PROBING THE CURE AND POSTCURE REACTIONS IN POLYURETHANES BY FTIR AND GPC

Salehi, Hamed*
Department of Chemistry, Faculty of Science, Tarbiat Modares University,
P.O.Box 14155-4838, Tehran, Iran.

Eslami, Mozaffar
Research Institute of Petroleum Industry, P.O.Box 18745-4391, Tehran, Iran.

Sarbolouki, Mohammad Nabi
Institute of Biochemistry and Biophysics, Tehran University,
P.O.Box 13145-1384, Tehran, Iran.

(Received: Jan. 28th 1994, Accepted: May 20th 1996)

ABSTRACT: Fourier transform infrared (FTIR) and gel permeation chromatography (GPC) were respectively utilized in determining the changes in isocyanate (NCO) concentration and molecular weight (MW) and its distribution (MWD) in polyurethanes during their cure and postcure stages. Samples, originally cured at 55°C, were taken through accelerated aging tests at various temperatures. The FTIR and GPC analytical conditions were optimized, for both molecular weight and molecular weight distribution and NCO group determination. In FTIR spectroscopy Beer’s law was obeyed over the ranges: 2.33–22.34 and 0.03–1.61 mmol lir⁻¹. RSD, detection limit and molar absorptivity were found to be 1.46%, 4.10⁻⁶ mol lir⁻¹, and 1095 lir⁻¹ cm⁻¹ respectively. It was found the NCO concentration decreases with the progress of polymerization and at the same time MW of the sol increases, going through a maximum and then decreases to a constant level. The time to reach this level and termination of NCO concentration, i.e., the end of polymerization decreases with the increase in temperature. The results obtained from GPC and FTIR methods in following the different steps of polymerization as well as those from the linear plots of the end time of reaction vs. the 1/T, were in good agreement.

KEY WORDS: Polyurethanes, GPC, FTIR, Cure, Postcure, Accelerated aging, NCO concentration.

※ This paper is dedicated to Professor Ali Akbar Moshfegh the founder of the chemistry department of Shiraz University on the occasion of his 70th birthday.
※ To whom correspondence should be addressed
※ Present address: Engineering Research Center, Jahad Sazandegi, P.O.Box 13445-754, Tehran, Iran.
1021-9986/96/2/87 6/ $ 1.260
INTRODUCTION

Polyurethanes (PU) are addition polymers formed via a step growth mechanism by a reaction between a di- or poly-isocyanate and a polyol:

\[
\text{OH} + \text{NCO} \rightarrow \text{NH-C-N} + \text{H}_2\text{O}
\]

PU is utilized in a great variety of commodities, from ships to footwear, constructions to cars, etc [1]. During the cure step the hydroxyl groups react with the isocyanate groups, leading to a gradual decrease in their concentrations. During the advancement of polymerization molecular weight (MW) increases while the molecular weight distribution (MWD) changes continuously. In this paper GPC and FTIR were utilized for studying the changes in isocyanate concentration and MW and MWD of the sol during the polymerization.

EXPERIMENTAL

Materials and methods

Polypropylene glycol (PPG) and polystyrene (PS) standards were used as GPC standards. Toluene and CCl₄ were used as solvents.

Polyurethane samples were prepared by the one shot polymerization technique [2] by using PPG as the polyol and TDI as the disiocyanate with other additives [3], then they were cast and cured for 93 hours. At different intervals the polyurethanes were sampled for GPC and FTIR studies. After the cure step, the samples went through accelerated aging tests at various temperatures (25, 45, 60, 70°C) and at different time intervals, tests were done to provide data for posture studies.

Instruments

GPC chromatograms and FTIR spectra were obtained using the instruments of LC-4A, CR-4AX (Shimazu, Kyoto, Japan) and FTIR IFS-88 (Brucker, Karlsruhe, Germany) respectively.

GPC method

Since toluene has a solubility parameter near to that of the PUs [4,5] and is thus a suitable solvent [3,4]. Also it is a common solvent used in GPC [6] and in this case gives the maximum difference with PPG in refractive index, relative to other solvents [7,8]. Hence it was selected as both the mobile phase and the solvent in these GPC studies. Sample solutions were prepared by cutting polyurethanes into thin shavings about 400μm thick and their soluble (sol) fractions was extracted with toluene in two stages followed by four toluene washes. The original extract was centrifuged and filtered by means of a Millex Filter, then injected into the GPC. After preliminary tests on the GPC columns [9], the optimum conditions were found to be as follows: Mobile phase: toluene, columns: 10³Å, 10⁴Å, detector: refractive index, flow rate: 1 mL min⁻¹. The mobile phase was degassed by ultrasonic vibration before using.

FTIR method

Sample preparation was similar to that of GPC save that CCl₄ was selected as the solvent. Operational conditions were as follows: liquid cell: CaF₂, detector: DTGS, pathlength: 210.5μ (pathlength determined by interference fringe technique [10]), resolution: 8 cm⁻¹, v_max = 2265 cm⁻¹ and triangular apodization.

RESULTS AND DISCUSSION

GPC

Calibration curves

A calibration curve was plotted by using PPG standards (MW=1200, 2000, 4000) for the low molecular weight range with R=0.9999 (Fig. 1). PS standards were used for plotting this calibration curve both in the low MW (R=0.99997) and the high MW range (R=0.9995) [11]. In order to obtain

![Fig 1: GPC calibration curve (column: 10³Å, standards: PPG with MW's: 1200-2000-4000)](image)}
a correlation between MW that is calculated from PPG and those from PS standards, six chromatograms were analysed for the interrelation between the MW's. The relation found was: $Q = \frac{\text{MW(PPG)}}{\text{MW(PS)}} = 0.70$ (Table 1).

**Cure stage**

GPC chromatograms during the cure stage are shown in Fig. 2. At time zero (after mixing) there are two peaks, peak (1) with MW=2220, this means that during mixing (30 minutes) most of PPG monomer has reacted at least with one TDI molecule. The existence of peak (2) with MW=4380, shows that there are two PPG monomers in some polymer chains. After 3 hours of curing a new peak appeared with MW=9460, this means that some of polymer chains have four PPG monomers present in this step. Gradually the MW from peak (1) and then peak (2)
Table 1: Calculation of Q coefficient (refer in text)

<table>
<thead>
<tr>
<th>Samples</th>
<th>MW(PS)</th>
<th>MW(PPG)</th>
<th>Q = MW(PPG)/MW(PS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3952</td>
<td>2920</td>
<td>0.71</td>
</tr>
<tr>
<td>2</td>
<td>4088</td>
<td>2906</td>
<td>0.71</td>
</tr>
<tr>
<td>3</td>
<td>4241</td>
<td>2986</td>
<td>0.70</td>
</tr>
<tr>
<td>4</td>
<td>4318</td>
<td>3040</td>
<td>0.70</td>
</tr>
<tr>
<td>5</td>
<td>4398</td>
<td>3089</td>
<td>0.70</td>
</tr>
<tr>
<td>6 (PPG-4000)</td>
<td>5096</td>
<td>3992</td>
<td>0.68</td>
</tr>
<tr>
<td>Average</td>
<td>—</td>
<td>—</td>
<td>0.70</td>
</tr>
</tbody>
</table>

decreases, however the MW from peak (3) increases shuch that the total average MW(MW-t) increases as the polymerization proceeds. Changes of MWD (three peaks (1), (2), (3)) and MW-t vs. time are plotted in Fig. 3. It is found that the MW of the sol increases with the progress in polymerization, going through a maximum and then decreases to a constant level (MW about 150000).

Fig. 3: MW and MWD changes during the cure stage
a) Changes in MW=2220 (peak 1)
b) Changes in MW=9460 (peak 2)
c) Changes in MW=4380 (peak 3)

γ2 is related to a, b and c

Similar changes have been reported [12,13] with different polymers. Probably this behaviour is due to the joining of high MW chains to crosslinked polymer (gel) or reaction of high MW chains to each other with subsequent gelation.

Postcure stage

The MW changes after each cure step at different temperatures were plotted vs. time (Fig. 4). At all temperature MW increases, and continuous through-out the postcure stage meaning that polymerization is not completed in the cure stage. After going a maximum, MW, decreases to a constant level. The time to reach this level, considered to be the end of polymerization, decreases with increasing temperature. These times for 25, 45, 60 and 70°C are 38, 8, 5 and 2 days respectively.

![Fig 4: MW changes during the postcure at different temperatuers](image)

FTIR

Elimination of the CO2 interference band

The isocyanate group has a \( \lambda_{\text{max}} = 2265 \text{ cm}^{-1} \) in the IR that interferes with the CO2 band (Fig. 5). To eliminate this interference, of a N2 gas was applied, then it was found that after two minutes the CO2 peak is eliminated.

![Fig 5: Elimination of CO2 peak by purging of N2 gas](image)

Calibration curves and study of beer's law

A calibration curve for NCO was plotted over the range 2.23-22.34 mmol lit\(^{-1}\) (R = 0.9999) and the average molar absorptivity, detection limit and RSD for 11 measurements were found to be 1095 lit mol\(^{-1}\)
cm$^{-1}$, 4 E-6 mol lit$^{-1}$ and 1.4% respectively. Interference of the polymer additives in quantitative analysis of NCO was studied (Fig. 6); no interference was found to occur. With the progress of polymerization, NCO concentration obviously decreases, therefore a second calibration graph was plotted for low concentrations, with increasing pathlength from 210.5 to 1070$\mu$m in the range 0.03-1.61 mmol lit$^{-1}$ (R = 0.9998).

![Fig. 6: Study of additive materials interference in quantitative analysis of NCO](image)

NCO(1): Calibration curve from pure TDI
NCO(2): Calibration curve from TDI + additive materials

Cure stage

FTIR spectra and NCO concentration during the cure time are shown in Figs. 7 and 8 respectively. It is found that the NCO concentration decreases to less than 1/2 of its initial value during the mixing time.

![Fig. 7: FTIR spectra showing the reduction in NCO group concentration as reaction time increases](image)

Fig. 8: NCO changes during the cure stage (45°C) (initial value of NCO is 104.09 mmol/100 g binder)

Postcure stage

FTIR spectra at different temperatures were obtained and changes of NCO concentration were plotted vs. the time (Fig. 9). It was found the polymerization is not completed in the cure stage. Similar results were found from GPC measurements of the postcure stage. The time to obtain NCO termination is considered to mark the end of polymerization and decreases with the increase in temperature. These times for 25, 45, 60 and 70°C are 38, 11, 5 and 2 days respectively.

![Fig. 9: NCO changes during the postcure at different temperatures](image)

The correlation between the polymerization time ($t_p$) and temperature was studied. Log($t_p$) vs. 1/T was plotted (Fig. 10) for data obtained from both FTIR and GPC methods. A good linear relationship between ($t_p$) and temperature was found, showing an Arrhenius correlation and a satisfactory agreement between the two methods.

CONCLUSIONS

For the same retention time, the ratio of molecu-
lar weight of PPG to molecular weight of polystyrene (PS) found was 0.7. For PPG and PS having the same MWs, the size (or hydrodynamic volume) of PS is found to be smaller than PPG. The isocyanate content of TDI is obtainable by FTIR. The molar absorptivity, detection limit and RSD were found to be 1056 lit mol\(^{-1}\) cm\(^{-1}\), 6×10\(^{-6}\) mol lit\(^{-1}\) and 1.46%, respectively. One can detect and measure through the FTIR and GPC results, the existence of the posture stage. During this stage a good linear relation is found between both methods, between the end of polymerization and temperature, showing an Arrhenius correlation, and as well a satisfactory agreement between the two methods.

Fig. 10: Correlation between time of polymerization and 1/T from GPC and FTIR methods

ACKNOWLEDGMENT

The support of this work by Engineering Research Center of Jahad Sazandegi is gratefully acknowledged.

REFERENCES


