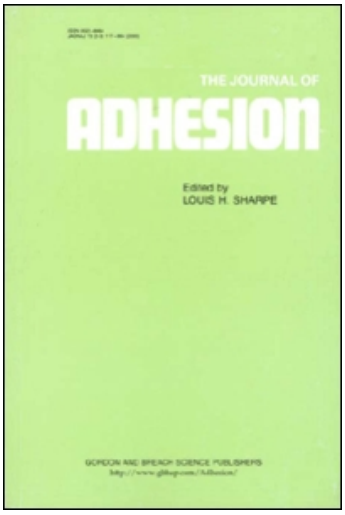

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Durability and Surface Analytical Studies of Adhesive Bonding to Wood

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Durability and Surface Analytical Studies of Adhesive Bonding to Wood†

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The effects of aging on adhesively bonded wood joints were examined using non-extracted, water-extracted and solvent-extracted wood. Surface analysis by XPS and SIMS were used to examine the various wood surfaces. The level of surface extractives is seen to be a major influence on the quality of the joints, both in terms of durability and strength.

KEY WORDS Wood, Urea formaldehyde; Phenol resorcinol formaldehyde; durability; XPS; SIMS.

INTRODUCTION

This paper summarises some of our investigations on the interactions between formaldehyde-containing adhesives and soft woods, the work being sponsored by The Building Research Establishment.

Two areas of the work will be considered here. Firstly, durability studies of joints constructed with woods extracted to different levels and secondly some surface analysis, by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS).

The adhesives used were urea-formaldehyde (UF), and phenol-resorcinol-formaldehyde (PRF) which were kindly supplied by Ciba-Geigy Ltd; they were free from any fillers or extenders. It has long been known that PRF adhesives are superior to UF's in both

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durability and strength.[1] Our principal interest, however, has been to discern the mechanism of adhesion to wood and to determine if possible which groups in wood may be involved in bonding.

DURABILITY

Scots pine (Pinus sylvestris) was cut and planed to a British Standard[2] single lap dimensions and subsequently prepared in one of the following ways.

a) Non-extracted;

b) Water-extracted. This was achieved by immersing the substrates in boiling water for 7 hours.

c) Solvent-extracted. This was achieved by extraction is a Soxhlet apparatus with each of the following solvents in sequence for more than 12 hours each[3]: dichloromethane, benzene/ethanol (2:1 by vol.), acetone, methanol. This procedure is responsible for the removal of extractives. Only a small amount of lignin is removed.

Single lap joints (25 mm × 25 mm overlap) of Scots pine wood were constructed with UF or PRF and left to cure. After two weeks, the bonded joints were placed in a glove box at >95% relative humidity and 30°C, and left for various lengths of time up to 1800 hours. The aged joints were then tested to destruction on a Monsanto Tensometer with a crosshead speed of 5 mm min^{-1}. Strengths of aged joints are shown in Figures 1 and 2.

X-RAY PHOTOELECTRON SPECTROSCOPY

This work was carried out on a VG ESCALAB Instrument using X-ray energy (AlK_α) = 1486.6 eV. The analysis area was approximately 5 mm × 5 mm and the beam diameter 6 mm. The samples were 100 μm sections of spruce (Picea abies) cut with a microtome. Some samples were aged at >95% RH at 30°C for six weeks. The results of these analyses are shown in Table I. XPS has a sampling depth of 5–10 nm.[4]

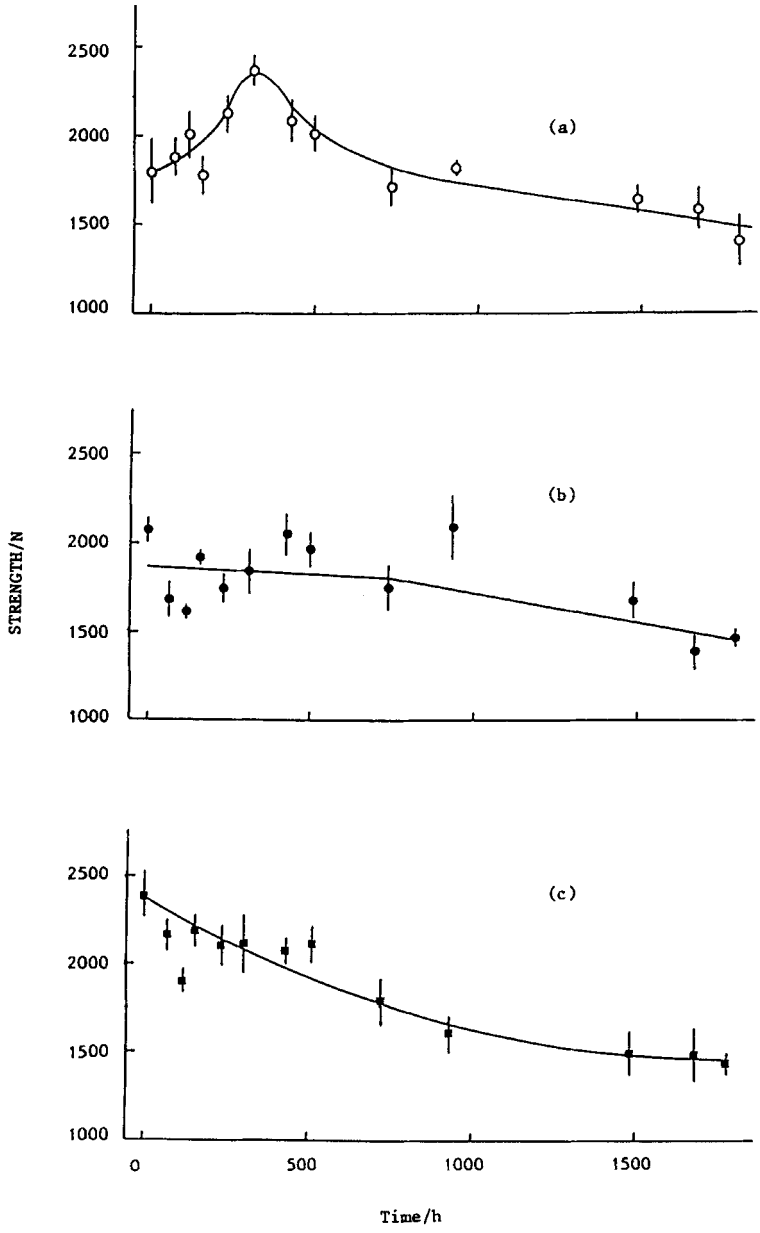

FIGURE 1 Strengths of UF bonded Scots pinewood joints on exposure to moist air at 30°C. (a) non-extracted, (b) water-extracted, (c) solvent-extracted.

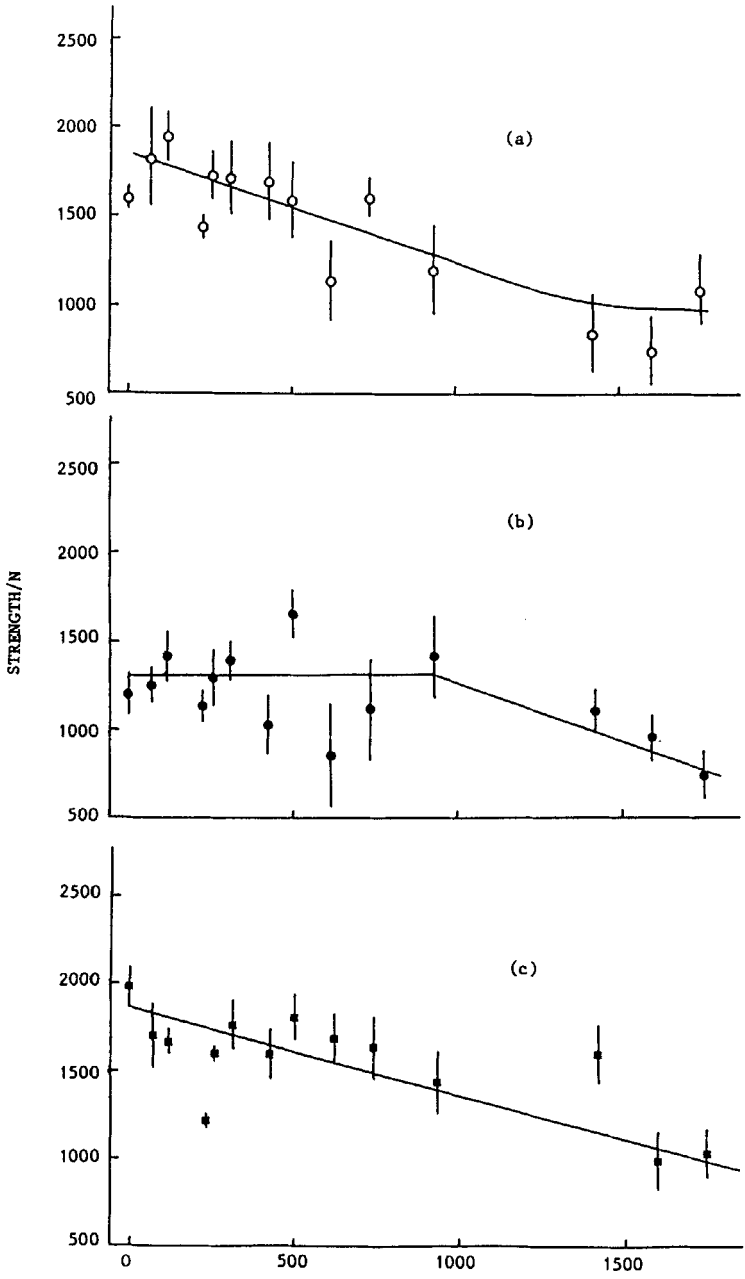

FIGURE 2 Strengths of PRF bonded Scots pinewood joints on exposure to moist air at 30°C. (a) non-extracted, (b) water-extracted, (c) solvent-extracted.

TABLE I
XPS analysis of non-extracted, water-extracted and solvent-extracted sprucewood, before and after aging

Sample	% Atom composition				O/C Ratio
	C	N	O	Contaminants	
Non-extracted	80.9	0.0	18.3	0.9 (Si)	0.23
Water-extracted	84.3	0.0	14.6	1.1 (Si)	0.17
Solvent-extracted	70.9	0.0	25.6	2.6 (Si)	0.36
Aged non-extracted	83.3	0.0	16.7	0.0	0.20
Aged water-extracted	69.5	1.7	27.1	1.7 (Fe)	0.39
Aged solvent-extracted	63.5	0.0	36.5	0.0	0.57

SECONDARY ION MASS SPECTROSCOPY

This work was undertaken on a VG instrument with a MM 12-12 quadrupole mass spectrometer. The analysis area was 6×6 mm, primary beam current 0.4×10^{-9} A and the primary ion was Xe^+ (2 keV). Secondary ions are ejected from the surface and analysed in a mass spectrometer. SIMS spectra of wood contain a large number of fragments and Figures 3 and 4 are given as examples.

Table II lists the samples that were studied by SIMS. In order to investigate the mechanism by which adhesives bond to wood, some samples were treated with the adhesive components, intermediates or model compounds which are listed in Table II. By comparing spectra of treated and untreated woods we were able to attribute changes to interactions between the adhesives and wood.

DISCUSSION

The results of tensile strength tests of aged joints (Figures 1 and 2) show a number of features common to both adhesives. Firstly, for the first 800 hours of aging, solvent-extracted wood provides stronger joints than non-extracted wood, and these in turn are stronger than water-extracted wood joints. Secondly, for approximately the first 1100 hours of aging, the water-extracted wood joints show no weakening. Finally, after approximately 1000 hours aging, joints with the three types of wood converge to approximately the same strengths.

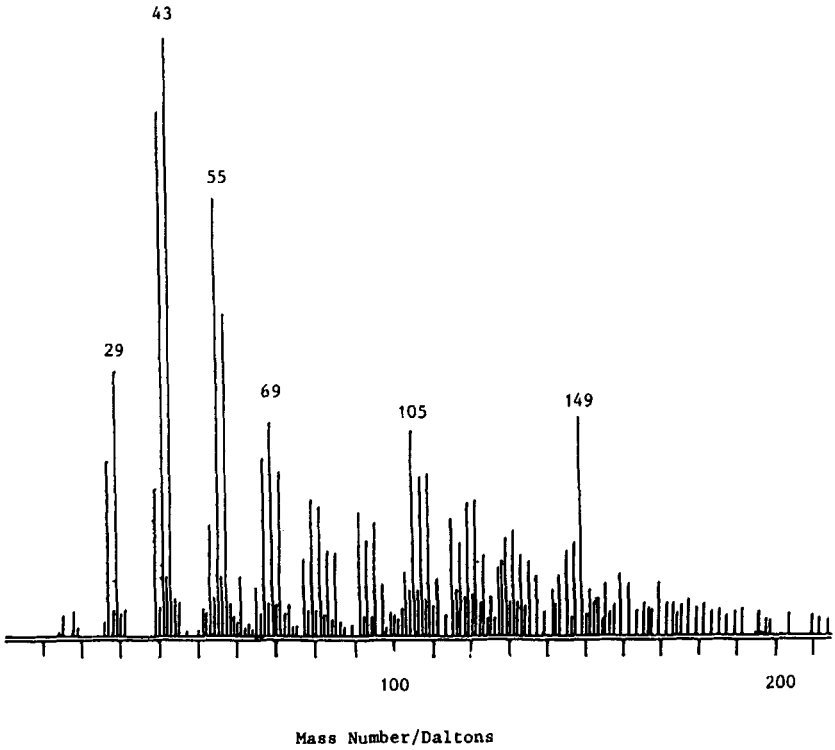

FIGURE 3 Positive ion SIMS spectrum of urea-doped, non-extracted spruce.

How can these changes be explained? It seems that the extractives content at the surface influences bond strengths. This is indicated by the XPS data which shows the oxygen to carbon ratio varying with level of extraction. However, the amounts of extractives are also related to the availability of cellulose; high levels of extractives may restrict adhesives entering the wood pores.

For water-extracted wood, resin penetration is reduced and some of the resin-extractive bonds will form to the detriment of the resin-cellulose bonds. Indeed, strengths of the water-extracted wood joints are initially stable and do not decrease. This suggests a certain amount of hydrolytic stability of these interactions.

The solvent-extracted and non-extracted woods allow increased adhesive penetration and have more cellulose available for bonding

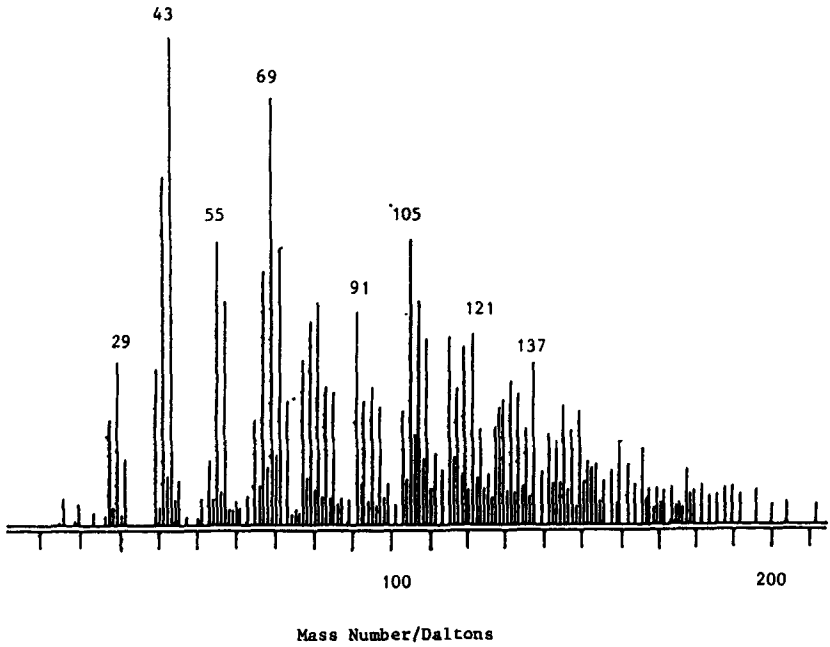

FIGURE 4 Positive ion SIMS spectrum of non-extracted spruce.

TABLE II
Samples analysed by SIMS

1. Solvent-extracted and non-extracted spruce.
2. Solvent-extracted and non-extracted Scots pine.
3. Softwood lignin.
4. Urea-treated, non-extracted spruce and urea.
5. Dimethylol urea-treated, non-extracted spruce and dimethylol urea.
6. Methylene diurea-treated, non-extracted spruce and methylene diurea.
7. Phenol-treated, non-extracted spruce.
8. 2-hydroxybenzyl alcohol (2-HBA)-treated, non-extracted spruce and 2-HBA.
9. Bis(2-hydroxyphenyl)methane (B2-HBM)-treated, non-extracted spruce and B2-HPM.
10. Paraformaldehyde-treated, non-extracted spruce and paraformaldehyde.
11. Cured detached films of UF, PRF and melamine-formaldehyde (MF) adhesives.

TABLE III
Number of SIMS spectral changes observed on doping non-extracted spruce

Dopant	Cellulose-lignin	Extractive
Urea	77	48
Phenol	9	20
Formaldehyde	41	47
Methylene diurea	23	33
Dimethylol urea	15	23
B2-HPM	14	32
2-HBA	47	51

compared to water-extracted wood. These two factors could account for the superior strengths of joints with these types of wood.

SIMS may provide information on the manner in which molecules are attached to wood and, as an example, spectra of non-extracted spruce both before and after treatement with urea are shown in Figures 3 and 4. These reveal the formation of new fragments (*e.g.* M = 64) and the loss of others (*e.g.* M = 148). Further, there are numerous changes in relative intensities (counts) of other fragments. By comparing non-extracted and extracted spruce spectra, we were able to identify whether the fragements originated from cellulose plus lignin or from the extractives. Thus, spectral changes on doping can be related to dopant-wood component interactions. In this way, Table III shows the number of spectral changes observed for urea and other dopants which indicate interactions with either cellulose-lignin or extractive components. We have regarded a spectral change as worthy of counting only when its intensity changes by more than 20%. Most of the intensity changes were in fact much greater than 20%. Also, for the doped wood, several new peaks appeared while others were lost when compared to the spectra of the dopant and the treated wood. These results indicate strong chemical interactions between the dopant and wood.

XPS has shown that, during aging, the remaining extractives migrate to the wood surface. Hence, the surfaces of the three types of wood come to resemble each other. This would account for the convergence of the strengths of joints constructed with the three types of wood.

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