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THERMOGRAVIMETRIC ANALYSIS OF CALCIUM MONTMORILLONITE TREATED WITH HEXAMETHYLENE DIISOCYANATE

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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

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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]:

$$RNCO + H_2O \rightarrow \underset{\substack{\text{carbamid acid}\\ \text{(unstable)}}}{[RNHCO_2H]} \rightarrow \underset{\text{amine}}{RNH_2} + CO_2 \qquad (1)$$

$$RNH_2 + RNCO \rightarrow \underset{\text{substituted urea}}{[RNH]_2CO} \qquad (2)$$

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 should be readily oxidizable in the thermobalance, whereas CM should not. This suggested that polymer content could be determined by thermogravimetry.

In quantitative thermogravimetry, the composition of a mixture is typically determined from the magnitude of the weight-loss steps for each component, providing that the steps are well separated on the temperature axis. The procedure is slightly more difficult if the weight-loss steps for the components of the mixture are only partially resolved. In these instances, the mgnitude of the individual weight-loss steps cannot be obtained by simple extrapolation to the percent weight axis. However, an algebraic method can be applied to overlapping weight-loss step data in order to obtain the composition of the mixture.

The method was developed by Mulley and Cavendish for the analysis of mixtures of brushite and monetite [9, 10]. Consider a sample consisting of a mixture of components A and B, with each component possessing a weight-loss step over a well-defined temperature range. To calculate the proportion of each material in the mixture, the two necessary equations are:

$$W_T = [\%A(W_A) + \%B(W_B)]/100 \quad (3)$$

$$\%A + \%B = 100 \quad (4)$$

where W_r is the total percent weight-loss of the mixture over the temperature range incorporating both steps, W_A and W_B are the respective percent weight losses for pure A and B, and %A and %B are the weight percentages of A and B in the mixture. In this system, the weight percentages are the unknown quantities, so Eq. 4 can be solved for %B and substituted into Eq. 3, which now becomes:

$$\%A = \frac{W_T - W_B}{W_A - W_B} \times 100\% \quad (5)$$

Because no assumptions were made during the derivation of Eq. 5, the equation can be applied to various two-component mixtures. For example, the method can be used for the analysis of mixtures of hydrates and carbonates, for which weight-loss steps arise from dehydration and decarboxylation reactions. In the present study, Eq. 5 was used to calculate the polymer content of calcium montmorillonite treated with catalyzed hexamethylene diisocyanate.

Experimental

All thermogravimetric analyses were conducted on a Mettler TA3000 system utilizing the TG50 thermobalance. A Mettler TC10A controller served as furnace control unit, data recorder and off line data evaluation module. Supplementary data evaluation was performed using a Lotus 123 database program

TG data were recorded between 20°C and 1000°C (except where indicated), using a heating rate of 25 deg/min. Oxygen was used to purge the furnace at a flow rate of 50 ml/min. TG blank measurements were made using uncovered, empty 70 μl alumina crucibles. The thermobalance was calibrated against the Curie temperatures of standard Mettler Alumel, Mumetal, and Trafoperm.

A sample of calcium montmorillonite, STx-1, was obtained from the Source Clays Repository of the Clay Minerals Society. The clay samples were not pretreated prior to analysis. Analyses were performed on samples of loosely packed powder, ranging from 10 to 100 mg in weight. Initial sample weights were measured on the external balance pan located outside of the purged TG furnace. This procedure was necessary because, for samples preweighed inside the furnace, desorption of water from the clay in the dry purge gas stream caused a gradual decrease in the initial weight readings.

The CM/HDI reaction products were prepared in the following manner. Five grams of STx-1, dried at 50°C for 3 days, was added to 70 ml of AR acetone, and the suspension was stirred vigorously. Approximately 1 ml of HDI monomer and 0.03% *v/v* dibutyltin dilaurate catalyst was added to 30 ml of acetone; this solution was added dropwise to the clay suspension over a period of 5 min. The suspension was stirred vigorously for a specified time, then centrifuged. The solution was decanted, and unreacted HDI was recovered by evaporation of the solvent. The solid reaction product was washed with acetone, centrifuged, and dried at 50°C for approximately 24 hours. To produce samples with varying polymer content, the process was repeated for a series of reaction times. Polymer content was initially estimated from the increase in weight of the CM after reaction.

Standards of polymer in clay were required for evaluating accuracy and precision. Pure HDI polymer was produced in the absence of CM using the aforementioned experimental procedure, and later ground in a mortar with clay to approximate the sample matrix of the reaction products.

Results

Untreated calcium montmorillonite STx-1

Thermogravimetric analyses of untreated calcium montmorillonite STx-1 showed three weight loss steps (Fig. 1a) ascribed to evolution of adsorbed water, chemically-bound water associated with exchangeable calcium ions, and structural water due to dehydroxylation of the silica lattice [7, 8, 11, 12]. The adsorbed water content of the clay samples often approached 15% by weight, depending on the relative humidity conditions of the ambient surroundings during storage. Chemically-bound water content was approximately 1.6%, and structural water loss was 4%.

Polyurea standards

The TG results for a polymer test standard appears in Fig. 1c. Oxidation of the polymer standards occurred between 225°C and 800°C via a multi-step reaction. Reaction of the polymer between 225°C and 460°C yielded a char residue, which subsequently underwent oxidation above 550°C. These observations are consistent with other thermoanalytic studies of polyureas [13].

Table 1 lists theoretical *vs.* experimentally-derived polymer content values (%P) for a series of test standards. For this series, the absolute error of the method was found to be 0.2%; the relative precision, determined by replicate analyses, was 1%.

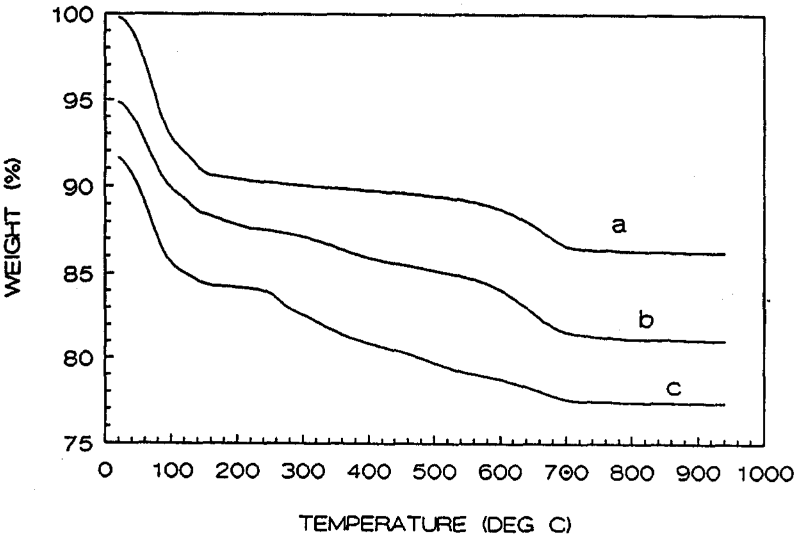

Fig. 1 Thermogravimetry curves for: *a*) untreated STx-1; *b*) reaction product; *c*) polymer standard. Curves offset and rescaled for overlay. Sample sizes approximately 10 mg

STx-1 and HDI reaction products

The results of thermogravimetric analysis for the series of HDI/CM products appear in Figs 1b and 2. A summary of the weight-loss data for the reaction products appears in Table 2. All of the samples exhibited large weight losses between 20°C to 225°C attributed to volatile desorption. In general, volatile content decreased with increasing reaction time (the time that HDI and CM were allowed to react).

Polymer content data were calculated by applying Eq. 5 to the weight-loss data over the range 225°C to 990°C. The results are listed in Table 3.

Table 1 Thermogravimetric analysis results for test standards

Polymer content/%	Weight loss/% 225°–800°C	Experimental polymer content/%
2.1	6.3	2.0
9.1	12.8	8.9
17.7	21.2	17.7
34.9	37.5	34.9

NOTE: Percent weight losses and polymer contents are based on dry sample weight at 225°C. Between 225°–800°C, untreated calcium montmorillonite exhibited a weight-loss of 4.4%, and pure HDI-derived polymer lost 99.3%.

Discussion

Regarding the preliminary attempts for using standard gravimetric analysis (weight by difference) to determine polymer content, the major cause of error was suspected to be variation in the adsorbed volatile content of the reaction products. In order for gravimetric analysis to yield accurate polymer content data, the volatile content of the reaction products and unreacted clay must be identical

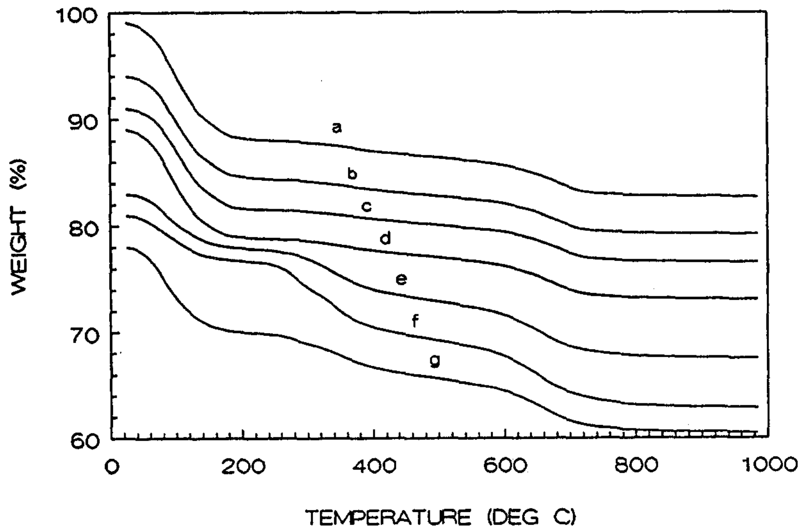

Fig. 2 Thermogravimetry curves for reaction products: *a*) 0.25 hr; *b*) 0.5 hr; *c*) 1 hr; *d*) 3.25 hr; *e*) 6.5 hr; *f*) 17 hr; *g*) 21 hr

Table 2 Thermogravimetric analysis data for products of the reaction between calcium montmorillonite STx-1 and hexamethylene diisocyanate

Reaction time/ hours	Weight loss/% 20° to 225°C	Weight loss/% 225° to 990°C
0.25	11.68	6.44
0.5	12.37	6.48
1.0	12.90	6.26
6.5	7.51	11.75
17	5.86	15.13
0*	14.47	4.65

NOTE: Percent weight-loss data based on sample weight at 225°C. Data marked with * denote samples of untreated clay.

Table 3 Polymer content results for products of the reaction between calcium montmorillonite STx-1 and hexamethylene diisocyanate

	Reaction time/hours				
	0.25	0.50	1.0	6.5	17
Polymer content /%	1.90	1.96	1.72	7.52	11.10
Recovery of HDI by TG /%	102	104	102	98	103
Recovery of HDI by gravimetry / %	97	97	96	74*	88

NOTE: The relative percent deviation for duplicate analyses was 1.9%. Percent recoveries were calculated from the initial weight of HDI monomer introduced into the reaction mixture, the weight of HDI recovered in the solvent, and the stoichiometry of equations 1 and 2 (85% yield of polyurea starting from HDI monomer).

On the contrary, a gradual decrease in volatile content with increasing reaction time was observed for the data in Table 2. It was postulated that as the polymer content of the reaction products increased, their surfaces became more hydrophobic and, hence, adsorbed less moisture from the atmosphere upon storage. Increase in sample weight due to the formation of polymer was thus offset by a reduction in volatile content, causing inexplicably low polymer content values.

It should be noted that mixtures of CM and polymer standard may react differently on TG than the reaction products, due to variation in the structure of the final polymerized product. These differences should primarily be manifested in the overall shape of the TG curve. Presumably, only a minor effect (if any) on the magnitude of the weight loss step would be observed.

Conclusions

Thermogravimetry provided an excellent means for determining the polymer content of calcium montmorillonite and hexamethylene diisocyanate reaction products. The discrepancy in the polymer content data obtained by traditional gravimetric analysis of the reaction products was presumed to be due to variation in adsorbed volatile content of the samples.

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Zusammenfassung — Zur Bestimmung der Menge des entstandenen Polymers wurde mittels Thermogravimetrie das Reaktionsprodukt aus der Reaktion von Calciummontmorillonit und Hexamethylendiisocyanat in Gegenwart von Dibutylzinndilaurat Katalysator untersucht. Die zur Bestimmung des Polymergehaltes der Tonerde entwickelte Methode ist sehr genau und präzise und liefert widerspruchsfreiere Ergebnisse als herkömmliche gravimetrische Methoden.