Difurfuryl Diisocyanates: New Adhesives Derived from Renewable Resources

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SYNOPSIS

The syntheses of difurfuryl diisocyanates [e.g., ethylidenebis(2,5-furandiylmethylene)diisocyanate (EDFI)] have been reported in the literature. Difurfuryl diisocyanates are structurally similar to diphenylmethane diisocyanate (MDI), which has proven to be an excellent adhesive for bonding wood composites. The MDI resin is synthesized from petroleum-derived chemicals; the EDFI resin is synthesized from biomass-derived chemicals. In this study, the mechanical properties of aspen flakeboards bonded with MDI and EDFI are compared. In general, results show that the strength properties of flakeboards bonded with MDI are only marginally better than those bonded with EDFI. Because EDFI is more viscous than is MDI, less than optimum atomization of the EDFI resin during spraying of the flakes is believed to be largely responsible for the differences in strength property values. The dry internal bond strength values of flakeboards bonded with MDI (1.33 MPa; 193 lb/in.^{2}) and EDFI (0.97 MPa; 140 lb/in.^{2}) at 3% resin content are significantly greater than the 0.41 MPa (60 lb/in.^{2}) required by the American National Standards Institute (ANSI/A208.1) for type-2 medium-density particleboard. © 1993 John Wiley & Sons, Inc.†

INTRODUCTION

Adhesives play an important role in the wood products industry. In 1988, this industry accounted for a 25% share of the total U.S. consumption of adhesives. The use of adhesives can increase the utilization of small and low-quality trees in a variety of bonded wood products.[1] The economic imperative to use available timber resources in as efficient a manner as possible will undoubtedly increase the demand for adhesives.

Several factors contribute to the necessity of investigating new types of wood adhesives. These factors include a need to decrease or eliminate formaldehyde emissions and to improve performance of composite panel products. Adhesives based on the isocyanate functionality were developed, in part, to address these needs. Diphenylmethane diisocyanate (MDI) has proven to be a versatile bonding agent. Initially, its high cost relative to those of phenol–formaldehyde (PF) and urea–formaldehyde (UF) resins and concerns about potential toxicity prevented the widespread use of MDI. However, in 1990, MDI accounted for a 15–20% share of the resin market for oriented strandboard (OSB) and waferboard.[2]

An additional factor that creates interest in new adhesive systems is a desire of the wood products industry to decrease its dependence on petroleum-based adhesives.[3] The desire for adhesive self-sufficiency provides the impetus for research and development of renewable adhesives based on biomass-derived materials. Renewable adhesive systems that rely on partial or total replacement of phenol in PF resins with constituents derived from lignins, tannins, or carbohydrates were reported.[4–6] However, difficulties in achieving consistent formulation of adhesive systems with such materials limit their commercial utilization.[7]

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Recently, the synthesis of difurfuryl diisocyanates from furfurylamine was reported.[8] These difurfuryl diisocyanates, which have potential use as wood adhesives, are of considerable interest for two primary reasons: (a) their chemical and structural similarities to MDI suggest that they may share the superior bonding properties of MDI; (b) they are derived from furfural, which is now produced in only modest quantities worldwide, but is potentially available in much larger quantities from a variety of renewable, biomass-based feedstocks.

To determine if difurfuryl diisocyanates are comparable to MDI in wood-bonding properties, the mechanical property values of flakeboards bonded with one difurfuryl diisocyanate reported in the literature [i.e., ethylidenebis(2,5-furandiylmethylene)diisocyanate (EDFI); Fig. 1] were compared with those of flakeboards bonded with MDI. In a previous study, flakeboards were bonded with EDFI that had been diluted with chloroform.[9] The chloroform lowered the viscosity of the EDFI resin and made it easier to spray, but chloroform also had a detrimental effect on the mechanical properties of the flakeboards. In the study reported here, the experiments from the previous study were repeated without dilution of the EDFI resin with chloroform.

EXPERIMENTAL

Adhesive Resins

The control resin for this study was Mondur-541[†] (Mobay), a polymeric MDI resin. The average molecular weight of this resin is approximately 350 g/mol.

The experimental resin was EDFI. The synthesis of this compound by phosgenation of ethylidenebis(2,5-furandiylmethylene)diamine was reported.[8] The IR, ^{1}H-NMR, and ^{13}C-NMR spectra (Figs. 2–4) of the compound isolated from the phosgenation reaction were consistent with its identity as EDFI.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) thermograms were obtained on approximately 10 mg of the total sample in sealed stainless-steel capsules (Fig. 5). For thermograms of the resins with wood, the resin-to-wood sample ratio was 1 : 1 by weight. The

[†] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

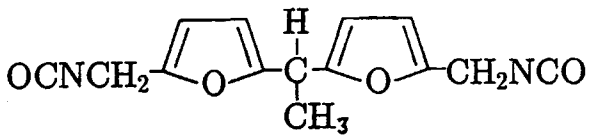

Figure 1 Chemical structure of EDFI.

aspen wood was prepared by grinding aspen flakes from the same source as that of the flakes used for the flakeboards. The temperature was programmed from 30 to 375°C at a rate of 10°C/min.

Flakeboard Construction

Flakeboards were constructed from disk-cut aspen (*Populus tremuloides* Michx.) flakes (38 × 12.7 × 0.51 mm; 1.5 × 0.5 × 0.02 in.). The flakes were preconditioned to 3% or 7% equilibrium moisture content (EMC). Because of a limited supply of resin, only 152 × 152 × 12.7 mm (6 × 6 × 0.5 in.) flakeboards (before trimming) were constructed. Using MDI, five flakeboards were constructed with flakes at 3% EMC and five were constructed with flakes at 7% EMC. Using EDFI, five flakeboards were constructed with flakes at 3% EMC and six were constructed with flakes at 7% EMC. The target density for the flakeboards was 720 kg/m^3 (45 lb/ft^3).

For each board, the appropriate quantity of flakes was weighed and placed in a rotary drum blender. The resin (3% based on the oven-dried weight of the flakes; 100% solids) was sprayed onto the flakes from a sprayhead mounted at the center of the blender drum. Compressed air was used to atomize the resin. The higher viscosity of EDFI, compared to the MDI, made it more difficult to force the resin through the sprayhead.

After blending, the flakes were matted by hand on cauls that were previously treated with Isostrip (QO Chemicals). A press temperature of 180°C was used in the cure of both resins. The time to reach stops was 5 s, and the pressing time was 5 min. After pressing, the flakeboards were allowed to cool at room temperature and then stored in a conditioned room at 27°C, 30% relative humidity (RH) until testing.

Specimen Testing

After conditioning, the flakeboards were cut into test specimens according to the pattern shown in Figure 6. All specimens were reconditioned to 27°C, 30% RH prior to testing. In the following tests, dry refers to specimens that were not treated with water before testing.

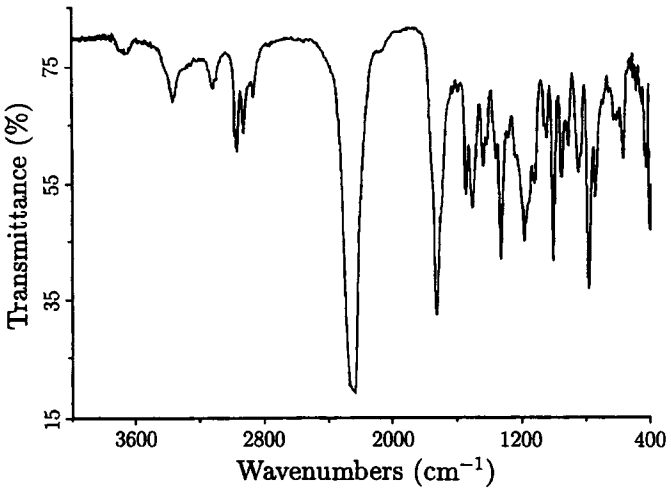

Figure 2 IR spectrum of EDFI.

Internal Bond

Internal bond strength was determined according to ASTM D 1037 Section 28.[10] One internal bond specimen was tested dry, and the other was tested after a vacuum-pressure soak (VPS) treatment. A VPS treatment consists of a 0.5 h submersion in tap water under a vacuum of 99 kPa (740 mmHg) followed by a 0.5 h submersion at a pressure of 413 kPa (3100 mmHg). The VPS-treated specimens were dried and reconditioned before testing.

Thickness Swell

The thickness swell specimens were tested according to ASTM D 1037 Section 103,[10] except that the test specimens were 50.8 × 50.8 mm (2 × 2 in.). Thickness measurements were taken at the midpoint of each edge (9.5 mm [0.375 in.] from the edge) and at the center of the sample.

Compression Shear

The compression shear specimens were tested dry according to ASTM D 1037 Section 143[10] using the

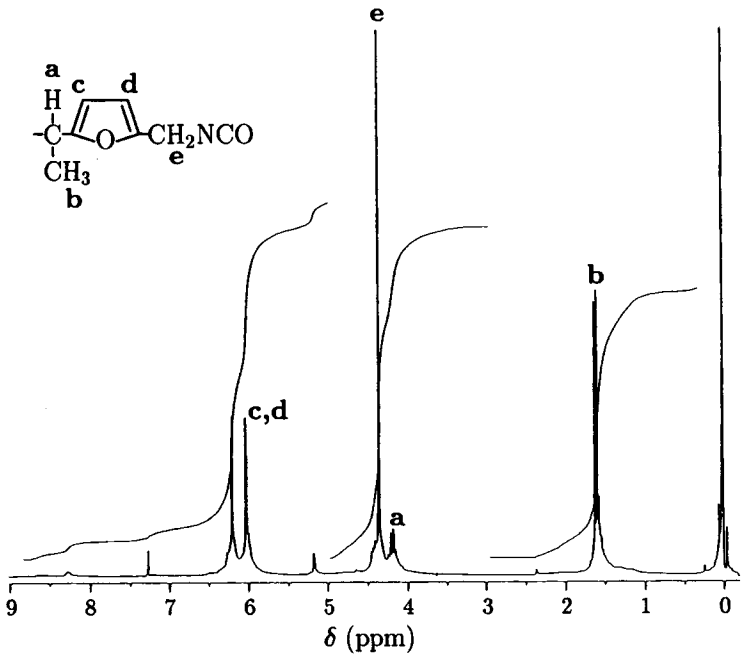

Figure 3 ^{1}H-NMR spectrum of EDFI.

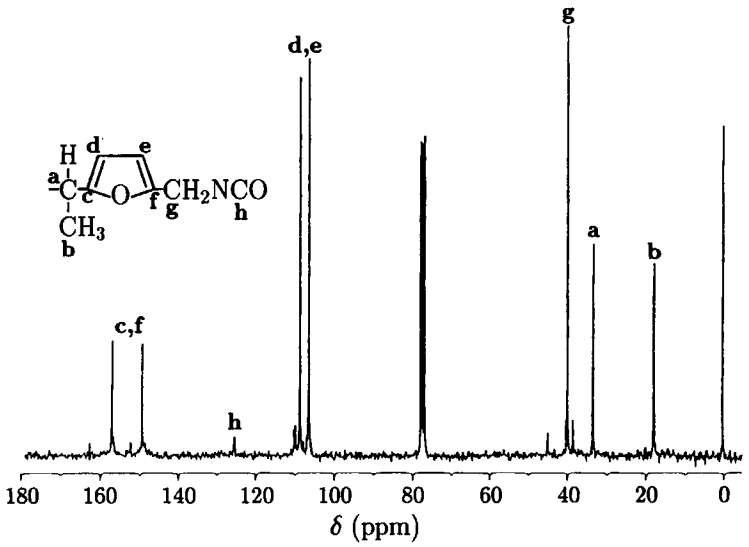

Figure 4 ^{13}C-NMR spectrum of EDFI.

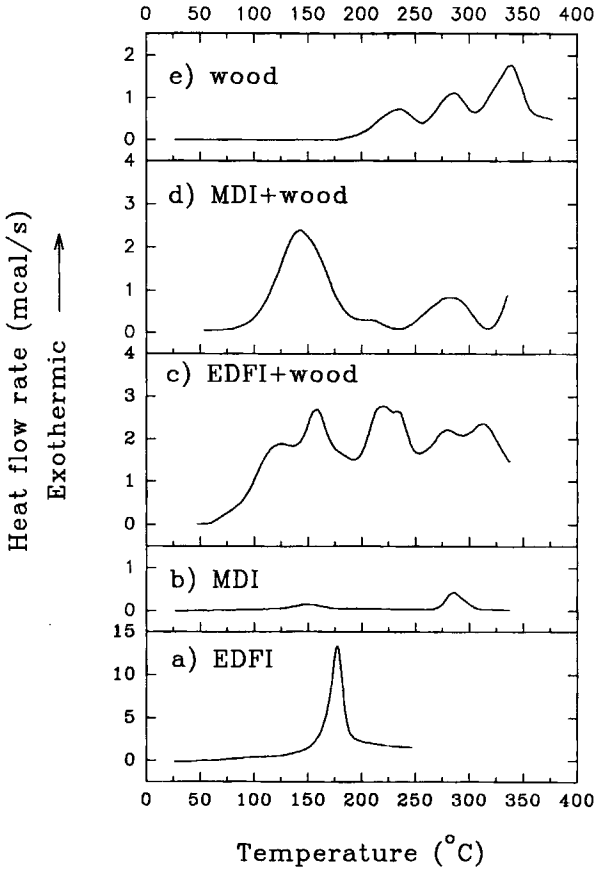

Figure 5 DSC thermograms of (a) EDFI, (b) MDI, (c) EDFI combined with an equal weight of aspen wood, (d) MDI combined with an equal weight of aspen wood, and (e) aspen wood.

Minnesota Shear Tester.[11] The thickness swell specimens were dried, reconditioned, and also tested using the Minnesota Shear Tester. These specimens were called wet to distinguish them from VPS-treated specimens.

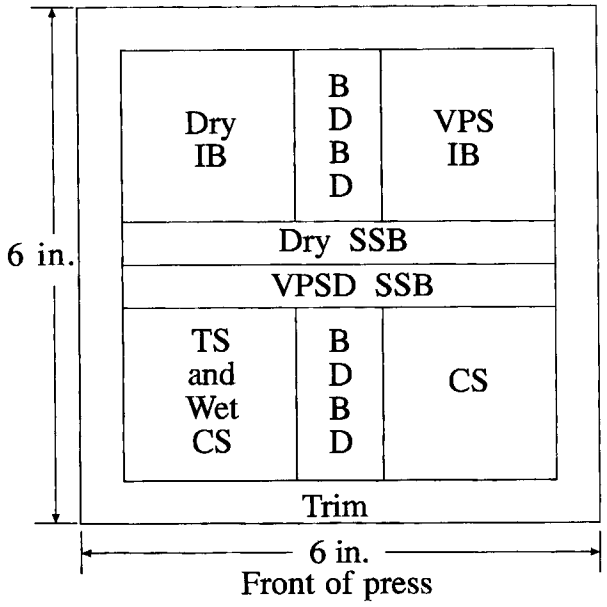

Figure 6 Pattern used for cutting test specimens from the flakeboards. The type of test performed on each specimen is indicated as follows: IB is internal bond; BDBD is boil–dry–boil–dry; SSB is small specimen bending; TS is thickness swell; CS is compression shear (1 in. = 25.4 mm).

Small Specimen Bending

Two bending specimens were tested on-edge according to APA Test Method S-6,[12] except that a 12.7 × 127 mm (0.5 × 5 in.) specimen was used instead of the standard 25.4 × 127 mm (1 × 5 in.) specimen. Smaller specimens were used so that two test specimens could be obtained from each flakeboard. One specimen was tested dry, and the other was tested after a VPS treatment. The VPS-treated specimens were dried and reconditioned before testing.

Boiling Endurance

Two specimens from each board were subjected to a boiling endurance test. This test consisted of a VPS treatment followed by two boil–dry cycles (10 min submersion in boiling water followed by 3.75 h in an oven at 107°C). The specimens were examined visually for crack formation and delamination.

RESULTS AND DISCUSSION

EDFI Characterization

Both the IR and ^{1}H-NMR spectra (Figs. 2 and 3, respectively) of EDFI closely matched the spectra of this compound that are reported in the literature.[8] The ^{13}C-NMR spectrum (Fig. 4) was also consistent with the proposed structure. However, no ^{13}C-NMR spectra of this compound are available in the literature for comparison. Stretching vibrations of the isocyanate group gave rise to the strong, broad absorption at 2240 cm^{-1} in the IR spectrum. The moderately strong carbonyl stretching vibration at 1730 cm^{-1} was associated with impurities, probably resulting from cleavage of the furan nucleus during synthesis. These impurities gave rise to a number of small resonances in the ^{1}H-NMR and ^{13}C-NMR spectra. The amounts of these impurities were relatively small as estimated from relative peak areas in the ^{1}H-NMR spectrum.

The DSC thermogram of EDFI [Fig. 5(a)] contained a large exothermic peak at 177°C. The DSC thermogram of MDI [Fig. 5(b)] contained a small exothermic peak at 287°C. Because these peaks occurred at temperatures that were not attained within the flakeboard mat, they are probably not associated with the bonding process. Rather, the peaks could be attributed to curing (cross-linking) reactions that occurred in the neat resin.

To investigate potential chemical interactions between the isocyanate resins and the wood during the bonding process, DSC thermograms were obtained for each resin in combination with ground aspen wood. The thermogram of EDFI with aspen wood [Fig. 5(c)] contained two exothermic peaks at 126 and 157°C. An exothermic peak appeared at 142°C in the thermogram of MDI with aspen wood [Fig. 5(d)]. These peaks occurred at temperatures likely to be attained throughout the flakeboard mat under the pressing conditions used. Furthermore, these exothermic peaks were absent in thermograms of the neat resins [Fig. 5(a) and (b)] and in a thermogram of aspen wood alone [Fig. 5(e)]. These observations provided strong evidence for chemical reactions of both isocyanate resins with wood and moisture in the wood. The importance of these reactions to the bonding process cannot be established from the present data.

Other researchers[13] attributed exothermic and endothermic peaks between 110 and 150°C in thermograms of MDI containing water to reactions that involved the formation of polyureas. These researchers also attributed an exothermic peak between 40 and 50°C in thermograms of MDI containing aspen to an unspecified reaction of MDI with wood. These researchers used open aluminum sample pans in their work, whereas sealed capsules were used throughout the present study. Consequently, it is difficult to draw definitive conclusions from comparisons of the results obtained in these two investigations.

The absence of an exothermic peak at 177°C in the thermogram of EDFI-containing aspen wood [Fig. 5(c)] implies that the EDFI was consumed by reactions occurring at lower temperatures. This observation provides additional confirmation that the exothermic peak at 177°C in the thermogram of neat EDFI was not associated with bonding. The thermograms of EDFI and MDI with aspen wood both contain exothermic peaks at temperatures greater than 180°C. Because these peaks occurred at temperatures greater than the pressing temperature, the reactions that produced these peaks were not considered to play a role in the bonding process.

Flakeboard Tests

A 2^2 full-factorial design was employed for this study. The two factors that were investigated were the type of resin (MDI compared to EDFI) and the EMC of the flakes (3% compared to 7%). The test specimens were evaluated for compression shear strength, internal bond strength, bending strength, water absorption, and boiling endurance. These

properties were found to be dependent on both the type of resin and the moisture content of the flakes.

Resin Effect

Results from the compression shear test are shown in Figure 7. The specimens labeled wet were the same ones used previously for the thickness swell tests. At 3% moisture content, flakeboards bonded with MDI exhibited significantly greater shear strength values, both dry and wet, than did those bonded with EDFI. However, at 7% moisture content, the shear strength values of flakeboards bonded with MDI decreased, whereas those bonded with EDFI increased marginally compared to the 3% moisture content flakeboards. At 7% moisture content, the differences in shear strength between flakeboards bonded with MDI or EDFI were not significant.

The internal bond strength values (tensile strength perpendicular to the board surface) of both dry and VPS-treated specimens are shown in Figure 8. The internal bond strength values exhibited the same trends with respect to the type of resin and the level of moisture content as were observed in the results of the compression shear tests. The lowest dry internal bond strength value that was observed for an individual flakeboard bonded with EDFI was 0.73 MPa (105 lb/in.^{2}). This value is well above the established standard of 0.41 MPa (60 lb/in.^{2}; Fig. 8)[14] for medium-density flakeboards. Hence, even the most poorly bonded EDFI flakeboard gave acceptable performance at 3% resin content. To the extent to which the internal bond test is a measure of the bonding efficiency of a resin, the results that were obtained with EDFI demonstrate its considerable potential for use as a wood adhesive.

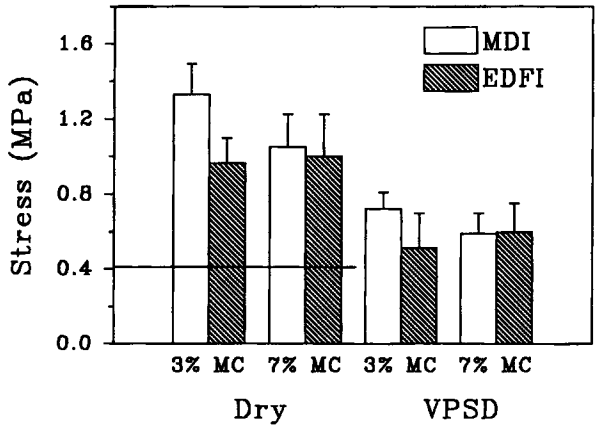

Figure 8 Results of internal bond test. T represents 1 standard deviation; horizontal line represents the ANSI A208.1 standard for type-2 medium-density particleboards; MC is moisture content.

For boards made from flakes with 3% moisture content, the internal bond strength of dry specimens averaged 1.33 and 0.97 MPa (193 and 140 lb/in.^{2}) for boards bonded with MDI and EDFI, respectively. Other researchers[15] reported a dry internal bond strength of 0.77 MPa (112 lb/in.^{2}) for aspen flakeboard made with MDI at a slightly lower density (700 kg/m^3) than those boards in the present study (720 kg/m^3). Even when an allowance was made for differences in density, the dry internal bond values obtained in the present study for flakeboards bonded with EDFI compared favorably with the results previously reported.

Data from the small specimen bending tests are shown in Figure 9. Although the test is called small specimen bending, it measures only breaking strength. Because the deflection of the sample was

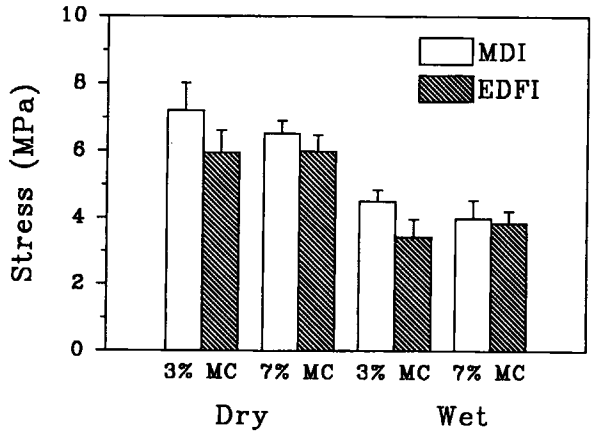

Figure 7 Results of the compression shear test. T represents 1 standard deviation; MC is moisture content.

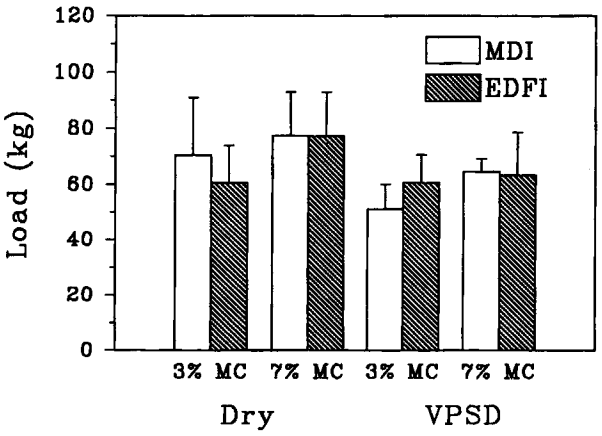

Figure 9 Results of small specimen bending test. T represents 1 standard deviation; MC is moisture content.

not measured as a part of this test, moduli were not determined. Data summarized in Figure 9 correspond to the averages of the maximum loads at failure. The breaking strength values of flakeboards bonded with the different resins were comparable. The only difference in breaking strength was that observed for boards constructed from flakes at 3% moisture content. The dry breaking strength was greater for flakeboards bonded with MDI than with EDFI. The breaking strength for VPS-treated specimens was greater for flakeboards bonded with EDFI than with MDI.

The percentages of thickness swell and weight gain are shown in Figures 10 and 11, respectively. After a 2 h soak, the flakeboards bonded with EDFI exhibited significantly greater water absorption and swelling than did the flakeboards bonded with MDI. After 24 h, this gap in water-absorption properties narrowed. The flakeboards made at the 7% moisture content no longer showed significant differences in thickness swell or weight gain.

All specimens remained bonded throughout the water-absorption experiment. In addition, all specimens survived the boiling endurance test. Although some EDFI specimens exhibited cracking along exposed edges, they did not delaminate. It should be noted that wax emulsions were not added to the flakeboards to impart water repellency.

Figures 7–11 indicate that considerable variability was associated with the experimental data. Much of this variability was probably introduced during the construction of the flakeboards. Approximately 5 mL of resin was used to make each flakeboard. Therefore, a variability of as little as 0.5 mL in the amount of resin between boards would be expected

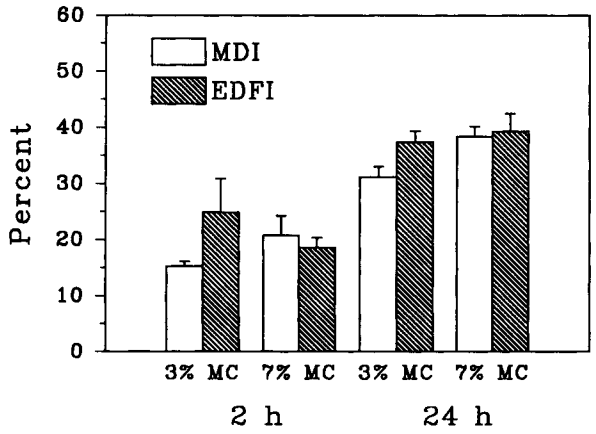

Figure 10 Percentage of thickness swell of flakeboards after 2 and 24 h submersions in water. T represents 1 standard deviation; MC is moisture content.

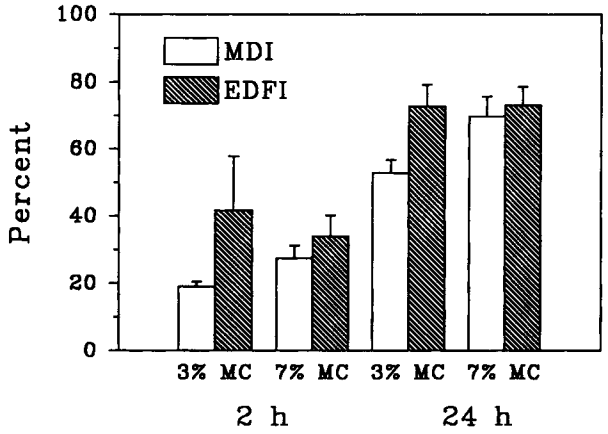

Figure 11 Percentage of weight gain of flakeboards after 2 and 24 h submersions in water. T represents 1 standard deviation; MC is moisture content.

to result in a large variability in mechanical properties. The retention of differing amounts of resin in the resin line of the blender between batches may have resulted in variabilities of this magnitude (±10%). The use of an undersized test specimen in the small specimen bending test may also have contributed to the high standard deviation in the data from that test.

The blending spray equipment produced a fine mist with the MDI resin that evenly coated the flakes. The EDFI resin did not atomize well, and the resulting mixture of small and large drops was not evenly distributed onto the flakes. Better mechanical properties of the finished board are generally associated with a finer, more even distribution of the resin onto the flakes. It is expected that optimization of the blending process for the EDFI resin will improve its bonding performance relative to MDI.

Flake Moisture Content Effect

In general, the properties of boards made at 3% moisture content were superior to those of boards made at 7% moisture content. This was true for all properties except breaking strength, which exhibited the opposite trend. Properties most affected by flake moisture content were internal bond strength and water absorption. The compression shear test was least affected by moisture content. The observed trends are in agreement with results that other researchers reported for the bonding of aspen flakes with isocyanate resins.[15–18] Experimental results indicated that the EDFI resin was less affected by flake moisture content than was the MDI resin.

CONCLUSIONS

Based on results of this study, the following conclusions are made:

1. The mechanical properties of flakeboards bonded with MDI are slightly superior to those of flakeboards bonded with EDFI. However, the differences in properties are small. Because EDFI is more viscous than is MDI, less than optimum atomization of the EDFI resin is probably responsible for some or all of the observed differences.
2. An increase in flake moisture content from 3 to 7% has an adverse effect on flakeboard properties. This result was observed with MDI, and to a lesser extent, with EDFI.

The results of this preliminary study demonstrate the considerable potential for use of difurfuryl diisocyanates obtained from renewable resources as wood adhesives. Optimization of resin distribution, press time, and press temperature for EDFI is expected to lead to improvements in its bonding performance. Additional research and development studies should be conducted to fully investigate the properties of difurfuryl diisocyanates and determine their suitability for use as adhesives for wood.

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