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A Universal Formulation for Tannin Adhesives for Exterior Particleboard

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ABSTRACT

A tannin-based adhesive formulation for particleboard based on the simultaneous reactions of small amounts of diisocyanates and formaldehyde with tannin extracts of the flavonoid type and useful to prepare good exterior grade particleboard is presented and discussed. The adhesive performs well when using any kind of flavonoid-type tannin extract.

INTRODUCTION

The use of polyflavonoid tannins as thermosetting adhesives for wood products is not new. Several examples of excellent tannin-based adhesives satisfying the requirements of various industrial applications have already been reported [5, 9, 10, 13, 14]. Most of these developments used the tannins from the bark extract of the black wattle tree (Acacia mearnsii formerly mollissima) [9-14], the wood extract of the quebracho tree (Schinopsis lorentzii and Schinopsis balansae), or the bark extract of the hemlock tree (Tsuga heterophylla) [5], which are, or have been, commercially available. Several attempts have also been made at utilizing the tannins of the bark of other Acacia species (i.e., Acacia Nigra [8]), of various pine species (i.e., Pinus Radiata [15, 16] and Loblolly pine [4, 16], i.e., Pinus

taeda and Pinus Elliotae), and of a variety of other vegetable species yielding a variety of condensed tannins such as mangrove [14] and sumach (Rhus Lancea). Other flavonoid-yielding species such as Eucalyptus camaldulensis, Mirica nagi, and Ouratea spp. [3], have not been investigated for adhesives. Fundamental studies carried out by different authors on the composition of the extracts of all these species and of the chemical structure of the polyflavonoid tannins in such extracts have shown that fundamentally important differences exist between all these extracts. The considerable difference in the structure of the flavonoid constituting the phenolic part of all these extracts has rendered impossible the development of universal formulations which would work for all the different extracts. Such differences effectively prevented the application of adhesive formulations developed for one extract to most of the other extracts.

On careful observation, all the difficulties encountered, be they due to different phenolic contents on the extracts, to different chemical structures of the flavonoid units and of the flavonoid polymers, or to differences in physical characteristics and properties such as viscosity, molecular size, and reactivity, are all and only related to the important fact that all the adhesives formulations conceived up to now are based on the reaction of these tannin extracts with formaldehyde.

Once this point is realized it becomes easier to understand that to arrive at a truly universal tannin adhesive formulation, it is necessary to use a reaction which is based on the common chemical characteristics of all the various tannins. The reaction with formaldehyde is only one of them. Together with the presence of phenolic nuclei, which is common to all the condensed-type tannins and which automatically leads to the choice of formaldehyde as a cross-linking reagent, all condensed tannins of the flavonoid type are rich in phenolic hydroxy groups. Furthermore, the impurities present in all tannin extracts are mainly sugars and hydrocolloid gums which are also rich in hydroxy groups. Hence a second type of common chemical group, the hydroxyl group, can be used for cross-linking adhesives based on condensed tannins. There are other chemical groupings common to all tannins, such as the ether group of the flavonoids etherocyclic ring, which can also be used; for instance, acid hydrolysis of the etherocyclic ring of all condensed tannins leads to autocondensation reactions and the formation of "phlobaphenes" [17]. It is of course unnecessary to rely on the use of one reaction or one type of reactive group only. Combination of two or more types of cross-linking reactions can considerably improve the practical results obtained. Because the scope of the work presented in this paper is to produce adhesives for exterior grade particleboard, and because wood rapidly deteriorates in acid conditions, it is safe to discard from the list of suitable reactions the acid autocondensation of tannins by hydrolysis of the flavonoid ring and consequent formation of "phlobaphenes."

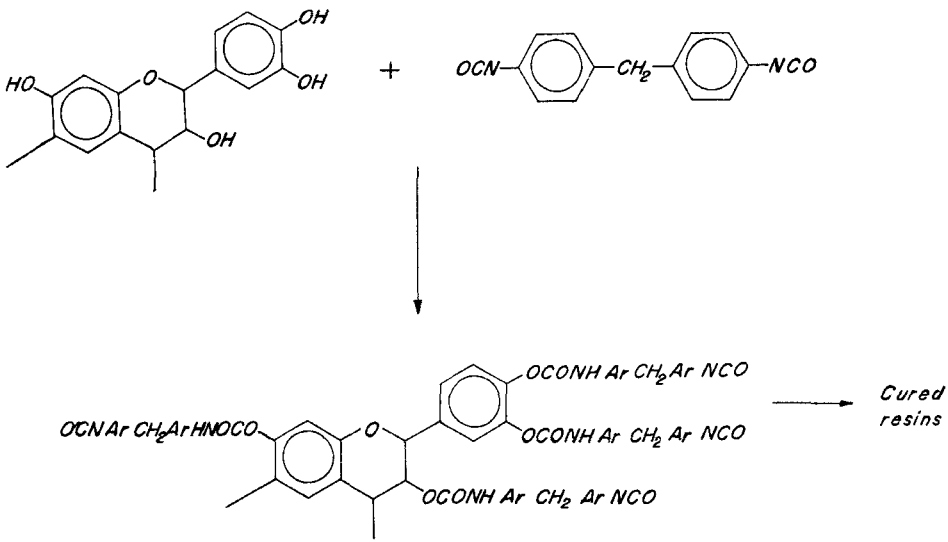
The hydroxyl group, common to all tannins, should instead deserve

closer consideration. Organic compounds carrying two or more hydroxyl groups of any nature can react with a variety of reagents such as epichloridrin to form epoxy resins and diisocyanates to form polyurethanes. While the former is indeed a very expensive reagent when used for the bulk manufacture of wood adhesives, the latter, the diisocyanates, if used in moderate amounts, is a more attractive economic proposition. Several factors must be kept in mind when trying to use diisocyanates.

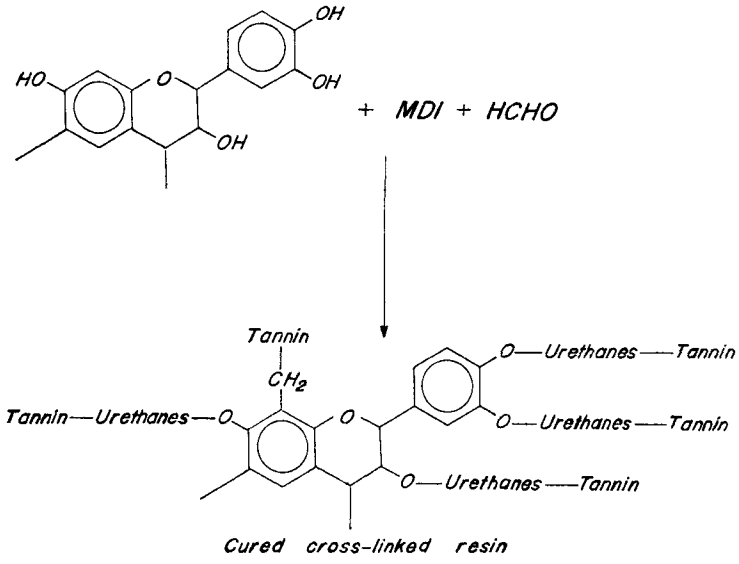
1. They are already used as wood adhesives though still presenting several practical problems [2].
2. They are true exterior grade adhesives though they are used in much greater amounts than at the low levels claimed [1].
3. The isocyanate group has been proved to be deactivated by water much less readily than previously thought when in presence of a phenol [11]. Consequently the reaction of a water solution of a tannin extract with a diisocyanate is a distinct possibility whether it is used alone or in combination with the reaction with formaldehyde.

The diisocyanate used in the experiments presented was commercial 4,4'-diphenylmethane diisocyanate, or MDI, which is readily available.

The reactions involved are the following:



By decreasing the amount of the relatively expensive MDI and combining the formation of the urethane with the reaction of the phenolic nuclei of the tannin with formaldehyde, the reaction will be



EXPERIMENTAL

The resin glue mix was obtained according to the following procedure: To a 44% water or water/methanol solution of any flavonoid-type tannin extract of a phenolic content of 55-60% or higher and containing 0.25% commercial defoamer are added, under continuous stirring, wax emulsion and water. Immediately before spraying, MDI is added to this mixture and the mixture is sprayed onto the wood chips. Paraformaldehyde is added simultaneously to the wood chips, in powder form, before resination, according to industrial procedures already reported [12]. In laboratory-type batch gluing experiments, the paraformaldehyde can best be added to the resinated wood chips after they have been sprayed with the liquid part of the adhesive, and the mixture stirred by mean of the glue blender.

The proportions, by mass, of the different materials in the glue mixes are shown in Table 1. The proportions of resin solids applied onto the chips, these being calculated as the sum of tannin extract solids + MDI, were 10 and 18% for core and surface chips, respectively, in glue mixes 1-4. This means that in glue mix 1, 10% tannin extract was added to the core chips; in glue mix 2, 9% tannin extract solids and 1% MDI; in glue mix 3, 8% tannin extract solids and 2% MDI; and in glue mix 4, 7% tannin extract solids and 3% MDI. Glue mixes 5, 6, and 7 were control glue mixes in which 1, 2, and 3% MDI alone were added to the core chips to study the contribution of MDI to the results obtained with glue mixes 2, 3, and 4, respectively. In glue

TABLE 1. Glue Mixes in Parts by Mass

Formulation type	1:100 tannin	2:90 tannin, 10 MDI	3:80 tannin, 20 MDI	4:70 tannin, 30 MDI	5:100 MDI	6:100 MDI	7:100 MDI
Tannin extract solutions 44%	250	225	200	175	-	-	-
Paraformaldehyde 96%	15	14	12.5	11	-	-	-
MDI	-	11	22	33	11	22	33
Wax emulsion	22	22	22	22	22	22	22
Water	60	80	110	135	100	100	100

TABLE 2. Particleboard Results

Glue mix no.	Adhesive type	Core glue solids (%)	Density (g/cm^3)	Swelling after 2 h boil measured wet (%)	Swelling after 2 h boil measured dry (irreversible swelling) (%)	Original internal bond (tensile perpendicular) (kp/cm^2)	Internal bond after 2 h boil (V100) (kp/cm^2)	Internal bond retention (%)
1	100 Tannin	10 Tannin	0.700	44.6	31.8	3.25	-	-
2	90 Tannin: 10 MDI	9 Tannin: 1 MDI	0.663	44.2	31.5	4.95	-	-
3	80 Tannin: 20 MDI	8 Tannin: 2 MDI	0.666	28.0	15.9	4.69	1.31	27.7
4	70 Tannin: 30 MDI	7 Tannin: 3 MDI	0.690	15.0	4.3	8.39	4.24	50.6
5	100 MDI	1 MDI	0.667	-	-	0.45	-	-
6	100 MDI	2 MDI	0.670	-	-	1.54	-	-
7	100 MDI	3 MDI	0.700	72.2	38.5	5.39	0.35	6.5
Commercial phenol/formaldehyde control		-	0.654	13.8	3.0	5.92	3.37	57.0
Commercial modified tannin/formaldehyde control		10 modified tannin	0.702	12.8	2.2	13.1	6.9	52.7
German standard DIN 68761 (2)							Minimum 1.5	

mixes 5, 6, and 7, 5.5% MDI was added to the surface chips. In glue mixes 5, 6, and 7, the water was sprayed onto the wood chips before the spraying of the MDI to avoid any deactivation of the isocyanate groups which would impair the efficiency of the adhesive.

The pressing conditions used to press duplicate 600 × 600 × 12 mm particleboard were the following: Moisture content (glue mixes 1, 2, 3, and 4), core = 18%, surface = 22%; (glue mixes 5, 6, and 7) core and surface = 10% maximum pressure = 25 kg/cm^2; pressing time = $7\frac{1}{2}$ min.; pressing temperature = 170°C.

TESTING

Twelve specimens, 50 × 50 mm, were cut from each of the duplicate boards. Six specimens were tested for internal bond in tensile perpendicular dry and the other six underwent the V100 treatment of the German standard DIN for exterior grade particleboard. The results obtained are shown in Table 2.

DISCUSSION

The results obtained for laboratory boards prepared with mixtures of a flavonoid-type tannin extract, a diisocyanate and formaldehyde, show that this type of formulation, in the case of a 70:30:mass:mass ratio of tannin extract:MDI, can be used for the production of good exterior grade particleboard. The results are very similar for all the tannin extracts used, and while excellent particleboard adhesive formulations of proven industrial reliability have already been reported [9] when using only the condensation reaction of the tannin with formaldehyde, these were obtained by the use of unmodified tannin extracts, in commercial use, and are somewhat easier to handle than the tannins yielded by some of the more unusual tree species. The advantages of the 70:30 tannin extract:MDI adhesive formulation are:

1. The ease of preparation. The tannin extract does not need to be chemically modified before use.
2. The adhesive does not need to be prepared by an adhesive manufacturer but can be assembled directly by the end user by purchasing materials easily available commercially.
3. Any tannin extract of the flavonoid type can be used with good results in this formulation, allowing the utilization of tannins more difficult to handle than those currently available and the use of materials which are currently considered as waste.
4. The tannin adhesive formulation described can be used industrially as described in this article or by spraying separately onto the wood chips the tannin solution and the diisocyanate in

(i) the same glue blender or (ii) each in a separate glue blender, with the two blenders in line as described for other wood adhesives [18]. The use of these techniques allows improved pot-life during industrial application.

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