2018 urethane foam
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THE UNIVERSITY OF TEXAS AT AUSTIN
DEPARTMENT OF CHEMICAL ENGINEERING
CHE 395E

PREPARATION OF URETHANE FOAMS: A STRUCTURE-PROPERTY CORRELATION

I.Object

The object of this experiment is to prepare semi-rigid poly- urethane foams and to explore the relationships between the chemical constituents in the foam and its physical properties.

II. References

l. Golding, B., "Polymers and Resins," Van Nostrand, N. J., (1959), pages 325-335.

2. Lyman, D. J., Rev. Macromol. Chem.,!, 191 (1966).

3. Arnold, R. G., et al., Chem. Rev., 57, 47 (1957).

4. McCaffery, E. M., "Laboratory Preparation for Macromolecular Chemistry," McGraw-Hill, New York (1970), pages 115-124.

5. Baker, J. W., and J. Gannt, J. Chem. Soc., 713 (1947); 9, 19, 24, 27 (1949).

III. Equipment and Supplies

l. Grade AA Castor Oil
2. Polyethylene glycol, MW= 400
3. Toluene, di-isocyanate (TDI)
4. Diethyl-amino-ethanol
5. Triethylamine
6. Silicone surfactant
7. Glycerol (U.C.L-520)
8. Hydrochloric acid
9. Drierite
10. 500 ml, 3-neck, round-bottom flask
11. Stirrer assembly
12. Air condenser
13. Thermometer, 0-l50°C
14. Heating mantle and rheostat

15. 6 oz size, paper cups

16. 250 cc Erlenmeyer flask

17. Drying tubes

18. Drying oven

19. Triple beam balance

20. Metal spatula

21. Stop watch

IV. Preliminary Work

1. Determine the toxicological properties of aromatic isocyanates such as TDI. Note that these compounds react strongly with nucleophiles in the order: amines>alcohols>water>mercaptans via the following:

$$\mathrm{R{-}N{=}C{=}O + R'{-}XH \rightarrow R{-}NH{-}COX{-}R'}$$

What health hazards could be ascertained from this knowledge?

2. Three reactions of isocyanates are most important in the preparation of urethane foams:

a. With water: $\mathrm{R{-}N{=}C{=}O + H20 \rightarrow R{-}NHCOOH + RNH2 + CO2\uparrow}$ (carbamic acid, amine and carbon-dioxide)

b. With alcohol: $\mathrm{R{-}N{=}C{=}O + R'{-}OH \rightarrow R{-}NHCOOR'}$ (urethane linkage)

c. with amine: $\mathrm{R{-}N{=}C{=}O + R'{-}NH2 \rightarrow R{-}N{-}C{-}N{-}R'}$ (urea linkage)

Explain how these reactions are used to prepare the foam. Note that water is di-functional in the foam reaction.

3. Read Baker and Gannt (5) to determine the roles of diethyl-amino- ethanol and triethylamine in the formation of polyurethane.

4. Successful foam production requires careful control of the molar ratios of OH to NCO. This is normally accounted for by use of the hydroxyl number: hydroxyl number - grams of KOH which have an equivalent number of OH units as 1000 grams of polyol. Free COOH groups are measured by use of the acid number: acid number: milligrams of KOH needed to neutralize 1 gram of COOH containing material. In the procedure below, a prepolymer found by reacting castor oil (hydroxyl No.= 160-170, acid no. 4, < .5% by weight free water), 2 400 m.w. polyethylene glycol, and TDI is formed. Calculate the weight percent of free NCO in the finished prepolymer accounting for the water likely to be in the mix. Stable foam production requires an NCO/OH ratio of 1.10. Fill out the table below to be sure that this ratio is approximately maintained.

5. Before beginning this experiment place the 500 ml reaction vessel, the air condenser, the stirrer bar, and the 250 cc Erlenmeyer flask in the air oven set at 120ºC and DRY OVER NIGHT.

V. Experimental Procedure

A. Preparation of Prepolymer

1. Remove reaction flask from air oven. Stopper and fit flask with drying tube containing Drierite. Allow flask to cool.

2. Introduce 85 g of Grade AA Castor Oil and 30 g of polyethylene glycol, MW=400, to flask.

3. Fit flask with air condenser topped by drying tube, and with stirrer and stirrer motor. Place assembly in hood.

4. Stir slowly and purge liquids with a slow stream of dry nitrogen.

5. Remove Erlenmeyer flask from oven and immediately stopper with a drying tube. Allow flask to cool.

6. Place Erlenmeyer flask in hood on triple beam balance. WEAR PROTECTIVE GLOVES (AND GLASSES,OF COURSE) and pour 110 g of toluene di-isocyanate into the Erlenmeyer flask. Quickly restopper the flask.

7. Remove nitrogen inlet tube from reaction flask, introduce the isocyanate into the flask, and position the thermometer.

8. The temperature will rise as the reaction proceeds. After the exotherm is over and the temperature begins to fall, place a heating mantle under the flask and raise the mixture temperature to 120 °C. Maintain the vessel at 120 °C for one hour. Remove mantle

9. and allow vessel to cool to room temperature.

10. The prepolymer is ready to use as soon as it has cooled.

B. Preparation of Semi-rigid Foam

I. Prepare a buffered catalyst by combining 35 g of diethyl-amino-ethanol, 16.6 ml of concentrated HCl, and 33 ml of water.

2. Calculate the quantity of water required for each formulation, taking into account that the buffered catalyst contains water and that the catalyst, glycerine, and the glycol all have free hydroxyl groups.

3. All the liquid ingredients, save for the prepolymer, are available in dropper bottles. Determine the number of drops per gram of each ingredient.

4. Dispense 20 g of prepolymer from the reaction flask into the paper cup (remember that the prepolyrner contains free isocyanate - handle carefully).

5. Add the remaining ingredients drop-wise to the cup. 6. Stir the components vigorously for 30 seconds with the blade of a steel spatula.

7. Determine the time between completion of mixing and commencement of the foaming reaction. Also determine the approximate time to complete the foaming reaction.

8. Determine the density of each foam, lb/ft3, by weighing and determining the volume of a regular section cut from the foam.

9. Examine a section of each foam formulation under a microscope to determine the relative degree of open to closed cells.

10. Repeat steps 4 through 9 for the following compositions:

Weight, grams/20 grams Prepolymer

Number	Buffered Catalyst	Diethyl-amino-ethanol	Glycerol	PEG 400	Water
1	0.7				1
2		0.4	1.8		
3		0.4	1.6	1.6	1
4*	0.7				1
5		0.4			1
6		0.4**	1.8		1
7	0.7				0.6

*with 0.1g surfactant

**replace diethyl-amino-ethanol with triethylamine

VI. Report

I. What changes would you make in the compositions of foams prepared above in order to render the foams more flexible.

2. How does the open-to-closed cell ratio vary with foam density? What controls foam density?

3. What effect does the surfactant used have on foam structure?

4. What effect does buffering the catalyst have on foam structure? Why?

5. What is the result of substituting tri-ethylamine for di-ethyl-aminoethanol? Why?

6. What would happen to the foam if a large excess of water were used in the formulation?