Interfacial Factors Affecting Polymeric Diphenylmethane Diisocyanate/Wood Bond Strength

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ABSTRACT: Polymeric diphenylmethane diisocyanate (pMDI) has been used for making wood board composites for over 30 years, although its growth in application has been limited mainly by the perception that it is a high-cost alternative to formaldehyde-based adhesives. Increased use of pMDI adhesive in making wood composites will require optimization of the process variables involved. One such factor is the unresolved question of the interfacial aspects most responsible for building strong wood composites. Some argue that adhesive surface coverage is primarily responsible for board strength; others assert that penetration of the pMDI into the wood matrix is a primary characteristic of strong boards. This article will provide evidence that the interfacial aspect most important in building board strength is surface coverage of the wood particles or fibers. Experiments controlling the depth of pMDI penetration into wood matrices and then measuring their adherend strength were performed. We also calculated the potential efficiencies to be obtained from maximizing the surface coverage and minimizing the matrix penetration using a spherical sector model. Neither high nor low pMDI viscosity offered a significant advantage in surface covering pine or oak, although it is speculated that minimizing the droplet size of pMDI in the resination step could lead to substantial efficiency improvements in adhesive coverage. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 449–455, 2005

Key words: adhesives; wood composites; interfaces; polymeric MDI (pMDI); resins

INTRODUCTION

Adhesive binders for composite wood manufacture have been the focus of numerous investigations because of their commercial and scientific interest.[1,2] Although formaldehyde-based resins remain the volume leader for bonding wood chips and wood flour,[3] polymeric diphenylmethane diisocyanates (pMDI) have been commercially applied to specialty wood boards and straw board.[4] Several aspects of pMDI limit market penetration. One restraint is the tendency of isocyanates to bond to steel press faces,[5] resulting in the need for copious application of release agents to the surface.[6] A second limitation is the relatively high price of pMDI compared to that of formaldehyde-based resins. Arguments have been made suggesting that the cost of pMDI adhesive is offset by its relative efficiency, faster processing speed, and improved board properties.[7] Nonetheless, the perception that pMDI is an expensive alternative wood binder remains.

We have recently reported on the use of polyurethane systems (the blend of pMDI and polyols) to reduce the cost of wood bonding and mitigate press sticking in these systems.[8] In many of these polyurethane systems wood bonding was purely a function of the mass fraction of pMDI in the adhesive. However, some polyurethane mixtures produced board strengths as much as 80% greater than would be predicted purely on the basis of pMDI addition. These pMDI/polyol mixtures were characterized by a fine dispersion of the two phases. Given the high equivalence ratio of isocyanate to polyol hydroxyl functionality, we speculated that the unexpectedly good performance was a result of improved pMDI dispersion of the pMDI on the wood surface. There was also the possibility of improved penetration of the isocyanate into the wood porous structure to make an enhanced composite phase.[9–12] The pMDI–wood composite could in principle boost the board's tensile strength. This article provides data that validates a model in which the main mechanism of board strength enhancement by pMDI is by interfacial interaction with the wood surfaces.[13–17] This result implies that pMDI properties or application techniques that ensure the widest spreading of the adhesive on the wood surface will provide the most cost-efficient use of this binder. We calculate the improvement in interfacial coverage

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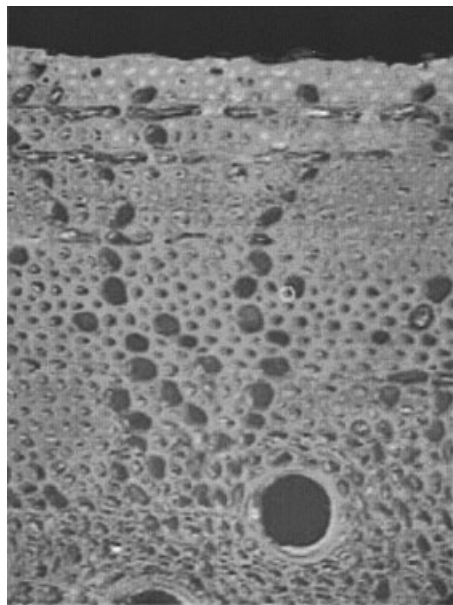
Figure 1 Penetration of pMDI (PAPI 27) into pine after 1 h. The white pore filling material at the top of the wood is the reacted polyurea phase.

as a result of enhanced spreading using a spherical sector model.

EXPERIMENTAL

pMDI was obtained from Dow Chemical (Midland, MI) under the tradename PAPI. PAPI-27 is nominally a 2.7 functional MDI oligomer having a molecular weight of 340 g/mol and a specified viscosity between 1.5 and 2.2 poise. We measured 2.16 poise with a calibrated viscometer (Brookfield Engineering Laboratories, Middleboro, MA). PAPI-94 is nominally a 2.3 functional oligomer having a molecular weight of 290 g/mol and a specified viscosity of 0.5 poise. We measured 0.65 poise with our particular sample (pMDI is

known to undergo viscosity increase with time as a result of reaction and chain extension with adventitious water). Southern pine and oak boards were obtained from a local hardware store. Samples as purchased were planed but not otherwise treated. Movies of pMDI spreading were collected on an M3z stereomicroscope (Leica-Wild, Wetzlar, Germany) connected to a DXM1200 digital camera (Nikon, Tokyo, Japan) and analyzed with Videum 2.9.2a software (Winnov USA, Santa Clara, CA). Penetration depth of pMDI was measured on pMDI-prepared wood samples that were subsequently frozen by liquid N_2 and sectioned by microtome. Penetration depth was measured with a Kaiser 785-nm laser Raman spectroscope (Kaiser Optical Systems, Ann Arbor, MI), which detected characteristic MDI ring bands. All spectra were calibrated with respect to wavelength and intensity.

Lap shear strengths were measured on specimens measuring $2 \times \frac{1}{2} \times \frac{1}{8}$ in. The long axis of each specimen was parallel to the wood grain. pMDI was spread on a surface area measuring $\frac{1}{4} \times \frac{1}{2}$ in. The pMDI was either wiped off immediately after application or allowed to penetrate the wood for a determined amount of time, after which the excess was wiped off. The spreading of the pMDI away from the application zone was prevented by applying a very viscous silicone sealant to the wood surface and end grain outside the overlap region. This sealant was subsequently removed before assembling the lap shear specimens. No spacer was used to control adhesive thickness because the samples had very thin film adhesive layers. Application rate was determined gravimetrically. Assembled lap specimens were subsequently held in place with new binder clips and cured in a convection oven at 150°C for 1 h. The cured specimens were then allowed to cool for 24 h at room temperature. Lap shear strengths were subsequently measured on an Instron 4202 frame with Series 9 software. Strain rate was 1 in./min. Lap specimens were prepared in standard format or in an

TABLE I
Lap Shear Energies for Wood Adherends with Controlled Penetration of pMDI into the Wood Matrix[a]

Sample	Application time	Application rate (mg/cm^2)	Wood	Lap shear (MPa)	Failure mode
1	5 s	9.3	Pine	9.35	Wood
2	5 min	13	Pine	9.68	Wood
3	30 min	24	Pine	9.1	Wood
4	1 h	33	Pine	9.0	Wood
6	21 h vacuum	175	Pine	9.1	Wood
7	5 s	9.7	Oak	9.5	Wood
8	1 h	31	Oak	8.2	Wood
9	1 h	18	Oak	9.1	Wood
10	1 h	20	Oak	8.1	Wood

[a] Samples 1, 3, and 9 were bonded with PAPI-94. The others were bonded with PAPI-27. Application rate is normalized to surface area exposed rather than to volume because the pMDI distribution in the wood interior is highly nonuniform (as described in the text). Independence of the failure mode on penetration depth (see Fig. 2) indicates that adhesion strength is derived primarily from interfacial interactions and not from formation of a composite phase.
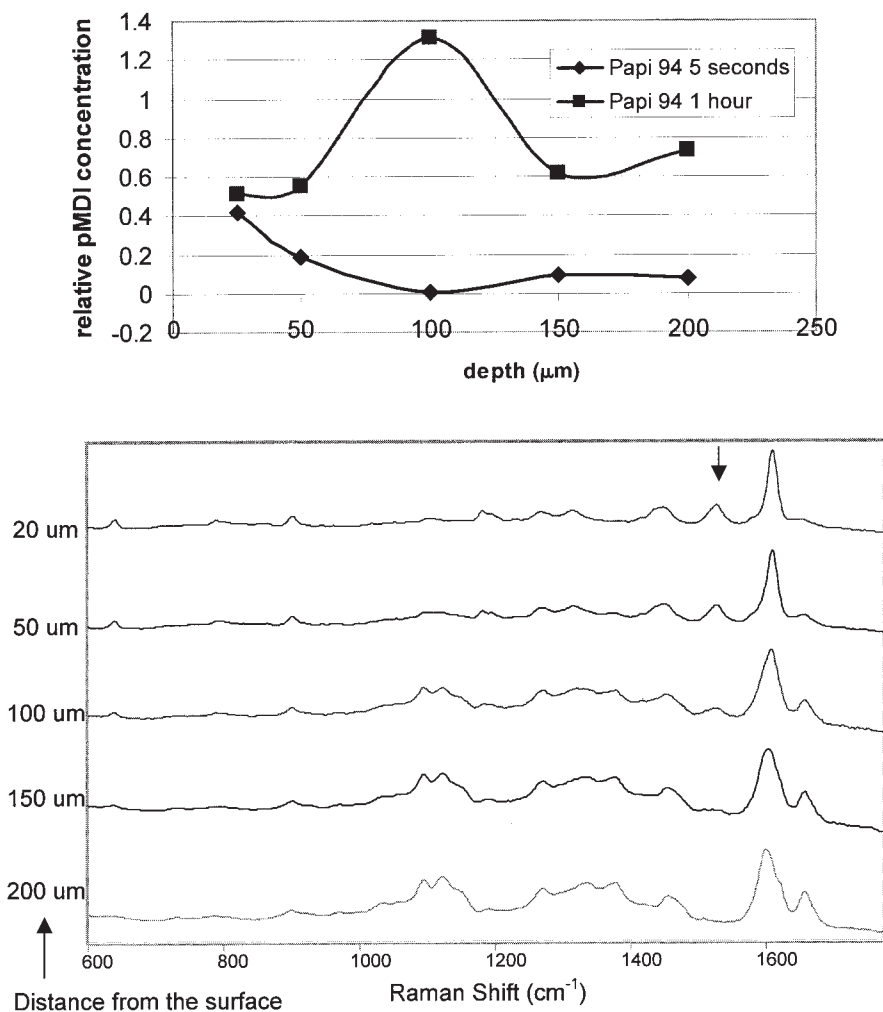
Figure 2 Representative depth profile for pMDI penetration into wood: (a) effect of exposure time on penetration into the wood sample for 5 s and 1 h exposure. The surfaces are both wiped and indicate similar surface concentrations. (b) Raman spectra of a 5-s exposure sample showing the steady drop off of the 1530 cm^{-1} pMDI ring Raman scattering signal.

overlap joint format.[18] Measured strengths were within experimental variation between these lap formats and no distinction is made in the data. Each sample is the average of at least three specimens. Variation from sample to sample was ±10%.

RESULTS AND DISCUSSION

A question being tested in this article is: does the penetration of wood binder resin into the wood's porous internal structure strengthen the wood, and so make the resulting board stronger? Implicit in the question is the idea that wood surfaces are weak, and tying this top layer to stronger lower layers increases tensile properties.[19] There is no question that pMDI is capable of wetting and penetrating the wood's surface and flowing to the interior structures (Fig. 1). The issue is whether it is desirable. It has been recently shown that pMDI is capable of bonding to the primary

hydroxyl groups intrinsic to wood structure, leading some to conclude that the mechanism of pMDI adhesion to the wood surface is by mechanical interlocking and covalent interactions.[20,21] However, previous work has shown only moderate increases in wood strength when an entire wood sample imbibes a resin.[16,22] This calls into question the ability of the very low mass fraction loadings (2–5%) in manufactured wood composites to appreciably enhance wood tensile properties, and further suggests that a strictly physical mechanism of adhesion may be of secondary importance in the overall board strength. Table I shows that wood samples adhered with pMDI give lap shear energies that are independent of the added adhesive mass over a factor of three. Furthermore, the measured lap shears are independent of pMDI viscosity within the range used in these experiments (65–216 cps).

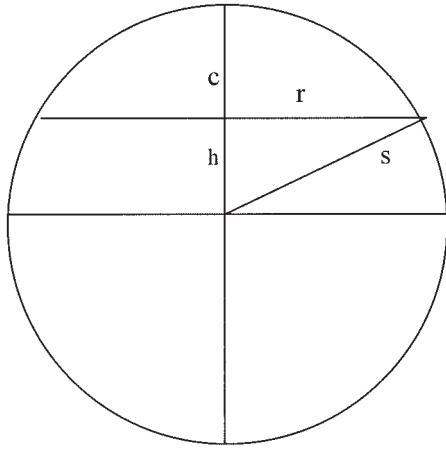Figure 2 in combination with Table I confirms that

Figure 3 Spherical sector model for calculating the increase in surface coverage for a droplet that spreads on a surface at constant volume. The droplet is described by the sector defined by $2r$ and c.

there is no functional relationship between the mass of pMDI within the wood structure and the depth of the wood failure. Figure 2 shows that the mass of pMDI imbibed into the wood is a function of the exposure time and that the maximum concentration of pMDI may be below the surface, given adequate exposure times. If formation of a wood–adhesive composite enhancing board tensile properties is an operational hypothesis, we would expect boards with substantial concentrations in the wood to exhibit greater adhesion energies. However, Table I shows no such correlation and we must assume that the variable most related to adhesion energy for these systems is adhered surface area.

These results indicate that the most efficient use of pMDI for composite wood boards is the procedure that most efficiently coats the wood chip surface with resin. Most application techniques involve spraying of the liquid pMDI onto the wood. These droplets then spread on the surface and penetrate the wood interior, or competitively spread and penetrate. Which process dominates will depend on the properties of the wood and the pMDI. It would be useful to ascertain the amount of additional surface that could be covered, if spreading were the primary mechanism. This knowledge would have a direct impact on the economic use of pMDI in composite board manufacture. Thus a question arises: For a droplet of given volume, how much surface area is incrementally covered as it spreads? This question can be approached from geometric considerations of a spherical sector model. In a reference to Figure 3, we seek to understand how the area under the spherical sector defined by chord r changes under the constraint that the total volume of that sector cannot change. With these assumptions the

total volume of the spherical cap and its right cylindrical cone is (definitions of variables are in Fig. 3)

$$V_t = 2/3\pi s^2 c \tag{1}$$

whereas the volume of the cone with top surface bounded by r is

$$V_c = 1/3\pi r^2 h \tag{2}$$

By subtraction, the volume of the drop defined by radius r and height c is

$$V_d = V_t - V_c \tag{3}$$

with the conditions that

$$c > 0 \tag{4}$$

$$s \geq r \tag{5}$$

$$h + c = s \tag{6}$$

$$s^2 = r^2 + h^2 \tag{7}$$

the volume of the drop can be rewritten as

$$\frac{3V_d}{\pi} = 2s^3 - 3s^2 h + h^3 \tag{8}$$

After solving for h for a given V_d and s, c can be calculated from conditional statement (6), after which r can be calculated from conditional statement (7). The total surface area of the droplet is then expressed as

$$A_t = 2\pi sc + \pi r^2 \tag{9}$$

Figure 4 illustrates that for a factor of 60% increase in droplet radius (spreading), the surface area under that droplet increases over 250%. Potential increases in spreading of the magnitude suggested by Figure 4 have practical significance to the economic use of pMDI in manufacture of composite boards. The following questions arise: What is the efficiency of pMDI as it is currently used? What remaining improvements are possible?

By visual inspection it is evident that pMDI spontaneously spreads on wood surfaces. The amount of this spreading could be, at least in principle, a function of the pMDI viscosity. It is also conceivable that the specific interaction of the isocyanate and the polar wood groups may facilitate transport along the surface. At the same time, wood is a very complex porous structure with a density of 0.4–0.7 g/cm³. The porosity can be described as trachids (softwood) or wood
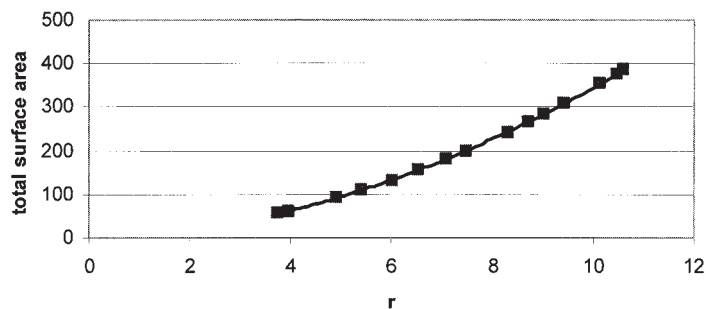
Figure 4 Results from spherical sector calculations for increasing total surface area with increasing spreading at constant volume. The decreasing slope at low *r* reflects the geometric requirement that a sphere at constant volume has a minimum radius.

rays (hardwoods), hollow tubule structures, interconnected by small windows (pits) (Fig. 5). Rheological aspects of pMDI may enhance penetration into the internal wood structure at the expense of its ability to spread. Penetration of pMDI into the wood is easily observed microscopically, as shown in Figure 1. Alternatively, there may be aspects of a specific wood sample that influences the spreading behavior of resin. For instance, as a droplet spreads it may encounter irregularities in the wood surface, pinning the edge and slowing its progress across the surface.[23] This behavior would promote the unproductive penetration of the pMDI into the wood interior.

Figure 6 shows that PAPI-27 and PAPI-94, with a threefold difference in viscosity spread to a similar extent over a period of 60 s on the pine surface used in this study. Not clearly visible on the pictures, but often seen through the microscope, is that pMDI is able to spread outside the droplet edge along open tubules. These tubules could then serve as a conduit not only to further spread the pMDI, but also to allow pMDI to escape into the wood interior through the system of

pits within the tubules.[24] Figure 6 also shows that the two different pMDI samples spread similarly on the oak surface, but noticeably ($\sim$ 30%) less than on the pine samples. SEM images of the wood end grain showed the oak wood rays to be significantly larger in diameter than the pine trachids, allowing the pMDI to penetrate the oak structure somewhat more readily. In fact, on the edge of the pMDI droplets on oak the escape of pMDI on intersecting wood rays along the surface is visible. These data indicate that enhancing the ability of pMDI to spread by for instance lowering viscosity may have the unintended consequence of accelerating the unproductive penetration into the wood interior. This leads to the conclusion that pMDI application methods that maximize the concentration of pMDI on the wood surface and minimize the penetration into the wood interior will result in more effective use of binder in the manufacture of composite boards. One approach is to apply preresinated wood flour to the wood furnish before pressing.[25] Another approach might be to minimize the drop size applied to the surface so that there is minimal volume to penetrate past the surface.

CONCLUSIONS

The research reported in this article demonstrates that there is a significant advantage to be gained from maximizing the spread of droplets of adhesive on the wood surface and minimizing the adhesive lost to subsurface penetration. Based on calculations, it is anticipated that limiting penetration of the adhesive below the wood surface, enabling a 50% increase in spreading, can result in a doubling of pMDI efficiency. The spread of pMDI on pine and oak surfaces at room temperature is not dependent on the pMDI viscosity after 60 s, suggesting strong specific liquid–solid interactions and the antagonistic competition between spreading and unproductive penetration into the wood's subsurface.
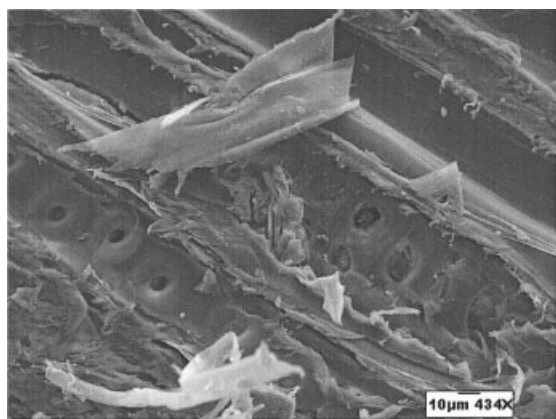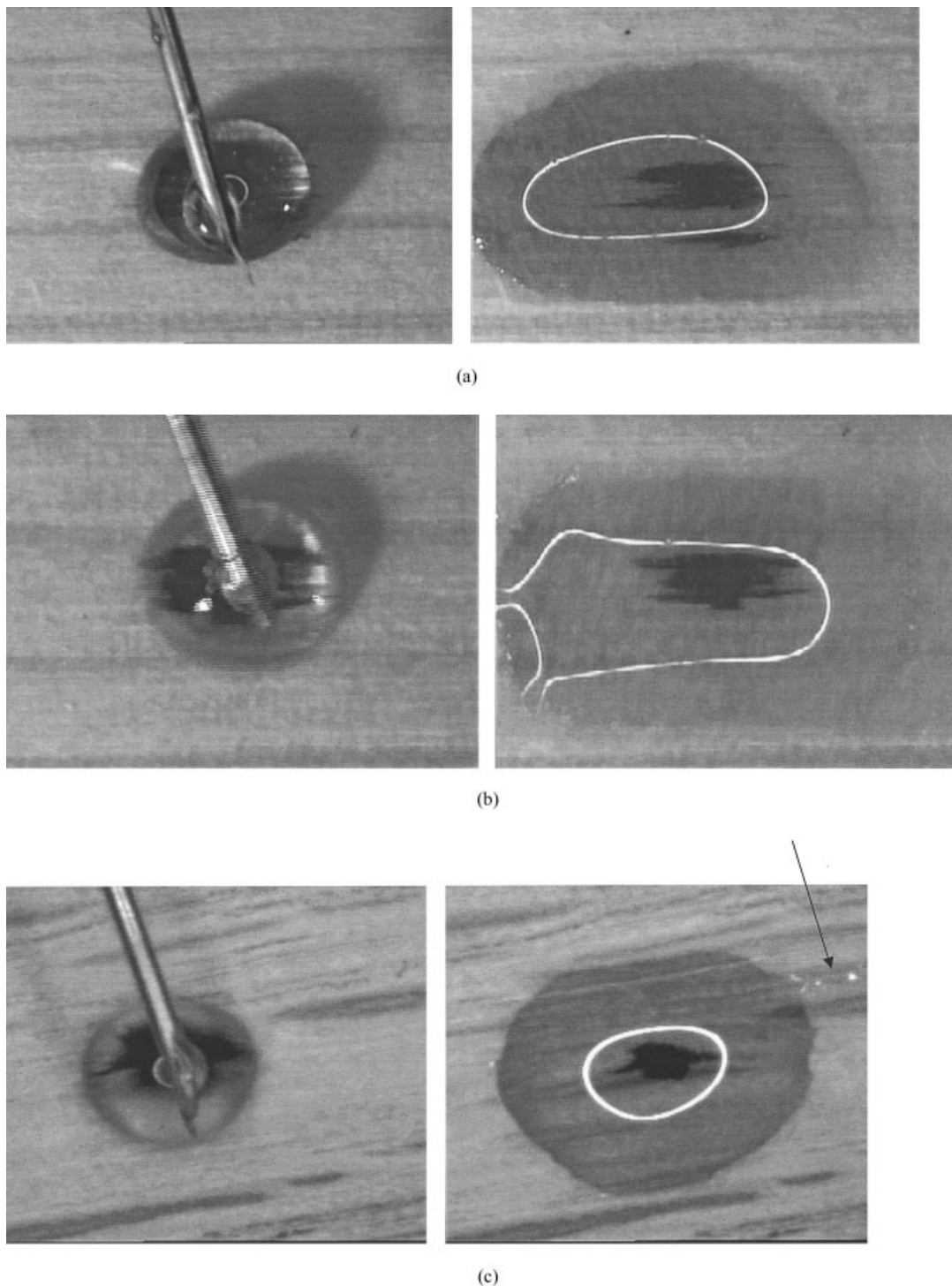

Figure 5 Surface of pine sample illustrating the trachid and pit conduits by which liquids such as pMDI may penetrate the wood surface into the wood interior.

Figure 6 Spreading of pMDI on wood. (a) PAPI-27 on pine at $t = 0$ and $t = 60$ s. (b) PAPI-94 on pine at $t = 0$ and $t = 60$ s. (c) PAPI-27 on oak at $t = 0$ and $t = 60$ s. The arrow indicates the transit of pMDI down a wood ray away from the drop. White circles on 60-s data are reflections from the light source.

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