

Analysis of compressively deformed poplar wood treated with PF resin by ESCA and FTIR

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The compression treatment of wood is useful to improve the properties of plantation wood and considered to be a good process for the efficient utilization of it. In previous report¹⁾, poplar wood was impregnated with phenol-formaldehyde(PF) resin and compressively cured by hot pressing. The PF resin treated wood (PFW) was improved on surface hardness, dimensional stability and mechanical properties. Furthermore chemical characteristics of PFW was analyzed by ESCA and FTIR in this paper. ESCA spectra of PFW were different from those of wood and PF resin according to the wave analysis method. With the increase of weight percent gain(WPG) of PFW, peak area of C_I decreased gradually while those of C_{II} and C_{III} increased gradually. The absorption bands in FTIR spectra of PFW were completely assigned to those of wood and neither separated absorption bands of PF resin nor novel bands were found in it. The relative intensity of some specific bands increased gradually with the increase of WPG. These results would be due to the changes in chemical structure and component of wood with the compressive curing of impregnated PF resin.

Key words : Wood, Compressive curing, PF resin, Impregnation, FTIR, ESCA

1. INTRODUCTION

Wood is a kind of natural high-molecular compound, which is made up of carbon (C), hydrogen (H), oxygen (O) and a small amount of nitrogen (N). Among these elements, carbon, hydrogen and oxygen constitute the main chemical composition of wood—cellulose, hemi-cellulose and lignin. In order to improve the properties of wood, it needs a certain modification treatment, chemical or physical modification treatment. In general, the chemical structure and composition changes through the chemical treatment. In this paper, phenol-formaldehyde(PF) resin treated wood(PFW) under different treatment conditions was analyzed using ESCA and FTIR^{2,3,4)}.

2. EXPERIMENTAL METHODS

2.1 Wood

Wood species was poplar, and the size of specimen was 20(T)×20(R)×30(L) mm.

2.2 PF resin

Water-soluble low-molecular weight PF resin was synthesized by ourselves. Molar ratio of phenol/formaldehyde is 1:2 and molecular weight of PF

resin is between 200 and 400 by GPC.

2.3 Impregnation of PF resin

Wood specimens were soaked in PF resin solution and vacuum for 30 min, then kept in it for 10 min at atmospheric pressure. PF resin concentration was 5%, 10%, 15% and 20%, respectively.

2.4 Compressive curing

PF resin impregnated wood was compressively cured at 180°C for 15min with hot press. Compression ratio was 20%. Weight percent gain(WPG) was calculated from the increase in weight of specimen.

2.5 ESCA

The size of PFW specimen was 6x6x1mm of tangential section. Shimadzu model 750 spectrometer with computer data treatment system was used for ESCA measurement. C_{1s} spectra of each specimens were detected and the bound energy and chemical shift of the peaks were determined by the wave analysis.

2.6 FTIR

FTIR was measured by KBr disc method and sample mesh was from 80 to 120.

3. RESULTS AND DISCUSSION

3.1 WPG of PFW

Four kinds of PFW with different WPG were prepared by impregnation of different concentrations of PF resin(Table I). It is very effective for the preparation of PFW with controlled WPG.

Table I WPG of PFW.

No.	WPG of samples
1	PF resin
2	wood
3	45.2%
4	31.8%
5	23.2%
6	11.4%

3.2 ESCA

ESCA spectra of specimen were obtained and C_{1s} spectra were analyzed by the computer curve fitting method(Fig.1). The spectra of wood and all the PFW were separated into four components, peak No. C_1 , C_{II} , C_{III} and C_{IV} from the lower binding energy. K.Setoyama^[5] analyzed wood surface by ESCA and attributed C_1 peak(285.5eV) to C-C, C_{II} peak(286.5eV) to C-O and C-OH, C_{III} peak(288.0eV) to O-C-O C=O, C_{IV} peak(289.2eV) to O-C=O, respectively. The results of our analysis showed that peak position of C_1 , C_{II} , C_{III} and C_{IV} was 285.1, 286.6, 288.1 and 289.1eV, respectively, and nearly the same as those of him.

On the other hand, the spectrum of PF resin was possible to be separated into both 3 and 4 components, and its attribution was unknown. We selected the separation into 3 components for lack of carboxyl group in PF resin and tentatively named them C_1 , C_{II} and C_{III} in accordance with wood, respectively.

Table II shows the peak position(PP, eV) and the relative peak area(PA, %) of separated peaks in each specimen.

It shows that PP of all the peaks, C_1 , C_{II} , C_{III} and C_{IV} shifted gradually to the higher binding energy with the increase in WPG of PFW. The increase in binding energy was small and ranged from 0.3 to 0.5eV. The reason of shift of PP is not clear, but we guess that it would occur because of the higher concentration of PF resin on the

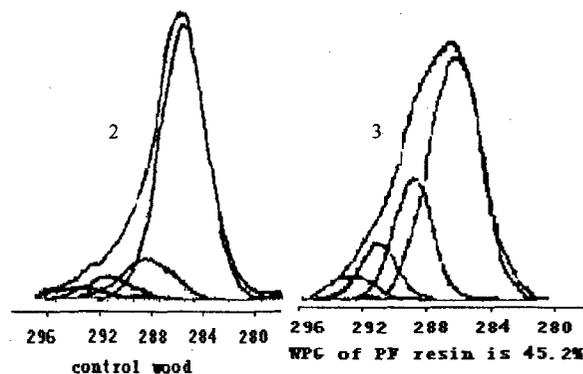
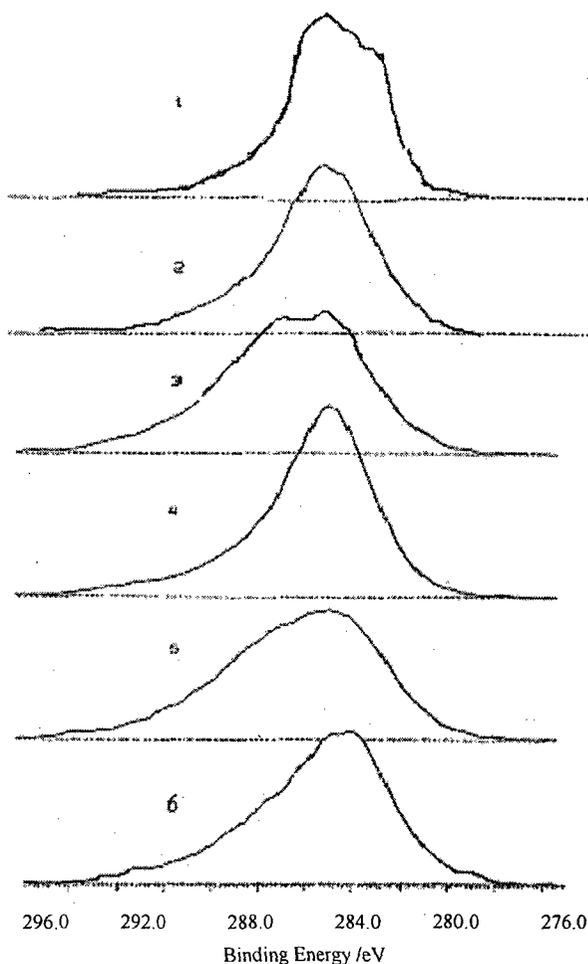


Fig.1 ESCA spectra of samples.

surface and the interaction of wood and PF resin during the compressed and high temperature curing of PF resin.

It also shows that PA of the peaks changed considerably except C_{IV} . With the increase in WPG of PFW, PA of C_1 decreased remarkably, PA of C_{II} increased considerably and PA of C_{III} increased slightly.

It is said that wood is composed of about 50% of C, 6% of H and 43% of O, respectively. The composition of PF resin is easily calculated from that PF resin is synthesized

Table II Spectra analysis of C_{1s} of samples by curve fitting method.

No.	Parameter	The number of peak			
		C _I	C _{II}	C _{III}	C _{IV}
1	PP/ev	284.6	285.7	288.6	-
	PA%	68.7	24.5	6.8	-
2	PP/ev	285.1	286.6	288.1	289.1
	PA%	79.9	11.7	5.0	4.3
3	PP/ev	285.5	287.1	288.4	289.5
	PA%	63.0	22.3	9.7	5.0
4	PP/ev	285.4	286.9	288.3	289.5
	PA%	70.2	16.5	9.1	4.2
5	PP/ev	285.4	287.0	288.3	289.5
	PA%	71.3	13.4	10.9	4.5
6	PP/ev	285.0	286.6	287.9	289.1
	PA%	72.9	16.2	7.9	3.0

Notes: The peak form of ESCA spectra was Gauss type. PP indicate peak place, which was the binding energy of this state; PA indicate relative peak area, which was relative content of each binding state. No. 1-- PF resin, No.2-- control wood, No.3-- WPG of PF resin is 45.2%, No.4-- WPG of PF resin is 31.8%, No.5-- WPG of PF resin is 23.2%, No.6-- WPG of PF resin is 11.4%.

by condensation reaction of phenol and formaldehyde. If the molar ratio of phenol and formaldehyde is either 1:1 or 1:2, PF resin should be composed of about 70% of C and 20% of O. It means that PFW would be changed to C rich and O poor material with the increase in WPG. From this theory, PA of C_I should be increased, and PA of C_{II} and C_{III} should be decreased, but the result obtained were opposite. It is concluded that the additive law does not apply to the discussion on change in PA.

The increase of PA of C_{II} and C_{III} means the formation of C-O, C=O and O-C-O derived from thermal oxidation of wood during compressive curing. So the elementary analysis and further characterization is necessary for the discussion on change in PA.

3.3 FTIR

Fig.2 shows FTIR spectra of all the samples and those of PFW were not obtained from the surface but from the whole.

It seemed that the figures of spectra of PFW were similar to those of wood. By comparing the wave-number of every peaks in spectra, it was recognized that all the

peaks of PFW was coincident with those of wood and that neither novel peaks nor specific peaks of PF resin except a common absorption band, 1373cm⁻¹, were found. It is considered that the peaks of PF resin were completely overlapped with those of wood and the specific peaks of PF resin were not detected even if WPG of PFW reached 45%. It also suggests that it may be impossible to detect the small amount of chemical change during the hot press for the curing of impregnated PF resin.

Then we tried to consider the effect of WPG on relative peak intensity of PFW. At first, we designated the band, 1736cm⁻¹, as the standard band because it was separated clearly from those of PF resin. Three bands were selected for the evaluation (Table3). The 1373cm⁻¹(CH flexural vibration) was only a common band. Others were 1460cm⁻¹(CH₂ deformation vibration) and 1596cm⁻¹(benzene ring stretching vibration) that were near to 1476cm⁻¹ and 1614cm⁻¹(both benzene ring extending vibration), the two biggest bands of PF resin in the fingerprint region, respectively, and were seemed to be influenced the most. As a result, all the relative intensity of three bands to the standard band increased gradually with the increase of WPG of PFW. But the additive law could not apply to this case totally because the relative intensity of all the three bands in wood was nearly the same as those of No.3, PFW of the highest WPG.

TableIII Relative intensity of selected three bands.

Wave number (cm ⁻¹)	Relative quantity /1736cm ⁻¹				
	2	3	4	5	6
1596	0.97	0.99	0.98	0.78	0.79
1460	0.83	0.84	0.63	0.55	0.53
1373	0.74	0.77	0.49	0.47	0.42

4. CONCLUSION

4.1 PFW with WPG ranged from nearly 10 to 45% were obtained by the impregnation of PF resin solution ranged from 5 to 20% concentration.

4.2 ESCA spectra was analyzed by the computer curve fitting method and C_{1s} spectra of wood and all the PFW were separated into four components, C_I, C_{II}, C_{III} and C_{IV}.

It was recognized that PP of all the peaks shifted gradually to the higher binding energy with the increase in

WPG of PFW. It would be caused by the interaction of wood and PF resin during the compressive curing.

It was also recognized that with the increase in WPG of PFW, PA of C_I decreased remarkably, PA of C_{II} increased considerably and PA of C_{III} increased slightly. Although the change in PA means the change in chemical structure and component of PFW, it is not clear because that the increase of oxygen containing bonds was not apparent and the additive law could not apply.

4.3 All the absorption bands of PFW was completely

attributed to those of wood and neither novel peaks nor specific peaks of PF resin except a common absorption band, 1373cm⁻¹, were found for the overlapping with those of wood.

The relative peak intensity of 1373cm⁻¹(CH flexural vibration), 1460cm⁻¹ (CH₂ deformation vibration) and 1596cm⁻¹ (benzene ring stretching vibration) to the standard band, 1736cm⁻¹, increased gradually with the increase of WPG of PFW. But the additive law could not apply to this case totally.

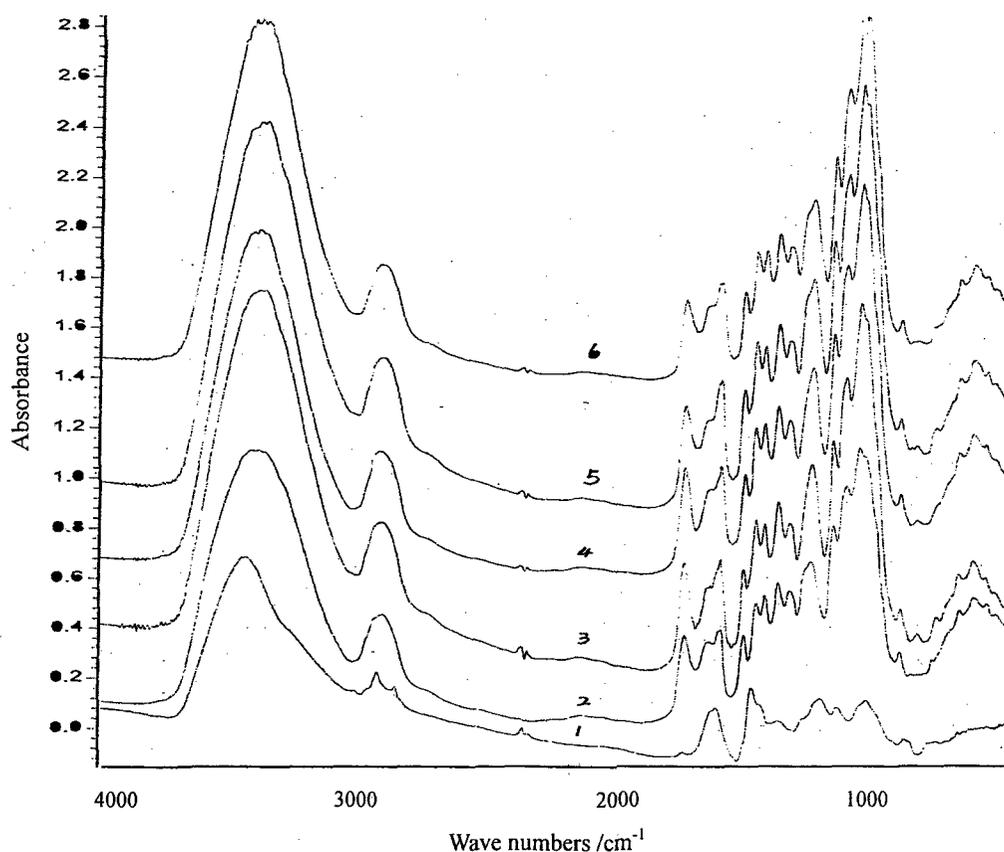


Fig.2 The FTIR spectra of PFW.

No.1: PF resin, No.2: wood, No.3: PFW (WPG-45.2%), No.4: PFW (WPG-31.8%), No.5: PFW (WPG-23.2%), No.6: PFW (WPG-11.4%).

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