each other, but different in the absorbance intensity of each chemical groups. As expected from condensation reactions of UF resin (Scheme 1), the methylene linkage ($-CH_2-$) between methylol groups ($-CH_2OH$) is formed by splitting off water molecules and the number of their linkage increases when UF resin advances into a large giant molecule via curing or cross-linking processes.

The band at 2970~2960 cm^{-1} was only detected for all UF resins, and could have resulted from a combined contribution of C-H mode from dimethylene ether ($-CH_2OCH_2-$), methylol group, or a methylene link ($–N-CH_2$). The carbonyl group (C=O) stretching of primary amides was the most dominant absorption band of the infrared spectra of UF resin which occurred at 1650 cm^{-1}, and did not appear to change with hardener levels and has been used as a reference band for quantitative comparison (Fig. 10, b). The occurrence of a band at 1400~1390 cm^{-1} band assigned to $–CH_2OH$ was detected for neat UF resins, while it was shifted to downfield to 1380~1330 cm^{-1}. The band at 1320 $cm^{-1}$was assigned to =C-N or -CH-N groups as reported [27].The spectra of three UF resins showed strong bands at 1050~1030 cm^{-1}, which could be assigned to methylene bridge ($-NCH_2N-$)[27].

Thus, a quantitative comparison of each chemical group has been made by normalizing the measured absorbance of each band to that of the carbonyl group (1650 cm^{-1}). Each absorbance at 2970~2960 cm^{-1}, 1400~1390 cm^{-1} or 1050~1030 $cm^{-1}$from CH stretching, methylol group or methylene linkage, respectively, of UF resins was quantified (Fig. 10, b). As expected from Scheme 1, the content of methylol group decreases while that of methylene bridge increases with an increase in the degree of cure of UF resin. In general, a greater hardener level accelerates the cure of UF resins because of a greater amount of acid produced by the hardener added, as shown in Scheme (4):

$$4NH_4Cl+6CH_2O \rightarrow (CH_2)_6N_4+6H_2O+4HCl \quad \text{------------------------------} \quad (4)$$

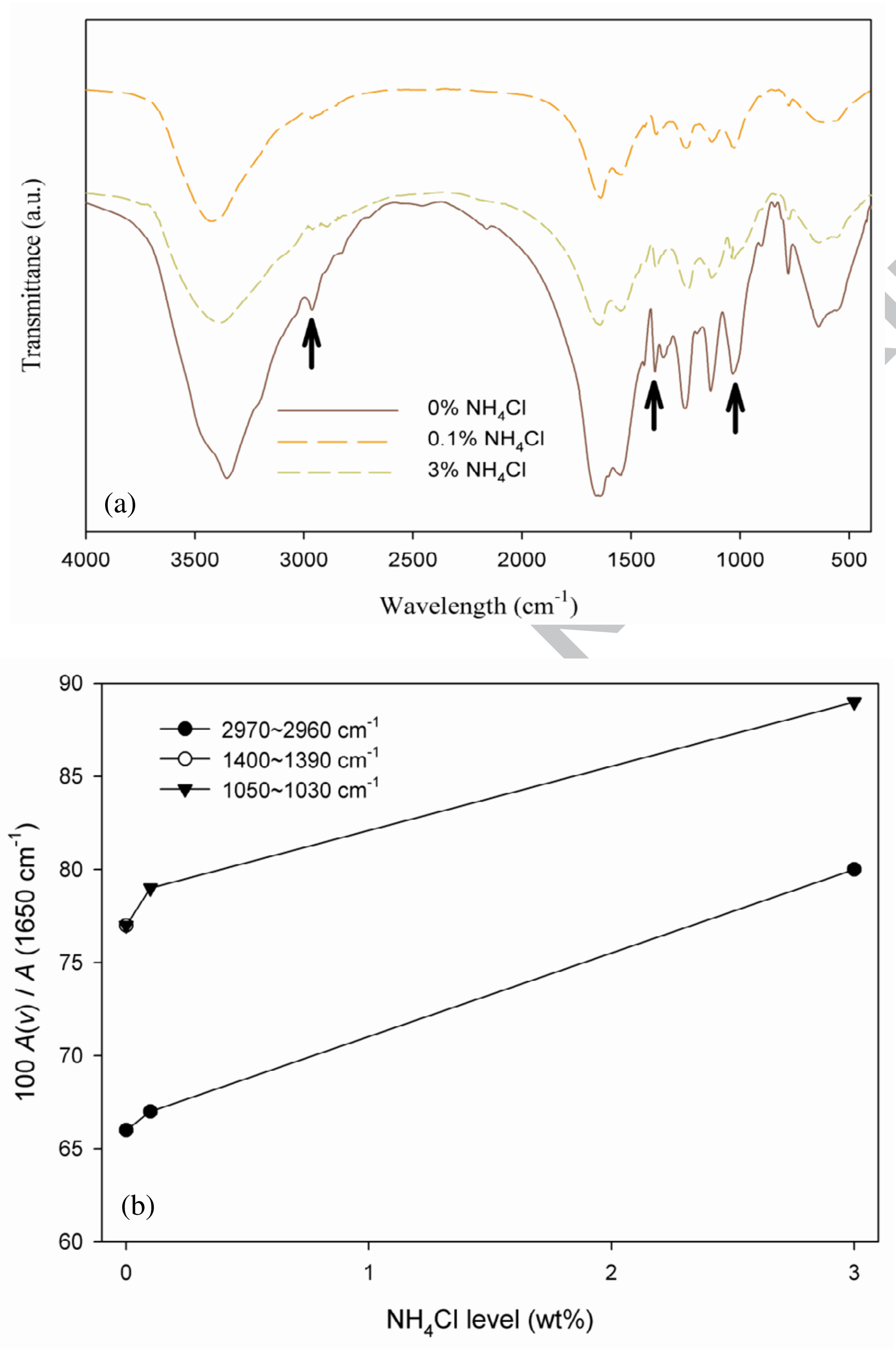


Fig. 10. FTIR spectroscopy of cured UF resins in the bond-line at different hardener levels. (a) Three absorbance bands of FT-IR spectra used for quantitative analysis (arrows), and (b) quantitative result of three absorbance bands of FT-IR spectra of (a). Quantitative comparison of

three absorbance bands (arrows in Fig. 10 a) shows an increase in methylene linkages and disappearance of methylol groups in the cured resins.

In order to confirm the presence of poly-crystalline structures, an X-ray based characterization was also undertaken. Fig. 11 compares the WAXD traces of the same resin cured with and without wood under the same condition. It shows that, in the presence of wood, the crystalline reflections are much less sharp and intense, although they are present and they reveal the occurrence of crystalline domains in the material. In the case of the resin investigated in this work, obviously wood acts as an obstacle to the regular ordering of the crystals and of their aggregates, and thus the SAXS pattern becomes featureless due to the absence of a periodical variation in electron density. In other words, as confirmed by electron micrographs, the crystalline domains are randomly arranged within the bond line because wood prevents their assembly into the bcc packing which characterizes the pure resin.

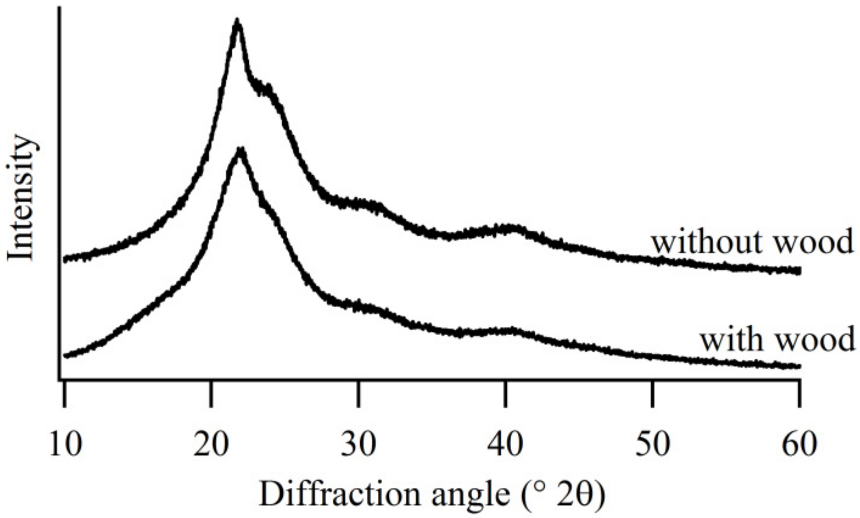


Fig.11.WAXD patterns of cured UF resinsin contact with and without wood.

4. Discussion

The majority of the studies on micromorphological characterization of UF resins have been undertaken on resins cured without contact with wood. As one important aspect of the performance of UF resin as an adhesive is how well it bonds with wood, it is crucial to understand resin behavior in contact with wood cell wall and its polymers and to find out if wood components have an influence on the physical, chemical and mechanical characteristics of the resin. For example, it has been suggested that when cured in the presence of wood UF resins are amorphous, even those based on a low proportion of formaldehyde to urea, which promotes crystallinity [19]. However, it is evident from the work presented here that crystalline regions were present in the UF resin contained within the lumens of tracheids. Therefore, the findings reported here significantly extend our understanding of the behavior of a low mole UF resin cured in contact with radiata pine wood veneers.

The presence of particulate structures in low mole UF resins has been reported before in several studies, with particles described variously as globular, spherical and nodular structures [1,13-16,26]. In our work, particles were both of globular and nodular forms. The latter type particles, which were in the majority, were associated with plate-like and other formations, with which they were confluent and appeared to protrude from their margins. Images suggestive of coalescence of globular particles into filamentous, beaded and other formations indicate that platy structures are likely end products of particle fusion, the maturation of which may not have fully completed under curing conditions, as the presence of undulations and protrusions from the margins of the platy structures would indicate. The discovery of the presence of nanometer size subparticles/substructures in fractured regions of both platy and protruding nodular structures was made possible by a novel technical approach employed for coating samples with plasma sputtered osmium [24], which essentially produces a structure-less film on the surface of coated samples, enabling ultra-high resolution imaging to be undertaken and nanometer scale structures to be resolved. In such situations coating with gold particles, which has been the most commonly used method for coating samples for SEM observations in the past, is either not suitable [25] or can obscure features similar or smaller in size to deposited gold particles.

TEM examination provided complementary data to those obtained using FE-SEM. TEM images showed the particles in the UF resin contained within the lumen of wood cells to be spherical (Fig. 9, a), which represent a sectional view of nodular structures observed by FE-SEM at the fractured surface (Figs. 3~5), thus providing further support for the view that particles are a dominant feature of UF resin architecture.

The presence of masses of crystalline structures in the UF resin contained within the lumens of tracheids was unexpected, as some reports suggest that crystallization of UF resins cannot occur when the resin is cured in contact with wood [19]. Crystalline nature of cured UF resins, particularly those of low formaldehyde to urea ratios, has been reported in several studies [14,19,20,22,28] and spatial arrangement of crystalline domains and distance between the domains for UF resins have been determined [21]. Majority of these studies have employed X-ray based techniques to assess crystallinity, and confirmation of the presence of crystals in UF resins based on morphological characterization has been obtained only on some occasions [1].

FE-SEM examination undertaken in the work presented here is therefore a necessary complement to X-ray based studies of crystalline characteristics of low mole UF resins, and makes significant advances to our understanding of the behavior of low mole UF resins during curing for following reasons. One, as far as we know this is the first record of crystallization of a UF resin in contact with and within the confinement of wood cell walls. Second, the physical association of what we consider as emerging crystals with globular/nodular particles suggests that the particles function as nucleation sites for crystals. This view is consistent with the suggestion of Pratt et al. [17] and Dunker et al. [29] that colloidal particles of UF resins represent crystalline or semi-crystalline regions. Absence of crystals in association with non-globular (platy) regions of the resin architecture suggests differences between globular/nodular structures and platy formations perhaps at the molecular level, although the two systems appeared to be physically confluent with each other and had a texture consisting of similar appearing nano substructures. The perceived differences may be related to the crystallization behavior of these crystals in a particular environment, which deserves further investigation.

There are likely practical implications of the presence of crystallinity, particularly relating to hydrolytic stability and adhesion strength. For example, improved hydrolytic stability of low mole UF resins is considered to be in part related to crystallinity of such resins [22], and micromorphological demonstration of the presence of crystalline structures in the 1.0 F/U mole UF resin in our work is significant also in this regard. It had been known that low F/U mole UF resins result in a deterioration of the adhesion strength compared to high F/U mole ratio UF resins [3, 30]. Various reasons, such as low degree of cross-linking [31], greater brittleness [32], or high residual stress [33] are believed to be responsible for reduction in adhesion strength. Thus it is possible that the crystallinity present in the UF resin we investigated may have a negative effect on adhesion strength, although crystals were not widespread but occurred in domains. Therefore, it is not expected that the crystals scattered in the matrix of cross-linked UF resin make a contribution in building elastically active network chains between two cross-links that mainly provides stiffness with cross-linked network of thermosetting polymers [34].

TEM-ED pattern of the cured UF resin in wood cell lumen, showing four-ring pattern in the image, is quite compatible with WAXD pattern. Taken together, TEM-ED and WAXD patterns suggest that the cured UF resin in contact with wood is polycrystalline in nature. Morphological variability observed in the form of the crystals (emerging vs. mature crystals) using FE-SEM is likely the basis for TEM-ED and WAXD patterns recorded, indicating poly-crytsallinity in the resin.

FTIR spectra (Fig. 10, a) suggest that methylol groups and methylene linkages are present for all UF resins, independent of the hardener level. Moreover the normalized absorbance of CH vibration increased with an increase in the hardener level, which resulted from the combinations of different chemical species such as dimethylene ethers, methylol groups or methylene bridges. It is not possible to compare the relative absorbance of methylol groups at different hardener levels because of its shift to downfield. However, the quantitative result of methylene bridges clearly increases with an increase in the hardener level, indicating that the UF resin in contact with wood was in a cured state. Confirmation of this by employing FTIR spectroscopy removes ambiguity as to whether or not we were investigating the features of resin in a cured state.

In a previous work, we obtained a much richer WAXD pattern with several sharp and defined crystalline reflections by focusing on the structure and morphology of UF resins in the absence of wood [21]. Caution should be exercised, though, in concluding solely from WAXD that crystallization of UF resins cannot occur when wood is present. The effect of wood within the samples greatly dilutes the contribution of the crystalline reflections to the diffractograms making it difficult to accurately assess the structure attained by the resin. The same can be said for SAXS. In the UF resin samples coming from the bond line of glued wood veneers, featureless patterns were obtained (not shown). As previously reported [21], the same resin cured in the absence of wood in the same conditions as in the present work yielded a very detailed SAXS spectrum. A major reflection followed by several other minor peaks was arranged according to a scheme characteristic of a bcc packing of spheres. Such ordered arrangement disappeared in the presence of wood. This is somewhat similar to what is observed on the SAXS signal of polymer lamellae in the presence of inorganic nanofillers such as montmorillonite. The peak due to the stacking of lamellae of the polymer matrix often is weakened and broadened to such an extent that it is no longer detectable [35-36]. This does not mean that the lamellae are not formed in nanocomposites, and in fact lamellae are clearly visible by TEM or atomic force microscopy AFM) [35-36]. The disappearance of a SAXS peak means that in these materials the lamellae are no longer arranged in an ordered fashion, due to the hindering role of clay [37-40]. In the case of the resin investigated in this work, obviously wood acts as an obstacle to the regular ordering of the crystals and of their aggregates, and thus the SAXS pattern becomes featureless due to the absence of a periodical variation in electron density. Our work shows the importance of combining high resolution microscopy technique with X-ray analysis in obtaining more complete and accurate information on crystallization characteristics of a polymer. In some earlier studies[14,17,23], failure to detect crystallization of UF resin cured in contact with wood is likely to have resulted from the reliance primarily on X-ray methods to assess crystallinity.

5. Conclusions

Obtaining detailed molecular and structural knowledge of UF resins, one of the thermosetting polymers most widely used as a wood adhesive, is important to fully understand the performance and properties of UF resins cured in contact with wood. Using FE-SEM, TEM, ED, FT-IR spectroscopy and WAXD techniques, we provide evidence that 1.0 F/U mole ratio UF resin that had been partially cured in contact with wood possessed crystallinity. Although globular/nodular particles in UF resins have been considered to exhibit crystallinity before, the exact site of crystal nucleation within the resin architecture was not known. Our FE-SEM observations provided micromorphological evidence of a spatial relationship of small emerging crystals with globular particles, suggesting that these particles may be the site of crystallization. Additionally, WAXD in combination with ED and FTIR suggested that 1.0 mole UF resin cured in contact with wood is likely to possess polycrystalline characteristics. Thus, our work employing a combination of microscopic, chemical and physical techniques has provided important new knowledge on the architecture and crystallization characteristics of a low formaldehyde mole UF resin that was cured in contact with wood. Regarding practical implications of the findings presented, it is likely that the presence of crystals may impact adhesion properties negatively as there is likely to be lower degree of cross-linking in crystal-containing regions of the resin.

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Supplementary Data

Additional micromorphologies of crystals in UF resin cured in contact with wood, including both globular/nodular particles and crystalline structures. In places, emerging crystals appear to be closely associated with globular particles (Fig. S1).

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Graphical Abstract

Morphological, Chemical and Crystalline Features of Urea-Formaldehyde Resin Cured in Contact with Wood

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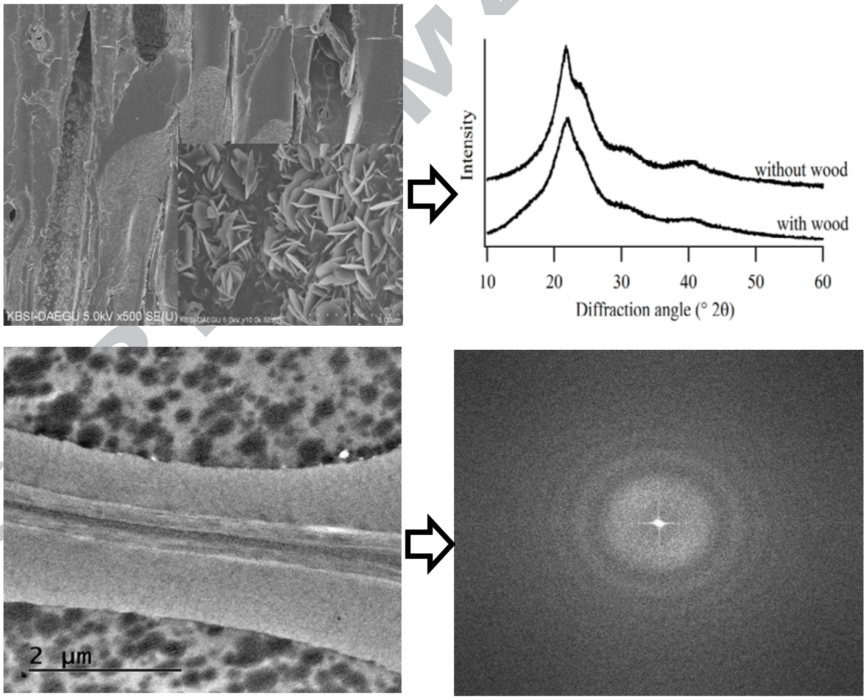

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Highlights

- FE-SEM shows crystal structures in UF resin cured in contact with wood.
- WAXD confirms that the cured UF resin possesses crystals in the presence of wood.
- ED coupled with TEM indicated that the cured UF resin contained polycrystals.
- FTIR spectra demonstrated that the cured UF resin has been advanced in its cure.
- These results confirm that UF resin cured in contact with wood does crystallize.