

# Impact of curing time on ageing and degradation of phenol-urea-formaldehyde binder

D.V. Okhrimenko<sup>a,\*</sup>, A.B. Thomsen<sup>b</sup>, M. Ceccato<sup>a</sup>, D.B. Johansson<sup>b</sup>, D. Lybye<sup>b</sup>, K. Bechgaard<sup>a,1</sup>, S. Tougaard<sup>c</sup>, S.L.S. Stipp<sup>a</sup>

<sup>a</sup> Nano-Science Center, Department of Chemistry, University of Copenhagen, 2100, Copenhagen OE, Denmark

<sup>b</sup> ROCKWOOL International A/S, Hovedgaden 584, 2640, Hedehusene, Denmark

<sup>c</sup> Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, 5230, Odense M, Denmark



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## ABSTRACT

Phenol-urea-formaldehyde (PUF) resin is one of the most important thermosetting polymers. It is widely used in many industrial and construction applications as an organic coating and adhesive. For example, in production of mineral wool for insulation, PUF is used together with the coupling agent (3-aminopropylsilane, APS) and serves as a binder for attaching mineral fibers to each other and to create the necessary mechanical integrity and shape of the final product. However, during ageing under high humidity (95%) and temperature (70 °C), hydrolysis can degrade PUF, decreasing product quality. A better understanding of the chemical processes caused by hydrolysis would promote development of more stable PUF binders. We investigated the composition and stability changes during ageing of cured PUF powder binder and mineral wool fibers where PUF binds the fibers together. We aged the samples in hot water (80 °C) or in a controlled climate chamber (70 °C; 91% RH) and analyzed them using X-ray photoelectron spectroscopy (XPS), element analysis and thermogravimetric (TG) analysis. We investigated the composition of species released from PUF during hydrolysis by electrospray ionization (ESI) of the aqueous solutions. The results show that the extent of PUF curing and the presence of APS as the coupling agent have an important impact on its stability. XPS revealed that poorly cured PUF contains a high fraction of  $\text{—NH—CH}_2\text{—O—CH}_2\text{—NH—}$  bonds which are easily hydrolyzed, while longer curing results mostly in more stable methylene bridges,  $\text{—NH—CH}_2\text{—NH—}$ . We also observed evidence for urea  $\text{—NH—CO—}$  bond decomposition by ESI analysis. Mineral wool fiber ageing studies showed that PUF rearranges on the fiber surface and detaches from it, together with the APS coupling agent. This improved understanding of the effects of ageing provides clues for designing a more robust binder, leading to increased quality and stability of mineral wool insulation.

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## 1. Introduction

Phenol-urea-formaldehyde (PUF) resole is used in many industrial applications such as wood adhesives [1] and mineral wool insulation production [2]. PUF is based on phenol-formaldehyde (PF) resole which is obtained from basic solutions with a phenol to formaldehyde ratio less than one [3]. Because of the high concentration of formaldehyde at the end of the reaction of the PF resole resin, an excess of free formaldehyde exists, which can cause

undesirable environmental pollution when the PF is cured. To reduce the amount of free formaldehyde, urea can be added to the PF resin to scavenge unreacted formaldehyde and bind to four formaldehyde molecules. Usually urea is added at the end of the reaction, when the phenol molecules have already reacted with the formaldehyde, forming methyl phenol oligomers with methylene bridges [4],  $\text{—CH}_2\text{—}$ . Under basic conditions, urea reacts with formaldehyde forming short urea-formaldehyde (UF) oligomers first through formation of  $\text{—CH}_2\text{—O—CH}_2\text{—}$  bonds [5] which transform to methylene bonds with heating. Thus, the PUF final product can be considered to be a mixture of PF and UF resins [6] where phenol-urea condensates are present [7,8], but there is no long range order. The inclusion of urea into the phenol-formaldehyde network alters some of the properties of the resulting resole,

\* Corresponding author.

E-mail address: [denisokr@nano.ku.dk](mailto:denisokr@nano.ku.dk) (D.V. Okhrimenko).

<sup>1</sup> Deceased.

such as flexural strength [9], shelf life and adhesion performance [10], and it accelerates curing rates [11]. It has been experimentally determined that urea content in the range of 16–20% maximizes the bending strength of the PUF resole [3]. To obtain a final binder that can be used as adhesive, PUF is usually mixed with coupling agents. In the case of mineral wool production, 3-aminopropylsilane (APS) coupling agent is used to enhance PUF adhesion to the mineral fiber surfaces [2]. APS reacts with mineral wool [12,13] or glass fiber [14–21] surface through silanol groups,  $-\text{Si}(\text{OH})_3$ , and with the polymer matrix [22] through its amino group  $-\text{NH}_2$ . This allows binding of mineral fibers together (Fig. 1) and creates the necessary mechanical properties for the mineral wool product, when the PUF binder is cured [2]. However, reactions between the silanol group of APS and polymer matrix have also been described [23–25].

One of the major problems with using PUF binder in mineral wool production is degradation of its mechanical properties over the long term. Ageing is assumed to be caused by hydrolysis of the binder, which is amplified by increased humidity and temperature, but the exact mechanism is unknown. The stability of PF, UF, PUF and their modifications have been studied mainly with thermal degradation [26–31], Fourier-transform infrared spectroscopy (FTIR) [32] and monitoring the release of formaldehyde [33–38].

This study focused on characterizing and quantifying the stability and the ageing processes that take place in cured PUF binder. To investigate the effects of ageing, the cured PUF binder was analyzed in powder form before and after ageing in hot water (80 °C) for 3 h. Cured binder powder samples were obtained with different amounts of coupling agent (3-aminopropylsilane, APS, ranging from 0, 0.2 and 2%) and were cured for 15 or 60 min. The purpose was to determine how APS presence and curing time would influence PUF binder stability with respect to hydrolysis. Previously it has been shown that APS can cause changes in physical properties of the PF resin, increasing viscosity by self condensation reactions forming siloxane bonds [39]. Curing conditions are

considered to be the most important for PUF stability [5,8,11]. We also studied ageing of mineral wool fibers treated with PUF and APS under similar conditions (3 h in water bath at 80 °C or 7 days in a climate chamber at 70 °C and 91% relative humidity) and compared the results.

Aged and unaged samples were analyzed by the same techniques to identify changes in the chemical structure. Solid fractions were investigated using X-ray photoelectron spectroscopy (XPS), thermogravimetric (TG) and elemental NHC (nitrogen, hydrogen and carbon) analyses. The aqueous solutions used for PUF powdered binder ageing were analyzed by electrospray ionization (ESI) to determine which species of cured PUF are released to the aqueous phase. Mineral wool samples were analyzed by X-ray photoelectron spectroscopy (XPS) and streaming potential to observe changes in the PUF binder layer caused by ageing.

## 2. Experimental methods

### 2.1. Materials

PUF binder was mixed to obtain 15% solid content binder using PUF prefab from the ROCKWOOL International A/S Doense factory (10 g, about 46% solid content) by adding concentrated ammonia solution (0.8 ml), ammonium sulphate (0.1 g) and ultra deionised water (20 ml, Milli-Q, MQ, specific resistivity of 18.2 MΩ cm at 25 °C) in accordance with the recipe used at the factory. The composition of the PUF prefab was similar to that described in Zafar et al., 2013 [40]. We prepared PUF binder with no coupling agent as well as PUF with a normal amount of APS used for mineral fibers treatment (i.e. 0.2% 3-aminopropylsilane, APS, Momentive, VS-142) and 10 times higher APS (2%).

Mineral wool fibers that had been treated with PUF binder were collected from ROCKWOOL International A/S. The fiber product also contains APS coupling agent (4.4 L of 40% solution per 1000 L of PUF) and oil (Shell Catenex Oil S 579), which is used to increase

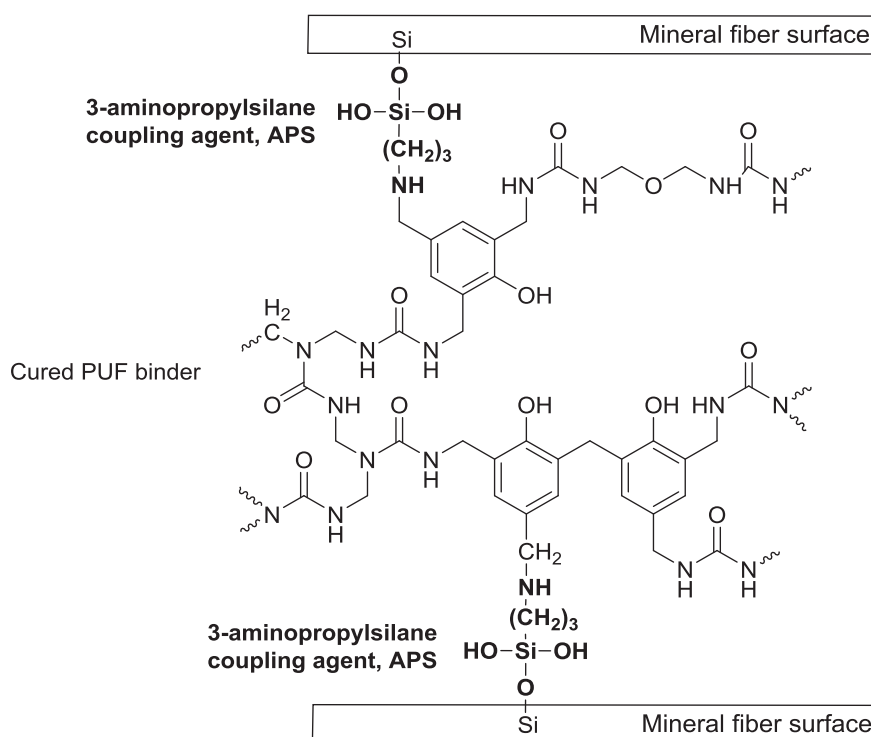


Fig. 1. The hypothetical structure of PUF binder attached to two mineral fiber surfaces with APS coupling agent.

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