Flexible Polyurethane Foam. I. FTIR Analysis of Residual Isocyanate

K. C. COLE and P. VAN GHELUWE, *National Research Council Canada,* *Industrial Materials Research Institute, 75 De Mortagne Blvd., Boucherville, Quebec, Canada J4B 6Y4,* and M. J. HÉBRARD and J. LEROUX, *Union Carbide Canada Ltd., 10455 Metropolitan Blvd., Montreal East, Quebec, Canada H1B 1A1*

Synopsis

A method for the measurement of residual isocyanate in flexible polyurethane foam by attenuated total reflectance Fourier-transform infrared spectroscopy is described. Residual isocyanate as a function of time was measured in freshly made foams of varying isocyanate index. The effect of relative humidity during storage on the decrease in isocyanate concentration was investigated. As expected, aging under humid conditions was found to decrease the isocyanate concentration faster than under dry conditions. However, even after long periods of time under high humidity, traces of bound isocyanate remained. The fate of the isocyanate is discussed.

INTRODUCTION

The operation of industrial processes always involves art. It is often acquired through experimenting and looking at the end results without fully understanding the mechanics of what is going on. The manufacture of flexible polyurethane foam during hot and humid summers is one such instance. To compensate for the damaging effect of changing climatic conditions on the mechanical properties of foam, an excess of toluene diisocyanate (TDI) is added to formulations. These high index foams cure to reach the desired properties.

Unreacted isocyanate (NCO) is present immediately after foaming, even in foams having less than the stoichiometric amount of TDI.[1] While the properties of foam improve with time under humid conditions, the concentration of isocyanate groups decreases.[2] The fast reactions involved in the blowing process and the rapid gel times ensuing prevent total consumption of the bound NCO groups. These are locked in the gelled matrix, but if sufficiently high temperatures are maintained long enough, greater mobility of the chain ensures a more complete reaction.[3]

By examining the reactivity of high index foaming mixtures and chemical composition of the resulting products we have sought to understand the fate of excess isocyanate. In Part I, we monitor the concentration of NCO groups during foam storage using Fourier transform infrared (FTIR) techniques. The foam spectra were obtained by attenuated total reflectance (ATR) and analyzed for chemical composition as a function of isocyanate index. In Part

II, the reactivity of high index foam systems will be examined through measurement and analysis of exotherms.

EXPERIMENTAL

Materials and Foaming Procedure

Foams were prepared with NIAX polyol 16-46 (Union Carbide Corp.), a secondary hydroxyl end-terminated polyether triol with a hydroxyl number of 47 ± 1 mg KOH/g. Toluene diisocyanate (TDI) with a 80/20 ratio of the 2,4- and 2,6-isomers was obtained from BASF. The amine catalyst was a 70% solution of 2,2'-oxybis(N,N-dimethylethaneamine) in dipropylene glycol (NIAX catalyst A-1, Union Carbide Corp.). Stannous octoate (T-9, M & T Chemicals, Ltd.) and Union Carbide silicone surfactant L-6202 were also used throughout.

Table I gives the foam formulation where the indicated amount of TDI corresponds to 1.05 eq (105 index) relative to the active hydrogen compounds present in the resin. Foams of different indices were made by varying the amount of TDI. The foaming[4] and temperature measurement[5] procedures are similar to those reported previously. Briefly, the polyol (500 g), water, amine, and surfactant are mixed for 60 s. The mixing is stopped for 15 s while the tin catalyst is added. The mixing is resumed for a final 15 s. The TDI is added 6 s before the end of mixing. The reacting mixture is poured in a 36 × 36 × 15 cm cardboard box suitably equipped for temperature measurements. Five minutes after the end of mixing the foam buns are cured for 15 min in an oven at 100°C.

Sample Handling

The foam buns were left to cool in a room kept at 50% relative humidity and 22°C for about 1 h. The buns were cut with an electric knife and examined by FTIR immediately. Time zero in these experiments thus represents roughly 1 h and 25 min after the end-of-mixing.

The small cut samples were stored in two glass jars to simulate dry and humid atmospheres. One jar contained a saturated calcium nitrate solution and was maintained at 23°C, generating 48% relative humidity. The other jar was desiccated with calcium sulfate. Uncut buns and large pieces of foam were kept in the controlled atmosphere room.

TABLE I
Polyurethane Foam Formulation[a]

NIAX polyol 16-46	100
Water	4.0
NIAX catalyst A-1	0.1
Surfactant L-6202	1.0
Stannous octoate	0.25
TDI (105 index)	48.6

[a]Quantities are in parts by weight based on 100 parts polyol.

Sample Handling for Evolution of NCO at Different Depths in a Sample. A bun of 105 index foam was cut into 14 slabs of about $15 \times 15 \times 5$ cm, which were kept in the controlled atmosphere room except for one slab. Three spectra were obtained immediately from three widely separated positions on this slab to obtain the range of NCO values. Since the slab was freshly cut, taking depth samples from within this slab was considered irrelevant. Only the surface was measured. Periodically, a slab which had been cut from near the center of the bun was taken and spectra obtained at three different depths: 0 (exposed surface), 4, and 25 mm.

Sample Handling for Evolution of NCO under Humid and Dry Conditions. Four samples from one 105 index foam bun were taken: two from the center and two from the side. They were identified as such. A center sample and a side sample were kept in the humid jar while the other pair was kept in the dry jar. The very same samples were monitored throughout. They were handled carefully to avoid contamination and replaced in their respective jars after each measurement. For monitoring the NCO group evolution in foams prepared at different indices, the samples were cut from the center of the buns. In this case, however, we only examined samples stored under humid conditions.

Infrared Spectroscopy

Infrared spectra of foam samples were measured by attenuated total reflectance spectroscopy. This is an excellent technique for obtaining spectra of the surface of deformable samples which are difficult to measure in transmission[6,7]; the surface is probed to a depth of a few micrometres. Spectra were measured on a Nicolet 170SX Fourier transform instrument equipped with a mercury cadmium telluride detector. The reflectance accessory consisted of a twin parallel mirror attachment from Harrick Scientific Corp. with a 45° KRS-5 (thallium bromoiodide) single-pass parallelogram prism ($50 \times 10 \times 3$ mm). Foam samples approximately $50 \times 10 \times 5$ mm were placed in contact with both sides of the prism using finger pressure to tighten the clamps. The foam spectra were obtained by taking the ratio of the measured transmission to that of the prism alone. This gave spectra with a transmittance of about 10% in the region of strongest absorption (the polyol band at 1091 cm^{-1}). The penetration depth, as defined by Harrick,[6] was estimated to be about 1.2 μm at the frequency of the isocyanate band (2270 cm^{-1}).

ATR spectra of liquid samples were measured using a single reflection prism liquid cell, also from Harrick Scientific, equipped with a 45° zinc selenide prism.

The recorded spectra were converted to absorbance units and, where necessary, corrected for atmospheric water vapor and carbon dioxide absorption by subtraction of the appropriate reference spectra. The CO_2 correction is particularly important since the main band overlaps the isocyanate band to some extent. After baseline correction the spectra were "normalized" by multiplying by $\bar{\nu}/1000$, where $\bar{\nu}$ is the frequency in wavenumbers. This corrects for the fact that in ATR the beam penetration is proportional to the wavelength. The resulting spectra were found to closely resemble transmission spectra measured on thin slices of foam, but were of better quality because of the
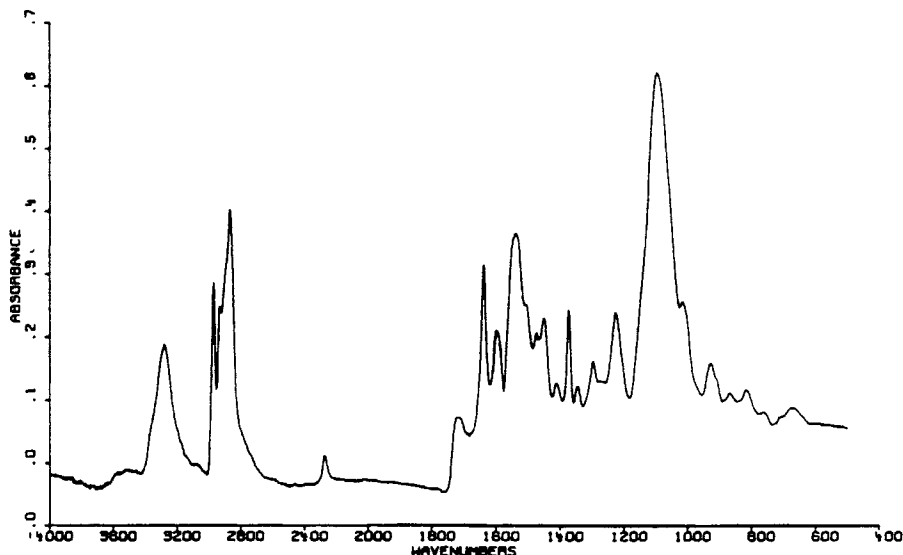
Fig. 1.   ATR spectrum of a typical 105 index foam.

scattering losses occurring in transmission. A typical spectrum of a 105 index foam is shown in Figure 1.

ATR FTIR Determination of Residual Isocyanate

A quantitative measure of the number of unreacted isocyanate groups in the foam was obtained through use of the NCO stretching band at 2270 cm^{-1}. Using the Nicolet software, the area A(NCO) of this band was calculated with respect to a baseline drawn between the points at 2334 and 2150 cm^{-1}. Similarly, the C—H stretching band was integrated to give A(CH) using a baseline drawn between 3012 and 2550 cm^{-1}. The ratio A(NCO)/A(CH) gives a figure which is directly related to the amount of unreacted isocyanate in the foam and independent of the overall spectrum intensity, which depends on the degree of contact between the foam and the prism. The CH band was chosen as reference because it is well separated from other bands and arises from vibrations of bonds (contributed for the most part by the polyol), which are not broken or formed in the foam-forming reactions.

To establish the precision of the NCO/CH ratio, a freshly cut sample of foam was measured 10 times in succession. After each measurement the sample was removed, the prism was cleaned and the sample reinstalled. The average value for the NCO/CH ratio was 0.0615 with a standard deviation of 0.0033 (5%).

The method was calibrated by preparing a blend of TDI and polyol in the proportion 48.6 to 100 parts by weight as in a 105 index foam. The spectrum of this blend (Fig. 2) was immediately obtained by ATR in a prism liquid cell. The NCO/CH ratio was measured to be 2.75. No absorption was observed in the 1700 cm^{-1} region, indicating that the two components had not reacted significantly to form a urethane. This value NCO/CH = 2.75 was thus considered to correspond to 100% unreacted NCO group in this blend. We
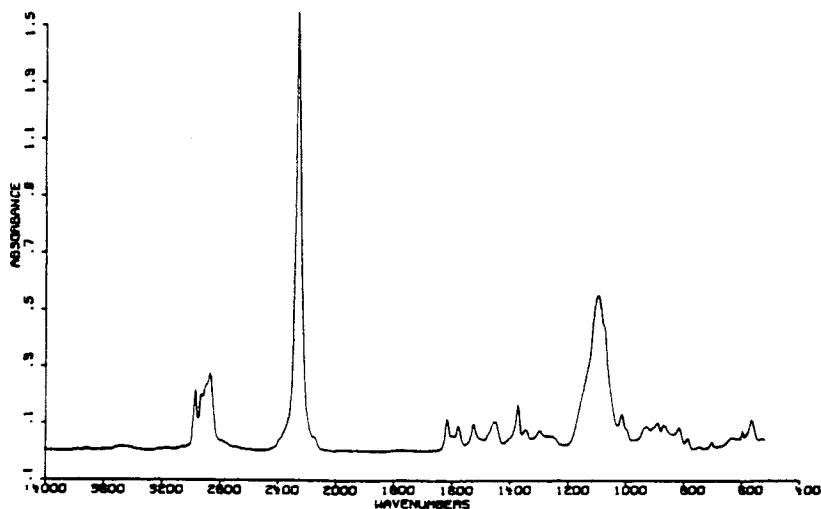
Fig. 2. Spectrum of TDI and polyol blend.

assumed that the differences between the band intensities of the liquid mixture and the foam are not significant. Thus, this NCO/CH ratio was used to estimate NCO levels in foams.

RESULTS AND DISCUSSION

Absolute Isocyanate Concentration

In a 105 index foam (Table I) the NCO/CH ratio after foaming is typically 0.04–0.06. This indicates that about 1.8% of the total NCO groups remain unreacted, based on an original ratio of 2.75. On a weight basis, these NCO groups represent roughly 0.30% of the total foam weight, taking into consideration CO_2 loss.

Interestingly enough, comparable values can be obtained by another method. In a 105 index foam, using TDI and polyol densities of 1.224 and 1.023 g/cm^3, respectively, the TDI/polyol volume ratio is 0.406 in the original mix. By adding the IR spectra of the two neat liquids using this volume ratio, a combination spectrum is obtained having a NCO/CH ratio of 3.03. By this method, in a 105 index foam, the unreacted NCO is 1.7% of the total original NCO groups and 0.28% on a foam weight basis.

Although relatively high levels of isocyanate have been measured in some fresh foams by dibutylamine titration,[8] low level residual isocyanate in a piece of foam is difficult to obtain by direct titration techniques.[3] The polymeric nature of the material prevents quantitative reaction with the target group buried within the matrix. Extraction of unreacted TDI followed by gas chromatography allows the measure of low levels of free TDI in foams but does not measure bound isocyanate.[9] In traditional IR methods, calibration using moisture sensitive materials is error prone, although laborious techniques achieve reasonable values.[1] For instance, 0.56% by weight residual isocyanate immediately after foaming is reported[1] in an albeit different 105 index foam; this is in the same range as the values reported here.
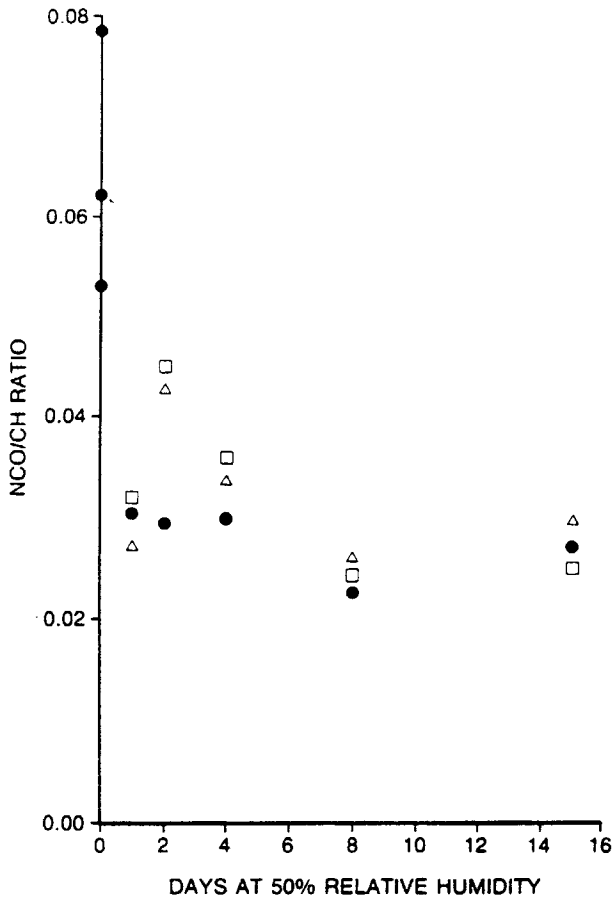
Fig. 3. Evolution of NCO/CH ratio at different depths in foams kept at 50% relative humidity: (●) surface; (□) 4 mm; (▵) 25 mm.

Evolution of Isocyanate at Different Depths

The NCO/CH ratios of foam samples taken at different depths are shown in Figure 3 (except for day zero where the depth is irrelevant and where the full circle symbol is used). In the first few days, the isocyanate values show considerable scatter. Should the foam have been homogeneous to start with, should the depletion of isocyanate have been due to the reaction with water, and should the diffusion of water vapor across the thickness of the foam be a rate limiting step, we could have expected a higher isocyanate level with the deeper samples. This expected correlation between sample depth and NCO/CH ratio was not apparent. The wide variation of the initial NCO values reflects significant differences in composition within the foam. We believe that this is not due to improper mixing but is rather the result of temperature gradients across the laboratory-made foam which affect the rates of reaction and thus the composition of the foam. This aspect is further discussed in the Effect of Temperature on Foam Composition section.

Beyond 4 days, the large differences in isocyanate concentration do not persist; the more accessible NCO groups have reacted fairly quickly. After 8

days, the scatter is disappearing, and the values converge to about 0.026. The effect of sampling depth is not seen. On this long time scale and for the thicknesses studied, the water vapor diffusion across the open cell structure does not appear to be a limiting factor in the consumption of isocyanate. In a subsequent section the diffusion of water within the polymer matrix is discussed.

Evolution of Isocyanate Under Humid and Dry Conditions

Figure 4 pertains to samples taken from the center of a 105 index foam and kept under humid and dry conditions. Since each set of data was obtained using the same exposed surface, effects of composition variation are eliminated. The scatter is thus substantially lower than in Figure 3. The decrease of the NCO ratio is much slower for the sample kept under dry conditions than for the one kept under humid conditions. The slow decrease in the sample kept under dry conditions is attributed to brief contacts with atmospheric moisture during handling. For samples taken from the same foam but at the side,
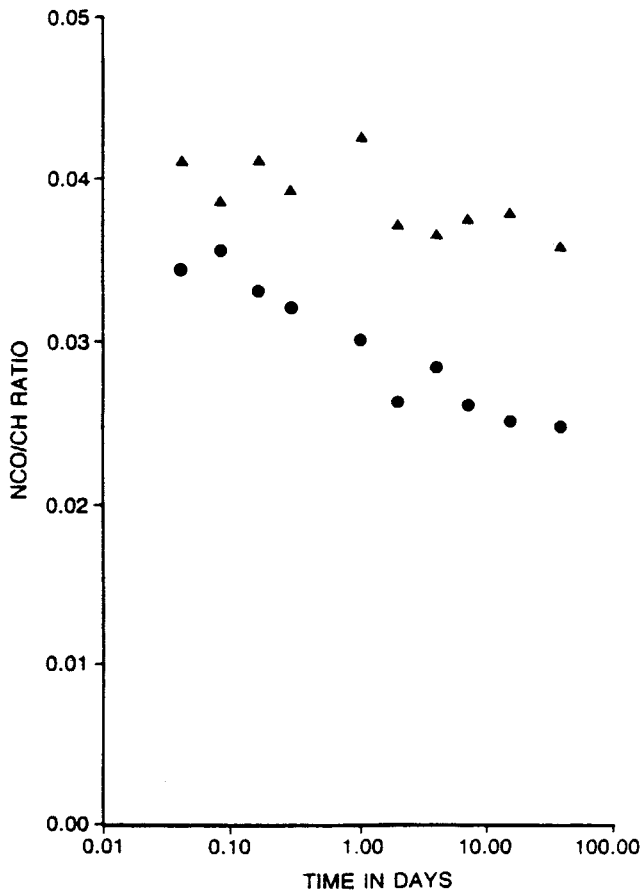

Fig. 4. Evolution of NCO/CH ratio under humid (●) and dry (▲) conditions for a center sample from a 105 index foam.
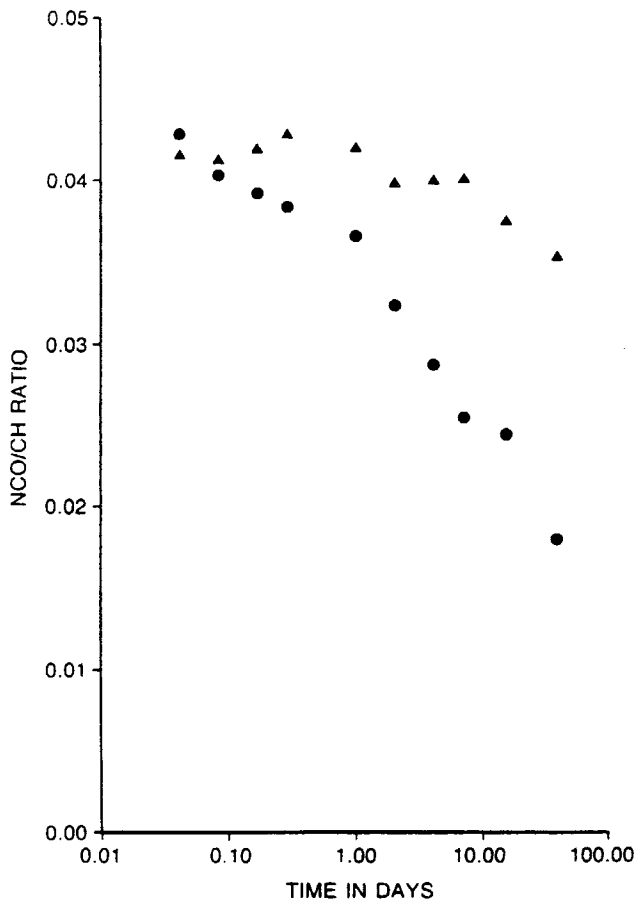
Fig. 5.   Evolution of NCO/CH ratio under humid (●) and dry (▲) conditions for a side sample from a 105 index foam.

results are shown in Figure 5. The trends are the same, although the initial bound NCO concentrations are slightly higher for the side samples.

It was suggested that water remaining in the matrix after foaming is responsible for the initial consumption of the NCO groups.[8] If this were the case, the rates of disappearance of the NCO groups, at least during the first few hours, would be similar regardless of atmospheric conditions. This was not observed. Under a dry atmosphere, the decrease in NCO groups during the first few hours is slower than for the sample kept under a humid atmosphere. Diffusion of moisture into the polymeric matrix appears to be the major factor in the reduction of isocyanate levels.

Evolution of Isocyanate in High Index Foams

Measurements of foams prepared at indices ranging from 100 to 115 showed that the higher the index, the greater the amount of isocyanate immediately after foaming (Fig. 6). Exposure to a humid atmosphere initiates a rapid decrease in the bound NCO values (Fig. 7). This rapid decrease tapers off in 10–15 days, after which the decrease is slow and gradual. After 79 days in 50%
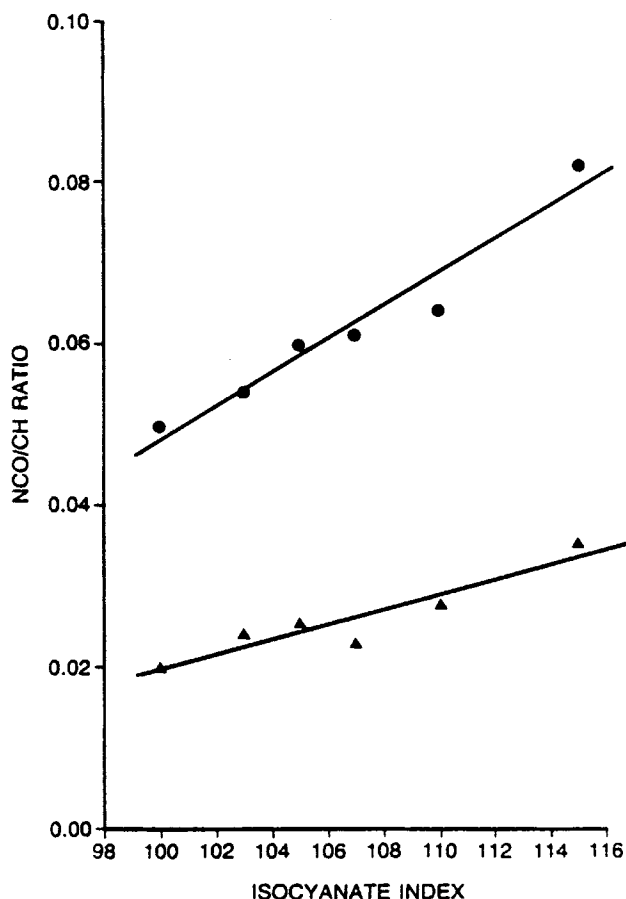
Fig. 6.   NCO/CH ratio for foams of various indices, after foaming (●) and after 79 days (▲) at 50% relative humidity.

RH at 22°C, the NCO/CH ratios still do not coincide, and their respective order on the concentration scale is still roughly maintained (Fig. 7). Those foams lying on the extremes of the index range (100 and 115) give no indication of a prompt convergence of their NCO/CH ratios.

Diffusion of water into the polymer matrix is the most probable mechanism whereby bound NCO groups are consumed. The migration of small molecules through polymers is generally discussed in terms of Fick's law[10]:

$$\frac{M_0}{M_t} \propto \frac{1}{t^{1/2}}$$

where M_0 is the total mass of the migrant and M_t is the mass diffused at time t. If the NCO/CH ratio is R_0 at time zero and R at time t, then the data of Figure 7 can be normalized as the ratio R/R_0. A plot of these values against the square root of time is shown in Figure 8. Despite some scatter in the points, the results for all indices tend to fall on the curve: $R/R_0 = 1/(0.18t^{1/2} + 1.0)$. Correlation was 0.994. This curve fits the data both in the initial stages, where the drop in isocyanate is rapid, and in the final stages, where it
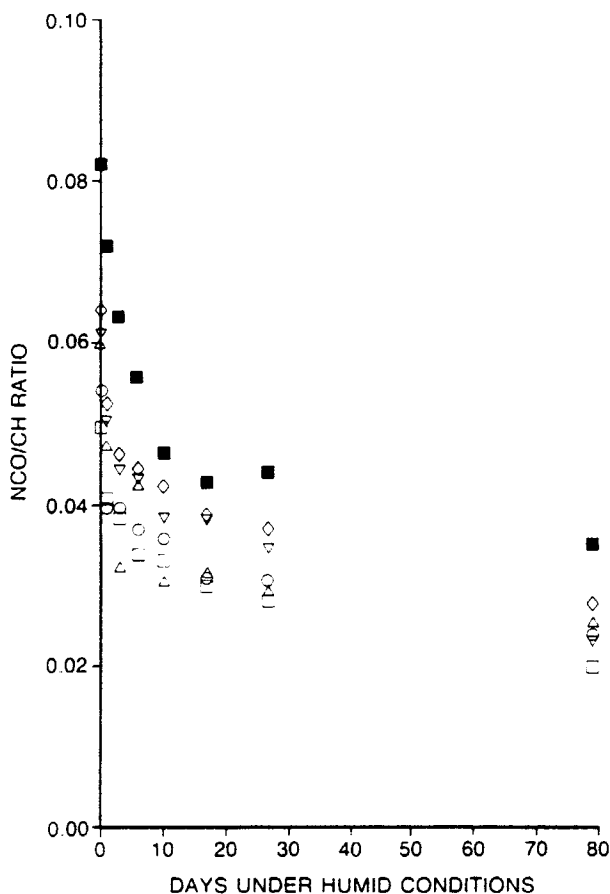
Fig. 7. Evolution of NCO/CH ratio for foams of various indices kept under humid conditions;
(□) 100; (○) 103; (△) 105; (▽) 107; (◇) 110; (■) 115.

is more gradual. Thus, in the index range of the present study ($I = 100–115$), water seems to reach the bound NCO sites by diffusion.

After about a month, the décrease in NCO/CH ratios becomes extremely slow. The bound residual isocyanate groups appear quite inaccessible to exogenous and endogenous reactants. For instance, the samples of 115 index foam after 80 days exposure to humid atmosphere had a NCO/CH ratio of 0.036. They were submerged in boiling distilled water for 3 h and dried in an oven at 110°C for 1 h. The NCO/CH ratio dropped to 0.016. An additional boiling water treatment for 6 h brought the ratio to 0.007. The need for such drastic conditions to reach the few remaining isocyanate groups emphasizes the remarkable hydrolytic stability of these polyurethane matrices.

Effect of Temperature on Foam Composition

By subtracting electronically two spectra of a 105 index foam, one obtained from a sample taken at the center of the bun and the other from a sample taken at the side, a differential spectrum (Fig. 9) is obtained. The temperature gradient between the two zones can attain 10°C. Foam from the cooler zone
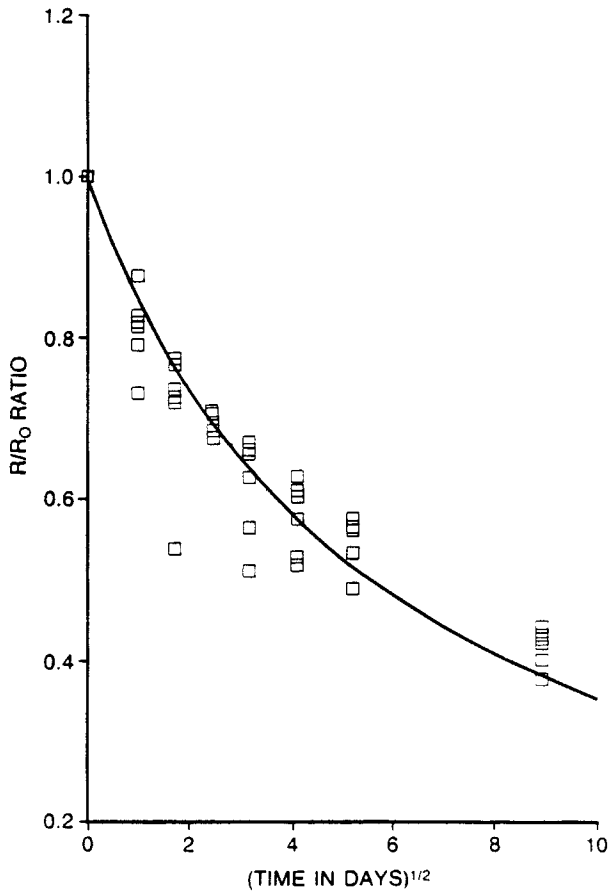
Fig. 8.   Normalized NCO/CH ratios as a function of square root of time and calculated curve.
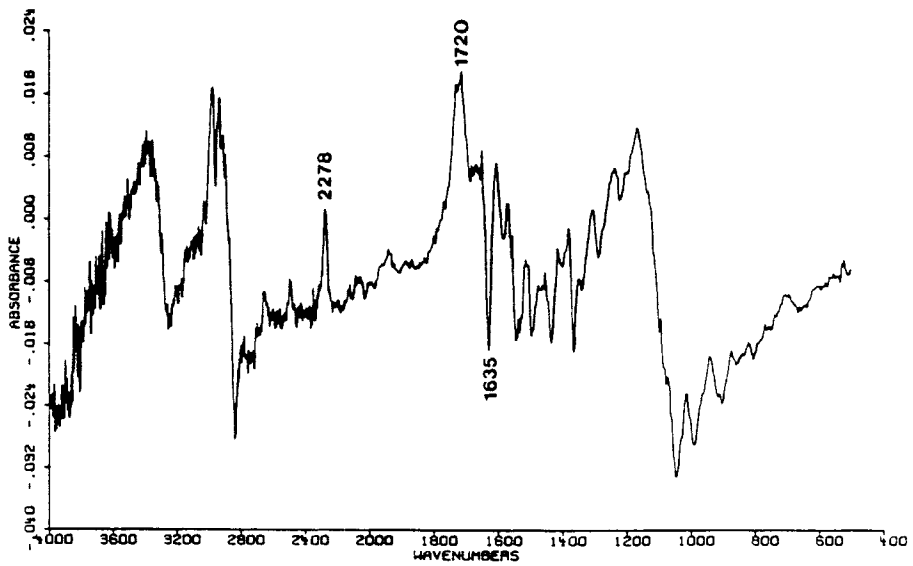

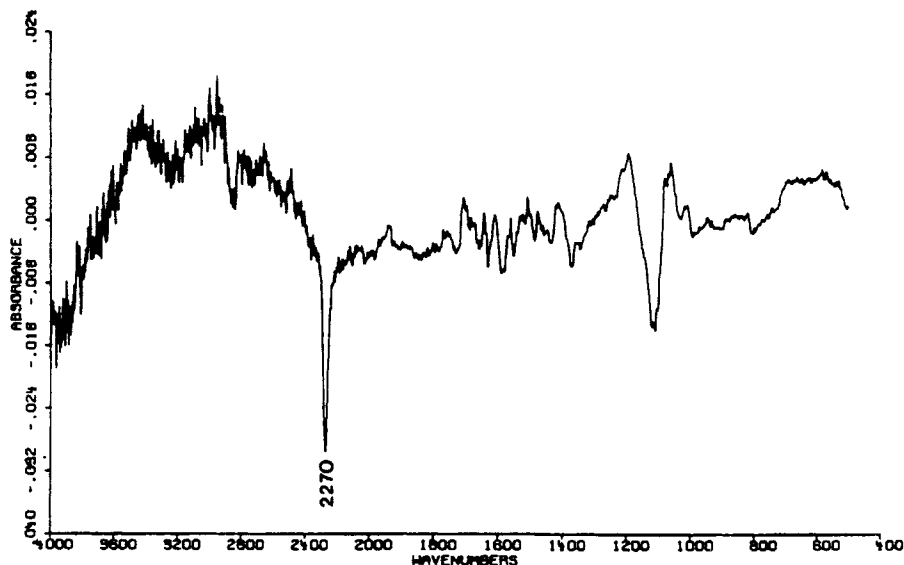Fig. 9.   Differential spectrum: side sample minus center sample.

Fig. 10.   Differential spectrum: after 15 days under humid conditions minus after foaming.

has a higher isocyanate concentration (2278 cm^{-1}) as well as a higher combined urethane, allophanate, and biuret concentration (1720 cm^{-1}); the urea concentration is lower (1635 cm^{-1}).

Fate of Isocyanate Under Humid Conditions

The spectrum of a freshly made 105 index foam was subtracted from a spectrum of the same foam aged for 15 days under humid conditions. The resulting differential spectrum (Fig. 10) shows clearly that the isocyanate groups in the polymer matrix are being consumed. The very strong negative absorbance of the NCO stretch and its position (2270 cm^{-1}) make this interpretation unequivocal. Each of the many possible products, such as biurets, allophanates, and amines, resulting from the depletion of residual isocyanate would be present at a fraction of the original NCO concentration (ca. 0.30%). Furthermore, the band absorptivities of these products are much lower than the NCO stretch.[11] The identification of the products becomes quite difficult. It has been suggested that, in the final stages of the cure, NCO groups merely react with available humidity to form —NH_2 groups with loss of CO_2.[12] Because of lack of mobility and progressively lower concentrations of available NCO groups, the amine groups cannot further react. Unfortunately, the 3000–3500 cm^{-1} region in this differential spectrum, where the N—H stretch is expected to absorb, is muddled by noise and possibly the —OH stretch of adsorbed water. It was not possible to assign with certainty the other peaks in this spectrum.

CONCLUSION

The depletion of residual bound isocyanate groups in flexible polyurethane foams relies mainly on the reaction with water. The rate of consumption depends on the relative humidity prevailing. The byproducts resulting from

the reactions with water or other chemical moieties within the polymer matrix remain difficult to identify. The rate of disappearance of the isocyanate groups in foams appears to follow a normal diffusion process, i.e., diffusion of water into the polyurethane matrix. After a period of approximately 1 week, the residual isocyanate concentration becomes virtually stable. Only severe hydrolytic conditions accelerate the depletion of the remaining isocyanate groups.

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