

DEVELOPMENT OF ISOTROPIC CARBON FIBER FROM WOOD TAR

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1. Introduction:

Compared with fossil fuel such as coal and petroleum, wood is a rich renewable source to provide readily available energy. Wood had become a part of our daily life and an important precursor for preparation of carbon material such as char. Its thermal decomposition reactions in the absence of air to provide charcoal, liquid, gas fuels. Oil phase in liquids are called wood tar, a kind of mixture including many organic compounds. Although some of these for example, phenols derived from biomass pyrolysis oils are very valuable and useful chemicals [1,2], their separation and purification are still complicated and difficult up to now [3-5]. Based on the presence of many kinds of phenol-containing fractions in wood tar, it is possible to develop wood tar resin by a similar process as the polymerization of phenols into thermal-setting resin [6,7] to prepare high performance carbon materials such as glass-like carbon, carbon fiber, binder with high carbonization yield and so on.

Many researches have been doing to analyze and utilize wood tar. Generally, GC-MS is very useful to analyze the composition of wood tar [7-13], however, it is not enough for the application. Except that, other methods such as IR, NMR, GC-FID and other methods were employed to analyze tar and separated phenols [7,14-17]. The combinations of GC-MS, IR, NMR, TOF-MS, TG are certainly more beneficial to get more information on the constituents of wood tar accurately to use it more effectively.

In the present study, the analyses of the molecular compositions of wood tar by TOF-MS, GC-MS, FT-IR, ¹H-NMR and TG, it was polymerized with formaldehyde solution by using oxalic acid and HCl acid as catalyst at 90°C for 1h and 35min respectively to prepare wood tar resin. The resultant resin was successfully spun, self-cured at 200°C and carbonized at 650~1000° to achieve isotropic carbon fiber.

2. Experimental

2.1. Analysis of wood tars.

In the present study, two kinds of wood tars (mixed wood tar and bamboo tar) were used. Their elemental composition was summarized in Table 1. GC-MS was employed to identify half-quantitatively the kinds of organic compounds in tar. TOF-MS was used to analyze molecular weight distribution of compounds in tar. NMR was employed to get information about aromatic index in tar. FT-IR was used to qualitatively analyze the functional groups in tar. TG was employed to determinate the carbonization properties.

2.2. Polymerization of wood tar (bamboo tar) into resin.

Wood tar of 120g was polymerized with 37% formaldehyde solution of 120g in three-mouth flasks placed in heater, using oxalic and HCl acid as catalysts at 90°C for 1h and 35min respectively to prepare wood tar resin. After polymerization and cooling, water over resin was taken out and further removed the

un-reacted small molecules under decompression.

2.3. Preparation and characterization of carbon fiber from wood tar resin.

The resultant resin was successfully spun (nozzle: D 0.3mmx L 0.9mm), self-cured at 200°C for 1h with a heating rate of 10°C/h and carbonized at 650~1000°C for 1h with a heating rate 1~3°C/min in a flow of argon to achieve isotropic carbon fiber. Properties of resin based CF were measured.

3. Results and Discussion

3.1. Composition

Wood and bamboo tars show high oxygen-containing amount, 28 and 30%, respectively. The carbon containing content of the former is higher than the latter. Hexane insoluble part of wood tar is much higher than bamboo one as shown in Table 1, indicating that wood tar contains more polar components.

The distribution of hydrogen derived from d ¹H-NMR spectra (not shown) was summarized in Table 2. The NMR ¹H-NMR spectra contained two major zones of chemical shift about 1-5ppm and 6-9 attributed to aromatic and aliphatic protons, respectively. Aromatic index of wood tar is slightly high than bamboo tar, 0.48 and 0.47, respectively.

Fig. 1 showed IR spectra of two kinds of tars, indicating that they contain a lot of functional groups, especially –OH groups. The groups play an important role during the polymer development from wood and bamboo tars. Strong absorption was observed at 3200-3600cm⁻¹, attributed to free phenolic OH and COOH groups. Two carbonyl bands demonstrated the presence of carboxylic acids and ketones (at 1700cm⁻¹) and ether and phenolic OH at 1100-1200cm⁻¹. Those peaks of 1400-1600cm⁻¹ were certainly ascribed to aromatic structures.

TOF-MS spectra of tars (not shown) demonstrated that wood tar displays a distribution varied from 200 to 600, in the meantime, bamboo tar shows a slight decrease distributed from 160 to 450. Their average molecular weights are 310 and 315, respectively.

GC-MS spectra of tars (not shown) displayed that the used tars are composed of the mixture of many kinds of organic compounds over 50 as shown in Table 3. Bamboo tar contains more amount of phenol, methyl phenol, 4-ethyl-4-methoxy phenol, 2,6-dimethoxy phenol than wood tar. Wood tar displays more amount of benzenediol, dimethyl phenol, 2-methoxy-4-propyl phenol, 2-methoxy-4-(1-propenyl) phenol. The areas of peaks containing phenol group in areas of all peaks for bamboo and wood tars amounts for 71% and 50%, respectively, indicating also the former contains more amount phenols than the latter.

TG results indicated that bamboo tar showed higher carbonization yield at 900°C than wood one, 16 and 12%, respectively. It is consistent with the information obtained from GC-MS.

3.2. Polymerization of wood tar.

TOF-MS spectra of tar resins (not shown) demonstrated that the molecular weight of products obtained from the polymerization of tars with formaldehyde under acid catalyst, trends to enlarge. Two kinds of resins derived from wood and bamboo tars display broader distributions of molecular weights from 200 to 800. Their average molecular weights are 386 (wood tar resin) and 406 (bamboo tar resin), respectively. The increase is certainly attributed to the polymerization of phenols contained in tars. Two precursors of tars are transformed from liquid into solid after the polymerization reactions. Bamboo tar resin shows a higher softening point than the other, 80°C and 60°C, respectively. The former displays a

higher atomic ratio of carbon to hydrogen as shown in Table 1. It should be noted that the molecular weight be not increase largely because the compounds except phenols do not react with formalin to obtain larger molecule. In the same preparation conditions, the resultant resin yields are 72 and 80% for wood tar and bamboo tar, respectively, demonstrating that the latter contains more phenols.

3.3. Preparation of carbon fibers.

The above resultant resins show a good spinnability at low temperature of 130°C-185°C. After curried at 200°C, spun fibers were successfully carbonized to develop carbon fibers as shown in Fig. 2. Some properties of fibers derived from resins are summarized in Table 4. The morphology of as-prepared carbon fibers was showed in Fig. 2, indicating a diameter varied from 10 to 20um. The curing results in a slight decrease of weight of about 10% due to the volatile of some compounds with small molecules. Slow heating rate may avoid the molting of fibers during carbonization. The cured resin derived from bamboo shows higher carbonization yield than the resin from wood tar, 48 and 40%, respectively. Based on tar amount, total yields of bamboo and wood tars are 43 and 35%, respectively, ascribed to more amount of phenols in the former, which can be polymerized into thermal setting resin to improve the yield. The prepared carbon fibers derived from bamboo tar resin show a larger interspacing of 0.385-0.417nm from XRD pattern and middle strength ratio of I_{1350}/I_{1580} of 0.72-0.96, from Raman spectroscopy. The prepared carbon fibers derived from wood tar resin display two interspacings of 0.350 and 0.385nm from XRD pattern, indicating that there are two kinds of crystallite structures, and larger strength ratio of I_{1350}/I_{1580} of 1.09. The properties of the carbon fibers are expected to be comparable with those of commercial carbon fibers.

4. Conclusion

In summary, the analyses of the molecular compositions of wood and bamboo tars reveal that two kinds of tars contain a few of phenol-group compounds. The components may be polymerized into a special thermal setting resin, which can be expected as a good precursor to develop high performance carbon materials such as carbon fibers, carbon film, carbon membrane, glass-like carbon, carbon binder and so on. In the present study, carbon fibers have been developed successfully from the resultant two kinds of tar resins, and their properties are found to be comparable to those of commercial carbon fibers. Careful investigation is still under research to achieve higher yield and improve further the properties of carbon fibers. In addition, tars derived from different trees and different conditions should be checked in the latter research.

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Table 1 Basic data of wood, bamboo tars and their resins after the polymerization

	Elemental analysis (wt%)				C/H	C/O	HI wt%	Ash wt%	SP °C
	C	H	N	O (by diff)					
Wood tar	64.66	6.92	0.16	28.26	0.78	3.05	61		
Bamboo tar	61.98	7.33	0.42	30.27	0.70	2.73	17	0.21	
Wood tar resin	68.98	6.78	0.14	24.10	0.85	3.82		0.17	60
Bamboo tar resin	70.02	6.56	0.52	22.90	0.89	4.08		0.10	80

HI: n-hexane insoluble

Table 2 ¹H-NMR analysis of wood and bamboo tars in CDCl₃

	Hydrogen distribution, %			f _a
	H _a	H _α	H _β +H _γ	
Tar	19.0	66.5	14.5	0.48
Pitch	25.8	56.3	17.8	0.47

H_a: aromatic hydrogen δ (¹H)=6~9ppm; H_α: α -hydrogen δ (¹H)=1.7~4;

H_β: β -hydrogen δ (¹H)=1~1.7; H_γ: γ -hydrogen δ (¹H)=0.5~1.

Table 4 Properties of carbon fibers derived from tar resins

Fiber	Curing conditions °C—h-°C/h	Curing yield* %	Carbonization conditions °C—h-°C/min	Carbonization yield** %	Total yield* %	d ₀₀₂ nm	R (I ₁₃₅₀ /I ₁₅₈₀)
	200-1-10	90	1000-1-1	49	44	0.388	0.914
	200-1-20	87	1000-1-1	47	41	0.385	0.967
Wood tar resin	200-1-10	87	1000-1-1	40	35	0.351 (25.4°) 0.386 (23.0°)	1.097
	200-1-10	87	1000-1-2	40	35	0.348 (25.6°) 0.385 (23.1°)	1.093

Yield base:*resin; **cured resin

Table 3 Compound contents of wood and bamboo tars followed by GC-MS analysis

No	RT min	Compound	MW	Formula	GC peak area, %	
					Wood tar	Bamboo tar
1	5.68	2-furancarboxaldehyde	96	C ₅ H ₄ O ₂		2.697
2	6.80	2-furanmethanol	98	C ₅ H ₆ O ₂		
3	7.96	2-methyl-2-cyclopenten-1-one	96	C ₆ H ₈ O		
4	8.13	1-(2-furanyl)-ethanone	110	C ₆ H ₆ O ₂		
5	8.18	Butyrolactone	86	C ₄ H ₆ O ₂	0.822	
6	8.77	3-methyl cyclopentanone	98	C ₆ H ₁₀ O		
7	9.64	5-methyl-2-furancarboxaldehyde	110	C ₆ H ₆ O ₂	0.461	
8	10.74	Tetrahydro-2-furanmethanol	102	C ₅ H ₁₀ O ₂	1.260	
9	11.29	3-methyl-1,2-cyclopentanedione	112	C ₆ H ₈ O ₂	2.358	
10	11.77	Phenol	94	C ₆ H ₆ O	1.195	5.420
11	12.72	Methoxy phenol	124	C ₇ H ₈ O ₂	8.315	7.080
12	12.93	No known				
13	12.99	Methyl phenol	108	C ₇ H ₈ O	2.106	2.403
14	13.20	Maltol	126	C ₆ H ₈ O ₆		
15	13.43	Methyl phenol	108	C ₇ H ₈ O ₂	1.355	2.926
16	13.52	Methyl phenol	108	C ₇ H ₈ O	2.544	2.417
17	14.63	Dimethyl phenol	122	C ₈ H ₁₀ O	1.185	
18	14.70	Dimethyl phenol	122	C ₈ H ₁₀ O	0.870	
19	14.77	Naphthalene	128	C ₁₀ H ₈		
20	14.78	2-methoxy-4-methyl phenol	138	C ₈ H ₁₀ O ₂	1.081	
21	14.86	2-methoxy-4-methyl phenol	138	C ₈ H ₁₀ O ₂	11.606	5.407
22	15.09	2-ethyl phenol	122	C ₈ H ₁₀ O		9.025
23	15.52	Dimethyl phenol	122	C ₈ H ₁₀ O	1.869	
24	15.53	1,4:3,6-dianhydro- α -D-glucopyranose	144			
25	16.47	4-ethyl-4-methoxy phenol	152	C ₉ H ₁₂ O ₂	0.768	7.222
26	16.89	Benzenediol	110	C ₆ H ₆ O ₂		
27	16.95	Benzenediol	110	C ₆ H ₆ O ₂	2.747	
28	17.66	Methyl-1,2-benzenediol	124	C ₇ H ₈ O ₂		
29	17.75	2,6-dimethoxy phenol	154	C ₈ H ₁₀ O ₃		11.339
30	18.03	2-methoxy-4-propyl phenol	166	C ₁₀ H ₁₄ O ₂	4.210	1.993
31	18.19	Methyl-1,2-benzenediol	124	C ₇ H ₈ O ₂		
32	19.36	4-hydroxy-3-methoxy benzoic acid	168	C ₈ H ₈ O ₄		6.491
33	19.46	2-methoxy-4-(1-propenyl)-phenol	164	C ₁₀ H ₁₂ O ₂	3.846	
34	20.06	1-(4-hydroxy-4-methoxyphenyl)-ethanone	166	C ₉ H ₁₀ O ₃	1.328	
35	20.54	1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone	182	C ₉ H ₁₀ O ₄		5.508
36	20.67	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	180	C ₁₀ H ₁₂ O ₃	4.572	
37	21.54	2,4-dihydroxy-3-methyl propiophenone	180	C ₁₀ H ₁₂ O ₃		
38	21.71	2,6-dimethoxy-4-(2-propenyl)-phenol	194	C ₁₁ H ₁₄ O ₃		1.200
39	21.81	No known				2.745
40	23.20	2,6-dimethoxy-4-(2-propenyl)-phenol	194	C ₁₁ H ₁₄ O ₃		2.672
41	24.14	No known				
42	24.69	No known				
43	25.01	No known				
44	26.90	(5 α , 9 α , 10 β)-kaur-15-ene	272	C ₂₀ H ₃₂		
45	29.67	2-(1,1-dimethylethyl)-anthracene	234	C ₁₈ H ₁₈		
46	30.27	No known				
47	30.90		286	C ₂₀ H ₃₀ O		
48	30.96		314	C ₂₁ H ₃₀ O ₂	2.404	
Other peak area, %					43.10	23.45
Peak area of phenol-containing group, %					49.60	71.10

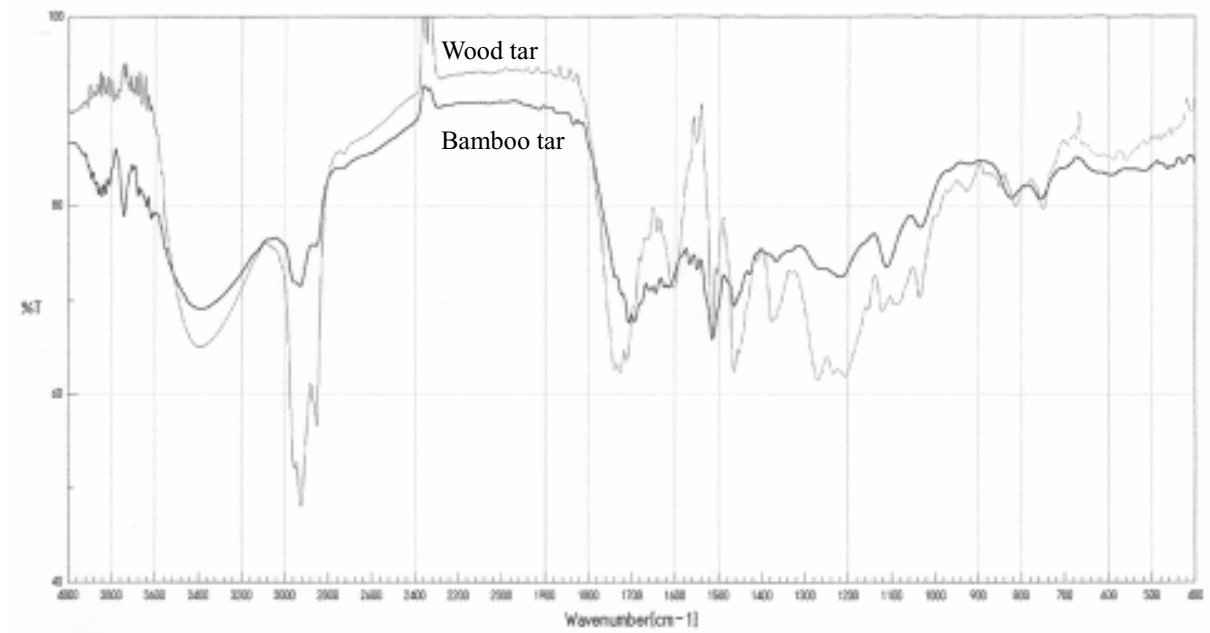
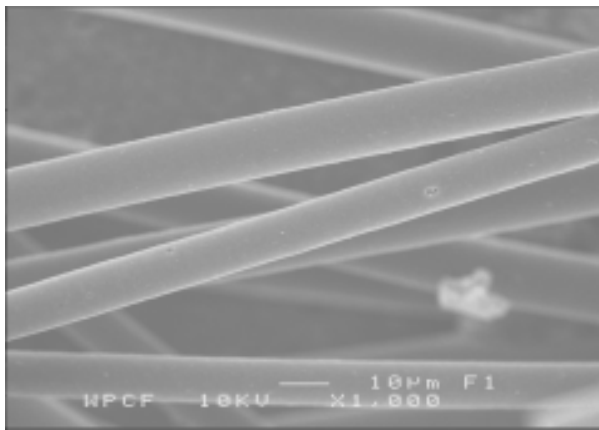
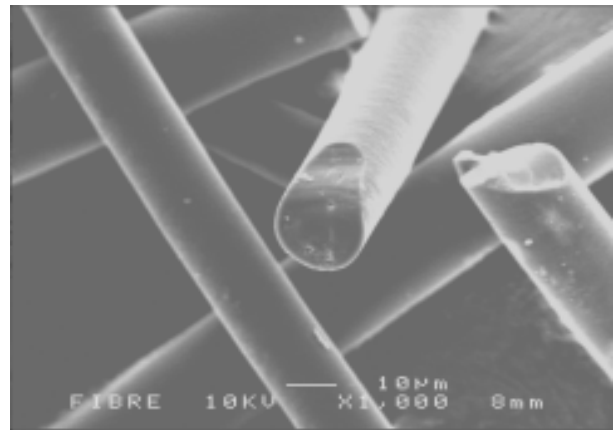


Fig. 1 FT-IR spectra of wood and bamboo tars



CF from bamboo tar resin



CF from wood tar resin

Fig. 2 Morphologies of carbon fibers derived from wood and bamboo tar resins