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Failure mechanisms in wood joints bonded with urea-formaldehyde adhesives

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Wood joints bonded with urea-formaldehyde (UF) are weakened by cyclic swelling and shrinking. To study the failure mechanisms in UF-bonded joints, specimens were bonded with unmodified, modified (amine), or phenol formaldehyde adhesive and subjected to accelerated aging. Modification of the adhesive properties increased the cleavage fracture toughness and shear strength of bonded joints and improved the resistance of joints to cyclic swell-shrink treatment and accelerated moist-heat aging. Joints bonded with some modified urea-formaldehyde adhesives were as resistant to these treatments as joints bonded with phenol formaldehyde. Physical and mechanical origins of the improved adhesive performance were determined by microscopic analysis. Cure-shrinkage stresses precracked unmodified adhesive layers and damaged the wood interphase. The damaged interphase was especially susceptible to the effects of cyclic swelling and shrinking stresses. Certain modifiers reduced or eliminated cure-shrinkage cracking and damage to the wood. Moist-heat aging caused molecular scission in the bulk unmodified adhesive layer as revealed by the onset of shear cracking in the adhesive layer and erosion of exposed surfaces. Certain modifiers reduced or eliminated molecular scission and erosion responsible for adhesive weakening in moist-heat aging. We conclude that incorporating flexible amines in the adhesive structure improves the durability and stability of UF-bonded joints.

Bruchmechanismus von Holz-Leim-Verbindungen auf der Basis von Harstoff-Formaldehyd-Harzen

Holz-Leim-Verbindungen auf der Basis von UF-Harzen verlieren an Festigkeit durch zyklisches Quellen und Schwinden. Zur Untersuchung des Bruchmechanismus wurden Proben mit unmodifizierten und modifizierten Harzen (Amin oder Phenol) verleimt und einer beschleunigten Alterung unterzogen. Die Modifizierung der Leimeigenschaften erhöhte die Bruchzähigkeit und die Scherfestigkeit der Leimverbindungen und erhöhte die Beständigkeit gegenüber der zyklischen Quell- und Schwinde-Behandlung sowie der Feuchte-Hitze-Alterung. Einige der modifizierten Leime erreichten die Festigkeit von Phenol-Formaldehyd-Verleimungen. Der Mechanismus der Rißbildung wurde im Rasterelektronenmikroskop verfolgt. Zunächst entstehen beim Aushärten Schwindungsrisse innerhalb der Leimschicht bei unmodifizierten Harzen. Diese Risse schädigen auch die Holz-Leim-Verbindung. Danach ist die Leim-Holz-Verbindung besonders anfällig gegenüber Quellungs- und Schwindungsbeanspruchung. Einige Leimzusätze reduzieren oder verhindern die Entstehung dieser Schwindungsrisse, die zu vermehrten Scherbrüchen führen sowie zur Erosion der freigelegten Bruchflächen. Einige Leimzusätze verhinderten diese Spaltungen der Leimschicht, welche für die Beständigkeit gegenüber der Feuchte-Hitze-Alterung verantwortlich sind. Daraus wird geschlossen, daß der Einbau von Aminen in die Leimstruktur die Stabilität und Dauerhaftigkeit von Harnstoff-Formaldehyd-Verbindungen erhöht.

1
Introduction

The poor durability of urea-formaldehyde (UF) bonded wood joints is attributable to hydrolytic degradation and cyclic swell-shrink stress-rupture of the joint. Previously, we demonstrated that resistance to these types of degradation can be greatly improved by the incorporation of flexible di- and tri-functional amines into the adhesive (Ebewele et al. 1991a,b; 1993a,b). Our hypothesis was that the flexible amines would interfere with the formation of hydrogen bonds and distribute flexible crosslinking uniformly in the cure. These changes should reduce shrinkage during cure and render a tougher and more flexible adhesive layer. The cured adhesive should also be more soluble in and more plasticized by moisture and thus better able to accommodate stresses caused by swelling and shrinking of the wood adherends. Reduction of hydrogen bonding and improvements in crosslinking would also reduce the cured adhesive's sensitivity to the loss of some crosslinks under hydrolytic conditions. We evaluated the effectiveness of the strategy by measuring the cleavage fracture toughness and the shear strength of unexposed joints and joints after cyclic vacuum-pressure-soak-dry treatment or moist-heat aging.

The purpose of this study was to develop an understanding of the failure mechanisms of wood joints bonded with unmodified and amine-modified UF adhesives and thereby learn how such modification improves the durability of UF-bonded joints.

2
Experimental

2.1
Adhesives

Specimens were made with an unmodified UF adhesive prepared in the laboratory (CONTROL), a commercially-produced unmodified UF adhesive (COMMERCIAL), several amine-modified UF adhesives produced in the laboratory, and a commercial phenol formaldehyde adhesive (PF). Methods for incorporating the amine into the adhesive have been described elsewhere (Ebewele et al. 1991a).

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2.2
Specimen preparation and testing

A composite contoured double-cantilever beam specimen was used to measure cleavage fracture toughness. A reduced-size compression block shear specimen was used to measure the shear strength of bonded joints. The details of specimen preparation and testing have been described elsewhere (River and Okkonen 1993, Ebewele et al. 1993a, Okkonen and River 1989).

2.3
Accelerated aging treatments

A set of test specimens was subjected to ten cycles of vacuum-pressure-soak-dry (VPSD) treatment before testing (Ebewele et al. 1991a). A second set of specimens was subjected to moist-heat aging at 70°C and 80 percent relative humidity for up to 40 days before testing. Only shear specimens were used in the moist-heat aging experiment.

3
Results and discussion

3.1
Crack-initiation energy and shear strength

The crack-initiation energy describes how much energy is required to start a crack growing or to develop a unit area of new fracture surface. The crack-initiation energy of untreated specimens ranged from 95 J/m^2 to 567 J/m^2. Energies above 400 J/m^2 were obtained from joints made with unmodified and modified resins cured with formic acid.

Ten cycles of VPSD treatment reduced the crack-initiation energy of specimens bonded by various adhesives by 16 to 72 percent. Specimens bonded with unmodified adhesives were the most severely affected and lost from 63 to 72 percent of their crack-initiation energy before VPSD treatment.

The shear strength of specimens ranged from 16 to 26 MPa when tested before treatment. Ten cycles of VPSD treatment reduced the shear strength from 5 to 80 percent depending upon the adhesive. Specimens bonded with two unmodified adhesives lost 40 and 80 percent; specimens bonded with the best modified adhesives did not lose strength. Forty days of moist-heat aging decreased the shear strength of joints made with unmodified adhesive by 78 and 83 percent. The strength of joints subjected to moist-heat aging and bonded with the best modified adhesives decreased in the range of 5 percent. In comparison, the strength of joints bonded with PF adhesive decreased 5 percent in both the cyclic soak-dry and moist-heat treatments.

3.2
Adhesive behavior during cure

Microscopic examination of unbroken and broken specimens revealed that the adhesive layers existed in one of three distinct conditions prior to any aging treatment or mechanical test. These conditions – Types I, II, and III – which are related to the degree of adhesive modification, have pronounced effects on stability and durability of the bonded joint.

TYPE I is characteristic of unmodified UF adhesive layers. The adhesive layer displays relatively straight cracks that run generally parallel or perpendicular to the adherend fiber. Crack intersections often form a right angle (Fig. 1). Thus, looking down on the surface of a tested specimen, the adhesive layer is broken into blocks or rectangles. The cracks in the adhesive are perpendicular to the wood surface (Fig. 1). The relative smoothness of a Type I crack surface is characteristic of a fast-moving brittle fracture in a polymer with restricted molecular mobility having little opportunity for plastic deformation (Ward 1971, Williams 1984). These cracks exhibit the release of cure-shrinkage stresses that build up in the adhesive layer as a result of restraint by the wood adherends. Greater restraint in the longitudinal wood direction causes more frequent cure-shrinkage cracking perpendicular to the fiber direction than parallel to the fiber direction.

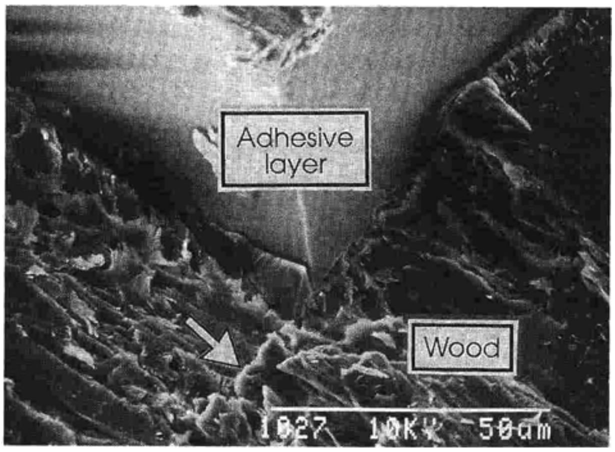

Fig. 1. Crack surfaces of adhesive layer in Type I condition. Arrow indicates crack. (M93 0025)

Bild 1. Bruchflache einer Leimschicht (unter Typ I Bedingung). Der Pfeil zeigt auf die Bruchlinie.

TYPE II is characteristic of moderately modified adhesive layers. Cure-shrinkage cracks, as observed in Type I layers, appear in the adhesive layer across, but seldom parallel to, the fiber direction. These cracks are farther apart than in Type I adhesive layers, but they have smooth surfaces and their faces are perpendicular to the wood surface. Some modified adhesives develop cure-shrinkage cracks across the fiber direction, but the crack arrests before it reaches the wood surface.

TYPE III layers are unbroken. No cracks develop prior to aging treatment or mechanical testing. Either the adhesive shrinks less or it has the flexibility and toughness to relieve shrinkage stresses without cracking. Type III behavior is characteristic of joints bonded with unmodified UF resins cured with formic acid

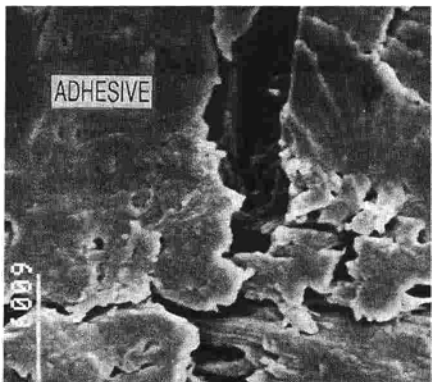

Fig. 2. Microcrack formation in wood surface at end of cure-shrinkage crack in adhesive layer.

Bild 2. Mikrorißbildung an einer Holzoberfläche. Der Riß erfolgte am Ende der Aushärtezeit innerhalb der Leimschicht.

and some modified resins cured with amine hydro-chloride. Conventional PF adhesives also produce a Type III layer.

Cracking relieves the cure-shrinkage stress in the adhesive, but damages the wood adherends. The force exerted by the adhesive layer as it contracts after cracking has sufficient energy to rupture cells near the adherend surface in tension parallel to the fiber direction (Fig. 2). (One of these cracks in the wood surface can also be seen in the lower portion of Fig. 1, arrow.) As a result, joints with Type I and II adhesive layers are highly flawed as they begin their service life. In contrast, joints with Type III adhesive layers are relatively unflawed and integral when entering service.

3.3
Effects of aging treatments

In view of the different conditions of adhesive layers as they enter service or, in this case, aging treatment, it is not surprising that the cyclic VPSD treatment had a much greater effect on specimens with unmodified adhesive (Type I) than on specimens with modified adhesives (Types II and III). Examination by scanning electron microscopy (SEM) revealed that VPSD had no apparent physical effect on unmodified adhesives themselves. The unmodified adhesive layers were already so highly cracked, perpendicular and parallel to the fiber direction, that swelling and shrinking of the wood adherends did not develop sufficient stress to further crack the adhesive. Some modified adhesives developed cracks parallel to the fiber direction and perpendicular to the adherend surface. The surfaces of these VPSD cracks were very rough in contrast to the smooth cure-shrinkage cracks (Fig. 3). Such rough surfaces should be expected of a tough flexible adhesive stressed to fracture while plasticized by heat and moisture. The occurrence of these parallel-to-fiber cracks apparently had little effect on joint strength.

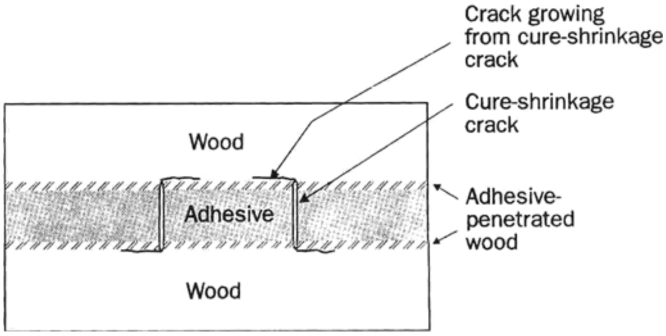

Fig. 4. Schematic of crack formation in wood interphase at root of cure-shrinkage crack growth and possible coalescence of cracks in wood interphase during subsequent swelling and shrinking.

Bild 4. Schema und Rißbildung innerhalb der Holz-Leim-Zwischenschicht, ausgehend von einem Aushärteriß, welcher zunächst wächst und sich während des anschießenden Quellens und Schwindens möglicherweise mit Rissen innerhalb der Holzschicht vereinigt.

Because joints bonded with unmodified adhesive lost most of their strength in a few VPSD cycles but appeared physically unchanged by that treatment, we think that the wood interphase must be weakened by the treatment. As discussed, adhesive cure-shrinkage cracking leaves myriad sharp, natural flaws in the wood surface. These flaws act as crack initiators in weak longitudinal planes between cells. Differences between adhesive and wood coefficients of expansion very likely cause cracks to grow in these weak planes (Fig. 4). In the extreme, as for example in the highly precracked unmodified adhesive layers, the cracks coalesce and the joints delaminate.

Moist heat has pronounced physical and chemical effects on UF adhesives. Preexisting cracks increased in width during 40 days of moist-heat aging. This widening of the cure-shrinkage cracks was caused by erosion of the crack surface by the hot, moist atmosphere (Fig. 5). Cracks may also be widened by shrinkage during aging. Narrow secondary cracks with smooth, uneroded surfaces were observed (Fig. 5, arrow). The smoothness of the secondary cracks and their proximity to older eroded cracks suggest secondary shrinkage and cracking late in the 40-day aging period.

3.4
Fracture behavior before aging

Unaged specimens failed differently depending upon whether the test was in cleavage or shear and upon the condition of the adhesive layer (Type I, II, or III) when the test occurred.

3.4.1
Cleavage

The cleavage test specimen was designed with the grain oriented to the crack growth direction, which forces the crack back toward

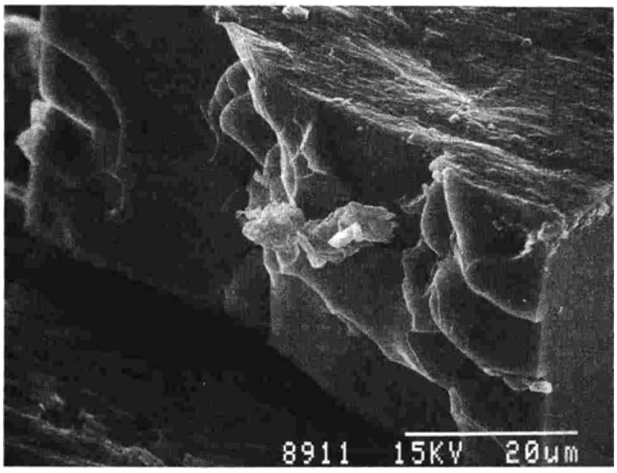

Fig. 3. Rough fracture surface of modified adhesive layer formed by adherend swelling or shrinking while adhesive was plasticized by heat and moisture in VPSD treatment. Portion of smooth cure-shrinkage crack surface is visible at right.

Bild 3. Rauhe Bruchfläche eines modifizierten Leims aufgrund von Quellen oder Schwinden des anhaftenden Leims während der plastischen Verformung durch Hitze und Feuchte innerhalb der VPSD-Bechandlung. Ein Teil der glatten Fläche eines Aushärterisses ist am rechen Bildrand sichtbar.

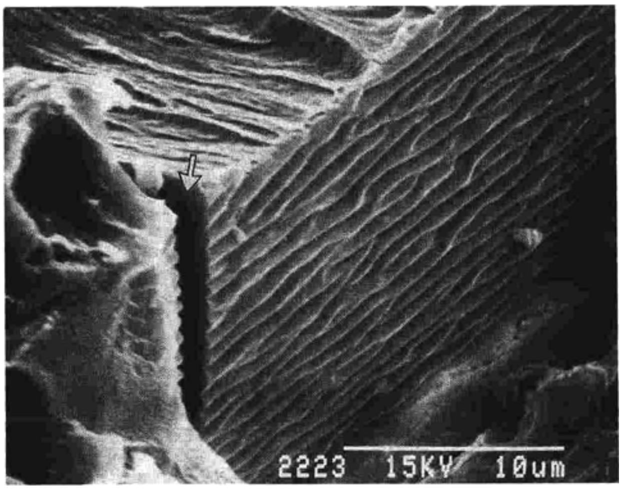

Fig. 5. Ridged erosion of cure-shrinkage crack surface and narrow aging-shrinkage crack (arrow) in unmodified adhesive layer caused by exposure to moist-heat aging.

Bild 5. Durch Erosion zerfurchte Oberfläche eines Aushärterisses und ein schmaler Schwindungsriss (Pfeil) aufgrund des Alterungsprozesses (Feuchte-Hitze-Zyklen) in einer Leimschicht (unmodifiziert).

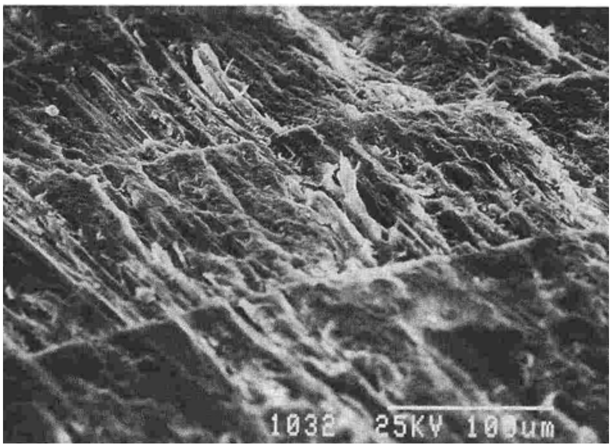

Fig. 6. Ramp-like fracture surface of wood adherend in cleavage fracture specimen caused by cure-shrinkage cracks in wood surface and grain orientation of adherend.
Bild 6. Stufenformige BruchflËäche einer Holz-Leim-Probe nach einem Bruchtest. Das Bruchbild ist verursacht durch Ausharterisse in der Holzoberflache und Faser-Orientierung des Leims.

the bondline. The intent was to force the crack to remain near the joint, thus providing the maximum opportunity for the adhesive to fail. Even strong joints produce shallow wood failure in such specimens. This specimen design produced distinctly different fracture surfaces depending on the preexisting condition of the adhesive layer.

In unmodified adhesive with a Type I layer, the fracture surface produced by cleavage consisted almost entirely of fresh shallow wood failure. The adhesive layer was already prefractured, but it was still strong. No new fractures occurred in the adhesive because the primary crack tip traveled along one weakened wood interphase or jumped from one interphase to the other through the preexisting cure-shrinkage cracks, as dictated by the local strengths. The shallow wood failure usually had a ramped appearance (Fig. 6) as the primary crack tip traveled down into the wood interphase along the wood portion of a cure-shrinkage crack and returned along the fiber direction to just below the adhesive layer.

Modified adhesives with Type II layers fractured predominately in the wood; some adhesive cracking occurred as the primary crack jumped from one interphase to the opposite. These adhesive crack surfaces were generally parallel to the fiber direction but sloped with respect to the plane of the adherend surface (Fig. 7). The crack surface changed gradually from smooth to striated (Fig. 7), or it was totally striated. Modified adhesives with Type III layers also fractured predominately in the wood and had less interphase jumping, but there were prominent striations where the crack passed through the adhesive layer.

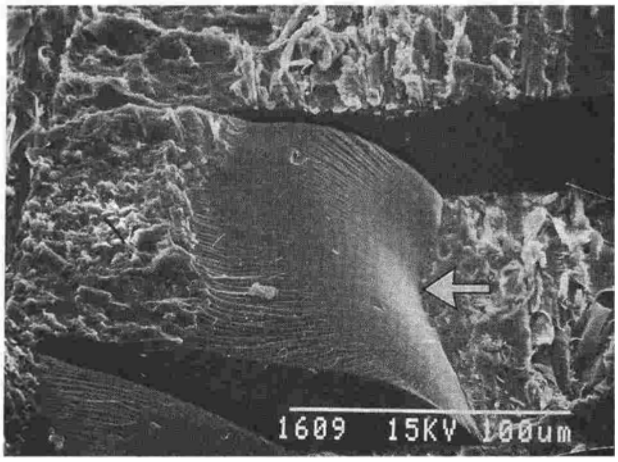

Fig. 7. Fracture of modified adhesive layer a primary crack jumped from one interphase to the other. Crack initiation began at lower interphase and traveled through adhesive layer (arrow) to upper interphase.
Bild 7. Bruch einer Leimschicht (modifizierter leim). Die Bruchbildung begann innerhalb der untren Zwischenschicht, verlief durch die Leimschicht (Pfeil) bis in die obere Holzschicht.

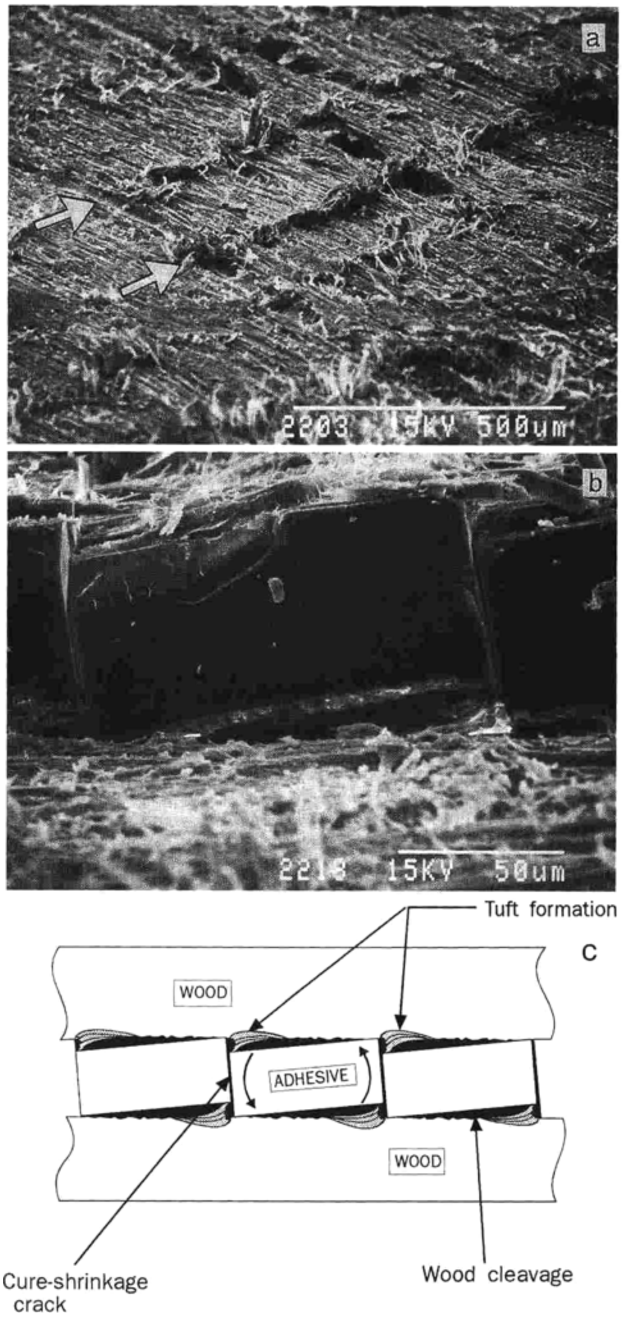

Fig. 8a–c. Wood failure in shear test: **a** lines of raised fiber fragments formed by cure-shrinkage cracks in wood surface and tendency of blocks of cure-shrinkage cracked adhesive to roll and cleave wood when sheared, **b** partially rotated blocks of cure-shrinkage cracked adhesive crack adhesive layer, and **c** schematic of cleaving action of rotating block fracture in unmodified adhesive.
Bild 8a–c. Holzbruch im Schertest: **a** die Reihen von aufgerichteten Faserfragmenten bilden sich aufgrund von Schwindungsrissen beim Aushärten und der Tendenz der durch Schwindungsrisse getrennten Leimblöcke, sich zu drehen und so das Holz zu spalten. **b** teilweise gedrehter Block einer Leimschicht, der durch Schwindungsrisse beim Aushärten der Leimschicht entsanden ist. **c** Schema zum Zustandekommen des Bruchbildes durch Aufspälten der Leimschicht und teilweise Drehung des entstandenen Bruchstücks (unmodifizierter Leim).

In modified adhesives, striations are evidence of ductile failure involving extensive plastic shear deformation in contrast to the smooth or minutely reticulated cure-shrinkage crack surfaces of the unmodified adhesive. The transition from a smooth to a striated surface results from a slip-stick type of fracture that is characteristic of a toughened thermosetting adhesive (Kinloch and Young 1983).

3.4.2
Shear

Unaged specimens of both unmodified and modified adhesives produced a high percentage of wood failure when tested in shear. Wood failure was shallow in joints made with unmodified adhesive. Wood surfaces exhibited peculiar rows of fibrous tufts (Fig. 8a), which resulted from two effects of the cure-shrinkage cracks in the Type I adhesive layer. First, the microcracks in the wood surface acted as crack initiators. Second, the low height-to-length ratio of the cure-shrinkage cracked blocks of unmodified adhesive allowed the blocks to rotate under the shearing action on the adhesive layer (Fig. 8b). Rotation tended to cleave the wood surface, with cleavage initiating at each microcrack (Fig. 8c).

Some modified adhesives were weaker than the wood and developed slanted shear cracks during testing (Fig. 9).

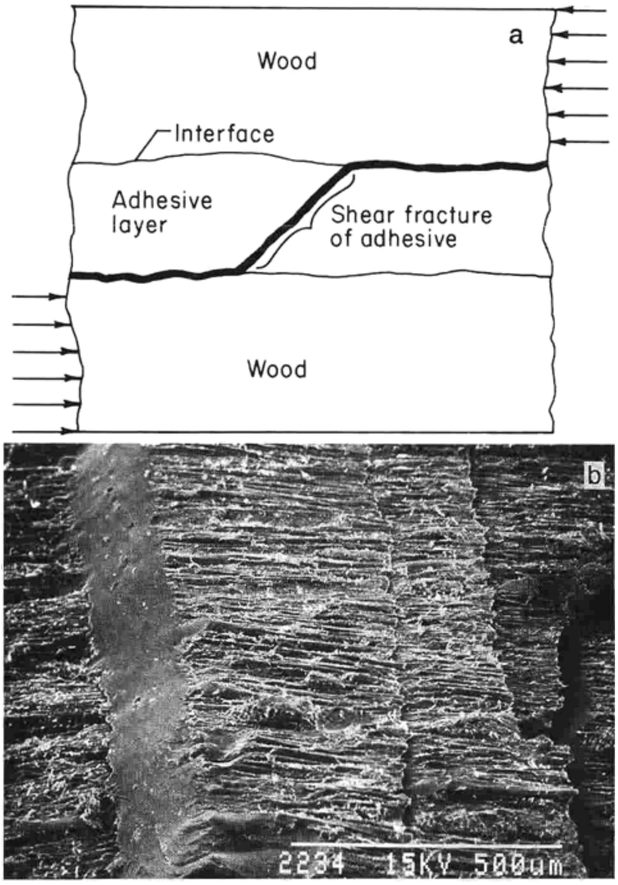

Fig. 9a, b. Slanted shear cracks in modified adhesives: **a** after shear testing, primary crack travels along one interphase, shears through the adhesive layer, and continues along opposite interphase; **b** a series of parallel shear fractures in a layer of modified adhesive.

Bild 9a, b. Gegeneinander versetzte Brüche in einer Leimschicht (modifiziert). **a** Bruchbild nach Schertest; der ursprungliche Riß verlauft zunächst innerhalb einer Zwischenschicht, schert dann durch die Leimschicht und setzt sich in der gegenüberliegenden Schicht fort. **b** Bruchbild innerhalb einer Leimschicht (modifiziert) nach einer Serie paralleler Schertests. **c** Schematische Skizze der Rißbildung.

3.5
Fracture behavior after aging

3.5.1
Vacuum-pressure soak-dry treatment

When cure-shrinkage cracks form in unmodified and some modified adhesive layers, the crack initiation and growth mechanism described in section 3.3 progressively weakens the wood interphase. The strength of a specimen tested before total delamination will diminish according to the amount of crack growth in the wood interphase. The primary crack formed by the overwhelming force of the testing machine simply follows one of these weakened wood interphases. The primary crack can readily jump between the interphases with little hindrance from the precracked adhesive layer. Joints made with modified adhesives suffer damage in proportion to the amount of cure-shrinkage cracking across the fiber direction. Fracture surfaces appear the same as joints tested to failure without VPSD treatment except for the additional VPSD cracks parallel to the grain.

It is clear that the improved resistance of joints made with modified adhesives is in proportion to the success in eliminating cure-shrinkage cracking. It is not coincidental that the adhesives most successful in eliminating cure-shrinkage cracking are also those that present the toughest, most integral barrier to the crossing of the primary crack from one interphase to the other.

3.5.2
Moist heat treatment

We previously described the erosive effect of moist heat upon the adhesive where it is directly exposed to the atmosphere. Strength tests show that a weakening or chemical effect also occurs in the bulk adhesive. This weakening can be readily seen by the onset of shear cracking in layers of adhesives that had not exhibited this characteristic prior to aging.

Adhesives subjected to moist-heat aging seem to differ in the time of onset and degree of shear cracking. Unmodified adhesive

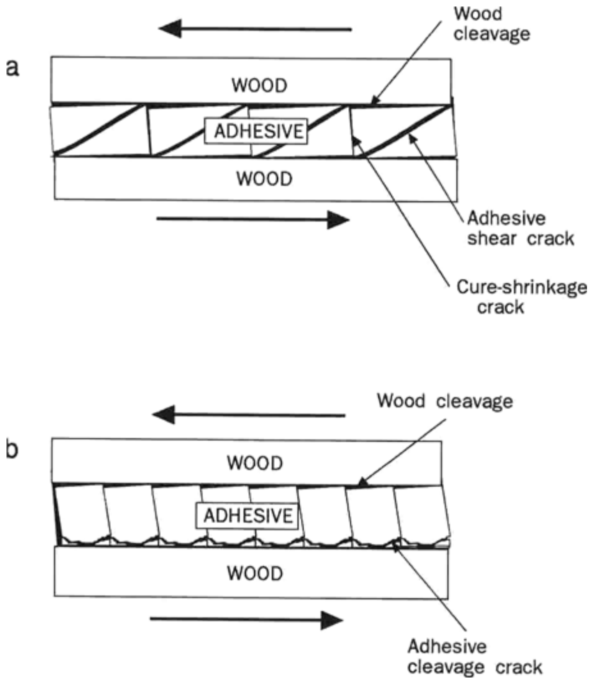

Fig. 10. Granulation of an unmodified UF adhesive layer is caused by **a** combination of cure-shrinkage (vertical) cracks and subsequent shear cracking (slanted cracks) or **b** cleavage cracks.

Bild 10. Die Aufrauhung einer Leimschicht aus unmodifiziertem UF-Harz ist verursacht durch **a** eine Kombination von senkrechten Aushärterissen und anschließenden Scherrissen (schräg versetzte Risse oder **b** Spaltungsrisse.

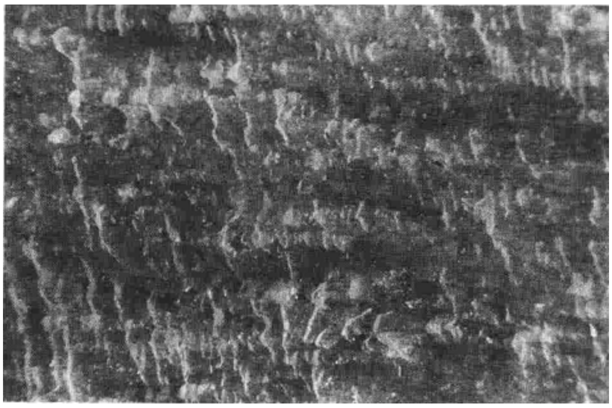

Fig. 11. Wavy shear cracks in moist-heat-resistant amine-modified adhesive layer after shear testing.
Bild 11. Wellenformige Scherrisse in einer Leimschicht aus feuchte- und hitze-bestandigem amin-modifizierten UF-Harz nach einem Schertest.

did not shear crack when tested prior to aging, but it developed closely spaced shear cracking after a short aging period. In this instance, the adhesive layer became granulated by one of the actions shown in Fig. 10. Some of the more flexible modified adhesives shear cracked before moist-heat aging and continued to shear crack after aging. But, without extensive cure-shrinkage cracking, the modified adhesive layers did not granulate. More-resistant modified adhesives developed scattered wavy and discontinuous shear cracking when tested after aging (Fig. 11). A few of the most resistant adhesives failed to develop any shear cracks and maintained high strength and wood failure through 40 days of moist-heat aging.

4
Conclusions

Modification of urea-formaldehyde adhesive by incorporation of flexible di- and trifunctional amines into the adhesive improves the resistance of bonded joints to cyclic swelling and shrinking environments by minimizing or eliminating cure-shrinkage cracking of the adhesive layer and consequent damage to the wood interphase. Modification by these flexible amines also improves resistance to moist-heat aging as shown by reduction of erosion. In the tests reported here, shear cracks occurred in moist-heat-aged unmodified adhesive. These cracks combined with preexisting cure-shrinkage cracks to granulate and completely destroy the integrity of the unmodified adhesive layer. Shear cracks occurred in some amine-modified adhesives before aging, but those without preexisting cure-shrinkage cracks suffered less damage and did not granulate. Some modified adhesives resisted moist-heat weakening and did not develop shear cracks during testing.

5
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