Preparation of Liquefied Bark-Based Resol Resin and Its Application to Particle Board

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ABSTRACT: Barks of Taiwan acacia (*Acacia confusa*) and China fir (*Cunninghamia lanceolata*) were liquefied in the presence of phenol with sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) as catalyst. The properties of resins prepared from liquefied bark and the feasibility of liquefied bark-based resol resins in particle board manufacturing were investigated. The viscosity and thermosetting property of liquefied bark-based resol resins were affected by the kind of bark species and the catalyst used. Liquefied bark-based resol resins using China fir bark as raw material had higher viscosity than the ones using Taiwan acacia bark. In the course of thermosetting, liquefied bark-based resol resins using Taiwan acacia bark as raw material had a higher maximum temperature of exothermic peak and onset temperature as well as a larger quantity of exothermic heat than those using China fir bark. Resol resins prepared from bark liquefied with H_2SO_4 as catalyst had higher viscosity, while resins with HCl as catalyst had a higher maximum temperature and height of exothermic peak and a larger quantity of exothermic heat at thermosetting. Particle board made with A-S adhesive that was prepared from liquefied Taiwan acacia bark with H_2SO_4 as catalyst had the best particle board properties than those made with other adhesives. For the particle board made with A-S adhesive, its static bending strength and internal bonding strength would be increased as the hot-pressing time extended. The particle board made with hot-pressing temperature of 150°C and hot-pressing time of 10 min had the maximum normal and wet static bending strength and internal bonding strength. Its normal static bending strength was 170.8 kgf/cm^2 and the particle board showed satisfactory wet static bending strength and internal bonding strength. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1837–1841, 2003

Key words: adhesives; biomaterials; differential scanning calorimetry; liquefied bark; resol resin

INTRODUCTION

Although wood is a renewable natural resource, how to utilize wood effectively is still an important subject. Petroleum is the resource people most heavily rely on nowadays, but it will be exhausted eventually. Tree bark is rich in phenolic material. If properly applied, it may substitute for the demand of petroleum in part. The authors have done a series of researches in the application of bark extractives to make wood adhesives.[1–4] Liquefaction of wood or bark in phenol and with inorganic acid as catalyst and using liquefied wood or bark to make wood adhesives can expand the applications of these biomaterials. Alma et al.[5,6] employed HCl as catalyst to liquefy wood in phenol, then used liquefied wood as the raw material for resin and molding. Mitsunaga et al.[7,8] and Santana et al.[9,10] investigated the feasibility of preparing wood adhesives using tannin and bark that liquefied in phenol. The authors also used Taiwan acacia and China fir barks as raw materials to investigate their liquefaction effects in phenol with HCl and H_2SO_4 as catalyst and made wood adhesives from these liquefied barks.[11,12] This study discusses the preparation of liquefied bark-based resol resin and its application in particle board manufacturing.

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EXPERIMENTAL

Materials

Taiwan acacia (*Acacia confusa*) and China fir (*Cunninghamia lanceolata*) barks were liquefied in this study. All barks were air-dried, ground to powder in a hammer mill with a screen of 2 mm diameter, and dehydrated with vacuum oven at 60°C. Chemicals used such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), phenol, formalin, sodium hydroxide, and methanol were reagent grades and were used without further purification. Particle boards were made with wood particles of China fir.

Liquefaction of bark in phenol

To liquefy the bark, phenol was charged into a four-neck separable glass flask (1 L) equipped with stirrer, thermometer, and reflux condenser. The reagent was stirring and heating to 120°C by electric heating mantle, then H_2SO_4 or HCl was dropped into with a separating funnel as catalyst. Dried bark powder was slowly added into the reacting flask. After all the bark powder was added, the temperature of reactant was elevated to 150°C; this temperature was maintained for 60 min to carry out liquefaction reaction. In the reaction of liquefaction, the weight ratios of Taiwan acacia bark and China fir bark to phenol were 1:3 and 1:3.5, respectively, and the amounts of H_2SO_4 and HCl were 5% and 10% based on the weight of phenol, respectively.

Preparation of liquefied bark-based resol resin

After liquefaction, the liquefied bark-based resol resins were prepared with 100 parts of the liquefied products, 155 parts of formalin (37% aqueous solution), and 64 parts of sodium hydroxide aqueous (40% concentration). Prior to liquefied bark-based resol resins preparation, liquefied bark, formalin, and one-third of sodium hydroxide aqueous were loaded into the reacting bottle; the temperature of reactants were elevated to 85°C within 30 min and held for 10 min. Then two-thirds of remnant sodium hydroxide were gradually dropped into reacting bottle with separating funnel; at this stage, the temperature of reactant was maintained at 85°C. Until all sodium hydroxide was added, the temperature was held at 85°C, and the reaction continued for 60 min; the resulting resin was then cooled to room temperature. Four kinds of liquefied bark-based resol resins were prepared.

Properties of liquefied bark-based resol resins

Properties such as solid content, viscosity (at 25°C), pH value, and gel time (at 135°C) of liquefied bark-based resol resins were measured.

Thermosetting of liquefied bark-based resol resins

The thermosetting properties of liquefied bark-based resol resins were measured by differential scanning calorimetry (Perkin-Elmer DSC-7). The capsule used was large-volume O-ring–sealed stainless steel sample container that could tolerate up to 24 atm of internal pressure. The samples weighed between 15 and 20 mg. The environment air was nitrogen. The heating rate was 10°C/min from temperature of 30 to 225°C. For all resins, the maximum temperature, onset temperature, and height of exothermic peak as well as the quantity of exothermic heat at thermosetting were analyzed.

Particle board production

China fir wood particles were dried to reach the moisture content approximately between 3% to 5%. The rate of adhesive applied was 10% of adhesive solid, based on oven-dried weight of wood particles. The liquefied bark-based resol resins were sprayed onto the surface of wood particles in a drum-type rotary blender by means of air-spread gun. The glued wood particles were hand-formed to a particle board mat. The construction of particle boards was single layer, 40 cm by 40 cm in size, 1.2 cm in thickness, and 0.6 g/cm^3 in target density. The parameters of particle board manufacturing investigated in this experiment were kinds of resin, hot-pressing temperature, and hot-pressing time. Particle boards made with A-S adhesive were pressed at 25 kgf/cm^2 at hot-pressing temperatures of 150, 165, and 180°C for 5, 8, and 10 min, respectively. For the other three adhesives, particle boards were pressed at hot-pressing temperature of 150°C for 10 min. Two boards were made for each experimental condition, for a total of 24 boards.

Properties of particle boards

All 24 particle boards were conditioned to their equilibrium moisture content at 20 ± 1°C and 65% ± 2% relative humidity. Then each board was tested for density (eight specimens, 5 cm by 5 cm), moisture content (eight specimens, 5 cm by 5 cm), normal and wet static bending strength (five specimens, 5 cm by 23 cm), internal bonding strength (five specimens, 5 cm by 5 cm), and thickness swelling in the 24-h water soak test (five specimens, 5 cm by 5 cm) according to the testing standard of CNS 2216 (Chinese National Standards[13]).

RESULTS AND DISCUSSION

Properties of liquefied bark-based resol resins

For bark liquefaction, two kinds of bark species (Taiwan acacia and China fir) and two kinds of catalyst (H_2SO_4 and HCl) were used. With these liquefied barks, four kinds of liquefied bark-based resol resins were prepared in this study. Table I illustrates the properties of liquefied bark-based resol resins prepared in this study. The viscosity of liquefied bark-based resol resins is affected by both the kind of bark species and catalyst used in liquefaction. The liquefied bark-based resol resins that used Taiwan acacia bark as raw material have lower viscosity than resins that used China fir bark. The liquefied bark-based resol resins prepared from liquefied bark that used H_2SO_4 as catalyst in liquefaction had higher viscosity than the one with HCl as catalyst. Resins of A-S and C-S prepared from liquefied bark with H_2SO_4 as liquefying catalyst have a viscosity of 350 and 840 mPa s, respectively, while resins of A-C and C-C prepared from liquefied bark with HCl as liquefying catalyst have a viscosity of 33 and 45 mPa s, respectively, significantly

TABLE I
Properties of Liquefied Bark-Based Resol Resins

	Liquefaction condition			Properties of resins			
Resins	Bark species	Catalyst	Catalyst added (%)	Solid content (%)	pH	Viscosity (mPa s)	Gel time (min) at 135°C
A-S	Taiwan acacia	H_2SO_4	5	43.0	11.36	350	16.4
A-C	Taiwan acacia	HCl	10	43.1	11.45	33	14.4
C-S	China fir	H_2SO_4	5	45.2	11.53	840	19.4
C-C	China fir	HCl	10	46.2	11.40	45	11.2

lower than A-S and C-S. The reason may be that, in the reaction of liquefaction, H_2SO_4 catalyst has higher acidity than HCl. The liquefaction with strong acid can promote degradation of wood lignocellulose and reduce its molecular weight, thus facilitating the combination of phenol with lignocellulose and help the bark liquefied. In our previous reports, the liquefied bark that using H_2SO_4 as catalyst had lower amount of unliquefied bark residue than HCl.[11,12] However, this strong acid will cause the recondensation of lignin after it is degraded and increase its molecular weight. The existence of these higher molecular components in liquefied bark will result in prepared resins with partial ingredients of larger molecular weight and produce greater viscosity.

The liquefied bark-based resol resins with H_2SO_4 as catalyst at the time of bark liquefaction require longer gel time at 135°C than the one with HCl as catalyst. As mentioned earlier, resins of A-S and C-S made with liquefied bark with H_2SO_4 as liquefying catalyst have higher viscosity, showing the existence of larger-molecular-weight ingredients in resins. The steric hindrance caused by this larger-molecular-weight structure may make further crosslinking reaction more difficult, therefore the reactivity of these resins are weaker and require longer gel time than the ones made with HCl as liquefaction catalyst.

Thermosetting of liquefied bark-based resol resins

Table II shows the results from DSC thermosetting analysis of various kinds of liquefied bark-based resol resins. The resins prepared from liquefied Taiwan acacia bark have a higher maximum temperature of exothermic peak than that prepared from liquefied China fir bark at the time of thermosetting. For both liquefied Taiwan acacia and China fir bark, resins prepared from liquefied bark using HCl as catalyst have a higher maximum temperature of exothermic peak than those using H_2SO_4. The onset temperature at which thermosetting reaction started is higher for the resins that used liquefied Taiwan acacia bark as raw material than the ones using liquefied China fir bark. For both bark species, however, liquefaction using HCl as catalyst produces resins having a lower onset temperature. Liquefied Taiwan acacia bark-based resol resins have a larger quantity of exothermic heat and a higher exothermic peak at thermosetting than liquefied China fir bark-based resol resins. For both bark species of liquefied bark-based resol resins, liquefaction with HCl as catalyst has a greater quantity of exothermic heat and a higher exothermic peak than liquefaction with H_2SO_4 as catalyst. Comparing these results with the ones in Table I, we can see that at the time of thermosetting, liquefied bark-based resol resins made from the same bark species have a higher viscosity and require a higher onset temperature and release a smaller amount heat at crosslinking reaction.

Figure 1 is the DSC thermograms of these four liquefied bark-based resol resins. Among these, A-S, A-C, and C-C resins all demonstrate only a single exothermic peak at thermosetting, while C-S resin made with liquefied China fir using H_2SO_4 as catalyst presents another smaller exothermic peak at low temperature region. It shows that the adhesive has not completed its addition reaction at resin preparing stage, so the exothermic peaks for both the addition reaction and the condensation reaction appear simul-

TABLE II
Thermosetting Properties of Liquefied Bark-Based Resol Resins

Resins	Maximum temperature of exothermic peak (°C)	Onset temperature (°C)	Exothermic heat at thermosetting (J/g)	Height of exothermic peak (w/g)
A-S	147.0	110.314	−66.095	−0.319
A-C	147.6	94.616	−81.565	−0.354
C-S	145.0	95.954	−61.209	−0.269
C-C	146.6	94.574	−76.658	−0.325

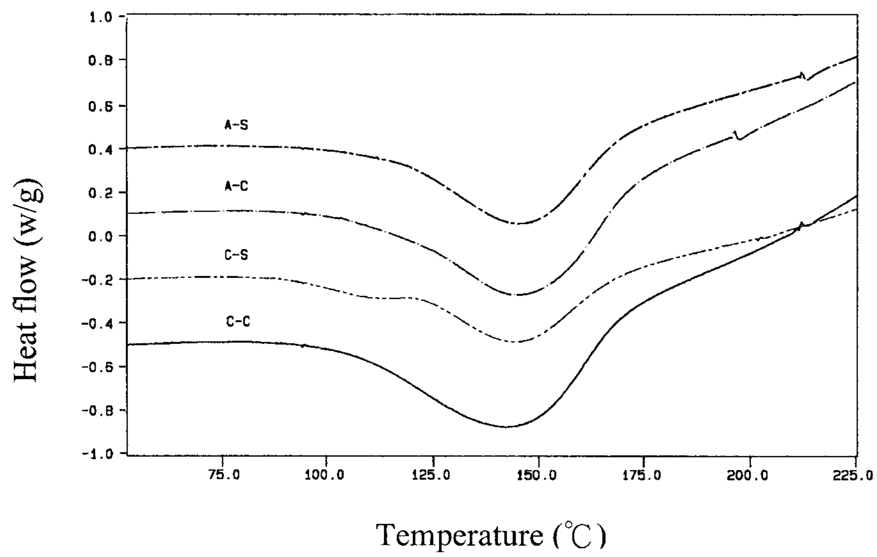

Figure 1 DSC thermograms of various kinds of liquefied bark-based resol resins.

taneously at thermosetting analysis. This phenomenon is the same in an earlier research by us.[12]

Properties of particle boards

Table III shows the properties of particle boards made with the liquefied bark-based resol resin of A-S with 10% of adhesive rate and hot-pressed at temperature of 150, 165, or 180°C for 5, 8, or 10 min. At hot-pressing temperature of 150°C, as the hot-pressing time extends, the static bending strength increases apparently. With hot-pressing time of 10 min, the particle board has the largest static bending strength than at others. The normal static bending strength reaches 170.8 kgf/cm^2, meeting the requirement of 130 kgf/cm^2 for the particle board of model 150 by CNS 2215 standard, and close to the requirement of 180 kgf/cm^2 for the particle board of model 200. After soaking in 70°C water, its wet bending strength is 115.5 kgf/cm^2, above the requirement of 90 kgf/cm^2 for the particle board of model 200 by CNS standard. At hot-pressing temperature of 165°C, static bending strength increases as hot-pressing time extends, but with a less apparent tendency than at 150°C. At hot-pressing temperature of 180°C, the normal static bending strength reaches the maximum after 5 min of hot-pressing time, but extending the hot-pressing time will only increase the wet static bending strength slightly. The internal bonding strength of particle boards made at three different temperatures all surpass the requirement of 3 kgf/cm^2 for the particle board of model 200 by CNS standard. Comparing the different hot-pressing times, lower internal bonding strength happens at hot-pressing time of 5 min, while not much difference shows between 8 and 10 min. Among all particle boards, the ones that hot-pressed at the temperature of 180°C

TABLE III
Properties of Particleboards Made with Liquefied Bark-Based Resol Resin of A-S under Various Boards Manufacturing Conditions

Hot-pressing				Bending Strength (kgf/cm^2)			
Temperature (°C)	Time (min)	Board density (g/cm^3)	Moisture content (%)	Normal	wet	Internal bonding strength (kgf/cm^2)	Thickness swelling (%)
150	5	0.59	8.0	117.0	75.2	3.3	16.7
	8	0.62	7.4	154.6	101.5	8.8	15.9
	10	0.61	7.2	170.8	115.5	8.7	15.2
165	5	0.63	7.5	111.1	69.2	5.9	16.6
	8	0.61	6.8	133.4	89.8	8.3	15.3
	10	0.63	6.5	136.2	93.7	7.8	15.3
180	5	0.60	6.9	153.4	101.2	6.2	14.9
	8	0.61	6.5	155.5	108.9	7.7	12.5
	10	0.62	6.5	152.0	113.4	8.6	12.2

The board density and moisture content were the means of eight specimens; the bending strength, internal bonding strength, and thickness swelling were the means of five specimens.

TABLE IV
Properties of Particleboards Made with Various Kinds of Liquefied Bark-Based Resol Resins

Adhesive	Board density (g/cm^3)	Moisture content (%)	Bending strength (kgf/cm^2)		Internal bonding strength (kgf/cm^2)	Thickness swelling (%)
			Normal	Wet		
A-S	0.61	7.2	170.8	115.5	8.7	15.2
A-C	0.61	7.1	117.5	77.2	3.1	20.2
C-S	0.59	7.8	125.3	75.5	6.3	16.3
C-C	0.66	7.4	152.8	88.2	4.2	16.1

Ten percent of adhesive rate, 150°C of hot-pressing temperature, and 10 min of hot pressing time.

demonstrate the minimum thickness swelling after 24-h water soak test and have a decreasing tendency in thickness swelling as hot-pressing time extends.

Table IV shows the properties of particle boards made with the four kinds of liquefied bark-based resol resins. The manufacturing conditions of particle board used are 10% of resin rate, 150°C of hot-pressing temperature, and 10 min of hot-pressing time. Comparing the two kinds of liquefied Taiwan acacia bark-based resol resin, particle boards made with A-S resin using H_2SO_4 as liquefied catalyst have obvious superior properties to the ones made with A-C using HCl. The properties of particle boards made with the two kinds of liquefied China fir bark-based resol resins showed slight differences. The particle boards made with C-C have static bending strength slight greater than the ones with C-S, but the internal bonding strength is greater for C-S. Among the four kinds of liquefied bark-based resol resins, particle boards made with A-S has the best normal and wet static bending strength, internal bonding strength, and thickness swelling.

CONCLUSIONS

The viscosity of liquefied bark-based resol resins are affected by the kind of bark species and catalyst used in bark liquefaction. Resins prepared from liquefied China fir bark have greater viscosity than the ones prepared from liquefied Taiwan acacia bark. The liquefied bark with H_2SO_4 as catalyst in liquefaction makes the resins have higher viscosity than the one with HCl as catalyst.

At the time of thermosetting, liquefied Taiwan acacia bark-based resol resins have a higher maximum temperature of exothermic peak and onset temperature and a larger quantity of exothermic heat than liquefied China fir bark-based resol resins. Resins prepared from liquefied bark that used HCl as liquefaction catalyst have a higher maximum temperature and height of exothermic peak and a larger quantity of exothermic heat at thermosetting than the ones with H_2SO_4 as catalyst.

Among the four kinds of liquefied bark-based resol resins, particle boards made with A-S have the best properties. As the hot-pressing time extended, the static bending strength and internal bonding strength of particle board will be increased. The particle board made at hot-pressing temperature of 150°C, and hot-pressing time of 10 min has the best mechanical properties.

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References

1. Lee, W. J.; Liu, C. T. For Prod Industries 1996, 15, 109.
2. Lee, W. J.; Liu, C. T. For Prod Industries 1996, 15, 251.
3. Lee, W. J.; Liu, C. T. For Prod Industries 1996, 15, 627.
4. Lee, W. J.; Liu, C. T. For Prod Industries 2000, 19, 363.
5. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. Wood Sci Technol 1995, 30, 39.
6. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. Holzforschung 1996, 50, 85.
7. Mitsunaga, T.; Abe, I. Mokuzai Gakkaishi 1992, 38, 585.
8. Mitsunaga, T.; Kondo, O.; Abe, I. Mokuzai Gakkaishi 1995, 41, 200.
9. Santana, M. A. E.; Baumann, M. G. D.; Conner, A. H. Holzforschung 1995, 49, 146.
10. Santana, M. A. E.; Baumann, M. G. D. J Wood Chem Technol 1996, 16, 1.
11. Lee, W. J. For Prod Industries 1998, 17, 681.
12. Lee, W. J.; Liu, C. T. For Prod Industries 2001, 20, 217.
13. Method of Test for Particle Boards. Chinese National Standards CNS 2216 (1984).