

# THE USE OF XPS TO INVESTIGATE THE AGEING MECHANISM OF THE PHENOL-UREA-FORMALDEHYDE (PUF) BINDER COATED MINERAL FIBERS

A. Zafar<sup>1\*</sup>, J. Schjødt-Thomsen<sup>1</sup>, R. Sodhi<sup>2</sup>, D. de Kubber<sup>3</sup>

<sup>1</sup> Department of Mechanical and Manufacturing Engineering, Aalborg University, Aalborg, Denmark, <sup>2</sup> Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Canada, <sup>3</sup> Rockwool International, R&D department, Hedehusene, Denmark

\* Corresponding author ([aza@m-tech.aau.dk](mailto:aza@m-tech.aau.dk))

**Keywords:** Ageing, Interfaces, XPS, Phenol-urea-formaldehyde binder, mineral fibres

## 1. Introduction

In the production of mineral wool insulation products, Phenol-Urea-Formaldehyde (PUF) binder has been used for many years to bind mineral fibres together and to give desired mechanical strength to the material. The mechanical properties of the binder are found to decrease during long term ageing. The goal of this investigation is to identify the chemical changes occurring in the material during ageing that causes decrease in its mechanical properties. X-ray Photoelectron Spectroscopy (XPS) has been used widely for the characterization of adhesion of binders, coupling agents, coatings and polymer matrices with different kind of fibres and substrates [1-3]. XPS was used in this study to observe chemical changes occurring due to ageing in the mineral wool products.

## 2. Experimental Methods

### 2.1 Material

The samples were taken from the original mineral wool products consisting of mineral fibres coated with PUF binder assisted by Amino Propyl Silane (APS) coupling agent. Pure PUF binder and uncoated mineral fibre samples were used in the investigation to identify the peaks belonging to these components in the mineral wool samples. Uncoated mineral fibres were obtained by heating original mineral wool samples at 590 °C for 4 hours to remove all the organic material from the fibres. Pure PUF binder was cured on a glass plate at 200 °C for 1 hour.

In PUF binder, the molar ratio of formaldehyde to phenol is in the range of 3.2 - 4. Urea is added to the

binder and the molar ratio of urea to phenol is in the range of 1.5 - 2.5. The main reactions between phenol, formaldehyde and urea groups can be found in [4-6]. The chemical structure of PUF binder is shown in Scheme 1.

### 2.2 Ageing condition

The accelerated ageing was carried out by placing the samples in a climate chamber at a temperature of 70 °C and 95% relative humidity for seven days.

### 2.3 XPS

All measurements were made with a Thermo Scientific K-Alpha XPS. The samples were analyzed with a monochromatic Al K-alpha X-ray source. The survey spectra were obtained at 90° angle with a pass energy of 150 eV. The compositions were taken from the spectra of each element collected in a snapshot mode with a pass energy of 150 eV. High resolution spectra of elements of interest were obtained in a scanned mode with a pass energy of 25 eV. Charge compensation was done using a low energy flood gun. The deconvolution of the peaks was performed by using the manufacture's software Avantage. The binding energy scale was calibrated to the C1s peak at 285 eV for charge correction. The peak shape is a combination of Lorentzian and Guassian in a ratio of 70 to 30 %.

## 3. Results and Discussion

### 3.1. Uncoated Mineral Fibres

The surface composition of the uncoated mineral fibres is given in Table 1. The main elements in the uncoated fibres are carbon, oxygen, silicon, aluminum, calcium, magnesium and sodium. Carbon concentration is 32 % attributed to adventitious

organic contamination. The high concentration of oxygen (44 %) arises from the oxides of aluminum, silicon, calcium, sodium, iron and magnesium. N1s signal is not detected in the spectrum, which indicates the complete removal of the organic material during heating since the nitrogen atom is present in urea groups of the PUF binder and present in APS as amino group. Furthermore, the absence of nitrogen peak also indicates that the silicon signal only originates from the fibre surface and not from the APS coupling agent.

### 3.2. Pure PUF binder

Pure PUF binder sample was characterized to get information about the contribution of the PUF binder in the XPS spectra of mineral wool products. The survey spectrum of the sample only detects carbon, oxygen and nitrogen elements and the atomic composition of these elements are not very different from the estimated values calculated from molar ratios given in Table 2.

Five peaks associated with carbon were fitted to the C1s high resolution spectra in the pure PUF binder sample. First peak at 285 eV is due to hydrocarbon groups (C-C/C-H), which is partly aromatic due to phenol groups and partly aliphatic due to present of urea groups. The second peak at 285.9 eV is due to –OH group attached with benzene ring, i.e. phenol. This peak also includes contribution of carbon atom attached to nitrogen (C-N) due to presence of urea group attached to methyl bridge as shown in scheme 1. Third peak at 286.5 eV is due to aliphatic carbon attached with oxygen (C-OH), which is present due to the reaction of formaldehyde group with urea or phenol. Fourth peak at 287.8 eV is due to presence of carbonyl or amide group (CO/NCO) and fifth peak at 289.1 eV is due to urea group (NCON), both peaks are due to presence of urea in the PUF binder. The fitting of the C1s spectrum is consistent with the chemical structure of the binder as shown in Scheme 1.

### 3.3. Unaged and aged mineral wool products

Atomic composition of surface of the unaged and aged samples evaluated from XPS survey spectra is shown in Table 1. In case of the unaged samples, carbon, oxygen, nitrogen, silicon, aluminum and calcium are main elements. The atomic composition of carbon, oxygen and nitrogen in the unaged

mineral wool sample was compared to pure PUF binder samples as shown in Table 2. It shows that the atomic composition of the mineral wool products is different from the atomic composition of the pure PUF binder sample. Although mineral wool products also contain contribution from the coupling agent and fibres, the concentration of nitrogen in mineral wool products (2.12%) is still very low as compared to pure binder (13%) or estimated value (18%). During curing of mineral wool product, it was expected that 20 % of urea was disappeared. It appears that evaporation of urea from the surface of the mineral wool products could be much more than expected.

The atomic composition of the unaged and aged mineral wool products was compared as shown in Table 1. It shows that oxygen, aluminum, silicon, calcium and nitrogen composition decreases and carbon composition increases after ageing when compared to the unaged mineral wool products. The changes in atomic composition show that chemical changes occurred during ageing of mineral wool products. The decrease in the composition of aluminum, silicon, calcium and oxygen is due to lower signals of these metal oxides on the fibres' surface of the aged samples. The cause of the decrease is not fully understood yet and should be further investigated. The decrease in the atomic composition of nitrogen in the aged samples is due to decrease in the concentration of urea groups in the binder, which is also observed by C1s high resolution spectra.

C1s high-resolution spectra were peak fitted to identify the differences in functionalities present at the surface of the unaged and aged samples. The results are presented for carbon high resolution spectra in Fig. 1. It can be clearly seen that the C1s spectrum of the aged sample is much narrower than unaged sample, which indicates the removal of some groups of carbon attached with oxygen and nitrogen in aged samples.

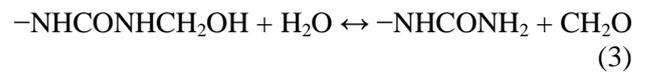
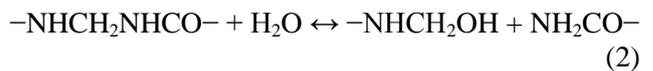
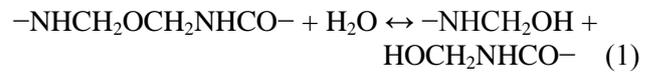
In case of the unaged sample, five peaks associated with carbon were fitted to the C1s spectra as shown in Fig. 1. The binding energy states at 285 eV is due to hydrocarbon groups (C-C/C-H) present in aromatic ring structure, propyl groups in APS coupling agent, methylene bridge between urea groups or phenol groups and also due to adventitious

hydrocarbon contamination. In literature, the peaks for aromatic and aliphatic hydrocarbon are also fitted separately but they lie very close to each other, making it impossible to fit both peaks accurately. The peak for C-Si group normally exists at 284.7 eV, but it lies so close to hydrocarbon peak at 285 eV that it overlaps with it. So, there is also contribution of the C-Si group to the peak at 285 eV. The peak at 285.8 eV is due to carbon attached with nitrogen (C-N) in the urea group of the binder or amino group of the APS coupling agent. This peak also has contribution of the bond between aromatic carbon and alcohol groups (C-OH). The peak at 286.7 eV is due to aliphatic carbon attached with oxygen as alcohol group or ether group (C-OH/C-O-C). The peak at 287.8 eV is due to carbonyl group (C=O) or amide group (N-C=O), which come from urea groups present in the binder. The peak at 289 eV is also due to a fragment of urea group (NCON).

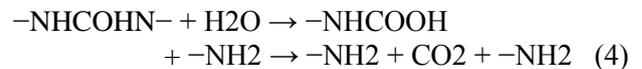
In case of the aged sample, fitting of C1s spectra is only done with four components as shown in Fig. 1. It was not possible to include a peak due to urea group at 289 eV (NCON) and a significant decrease from 1.90% to 0.40% was also observed for the peak at 288 eV (C=O/N-C=O), which indicates the significant decrease in urea group concentration after ageing. The concentration of the peak at 286.7 eV (aliphatic C-OH/C-O-C) was decreased from 7.16 % to 4.02 % after ageing as shown in Table 3. This decrease is also linked with hydrolyzation of urea because the decrease in urea group concentration can lead to a decrease in aliphatic carbon attached to oxygen. The urea group, present in the binder, can hydrolyze in the presence of moisture since the hydrolytic stability of the urea-formaldehyde bond is low. This results into hydrolytic degradation of the binder under humid environment. The susceptibility to hydrolysis of a cured resin depends on its chemical nature and the degree of cross linking. Furthermore, the hydrolytic reactions occurred in the presence of moisture and are accelerated by heat and acids [7].

Many of the reactions that form Urea-Formaldehyde products are reversible condensation processes that eliminate water in the forward direction and therefore, involve hydrolysis in the reverse direction [8]. The reversibility of the ether bridge and methylene bridge explains the low resistance of UF resins against the influence of water and moisture.

Hydrolysis of the cured resin will cause splitting of ether bridges into urea methylol groups, which can further split into urea and formaldehyde as shown in Eq. 1 and Eq. 3 [9-12]. Although methylene bridge is relatively stable, this reaction will be visible under the conditions used for the ageing. Slonim et al. [13] studied the acid catalyzed hydrolysis of carefully characterized methylene-diurea (UFU) and they found that the initial hydrolysis products are urea and monomethylol; the later degrade further into urea and formaldehyde as shown in Eq. 2 and Eq. 3. Allan et al. [14] also observed the hydrolytic cleavage of methylene bridge between two nitrogen atoms. These reactions contribute to the subsequent formaldehyde emission from the cured resin [7-15].



Some evidences also exist for acid catalyzed hydrolysis of the amide bond, in which the products are amines and carbon dioxide [8, 14-16]. Allan et al. [14] showed that the amide linkage between two nitrogen atoms can also be cleaved in the presence of moisture. Dutkiewicz [15] also observed by using infrared analysis that the acid catalyzed hydrolysis of urea formaldehyde polymer leads to a decrease in the concentration of carbonyl groups. The reaction of carbonyl group with water leads to the formation of amino and cerbamic acid. The cerbamic acid groups are unstable and can lead to the evolution of carbon dioxide as shown in Eq. 4.



The decrease in the concentration of urea group at 289 eV along with the decrease in the concentration of carbonyl or amide group (C=O/N-C=O) at 287.8 eV is due to occurrence of these reactions in the binder. The splitting of ether bridges between the urea groups and terminal methylol groups results in a decrease in the concentration of aliphatic alcohol and ether groups at 286.7 eV.

#### 4. Conclusion

The chemical changes occurring in the mineral wool products due to ageing were investigated by XPS. XPS survey spectra of the surface of the aged samples showed some significant changes in atomic composition compared to the unaged samples. C1s high resolution spectra showed a significant decrease in the urea and carbonyl group concentration during ageing. This decrease attributes to the hydrolyzation of urea present in the Phenol-Urea-Formaldehyde (PUF) binder. This study provides a better understanding of the ageing mechanism of the mineral wool products.

#### 5. Acknowledgements

The author (AZA) wishes to acknowledge financial support from Rockwool International A/S.

#### 6. References

- [1] C.E.Moffitt, Q.S. Yu, C.M. Reddy, D.M. Wieliczka and H.K. Yasuda, XPS analysis of aging of thin adhesion promoting, fluorocarbon treatments of DC plasma polymers, *Plasmas and Polymers*, Vol. 6, 193-209, 2001.
- [2] D. Wang and F. R. Jones, ToF-SIMS and XPS Studies of the Interaction of Silanes and Matrix Resins with Glass Surfaces, *Surface and Interface Analysis*, Vol. 20, 457-467, 1993.
- [3] C.L. Weitzsacker, M.X. and L.T. Drzal, Using XPS to Investigate Fiber/Matrix Chemical Interactions in Carbon-fiber-reinforced Composites, *Surface and Interface Analysis*, Vol. 25, 53-63, 1997.
- [4] A. Gardziella, L.A. Pilato, A. Knop, *Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology*, 2<sup>nd</sup> edition, 2000.
- [5] Guangbo He, Ning Yan, 13C NMR study on structure, composition and curing behavior of phenol-urea-formaldehyde resole resins, *Polymer* 45 (2004) 6813-6822.
- [6] Bunichiro Tomita, Chung-Yun Hse, Phenol-urea-formaldehyde (PUF) co-condensed wood adhesives, *International Journal of Adhesion & Adhesives* 18 (1998) 69-79.
- [7] P. K. Kavvouras, D. Koniclitsiotis and J. Pctinarukis, Resistance of Cured Urea-Formaldehyde Resins to Hydrolysis: A Method of Evaluation, *American Chemical Society*, Vol. 14, (1980) 1235-1240.
- [8] G. E. Myers, Resin Hydrolysis and Mechanisms of Formaldehyde Release from Bonded Wood Products, *Forests Products Research Society* (1986) 119-156.
- [9] Z.A. Abdullah, B.D. Park, Hydrolytic Stability of Cured Urea-Formaldehyde Resins modified by additives,

*Journal of Applied Polymer Science*, Vol. 114, 1011-1017, 2009.

[10] M. Dunky, Urea-formaldehyde (UF) adhesive resins for wood, *International Journal of Adhesion & Adhesives* 18 (1998) 95-107.

[11] P. K. Kavvouras, D. Koniclitsiotis and J. Pctinarukis, Resistance of Cured Urea-Formaldehyde Resins to Hydrolysis: A Method of Evaluation, *American Chemical Society*, Vol. 14, (1980) 1235-1240.

[12] I. Chung, G. E. Maciel, NMR study of the stabilities of urea-formaldehyde resin components toward hydrolytic treatments, *Journal of Applied polymer Science*, Vol. 52 (1994) 1637-1651.

[13] I.I. Slonim, S.G. Alekseeva, I.G. Urman, B.M. Arshava, B.I Aktselrod, A study of equilibria in the UF system using C-13 NMR, *Vysokomol. Soed.* 29 (1978) 1477-1485.

[14] G.G. Allan, J. Dutkiewicz, E.J. Gilmartin, Long-Term Stability of Urea-Formaldehyde Foam Insulation, *American Chemical Society*, Vol. 14, 1980.

[15] J. Dutkiewicz, Hydrolytic degradation of cured urea-formaldehyde resin, *Journal of Applied Polymer Science*, Vol. 28 (1983) 3313-3320.

[16] G. Camino, L. Operti, L. Trossarelli, Mechanism of Thermal Degradation Urea-Formaldehyde Polycondensates, *Polymer Degradation and Stability* 5 (1983) 161-172.

Table 1: Surface composition (at %) for the unaged and aged Rockwool samples with PUF binder

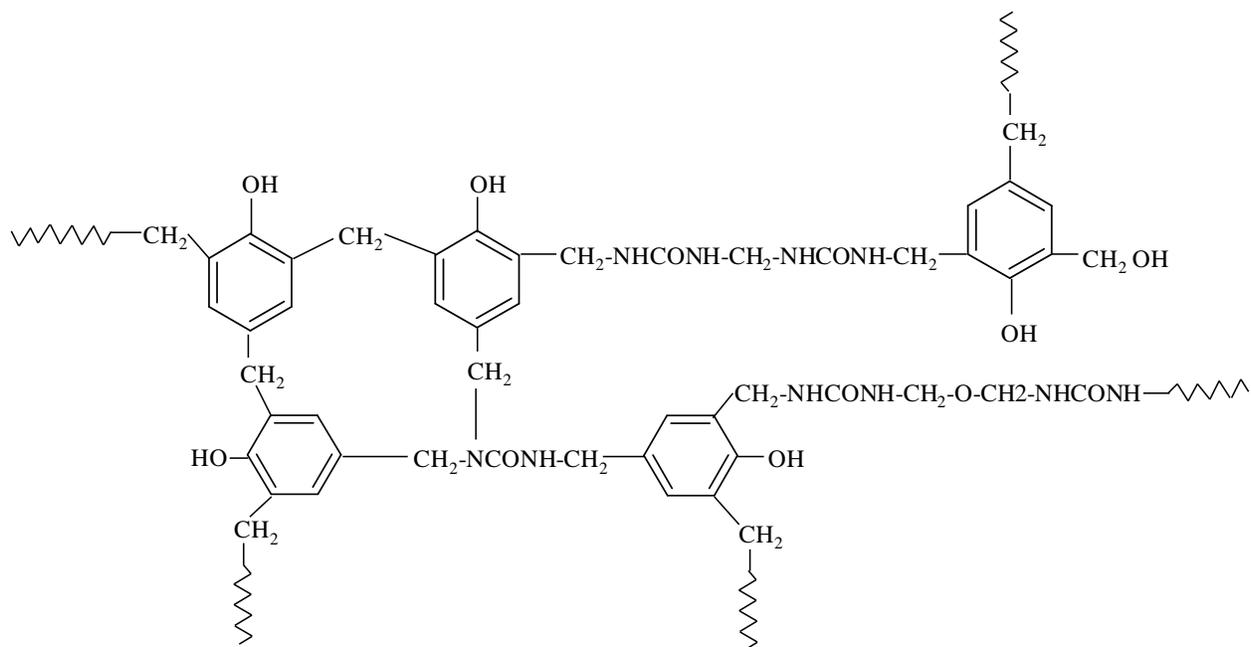
Elements	Uncoated	Pure	Unaged	Aged
	Mineral fibres	PUF binder	PUF binder	PUF binder
<b>C</b>	32.38	72.97	80.55	95.59
<b>N</b>	-	13.24	1.97	0.62
<b>O</b>	44.37	13.64	10.2	2.58
<b>Si</b>	7.65	-	4.04	0.56
<b>Al</b>	3.70	-	2.12	0.25
<b>Ca</b>	8.04	-	1.12	-
<b>S</b>	0.69	-	-	0.39
<b>Na</b>	2.01	-	-	-
<b>Mg</b>	1.04	-	-	-
<b>Fe</b>	0.13	-	-	-

Table 2: Comparison of estimated value of atomic composition of C, O and N with actual atomic composition of PUF binder, mineral wool products

Atom	Pure binder %	Mineral wool %	Estimated %
C	72.97	86.87	66.12
O	13.64	11.00	15.19
N	13.24	2.12	18.69

Table 3: Peak fitting data from the C 1s spectra of unaged and aged mineral wool products and pure PUF binder

Sample	Surface concentration of C1s peak fitting (at. %) (The binding energies of peak fitting (eV))				
	C-C/C-H/ C-Si	C-N / Aromatic C- OH / C-O-C	Aliphatic C- OH/C-O-C	C=O/N-C=O	NCON
Unaged PUF coated fibres	74.0 (285)	15.3 (285.8)	7.2 (286.7)	1.9 (287.8)	1.6 (289)
Aged PUF coated fibres	83.8 (285)	11.8 (285.8)	4.0 (286.7)	0.40 (288)	- -
Pure PUF binder sample	55.2 (285)	20.00 (285.9)	17.2 (286.5)	2.4 (287.8)	5.2 (289.1)



Scheme 1: The chemical structure of the cured PUF binder

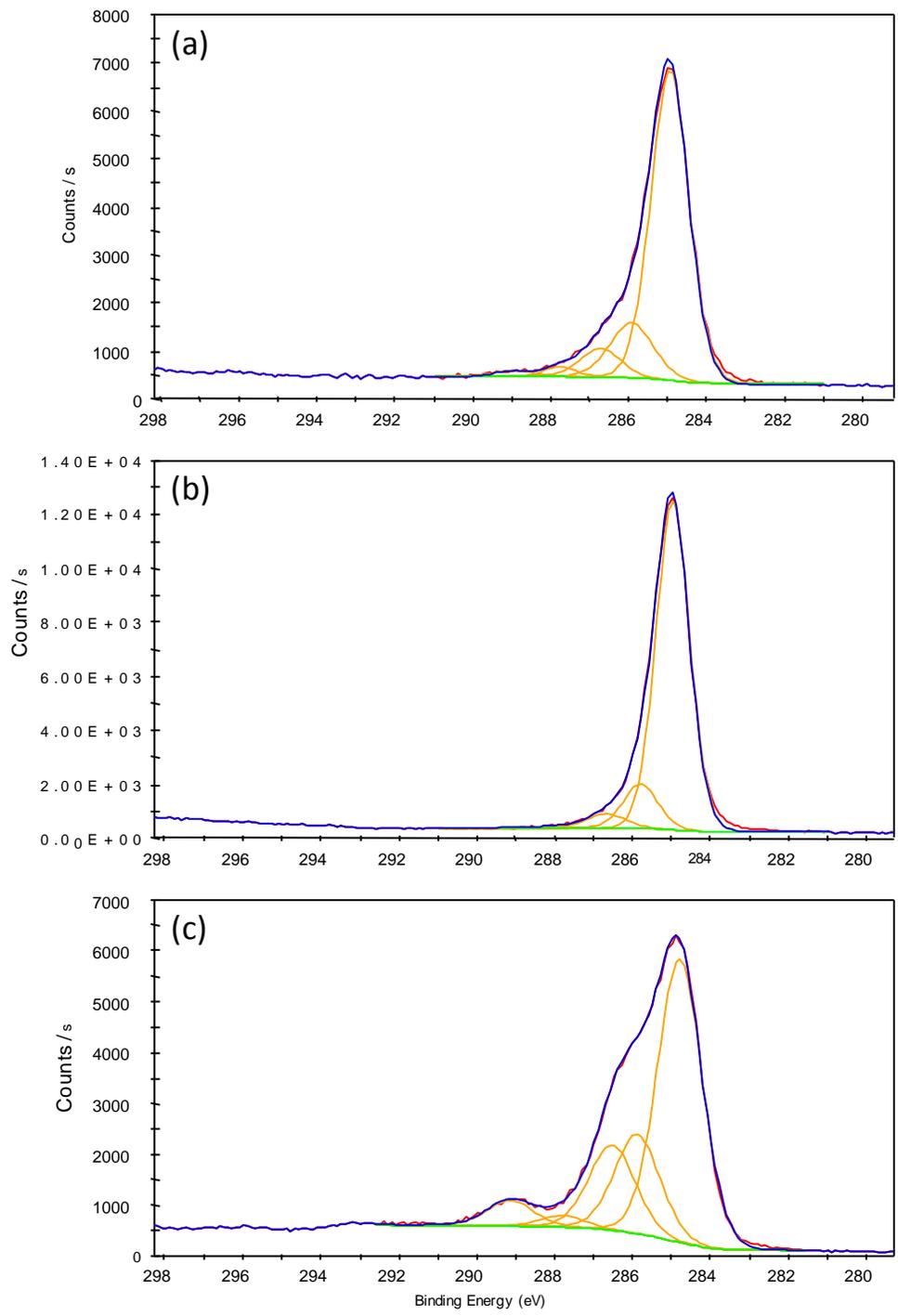


Fig. 1: The high resolution C 1s spectra of the (a) Unaged mineral wool product (b) Aged mineral wool Product (c) Pure PUF binder sample