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Investigation of the ageing effects on phenol-urea-formaldehyde binder and alkanol amine-acid anhydride binder coated mineral fibres

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ABSTRACT

Phenol-Urea-Formaldehyde (PUF) binder coated mineral fibres' mechanical properties have been observed to degrade during ageing at elevated temperatures and humidity, while alkanol amine-acid anhydride binder based mineral fibres exhibited better ageing properties for same duration of ageing. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were employed to identify the chemical changes occurring in the PUF binder coated mineral fibres and alkanol amine-acid anhydride binder coated mineral fibres during that ageing. The samples were aged in a climate chamber for 7 days at 70 °C and 95% relative humidity. In the case of the PUF binder coated fibres, quantitative XPS measurements showed some significant changes in the atomic composition of the PUF binder coated mineral fibres after ageing, including decreased urea and carbonyl groups concentrations. Principal Component Analysis (PCA) was applied on the positive and negative ToF-SIMS spectra of the PUF binder coated mineral fibres, showing a decrease in the concentration of the nitrogen containing peaks during ageing. This decrease was attributed to the depolymerisation of the binder due to hydrolysis of amide, methylene ether and methylene linkages between urea groups present in the PUF binder. In the case of the alkanol amine-acid anhydride binder coated mineral fibres, both XPS and ToF-SIMS techniques consistently showed that the surface chemical composition of the organic components of the alkanol amine-acid anhydride binder coated mineral fibres did not change appreciably after 7 days of climate ageing, which is relevant to the good retention of mechanical strength for products formulated with the alkanol amine-acid anhydride binder.

1. Introduction

Mineral wool is considered to be the best known insulation material among a variety of insulation materials. Mineral wool products consist of either glass fibres or stone fibres bonded together by a binder that is often a cured thermoset polymer. Different processes are involved in which the molten inorganic composition flowing from a melt furnace is spun into fibres by means of centrifugal forces and very high air speed. The fibres are collected onto a conveyor belt in an irregular manner to form a mat and sprayed with the resin binder. The coated fibrous mat is transferred to a curing oven where hot air is blown through the wool to cure the binder and rigidly bond the fibres together. Thus, thermal insulation mats, acoustical tiles and similar structures contain binder of 0.5–20% to provide strength to the structure and to preserve insulating, acoustical and dimensional properties [1].

The Phenol-Urea-Formaldehyde (PUF) binder has been used for many years in the production of mineral wool products. However, the desire to minimize the emissions of volatile organic compounds (VOC) from the mineral wool products in conjunction with existing and proposed legislation directed to the lowering of formaldehyde have led to the development of formaldehyde free binders such as binder based on polycarboxypolymers and polyols as described in [2]. Another formaldehyde free binder for mineral wool products is based on aliphatic and/or acid aromatic anhydride with alkanol amines [3–5], which are water soluble and exhibit excellent binding properties in terms of curing speed and cross-link density.

The understanding of the binder chemistry is closely coupled with the mechanical properties of the mineral wool products. The mechanical properties of mineral wool products are found to degrade during long term ageing. Previous studies [4] showed that mineral wool products based on alkanol amine-acid anhydride

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binder retain 90% of their initial strength after 7 days of the accelerated ageing; whereas the products based on PUF binder retain only 60% of their initial strength after the same duration of accelerated ageing. More knowledge about the effects of ageing on surface chemistry of the binder needs to be acquired in order to understand why (or why not) the binder based products lose or retain its mechanical properties during ageing.

In the current research work, advanced surface sensitive techniques, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are used as the main analytical tools in order to study the surface chemistry of the binder. XPS and TOF-SIMS have been used widely for the characterization of adhesion of binders, coupling agents, coatings and polymer matrices with different kind of fibres and substrates [6–9]. XPS is a technique to obtain quantitative relative surface composition information through the use of photoelectron peak intensities and corresponding empirical relative sensitivity factors. On the other hand, ToF-SIMS provides detailed information about the surface composition, molecular structure and chemical bonding of the materials [9]. In cases where ToF-SIMS spectra of different samples cannot be distinguished by the absence or presence of obvious unique peaks, Principal component analysis (PCA) has been shown useful to assist with data interpretation by capitalizing on the differences in the relative intensities from spectrum to spectrum [10]. The goal of this investigation is to identify the chemical changes occurring in the phenol-urea-formaldehyde binder and alkanol amine-acid anhydride binder coated mineral fibres being subjected to ageing.

2. Experimental methods

2.1. Materials

PUF binder coated mineral fibres and alkanol amine-acid anhydride binder coated mineral fibres were collected from Rockwool International A/S. The PUF binder and alkanol amine-acid anhydride binder coated mineral fibres were also assisted by APS coupling agent. The amount of APS is 4.4 L (of 40% solution) per ton of the resin solid. The binder coated fibres were also treated with mineral oil, which is used as water repellent. The binder and mineral oil were simultaneously sprayed onto the fibres using separate nozzles.

Uncoated mineral fibres were obtained by heating original mineral wool samples at 590 °C for 4 h to remove all the organic materials from the fibres. Pure PUF binder samples were prepared without APS and mineral oil to get information about the spectral contributions of the PUF binder in the XPS and ToF-SIMS spectra of the mineral wool products. Pure PUF binder solution was also received from Rockwool International A/S. It was cured at 200 °C for 1 h.

The PUF resin was prepared by mixing phenol, formaldehyde and catalyst, and heating it up to ±80 °C until the desired condensation degree was reached. Molar ratio of formaldehyde to phenol is in the range of 3.5–3.9. After condensation between phenol and formaldehyde, urea was added to react with the remaining formaldehyde. The molar ratio of urea to phenol was in the range of 1.5–2.5. More information on the preparation of the binder and the main reactions between phenol, formaldehyde and urea groups can be found in [1,11,12]. The chemical structure of cured PUF binder is shown in Scheme 1.

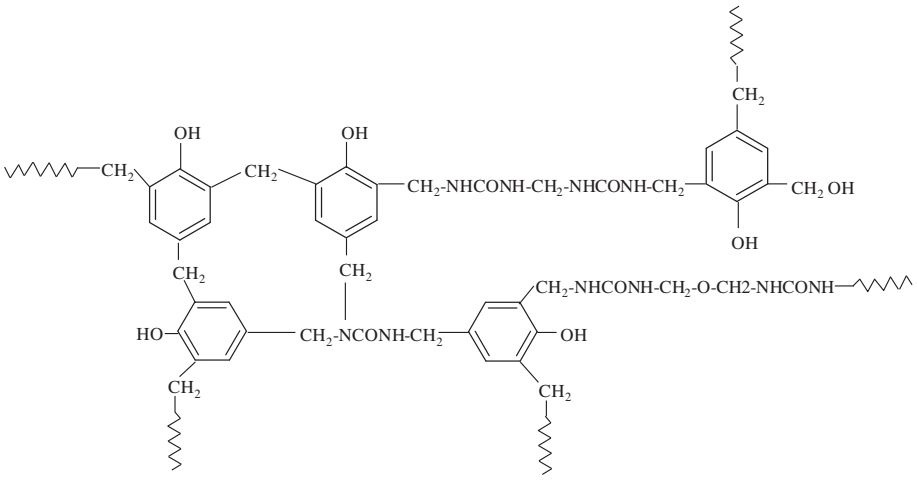
The hypothetical chemical structure of the cured alkanol amine-acid anhydride binder is shown in Scheme 2. The binder resin is prepared by condensation reactions of diethanolamine (DEA) with tetrahydrophthalic acid anhydride (THPA) and trimellitic acid anhydride (TMA). The functional groups in the resin are amino, hydroxyl and carboxylic acid groups, which crosslink during heating from 130 °C to 300 °C. When the resin is cured, condensation reactions take place between carboxyl acid and hydroxyl groups to form ester bonds, and between the carboxylic acid and secondary amine to form the amide bonds. The detailed information about the chemistry of the binder and its processing can be found in [5].

2.2. Ageing condition

The accelerated ageing was carried out by placing the samples in a climate chamber containing atmospheric air at a temperature of 70 °C and 95% relative humidity for seven days. Unpublished proprietary reports showed that these ageing conditions are appropriate for a considerable duration of ageing.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS 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° take-off angle with a pass energy of 150 eV. The atomic 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



Scheme 1. The chemical structure of the cured PUF binder.