Tannin/Polyurethane Adhesives for Bonding Aluminum

Tannin-based adhesives for wood have already been reported by different authors[1,2,4,5]. These tannin-based adhesives behave similarly to synthetic phenol/formaldehyde or phenol/resorcinol/formaldehyde resins. This similarity in behaviour could be extended to the preparation of phenolic-modified urethane adhesives for metal bonding. A tannin-based adhesive could be used as the modifying phenolic resin as compatibility of certain types of polyurethanes with condensed tannins has already been reported.[3] This paper deals with the preparation of a modified tannin/formaldehyde/polyurethane hot-curing adhesive to bond aluminum to aluminum.

EXPERIMENTAL

Preparation of Tannin/Formaldehyde Adhesive

A tannin/resorcinol/formaldehyde adhesive already reported[4] for wood application was prepared as follows:

A mixture of 259 parts of a 59% aqueous solution of commercial wattle extract powder (extract of the bark of *Acacia mearnsii*), 42.2 parts methanol, 0.8 parts commercial defoamer, and 74.9 parts 99% resorcinol was prepared at ambient temperature. To this mixture 24.5 parts 38% formalin solution and 20 parts of a 45% aqueous sodium hydroxide solution were added still at ambient temperature. The mixture was brought to 70°C and held there for 1 hr, then cooled and stored.

Polyurethane Adhesive

The polyurethane adhesive used is a commercially available product having the following composition: adipic acid/butadienediol/MDI polyurethane; adipic acid/hexanediol/MDI polyurethane; Morthane CA 11 (crystallizing thermoplastic polyurethane adhesive, Morton Chemical Co., Morton-Norwich Products, U.S.A.); Aerosil silica smoke to increase thixotropy; vinylacetate/vinylchloride copolymer (Vynilite VMCH, Union Carbide); ethyl acetate:acetone 50:50 as solvent.

Adhesive Mixing

To 75 parts by weight of the polyurethane adhesive were added 25 parts by weight of the tannin/formaldehyde adhesive prepared and 1.6 parts 96% paraformaldehyde powder as hardener for the tannin-based adhesive. The two adhesives are compatible and form a homogeneous high-viscosity solution.

Testing

Aluminum blocks 30 mm × 25 mm in size were etched with a 15% sodium dichromate/conc. H_2SO_4 mixture (4:1) and then coated with the mixed adhesive and left to dry as indicated in Table I (assembly time), and pressed together at 200–250 psi in a G-clamp. Each two aluminum blocks are glued in such a way that the glued overlap is 25 mm × 25 mm and steps of 5 mm on each side of the glued blocks are left unglued to facilitate gripping of the specimens during shear strength testing. The appearance of the specimens before shear strength testing is the same as shown for block shear strength specimen in the Federal test methods standard 175, Method 1031.[6] The specimens, still clamped, are cured in an oven for different lengths of time and at different temperatures (Table I).

After cooling to ambient temperature and releasing from the holding clamp, the specimens are tested for shear strength in a Universal testing machine at a constant speed of 2.5 mm/min. The results are shown in Table I.

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TABLE 1
Shear Strength Results of Aluminum Blocks Bonded with Tannin/Polyurethane Adhesive

Adhesive type	Open assembly time, min	Curing time, min	Curing temperature, °C	Shearing strength (average), psi
Tannin/polyurethane	5	25	145	786
	5	60	145	1199
	0	15	175	663
	0	35	175	627
	0	45	175	614
	5	15	175	1274
	5	35	175	2283
	5	45	175	2158
	45	15	175	1641
	45	35	175	2235
	45	45	175	1982
Polyurethane control	5	35	175	766

DISCUSSION

The results shown in Table I indicate that addition of a small amount of a tannin/formaldehyde adhesive to a polyurethane adhesive that is compatible with it will greatly increase the strength of aluminum to aluminum joints glued with the polyurethane adhesive. Optimum conditions of cure appear to be 35 min at 175°C. The upgrading effect that the tannin-based adhesive has on the polyurethane is open to discussion. However, it may be assumed that three crosslinking mechanisms are present: (i) the tannin crosslinking through the formation of methylene bridges during the reaction with formaldehyde, (ii) the polyurethane crosslinking with itself, and (iii) the polyurethane crosslinking with the tannin by reaction of the free isocyanate groups present in the polyurethane adhesive with the alcoholic and phenolic hydroxyl groups present in the tannin. The latter crosslinking mechanism is probably the one giving the considerable higher joint strength than that given by the polyurethane adhesive alone. The presence of water and methanol contributed by the tannin-based adhesive will deactivate part of the isocyanate groups of the polyurethane adhesive, but from the results obtained it can be deduced that the reactive isocyanate groups do react at least to some extent with the tannin hydroxyl group. The tannin-based adhesive alone cannot be used for metal bonding as it presents little or no adhesion to metallic substrates. Furthermore, the highest strength recorded for this type of tannin-based adhesive on wood is of the order of about 1200 psi, considerably lower than what has been obtained by mixing the tannin and the polyurethane adhesive. It cannot be excluded that tannin/polyurethane adhesives could be used for other metallic or nonmetallic adherends.

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