THERMOGRAVIMETRIC ANALYSIS OF CALCIUM MONTMORILLONITE TREATED WITH HEXAMETHYLENE DIISOCYANATE

M. R. Schilling*, F. Preusser* and G. Gutnikov+

*THE GETTY CONSERVATION INSTITUTE, 4503 GLENCOE AVENUE, MARINA DEL REY, CALIFORNIA, 90292-6537 USA
+DEPARTMENT OF CHEMISTRY, CALIFORNIA STATE POLYTECHNIC UNIVERSITY, POMONA, CALIFORNIA, 91768 USA

(Received June 22, 1991; revised form December 30, 1991)

The product of the reaction between calcium montmorillonite and hexamethylene diisocyanate in acetone, catalyzed with dibutyltin dilaurate, was studied by thermogravimetry to determine the amount of polymer produced. The method developed to determine polymer content in the clay possessed excellent accuracy and precision, and produced more consistent results than traditional gravimetric methods.

Keywords: montmorillonite, polymers, TG

Introduction

The preservation of archaeological and historic adobe structures continues to attract considerable attention in the field of art conservation [1, 2]. In essence, adobe is a composite of sand, silt and organic debris, bound together by clay. If left untreated, a large number of adobe structures throughout the world would be destroyed by the effects of water and weathering. Many treatment methods attempt to consolidate and preserve adobe surfaces with reactive monomer or polymer solutions, applied to the structure by spraying or by other methods. Ideally, such treatments impart water repellency and improved structural stability to adobe [3].

A number of commercial products are currently available that can be used to consolidate adobe. Many of these products are based on polymers such as silanes, epoxies, acrylics, or polyurethanes [3]. However, the majority of these products
are unacceptable for use in conservation because they impart objectionable qualities to the treated structures, such as discoloration, cracking or spalling of the surface [3].

Because it is difficult to find one product that meets all conservation requirements, it is important to evaluate new products as they become available in the market. One of a number of materials currently being evaluated at the Getty Conservation Institute (GCI) for use in the treatment of adobe is hexane-1, 6-diisocyanate, commonly known as hexamethylene diisocyanate or HDI [3].

Difunctional isocyanates such as HDI react with adsorbed water present in the clay component of the adobe material to form a polyurea according to the following equations [4, 5]:

\[
\begin{align*}
RNCO + H_2O & \rightarrow [RNHCO_2H] \rightarrow RNH_2 + CO_2 \\
\text{carbamid acid amine} & \text{(unstable)} \\
RNH_2 + RNCO & \rightarrow [RNH]_2CO \\
\text{substituted urea}
\end{align*}
\]

where \( R \) is \(-(CH_2)_6NCO\). Ultimately, polymerization occurs due to the difunctionality of the HDI molecule. Considering that one mole of CO\(_2\) is evolved for every two moles of diisocyanate converted to polyurea, the theoretical yield of reactions 1 and 2 with respect to HDI monomer is 85%. By these reactions, HDI produces a polymeric network that imparts structural stability and increased water repellency to the adobe substrate [3, 6].

As part of the GCI research [3], the reaction of HDI monomer with calcium montmorillonite (CM), a clay mineral commonly found in adobe, was studied. Calcium montmorillonite can be represented by the formula \((Al, Mg, Fe)_{4}(Si, Al)_8O_{20}(OH)_4(Ca)_{0.7}\). In these studies, a known quantity of CM, previously dried at 50°C, was slurried in acetone and allowed to react with monomer in the presence of dibutyltin dilaurate catalyst for a pre-determined time period. The product was washed, dried at 50°C, and weighed to determine the amount of polymer produced. Unexpectedly, the polymer content was less than the stoichiometric amount of HDI monomer consumed. In some cases, the clay weight actually decreased after reaction.

It thus became necessary to find an alternative method for determining polymer content. Direct spectrophotometric determination of polymer loading proved to be a difficult undertaking. Fourier-transform infrared (FTIR) spectrometry of the products of the reaction revealed complex mixtures of polyureas which were not amenable to quantitative analysis using this method [6].

Thermogravimetry has been used with much success for the examination of clays [7, 8] and polymers [9]. It was speculated that the HDI-derived polymer...