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Evaluation of Bonding Performance and Interface of Birch with API Adhesive

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Abstract: This paper aims at making a study on the bonding properties of birch with API adhesive. A non-formaldehyde adhesive to improve the bonding strength and water resistance of the emulsion was investigated. The adhesive was a composite system that was formulated from polyvinyl acetate (PVAc) emulsion, PVA, isocyanate and some other additives. In this study the effect of isocyanate at room temperature on the curing behavior of PVAc was investigated. The research conclusion that a proper mole ratio of –NCO group and hydroxyl groups is 25/1. And the isocyanate percent have arrived at 15%, the dry and wet shear strengths of birch is the highest. From the cost of API adhesive we choose TiO_2 and $CaCO_3$. A XPS technique has been established to analyze structure of crosslinking in bonding interface. The experimental results indicated that the occurrence for chemical reaction between PVAc-based API adhesive and birch wood.

Keywords: Isocyanates, bonding strength, PVAc, interface.

1. INTRODUCTION

Polyvinyl acetate (PVAc) is one of the most important commercial polymers, which has many advantages, such as safe operation, low coat, and room temperature cure [1]. Therefore, it is suitable for population in birch process. PVAc acquire special attention in the areas of drug delivery, adhesives, membrane, paper and many other applications [2]. Isocyanate adhesive has the higher adhesion strength and the better water-resistant to wood and other products [3]. Aqueous polymer isocyanate (API) adhesive is a water medium, with the convenience and safety, environmental pollution (excluding formaldehyde, phenol and other toxic substances) and the adhesive material is non-acid pollution (API system was neutral) and so on, can be used as green-type adhesive [4]. Another outstanding feature is the API can be cured at room temperature and has excellent water resistance, heat resistance and aging resistance [5]. In addition, API is a two-component adhesive, require on-site mix before using. In this study, a aqueous emulsion polymer adhesive is described, which comprise modified PVAc emulsion by using esters of high fatty acid, and cross linking pMDI.

2. EXPERIMENTS

The wood material in this study was birch, collected from Forestry Bureau of Heilongjiang Province in China. Adhesive used in this study was polyvinyl acetate and polymer isocyanate adhesive. Polyvinyl acetate and polymer isocyanate used in this study were made in adhesive laboratory in Northeast Forestry University of China and is composed of two components, matrix and crosslinker. The main component of crosslinking is polymeric diphenylmethane diisocyanate (pMDI). The average functionality of pMDI used in this study was 2.5.

Adhesive used in this study was aqueous polymer adhesive (API). API adhesive used in this study were made in our laboratory. And adhesive is composed of two components, matrix and crosslinker. The main component of crosslinking is polymeric diphenylmethane diisocyanate (pMDI). Specimens used for testing compressing shear strength of glue-blocks. Birch wood boards were cut to a size of 10mm thick, 25mm wide and 30mm long.

XPS measurements were performed at room temperature with monochromatic AlKα radiation (1486.6eV) using a K-Alpha X-ray photoelectron spectrometer (supplied by Thermo Fisher Scientific Co., Ltd). The X-ray beam was a 100-W, 200mm-diameter beam raster over a 2mm by 0.4 mm area on the sample. High-energy photoemission spectra were collected using pass energy of 50eV and resolution of 0.1eV. For the $Ag3d_{5/2}$ line, these conditions produced an FWHM of 0.80eV.

3. RESULTS AND DISCUSSION

3.1. Bonding Strengths of Birch Between Different Isocyanates Prepolymer with API Adhesives

Curing of API adhesive relies on loss of water whereas the reaction of isocyanate with hydroxyl compounds such as PVAc and water. When API adhesive was used, matrix and crosslinker were each other with to weight rate of 100:15:5. The isocyanate group (-NCO) of the crosslinker could react with the components of the water-based polymer mixture and wood substrate during composite adhesive preparation and application. It is known that the major -NCO reactions in these adhesive systems are those with water or a hydroxyl group which made the formation of urea or urethane possible [6].

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Allophanate and biuret groups are possible by-products; however, such reactions are rare. So attention should be paid to the fact that matrix and crosslinker were mixed just when composite adhesive were used. And also all glued-blocks should be put into presser in 10 minutes in order to improve adhesive properties [7]. Results of shear strengths of birch glued blocks with composite adhesives were shown in Table **1**. Prepolymer isocyanates were prepared by different NCO/OH mole rate with 50/1, 25/1, 10/1, 5/1, which renamed PU_1, PU_2, PU_3, and PU_4 respectively. The results show that shear strengths and wood failure increase with the increasing of the ratio of NCO/OH. This is due to isocyanate-NCO content increased, resulting in faster response, increased bonding strength. However, the subsequent application of adhesive is shortened, higher costs. In order to improve the shear strength of API, to extend the application period, and to increase utilization performance, the NCO/OH ratio of prepolymer is 25/1. Blocks were boiled on boiling water of 100°C for 5h, soaked in water at room temperature for1h, and then placed in drying oven at 60°C for 18h. In the boiling and drying test strip does not appear in the specimens. As the isocyanate reacts with the wood frame structure, which led to the increase with the isocyanate, wet shear strengths is also increasing. But NCO/OH ratio of prepolymer isocyanate, relative content of soft and rigid part and crosslinking density all have effects on the bonding behaviors of samples apparently. To sum up the above arguments, I think a proper mole ratio is 25/1.

3.2. Bonding Strengths of Birch Between Different Percent Isocyanates

When API adhesive was used, PVAc and crosslinker were mixed with each other with the weight rate of 85/5, 85/7.5, 85/10, 85/12.5, 85/15, and 85/17.5 respectively.

Table **2** and Figs. (**1**, **2**) show the shear strengths of birch with different percent isocyanate.

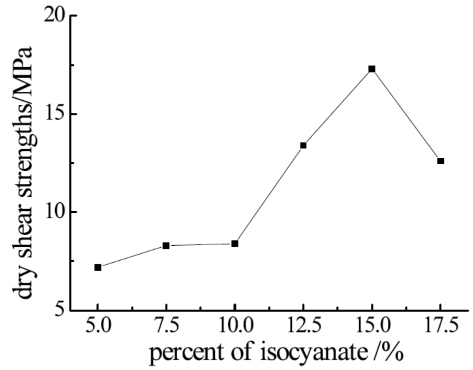


Fig. (1). Dry Shear strengths of birch with different isocyanate of API adhesive.

With the increase of isocyanate, the dry shear strength of birch increased first and then decreased. When the isocyanate percent have arrived at 15%, the dry shear strengths of birch is the highest. In addition, with the increase of the –NCO groups, the urea or urethane group were format much more. Dry shear strength of birch with 15% percent isocyanate was 17.3MPa.

From the Table **2** and Fig. (**2**) we can see that with the increase of isocyanate, the dry shear strength of birch increased first and then decreased. When the isocyanate percent have arrived at 15%, the wet shear strengths of birch is the highest. Wet shear strength of birch with 15% percent isocyanate was 2.7MPa, which meant that breakage of chemical bond between API adhesive and birch wood almost.

Table 1. Shear Strengths and Wood Failure of Birch Glued Blocks with API Adhesive

Different Isocyanate Polymer	Dry Shear Strength/MPa	Wet Shear Strength/MPa	Wood Failure (%)
PVAc	9.8	0	0
PU_1	15.8	2.6	78
PU_2	12.3	2.0	85
PU_3	19.2	3.5	92
PU_4	13.2	3..8	87

Table 2. Shear Strengths of Birch with Different Percent Isocyanate of API Adhesive

Isocyanate Percent (%)	Dry Shear Strengths/MPa	Wet Shear Strengths /MPa
5	7.2	0
7.5	8.3	0.3
10	8.4	1.1
12.5	13.4	1.2
15	17.3	2.7
17.5	12.6	2.3

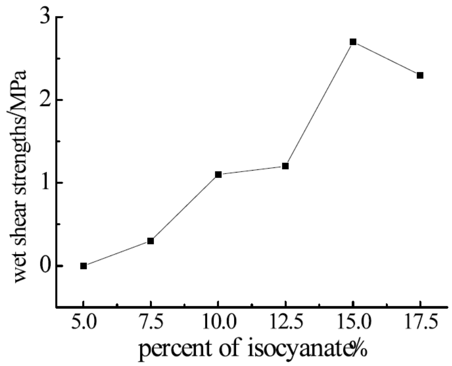


Fig. (2). Wet Shear strengths of birch with different isocyanate of API adhesive.

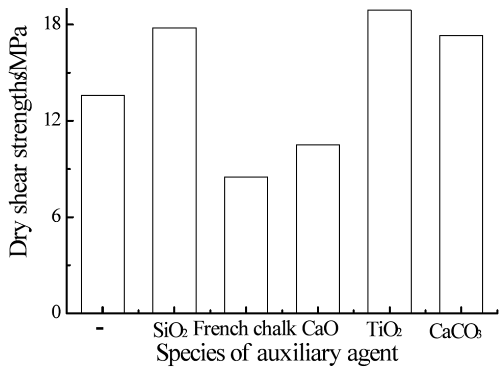


Fig. (3). The effect on dry Shear strengths of birch with different auxiliary agent.

3.3. The Effect on Bonding Strengths by Different Auxiliary Agent

Comparing with no auxiliary agent, the dry shear strengths for added French chalk and CaO were lower, but added nano-SiO_2, and TiO_2 and $CaCO_3$ were higher, and the best the auxiliary agent is nano-SiO_2.

The Table **3** and Fig. (**4**) illustrated the auxiliary agent for API adhesive could be poor water resistance. Because the auxiliary agents have a plenty of hydrophilic group that lead to the poor water resistance of API adhesive. But from the cost of API adhesive for the industry application, the cheap auxiliary agent could be the optimum under satisfactory to shear strengths technological requirements. From the results of the study on the auxiliary of the API adhesive into birch, we could see that the optimum the auxiliary agent play important role in the API adhesive cost. To sum up, TiO_2 and $CaCO_3$ were the best auxiliary in this study.

3.4. X-Ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) analysis was used to characterize the chemical changes of the glued blocks. In the high resolution spectra of C1s, N1s, O1s, as shown in Figs. (**5-7**) and Table **4**, it is evident that the C1s spectra of the samples consist of four well-resolved peaks. The curve-fitting simulation was carried out after subtracting the baseline correction. The peaks of carbon atoms at 284.6eV, 285.9eV, 287.8eV, 298.9eV is corresponding to the carbon atoms in abbreviated C-C or C-H, the carbon atoms a singly bonding to oxygen and nitrogen(ether group -C-C-O or -C-N), the carbon atoms double-bond to oxygen and nitrogen in the urethane linkage (-O-C=O) and the carbon atoms double-bonded to oxygen and nitrogen (-N-C=O) in the imides group respectively [8]. Chemical reactions and structure in the equation are as follows in Schemes **1-4**.

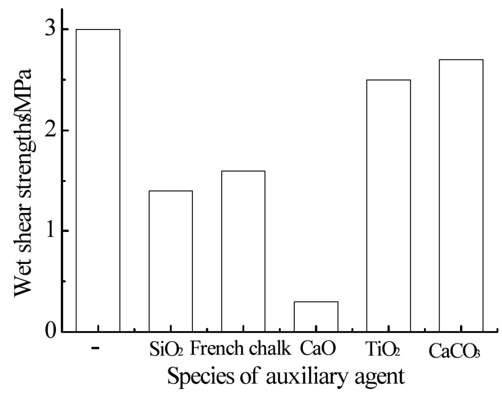


Fig. (4). The effect on wet shear strengths of birch with different auxiliary agent.

To assume that the API adhesive and birch gluing interface layer has happened in any chemical changes, gluing interface layer of the main base of the basic content should be marked with the API and wood with relatively simple. API and wood, a user interface layer of the draft basic base ball is notable changes have taken place in the wood C1sA of the content of the 49.32%, while gluing interface layer C1sA the regiment 40.25 %, compared with the user interface layer C1sA base of 9.08% decrease. The C1sB atomic percent of birch is 12.17%, and API adhesive is 29.04, while the interface gluing is 17.53% situated between the two. From the chemical of API adhesive and that, it is a different API isocyanate group, or wood on the hydroxyl group there was a nuclear reactions and a quantitative urethane base isocyanate group that interface in an oxygen content of the increase. Therefore, chemical changes of surfaces interfere with API

Table 3. Shear Strengths of Birch with Different Auxiliary Agent

Species of Auxiliary Agent	Dry Shear Strengths/MPa	Wet Shear Strengths/MPa
-	13.6	3
SiO_2	17.8	1.4
French chalk	8.5	1.6
CaO	10.5	0.3
TiO_2	18.9	2.5
$CaCO_3$	17.3	2.7

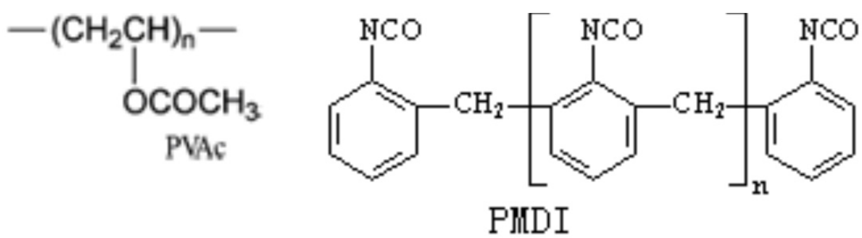
Table 4. Percent Content of Elements in the Bonging Interface

Name	Peak BE(eV)	Group	Wood (At %)	Adhesive (At %)	Bonding Interface (At %)
C1sA	284.6	-C-C-	49.33	24.2	40.25
C1sB	285.9	-C-Nor -C-O	12.17	29.04	17.53
C1sC	287.8	-O-C-O-	13.8	18.25	13.16
C1sD	298.9	-N-C=O or O=C-O	4.12	4.51	7.74
N1sA	399.66	-C-N-	1.57	2.91	1.46
N1sB	400.32	-N-C=O	-	1.2	1.79
O1sA	531.84	-N-C=O	8.18	6.15	5.93
O1sB	532.61	-O-C-O-	10.83	9.48	9.35

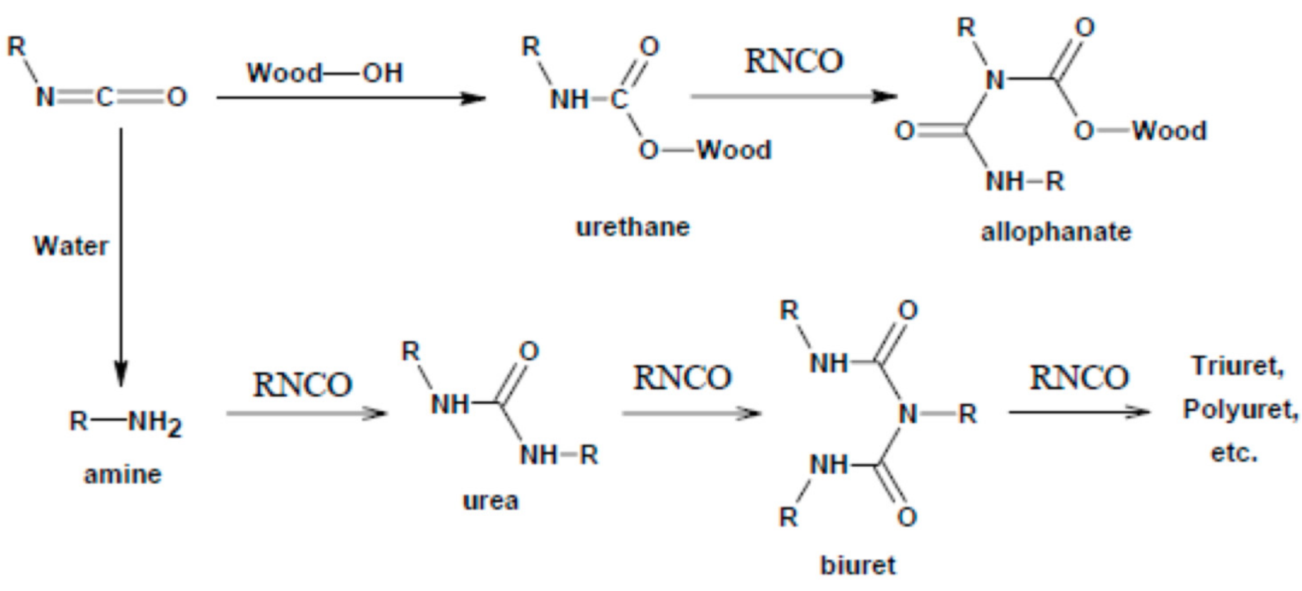
adhesion strength of the adhesive consequently. From the results of XPS analysis, it was clear that the urethane groups (-NH-C=O)) attached onto the surface of the wood and main agent PVAc, and these groups were useful for improved the strength of polymers to make bonding.

4. CONCLUSIONS

Prepolymer isocyanate was used as a crosslinker to crosslink PVAc in this study. By changing the ratio of the prepolymer isocyanate, PVAc two-groups of adhesive have been prepared successfully. Different kinds of prepolymer on to the performance effects of different dry and wet bonding strength are higher. The isocyanate play an important role for API adhesive bonded into birch. Dry and wet shear strength of birch with 15% percent isocyanate was 17.3MPa and 2.7MPa. TiO_2 and $CaCO_3$ was the best auxiliary in this study. And the ratio of auxiliary agent was 5% of API adhesive. The dry shear strengths for TiO_2 and $CaCO_3$ were



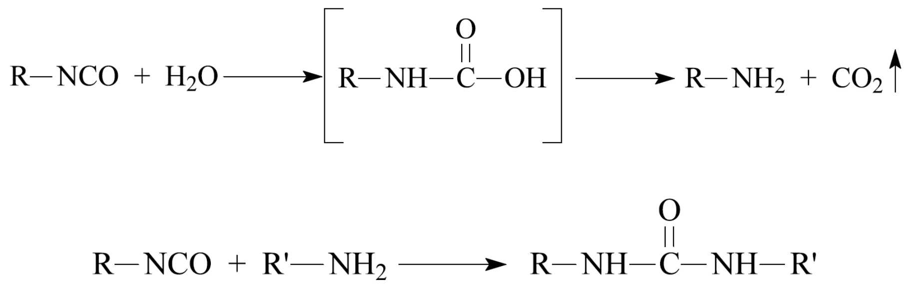
Scheme 1. The structure of isocyanate and PVAc.



Scheme 2. Reaction equation of pMDI resin with wood.

$$R{-}NCO + R'{-}OH \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{||}}{C}{-}OR'$$

Scheme 3. Reaction equation of isocyanate with hydroxyl compounds.



Scheme 4. Reaction equation of isocyanate with water.

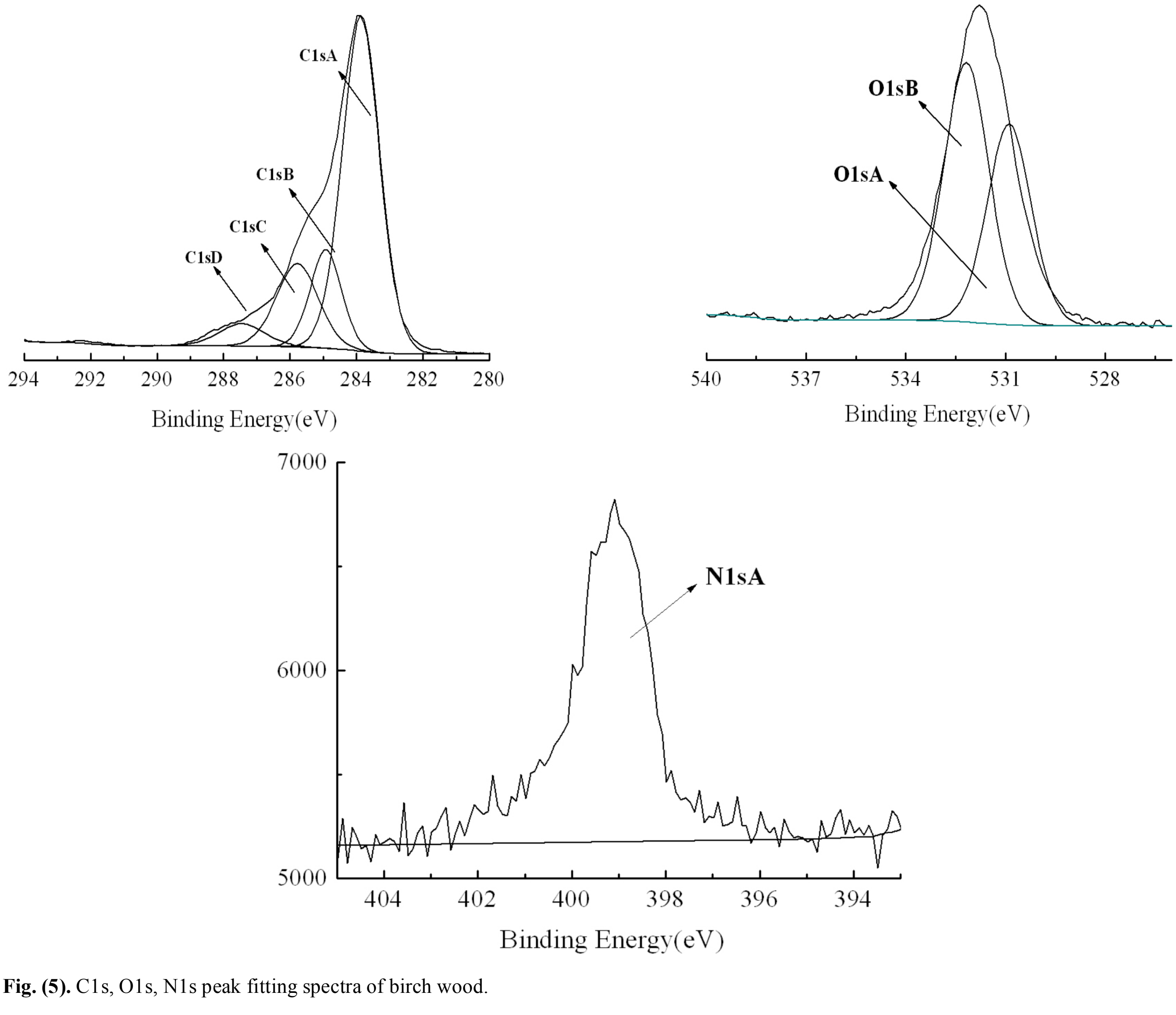


Fig. (5). C1s, O1s, N1s peak fitting spectra of birch wood.

18.9 and 17.3MPa, while the wet shear strengths for TiO_2 and $CaCO_3$ were 2.5 and 2.7MPa. The carbon, oxygen and nitrogen element of gluing interface layer studied by XPS, the results show that the nitrogen atomic percent of the interface lower than API adhesive, but higher in the wood, and carbon atomic percent of the interface bonding is not simple piling up with the API and birch, but the birch and API adhesive create some changes in the interface to make some fundamental base of content have increased and make some fundamental base of the content of less.

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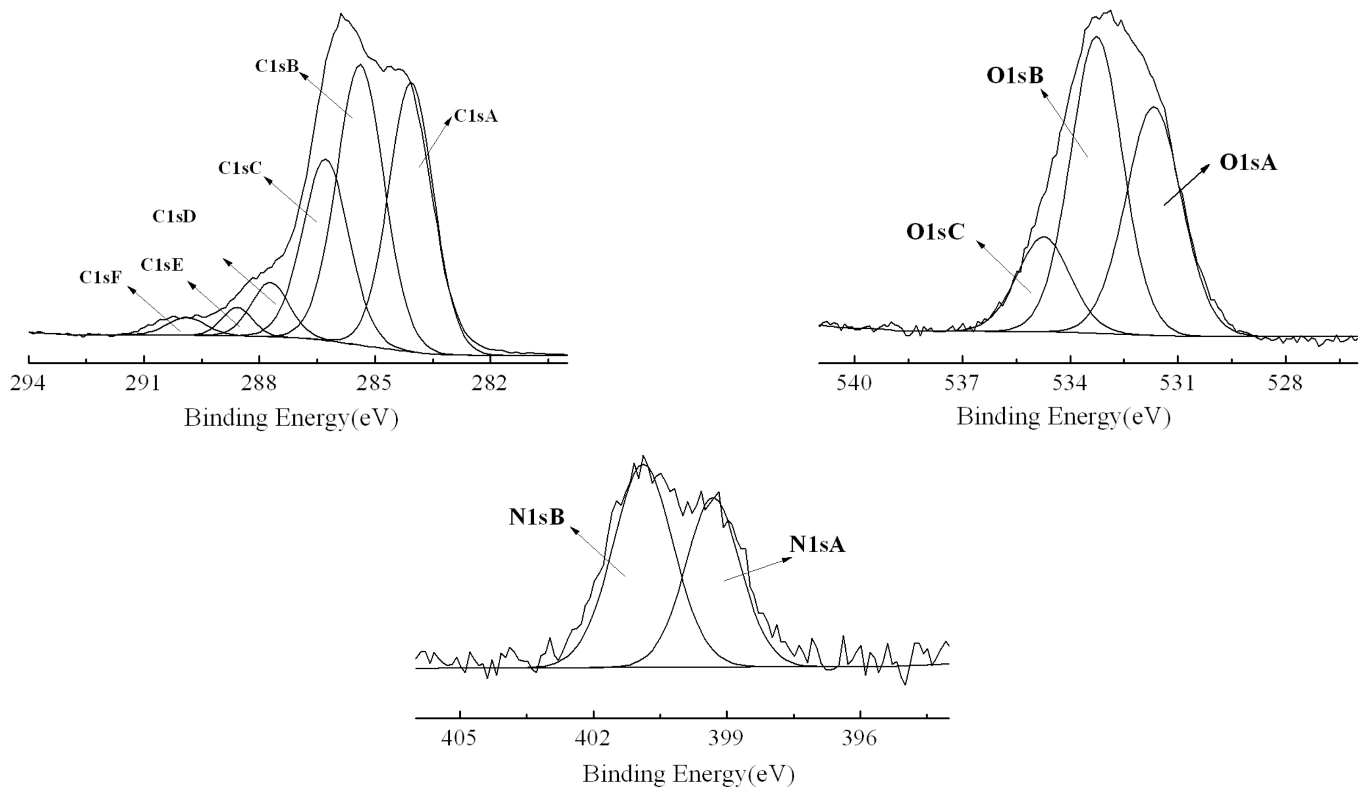

Fig. (6). C1s, O1s, N1s peak fitting spectra of API adhesive.

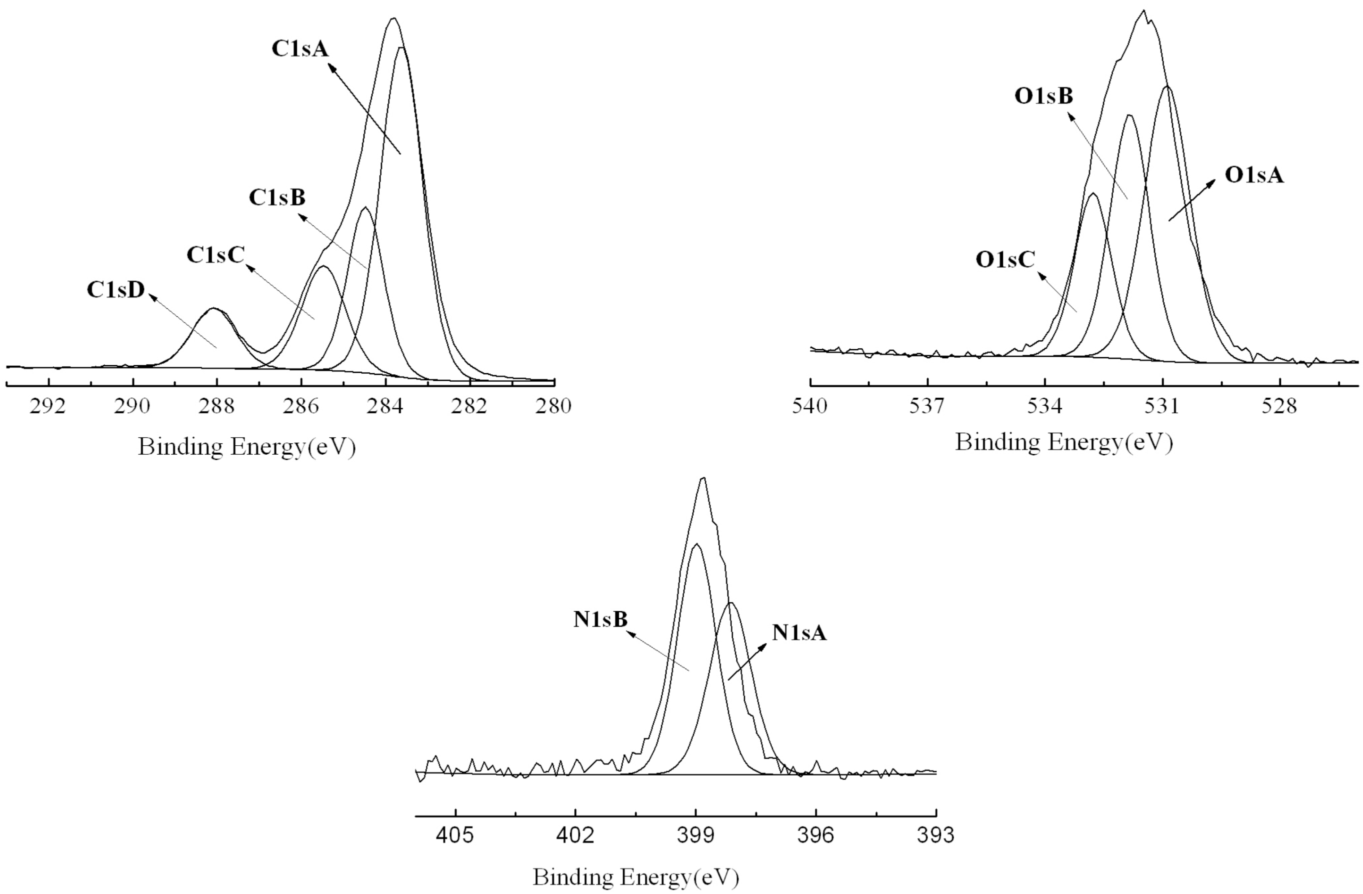

Fig. (7). C1s, O1s, N1s peak fitting spectra of bonding interface.

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