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Termite resistance and wood-penetrability of chemically modified tannin and tannin–copper complexes as wood preservatives

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Abstract We examined the ability of chemically modified tannin and tannin–copper complexes to penetrate wood and the ability of the treated wood to resist termites. Only the tannin-treated wood retained the agents after treatment. Wood with untreated mimosa tannin (MT) retained the least amount, followed by wood with resorcinolated tannin (RMT) and that with catecholated tannin (CMT). When RMT or CMT was mixed with ammonia–copper, the wood retained twice as much of these solutions as the MT – ammonia–copper solution. The degree of retention of RMT–NH_3–Cu and CMT–NH_3–Cu ranged from 268 to 326 kg/m^3. The solutions penetrated 2–13 mm from the tangential sections of the logs. We also measured the termite resistance conferred by these solutions. Most of the tannin–NH_3–Cu solutions showed contact lethality for termites in the contact toxicity test. However, the termites were fed cellulose treated with those solutions and most survived the oral toxicity test (14 days). Moreover, these solutions reduced the amount of damage to the wood by termites. However, the mortality rate of the termites during the eating-damage test (>21 days) did not reach 100% for any of the solutions except for RMT. As a result of the field stake test with the same log's used for the penetrability test, the mass loss of wood treated with RMT or CMT alone or with RMT + NH_3 + $CuCl_2$, was about one-third to one-half that of the controls. Because these solutions have good wood penetrability and good termite resistance, they have potential use as low-toxicity wood preservatives.

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Key words Chemically modified condensed tannin · Tannin–copper complex · Penetrating ability · Pressure treatment · Termite resistance

Introduction

It is well known that tannin exhibits antibacterial action and enzyme inhibition. Laks et al.[1] studied the use of condensed tannin and copper as wood preservatives and reported that injecting sulfited bark extract followed by $CuCl_2$ solution made wood blocks resist decay by *Trametes versicolor*. However, the decay-resisting ability of one-step-treated wood blocks was no greater than that of two-step-treated blocks using a solution of sulfited bark extract mixed with copper–ammonia.

Ohmura et al.[2,3] examined the termite-resisting ability of flavonoids and noted the following. Although taxifolin is the main feeding deterrent for termites in Japanese larch, taxifolin is disintegrated by steam treatment. Furthermore,[3] for the relations between the structure of some flavonoids and antifeeding activity, it was found that compounds containing two hydroxyl groups at C-5 and C-7 in A rings showed high antifeeding activity. The presence of a carbonyl group at C-4 in the pyran rings of the compounds was necessary for the high activity.

We have done developmental research on a wood preservative using chemically modified tannin and tannin – metal complexes that can be injected for a one-step treatment. As a result, preservatives have been developed using chemical pretreatment of mimosa tannin (MT), resorcinolated MT (RMT), and catecholated MT (CMT) with the addition of copper. The antidecay superiority of these preservatives has already been reported.[4,5]

In this investigation, to put these tannin and tannin–copper complexes to practical use as low-toxicity wood preservatives, we assessed the ability of these solutions to penetrate wood during pressure treatment. We also measured the ability of the treated wood to resist the termite *Coptotermes formosanus* Shiraki.

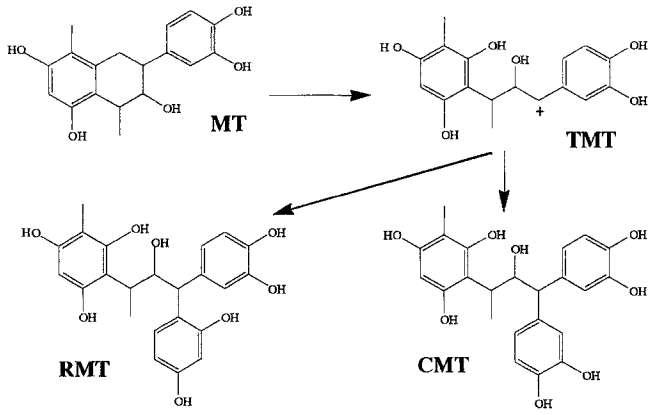

Fig. 1. Chemically modified tannins. *MT*, untreated mimosa tannin; *RMT*, resorcinolated; *CMT*, catecholated; *TMT*, intermediate (trichloroacetic acid treated)

Experiments

Preparation of chemically modified tannin

MT, RMT, and CMT were prepared as described in a previous report.[4] Structures of the chemically modified tannins are shown in Fig. 1.

Preparation of treatment solution

The pressure treatment solutions containing unmodified or chemically modified tannin were mixed with an ammonia and cupric chloride aqueous solution.

Tannin–NH_3–copper solutions (MT–Cu, RMT–Cu, CMT–Cu): An 18% ammonia aqueous solution was added to a 5% tannin solution, and then 0.1 M $CuCl_2$ aqueous solution was mixed with the tannin–ammonia solution in a volume ratio of 15:14:15.

Tannin–NH_3 solution (MT–NH_3, RMT–NH_3, CMT–NH_3): A 5% tannin solution, 18% ammonia aqueous solution, and deionized water were mixed in a volume ratio of 15:14:15.

Tannin solution (MT, RMT, CMT): A 5% tannin solution and deionized water were mixed in a volume ratio of 15:29.

Copper solution (Cu): A 0.1 M $CuCl_2$ aqueous solution and deionized water were mixed in a volume ratio of 15:29.

NH_3 solution (NH_3): An 18% ammonia aqueous solution and deionized water were mixed in a volume ratio of 14:30.

Penetrability test

Wood for penetrability test

Four log specimens (45 cm long) were prepared from an air-dried Japanese cedar (sugi, *Cryptomeria japonica* D. Don) log (10 cm diameter, 2 m long) from which the cambium layer had been removed. The specimens for comparison were prepared from the same log. The cross sections of two log specimens used to examine the penetrability from both cross sections and tangential sections were not sealed with silicon resin. The cross sections of the other two specimens were sealed with silicon resin.

Pressure treatment, retention of solution, and observation of penetrated area

Pressure treatment was used a reduced-pressure treatment apparatus (SBK-300; Yasujima). MT, RMT, and CMT and the complex solutions of these tannins and Cu ions were used as pressure treatment solutions. Unmodified MT, RMT, and CMT solutions were pressure treated into the log specimens in a one-step procedure.[4] Four log specimens were placed in a specimen container with each treatment solution in the pressure treatment apparatus. A weight was placed on the specimens to prevent them from rising from the solution. The pressure treatment apparatus was decompressed to 60 mmHg and maintained at this pressure for 30 min. Pressurization in the apparatus was then increased with an air compressor. Each 2 kg/cm^2 increase was maintained for 5 min up to 6 kg/cm^2. The highest pressure reached was 9.3 kg/cm^2, which was maintained for 30 min; then the pressure was returned to ambient pressure. Retention of the agent (kg/m^3) was calculated from the weight differential of each log specimen before and after pressure treatment.

Five disks (each 2 cm in thickness) were cut from the cross section of each log. The color change in each disc section was filmed with a digital camera. A printout was made of the image which was cut and divided into the penetrated part and the unpenetrated part. The penetrated area of the treatment solution was calculated from the weight of each part.

Termite resistance test

The tests of contact and oral toxicity and the wood eating-damage test followed Standard 12 (1992) of the Japan Wood Preserving Association's "Examination method of termite prevention competence of termite inhibitor for wood by coating, spraying, or soaking." Furthermore, the logs used to evaluate the penetrability were submitted to the field stake test. *C. formosanus* Shiraki was used for the tests.

Contact toxicity test

A 1.5% Bacto Agar aqueous solution (1 ml) was added to 3 g of quartz sand, and the mixture was dried and used as the control quartz sand. These samples of control quartz sand were treated with 1 ml of each agent solution and dried. A 2-g portion of the control and of the treated quartz sands were spread in half the area of a Petri dish. A separation 5 mm wide was established between the sands.

Ten worker termites were put in each Petri dish. The dishes were placed in an incubator (28° ± 2°C) and left

for 14 days. The initial moisture levels were maintained. Observations of termite health status and the number of dead termites were made every 2h for 8h on the first day and every 24 hours from the second day onward. Each examination was repeated three times.

Oral toxicity test

Cellulose powder dyed with Oil Red BB was treated with each agent and then dried. Tablets (5mm in diameter × 2mm thick) were prepared from each cellulose powder sample by packing and hardening in a plastic pipe (inside diameter 5mm). One tablet was placed in an acrylic vessel with an open pore at the center of the bottom, and gypsum was used to cover the pore.

Twenty-five worker termites were placed in the vessel and bred for 14 days in an incubator (28° ± 2°C); any moisture lost was supplied from the bottom of the vessel. The color and health of the termites and the number of dead termites were observed during the breeding period at the same schedule described above. Each examination was repeated three times.

Wood eating-damage test

The wood used in this test was sapwood [two radial sections, 20 (L) × 10 (R) × 10 (T) mm] from Japanese black pine (*Pinus thumbergii* Parl). For each test solution, ten specimens were placed in a desiccator. A weight was placed on the specimens to prevent them from floating to the surface. The desiccator was depressurized with a vacuum pump (exhaust velocity 100l/min) for 30min. The pump was stopped, and an agent solution was added through a vinyl pipe. The desiccator was returned to ambient pressure and left overnight. The excess solution was removed from the specimens, and they were then air-dried. The specimens were dried at 60°C for 48h before and after pressure treatment and weighed after drying.

Five treated specimens were subjected to a leaching test, which was repeated ten times. Each time the specimen was dipped in distilled water for 30s, then kept in a desiccator at 26°C for 4h, and dried at 40°C for 20h. The weight of each specimen was measured after drying at 60°C for 48h. The degree of retention (i.e., weight gain, WG) of the agent was calculated from the difference in the weights of the specimen before and after pressure treatment and the leaching test.

Each specimen was placed in a vessel (8cm in diameter, 5.5cm deep) made from an acrylic pipe blocked at one end with gypsum. Altogether, 150 worker termites and 15 soldier termites were selected at random and placed in the vessel. They were bred in an incubator (28° ± 2°C) for 21 days. Any water lost was replenished from the bottom of the vessel.

The fouling that had adhered to the specimens during the breeding period was removed, and the specimen was dried at 60°C for 48h. The weight loss of the specimen was calculated from its weight before and after the eating-damage test. The number of dead termites was recorded. Each test was repeated five times.

Field stake tests

Logs (35cm long) that had been removed 10cm from the cross section to measure the penetrated area in the penetrability test were used for the field stake tests. The logs were buried about 20cm in soil from the cross section (without sealing). The logs were inserted into soil 2–5m from a scrap wood storage place where *C. formosanus* was known to live in thickets of bamboo and shrub at Kyushu University (Higashi-ku, Fukuoka, Fukuoka-ken, Japan). The logs were separated by at least 30cm. Control logs were installed in soil within 4m from the scrap wood and were left there for 40 months, from October 9, 1997, to February 8, 2001. After the test period, the stakes were dug out and any adhering mud brushed away. Termite resistance was later evaluated. The weight of the specimens before and after the field test was measured after drying at 23°C and relative humidity (RH) of 55%; the mass loss was then calculated.

Results and discussion

Ability to penetrate wood

Comparisons of MT, RMT, and CMT and the effects of ammonia–copper treatment were undertaken. Table 1 shows the retention of each agent. We also compared the area penetrated by each agent in sections 2, 4, 6, 8, and 10cm from the cross section (root side) of the log (Table 2).

The retention of the penetrating agent in samples with unsealed cross sections increased in the order MT, RMT, and CMT. There was little difference in retention levels of MT, RMT, and CMT solutions in samples with unsealed cross sections. However, retention of NH_3–Cu combined with RMT or CMT were about 1.3–1.7 times higher than that of the agent with MT. The retention of specimens with sealed cross sections were about 1.7–2.1 times higher than that of the NH_3–Cu combined agent with MT.

During the pressure treatment of log specimens in which the cross section was sealed, the agent had penetrated 2–13mm from the tangential section of the log (the surface of the log). When the penetrated areas in the cross section were compared (Table 2), for the tannin solution only and

Table 1. Retention of agent

Tannin	Tannin		Tannin–NH_3–Cu	
	Open	Sealed	Open	Sealed
MT	462	206	472	159
RMT	497	239	614	268
CMT	535	235	822	326

Retention as expressed as kilograms per cubic meter
Data are for open and sealed cross sections
MT, untreated tannin; RMT, resorcinolated tannin; CMT, catecholated tannin

the unsealed cross section the penetratied area suddenly decreased with increased distance from the cross section. However, in the case of CMT–NH_3–Cu and RMT–NH_3–Cu in particular, there was a slight decrease in the amount of penetration with distance from the cross section. Even in specimens with sealed cross sections, the penetrated area of the cross section 10 cm from the log end comprised 22% and 13% of the area of the cross section, respectively, in specimens treated with CMT– and RMT–NH_3–Cu.

We believe that the increased retention of the solution was due to chemical modification of tannin. The chemical modifications were accompanied by cleavage of the tannin C-ring and the increment in hydrophilicity with the addition of catechol and resorcinol to the structure of the tannin (Fig. 1). The reason for increased retention of the tannin–ammonia–copper solutions was also probably due to an alteration in the solubility of tannin with the addition of ammonia.

Table 2. Effect of pressure treatment conditions on the penetrated area

Tannin	Distance from cross section (cm)	Penetrated area (%)			
		Tannin		Tannin-ammonia-copper	
		Open	Sealed	Open	Sealed
MT	2	100	6	94	7
	4	95	4	69	3
	6	91	5	58	4
	8	30	6	28	7
	10	19	5	27	7
RMT	2	95	17	79	17
	4	77	15	69	13
	6	35	15	62	9
	8	32	14	57	10
	10	29	16	58	13
CMT	2	84	15	96	16
	4	76	9	95	14
	6	41	10	84	11
	8	22	9	63	15
	10	19	11	69	22

The retention levels of the specimens treated with chemically modified tannin–NH_3–Cu, which showed superior preservative ability,[4] was 268–326 kg/m^3 for specimens from sealed logs. These levels of retention were equivalent to those demonstrated by pressure treatment of a pole of *C. japonica* with chromated copper arsenate (CCA) to be 180–300 kg/m.[3,6]

Termite-resisting ability

Contact toxicity test

Table 3 shows the mortality of termites during the contact toxicity test. The mortality was 100% for CMT– and CMT–NH_3-exposed termites at the third day. The ability of a series of CMT and RMT agents to protect wood from termites was equal to that of agents with copper. There was no difference between termite mortality with control quartz sand and that with the agent-treated quartz sand for any agent tested.

Oral toxicity test

Table 4 shows the mortality of termites in the oral toxicity test. The mortality of the termites that ate cellulose powder pellets treated with MT–NH_3 or RMT–NH_3 was 100% by the 12th day. However, when the termites were fed cellulose powder treated with other agents, the mortality was less than 100% by the 14th day. The bodies of all termites that had been bred with the pellets were dyed red, and thus it was clear that the termites had eaten those pellets.

Wood eating-damage test

Figure 2 shows the retention (WG) of each agent in the Japanese black pine specimen for the eating-damage test. The reduction of WG by the leaching test was marked only in the specimens treated with $CuCl_2$ and MT–NH_3–$CuCl_2$.

The mass loss of the specimens and termite mortality in the eating-damage test after the leaching test are shown in

Table 3. Mortality rate of termites in the contact toxicity test

	Mortality (%)								
	6 h	8 h	2 days	3 days	4 days	5 days	6 days	7 days	14 days
Agent									
Control	0	0	3.33 ± 5.77	10 ± 10	16.7 ± 5.77	16.7 ± 5.77	16.7 ± 15.28	23.3 ± 5.77	40 ± 20
MT	0	0	0	26.7 ± 5.77	56.7 ± 5.77	93.3 ± 11.55	100	100	100
RMT	3.33 ± 5.77	3.33 ± 5.77	13.3 ± 5.77	86.7 ± 11.55	100	100	100	100	100
CMT	0	0	50 ± 10	100	100	100	100	100	100
MT–NH_3	0	0	3.33 ± 5.77	6.67 ± 5.77	10 ± 10	36.7 ± 5.77	63.3 ± 5.77	100	100
RMT–NH_3	0	3.33 ± 5.77	23.3 ± 5.77	80 ± 10	100	100	100	100	100
CMT–NH_3	0	3.33 ± 5.77	53.3 ± 15.28	100	100	100	100	100	100
MT–NH_3–$CuCl_2$	0	0	3.33 ± 5.77	73.3 ± 15.28	90 ± 10	100	100	100	100
RMT–NH_3–CuCl	0	0	16.7 ± 5.77	76.7 ± 5.77	100	100	100	100	100
CMT–NH_3–CuCl	0	0	16.7 ± 5.77	73.3 ± 11.55	86.7 ± 11.55	100	100	100	100
$CuCl_2$	0	0	16.7 ± 5.77	56.7 ± 11.55	93.3 ± 5.77	100	100	100	100
NH_3	0	0	6.67 ± 5.77	80 ± 0	96.7 ± 5.77	100	100	100	100

Results are the mean ± SD
There was zero mortality at 2 h and 4 h

Table 4. Mortality rate of termites in the oral toxicity test

Agent	Mortality (%)					
	1 day	3 days	6 days	9 days	12 days	14 days
Control	0	0	4 ± 0	4 ± 0	4 ± 0	4 ± 0
MT	2 ± 1	6.0 ± 1.7	8 ± 0	12 ± 4	16 ± 4	26.0 ± 5.1
RMT	1.3 ± 2.3	2.7 ± 4.6	4 ± 4	8 ± 4	12 ± 4	18.7 ± 6.1
CMT	2.7 ± 2.3	8 ± 0	12 ± 0	14.7 ± 2.3	29.3 ± 1.7	33.3 ± 3.1
MT–NH_3	0	1.3 ± 2.3	2.7 ± 2.3	77.3 ± 3.1	100	100
RMT–NH_3	0	8 ± 4	52 ± 4	100	100	100
CMT–NH_3	1.3 ± 2.3	18.7 ± 2.3	45.3 ± 2.3	73.3 ± 2.3	73.3 ± 2.3	81.3 ± 2.3
MT–NH_3–Cu	0	0	6.7 ± 2.3	8 ± 0	10.7 ± 2.3	14.7 ± 2.3
RMT–NH_3–Cu	2.7 ± 2.3	6.7 ± 2.3	6.7 ± 2.3	9.3 ± 2.3	21.3 ± 2.3	24 ± 4
CMT–NH_3–Cu	0	1.3 ± 2.3	1.3 ± 2.3	4 ± 4	17.3 ± 2.3	29.3 ± 2.3
$CuCl_2$	4 ± 0	8 ± 0	8 ± 0	9.3 ± 2.3	16 ± 4	18 ± 2
NH_3	0	0	5.3 ± 2.3	10.7 ± 2.3	13.3 ± 2.3	18.7 ± 2.3

Results are means ± SD

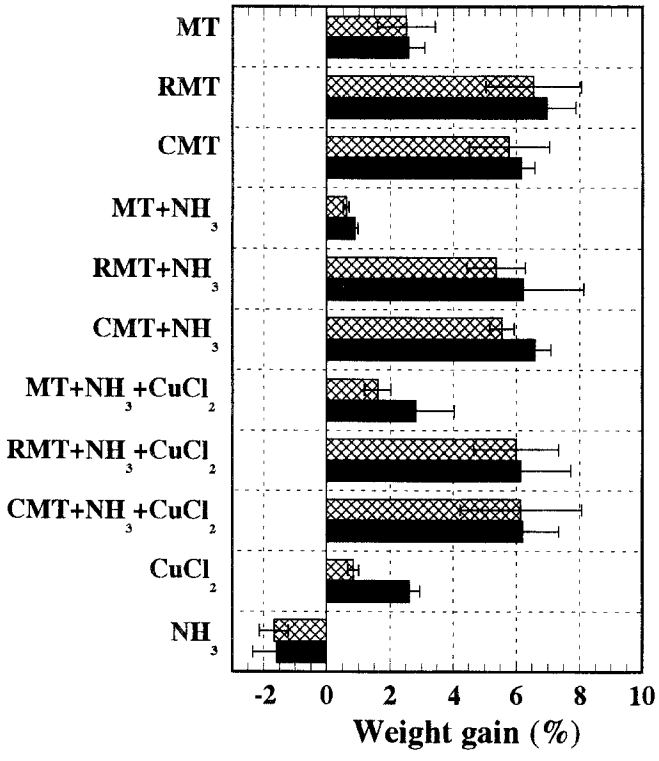

Fig. 2. Weight gain of agent in specimens in the eating-damage test. *Filled bars*, before the leaching test; *crosshatched bars*, after the leaching test

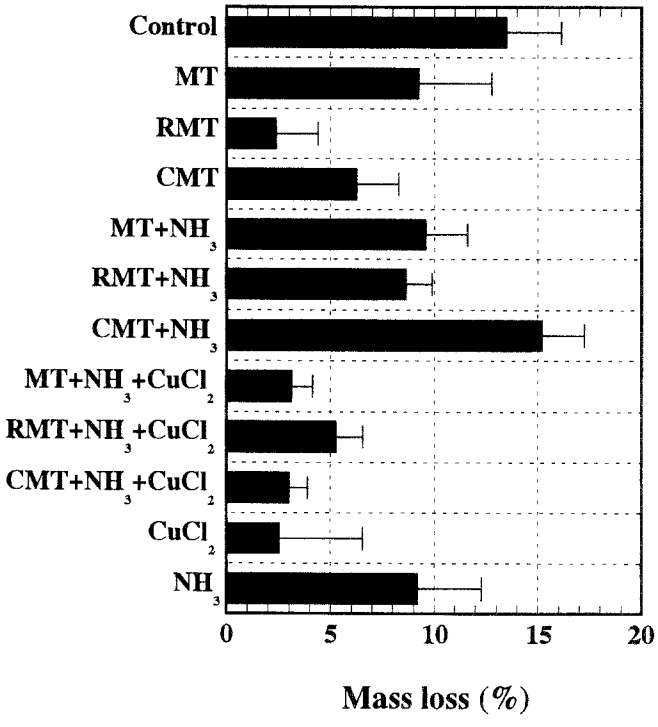

Fig. 3. Mass loss of wood specimen in the eating-damage test after the leaching test

Figs. 3 and 4, respectively. Treatment with the agents bestowed protection from termites in most cases. The termite-resisting ability of specimens before the leaching test showed the same tendency as that after the leaching test. In other words, it was suggested that the leaching test had no effect on resistance ability. In particular, RMT, CMT, and the tannin–ammonia–copper solutions had excellent termite-resisting ability, even after the leaching test. The specimens treated with $CuCl_2$ alone also had excellent termite-resisting ability. However, even after leaching, color from the copper that had been leached out of the specimen was observed during the eating-damage test. Therefore, the leached copper might repel termites in the test area.

The mortality of termites did not reach 100%, except in specimens treated with RMT and before the leaching test. Even when the mortality was 100% in the contact and oral toxicity tests, the overall mortality did not reach 100%. This indicates that some termites remained alive, and that tannin–ammonia–copper did not have superior protective ability against termites.

Field stake tests

The mass loss of logs in the field stake test is shown in Fig. 5. After the test, almost all logs maintained their initial

shape except for the control logs and logs treated with MT, although there were also a few holes made by termites. However, when those logs were cut 5 cm from the end to be buried underground, eating damage by termites occurred in sapwood even in logs that appeared healthy. When mass loss was compared, termite-resisting ability improved in the order controls, MT series, CMT series, and RMT series. Even in wood treated only with RMT, the mass loss over 40 months was less than 10%. However, because in the wood eating-damage test the mortality rate of termites did not reach 100%, even this RMT series agent cannot be called a completely successful antitermite agent.

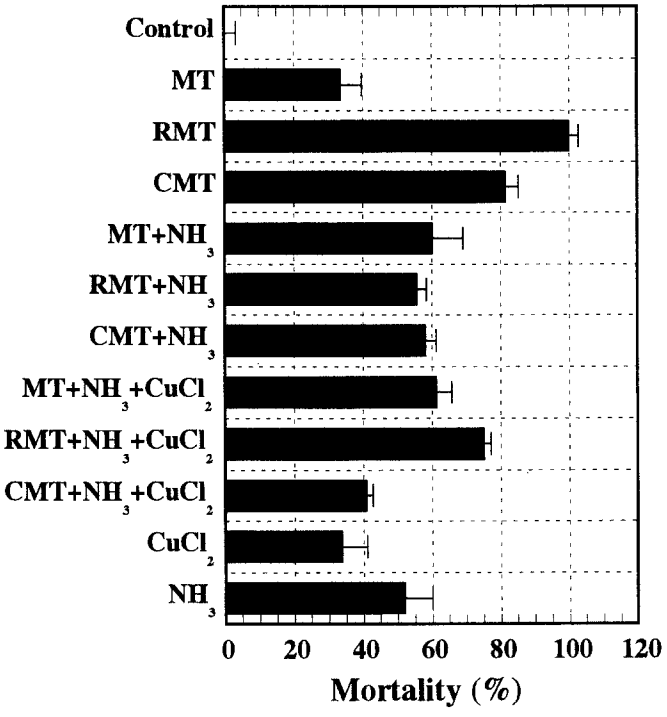

Fig. 4. Mortality of termites in the eating-damage test after the leaching test

Conclusions

We examined the ability of a series of tannin, tannin–copper, and tannin–ammonia–copper solutions to penetrate wood and the termite resistance of the treated wood.

1. Levels of retention of the chemically modified tannin increased in the order MT, RMT, and CMT. However, when the cross sections of the logs were sealed, there was little difference among retention levels of MT, RMT, and CMT solutions.
2. The retention levels of ammonia–copper solution with RMT or CMT were about 1.3–1.7 times that of ammonia–copper solution with MT.
3. All agents penetrated 2–13 mm from the tangential sections of the logs. In particular, CMT–NH_3–Cu and RMT–NH_3–Cu solutions easily penetrated about 20% of the area of the cross section from the tangential section of the logs.
4. The retention levels of the chemically modified tannins RMT–NH_3–Cu and CMT–NH_3–Cu ranged from 268 to 326 kg/m^3 for sealed logs.
5. In the contact and oral toxicity tests, some agents exhibited 100% termite mortality. However, it became clear that most of the tannin–ammonia–copper solutions did not have contact toxicity because the termites had eaten the treated cellulose pellets and remained alive.
6. During the wood eating-damage test, the weight loss of the treated wood suggested that the tannin–ammonia–copper agents gave a high level of protection against termites. However, the mortality of the termites during the eating-damage test (>21 days) did not reach 100% with any solution except RMT before the leaching test.

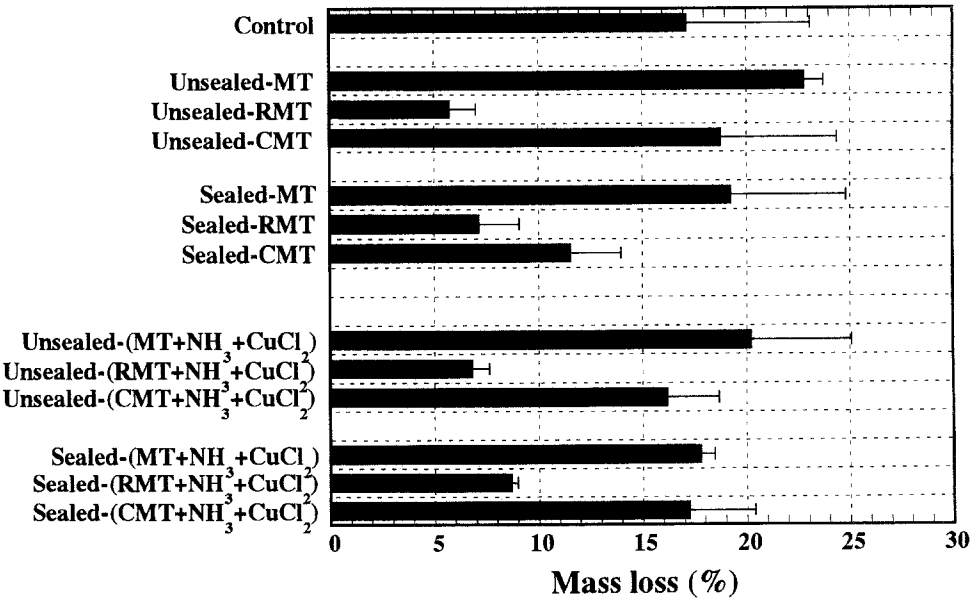

Fig. 5. Mass loss of logs in the field stake test. *Unsealed*, open cross section; *Sealed*, sealed cross section

7. The fact that living termites remained suggests that the tannin–ammonia–copper agents tested were not completely successful antitermite agents.

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