A Novel Biodegradable Antimicrobial PU Foam from Wattle Tannin

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ABSTRACT: A new kind of polyurethane (PU) foam was synthesized from wattle tannin (WT), which has good prospects of application for its biodegradation and bacteriostasis. The effects of WT content, diisocyanate dosage, and chemical modification of WT on properties of PU were investigated. It was found that WT could contribute not only to bacteriostatic activity, but also to biodegradability during soil micro-organism treatment for the polyurethane foams. Furthermore, the bacteriostasis of PU is improved by modifying the chemical structure of WT. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2756–2763, 2003

Key words: polyurethane; biodegradable

INTRODUCTION

With the development of the polymer industry, polyurethane has been widely used in the fields of fibers, foams, elastomers, and protective coatings for its steady quality and excellent performance. The ability of micro-organism growing on the polyurethane presents a human health problem during the usage and storage of PU. In an effort to address this problem, antibacterial agents have been applied into the polymers.

In general, two major methods have been used to produce antimicrobial polymers: the antimicrobial materials are mixed with the polymer or laid on the surface of polymer.[1] Those methods have disadvantages of a short useful life and undesirable washability. Therefore, it has become very important to find a natural antimicrobial material that can be incorporated into the formulation of PU and retain its bacteriostatic ability.

There is a noticeable and interesting phenomenon in the plant kingdom. The bark can protect the tree from plant diseases and insect pests during growing. However, bark can be degraded by natural micro-organisms after death or disused. This phenomenon suggests the possibility to develop a new kind of polymer with biodegradation and micro-organism resistance.

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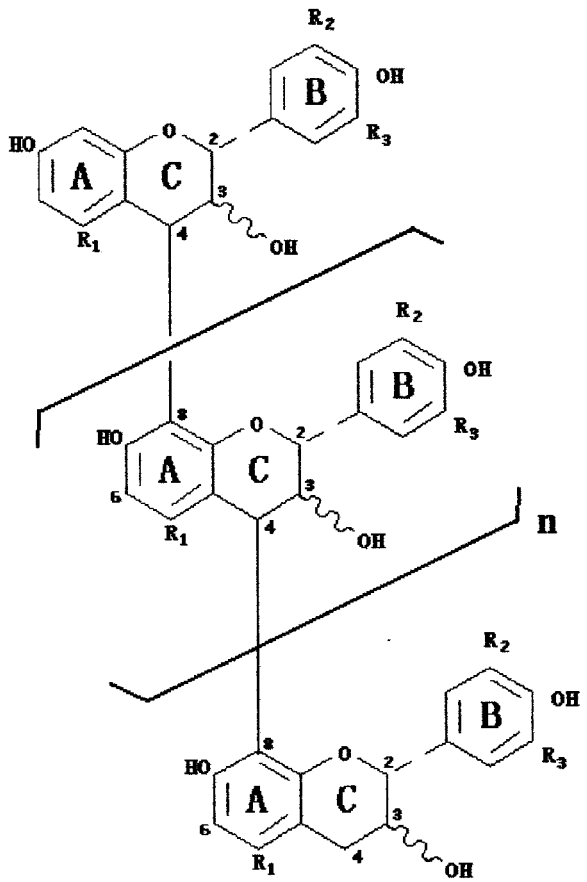
Some investigations have indicated that tannin is the efficient antimicrobial agent in the bark. "Tannin" is a general descriptive name for a group of polymeric phenolic substances, which can be found in almost every plant part: bark, wood, leaves, fruits, and roots. Its molecular weights range from 500 to 3000.[2] Generally, tannin can be classified into hydrolyzable and condensed (or nonhydrolyzable) tannin. Hydrolyzable tannins contain either gallotannins or ellagitannins, while the more numerous condensed tannins are the polymerized products of flavan-3ols and flavan-3, 4-diols, or a mixture of the two[3] (Scheme 1). Tannins in plants can inhibit the growth of fungi, bacteria, and viruses, and serves as a natural defense mechanism against microbial infections.[4] Condensed tannins have been determined to bind cell walls of ruminal bacteria, preventing growth and protease activity.[5]

The Acacia mearnsii bark contains significant amounts of wattle tannin (WT), a kind of condensed tannin, and is in large area of plantation forests in China, Africa, and America because of its fast growth rate. The introduction of plant components into PU formulation has been reported.[6] WT can be successfully incorporated into PU foams formulation, which enhances the biodegradability and micro-organism resistance.[7] Also, WT is utilized as a polyol component in polyurethane synthesis, because it has both aliphatic and aromatic hydroxyl groups.

In this study, we tried to synthesize a novel WT polyurethane (WT-PU), which included the bacteriostatic activity and biodegradation together. Furthermore, the bacteriostatic activity of WT-PU was improved by modifying the chemical structure of WT.



Progibourtinidin

R_1=H, R_2=H, R_3=H

Profisetinidin

R_1=H, R_2=OH, R_3=H

Prorobinetinidin

R_1=H, R_2=OH, R_3=OH

Propelargonidin

R_1=OH, R_2=H, R_3=H

Procyanidin

R_1=OH, R_2=OH, R_3=H

Prodelphinidin

R_1=OH, R_2=OH, R_3=OH

Scheme 1 The structure of tannin.

The effects of WT content, diisocyanate dosage, and chemical modification on properties of WT-PU are discussed.

EXPERIMENTAL

Preparation of WT-PU

The biomass PU was prepared using the same procedures as described previously.[7] WT polyol was obtained using the liquefaction method. WT (or modified WT) meal and the liquefied solvent (consisting of PEG400 and glycerol with a weight fraction of 94/6) were weighed into a flask. Liquefaction was performed with stirring and refluxing at 120°C for 60 min. After cooling, the biomass polyol was premixed thoroughly with a catalyst and other additives, and then methylenediphenyl diisocyanate (MDI) in variable amounts was added to yield PU foam containing different WT content (10%, 20%, and 30% WT) with stirring at 2400 rpm. The resulting foam was removed from the mold after 1 h, and was allowed to cure at room temperature for 1 week before the test. WT was replaced by trimethylolpropane (TMP) to prepare TMP polyurethane (TMP-PU) for the control tests.

The MDI index (NCO/OH ratio) and WT content are defined as follows:

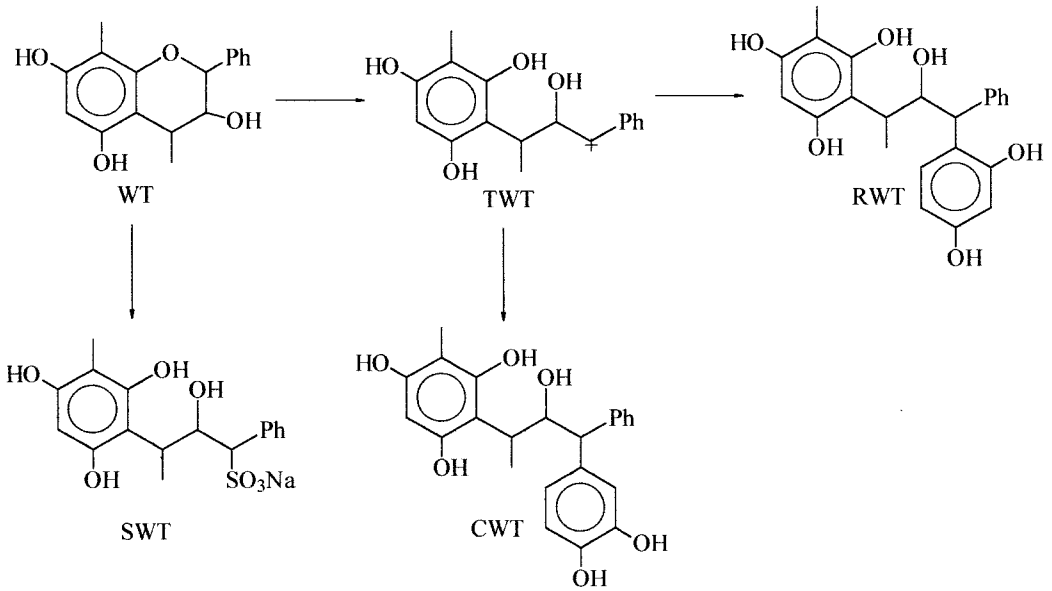
$$\text{MDI index} = \frac{W_{\text{MDI}} \times I_{\text{MD}}}{W_{\text{Bio}} \times H_{\text{Bio}} + W_{\text{Add}} \times H_{\text{Add}}}$$

$$\text{WT}(\%) = \frac{W_{\text{WT}}}{W_{\text{Bio}} + W_{\text{Add}}} \times 100$$

where I_{MDI} is the content of the isocyanate group in the MDI, and H_{Bio} and H_{Add} are the content of total hydroxyl groups in biomass polyol and other additives, respectively. W_{MDI}, W_{Bio}, and W_{Add} denote the weights of MDI, biomass polyol, and other additives, respectively.

Chemical modification of WT

The chemical modified tannins were prepared according to Yamaguchi.[8] For purifying the raw tannin, a



Scheme 2 Chemical modification of WT.

20% aqueous solution of commercial WT was centrifuged at 3000 rpm for 30 min, and then the supernatant was lyophilized. Sulfonated tannin (SWT), trichloroacetic acidtreated tannin (TWT), resorcinolated tannin (RWT), and catecholated tannin (CWT) were prepared as follows (Scheme 2).

SWT: 20% Na_2SO_3: WT and 0.4% octyl alcohol: WT were added to a 50% WT solution and allowed to react for 100 min in a water bath at 90°C with stirring.

TWT: Trichloroacetic acid (0.257 mol) was react in a water bath with stirring at 86°C for 120 min. After cooling, the reaction mixture was neutralized with 2*N* NaOH. The residual trichloroacetic acid in the reaction mixture was decomposed to CO_2 and chloroform.

RWT or CWT: resorcinol (1.54 mol) or catechol (1.54 mol) and trichloroacetic acid (0.257 mol) were added to WT (1 mol, 65% aqueous solution), and then the mixture was heated under reflux for 90 min at 86°C. After cooling, the reactant was neutralized with 2*N* NaOH. All of the products for preparing WT polyurethane were lyophilized following above method.

Assay of bacteriostatic activity

Different mediums were used for different micro-organisms. Beef extract peptone medium (BPA) was taken for the bacteria of *Salmonella typhi*, *Shigcila dysenteriac*, *Eschercihia Coli*, *Pseuodo monas aeruginosa*, and *Staphylococcus aureus*. Alcohol (95%) was added into BPA (1:20, BPAE) for *Proteus valgaris*, and the potato extract glucose medium (PSA) was used for *Aspergillus flavus*, *Aspergillus niger*, *Rhinpus oryzac*, *Mucor kacilliformis*, and *Paccilomgces uarioti*.

The bacteriostatic activity was pursued with the shake culture method.[9] That is, the PU samples (0.75 g) was put into a 250-mL flask, then 70 mL phosphate buffer solution (PBS, 0.03 mol/L, pH 7.2–7.4), and 5 mL fungi soliquoid were added, and the concentration of which in the buffer media was 1×10^4–2×10^4 cfu/mL. The flask was fixed to the mechanical shaker and shaken at 300 rpm for 1 h. The mixed solution (0.5 mL) was taken out, and was inoculated on a Petri dish by the agar pour-plate method, then counts of the living cultured fungi before (N_0) and after shaking (N_1) were taken. The bacteriostatic activity was calculated by the following equation:

$$\text{Bacteriostatic Rate} = \frac{N_0 - N_1}{N_0} \times 100\%$$

More than three replications were conducted, and the same assessments of TMP-PU were carried out for control. Generally, the sample was considered having bacteriostatic activity when the bacteriostatic rate was over 26%.

Assay of biodegradation

After removal of hardened clumps, plant debris, and other things, the soil was obtained from the field and was put into a plastic box with holes in the cover. The samples were buried in the soil at ambient humidity and temperature (37–92%, 20–35°C) for different periods. The control experiments were carried out using TMP-PU under the same conditions.

After soil treatment, the samples were washed in deionized water and dried at 50°C for 24 h. Then the samples were equilibrated for 24 h before testing at least.

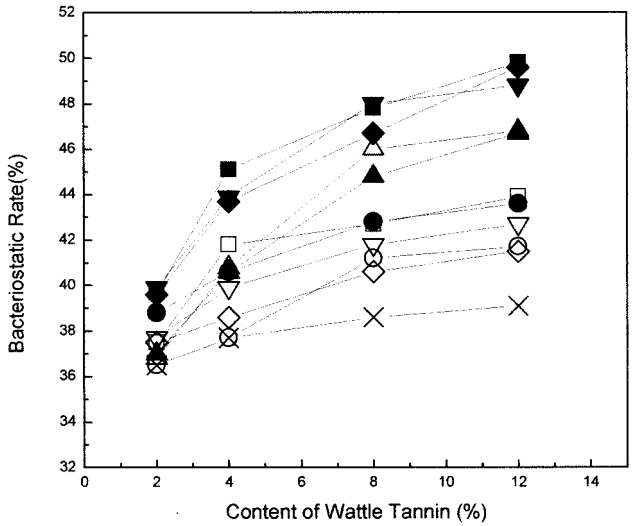


Figure 1 Bacteriostatic rates of WT. Notes: ■ *Staphylococcus aureus*, □ *Eschercihia coli*, ▲ *Pseudo monas aeruginosa*, △ *Salmonella typhi*, ● *Shigcila dysenteriac*, ○ *Bacillus subtilis*, ▼ *Proteus valgaris*, ▽ *Bacillus cereous*, ◆ *Staphylococcus albus*, ◇ *Salmonella typhimurium*, × *Aspergillus flavus*.

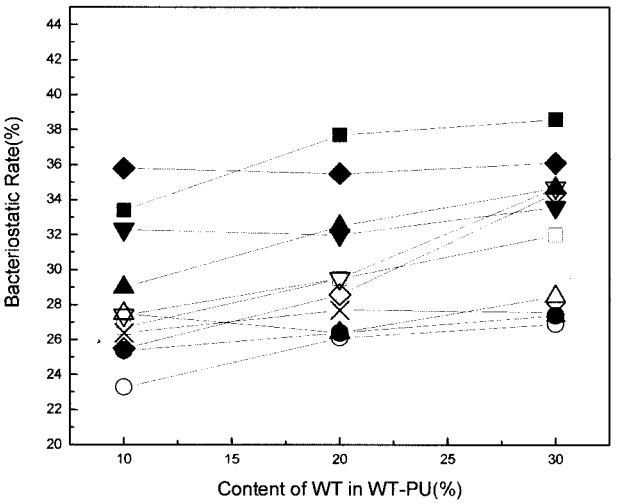


Figure 2 Effects of WT content in WT-PU on bacteriostatic rates. Notes: ■ *Staphylococcus aureus*, □ *Eschercihia coli*, ▲ *Pseudo monas aeruginosa*, △ *Salmonella typhi*, ● *Shigcila dysenteriac*, ○ *Bacillus subtilis*, ▼ *Proteus valgaris*, ▽ *Bacillus cereous*, ◆ *Staphylococcus albus*, ◇ *Salmonella typhimurium*, × *Aspergillus flavus*.

The weight loss of WT-PU can be defined as the following equation:

$$\text{Weight loss (\%)} = \frac{W_o - W_s}{W_o} \times 100$$

where W_0 and W_S are the weight of WT-PU foam before and after soil treated, respectively.

The IR spectra and SEM (Scanning Electronic Microscope) photos of PU were performed with a Nicolet IR-550 FTIR Spectrometer and Hitachi S-520 SEM, respectively.

RESULTS AND DISCUSSION

Bacteriostasis of WT and WT-PU

The bacteriostasis of tannins had been well documented, and was validated in this study.[4] The results showed that WT had evidently bacteriostatic activity to 10 kinds of germs and one kind of yeasts, which were *Staphylococcus aureus, Staphylococcus albus, Proteus valgaris, Salmonella typhi, Pseudo monas aeruginosa, Eschercihia coli, Shigcila dysenteriac, Bacillus cereous, Salmonella typhimurium, Bacillus subtilis*, and *Aspergillus flavus* (Fig. 1).

When WT was incorporated in the preparation of PU, WT-PU retained the activity of WT to above bacteria (Fig. 2), and the activity increased with the enhancement of WT. However, when TMP replaced WT, TMP-PU was considered no bacteriostatic activity, because its bacteriostatic rate was below 26%.[9] The results indicated that the WT component contributes mainly to the bacteriostatic activity of PU. But the activity obviously decreased with an increasing isocyanate dosage in the formulation of WT-PU (Fig. 3).

The reason seemed to be that the hydroxyl group of WT decreased with the enhancement of isocyanate in the WT-PU system. Three major urethane derivatives (CU-IA, CU-IB, CU-II) were prepared in the reaction of phenylurethane formation from catechin as a model reaction for polyurethane synthesis from WT[10] (Scheme 3). The CU-IA and CU-IB were tautomeric isomers in which the free hydroxyl group might be involved. CU-II became the main product if phenyl isocyanate is in enough amounts. It could be seen that

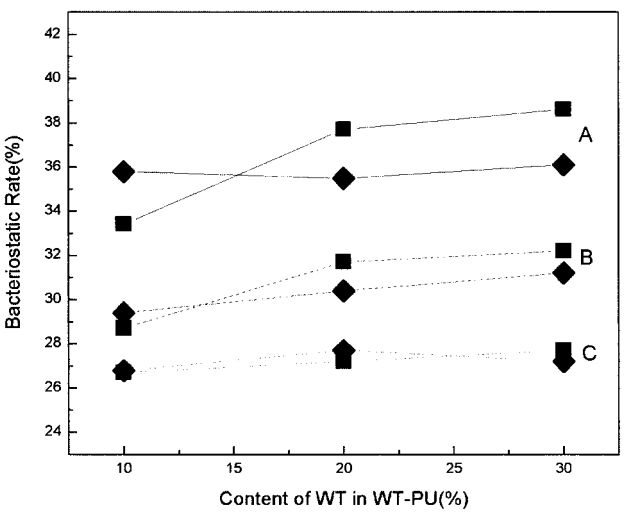
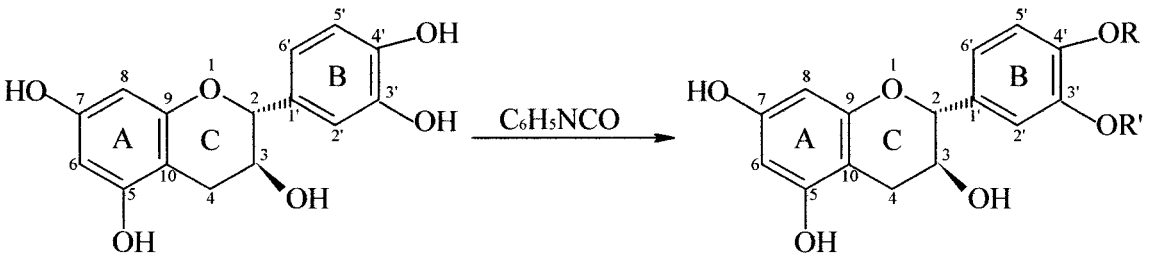


Figure 3 Effects of MDI index on the bacteriostatic activity of WT-PU. Notes: ■ *Staphylococcus aureus*, ◆ *Staphylococcus albus*; MDI index: 0.9 (A); 1.0 (B); 1.1 (C).



Scheme 3 Reaction of (+)-catechin with phenyl isocyanate as a model reaction of tannin and diisocyanates.

B ring of catechin was easier to form urethane bonding than A ring as described in our previous article.[10] So the main functional group of bacteriostatic activity was the phenolic hydroxyl group of the A ring in the WT structure. Therefore, it was very important to protect the free phenolic hydroxyl group of the A ring in preparation of antimicrobial PU.

The bacteriostatic activity of WT-PU had been verified in the above study. Therefore, we tried to enhance the activity of WT-PU for further practical application by introducing the chemically modified WT into PU.

Effects of chemical modification

H. Yamaguchi et al. had chemically modified the tannin to improve the preservative activity to wood.[11] So WT and chemical modified WT (TWT, SWT, CWT, and RWT) were prepared in PU and their contents were all 10%.

The bacteriostatic activity of modified WT was shown in the Figure 4. It suggested that the activity of modified WT was improved. Above all, the activity of RWT had enhanced uppermost, and the following was CWT, SWT, and TWT. The changes of bacteriostatic

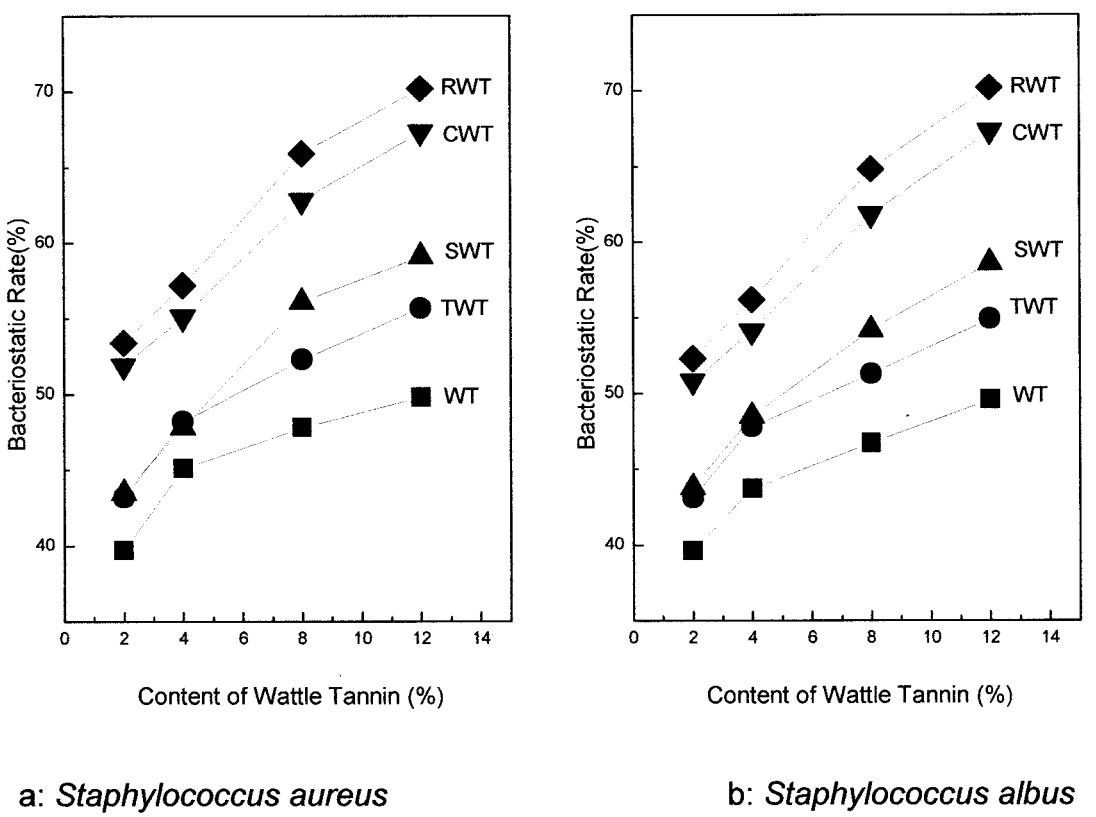


Figure 4 Effects of chemical modification of WT on bacteriostatic rates to *Staphylococcus aureus* and *Staphylococcus albus*.

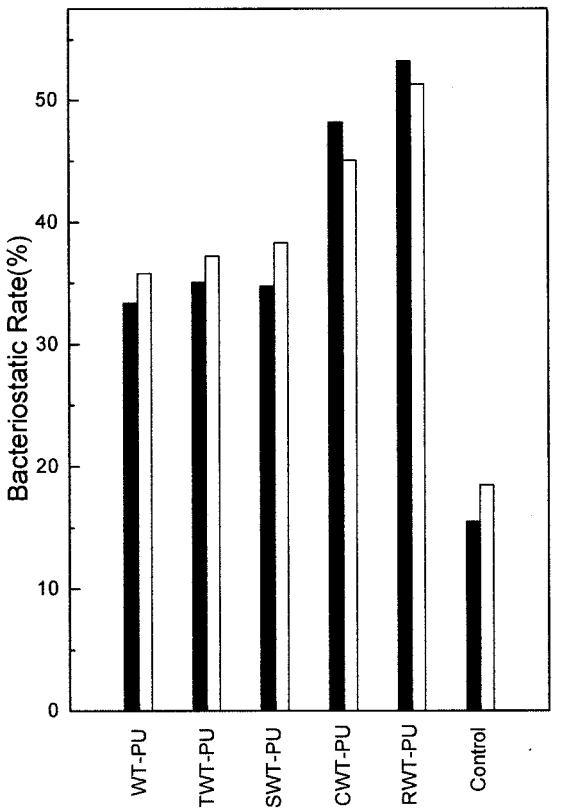


Figure 5 Effects of chemical modification of WT on bacteriostatic rates. Notes: The content of WT(or chemical modified WT) in PU: 10%; ■ *Staphylococcus aureus*, □ *Staphylococcus albus*.

activity of WT-PU were observed before and after chemically modification of WT. The effects of PU on the growth of *Staphylococcus aureus* and *Staphylococcus albus* during shaking flask test were shown in Figure 5. It was considered that the antimicrobial properties of the PU containing modified WT were improved by changing the chemical structure of WT.

Therefore, the bacteriostatic activity of WT-PU was increased by chemically modification of tannin, which could lay the foundation for its application in the future.

Biodegradation of WT-PU

WT-PU can retain bacteriostatic activity of WT to some pathogens during the normal usage, which has been basically confirmed by the shake culture experiment. Furthermore, we expect the WT-PU has certain biodegradation in the soil after disuse to reduce the pollution to environment caused by undegradable polymer materials. So the soil burial test was carried out in WT-PU, for evaluating its biodegradability under natural soil micro-organism treatment. In this study, the weight losses and the losses of compressive strength (σ) were calculated from respective differences of weights and compressive strength before and after the soil burial. Meanwhile, the surfaces of PU

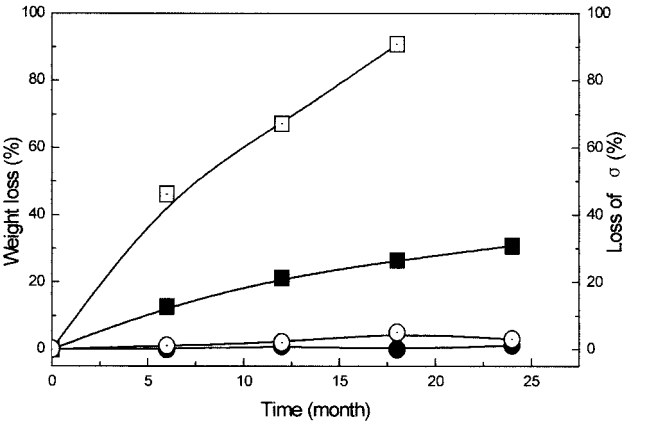


Figure 6 Effects of periods of the soil burial treatment on weight losses and losses of compressive strength (σ) of WT-PU and TMP-PU. Notes: ■, □ Weight loss and loss of σ of WT-PU; ●, ○: weight loss and loss of σ of TMP-PU.

were observed under SEM. All of results indicate that WT-PU could be degraded to some extent, in soil, and the WT component contributed mainly to the biodegradation.

The loss of σ and weight loss of WT-PU and TMP-PU during the soil treatment are shown in the Figure 6. The samples after 24-month treatment had become very fragile, and could not be used for the mensuration of compressive properties. For WT-PU, both the weight loss and the loss of σ obviously increased with increasing periods of soil treatment, whereas they were very small for TMP-PU. At the beginning, the decrease was fast, and then it was slowed down. It may be related to the increasing difficulty for deep entrance of the micro-organism and expelling of the degraded product. Also, the half-life of WT-PU was about 39 months based on the weight loss. The change of σ loss was consistent with the weight loss, and much larger than corresponding weight loss. These results suggested that WT could be acting as crosslinking points in PU. The degradation broke the net-like

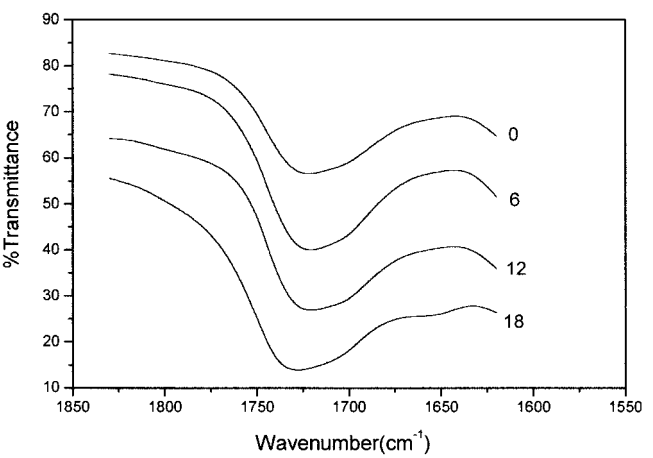


Figure 7 IR spectra of WT-PU foams treated with soil microorganisms after 0, 6, 12, and 18 months.

TABLE I
The Values of $(X_b)_{CO}$ and C_n of WT-PU and TMP-PU

Months		0	6	12	18	24
$(X_b)_{CO}$	WT-PU	0.36	0.31	0.29	0.26	0.24
	TMP-PU	0.34	0.33	0.33	0.34	0.32

structure of PU, and brought on the larger losses of compressive strength.

The hydrogen bond was very important to the structure and its biodegradable properties of PU. Two discernible peaks assignable to free and hydrogen-bonded carbonyls near 1720 cm^{-1} had been studied to characterize the molecular-level mixing of the hard segments. The band of C═O in urethane was divided into double bands due to the existence of a hydrogen bond in the PU (Fig. 7). The band at 1730 cm^{-1} was assignable to the free carbonyl, and the lower frequency one at 1710 cm^{-1} was associated with hydrogen-bonded carbonyl. Using the peak at 1600 cm^{-1} (the absorption of C═C in phenyl) as a standard, it could be seen that the peaks of urethane carbonyls were both weakened during soil treatment. However, as a control, no changes were obtained in the IR spectra of TMP-PU at the same condition (data not shown). The fraction of hydrogen bonding in PU can be given by the following equation:[12]

$$(X_b)_{CO} = \left[1 + 1.2 \times \frac{(A_f)_{CO}}{(A_b)_{CO}}\right]^{-1}$$

where $(A_f)_{CO}$ and $(A_b)_{CO}$ are bond areas of free carbonyl bond and hydrogen-bonded carbonyl, respec-

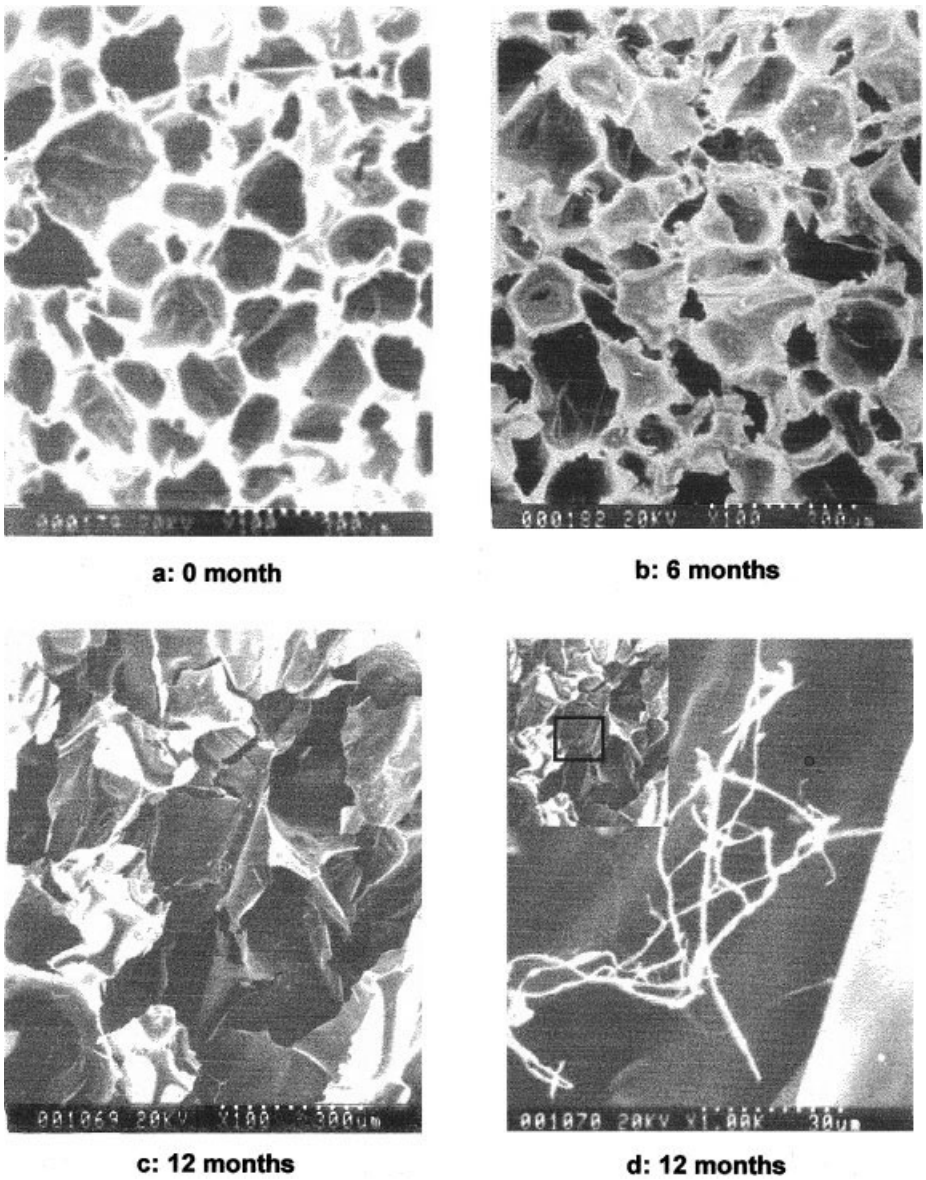


Figure 8 SEM photographs of WT-PU foams treated with soil micro-organisms after 0 [(a), ×80], 6 [(b), ×80], 12 [(c), ×80], and 12 [(d), 800] months.

tively. The results were listed in Table I. With the delay of the biodegradation periods, $(X_b)_{CO}$ of WT-PU was obviously decreased. That is, the hydrogen bond in WT-PU was weakened after degradation, which could improve biodegradability of PU foam.

Furthermore, the changes of WT-PU surfaces during soil treatment were shown in Figure 8. The integrity and uniformity microcell was a representative structure of PU before decay [Fig. 8(a)]. After biodegraded, the cells were damaged, and the cells of the foams had been expanded with soil treatments [Fig. 8(b) and (c)]. The decay of the microcell may be mostly induced by the decline of mechanical properties. There was an interesting phenomenon that some micro-organism was growing in the cells of WT-PU after being seriously destroyed [Fig. 8(d)]. It suggested that the WT-PU had provided proper growing conditions for the micro-organism. However, the decay was not observed in TMP-PU.

From the above experiments we found that WT-PU also has considerable biodegradability in soil after disuse, in addition to the bacteriostatic activity during the normal usage. The feasibility of preparing a novel biodegradable antimicrobial PU was basically confirmed in this pilot study. However, the mechanisms of antimicrobial activity or biodegradation of WT-PU is not clear in some degree, and further study will be needed.

CONCLUSIONS

1. It was found that WT-PU retained the bacteriostatic activity of WT to some pathogens, and the activity increased with the enhancement of WT. However, the activity obviously decreased with an increasing isocyanate dosage in the preparation of WT-PU.
2. The main functional group of bacteriostatic activity was the phenolic hydroxyl group of the A ring in the WT structure. Therefore, it was very important to protect the free phenolic hydroxyl group of the A ring in preparation of antimicrobial PU. Furthermore, the antimicrobial properties of the PU containing chemically modified WT were improved.
3. WT can enhance biodegradability of the PU foams by soil micro-organism, and be degraded randomly. The half-life of WT-PU was 39 months based on the weight loss. The hydrogen bond in WT-PU was weakened after degradation. Thus, a way was showed to prepare a new kind of biodegradable antimicrobial PU with good prospects of application.

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