

Exterior Wood Adhesives by MDI Crosslinking of Polyflavonoid Tannin B Rings

Tannin-based exterior wood adhesives prepared by alkali- or acid-catalyzed condensation of polyflavonoid tannins with formaldehyde have already been described as substitutes for synthetic phenolic resins.^{1,2} The distinguishing characteristic of many of these adhesives is the necessity of increasing crosslinking by means of small amounts of simple phenolic or aminoplastic resins.^{1,2} In all industrially meaningful tannin-formaldehyde adhesives which have been developed, with one exception,² only the highly reactive resorcinolic A rings of the flavonoids are utilized, the catecholic or pyrogallolic B rings presenting such a low reactivity that only in extreme conditions of pH, time, and temperature would they be able to condense with formaldehyde.³ In order to increase crosslinking by involving the flavonoid B ring in the cured adhesive network, it is then necessary to use a reaction different from the condensation of the tannin with an aldehyde. 4,4-Diphenylmethane diisocyanate (MDI) and commercial "polymeric" methylene diisocyanate (MDI) can be used to react with the phenolic hydroxy groups of polyflavonoids. The MDI has been defined as "polymeric" since the commercial product is a complex mixture of the isomers of di- and triisocyanates and higher polymeric aromatic species.⁴

Both the A and B rings of the flavonoids will then be involved in the reaction with MDI since such a reaction is not dependent on the higher or lower nucleophilicity of such rings as in the case of the reaction with formaldehyde. Considering that the A rings can still be crosslinked by reaction with formaldehyde, the use of MDI will involve B rings crosslinking with further increase of strength of the cured tannin adhesive network. A new problem introduced with this system is the deactivation of isocyanate groups caused by the aqueous solvent used for tannin-based adhesives. The problem can be solved by partial benzylation of the tannin, before adhesive compounding, in order to dissolve the tannin extract in a more suitable solvent; but this system, though effective, is not economical.⁵

However, there are indications that even in presence of considerable amounts of water, isocyanate groups can still react with the hydroxy groups of the tannins. This note sets out to show that MDI can condense with tannin-formaldehyde resins, in the presence of water, to give cured exterior-grade wood adhesives networks of higher strength. The tannins of the hot-water extract of the bark of the black wattle tree (*Acacia mearnsii*, formerly *mollissima*) and Bayer Desmodur 44V20 "polymeric" methylene diisocyanate (MDI), both commercially available, were used for this study.

EXPERIMENTAL

To investigate if MDI is capable of reacting with phenolic hydroxy groups in the presence of the amount of water generally used in tannin-based adhesives solutions, the two following reactions were carried out: (1) Molten phenol, 15.7 parts by mass, were reacted under reflux for 30 min with 10.2

TABLE I
Resin Glue Mixes

Resins	Parts by mass weight					
	1	2	3	4	5	6
Wattle extract, spray-dried powder	60	60	60	60	60	60
Defoamer	0.3	0.3	0.3	0.3	0.3	0.3
Water	52	52	52	52	52	52
UF resin syrup, 63.8%	—	9.7	—	—	9.7	9.7
Commercial MDI (Bayer Desmodur)	—	—	18.1	12.0	18.1	18.1
Paraformaldehyde 96% powder	8.4	6.2	3.4	5.1	3.4	6.2
Water	10	10	25	35	25	30

parts of commercial "polymeric" MDI. (2) The same reaction was repeated after dissolving the phenol in 15.7 parts of water.

Light-brown precipitates were formed in both reactions, and after drying in a rotary evaporator, mass spectra were done by direct-probe insertion of the samples. Scanning was for a period of 10 min every 2 sec. The fragmentation pattern of the condensates formed showed that reaction of phenol with MDI had taken place in the presence of the considerable amount of water used for reaction. The fragments found indicating the occurrence of the MDI/phenolic hydroxyl reaction in the presence of water as well as their *m/e* percentages are listed in Table I.

Glue mixes in parts by mass, were prepared in order to test the effect of MDI/tannin crosslinking on the strength of tannin-formaldehyde adhesives (Table II). These glue mixes were used to glue beech strips 125 × 25 × 3 mm with a glued overlap at 25 × 25 mm, cured for 4 hr at 90°C at an equilibrium moisture content of 12%. The glued beech strips prepared and tested according to British Standard 1204, Part 2, for synthetic resin adhesives for wood gave the results shown in Table II.

Glue mixes 2 (control) and 6 were used to prepare triplicate plywood panels 60 × 60 cm in dimension using beech, pine, and okumé veneers under the following conditions: veneer moisture

TABLE II
Mass Spectra Fragment. "Polymeric" MDI/Phenol Reaction

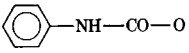
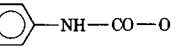
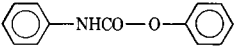
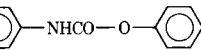
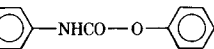
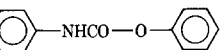
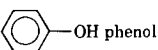
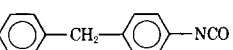
	MW	<i>m/e</i> percentage	
		A ring—no water present	B ring—water present
	136	0.9	6.9
HC- 	148	1.3	9.3
OCN—Ar—CU ₂ —Ar—OCONH	267	2.0	—
OCN—Ar—CU ₂ —Ar—OCONH—Ar	343	8.0	—
	213	1.1	3.4
C- 	224	1.1	12.8
CH- 	225	1.0	3.6
CH ₂ - 	226	0.9	—
	94	66.0	100.0
OCN-  -NCO	250	100.0	21.1
MDI ("dimeric")			

TABLE III
B.S. 1204 Beech Strips Test Results

	Glue Mix No.					
	1	2	3	4	5	6
Dry						
Shear strength, psi	731	765	759	786	829	840
Wood failure, %	98	100	99	100	96	100
Cold-water soak						
Shear strength, psi	626	551	591	595	613	735
Wood failure, %	75	98	64	85	92	85
Boil test						
Shear strength, psi	423	533	400	505	562	602
Wood failure, %	75	73	25	63	81	75

TABLE IV
B.S. 1088 Plywood Results

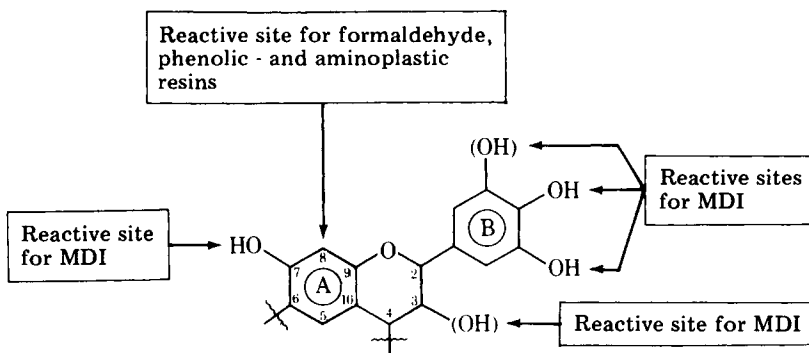
Veneer species	Glue mix no.	Assembly in mm	Pressing time, min	Knife test		Shear strength (in tension) test						
				Dry	24-hr cold soak	72-hr boil	Dry		24-hr cold soak		72-hr boil	
							Strength, psi	Wood failure, %	Strength, psi	Wood failure, %	Strength, psi	Wood failure, %
Beech	2	1 × 1 × 1	6½	0	0	0	337	5	280	13	214	0.0
	6	1 × 1 × 1	6½	4	6	4	441	95	425	90	287	0.0
Okumé	2	1.5 × 1.5 × 1.5	5	9	6	6	—	—	—	—	—	—
	6	1.5 × 1.5 × 1.5	5	10	8	9	—	—	—	—	—	—
Pine	2	3 × 3 × 3	5½	6	6	6	239	71	214	92	194	51
	6	3 × 3 × 3	5½	7	7	8	274	81	214	93	210	83

content, 5%; glue spread, 220–250 g/m² single glue-line; panel construction, 3-ply; veneer thickness, 1, 1.5, and 3 mm; pressing temperature, 125°C; no prepressing; open assembly (assembled, unpressed panel) time, 15–20 min; pressing time, 5, 5½, and 6½ min at 230 psi. Detailed conditions for each type of panel are shown in Table III.

After manufacture the plywood panels were hot-stacked overnight and then trimmed and cut into three 12.5 × 12.5-cm squares and in 15 × 2.5-cm strips. All the samples were tested dry, after 24 hr of cold-water soak and after 72 hr of boiling. The 12.5 × 12.5-cm samples were knife-tested according to British Standard 1088, 1957, for marine-grade plywood in which a bond rating from 0 to 10 is assigned, 0 indicating complete glue failure and 10 complete wood failure and stating that no glue line shall have an overall quality of less than 2 and the average value for all glue lines tested shall not be less than 5. The 15 × 2.5-cm strips were instead tested in tension according to the South African Bureau of Standards specification SABS 096-1965 for marine-grade plywood and the British Standard 1203, 1963, for synthetic resins for plywood, requiring an average strength in tension of not less than 200 psi for each glue-line. The results are shown in Table IV.

DISCUSSION AND COMMENTS

The strength test results in Tables III and IV as well as the types of fragments obtained by mass spectrometry show that commercial "polymeric" MDI is capable of reacting quite easily with the hydroxy groups of flavonoid A and B rings of tannins in water solution.



The best combination appears to be given by fortified (in this case by an aminoplastic resin) tannin-formaldehyde adhesives to which commercial "polymeric" MDI has been added and reacted with. The increase in strength of the tannin-based adhesive is probably due by the further crosslinking brought about by the reaction of MDI with the hydroxy groups of the flavonoids B rings. It is certain that part of the MDI will react with the hydroxy groups of the flavonoids A rings, but such reaction should not be reflected in significant strength improvements as the flavonoids A rings are more than sufficiently crosslinked through their reaction with formaldehyde and the hydroxymethylene groups of the fortifying aminoplastic resin.¹¹ The statistically significant improvement in strength observed is then mainly due to flavonoid B ring hydroxy groups and possibly the 3-hydroxy group in the heterocyclic ring.

"Polymeric" MDI performs better than pure 4,4'-diphenylmethane diisocyanate (MDI) as the distribution of aromatic polymeric species affords better probabilities of crosslinking and fortification. On the more practical side, an added advantage is the considerable improvement in the ease of spread of the adhesive afforded by the addition of MDI to tannin-based adhesives solutions, notwithstanding the significant increase in viscosity caused by MDI/tannin condensation and copolymerization. Furthermore, deactivation of isocyanate groups by the water present, which certainly does occur, does not appear to interfere significantly.

References

1. A. Pizzi and H. O. Scharfetter, *J. Appl. Polym. Sci.*, **22**, 1745 (1978).
2. A. Pizzi, *J. Appl. Polym. Sci.*, **23**, 2777 (1979).
3. A. Pizzi, *J. Polym. Sci. Polym. Polym. Lett. Ed.*, **17**, 489 (1979); *J. Appl. Polym. Sci.*, **24**, 1257 (1979).

4. G. W. Ball and R. P. Redman, Paper presented at FESYP Symposium, Hamburg, September 1978.
5. A. Pizzi, *J. Appl. Polym. Sci.*, to appear.
6. M. Gamo, S. Kocho, M. Kondo, and Y. Katsuzawa, *Nippon Setchaku Kyokaiishi*, **14**, 420 (1978).
7. British Standard BS 1204; 1965, Part 2, Specification for Synthetic Resin Adhesives for Wood.
8. British Standard BS 1957, Specification for Marine Grade Plywood.
9. South African Bureau of Standards SABS 096-1965, Specification for Marine Grade Plywood.
10. British Standard BS 1203; 1963, Specification for Synthetic Resin Adhesives for Plywood.
11. A. Pizzi, *Adhes. Age*, **20**, 27 (1977).

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