

Mikroskopische Charakterisierung der Klebstoffverteilung in Holzwerkstoffen – in Bezug zu mechanischen Holzwerkstoffeigenschaften

Microscopical characterisation of adhesive distribution in
wood based panels – relating to mechanical board properties

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1. Vorwort

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2. Zusammenfassung

Die Klebstoffverteilung wird als ein wichtiges Werkzeug in der gezielten Produktentwicklung und -optimierung von Klebstoffsystemen und Holzwerkstoffplatten gesehen. Sie stellt einen ersten Handlungsansatz dar mechanische Platteneigenschaften interpretieren zu können. Bisherige Untersuchungen zur Leimverteilung basierten auf Methoden, bei der der Klebstoff vor der Plattenherstellung markiert oder angefärbt worden ist. Besonders für Untersuchungen im industriellen Maßstab bedeutet das einen großen Aufwand und hohe Kosten. Darauf aufbauend, wird die Wechselwirkung zwischen der Klebstoffverteilung in Holzwerkstoffen und den mechanischen Platteneigenschaften untersucht. Dafür wird eine mikroskopische Methode vorgestellt mit der es möglich ist, die Leimverteilung in Span- und Faserplatten zu bestimmen ohne den Klebstoff vor der Plattenproduktion anfärben zu müssen. Des weiteren wird der Einfluss von direkten Klebstoffmodifizierungen, chemisch oder durch Zugabe von fibrillierter Zellulose, auf die mechanischen Werkstoffeigenschaften untersucht.

3. Abstract

Resin distribution is seen as an important instrument towards a targeted product development of resin systems and wood based panels. It is the fundamental approach in analysing mechanical board properties. Previous methods to determine resin distribution comprise staining the resin before board producing. In terms of analysing industrial wood based panels these procedures causes high costs and effort. Based on this, it is attempted to examine the interaction between resin distribution and mechanical board properties. Therefore a microscopic method is presented in which the resin distribution of particle boards can be estimated without the need of staining the resin in advance. Additionally the influence of chemical adhesive modification or an addition of fibrillated cellulose in order to enhance mechanical board properties is investigated.

4. Einleitung

Für die mechanischen Eigenschaften von Holzwerkstoffen ist die Bindefestigkeit, d.h. eine ausreichende Adhäsion zwischen Holz und Klebstoff von entscheidender Bedeutung. Die am häufigsten eingesetzten Klebstoffe in der Holzwerkstoffindustrie sind Aminoplastische Klebstoffe auf Basis von Harnstoff-Formaldehyd (Diem et al. 2010). Obwohl diese Harze viele Vorteile für eine industrielle Anwendung aufweisen, wie hohe Reaktivität und einfache Handhabung zu moderaten Kosten (Dunky 1998, Dunky and Niemz 2002), erfordern mitunter auftretende Einbußen in der Bindefestigkeit und das Streben nach immer niedrigeren Formaldehydmissionen eine ständige Optimierung des Systems. Um gleichbleibende mechanische Platteneigenschaften zu gewährleisten, wird in der Holzwerkstoffproduzierenden Industrie ein Überschuss an Klebstoff eingesetzt, um Festigkeitsschwankungen auszugleichen und die Festigkeitsstandards durchgehend zu erfüllen.

Im Zuge von Produkt- und Klebstoffoptimierungen ist es ein anhaltendes Ziel der Holzwerkstoffindustrie Ressourcen zu reduzieren, sprich den Klebstoffeinsatz zu verringern oder Klebstoff so zu modifizieren, dass bei weniger Klebstoffeinsatz gleiche oder sogar verbesserte Platteneigenschaften erzielt werden. Klebstoffeigenschaften können, abhängig von der Produktanwendung, auf unterschiedliche Weise verbessert werden. Die chemische Modifizierung der Klebstoffe ist dabei am naheliegendsten. Daneben können Füllstoffe eingesetzt werden, um die Klebstoffeigenschaften nach Bedarf zu verändern. Die Zugabe von Nanozellulose zu Holzklebstoffen ist relativ neu, zeigt aber in ersten Versuchen positive Effekte der Klebstoffe in ihrer „bond performance“ (Veigel et al. 2011, Kaboorani et al. 2012,

Veigel et al. 2012). Besonders spröde Klebstoffe wie UF, weisen durch die Zugabe von Nanozellulose eine erhöhte Belastbarkeit auf (Veigel et al. 2011, Veigel et al. 2012). Diese verbesserten mechanischen Eigenschaften können sich wiederum positiv auf den Klebstoffeinsatz auswirken und demnach Klebstoffkosten senken.

Eine erste Herangehensweise für eine Klebstoffoptimierung und -reduzierung ist die Kenntnis der Klebstoffverteilung innerhalb der Holzwerkstoffe. Die Klebstoffverteilung innerhalb plattenförmiger Holzwerkstoffe wird als eine der maßgeblichen Einflußfaktoren für die Platteneigenschaften gesehen (Riegler et al. 2012). Ihre Optimierung führt zu einer steigenden Klebstoffeffizienz und geringeren Produktionskosten (Xing et al. 2006). Für Spanplatten wurde nachgewiesen, dass nur etwa die Hälfte des eingesetzten Klebstoffes direkt zur Bindung zwischen den Spänen beiträgt. Der Rest penetriert in die Späne oder bildet Agglomerationen (Mahrtdt et al. 2015). Ist die Leimverteilung bekannt, kann davon ausgehend, der Klebstoff so modifiziert werden, dass er die gewünschten Anforderungen erfüllt.

Methoden, die Klebstoffverteilung in Holzwerkstoffen beschreiben, sind in der Literatur umfangreich vorhanden (Pakdel et al. 2008). Hierbei hat sich herausgestellt, dass besonders die Anwendung der Fluoreszenzmikroskopie einen guten Kontrast zwischen Holz und Klebstoff liefert (Kamke und Lee 2007).

Da UF basierende Klebstoffe im ausgehärteten Zustand eher transparent erscheinen müssen sie markiert werden, um einen ausreichenden Kontrast zwischen Holz und Klebstoff zu erreichen (Xing et al. 2005). Dazu können bestimmte Fluoreszenzfarbstoffe wie Acriflavine, Rhodamin und Brilliant Sulphaflavine verwendet werden und der Klebstoff kann mittels Fluoreszenzmikroskopie charakterisiert werden (Sernek et al. 1999; Kamke et al. 2000; Loxton et al 2003). Die meisten in der Literatur beschriebenen Färbungsmethoden wurden durchgeführt indem der Klebstoff, bevor er auf die Fasern oder Späne aufgesprüht wurde, angefärbt worden ist. Diese Vorgehensweise schließt jedoch aus, dass man Chargen, die besonders gut oder schlecht ausfallen im Nachhinein nicht mehr auf ihre Leimverteilung prüfen kann. Klebstofffärbungen, die im industriellen Maßstab durchgeführt werden sollen, führen zu hohen Kosten aufgrund der großen Leimmenge, die angefärbt werden muss. Zudem erhält man farbige Werkstoffplatten, die nicht verkauft werden können (Ginzel und Stegmann 1970).

Das Ziel der vorliegenden Arbeit ist eine einfache Methode vorzustellen, mit der die Leimverteilung in Holzwerkstoffen, auch an bereits produzierten Platten, nachträglich noch bestimmt werden kann. Die Methode soll gezielt eingesetzt werden um als Kontrollwerkzeug

für Klebstoffmodifizierungen zu dienen, um deren Auswirkungen auf die Leimverteilung sichtbar zu machen. Darüber hinaus soll der Frage nachgegangen werden, welchen Einfluss die Leimverteilung in Holzwerkstoffen auf die Werkstoffeigenschaften und hier gezielt auf die Plattenfestlichkeit hat. Dafür sollen folgende Arbeitshypothesen überprüft werden. Zum einen die Vermutung, dass die Leimverteilung einen Einfluss auf die Festigkeit plattenförmiger Holzwerkstoffe hat. Zum anderen, dass eine hohe Anzahl kleiner Leimpartikeln zu einer homogenen Leimverteilung und zu höheren Plattenfestigkeiten führt. Dafür wird die Leimverteilung in diversen Holzwerkstoffen, u.a. hergestellt mit modifiziertem Klebstoff, bestimmt und in Zusammenhang mit ermittelten Plattenfestigkeiten betrachtet und interpretiert.

Die Ergebnisse der vorliegenden Arbeit wurden in drei Publikationen in wissenschaftlichen Journalen veröffentlicht.

5. Material und Methoden

5.1 Material

5.1.1 Holzarten

Im Rahmen einer Untersuchung (Publikation II) wurden Spanplatten im Labormaßstab produziert. Für die produzierten Spanplatten wurden industrielle Mittelschichtspäne aus verschiedenen Holzarten mit einer Partikelgröße von 1 bis 6 mm verwendet.

5.1.2 Klebstoffe

Für die Herstellung der untersuchten Holzwerkstoffe wurden wässrige Klebstoffsysteme verwendet. Eingesetzt wurde Klebstoff auf Basis von Harnstoff-Formaldehyd (UF)-Harzen (Primere, Metadynea GmbH, Krems). Für die Einbettung des Probenmaterials wurde ein niedrig viskoser Epoxidklebstoff verwendet.

5.1.3 Mikroskopieproben

Die Herstellung von Dünnschnitten aus Holzwerkstoffproben ist ausführlich beschrieben in Publikation I. Eine leichte Abwandlung des Prozesses wird in Publikationen III für Faserplatten beschrieben.

Der Prozess von der Probenpräparation zur mikroskopischen Bildaufnahme ist in Abbildung 1 dargestellt.

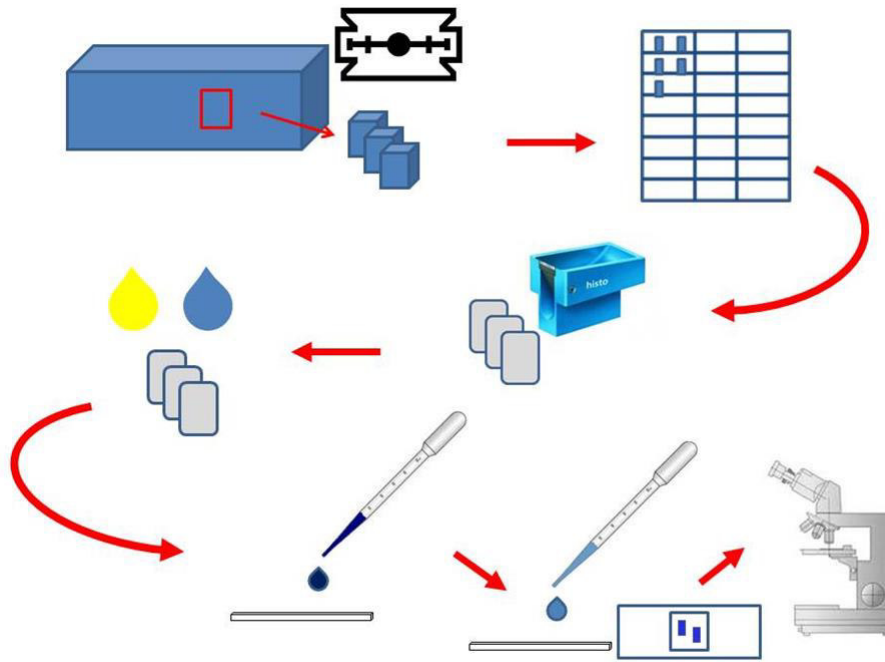


Abbildung 1 Schematisierter Prozess von der Probenpräparation zur Lichtmikroskopie

5.2 Methoden

5.2.1 Dünnschnittpräparation

Die neue Methode beginnt mit der Probenvorbereitung, indem 2×2×3 mm große Proben aus plattenförmigen Holzwerkstoffen herausgeschnitten werden. Die Probenkörper werden in niedrig viskosen Epoxyd-Klebstoff eingebettet. Das einbetten stabilisiert die empfindlichen Proben und verhindert ein vorzeitiges Zerschneiden während der Herstellung der Dünnschnitte und ein Quellen während der Färbung. Die Epoxyd-Matrix schafft ein stabiles Gebilde von dem recht einfach Dünnschnitte hergestellt werden können. Die 2 µm dicken Schnitte werden mit einem Ultramikrotom (Leica Ultracut R) geschnitten. Die Schnitte werden anschließend in einer Doppelfärbung angefärbt. In einem ersten Schritt werden die Schnitte mit einer 0,1%-igen Lösung Brilliant Sulphaflavine (BSF) angefärbt. Der Fluoreszenzfarbstoff wird verwendet um den Klebstoff zu markieren. Danach wird der überschüssige Farbstoff mit deionisiertem Wasser ausgewaschen. Anschließend werden die Dünnschnitte zwischen Objektträger und Deckglas platziert und mit einer 0,2%-igen Gentianaviolett Lösung eingefärbt. Der zweite Farbstoff wird verwendet, um die Holzsubstanz anzufärben und um so einen ausreichenden Kontrast zwischen Holz und Klebstoff für die nachfolgende Bildauswertung zu schaffen. Der überschüssige Farbstoff wird wie bei der ersten Färbung ausgewaschen. Nachdem der Dünnschnitt getrocknet ist, werden Mikroskopiebilder mit

einem Fluoreszenzmikroskop (Zeiss Axioplan 2Imaging) gemacht. Das Mikroskop wird verwendet mit einer Halogenlampe HAL 100 und einer Fluo Arc HBO 100 Ultraviolettlampe. Für die Verwendung der HBO 100 wird ein Filtersystem mit einer Anregungswellenlänge von 438 nm und einer Emissionswellenlänge von 520 nm verwendet. Während der Aufnahme wird zwischen den beiden Lichtwegen gewechselt, weil für die weitere Bildauswertung die Information beider Bildinhalte notwendig ist. Für die Bildaufnahme wird eine Zeiss AxioCam HRc verwendet, mit der Bilder im Hellfeld und Fluoreszenzlicht mit einer Auflösung von 0,943 $\mu\text{m}/\text{pixel}$ gemacht werden können. Um den gesamten Dünnschnitt fototechnisch zu erfassen, wurde dieser rasterartig abfotografiert. Dabei werden die gleichen Bildbereiche sowohl im sichtbaren Licht als auch im fluoreszenzlicht aufgenommen, übereinandergelegt und mit Bildbearbeitungssoftware (Photoshop CS3) zu einem neuen Bild verbunden (Abb.2).

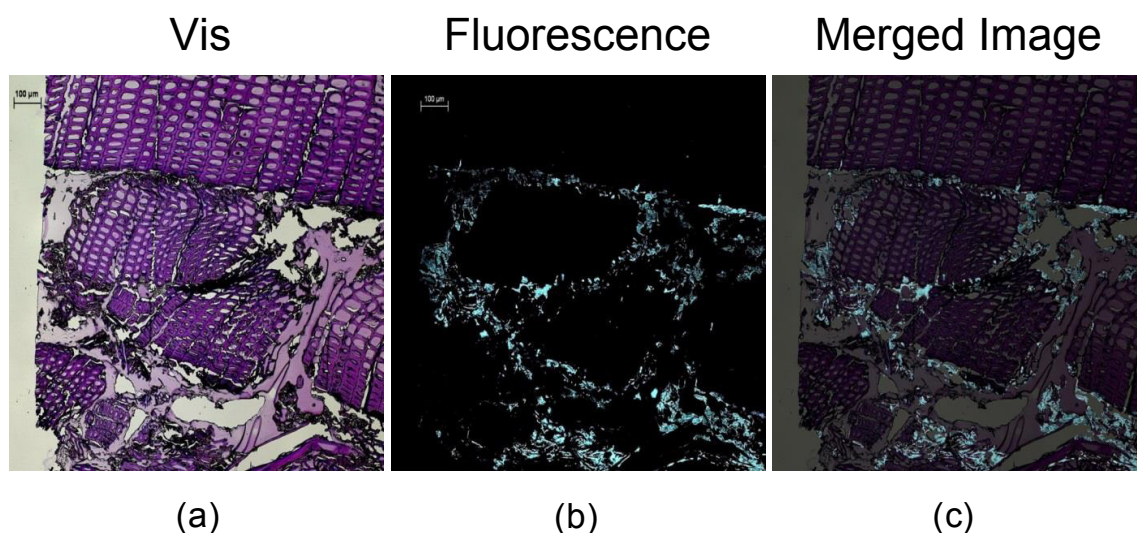


Abbildung 2 **a** Querschnittsbild, gefärbt mit Gentiana Violett, aufgenommen im sichtbaren Licht, **b** Dünnschnitt angefärbt mit BSF und aufgenommen unter Fluoreszenzlicht, **c** die Kombination der Bilder **a** und **b** zeigt beide Aspekte Holz und Klebstoff

Um beide Bildinformationen nutzen zu können, wird bei einem der Bilder die Deckkraft reduziert. Die so erhaltenen Mosaicbilder werden dann mit benachbarten Bildern aus dem Aufnahmeraster, mit der Bildbearbeitungssoftware MosaicJ, einem erweiterten Werkzeug von ImageJ, verbunden (Abb. 3).

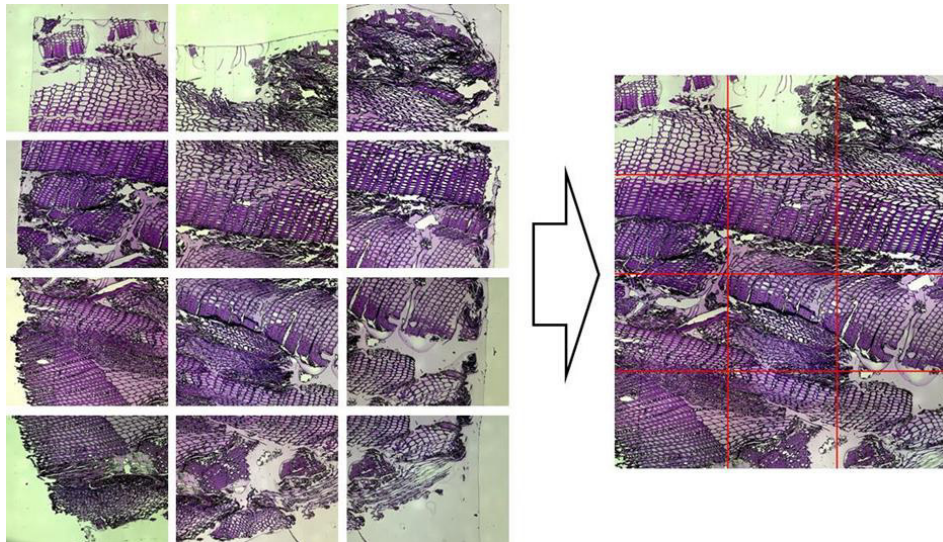


Abbildung 3 Einzelbilder, aufgenommen in einem Raster und verbunden mit angrenzenden Bildern, um den ganzen Dünnschnitt zu erfassen

Die erhaltenen Querschnittsbilder werden dann weiter mit Photoshop bearbeitet. Dabei werden die Spanoberflächen mit einem linienförmigen Band so markiert, dass eine genaue Zuordnung des Klebstoffes zur Leimfuge oder Penetration möglich ist. Ebenso möglich ist die Bestimmung des überschüssigen Klebstoffes, der weder in der Leimfuge noch im Span penetriert vorliegt. Einzelne Binärbilder vom Klebstoff, Spaninneren und der Klebefuge an sich werden erzeugt und mit ImageJ quantifiziert und den einzelnen Spanbereichen relativ zugeordnet (Abb. 4).

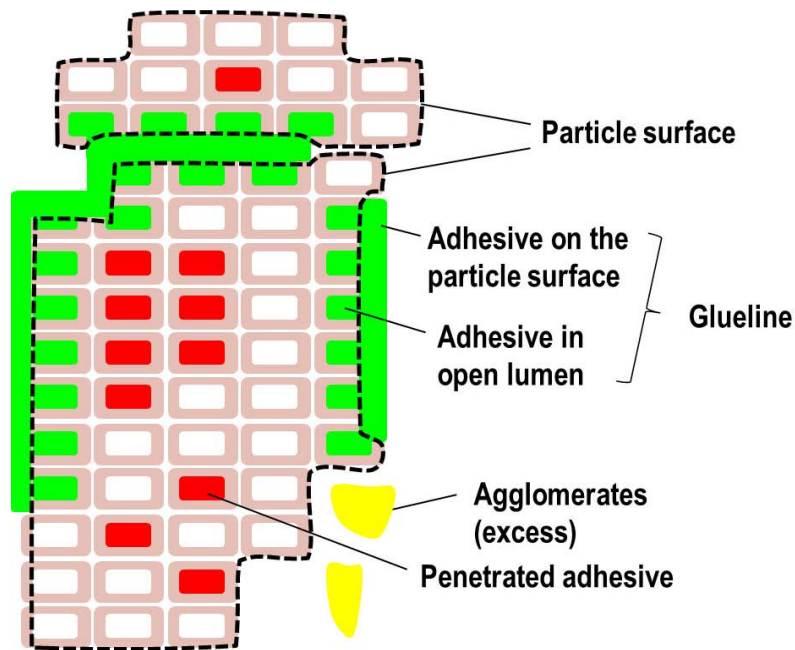


Abbildung 4 Querschnittsmodell von Holzspänen und wie der Klebstoff daran angeordnet sein kann

5.2.2 Fluoreszenzmikroskopie

Für die mikroskopische Klebstoffdetektion in Holzwerkstoffen (Publikation I, II, III) wurde ein Fluoreszenzmikroskop Axionplan 2 imaging (Carl Zeiss Microimaging GmbH, Jena, Deutschland) verwendet. Für die quantitative Auswertung der Mikroskopiebilder, wie etwa der Bestimmung der Klebstoffverteilung, wurde die Software ImageJ und Photoshop verwendet.

5.2.3 Klebstoffcharakterisierung

Um einen Einfluss der Zellulosezugabe auf die rheologischen Eigenschaften der Klebstoffe zu untersuchen, wurden Viskositätsmessungen durchgeführt. Die Messungen erfolgten mit einem Rotationsrheometer (Bohlin CVO, Bohlin Instruments GmbH, Pforzheim, Deutschland) und einer Kegel/Platte Meßanordnung. Dabei rotiert der obere Kegel im Abstand von 0,15 mm (Scherrspalt) über der feststehenden Platte. Die Messungen wurden mit einer steigenden Scherrate von 0,1 bis 200 s⁻¹ gemessen.

Um den Einfluss der Zellulose auf die Aushärtengeschwindigkeit des Klebstoffes unter Pressbedingungen zu simulieren, wurden dynamische mechanische Analysen (DMA) und dynamische Differenzkalorimetrie (DSC) -Messungen durchgeführt. Die DMA-Messungen wurden mit einer Netz DMA 242 C (NETZCH-Gerätebau GmbH, Germany) durchgeführt. Dafür wurden mit definierten Furnierverklebungen 3-punkt-Biegeversuche in einem Temperaturbereich von 10 bis 180 ° C, bei einer statischen Last von 0,5 N durchgeführt. Die

DSC-Messungen wurden mit einer Netz DSC F3 Maia (NETZCH- Gerätebau GmbH, Germany) durchgeführt.

5.2.4 Mechanische Charakterisierung

Die Prüfung der in Publikation II hergestellten einschichtigen Spanplatten erfolgte nach dem entsprechenden Prüfnormen. Die Dichte der Platten wurden nach EN323 (1993) bestimmt. Die Bestimmung der Querkzugfestigkeit wurde nach EN319 (1993) bestimmt und an der Universalprüfmaschine der Firma Zwick/Roell Z100 (Ulm, Deutschland) durchgeführt. Die mechanischen Daten der übrigen Publikationen wurden vom Holzwerkstoffproduzenten bezogen.

6. Zusammenfassung der Ergebnisse

Im Zuge der vorliegenden Arbeit wurde eine neue Methode zur Leimdetektion in industriellen Spanplatten vorgestellt (Publikation I). Mit der Methode ist es möglich die Klebstoffverteilung quantitativ zu bestimmen ohne den Klebstoff vor der Holzwerkstoffproduktion anzufärben. Bestimmt wurden Parameter wie Klebstoffpartikelgröße, Bedeckungswerte, der Anteil des Klebstoffes in den Spänen und der Anteil der Klebstoffes in der Leimfuge. Es konnte für die untersuchten Proben nachgewiesen werden, dass der Klebstoffanteil der Leimfuge, der zur Verklebung der Holzpartikeln maßgebend beiträgt, bei weniger als der Hälfte des Gesamtanteils liegt. Dennoch wird davon ausgegangen, dass penetrierter Leim zur Dimensionstabilität bei Feuchteinfluss beiträgt (Frihart 2009).

In Publikation II wurde der Effekt einer 5%igen Zugabe von mikrofibrillierter Zellulose (MFZ) auf die Querkzugfestigkeit von einschichtigen Laborspanplatten untersucht. Dabei konnte eine um 30% höhere Querkzugfestigkeit der Platten mit Modifizierung ($0,63 \pm 0,07$ MPa) zur Referenz ($0,47 \pm 0,1$ MPa) bei gleicher Plattendicke festgestellt werden.

Um einen Erklärungsansatz für die deutliche Verbesserung der mechanischen Plattenfestigkeit bei einer Zugabe von fibrillierter Zellulose zu finden, wurde zunächst die Leimverteilung in Spanplatten mit unmodifizierten UF und MFZ-modifizierten UF lichtmikroskopisch untersucht. Zusätzlich wurde die Viskosität und das Aushärteverhalten von beiden Klebstoffsystemen untersucht. Der MFZ-modifizierte Klebstoff hatte eine höhere Viskosität, die mit steigender Scherrate abnahm (shear thinning), was in guter Übereinstimmung mit anderen Experimenten ist (Iotti et al. 2011; Puisto et al. 2012; Dimić-

Mišić et al. 2013; Katarina et al. 2013; Grüneberger et al. 2014). Im Vergleich zur Referenz zeigte der modifizierte Klebstoff ein chemisch und mechanisch verzögertes Aushärteverhalten. Letzterer zeigte mikroskopisch betrachtet, größere zusammenhängende Klebstoffpartikel in der Leimfuge und eine höhere Klebstoffbedeckung der Holzspäne. Dementsprechend weist der modifizierte Klebstoff auch einen höheren Anteil an Klebstoff in der Leimfuge ($53\pm 8\%$) auf, als die Referenz ($42\pm 9\%$).

Nicht nur in Spanplatten, sondern auch in anderen Holzwerkstoffen, wie Faserplatten, ist die Leimverteilung von Interesse, um etwa die Güte von Klebstoffmodifizierungen bewerten zu können. Dafür wurden in einem Projekt industrielle HDF Platten, die teils mit modifiziertem Klebstoff (mUF) hergestellt wurden, auf ihre Leimverteilung hin untersucht (Publikation III). Mechanische Tests ergaben Platten mit einer Zugfestigkeitssteigerung um 15% bezogen auf die Referenzplatten. Zudem wurde eine 7%-ige Reduktion der Dickenquellung nach 24 Stunden Wasserlagerung gemessen. Die mikroskopische Größenbestimmung von Klebstoffpartikeln ergab für den modifizierten Leim größere Partikel, die ihrerseits für eine höhere Klebstoffbedeckung auf den Fasern sorgten. Die durchschnittliche Querschnittsfläche der Klebstoffpartikel beträgt für die Referenz $4\ \mu\text{m}^2$ und $10\ \mu\text{m}^2$ für die Platten mit modifiziertem Klebstoff.

Die Untersuchungen zur vorliegenden Arbeit haben gezeigt, dass mit der vorgestellten Methode die Bestimmung der Klebstoffverteilung in Holzwerkstoffen möglich ist und ein relativer Vergleich zwischen unterschiedlichen Beileimungssystemen durchgeführt werden kann. Mit der genauen Kenntnis der Leimverteilung (Ist-Verteilung) kann in einem weiteren Schritt versucht werden durch eine gezielte Klebstoffmanipulation, -modifikation die gewünschte Verteilung (Soll- Verteilung) zu erreichen, immer mit der Möglichkeit, die gegenwärtige Klebstoffverteilung abzubilden. Da bei allen durchgeführten Plattenvergleichen alle Parameter, wie Holzmaterial, Prozessbedingungen und Plattendichten gleichgehalten worden sind, sich aber unterschiedliche Festigkeitseigenschaften ergaben ist es sicherlich gerechtfertigt den Grund für die geänderten Platteneigenschaften in der Klebstoffmodifizierung zu suchen, und hier besonders in ihrem Einfluss auf die Leimverteilung. Untersuchungen mit modifizierten Klebstoffen konnten die Funktionalität der Methode bestätigen und eine der aufgestellten Arbeitshypothesen verifizieren nämlich, dass die Leimverteilung einen Einfluss auf die Platteneigenschaften, in unserem Fall, die Festigkeitseigenschaften hat. Es konnte mit den vorgestellten Arbeiten gezeigt werden, dass durch eine Modifizierung der Klebstoffe, ob durch eine Zugabe von Nanozellulose oder einer chemischen Modifikationen, die zu größeren zusammenhängenden Klebstoffflächen in der

Leimfuge führen, höhere Plattenfestlichkeiten erzielt werden können. Für den mit Nanozellulose modifizierten Klebstoff dürfte wahrscheinlich die erhöhte Viskosität für die Ausbildung größerer Leimflächen und einen höheren Anteil an Klebstoff in der Leimfuge verantwortlich sein. Demnach scheint mehr Klebstoff für die Bindung zwischen den Partikeln verfügbar zu sein, was eine höhere Plattenfestigkeit begünstigt. Die zweite Hypothese, dass eine große Anzahl an kleinen Leimpartikeln die Plattenfestigkeit begünstigt konnte nicht verifiziert werden. Vielmehr wird für die Platten mit erhöhten Festigkeitseigenschaften angenommen, dass größere zusammenhängende Leimflächen, die zwar weniger häufig vorhanden sind, aber in den Bereichen in denen sie auftreten für feste Bindungen innerhalb der Platten sorgen und so einen größeren Beitrag zur Plattenfestigkeit leisten als viele kleine Leimtropfen, die individuell betrachtet schwächere Faserbindungen aufweisen. Mit den gewonnenen Erkenntnissen und einer geeigneten Methoden zur Bestimmung der Leimverteilung im Holzwerkstoffen können in zukünftigen Versuchen z.B. weitere Klebstoffmodifizierungen durchgeführt werden um die Klebstoff- und somit auch die Platteneigenschaften gezielt verbessern und Ressourcen einsparen zu können.

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8. Publikationen

8.1 Paper I

Mahrdt, E., Stöckel, F., van Herwijnen, H. W. G., Müller, U., Kantner, W., Moser, J. and Gindl-Altmutter, W. (2015). Light microscopic detection of UF adhesive in industrial particle board. Wood Science and Technology 49: 517-526

Light microscopic detection of UF adhesive in industrial particle board

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Abstract A new procedure to detect urea–formaldehyde adhesive in industrial particle board is presented. The method uses thin sections stained with a visible dye (gentian violet) and a fluorescent dye (brilliant sulphaflavine), respectively, in a two-step procedure. Microscope images of a selected area of interest acquired in visible and fluorescence modes are combined to obtain sufficient contrast, enabling semi-automated detection of adhesive by means of image analysis. No addition of dye prior to particle board production is necessary.

Introduction

The quality of a particle board depends on a variety of material and process parameters. Adhesive distribution within boards is considered to play an important role in board properties, and optimisation of adhesive distribution leads to increased resin efficiency and lower costs (Xing et al. 2006). Penetration of adhesive into wood particles is one factor of particular interest. On the one hand, excessive penetration is considered a severe disadvantage in bonding particle board, because penetrated adhesive does not directly contribute to particle bonding. It is believed

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that excessive penetration leads to a starved bondline with deficient adhesive and subsequent low resin bonding performance (Xing et al. 2005). On the other hand, resin penetration into particles may also lead to stabilisation in terms of reduced hygro-expansion and thus thickness swelling. The panel-producing industry is therefore highly interested in optimising the content of adhesive in order to comply with quality requirements while keeping cost at a minimum. Therefore, the knowledge of resin distribution within wood-based panels such as particle boards is an essential tool for screening effects of different or modified adhesives. Ideally, such a method should not be limited to boards produced at small laboratory scale, but it should be applicable to the full range of boards produced at industrial scale.

For producing panel boards such as particle boards, the most common adhesive is urea–formaldehyde (UF) (Dunky 1998). UF is colourless when cured and therefore difficult to detect by simple light microscopic methods (Xing et al. 2005; Riegler et al. 2012). In order to obtain good contrast between wood and adhesive under microscopic conditions, the resin has to be treated. To visualise UF resin within particle boards, various methods have been employed such as the use of stains, dyes, or chemical labelling (Niemz et al. 1990; Pakdel et al. 2008). In this context, fluorescent microscopy has been proven to provide perfect contrast between adhesives and wood (Kamke and Lee 2007). A number of fluorescence-staining methods have been reported in the literature. Kamke et al. (2000) introduced a fluorescent dye named acriflavine, and Grigsby and Thumm (2004) as well as Loxton et al. (2003) reported the usage of rhodamine. Another very promising fluorescent dye called brilliant sulphaflavine (BSF) was used by Sernek et al. (1999) to study the penetration of UF into beech plywood, two-layer parallel laminated wood, and solid wood. BSF reacts with basic amine groups and easily penetrates into tissue (Leemann and Ruch 1972), and therefore, the staining can be done after gluing wood particles (Riegler et al. 2012). Riegler et al. (2012) used the dye to stain particle board samples and single wood particles. Apart from conventional fluorescent microscopy as a technique for detecting UF resin, further methods for detecting UF adhesive in particle boards and fibreboards as well as on chips and fibres were confocal laser scanning microscopy (CSLM) (Loxton et al. 2003; Grigsby et al. 2005; Cyr et al. 2006), X-ray photoelectron spectroscopy (XPS) (Grigsby et al. 2004; Pakdel et al. 2008), microcomputed tomography (μ CT) (Walther et al. 2006; Evans et al. 2010; Standfest et al. 2010; Hass et al. 2012), scanning electron microscopy (SEM) (Wilson and Krahmer 1976; Thumm et al. 2001), and confocal Raman microscopy (Gierlinger et al. 2005).

Unlike fluorescence microscopy, most of the aforementioned methods either involve a considerable amount of experimental work and analysis or cannot achieve the desired resolution. Unfortunately, most of the reported staining methods with fluorescent dyes were carried out either by pre-staining resin before gluing particles or fibres or by staining single wood particles after gluing. So far, only boards made with pre-stained glue can be analysed. It was assumed that it is not possible to investigate an industrial lot made without pre-stained glue. This excludes the potential to apply the fluorescence method on many occasions when, for example, a lot is exceptionally good or bad. Staining resin under production conditions causes high costs because of the huge amount of resin that has to be stained. In addition to

the high staining costs, it leads to coloured boards which may be unacceptable to customers (Ginzel and Stegmann 1970).

Therefore, the aim of the present paper is to introduce a new method for detecting resin distribution in industrial particle board without the need for adding dyes prior to production.

Materials and methods

Sample preparation

The process from sample preparation to microscopy is illustrated in Fig. 1. Specimens were prepared from three-layer particle boards (PB) which were manufactured under laboratory conditions by Metadynea Austria GmbH, Krems, using commercial urea–formaldehyde adhesive. The amount of resin applied was 8 % in the core layer and 11% in the surface layer ([g] solid resin to [g] absolutely dry particles). The particle boards were pressed at a temperature of 220 °C and a pressure of 120 bar. Pressing time was 152 s for all boards. The boards of dimension 450 mm × 450 mm × 16 mm had a raw density of 650 kg/m³. Two different sample sets were produced with varying degree of condensation (DOC) and solid resin content (low DOC with high solid resin content and high DOC with low solid resin content). Specimens (app. 2 × 3 × 4 mm) were cut from the particle boards at

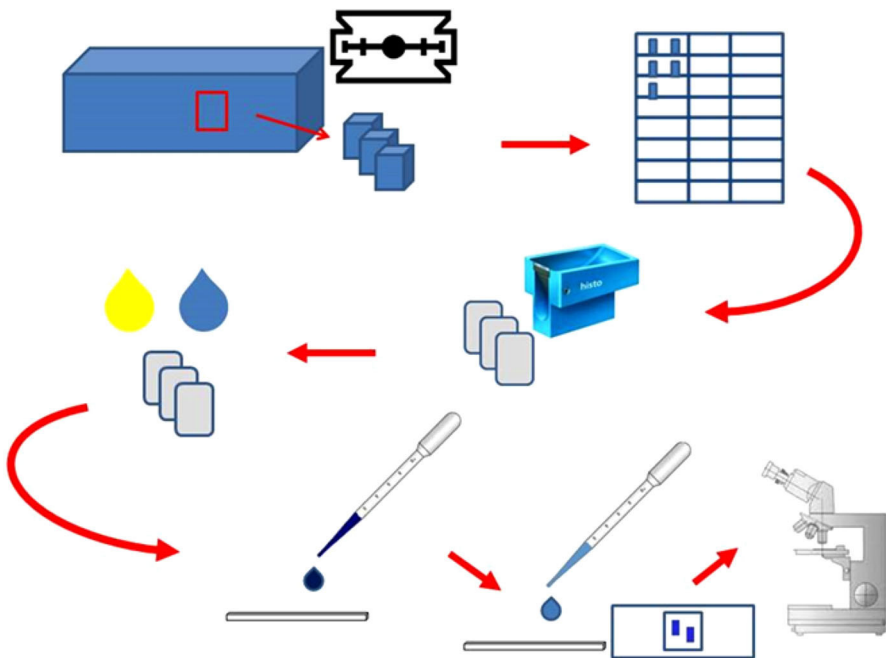


Fig. 1 Schematic process from sample preparation to light microscopy

different places in the core layer. All specimens were embedded in low-viscosity epoxy resin (Agar Scientific Ltd.) to prevent the samples both from rupturing during the cutting process and swelling during colouration. The resin was absorbed by the samples under vacuum and atmospheric pressure and was cured at 60 °C for 24 h. The epoxy matrix creates a stable object that could easily be cut into thin sections. An ultramicrotome (Leica Ultracut R) was used to cut 2- μm -thick sections of the specimens. After cutting thin sections, they were placed onto a 0.1 % solution of the fluorescent dye BSF, CAS registry number 2391-30-2. BSF was used for labelling the adhesive. After 1 min, the samples were removed and put into demineralised water for 10 min until the excessive dye was removed. Afterwards, the sections were placed between slide and cover slip. For staining the wooden parts of the section, a drop of gentian violet 0.2 % was placed on the outer edge of the cover slip for pulling the stain underneath the cover slip. Afterwards, the unnecessary dye was removed in the same way with demineralised water and subsequently dried.

Microscopy

After drying, images of the microsections were taken using the fluorescence microscope Zeiss Axioplan 2 Imaging equipped with an ultraviolet lamp FluoArc HBO 100, a halogen lamp HAL 100, and the object lens LD Epiplan 10 $\times$ /0.25 HD DIC M27. The halogen lamp HAL 100 for transmitted and incident light was used in transmitted light in this case. Additionally, for HBO 100, a 438-nm excitation filter and a 520-nm emission filter were used. When working with the microscope Axioplan 2 Imaging, it is required to switch between the two light channels because two distinct light sources are needed. A Zeiss AxioCam HRC was used to acquire images in brightfield and fluorescent light with a resolution of 0.943 $\mu\text{m}/\text{pixel}$. Several images were taken in a grid for each microsection in order to cover a large sample area. Visible light and fluorescence images (Fig. 2) from the same spot were matched and merged to one new image with image processing software (Photoshop

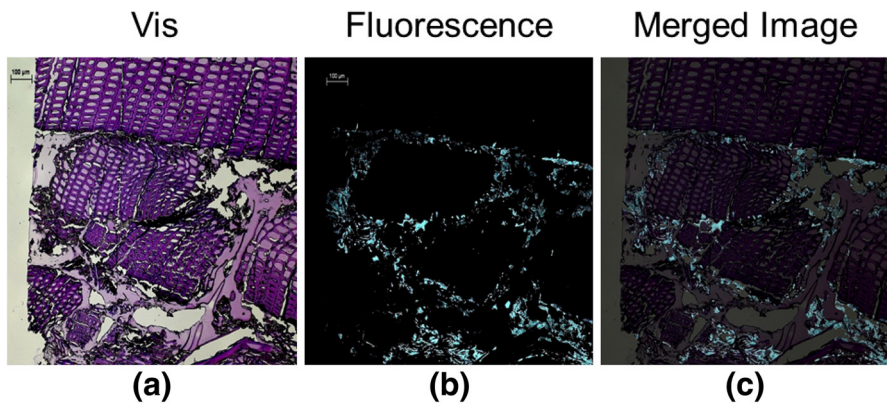


Fig. 2 **a** Cross-sectional image stained with gentian violet and taken under halogen light, **b** section stained with BSF and taken under fluorescence light, and **c** combination of the images a and b shows both wood and adhesive

CS3). In order to see both image aspects, the opacity of one of them was reduced. The merged images were then matched with respective neighbouring images from the grid in order to represent the whole microsection using the open source image processing software MosaicJ, a plugin from ImageJ (Fig. 3). The obtained cross-sectional images were further analysed using image processing software (Photoshop and ImageJ). In order to improve the contrast between wood particles and adhesive, respectively, and to decrease background fluorescence, a threshold was set in the Lab colour space at L 80/255, a 0/255 and b 0/255. A threshold setting is important in order to measure only adhesive without the bias of other image regions of variable brightness. All particle surfaces were contoured with a 1-pixel-wide line to designate the particle circumference, corresponding to the potential glueline. A 25- μm band following that surface line (12 μm in both directions including the 1- μm -wide line) (Fig. 4) was defined as covering the glueline region consisting of adhesive phase and wood–adhesive interphase. Adhesive occurring within this 25- μm -wide band around the circumference of particles was defined as pertaining to the glueline. Adhesive detected within the respective wood particle but outside the 25- μm band was defined as penetrated adhesive, and adhesive detected neither located inside wood particles nor within the 25- μm glueline band was defined as agglomerates (excess adhesive outside particles and gluelines, Fig. 5). Separate binary images of adhesive, inner areas of wood particles delimited by the glueline, and the 25- μm glueline itself were generated in Photoshop, quantified in ImageJ and adhesive classified according to Fig. 5. As an additional parameter, coverage is defined as the percentage of an individual wood particle circumference covered by adhesive.

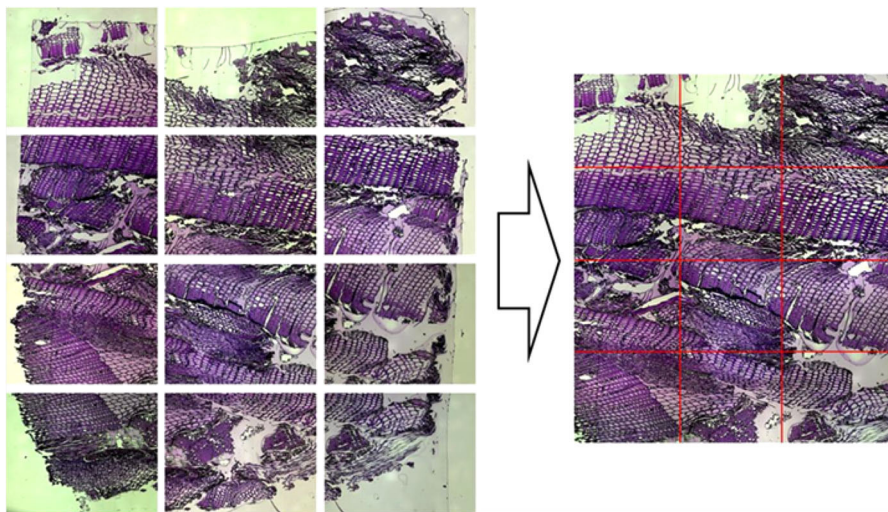


Fig. 3 Images taken in a grid and matched with neighbouring images in order to represent the whole microsection

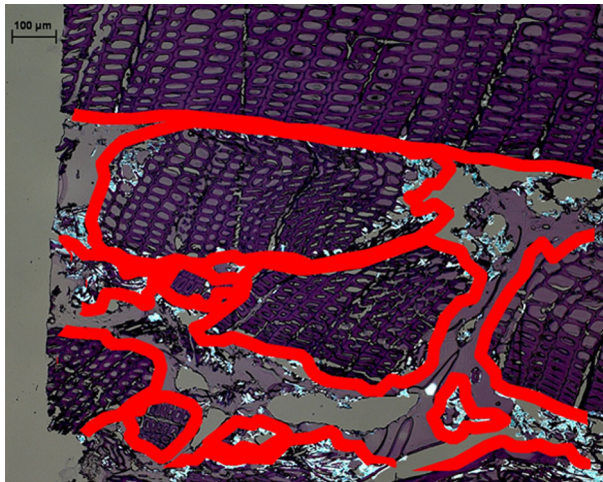


Fig. 4 Bondline region (25 μm width) of adhesive phase and wood–adhesive interphase

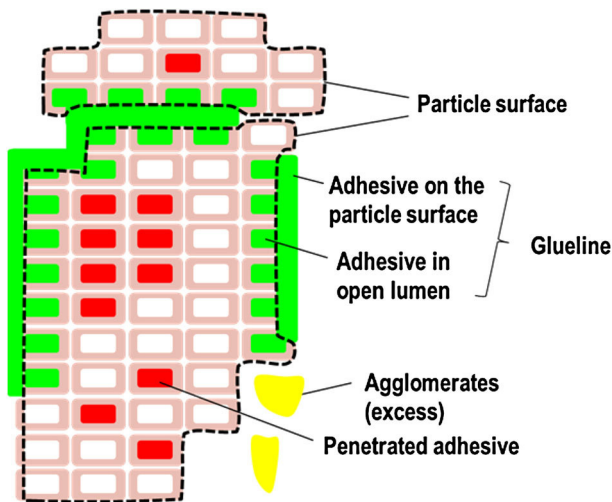


Fig. 5 Cross-sectional model of wood particles and how the adhesive could be arranged in, between, and around particles

Results and discussion

Figure 2a shows a microscope image of a thin section taken from an embedded particle board sample treated with BSF and gentian violet. Photographed under brightfield illumination, the adhesive appears lucent, whereas the wood shows a strong violet colour. Gentian violet is selectively bonded to wood components and suppresses fluorescence in stained cell walls. An image of the same section taken

under fluorescent light shows bright areas (Fig. 2b). These luminous regions represent the dye BSF, which is selectively bonded to amino groups in UF (Leemann and Ruch 1972). Under these conditions, no threshold settings would be necessary, the contrast in this detail is sufficient. However, especially in transition regions between wood and epoxy resin, a setting is recommendable, as some fluorescence of the epoxy resin occurs.

The combination of both images reveals both wood and adhesive (Fig. 2c). In this context, accuracy is important as both images need to be combined precisely. To obtain this, both image acquisitions should be taken consecutively without moving the image section as described above.

The first parameter evaluated is coverage, i.e. the average percentage of the circumference of all particles covered by adhesive (Fig. 6). Coverage can be interpreted as an indicator of how efficiently resin was spread over the surface of wood particles in the process. Only 5–15 % of the particle surface appears to be covered with resin based on these microscopic images. No significant difference between the coverage values calculated for both resins could be found (p value 0.71 in one-way ANOVA). Clearly, the difference in degree of condensation between the two resins used does not result in significantly different coverage values.

The size distribution of adhesive particles detected is a second parameter easily generated from the acquired data set. At a given resin loading, a high number of very small resin particles enable a more homogeneous distribution of adhesive throughout the board volume compared to a few large resin particles. Figure 7 shows resin particle size distribution for the two adhesives investigated in the present study. For practical purposes, the particles were assigned to size classes ranging from 25 up to 100.000 μm^2 . The low-condensation resin (UF1) exhibits a trend towards larger resin particle areas compared to high-condensation resin (UF2). However, with the exception of the size class around 10.000 μm^2 , differences are small.

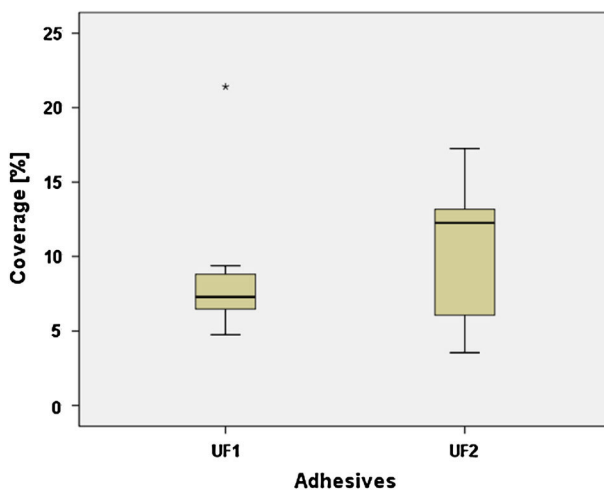


Fig. 6 Coverage of the particles with UF resin in the core layer of three-layer particle boards

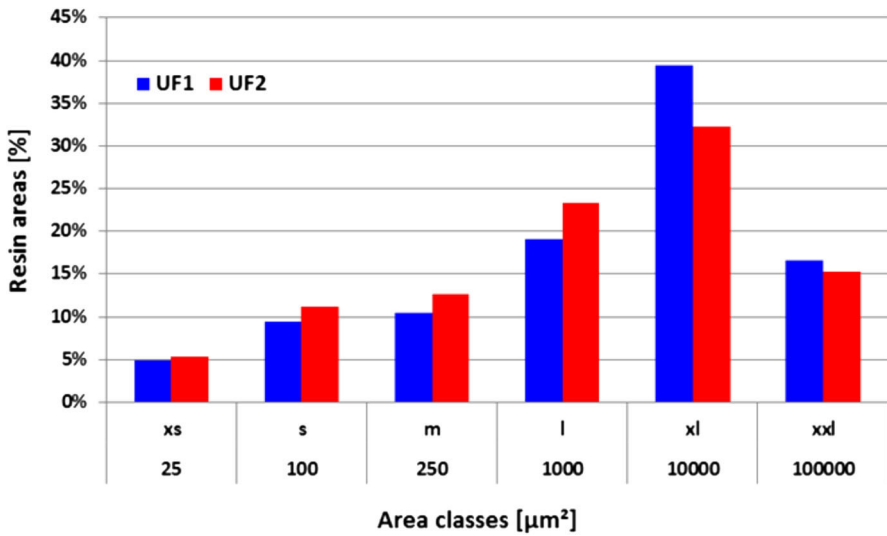


Fig. 7 Resin area classes in the core layer of three-layer particle boards

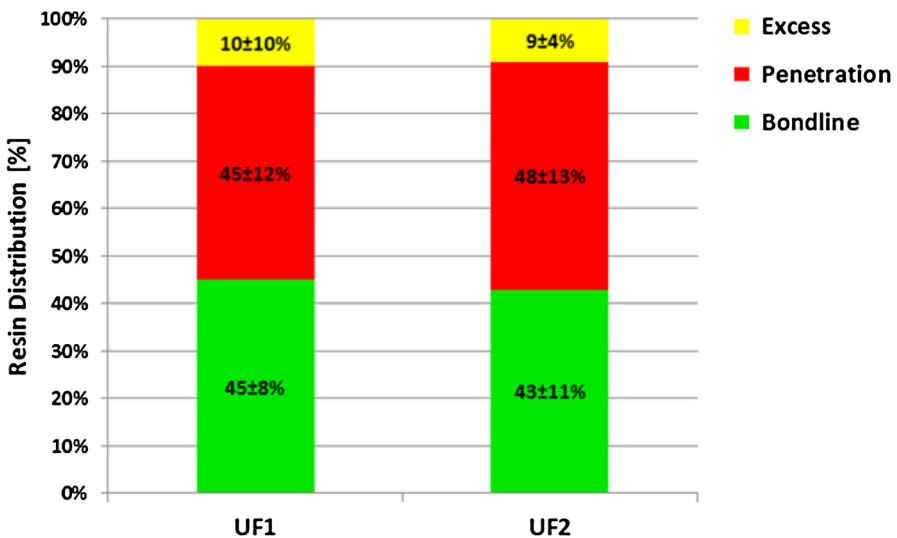


Fig. 8 UF resin distribution within the core layer of three-layer particle boards

Finally, the result of the assignment of adhesive to regions inside particles, inside the glueline, and agglomerates is shown in Fig. 8. Remarkably, only approximately 45 % of the adhesive detected with this method is associated with the glueline region, whereas another 45 % is penetrated into particles and roughly 10 % is found in agglomerates neither penetrated inside particles nor contributed to adhesive

bonding. Again, only slight differences far from statistical significance were observed for the resins studied here. This finding may be interpreted such that only half of the resin used in the boards produced here contributes to adhesive bonding, while the other half is not. However, it should be mentioned that adhesive penetrated deeply into wood particles may contribute to stabilising these particles against hygro-expansion and thus benefit the overall mechanical stability of the board.

Conclusion

The new method presented allows analysis of adhesive distribution in industrial boards without the need of adding any dye before production. The parameters evaluated may provide very useful information concerning the optimisation of adhesive bonding of particle board, in particular with regard to improving the amount of adhesive actually contributing to adhesive bonding in the glue-line, which was found to be surprisingly low at less than half the total amount of adhesive used.

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8.2 Paper II

Mahrtdt, E., Pinkl, S., Schmidberger, C., van Herwijnen, H.W.G., Veigel, S., Gindl-Altmutter, W. (2016) Effect of addition of microfibrillated cellulose to urea-formaldehyde on selected adhesive characteristics and distribution in particle board. *Cellulose* 23:571-80.

Effect of addition of microfibrillated cellulose to urea-formaldehyde on selected adhesive characteristics and distribution in particle board

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Abstract Several studies demonstrate that the addition of microfibrillated cellulose (MFC) to urea-formaldehyde (UF) wood adhesive improves the mechanical bond strength of wood particle board. In order to elucidate potential underlying mechanisms, the distribution of unmodified UF as well as MFC-modified UF (UF-MFC) in particle board was studied by means of light microscopy. The viscosity and cure characteristic of the adhesive systems were also characterised. UF-MFC showed high viscosity and shear thinning compared to UF. Both chemical and mechanical cure of adhesive were delayed in the presence of MFC. In UF-MFC, the size distribution of adhesive particles shifts towards larger particles compared to UF. More adhesive is directly available for adhesive bonding, and a larger part of the wood is covered with adhesive. This may be the cause for the better mechanical performance of particle board bonded with UF-MFC compared to UF.

Keywords Adhesive distribution · Microfibrillated cellulose · Particle board · Urea-formaldehyde wood adhesive

Introduction

By volume, particleboard is the most important product of the European wood-based panel industry. The standard binders used for this wood composite are aminoplastic adhesives on the basis of urea-formaldehyde (UF). The European production of amino resins was estimated to be 5.5×10^6 metric tons, of which about 95 % were used in particle board and MDF production (Diem et al. 2010). Urea-formaldehyde resins offer many advantages for industrial applications, such as high reactivity, ease of processing, and moderate cost (Dunky and Niemz 2002). On the downside, limited adhesive bond performance and post-production emission of potentially harmful formaldehyde require constant optimisation of this well-established adhesive system. Adhesive properties can be optimized in different ways depending on the application. The most obvious way is the modification of their chemistry. Another alternative approach to adhesive modification is the addition of fillers. Filler materials are non-volatile, non-gluing substances, which are insoluble in the adhesive. Common fillers are powders (cellulose, aluminium oxide, and silica), fibres (glass fibre, mica), sheet like materials (talc), and cubic materials (chalk, barytes) (Clauß et al.

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2011). Fillers enable to overcome limitations imposed by polymer chemistry. Especially in high performance adhesives nanoparticles or nanofibers from high strength materials are used to strengthen the material. For wood adhesives a number of studies exist in which particulate or fibrous fillers were used. Nanoclay-filled urea-formaldehyde showed positive results in a number of studies. In this case the addition of nanoclay reveals improved thermal stability (Zahedsheijani et al. 2012), increased water resistance and internal bonding of panels (Lei et al. 2008).

Another filler, similar to nanoclay is nano-SiO₂. This filler revealed performance improvements in the bonding of OSB-panels with urea-formaldehyde (Salari et al. 2013). In a different experiment nano-SiO₂ was used as a filler for MUPF-adhesive in the process of manufacturing water-resistant plywood. It was possible to optimize the process of gluing the sheets of veneer and to achieve a specific water-resistant level with a reduced amount of adhesive by 30 % (Dukarska and Czarnecki 2015). These improvements do not appear by using phenol-formaldehyde instead (Lei et al. 2010). Beside these rather new fillers the classic approach to improving adhesive performance is the addition of organic flours to urea-formaldehyde.

Recently it was shown that the addition of nanocellulose to wood adhesives may have significantly beneficial effects on their bond performance (Veigel et al. 2011, 2012; Kaboorani et al. 2012). In particular, brittle adhesive may benefit from the addition of MFC in terms of significantly improved toughness (Veigel et al. 2011, 2012). Due to its versatility and performance, offering a plethora of exciting application routes, nanocellulose has established itself as a major trend in cellulose research, as documented in recent reviews of the literature (Eichhorn et al. 2010; Klemm et al. 2011; Moon et al. 2011; Dufresne 2012; Liu et al. 2012; Kaboorani et al. 2012; Charreau et al. 2013; Salas et al. 2014; Wei et al. 2014; Jorfi and Foster 2015). The term nanocellulose comprises two variants of nano-scale cellulosic objects. i.e. microfibrillated cellulose (MFC) and cellulose nanocrystals (CNC). While MFC, cellulosic objects with typical diameters between 10 and 50 nm and length in the micrometer range, are usually obtained by purely mechanical processing of pulp, CNC production involves an additional acid hydrolysis step, where predominantly non-crystalline cellulose is removed, resulting in

comparably short, highly crystalline cellulose whiskers. While CNC production is still on the pilot scale, MFC availability will be greatly boosted by a recently announced production site in Norway (<http://www.borregaard.com/News/Borregaard-invests-NOK-225-million-in-a-production-facility-for-Exilva-microfibrillar-cellulose>). Therefore, also potential high-volume applications such as wood adhesive modification seem realistic using MFC.

Richter et al. (2009) used MFC for reinforcing one-component polyurethane, but their results remained not fully conclusive. In the case of polyurethane adhesive, surface hydrophobisation of MFC is necessary in order to provide surface chemical compatibility with the adhesive whereas aqueous MFC suspensions can be dispersed in aqueous adhesive systems such as UF. In the adhesive bonding of solid wood, it was demonstrated that an addition of 2 wt% MFC to UF may improve the specific fracture energy of adhesive bonds by up to 45 % compared to unmodified UF solid wood bonds (Veigel et al. 2011). Also in the bonding of wood composites, positive effects of MFC addition to aminoplastic adhesives were observed (Veigel et al. 2012). For both particle board and oriented strand board (OSB), significant positive effects of MFC addition on industrially relevant board properties, in particular internal bond strength, were observed. This is of particular interest, because improved adhesive performance could result in adhesive required, leading to significant cost reduction. Furthermore, a reduced amount of adhesive required—currently particleboard is typically produced with an adhesive content of 9 %—also directly translates to reduced formaldehyde emission.

Concerning the mechanism behind the positive effect observed for MFC addition to UF, one observation is that the overall deformability (i.e. strain to failure) and toughness of adhesive bonds increases upon MFC addition, which may be one cause for improved mechanical strength. Other potential effects, such as reduced shrinkage of UF upon cure due to the presence of MFC, analogous to a mechanism proposed for various nanogel-reinforced resin systems (Liu et al. 2012), or reduced microcracking, remain subject of speculation. Specifically in particle board, adhesive distribution is one of the critical parameters with regard to board performance (Riegler et al. 2012) and efficient use of adhesive. In particleboard, roughly only half of the adhesive used directly contributes to

particle–particle bonding, whereas the remainder penetrates into inner cavities of particle or forms individualised agglomerates (Mahrtdt et al. 2015). In the present study, we investigate potential effects of microfibrillated cellulose addition on the distribution of UF adhesive in particleboard, in order to further elucidate potential mechanisms behind the beneficial effects on board strength observed for MFC addition to UF. Furthermore, relevant adhesive properties such as viscosity and cure characteristics were also determined.

Materials and methods

Adhesive formulation and board preparation

The adhesive used in the present study was a commercially available UF adhesive (Primere, Metadynea GmbH, Krems, Austria) with a solid resin content of 65.5 %. This resin is a standard product widely applied in the particle board producing industry. MFC with the trade name Celish (grade KY100G) was purchased from Daicel Finechem Ltd. The product comes with a solid content of 10 %, has a fiber thickness between 1 and 0.01 μm and was used as received. For viscosity, DSC, and DMA experiments, MFC-modified UF was produced with a MFC content of 5 % (by weight of solid resin) by mixing with an Ultra-Turax device to achieve a homogeneous distribution of MFC in the UF matrix. Due to necessity of processing MFC in wet state, additional water was added to the formulation, which results in a final solid resin content of 53.5 %. In order to account for this fact, also the solid content of the unmodified reference-UF was adjusted to 53.5 % by diluting it with deionised water. Aqueous ammonium nitrate (60 wt%) was added as a hardener in a concentration of 3 wt% of solid UF-resin.

For the manufacture of one-layer particle boards, coarse softwood particles typically utilised in the core layer of industrial boards were provided by a particleboard mill. The particles, with typical length between 1 and 6 mm and thickness of 0.1–0.5 mm, were conditioned to a moisture content of 4.2 % and put into a ploughshare mixer (Gebrüder Lödige Maschinenbau GmbH, Paderborn), defined amounts of adhesive and subsequently MFC were added separately and mixed for 10 min in order to achieve

spreading of the adhesive onto the particle surfaces. Parallel trials with spray-application of adhesive yielded similar results. The target adhesive content was 7 % of cured UF resin based on oven-dry wood. The target MFC content was set to 5 % of the total mass of cured adhesive. The adhesive-coated particles were subsequently spread manually onto the press plate. Thereafter the press (LZT-OK by Langzauner GmbH, Lambrecht, Austria) was closed and the adhesive was cured at 220 °C and maximum pressure of 4 MPa for 140 s. During pressing, the final board thickness was set by means of 14 mm thick steel distance strips, i.e. pressing was done in distance-controlled mode rather than pressure-controlled mode. In total, 4 boards with a target density of 0.65 g cm^{-3} and dimensions of 500 × 430 × 14 mm were produced, i.e. two boards each with pure UF and MFC-modified UF.

Adhesive viscosity

Viscosity measurements of the two adhesive formulations used were performed on a Bohlin CVO Rheometer (Bohlin Instruments GmbH, Pforzheim, Germany) using the Bohlin Software. A cone/plate measuring geometry CP4/40 was selected consisting of a rotating upper cone with a diameter of 40 mm and a fixed lower plate 60 mm in diameter. The cone angle was 4° and the gap between cone and plate was 0.15 mm. A quantity of 1.3 mL of liquid adhesive was used and the measurements were run over a 180 s time span. The shear rates were between 0.1 and 200 s^{-1} recording a shear ramp. Three replicate measurements each were performed at 20 °C.

Adhesive cure

In order to study potential effects of MFC on adhesive cure, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) experiments mimicking cure conditions during hot-pressing were carried out. For DMA, 220 gm^{-2} adhesive was spread onto a strip of beech wood veneer with a length of 55 mm, a width of 10 mm, and a thickness of 1.1 mm and covered with a second strip of veneer of identical size. This sandwich was then mounted to the sample holder of a Netzsch DMA 242 C (Netzsch-Gerätebau GmbH, Germany). Three-point bending experiments at a free sample length of 40 mm between the supports

were performed with a constant heating rate of 10 K min^{-1} in the temperature range from 10 to 180°C . Samples were loaded with a static load of 0.5 N and then tested at a target amplitude of $30 \mu\text{m}$ with a frequency of 1 Hz. The oscillation amplitude was $30 \mu\text{m}$ for all specimens. During the experiment, the storage modulus E' of the sandwich increases in parallel to the progress of adhesive cure. Since E' is a measure of mechanical stability of the adhesive bond, the degree of mechanical cure (β) can be derived from such experiments by relating E' at a given temperature to the final maximum E' attained after complete cure. For a precise description of the method, the reader is referred to Wang et al. (2011).

For DSC measurements performed on a Netzsch DSC F3 Maia (NETZSCH-Gerätebau GmbH, Germany), again a sandwich set-up was chosen. This was deemed useful in order to account for a potential influence of woody substrate on cure kinetics e.g. due to pH of buffer capacity of wood. The adhesive was placed between two beech wood disks with a diameter of 3.5 mm and a thickness of $1.0 \pm 0.05 \text{ mm}$ prepared from the same piece of wood as the respective DMA sample, applying the same adhesive quantity. The resulting 3-layered specimen was then placed into a $30 \mu\text{L}$ gold-plated high-pressure steel crucible, sealed, and measured immediately. The same parameters for temperature range and heating rate as used for DMA were chosen. The progress of cure was evaluated from ratio between the reaction enthalpy released at a given temperature and the total reaction enthalpy released during the experiment. Since cure in the context of DSC relates to chemical reactions in the adhesive, it is termed chemical cure (α). Again the reader is referred to Wang et al. (2011) for more details.

Characterisation of boards

The density of the boards produced was determined according to the European standard EN 323 (1993). For each adhesive group 6–10 samples were tested. Internal bond strength, which is the inner strength of a board tested at an angle of 90° with respect to the plane of the board, was determined according to EN 319 (1993). A Zwick/Roell Z100 universal testing machine equipped with a 5 kN load cell was used for this purpose. For each group of specimens, mean values were calculated and compared by one-way analysis of variance (ANOVA, $p \leq 0.05$).

Concerning the analysis of adhesive distribution, the process from sample preparation to microscopy is illustrated in Fig. 1.

Sample preparation starts with the cutting of 8 small prisms of each adhesive group with dimensions between 1.5 and 2 mm from the core of the boards. These blocks were then impregnated with epoxy resin by means of repeated vacuum-pressure treatment. Sinking of the blocks into the liquid epoxy was taken as an indication of satisfying impregnation. After curing of the epoxy at 60°C , the blocks were trimmed and sectioned with a diamond knife mounted to an ultramicrotome. The thickness of the thin sections was set to $2 \mu\text{m}$. In order to provide contrast between cured adhesive, cell wall substance, and empty cavities, the sections were stained twice. Firstly, Brilliant Sulphaflavine, a yellow fluorescent dye which bonds selectively to basic amino-groups (Leemann and Ruch 1972), was used to stain the adhesive. Secondly, Gentian Violet was applied to stain cell wall material. Between and after the staining steps, the specimens were repeatedly washed with deionised water, and finally mounted to glass slides. With a fluorescence microscope (Zeiss Axioplan 2 Imaging) two images were taken at each selected position. One image was taken in incident light mode using an ultraviolet lamp Fluo Arc HBO 100 in order to capture fluorescence originating from stained adhesive. A 438 nm excitation filter and a 520 nm emission filter were used. A second image was then taken in transmitted light mode using a halogen lamp HAL 100. In this mode, image

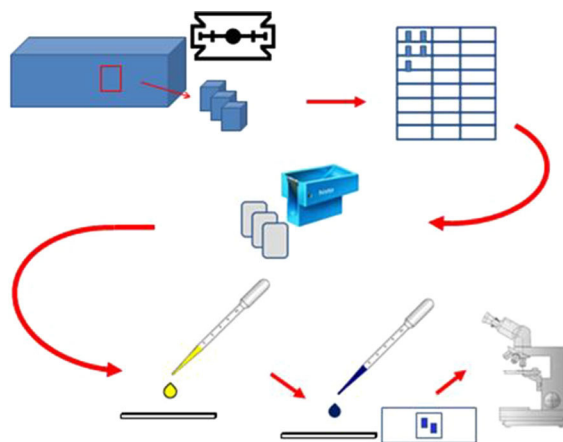


Fig. 1 Schematic process from sample preparation to light microscopy

contrast originates primarily from stained wood cell walls. All images were taken with a magnification factor of $100\times$ and a resolution of $0.943\ \mu\text{m}/\text{pixel}$. In order to cover a large representative sample area several overlapping images were taken. Prior to image analysis, visible light and fluorescence images from identical locations were matched and merged to one new image with image processing software (Photoshop CS3). The merged images were then matched with respective neighbouring images from the same grid in order to represent the whole micro section using the image processing software MosaicJ, a plug in from ImageJ. Further analysis was then done with Photoshop and ImageJ. Briefly, the sized and size distribution of adhesive particles was evaluated as well as the positioning of adhesive inside particles, at the interface between particles, or in disconnected agglomerations, respectively, was evaluated. The whole process was recently described in more detail by Mahrdt et al. (2015).

Results and discussion

Adhesive viscosity

As expected based on earlier studies (Veigel et al. 2012), the addition of MFC significantly changes the viscosity of UF adhesive (Fig. 2). While UF adjusted to the same water content as UF-MFC shows

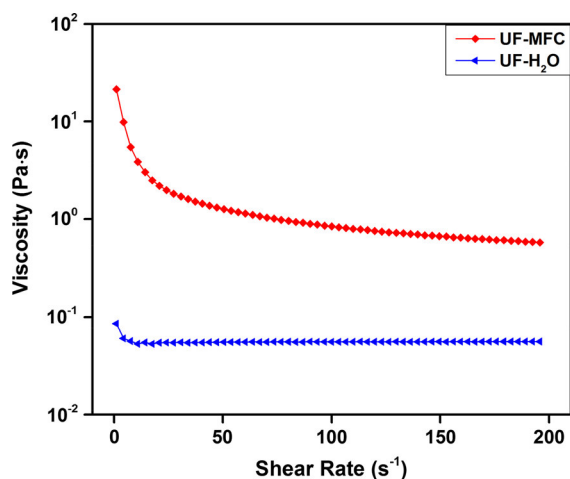


Fig. 2 Shear rate-viscosity curves with MFC-modified UF and diluted UF

essentially Newtonian behaviour, with a viscosity of $56\ \text{mPa}\ \text{s}^{-1}$ independently of the shear rate applied, UF-MFC exhibits very clear shear thinning. Starting with values up to $20\ \text{Pa}\ \text{s}$, viscosity rapidly decreases below $1\ \text{Pa}\ \text{s}$ at a shear rate $>80\ \text{s}^{-1}$. This behaviour is in good agreement with similar studies (Iotti et al. 2011; Puisto et al. 2012; Dimić-Mišić et al. 2013; Grüneberger et al. 2014). The high initial viscosity of UF-MFC is caused by the presence of a fibrillary network with substantial interfibrillar interaction. According to (Iotti et al. 2011), long and thin MFC fibrils are covered by hydroxyl groups that can take part in formation of temporary bonds between the fibrils. With increasing shear rate, shear thinning is observed as fibrils align in a reaction to the acting shear forces. For MFC suspensions in water, Iotti et al. 2011 also report a region of increasing viscosity, which was not observed in our experiment. Shear thinning may be beneficial to the processing of UF-MFC, as it can be pumped and sprayed onto wood particles without any adaptations to existing equipment.

Adhesive cure

The results of DMA and DSC experiments with wood-adhesive-wood sandwich specimens are summarised in Fig. 3.

As observed in literature (Wang et al. 2011), the formation of a polymer network (DSC signal termed chemical cure) precedes the build-up of mechanical adhesive strength (DMA signal termed mechanical

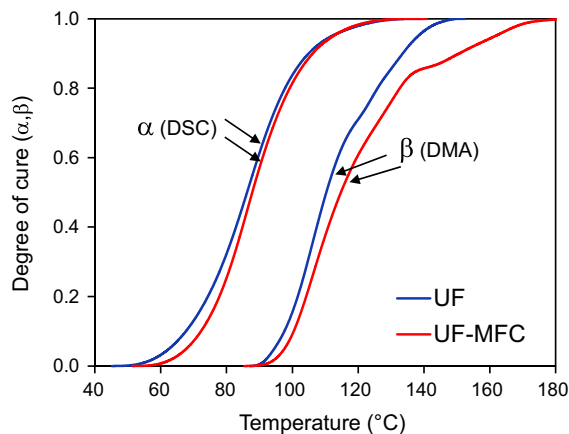


Fig. 3 Evolution of chemical cure (α) and mechanical cure (β) of UF and UF-MFC adhesive with increasing temperature

cure). An effect of MFC-addition to UF is clearly visible both with regard to the progress of the exothermal polycondensation reaction as measured by DSC, and also with regard to the increase in shear stiffness of the adhesive as measured by DMA. In both cases, UF-MFC lags behind UF (Fig. 3). One may speculate that the presence of MFC has a certain effect on cure kinetics. Adsorption onto the large surface that nanocellulose presents is related to highly localized intermolecular forces (Gardner et al. 2008). These forces could lead to temporary bonding of methylolated urea and UF oligomers at various stages of the polycondensation reaction. The reduced mobility of these molecules would then result in a lower reaction speed. Furthermore, as hydrophilic MFC prevents water from evaporating, the equilibrium reaction, generating water, may shift slower towards completion. However, such considerations are beyond the scope of the present study.

Technologically, any delay in adhesive cure is considered disadvantageous from a viewpoint focussed on productivity, as press cycles should be as short as possible in order to guarantee maximum throughput.

Mechanical board properties

In good agreement with the target density set to 0.65 g cm^{-3} , the average density of all boards prepared is $0.64 \pm 0.02 \text{ g cm}^{-3}$. Statistical analysis by means of one-way Anova indicates no difference in board density between reference boards bonded with pure UF and boards bonded with MFC-modified UF (Fig. 4).

Because of the strong effect of density on many board properties, particularly internal bond strength, it is an essential prerequisite for further analysis that there is no statistical difference in density between the two groups of boards studied. Internal bond strength (Fig. 4) of the MFC-modified boards shows about 30 % higher average values ($0.63 \pm 0.07 \text{ MPa}$) than the reference boards ($0.47 \pm 0.1 \text{ MPa}$). These results are in good agreement with already published results for wood composites (Veigel et al. 2012), which also revealed an improvement of internal bond strength when MFC-modified UF was used. Since density of the two groups of boards is not significantly different, other effects than variations in density must be investigated in order to reveal the cause behind the

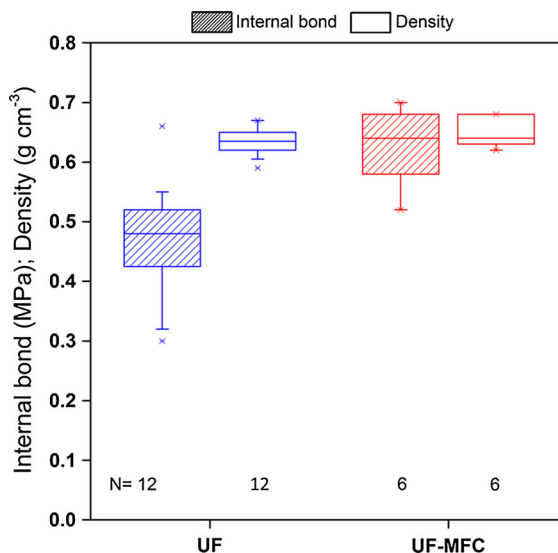


Fig. 4 Mechanical properties: internal bond and density

observed clear difference in board mechanics. The following analysis of adhesive distribution may contribute to elucidating these causes.

Adhesive distribution

Figure 5 shows typical microscope images of adhesive distribution in boards bonded with reference UF compared to boards bonded with MFC-modified UF. These images were obtained by merging two pictures taken in visible light and fluorescent mode, respectively. The yellowish background in all images originates from the epoxy resin used for embedding prior to thin-sectioning. UF adhesive shows bright greenish-light blue fluorescence and can thus be easily discerned from the intensely violet stained cell wall material.

The first parameter evaluated quantitatively from such images is the size distribution of adhesive particles. This parameter implies that a high number of very small resin particles enable a more homogeneous distribution of adhesive throughout the board volume than few large resin particles.

As shown in Fig. 6, the size distribution is clearly different for the two groups of boards investigated. In the reference boards, the distribution of particle sizes is rather even across all size classes defined. In comparison, a clear trend towards larger particles is evident for MFC-modified UF. Notably, small size

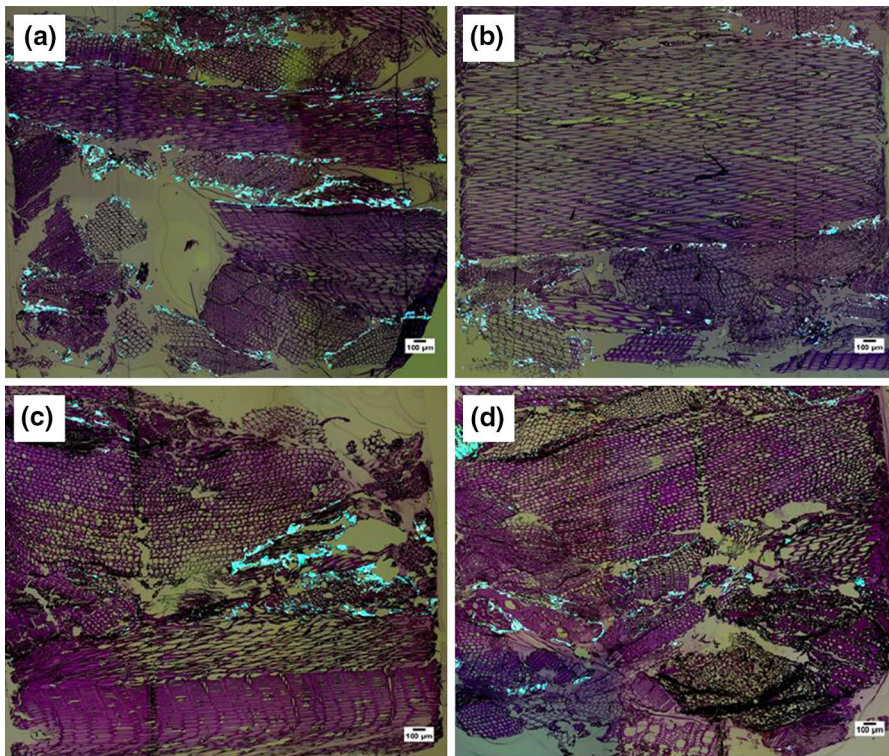


Fig. 5 Microscope images of adhesive distribution in boards bonded with reference UF (a, b) and with MFC-modified UF (c, d)

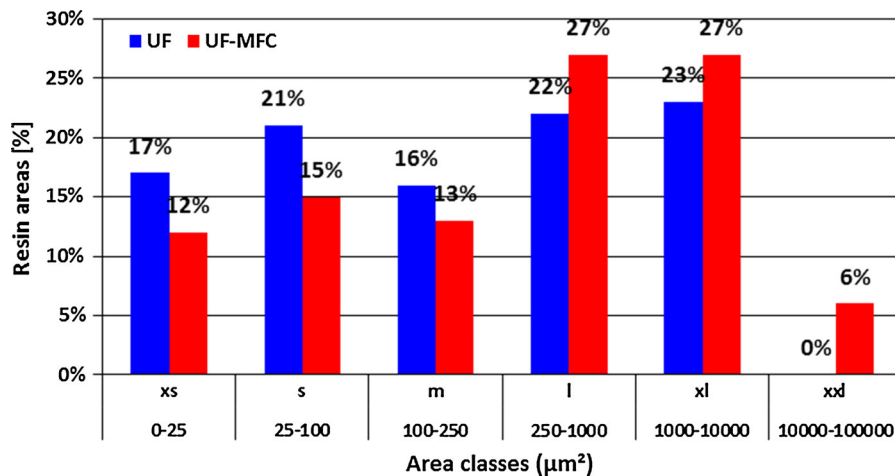


Fig. 6 Resin area classes of one-layer lab scale particleboards (12 microscope images were evaluated)

classes of $250 \mu\text{m}^2$ and smaller decrease, whereas larger size classes increase in frequency, which contradicts our assumption that a more homogeneous adhesive distribution in terms of numerous small particles instead of a smaller number of bigger particles may be favourable to internal bond strength.

On the contrary, an increase in the frequency of large particles correlates with an increase in bond strength in the present set of specimens.

However, not only the frequency of resin spots but also their location is of importance. Therefore we also investigated the coverage, i.e. the average percentage

of the circumference of all wood particles covered by adhesive (Fig. 7). In case of MFC-modified UF, a significantly larger part of the wood surface is covered by adhesive.

This is supported by the third parameter evaluated from 12 microscope images acquired, which refers to the assignment of adhesive to defined areas inside particles, at the interface between particles (i.e. actual adhesive bond line), or in disconnected agglomerations (Fig. 8).

In the reference boards bonded with unmodified UF, roughly 40 % of the adhesive is directly located in adhesive bond lines between neighbouring wood particles and thus provides mechanical strength to the composite. A surprisingly large fraction of 35 % of the adhesive is found within inner cavities of wood particles and thus does not directly contribute to adhesive bonding. However, this fraction of adhesive is probably not without use in the whole composite, since it somewhat stabilises the particles with regard to dimensional changes due to hygroexpansion (Frihart 2009). Finally, more than 20 % of the adhesive was found in disconnected agglomerations which apparently do not contribute to adhesive bonding. By comparison, UF-modification with MFC significantly changes the distribution of adhesive. Significant differences exist between the two groups regarding agglomerations (p value 0.008) and bond line adhesive (p value 0.034) in T Test. The fraction of adhesive directly contributing to particle–particle bonds increases to more than 50 % at the expense of disconnected agglomerations of adhesive, which are

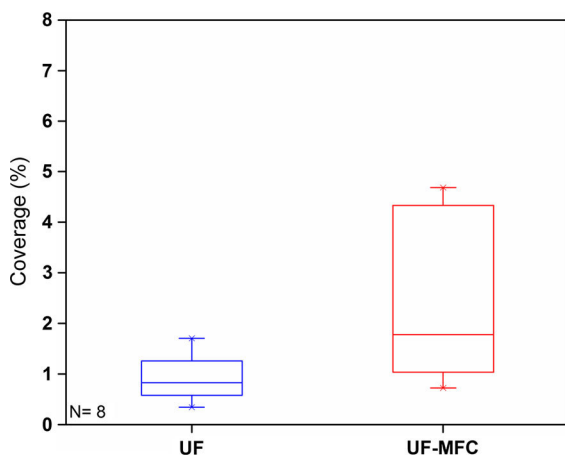


Fig. 7 Part of wooden particles covered with adhesive

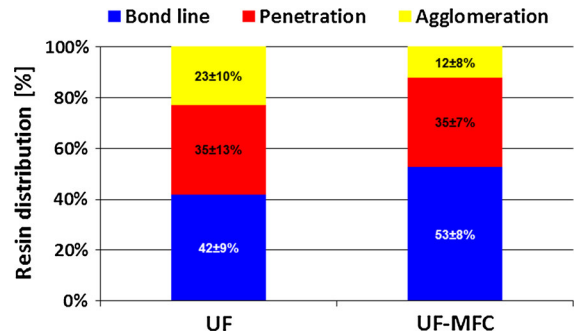


Fig. 8 UF resin distribution within one-layer lab scale particleboards (average values and standard deviations are given)

reduced to half the value found in the reference. With 35 % the fraction of adhesive penetrated into wood particle cavities remains unchanged.

Thus the change in adhesive distribution observed upon MFC addition is most probably attributed to a change in viscosity and the ability of MFC to bond water to its high specific surface. Increased adhesive viscosity may well explain the higher fraction of adhesive in the bondline and the trend towards larger adhesive particle size upon MFC addition. However, we have no explanation for the reduced fraction in agglomeration of UF-MFC. With regard to the improvement in board mechanics, it is proposed that this change in adhesive distribution exerts a positive influence and reinforces the already known effect of toughness improvement of UF modified with MFC (Veigel et al. 2011, 2012).

Conclusions

In summary, the results presented above show that MFC-modified UF is more viscous than unmodified UF, and adhesive cure is delayed by the presence of MFC. We conclude from the results of adhesive distribution characterisation that the interaction of UF with MFC leads to a shift in the size distribution of adhesive particles towards larger particles in UF-MFC compared to UF. A higher fraction of adhesive is available for bond-line formation and a larger part of the wooden particles is covered with adhesive. Changed adhesive distribution together with improved adhesive toughness are proposed to contribute to improved board strength.

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8.3 Paper III

Mahrtdt, E., van Herwijnen, H. W. G., Kantner, W., Moser, J., Giesswein, J., Mitter, R., Gindl-Altmutter, W. (2016) Adhesive distribution related to mechanical performance of high density wood fibre board. *International Journal of Adhesion and Adhesives*, in review

Adhesive distribution related to mechanical performance of high density wood fibre board

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Abstract

In a full-scale mill experiment two groups of high density wood fibre boards were produced. While one group was bonded with a standard melamine-urea-formaldehyde adhesive, a second group was bonded with a modified adhesive yielding systematically improved board properties at identical amounts of adhesive applied. By means of a fluorescence-microscopic method using the dye Acriflavine, adhesive distribution within the boards was evaluated and quantified. Very clear differences in the size distribution of the two adhesives were found, leading to the conclusion that a relationship exists between adhesive distribution and mechanical board performance.

1. Introduction

The disintegration of wood into particles and fibres, followed by re-assembly and adhesive bonding, leads to wood composite products with high structural homogeneity, dimensional stability, and standardised processing characteristics within very narrow limits of variability. Besides the nature of wood particles or fibres used, and processing parameters such as assembly, pressure and duration of hot-pressing, the type of adhesive applied plays a crucial role in the economic production and the technological performance of wood composite panels. Wood fibre boards may be produced with very little or no adhesive, relying on

intrinsic fibre-fibre bonds built-up in wet processing. However, modern state of the art wood fibre panels such as medium density fibre board (MDF) or high density fibre board (HDF) rely on efficient adhesive bonding. Besides a minor fraction of phenolic adhesive bonded boards, amino resins are the adhesive of choice due to its highly competitive price, high reactivity, and good bonding performance. Since the amount of adhesive spent contributes significantly to the overall product cost, any optimisation of adhesive use is welcome. In order to do so, the relationships between adhesive mechanics, interfacial adhesive-wood fibre interactions, and adhesive distribution on the one hand, and fibre board performance on the other hand need to be studied. With regard to adhesive distribution in UF-bonded boards, the lack of natural colour contrast between UF and wood poses a challenge for microscopic studies.

X-ray photoelectron spectroscopy (XPS) technique was used for high resolution imaging of elemental concentrations [1, 2]. For comparison, the same authors used confocal laser scanning microscopy (CSLM) for adhesive detection. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) was used in combination with energy-dispersive X-ray spectroscopy (EDXS) [3, 4]. Thumm et al. [5] used scanning electron microscopy (SEM) to investigate the penetration of urea melamine formaldehyde adhesive in wood fibres. With the same intention Cyr et al [6] used CLSM. Various researchers reported the adhesive coverage ratio of MDF fibres by using CLSM and fluorescence labelling [5, 7-13]. Electron energy loss spectroscopy (EELS) in combination with transmission electron microscopy (TEM) was used to determine the distribution of melamine-formaldehyde adhesive in wooden cell walls [14]. Gierlinger et al. [15] studied the melamine-formaldehyde adhesive content within cell walls of impregnated spruce wood by using UV microscopy and confocal Raman microscopy. UV microscopy was also used by Gindl et al. [16, 17]. Finally, UF resin distribution in wood composites has also been determined by light and fluorescence microscopy [8, 18-20].

In the present study we show that a new method involving a combination of fluorescent and Vis stains recently applied with success to UF-bonded particle board [19, 20], is capable of delivering valid information on adhesive distribution in HDF board. Furthermore, adhesive distribution data will be discussed with respect to potential relationships with mechanical board performance.

2. Experimental details

HDF boards were produced under exactly the same conditions in a full-scale mill trial using a standard melamine-reinforced UF (mUF) termed adhesive (A), and a modified optimised mUF termed adhesive (B). The viscosity of both adhesives (A) and (B) was the same. The resin loading in the HDF boards was set in the common industrial range of 10-13% solid resin on dry wood, and was equal for boards produced with (A) and (B).

Mechanical characterisation was carried out in three-point bending according to EN 310.. Internal bond strength was evaluated according to EN 319. and thickness swelling after 24h immersion in water was measured according to EN 317. Overall, 78 reference specimens (adhesive mUF A) and 100 modified specimens (adhesive mUF B) were tested.

The sample preparation for microscopic analysis of adhesive distribution described in Fig. 1 starts with cutting 8 small prisms with an edge length of 3 mm from the core of boards of each adhesive group. These blocks were then impregnated with epoxy resin after all air was removed during a vacuum step. After curing the epoxy at 60°C the blocks were trimmed and sectioned with an ultramicrotome equipped with a diamond knife. The thickness of the thin sections was set to 2 μm . For a better contrast between adhesive and fibres the sections were stained twice. Firstly, Acriflavine, an orange fluorescent dye, was used to stain the adhesive. Secondly, Gentian Violet was applied to stain cell wall material. Between and after the staining steps, the specimens were repeatedly washed with deionised water, and finally mounted to glass slides. With a fluorescence microscope (Zeiss Axioplane 2 Imaging) images were taken in incident light mode using an ultraviolet lamp Fluo Arc HBO 300 in order to capture fluorescent areas originating from stained adhesive. A 450-490 nm excitation filter and a 515 nm emission filter were used. All images were taken with a magnification factor of 200x and a resolution of 0.528 $\mu\text{m}/\text{pixel}$. In order to cover a large sample area several overlapping images were taken. The images were matched with correspondent neighbouring images using the image processing software MosaicJ, a plug in from ImageJ. Further analysis was done with Photoshop and ImageJ. In order to improve the contrast between wood fibres and adhesive, respectively, and to decrease background fluorescence a threshold was set in the Lab colour space at L 110/255, a 0/255 and b 0/255. With binary images it was possible to quantify the size and size distribution of adhesive areas within the HDF boards.

3. Results and discussion

3.1. Mechanical board properties

A summary of the most relevant physical parameters characterised is given in Table 1. Since typically, board properties vary significantly with density [21, 22], comparable density is prerequisite when possible causes for mechanical variability of boards are being discussed. In case of the two variants of HDF examined in the present study, no statistically significant difference in density was observed, with an average density of 0.90 g cm^{-3} for both variants. Despite roughly identical densities, mechanical board properties varied significantly. Consistently, improved performance was observed for the variant bonded with modified mUF adhesive, compared to the unmodified reference. While the trends towards improved properties in 3-point bending are not significant in a statistical sense, a very clear and highly significant improvement in internal bond strength of 15 % on average was seen (Fig. 2). In parallel, a 7 % reduction of thickness swelling after 24 h immersion in water was measured. Since identical amounts of adhesive were applied and no differences in density were found, an examination of adhesive distribution may help to identify possible causes for the variability in physical properties observed.

3.2. Adhesive distribution

Representative images captured in Vis and fluorescence mode demonstrate the very significant improvement in optical contrast between wood and adhesive achieved by means of fluorescence staining. In Vis mode (Fig. 3a) the general structure of HDF board, consisting of individualised fibres and fibre-bundles, is easily discernible due the very efficient staining of wood cell walls by means of Gentian violet. However, even at close inspection, adhesive cannot be easily identified in Vis mode due to lack of contrast. When switching to fluorescence mode in the same specimen region (Fig. 3b), cell walls appear in bright red, whereas small spots of adhesive may be easily discerned due to their greenish fluorescence. At higher magnification (Fig. 3c-d), adhesive is predominantly found in inter-fibre spaces, whereas internal fibre cavities (lumina) appear mostly free of adhesive. Notably, inter-fibre cell-corner regions often appear to be filled with adhesive. Overall, individual disconnected adhesive spots are more numerous compared to larger interconnected adhesive areas. Clear

adhesive bond lines between fibres are sparse as opposed to more frequent local adhesive particles bridging fibre-fibre gaps.

Microscope images taken at the same staining and illumination as Fig. 3, but at lower magnification, are shown for both HDF variants in Fig. 4. Even upon only superficial observation, a very clear optical difference in the pattern of adhesive distribution between the two variants is obvious. While numerous comparably small adhesive spots predominate in the board bonded with unmodified adhesive, significantly larger interconnected adhesive regions and larger individual spots are apparent with the modified adhesive. Due to the excellent colour contrast between wood cell walls, adhesive spots, and empty cavities, images as shown in Fig. 4 can be easily converted to binary images showing adhesive in white and non-adhesive regions (i.e. cell walls and empty cavities) in black (Fig. 5). From these binary images, the size of individual adhesive spots can be determined by straightforward image analysis. A representative result of this analysis is given in Fig. 6. Overall, adhesive spots with cross-sectional sizes between $1 \mu\text{m}^2$ up to $8000 \mu\text{m}^2$ were detected. The arithmetic mean of adhesive spot cross sectional area was $4.19 \mu\text{m}^2$ for the reference board and $10.36 \mu\text{m}^2$ for the board bonded with modified adhesive. As seen in Fig. 6, the shape of the adhesive spot size distribution curve is similar for both types of adhesive employed, with the notable difference of a clear shift towards larger adhesive spots in the modified variant.

In summary, improved bond performance in the modified HDF board coincides with a trend towards larger adhesive spots compared to the unmodified reference. Since identical wood material was used, processing conditions were the same, adhesive spreading rate was the same, and comparable board density was achieved, it is apposite to look into the adhesive as such with regard to identifying the cause for the differences in board performance observed. Studies found in literature give somewhat contradicting information on potential relationships between adhesive distribution in wood composites and mechanical board performance. Seminal studies by Loxton et al. [10] and Grigsby et al. [12] imply that a high number of small resin particles allows for a more homogeneous distribution throughout the board volume and greater proportions of smaller resin particle sizes were deemed beneficial for mechanical board properties. On the contrary, a recent study with urea-formaldehyde adhesion showed that the addition of nanocellulose to the liquid adhesive resulted in clearly larger adhesive spots in wood particle board produced with this adhesive in parallel to very significantly improved board mechanics [20]. In the present study, the latter observation is confirmed, hinting at a complex relationship between adhesive distribution and board mechanics. The predominance of larger adhesive spots in the better-performing variant could

be interpreted in a way that fewer well-bonded board areas provide a more significant contribution to board strength compared to more numerous but small adhesive spots, which – individually - provide comparably weak fibre-fibre linkages. However, no direct proof for this assumption can be provided yet.

4. Conclusion

A new approach to the elucidation of adhesive distribution in wood composites developed with particle board was successfully applied to high density fibre board. Clear differences in adhesive distribution were identified, which coincide with differences in physical board performance. Adhesive modification resulted in larger average adhesive particles and improved physical performance. This leads to the conclusion that the size distribution of adhesive spots within wood composites plays a crucial role with regard to the mechanical performance of the composite.

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Table 1 – Comparison of important physical characteristics of HDF boards bonded with two different mUF resins (average values and standard deviation are shown, 80 specimens each were tested)

Adhesive type	Density (g cm ⁻³)	Flexural strength (MPa)	Flexural modulus (GPa)	Internal bond strength (MPa)	24h thickness swelling (%)
mUF A	0.90 +/- 0.009	50 +/- 1.7	4.9 +/- 0.18	1.69 +/- 0.070	10.4 +/- 0.26
mUF B	0.90 +/- 0.009	52 +/- 1.5	5.1 +/- 0.21	1.94 +/- 1.127	9.7 +/- 0.30

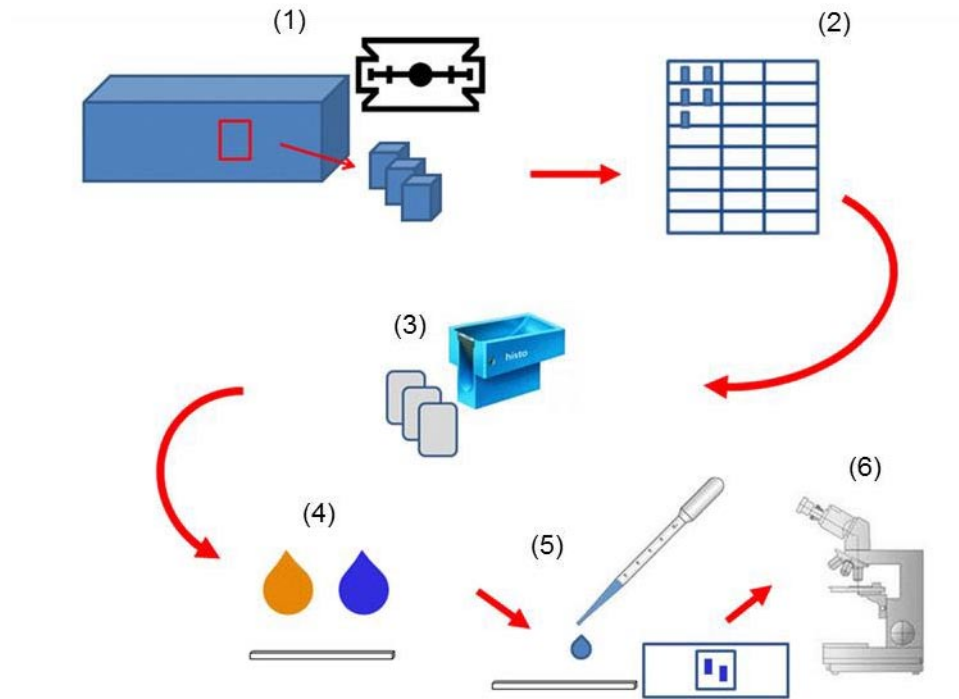


Fig. 1 Schematic of the sample preparation process. Small cubes are prepared from the HDF boards (1), embedded in epoxy resin (2) and cut into thin sections (3). The thin sections are deposited onto glass slides where they are stained (4) and washed (5), before being observed in the light microscope (6).

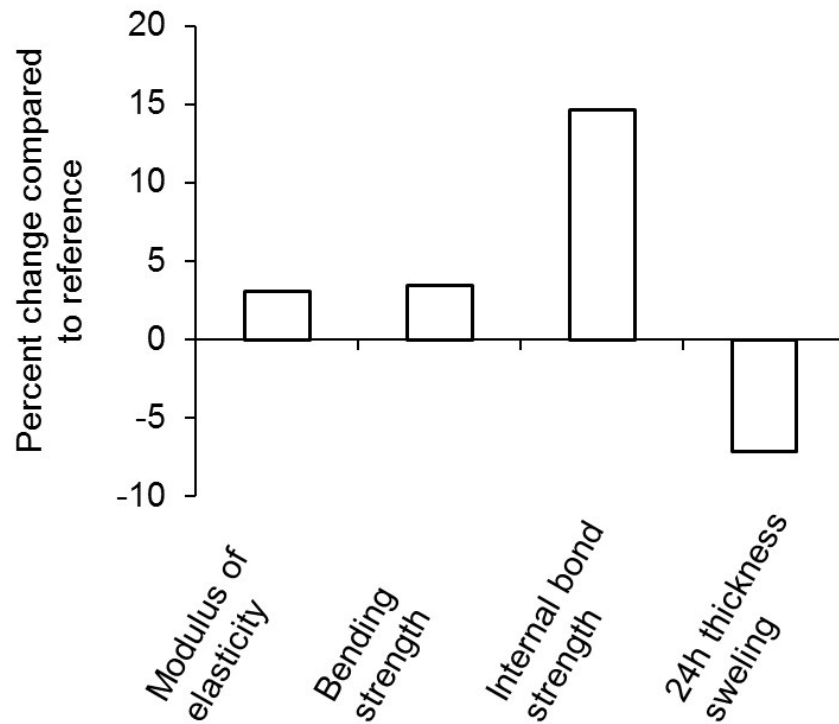


Fig. 2 Differences in physical board properties between boards bonded with unmodified reference adhesive compared to boards bonded with modified adhesive. The values shown were calculated by setting the performance of the reference boards to 100%.

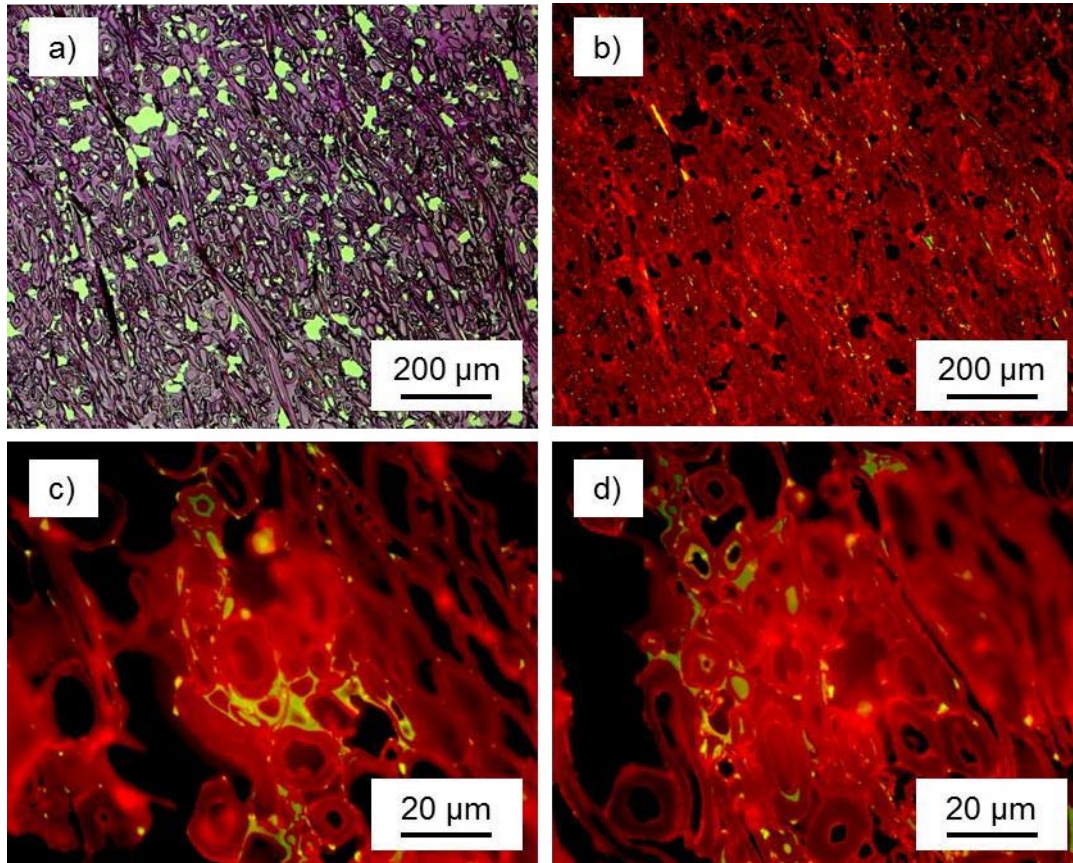


Fig. 3 Representative microscope images of adhesive distribution in HDF board in Vis (a) and fluorescence (b-d) modes, respectively. In Vis mode, wood cell walls appear in violet colour. In fluorescence mode, cell walls are stained in bright red, whereas adhesive shows greenish fluorescence.

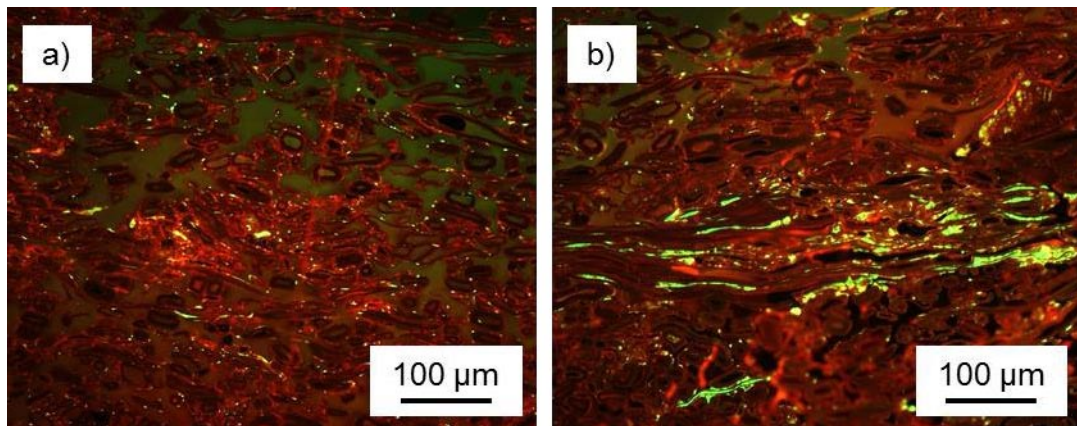


Fig. 4 Representative images of adhesive distribution in a board bonded with reference adhesive (a) compared to an image from a board bonded with improved modified adhesive (b).

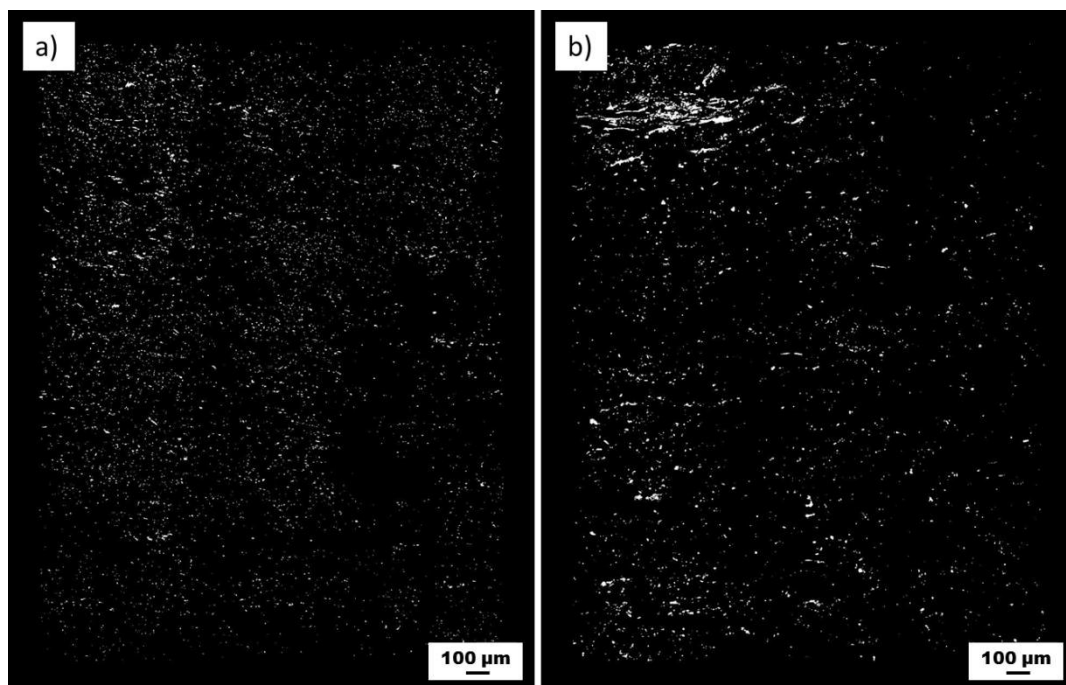


Fig. 5 Representative composite images of adhesive distribution across an area of 2.25 x 3.0 mm from a board bonded with reference adhesive (a) compared to an image from a board bonded with improved modified adhesive (b).

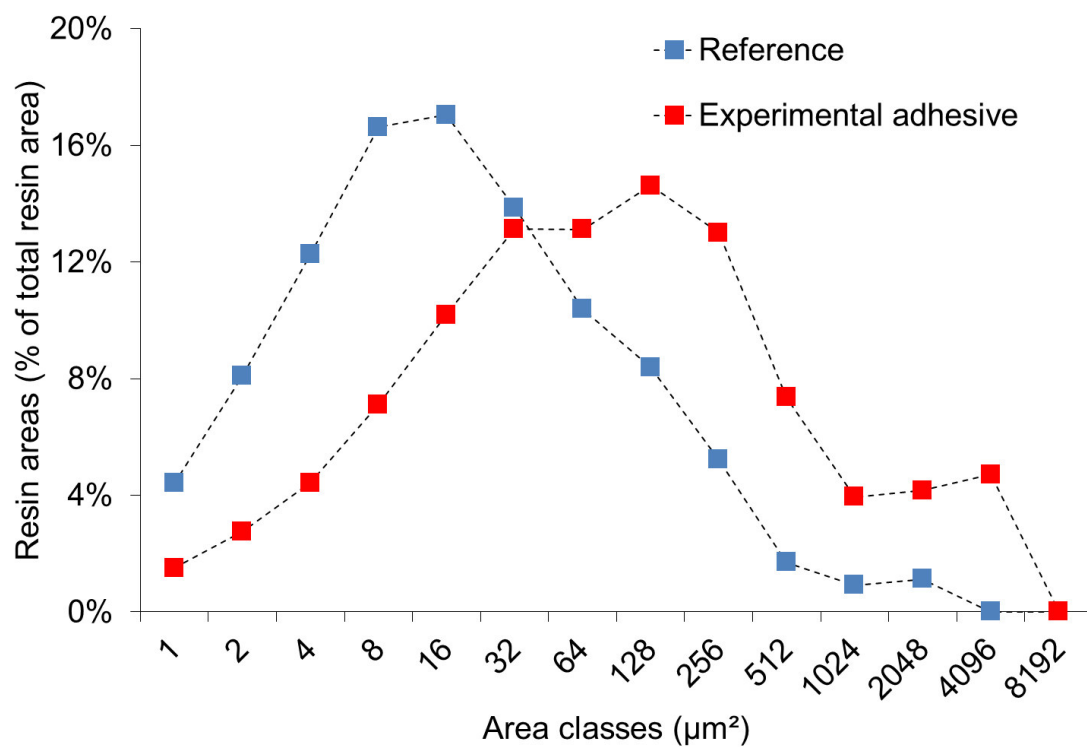


Fig. 6 Frequency distribution of adhesive spots of different size classes detected in the HDF boards investigated.