

Bamboo Tar-Based Polyurethane Wood Coatings

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ABSTRACT: Bamboo tar is a natural resource of aromatic polyol obtained from a residue of by setting or distilling crude bamboo vinegar. In this study, the two-packed polyurethane (PU) coatings were prepared by blending bamboo tar and castor oil varying with different weight ratios and polymeric toluene diisocyanate (PTDI) was used as a hardener at the NCO/OH molar ratio of 1.0. Six kinds of PU coatings were formulated and the viscosity, pot-life, drying time, mechanical properties (hardness, tensile strength, impact resistance, adhesion, and abrasion resistance), gel content, durability, lightfastness, FTIR, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were characterized. The results indicated that the bamboo

tar containing PU film appearance is semitransparent yellow-brown color and the wood texture could be kept after finishing. All PU films possessed excellent adhesion as well as durability. The increase in bamboo tar content led to shorten drying time of coatings and to increase in hardness, tensile strength, lightfastness, and thermal stability of films. From these results and due to a light smell flavor, it is suggested that the bamboo tar-based PU coatings is suitable to be used as an exterior wood coatings. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3718–3724, 2010

Key words: bamboo tar; coatings; films; polyurethanes; wood

INTRODUCTION

Today's dwindling oil supplies and the environmental concern of industries and governments from all over the world have highlighted the need to develop new coatings aiming to use the renewable raw material sources in the composition of polymers instead of conventional petroleum chemical ones and reduce their environmental impact.

Bamboo, a perennial lignified plant that belongs to Bambusoideae, is one of the most important forest resources, as it grows faster than any other woody plant on earth. There are many genera of bamboos cultivated in Taiwan. The total area of bamboo cultivation is about 152,300 hectares, which is 7.24% of the total forest area in Taiwan.¹ Among them, moso bamboo (*Phyllostachys pubescens*) is one of the most popular and valuable bamboo species. The traditional industry of bamboo in Taiwan is depressed in recent years, owing to the cheap labor competition of China and Southeast Asian country. To increase the economic income of bamboo products, the Council of Agriculture has been pushing new high-technology applications of this tropical plant, and hope that it could completely transform and foster the

continuous development of the traditional bamboo industry. Bamboo charcoal and vinegar are the potential candidates for increasing the economic value of bamboo products.

The crude bamboo vinegar, a brown-red transparent liquid with smoke flavor, is obtained from bamboo, carbonized and then cooled through the exhaust hole of a charcoal kiln. Bamboo tar is a dark-brown residue of the precipitation part derived from by setting the crude bamboo vinegar for 6 months or by distilling the crude bamboo vinegar under a reduce pressure. Meanwhile, the transparent part is called bamboo vinegar or distilled bamboo vinegar. The acidic liquid, which is composed of 80–90% of water and a mixture of more than 200 organic ingredients with acetic acid being the main one, has recently received increasing attention due to its potential characteristics of promoting the growth of crop, disinfections, sterilization against germ and mold, and as insect repellent agent for medicinal, agricultural, and industrial utilization.^{2–6} However, the about 30% yield of residue bamboo tar has not been utilized in Taiwan. The Taiwan bamboo tar production potential is about 50 tons/year and it will be increased year after year, enough to synthesize wood coatings with this low-cost raw material for domestic exterior wood finishing.

The ingredients of bamboo tar had been examined in our laboratory and shown its high hydroxyl value (over 200 mg KOH/g), and its main organic compositions are phenol derivatives such as 2, 6-dimethoxy phenol, phenol, and 2-methoxy phenol etc. Qiao et al.,⁷

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also found that the moso bamboo tar possessed 71% the relative phenolic content of total organic compound of bamboo tar by GC-MS analysis. In addition, some macromolecular networks which are similar to the lignin (guaiacyl and syringyl units) are also preserved in the bamboo tar. Therefore, bamboo tar can be as a natural aromatic polyol.⁸⁻¹⁰ It shows a great potential for using as a raw material of phenolic resins, polyurethane (PU) and carbon fibers. Similar studies about using the residue of the slow pyrolysis of eucalyptus wood for charcoal production, the characteristic and application of *Eucalyptus* tar pitch have been widely examined in Brazil.⁸⁻¹⁵

PU resin designates a polymer wherein the repeating unit is a urethane linkage ($-\text{NHCOO}-$). The synthesis of such polymers is performed by reacting with di- and polyfunctional hydroxyl compounds (polyols) with di- or polyisocyanates through addition polymerization. The PU resins have found extensive applications in many industries mainly because they possess excellent adhesion, abrasion resistance, chemical resistance, a wide range of mechanical strength and very low-temperature cure.^{16,17} Thus, it is very suitable for wood coatings.

Castor oil, obtained from the Castor nut (*Ricinus communis*) (oil content $\sim 50\%$), is an unusual oil in that it contains a very high amount (90%) of ricinoleic acid: a hydroxy moiety-containing fatty acid (12-hydroxy-9c-octadecenoic acid). It is at present the only commercially available source of natural hydroxylated triglycerides.¹⁸ The castor oil can be used as a polyol to react with isocyanate and form PU. In this study, it was also used as a flow modifier or a solvent¹² to reduce the viscosity of bamboo tar. Varying proportions of bamboo tar, along with castor oil and adding the polyisocyanate to synthesize two-packed PU coatings and the feasibility of the PU for wood coatings were assayed in this research.

EXPERIMENTAL

Materials

Bamboo tar was obtained by further distilling (70 mmHg, 90°C) the sedimentation tar of crude moso bamboo vinegar which had been set for 6 months. The crude moso bamboo vinegar was prepared by using an earth kiln and was supplied by Rui-Zhu Association, Taiwan. The bamboo tar had the hydroxyl value of 233 mg KOH/g, acid value of 24 mg KOH/g, viscosity of 1,128 cps (25°C), and its elemental compositions including C: 52.6%, H: 6.2%, O: 40.3% (by difference), N: 0.8% and S: 0.1% by elemental analysis.

Blown castor oil with hydroxyl value of 159 mg KOH/g, and acid value of 2 mg KOH/g, was purchased from Deuchen Company, Taiwan. Polymeric

toluene diisocyanate (PTDI) with the $-\text{NCO}$ value of 13.0%, viscosity of 1600 ± 400 cps (25°C), and solid content of $75.0\% \pm 1.0\%$, was supplied by Ann Feng Company, Taiwan. Tetrahydrofuran (THF) was obtained by Kanto Company, Japan. The specimens tested for coating include red oak (*Quercus* spp., moisture content: 12.6%), glass panel, and white card board. There were treated according to different requirements.

Preparation and characterization of PU coatings

Six kinds of polyols based on the weight ratios of bamboo tar/castor oil = 0/100, 20/80, 40/60, 60/40, 80/20, 100/0, were prepared. The calculated amounts of each polyol was blended with PTDI by the molar ratio of $\text{NCO}/(\text{OH}+\text{COOH}) = 1.0$, respectively. Then, an appropriate amount of THF was added to the mixture to adjust the solid content to about 50% and six kinds of PU coatings were obtained.

Test of viscosity for PU coatings was carried out on a Gardner bubble viscometer at 25°C. The pot-life of each coating was identified by its flowing characteristics at room temperature i.e., a fixed amount of each coating was put into a test tube to identify the flowing behavior of coating by vision at a time interval. The pot-life is defined as the time of the coating ceasing flowing. Drying time of coating was performed on a three-speed BK drying time recorded at 25°C, 65% relative humidity and the thickness of wet film was 76 μm .

Preparation and characterization of PU films

The resultant coatings were kept at room temperature until all bubbling ceased and then finished on different kinds of substrates with film applicator. The thickness of the wet films was adjusted to 200 μm . All finished specimens were conditioned at room temperature for 3 days before testing.

The hardness of the PU films on wood panels was investigated on a König hardness tester (Braive) according to DIN 53,157, and at least five points were tested with the values averaged for each specimen. The tensile strength and elongation at break of free films were determined on an EZ Tester (Shimadzu) with a crosshead speed of 5 mm/min. All specimens were of a specified shape and size in accordance with ASTM D638, and five samples were tested for each film and the values were averaged. The impact resistance of the tested films was determined using a Dupont Impact Tester IM-601, based on the height of striking of the coated wood panels that do not crack on a knowing falling weight of 300 g and impact hammer diameter of 1/2 inch.

The adhesion of tested films on wood panels was determined by the cross-cut method according to CNS K 6800, and the best adhesion is grade 10 followed by grades 8, 6, 4, 2, and 0. The abrasion resistance of the tested films was measured in terms of the weight loss per 1000 revolutions on a Taber Model 503 Abraser and the CS-10 wheel and load of 500 g were used. Gel content was measured by putting each given weighted films into a Soxhelt extractor containing 250 mL acetone. The solution was siphoned four times per hour (total 6 h) and the soaked film was further dried in an oven at 50°C for 6 h and the weight retention was calculated. The durability of films coated on wood panels was evaluated using hot-and-cold cycles test, in which the specimens were first placed into a -20°C refrigerator for 2 h, and then transferred to a 50°C oven for another 2 h. The cycle number was recorded if the films were cracked. After performing 20 cycles on the coated specimens, the gloss was measured and gloss retention was calculated. The gloss of films coated on wood panels and parallel to wood grain was detected by using Dr. Lange Reflectometer 60° Gloss Meter.

The lightfastness of films coated on white card paper was determined with a Paint Coating Fade Meter (Suga Test Instruments Co. Japan), the light source was mercury light (H400-F) and chamber temperature was at 32°C ± 4°C. After 100 h exposure, the change in color of the specimens was measured at five different points for each sample by using a spectrophotometer (CM-3600d, Minolta, Osaka, Japan) fitted with a D₆₅ light source with a measuring angle of 10° and a test-window diameter of 8 mm. The tristimulus values X, Y, and Z of all specimens were obtained directly from the colorimeter. The CIE L*, a*, and b* color parameters were then computed, followed by calculating the color difference (ΔE^*) directly from the Minolta MCS software system.

Fourier transform-infrared (FTIR) spectroscopy was carried out using a Mattson Genesis II spectrophotometer incorporating a Spectra Tech diffuse reflectance accessory unit. The samples were then mixed with KBr with the weight ratio of 1 : 100, and were ground into a pellet. Data were collected from 4000 cm⁻¹ to 400 cm⁻¹ with 16 scans for each sample. Thermal stability determinations of PU films were carried out on a thermogravimetric analysis (TGA) instrument, a Perkin-Elmer Pyris 1, in a nitrogen atmosphere from 50 to 550°C at a heating rate of 10°C/min, and the weight of tested samples was about 1.0 mg. Dynamic mechanical analysis (DMA) of the films to determine glass transition temperature (T_g) and maximum loss tangent ($\tan \delta_{\max}$) were performed in a nitrogen atmosphere from 0 to 250°C on a Pyris Diamond DMA according to the tension

TABLE I
Viscosity, Pot-Life, and Drying Time of PU Coatings With Different Bamboo Tar/Castor Oil Weight Ratios

Bamboo tar/castor oil (wt ratio)	Viscosity (Gardner, 25°C)	Pot-life (min)	Drying time (h)
0/100	X	200	5.5
20/80	X	110	5.2
40/60	X	45	5.2
60/40	Y	15	5.2
80/20	Z-6	10	3.0
100/0	Z-6	8	2.7

method. The heating rate was set at 5°C/min, and the resonance frequency was adjusted to 1 Hz. The sample size was 5 × 15 mm.

RESULTS AND DISCUSSION

Fundamental properties of PU coatings

The viscosity, pot-life, and drying time of PU coatings with different bamboo tar/castor oil weight ratios are listed in Table I. In this study, the solid content of PU coatings was 50% by using THF as a solvent. The PU coatings containing more castor oil (e.g., 0/100, 20/80, and 40/60) had the lower viscosity of X grade. However above the bamboo tar/castor oil weight ratio of 40/60, the viscosity of PU coatings increased with increasing the bamboo tar content. The result is in accordance with the study of *Eucalyptus* tar-derived PU coatings by Araújo and Pasa.¹⁰ The PU coatings with more bamboo tar had the shorter pot-life such as the one with 100% bamboo tar PU coating was only 8 min, while the one containing 100% castor oil reached to 200 min. However, the pot-life could be extended by adding the THF to reduce the solid content. The drying time of PU coatings had the tendency of the more bamboo tar containing the shorter drying time was. The 100% bamboo tar-based PU coating could be dried at 2.7 h, owing to the reactivity of phenolic hydroxyl group of bamboo tar higher than the hydroxy of castor oil with -NCO of PTDI.

Fundamental properties of PU films

Except the ratio 0/100 shows a transparent and clear appearance, the other PU films appearance are semi-transparent, yellow-brown color and the higher bamboo tar content caused become darker color. However, for each coating, the finished wood figures is clearly i.e., the wood texture could be kept after bamboo-tar based PU coating finished. The mechanical properties of PU films with different bamboo tar/castor oil weight ratios are shown in Table II. The results indicated that the 100% castor oil

TABLE II
Mechanical Properties of PU Films with Different Bamboo Tar/Castor Oil Weight Ratios

Bamboo tar/castor oil (wt ratio)	Hardness (König, sec)	Tensile strength (MPa)	Elongation at break (%)	Impact resistance (cm)	Adhesion (grade)	Abrasion resistance (mg)
0/100	33 ± 1	8.5 ± 1.6	211 ± 36	30	10	7.7 ± 1.2
20/80	45 ± 4	8.1 ± 1.6	258 ± 29	30	10	15.0 ± 1.8
40/60	55 ± 6	9.1 ± 1.0	94 ± 25	25	10	26.9 ± 3.8
60/40	64 ± 3	21.2 ± 2.2	11 ± 1	20	10	23.2 ± 1.2
80/20	76 ± 4	13.4 ± 1.4	3 ± 1	10	10	35.8 ± 3.2
100/0	79 ± 6	15.4 ± 1.8	3 ± 1	10	10	43.9 ± 2.4

based PU film had the lowest hardness of 33 sec. However, higher bamboo tar content caused increased the hardness, because of the introduction of more rigid aromatic rings into the system. The tensile tested showed that the tendency of more bamboo tar content, the larger tensile strength observed, especially for the bamboo tar/castor oil weight ratio of 60/40 PU film of 21.2 MPa. The results also showed that PU films containing more bamboo tar had the lower elongation at break as well as the impact resistance, such as the ones containing more than 60% bamboo tar possessed of hard and brittle characteristic which due to the presence more aromatic structures. The cross-cut assay of PU films on the wood panel showed no detached area was observed, indicating the excellent adhesion (i.e., 10 grade) obtained for all specimens. The 100% castor oil and 100% bamboo tar containing PU films had the best and worst abrasion resistance of the weight loss of 7.7 and 43.9 mg/1000 revolutions, respectively. The result showed the negative effect of the addition of bamboo tar to the PU coating for the abrasion resistance of film.

Some film properties of PU coatings with different bamboo tar/castor oil weight ratios are listed in Table III. The gel content represents the extent of cross-linking of —NCO with —OH group. The reactivity of pure castor oil with PTDI is more completely than that of bamboo tar, therefore, the gel content increased as castor oil content rose. This is due to the bamboo tar possesses some lignin-like macromolecule and less crosslinked structure obtained. For all PU films after 20 hot-and-cold cycles test, no film cracking was found on coated wood panels and the gloss retention of all specimens were retained at above 80%, indicating that all of the PU films had an excellent durability. After 100 h UV light exposure, the PU films with more bamboo tar content had the lower ΔE^* value. It is due to the natural dark color of the film itself, the color changes are unobviously after UV exposure. The results revealed that the film with higher bamboo tar content had a superior lightfastness, especially for the ones more than 60%.

Figure 1 shows the FTIR spectra of PU films with different bamboo tar/castor oil weight ratios. The

100% castor oil containing PU film (0/100) had an intense saturated aliphatic bands at 2980 and 2850 cm^{-1} associated with —CH_2 and —CH_3 , respectively. In addition, the 3010 cm^{-1} band represents an unsaturated aliphatic absorption. It was observed that an increase in bamboo tar content lead to a decrease in the absorption intensity of 2980 and 2850 cm^{-1} due to the reduction of the aliphatic groups of castor oil. The urethane linkage (—NHCOO—) was found for all specimens, such as 1070 cm^{-1} (C—O—C stretching vibration), 1220 cm^{-1} (C=O stretching vibration), 1535 cm^{-1} (N—H bending vibration), 1730 cm^{-1} (C=O stretching vibration), and 3350 cm^{-1} (may be O—H bonds overlapped with N—H bonds of urethanes). The spectra also showed the aromatic C=C at 1600, 1500, and 1450 cm^{-1} of PTDI and bamboo tar. Besides, the characteristic absorption of —NCO group at 2275 cm^{-1} was not appeared due to the complete reaction of PTDI with polyol to form urethane bonds for all specimens.

The thermal stability of PU films with different bamboo tar/castor oil weight ratios was carried out by TGA in nitrogen atmosphere are shows in Figure 2, and the T_{onset} and weight retention for each PU film are summarized as Table IV. The PU films degradation occurred in three events at the temperature range of 100–200, 220–320, and 320–400°C, as shown in derivative TG (DTG). In the first event, at about 100–200°C, there was no degradation event for 0/100 (100% based only on castor oil) and 20/80 PU films. While, the T_{onset} of after 40/60 PU films

TABLE III
Gel Content, Cycle Test, Gloss Retention, and Color Difference of PU Films with Different Bamboo Tar/Castor Oil Weight Ratios

Bamboo tar/castor oil (wt ratio)	Gel content (%)	Cycle test (cycles)	Gloss retention (%)	ΔE^*
0/100	90.9 ± 0.5	>20	94.9 ± 4.7	21.84
20/80	87.2 ± 0.6	>20	91.7 ± 6.6	16.49
40/60	69.4 ± 1.2	>20	80.4 ± 3.2	12.98
60/40	68.6 ± 1.7	>20	82.2 ± 4.1	4.52
80/20	66.8 ± 1.8	>20	81.3 ± 3.3	2.91
100/0	68.1 ± 0.5	>20	84.0 ± 2.7	5.28

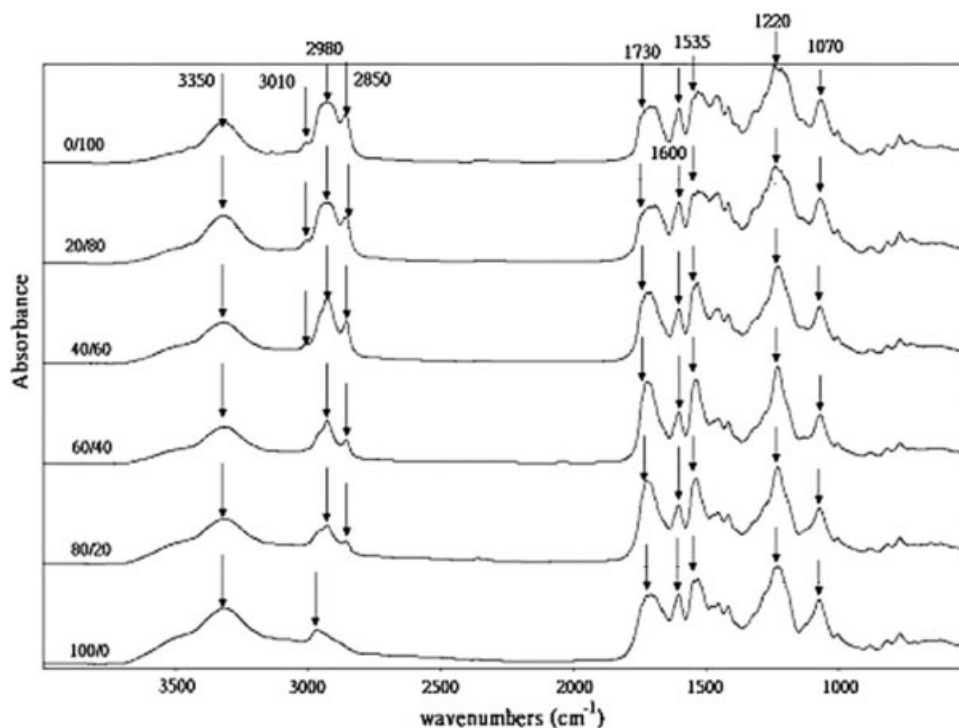


Figure 1 FTIR spectra of PU films with different bamboo tar/castor oil weight ratios.

decreased with increasing the bamboo tar content i.e. the T_{onset} for 40/60, 60/40, 80/20, and 100/0 were 129.0, 123.5, 111.4, and 97.3°C, respectively. The reduction of T_{onset} is due to the high oxygen content of bamboo tar (40.3% oxygen by methoxyl and hydroxyl group of phenolic derivatives) and due to the distillation of small amount of volatiles with low molecular weight.^{11,12}

The second event, at about 220–320°C, can be related to the degradation of the urethane linkage which derived from the reaction of castor oil and bamboo tar with PTDI. The result showed that the T_{onset} increased with higher bamboo tar content, e.g., the T_{onset} for 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0 were 220.2, 228.9, 229.1, 231.1, 233.0, and 239.8°C, respectively. It could be explained that during the thermal process, the aromatic rings of bamboo tar generates a carbon layer which retards the degradation of higher bamboo tar containing PU films.¹⁰

The third event, at about 320–400°C, can be attributed to the degradation of the castor oil aliphatic structure.¹² The tendency of T_{onset} was similar to those of the second event, while for the 100/0 PU film (100% based on bamboo tar) no degradation was found owing to no castor oil containing. At the final temperature 550°C, the weight retention for 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0 were 1.7, 1.8, 5.4, 7.0, 9.8, and 13.1%, respectively. The carbonaceous residue increased with increasing bamboo tar content due to its aromatic structure.

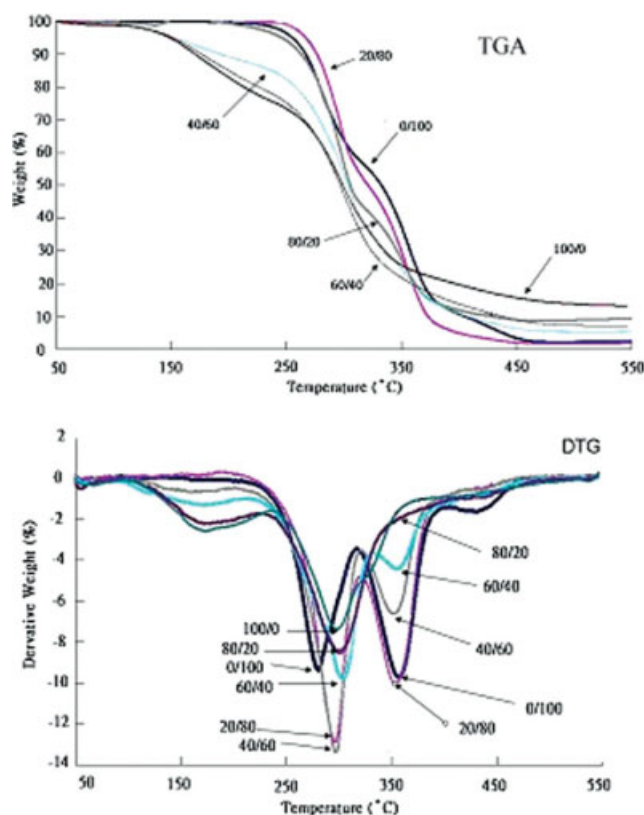


Figure 2 TGA and DTG curves of PU films with different bamboo tar/castor oil weight ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
 T_{onset} and Weight Retention of PU Films with Different Bamboo Tar/Castor Oil Weight Ratios

Bamboo tar/castor oil (wt ratio)	Area A (100–200°C)		Area B (220–320°C)		Area C (320–400°C)		550°C
	Onset (°C)	Weight retention (%)	Onset (°C)	Weight retention (%)	Onset (°C)	Weight retention (%)	Weight retention (%)
0/100	–	–	220.2	99.3	318.7	55.7	1.7
20/80	–	–	228.9	99.7	321.2	49.3	1.8
40/60	129.0	98.8	229.1	94.4	350.1	38.0	5.4
60/40	123.5	97.7	231.1	85.7	332.1	31.4	7.0
80/20	111.4	98.4	233.0	78.7	343.1	23.4	9.8
100/0	97.3	98.8	239.8	75.3	–	–	13.1

In DMA experiments, the $\tan \delta$ versus temperature of PU films with different bamboo tar/castor oil weight ratios are shown in Figure 3 and the $\tan \delta_{\text{max}}$ and T_g values are listed in Table V. According to Melo and Pasa,¹² the morphology PU film containing 100% castor oil is a uniformity of fracture and as the biopitch content increasing it becomes less segmented, and increases the heterogeneity of the domains, and reaches a lamellar fracture morphology in PU film based on 100% *Eucalyptus* tar pitch. In our study, the similar results were obtained. The 100% castor oil based PU film (0/100) was a uniformity domains of a homogeneous material. It possessed a broad peak of $\tan \delta$ and a lower $\tan \delta_{\text{max}}$ of 0.1877, resulting a higher cross-linking density which is in accordance with a higher gel content as shown in Table III. The 100% bamboo-tar based PU film (100/0) had a T_g of 63°C only insignificant higher than 100% castor oil based PU film of 61°C. Even the PU film (100/0) had a higher hard-

ness, but also higher in $\tan \delta_{\text{max}}$ of 0.3950, showing a more aromatic structures contributing to the hardness but less cross-linking density in the system.

The results also found that the T_g s showed great variation with bamboo tar addition and not regulation was observed. This may be due to the quantity and compatibility of the two polyols, castor oil and bamboo tar, which affects the reactivity of —NCO group with —OH for each polyol. The PU film (60/40) showed two T_g s of 37 and 130°C. The 37°C referred to the soft segments present in PU and were attributed to the less cross-linking part of castor oil in the system. While, the 130°C was probably due to the hard segments formed by bamboo tar and also derived from the better interpenetrating of two types of urethane linkage which made from castor oil and bamboo tar with PTDI, respectively. The results is in agreement with the PU film (60/40) had the highest tensile strength as shown in Table II. In addition, the other samples showed only one T_g , resulting a better homogeneity of the polymeric systems.

CONCLUSIONS

The PU coatings based on bamboo tar, along with castor oil and PTDI, showed a semitransparent film and yellow-brown color for wood finishing and possessed excellent adhesion as well as durability of films. The increase in bamboo tar content led to

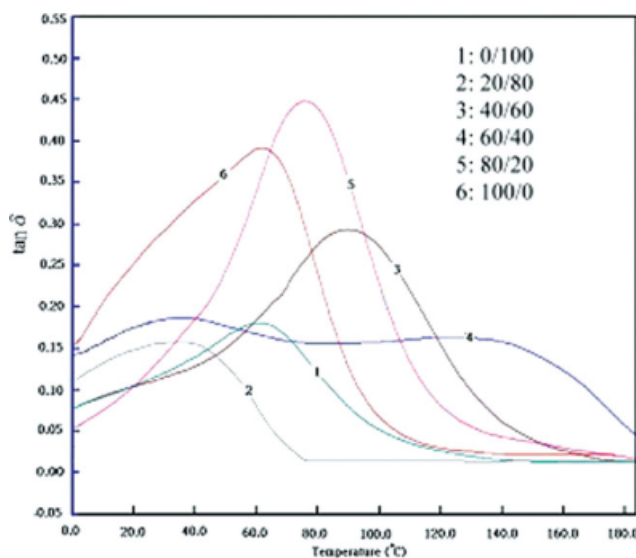


Figure 3 $\tan \delta$ versus temperature of PU films with different bamboo tar/castor oil weight ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
 T_g and $\tan \delta_{\text{max}}$ of PU Films with Different Bamboo Tar/Castor Oil Weight Ratios

Bamboo tar/castor oil (wt ratio)	T_g (°C)	$\tan \delta_{\text{max}}$
0/100	61	0.1877
20/80	34	0.1593
40/60	89	0.2923
60/40	37, 130	0.1862, 0.1625
80/20	77	0.4611
100/0	63	0.3950

shorten drying time of coatings and to increase in hardness, tensile strength and lightfastness of films. The thermal stability and carbonaceous residue of PU film increased with increasing bamboo tar content due to its aromatic structure. However, owing to obtain the lower gel content, it is a disadvantage of using too high amount of bamboo tar in coatings. From the above mentioned results and a light smell flavor, it suggests that the bamboo–tar based PU coating is suitable to be used as an exterior wood coating.

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