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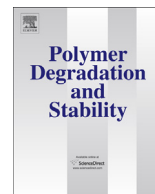
Degradation of polyurethane ester foam artifacts: Chemical properties, mechanical properties and comparison between accelerated and natural degradation

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ABSTRACT

Polyurethane foams deteriorate rapidly; the effects of degradation can appear after 20–30 years. Conservation issues mainly related to the loss of polyurethane foam mechanical properties frequently affect museum artifacts. Many studies dealt with degradation of polyurethane, but no one correlated the polyurethane chemical changes with the mechanical properties loss of the foam structure. In order to find a degradation indicator permitting to obtain simultaneously information on the chemical and mechanical condition of the foam with a non-invasive method, we performed accelerated degradation at different relative humidity conditions. Chemical modifications have been observed by Attenuated Total Reflection–Fourier Transform Infrared Spectroscopy (ATR–FTIR). Differential Scanning Calorimetry (DSC) has been used to follow polyurethane glass transition temperature variations. Mechanical properties of degraded and undegraded samples have been studied by Compression Force Deflection Test (CFDT) and Scanning Electron Microscopy (SEM) allowed visualizing foam surface modifications during the entire degradation period. ATR–FTIR spectra analysis of artificially degraded samples allowed identifying the ester/hydroxyl band ratio as a good indicator of polyurethane ester foam degradation. A correspondence was found between the decrease of the ester/hydroxyl ratio value and the loss of elasticity of the foam structure. The reliability of this indicator (ester/hydroxyl band ratio) has been validated by ATR–FTIR analysis performed on naturally degraded TDI based polyurethane ester foams.

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1. Introduction

Since the 1960s, because of the variety of applications, polyurethanes (PURs) attracted artists and designers, who utilized them for sculptures, paintings, design furniture, textiles and accessories [1,2]. PUR foams deteriorate rapidly; visible consequences of degradation can appear after 20–30 years of natural degradation. The main visual signs of degradation are discoloration, loss of flexibility and crumbling, which occur under influence of moisture, heat and light [3]. Consequently, conservation issues that now affect these artifacts, are mainly related to the loss of their mechanical properties.

During degradation, PURs undergo both chain scission and cross-linking. 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 [4–6]. Several studies concerning degradation and conservation strategies for PUR foams are reported in the literature [7–12]. However, while van Oosten [13] reported that impregnation of PUR ether foam with a mixture of Impranil DLV and vitamin E (antioxidant) inhibits photo-oxidation and gives flexibility to PUR ether foam, no convenient 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.

In a recent study, it was showed that treatments based on aminoalkylalkoxysilane (AAAS) monomers improve the mechanical compression properties of PUR ester foam [14]. In a previous preliminary study, this kind of treatment appears to be effective even on degraded PUR ester foams [15]. Reliable investigation on the ability of AAAS to consolidate PUR degraded foam was necessary.

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However, such investigation is not possible without an accurate study of artificial degradation of PUR foam used in the research. Although many studies deal with PURs degradation, none correlate PUR chemical changes with the mechanical properties loss of the foam structure during artificial degradation. This is the first aim of this research. ATR—FTIR analysis, mechanical tests and thermal analysis will be used to point out this correlation.

The second aim of the research is to find a degradation indicator to non-invasively obtain information on the chemical and mechanical condition of a foam. Such a tool would be very useful for conservators: first of all, the information about the condition of foams in collections would be obtained without damaging the structures. Secondly, such a tool could have a preventive function suggesting conservators to undertake an intervention before the collapse of a foam structure. With this in mind, ATR—FTIR spectra taken from the artificially degraded samples have been examined and different band ratios calculated.

The data obtained in this research made it possible to evaluate the degradation of a PUR reference foam during accelerated degradation and to define conditions that simulate, as closely as possible, degradation observed during natural degradation of PUR ester foams of the same composition.

2. Material and methods

2.1. Samples and chemicals

The PUR ester reference foam was obtained from *New Dimension Industries LLC (NDI LLC)*. The open-cell flexible foam, made from 2,6- and 2,4-toluenediisocyanates (TDI) and poly[di(ethylene glycol) adipate], has a density of 30 kg/m^3. The foam was pre-cut by NDI LLC in cubic samples (50 mm $\times$ 50 mm $\times$ 30 mm) suitable for compression tests.

Naturally degraded PUR ester foam samples (different degradation conditions) were collected for comparison with the artificially degraded samples. The majority of the naturally degraded samples were taken from PUR ester foams used for storage enclosures.

Deuterated water (D$_2$O) (CAS 7789-20-0) from *Euriso-top* was used for extraction of the polyol fraction of the PUR foam reference.

Polydiethyleneglycol adipate (CAS 9010-89-3, C$_{10n}$H$_{16n+2}$O$_{5+1}$) from *Sigma—Aldrich* was used as a reference for identification of the polyol fraction.

Adipic acid (CAS 124-04-9, C$_6$H$_{10}$O$_4$, MM 146.1 g/mol) from *Sigma—Aldrich* was used as a reference for one of the degradation products of PUR hydrolytic de-polymerization.

2.2. Accelerated degradation

Accelerated degradation in humid atmosphere has been carried out in a *Vötsch Industrietechnik VC0020* aging chamber. This chamber can control temperature and humidity with an accuracy of ± 0.3 °C for the temperature and of ± 1 to 3% *RH* for relative humidity.

Samples degraded in dry atmosphere were put in a chamber *Memmert ULM 400* that controls only temperature with the accuracy of ± 1 °C. Electronic sensors (hygrothermal button *PLUG&-TRACK* from *PROGES PLUS*) were placed in the chamber at 90 °C and recorded fluctuation in humidity $<1\%$ *RH*.

2.3. Mechanical tests

Mechanical properties have been studied by Compression Force Deflection Test according to the ASTM Standard D 3574-03 test C method [16] using an Adamel Lhomargy DY.20 B tensile/compression instrument. At least three specimens per sample were tested and mean values are reported. 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 compression strength determined (this value corresponds to the force after 60 s of compression). The elastic limit, another mechanical property of the foam corresponding to the force at the end of the linear elastic region, was determined from the stress—strain curves.

2.4. SEM imaging

Backscattered electron images of PUR foam were obtained with a SEM Jeol JSM-5410LV. Foam samples were cut with a scalpel blade into pieces of approximately 5 mm $\times$ 3 mm $\times$ 2 mm to fit into the SEM chamber. 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 300Å. The following experimental conditions were kept constant for all samples: high vacuum, 20 mm working distance, 20 kV accelerating voltage.

2.5. 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 homogeneity of degradation, artificially degraded samples were cut in slices to allow for infrared analysis at different 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.

2.6. GC-MS

For GC-MS analysis, an extract of the PUR foam reference sample was prepared. 200 mg of PUR foam were immersed in deuterated water (D$_2$O) and stirred for 24 h using a megnetic stirrer. The solution was then filtered using a glass syringe and a Teflon membrane filter of 0.45 μm porosity. Analysis of the extract was performed with a gas chromatograph *Thermo Trace GC Ultra* coupled to a mass spectrometer *Thermo Trace DSQ* in split mode with a flow ratio of 10:1 and an injector temperature of 270 °C. The carrier gas used was He at a constant flow of 1 mL/min. The column was a *Zebron ZB-5MS* (95% dimethylpolysiloxane and 5% phenilarylene) capillary column with a length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 μm. The oven temperature was programmed as follows:

- Initial temperature of 100 °C maintained for 2 min,
- Ramp at a rate of 10 °C/min up to 320 °C,
- Final temperature 320 °C maintained for 10 min.

The interface temperature was set at 280 °C and the source temperature at 200 °C. Mass spectra were acquired in electron impact mode at 70 eV with *m/z* scanned between 30 and 600.

2.7. Py-GC-MS

Py-GC-MS of the PUR reference foam was performed with a gas chromatograph *Shimadzu GC2010* coupled to a mass spectrometer *Shimadzu GCMS-QP2010 Plus* with a pyrolyzer *Frontier Lab PY-2020iD*. The pyrolysis temperature was set at 610 °C for 0.1 s and the pyrolyzer interface temperature was 320 °C. The analyses were