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Reinforcement properties of 3-aminopropylmethyldiethoxysilane and N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane on polyurethane ester foam

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ABSTRACT

Museum artifacts made of polyurethane foam are frequently affected by conservation issues mainly related to the loss of their mechanical properties. While effective polyurethane ether foam treatments already exist, no convenient consolidation treatment exists for polyurethane ester foams. The possibility of a reinforcement effect expected to prevent the mechanical properties loss has been evaluated. Two aminoalkylalcoxysilanes (AAAS), the 3-Aminopropylmethyldiethoxysilane and the N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane, which gave promising results for consolidation of paper, have been tested on modern industrial flexible polyurethane ester foam samples. AAAS solutions at different concentrations have been applied, by immersion, on polyurethane ester foam samples. Mechanical properties have been studied by Compression Force Deflection Test, which shows that after AAAS treatment the resistance of the foam to compression improves. The color of the samples before and after consolidation has been monitored to assess the impact of the treatment on the visual aspect of the foam. The AAAS distribution in the thickness of the samples has been investigated by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Magic angle spinning nuclear magnetic resonance (MAS NMR) has been used to confirm AAAS polymerization and to evaluate its average polymer chain length. The promising results obtained suggest that AAAS could be an efficient solution for the consolidation of polyurethane ester foams.

1. Introduction

Because of their multiple applications, since the 1960s, polyurethanes (PURs) attracted artists and designers, who utilized them for sculptures, paintings, design furniture, textiles and accessories [1,2]. PUR foams deteriorate rapidly; the effects of degradation can appear after 20–30 years of natural aging. Consequently, conservation issues mainly related to the loss of their mechanical properties now affect these artifacts. The main symptoms of degradation are discoloration, loss of flexibility and crumbling, which occur under influence of moisture, heat and light [3]. During the degradation process, PURs undergo both chain scission and cross-linking phenomena. For the two main families, PUR ester and PUR ether, several studies demonstrated that the esters are more sensitive to hydrolysis while the ethers are more sensitive to oxidation [3–6]. Several studies concerning degradation and conservation strategies for PUR foams used by artists are reported in the literature [7–11]. However, while van Oosten [12] reported that impregnation of PUR ether foam with a mixture of Impranil DLV and vitamine E (an anti-oxidant) inhibits the photo-oxidation and gives flexibility to PUR ether foam, no convenient consolidation treatment exists for PUR ester foams. Conservators of modern and contemporary art are still seeking solutions to extend the lifetime of works of art made from this material. Two aminoalkylalcoxysilanes (AAAS), the 3-aminopropylmethyldiethoxysilane (AMDES) and the N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (DIAMINO), already used for deacidification and consolidation of paper [13,14], were tested on modern industrial flexible PUR ester foam samples. For paper conservation the use of AAAS provides an alkaline buffer on the

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cellulosic network, improves the mechanical resistance of the paper and remains effective even after artificial aging [15]. In a preliminary study, it was showed that AMDES treatment improves the mechanical compression properties of PUR ester foam [16]. A reinforcement effect is obtained after the treatment of modern industrial PUR ester foam both unaged and after artificial aging.

In this study AMDES and DIAMINO treatments are compared; they were tested on modern industrial PUR ester foam samples to evaluate their reinforcement effect, the possibility to employ these products in the case of a preventive conservation treatment and their interaction with the PUR structure. This paper will present the results of the analysis performed on treated samples in comparison with the reference (untreated modern industrial PUR ester). Colorimetric measurements, stress/strain compression curves, scanning electron microscopy (SEM) images, Fourier transform infrared (FTIR) spectra, and ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) spectra will be discussed to evaluate the effectiveness of the two AAAS treatments for PUR ester foam reinforcement.

2. Material and methods

2.1. Samples

New Dimension Industries LLC (NDI LLC) supplied the PUR ester foam. It is an open-cell flexible foam with a density of 30 kg/m^3, PUR ester formulated with 2,6- and 2,4- toluenediisocyanates (TDI) and poly[di(ethylene glycol) adipate]. Nowadays this formulation is the most common in PUR ester flexible foam industry. From an internal study on foams from museum collections it was found that PUR ester flexible foams used by artists were usually formulated with TDI isocyanates as well. For this reason a 2,6-,2,4-TDI based PUR ester was selected for investigations. The foam was pre-cut by NDI LLC in cubic regular samples (50 mm × 50 mm × 30 mm) suitable for compression tests.

2.2. PUR impregnation treatment

Hexamethyldisiloxane (HMDS) was the solvent employed for the AAAS monomer solutions. It was primarily chosen for its low cohesive energy density and low surface tension, that permit a good wetting of the sample surfaces, and secondly for its weak van der Waals interactions that assure a good dimensional stability of the sample structure after solvent evaporation. HMDS solvent, AMDES and DIAMINO monomers were provided by Abcr GmbH. All the compounds were used as received from the producer, without further purification. Solutions of AMDES and DIAMINO in HMDS solvent were prepared at different AAAS concentrations (2.5%, 5% and 10% vol/vol). The effect of HMDS solvent alone on PUR ester foam was also evaluated. The foam samples were weighed and immersed for 24 h in each solution using closed polypropylene containers. To avoid foam flotation, an aluminum grid fixed inside the polypropylene container was used to maintain the samples dipped in the solution. After immersion the samples were dried under vacuum for 6 h at ambient temperature. Once completely dried they were weighed once more in order to determine the AAAS uptake. To be sure of the complete evaporation of the solvent all the measurements were performed two weeks after the treatment.

2.3. Colorimetric measurements

The foam flexible structure is easily deformed by the weight of the spectrophotometer when this is applied directly in contact with the sample upper surface. This deformation could affect the chromaticity coordinate value measurements [17]. To avoid any deformation of the foam cell structure, a rigid black box with a hole of 53 × 53 mm on the top is used as an additional device to the spectrophotometer X-Rite. For the measurements, the samples are inserted in the central hole of the box. The portable spectrophotometer is then positioned onto the box in close contact with the foam surface and can analyze it without any deformation of the foam cell structure.

The CIE L^*, a^* and b^* coordinates were measured with a portable sphere spectrophotometer X-Rite SP64 using the following set–up parameters: 4 mm measurement area (6.5 mm target window), illuminant type $D65$, 10° standard observer angle and specular component included (SPIN). The measurements were repeated on the top surface of 3 replicate samples at 5 different locations on each. The mean values were used to calculate the total color difference ΔE^*_{ab} and the metric chroma difference ΔC^*_{ab} between the treated samples and the reference using the standard colorimetric equations according to the ASTM Standard D 2244-93 [18]:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2}, \quad (1)$$

$$C^*_{ab} = \sqrt{(a^*)^2+(b^*)^2}, \quad (2)$$

$$\Delta C^*_{ab} = (C^*_{ab})_{\text{treated sample}} - (C^*_{ab})_{\text{reference}}. \quad (3)$$

2.4. Mechanical tests

Mechanical properties have been studied by Compression Force Deflection Test according to the ASTM Standard D 3574-03 test C method [19] using an Adamel Lhomargy DY.20 B tensile/compression instrument. At least three specimens per sample were tested and the value reported is the mean value of those observed. Every specimen was compressed down to 50% of its thickness (15 mm) at 50 mm/min and kept under compression for 60 s. The entire *stress/strain* curve was recorded and the final force after 60 s determined.

2.5. SEM imaging

Backscattered electron images and Silicon (Si) surface elemental analysis of PUR foam before and after treatment were obtained with a SEM Jeol JSM-5410LV equipped with an Oxford Link Isis – Energy Dispersive X-ray Spectrometer (EDS). Foam samples were cut with a scalpel blade in pieces of approximately 5 mm × 3 mm × 2 mm to fit in the SEM vacuum chamber. The cutting of the foam allowed thus to expose and visualize cross sections of the cell branches on the cut surfaces. The samples were mounted on aluminum sample holders with double-sided carbon tape (NEM tape, Nisshin EM Co. Ltd.) and coated with gold to a thickness of approximately 300 Å. The following experimental conditions were kept constant for both backscattered images and elemental analysis: high vacuum, 20 mm working distance, 20 kV accelerating voltage.

2.6. FTIR spectroscopy

FTIR spectra were recorded on a Nicolet 6700 spectrophotometer, equipped with a diamond ATR macro-system (Smart Endurance) scanning from 600 to 4000 cm^{-1}, 36 scans were recorded for each spectrum at a resolution of 8 cm^{-1}. To obtain information about the homogeneity of the treatment, treated samples were cut in slices allowing infrared analysis to different points of the sample thickness. Five spectra were collected from each sample; two near the external surfaces, one from the top and one from the bottom, and three from the bulk at regular intervals. To identify poly-