

LA-UR- - 9 8 - 5 0 6

Title:

**Infrared Spectroscopy of a Polyurethane
Elastomer Under Thermal Stress**

CONF-970812--

Author(s):

**A.L. Marsh
J.R. Schoonover**

Submitted to:

American Institute of Physics

MASTER

jsw

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos
NATIONAL LABORATORY



Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Infrared Spectroscopy of a Polyurethane Elastomer Under Thermal Stress

RECEIVED
JUL 01 1998
Q.S.T.I

A. L. Marsh¹ and J. R. Schoonover²

¹Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, Virginia 23943

²Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

FTIR spectroscopy was used to study changes in hydrogen bonding in estane, a polyurethane elastomer used as a binding agent in high explosive systems, as a function of temperature. Hydrogen bonding in estane has been observed to decrease with an increase in temperature.

INTRODUCTION

Infrared spectroscopy has been used to study morphology, particularly changes in hydrogen bonding, in polyurethanes and polyurethane elastomers. This technique is useful because certain absorption bands characteristic of polyurethanes are influenced by the environment in which the polymer is located. Specifically, changes in hydrogen bonding can be observed through the N-H and C=O stretching regions of the spectrum. Hydrogen bonding is known to occur between the N-H group of the urethane segment and the C=O group of the urethane or ester segment, and is also known to decrease with an increase in temperature. Several different types of polyurethanes have been studied by infrared spectroscopy. These types include poly(ether-urethanes) (1-15), poly(ester-urethanes) (3, 16), poly(urethane-urea)s (17, 18), and a simple polyurethane(19).

Srichatrapimuk and Cooper studied temperature dependent behavior of poly(ether-urethane) and poly(ester-urethane) elastomers as a function of hard and soft segment lengths (3). The IR absorptions in the N-H and C=O regions were monitored with temperature change in order to provide a quantitative measurement of phase separation. The enthalpy of hydrogen-bond dissociation was determined from the fraction of bonded groups at different temperatures. The H-bonded N-H stretch was located at 3320 cm⁻¹, and the non-bonded N-H stretch was a shoulder at 3420 cm⁻¹. The intensity of the bonded N-H stretch was observed to decrease, or shift to higher frequency, with an increase in temperature, indicating a decrease in hydrogen bonding. No splitting in the C=O region was observed in the poly(ester-urethanes). About 80% of N-H groups were calculated to be hydrogen-bonded at room temperature. More interurethane bonding occurred in polymers with longer hard and soft segments, and the hard-soft bonding was determined to dissociate

first.

Siesler observed similar results as Srichatrapimuk and Cooper observed(16). He conducted rheo-optical FTIR experiments of poly(ester-urethanes) at different temperatures by stretching and relaxation along a single axis. Temperature dependence of hydrogen bonding and structural organization of the hard segments were also studied. The change in the N-H region was attributed to a dissociation of hydrogen bonds and the small change in the C=O region was attributed to the functional group being less displaced. A shift of the N-H bending and C-N stretching band to lower frequency was observed, and was attributed to the inverse effect of hydrogen bonding on deformation vibrations.

The present work is a study of estane, a poly(ester-urethane) used as a structural support in industrial applications and as a binding agent in various high-explosive systems. Over time, possibly due to the presence of certain environmental agents, changes develop in the bulk properties of estane and in the mechanical and sensitivity properties of the explosive composites. The relationship between the bulk properties and the molecular structure of estane are not well understood, and questions regarding the effects of aging of estane-based, high-explosive binding matrices have been difficult to answer. FTIR studies have been used to fundamentally relate molecular vibrations of estane, in its pure form at various temperatures, to its macroscopic structural and binding properties.

EXPERIMENTAL

Estane 5703, a polyurethane elastomer consisting of urethane hard segments and ester soft segments, was obtained from B.F. Goodrich. The repeating unit of this polymer is

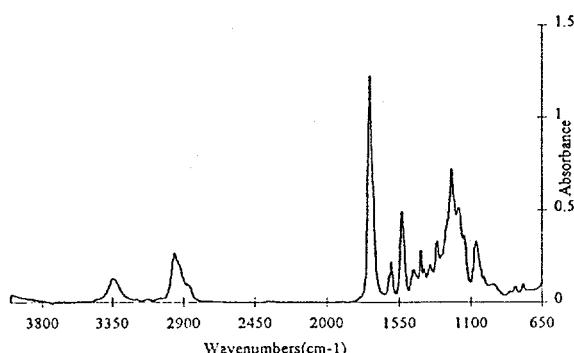
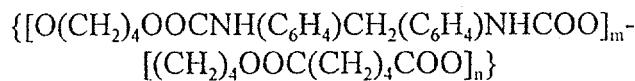


FIGURE 1. Infrared absorption spectrum of estane at 32.0 °C.



where $m = 4-6$ and $n = 1-3$. Samples were prepared by casting a dilute solution of the polymer onto 13mm x 2mm NaCl windows. Sample thickness was sufficient to yield an absorbance of under 1.5 absorbance units.

Samples were mounted between two NaCl windows in an aluminum block cell which contained a cartridge heater and was connected to a temperature controller. The temperature was monitored through a Type K thermocouple placed next to the sample in the temperature cell. Temperature readouts were to an accuracy of 0.1 °C. Spectra were taken with a Nicolet 20SXB FTIR spectrometer. 200 scans were measured with resolution of 8cm⁻¹. Difference spectra were calculated by subtracting the spectrum at 100.0 °C from the spectrum at 32.0 °C.

RESULTS AND DISCUSSION

Figure 1 is a spectrum of estane taken at 32.0 °C.

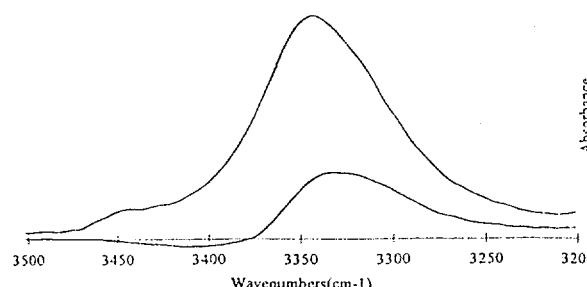


FIGURE 2. Relative change in the N-H stretching region at 100.0 °C.

TABLE 1. Absorption Band Assignments

Frequency (cm⁻¹)	Relative Intensity	Assignment
3440	weak, shoulder	free N-H stretch
3340	strong	bonded N-H stretch
3190	weak	CIS-TRANS bonded N-H stretch
3120	weak	overtone of 1531 cm⁻¹
2951	strong	CH ₂ asymmetric stretch
1732	very strong	free and bonded C=O stretch in urethane and ester
1597	strong	C=C(benzene) stretch
1531	very strong	N-H bend/C-N stretch
1415	strong	C-C(benzene) stretch
1315	strong	N-H bend, C-N stretch, C-H bend
1223	strong	N-H bend/C-N stretch
1180	strong	C-O-C(ester) stretch
1068	strong	C-O-C(hard) stretch

Table 1 summarizes the band assignments, for this spectrum, as made by Srichatrapimuk and Cooper (3). The N-H region consists of two bands, one at 3340 cm⁻¹ representing hydrogen-bonded N-H stretching and the other at 3440 cm⁻¹ representing non-hydrogen-bonded, or "free," N-H stretching. The "free" N-H band appears as a shoulder on the higher frequency side of the H-bonded N-H band. A strong band at 1732 cm⁻¹ represents "free" and H-bonded C=O stretch in both the urethane and ester segments. Two bands at 1531cm⁻¹ and 1223 cm⁻¹ represent both N-H bending and C-N stretching.

The relative change in the N-H stretching region at 100.0 °C is shown in Fig. 2. The difference spectrum shows a decrease in intensity of the bonded N-H stretch and an increase in intensity of the "free" N-H stretch. The N-H band is shifting to a higher intensity, indicating a decrease in hydrogen bonding.

The relative change in the C=O stretching region at 100.0 °C is shown in Fig. 3. The difference spectrum shows three bands are changing in intensity. Hydrogen bonding between N-H of the urethane segment and C=O of

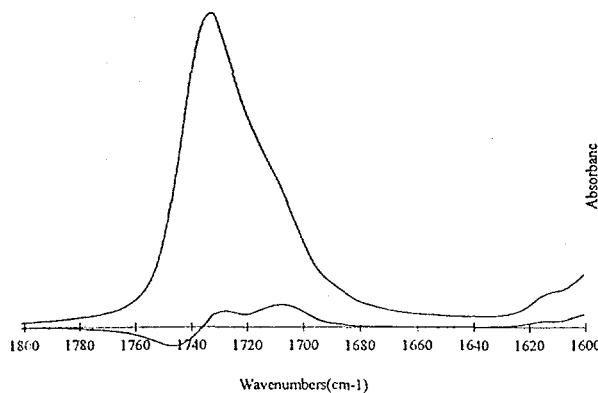


FIGURE 3. Relative change in the C=O stretching region at 100.0 °C.

both the urethane and ester segments must be decreasing. The overall band is shifting to a higher frequency with the measured temperature. The relative change in intensity, however, is small compared to the change for the N-H stretching region.

The relative changes in the N-H bending and C-N stretching regions are shown in Fig. 4 and Fig. 5. These bands are shifting to a lower frequency, due to the inverse effect of hydrogen bonding as noted by Siesler (16). These relative changes are not small compared to the changes in the C=O stretching region.

CONCLUSION

Morphological changes in a poly(ester-urethane) were observed by infrared spectroscopy as changes in absorbance intensity of N-H, C=O, and C-N bands as a function of temperature. The N-H stretching and C=O stretching bands shifted towards higher frequency with an

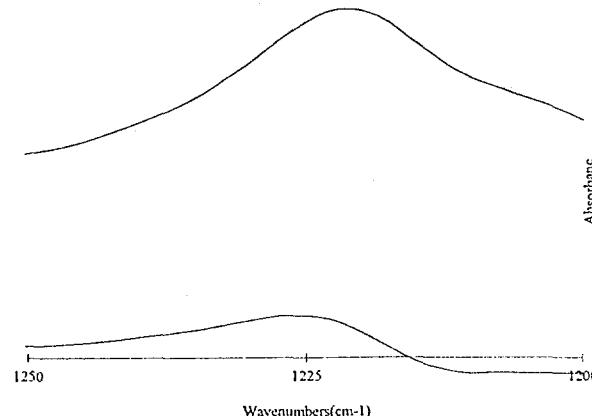


FIGURE 5. Relative band changes in the lower-frequency N-H bending and C-N stretching region at 100.0 °C.

increase in temperature, while the two N-H bending and C-N stretching bands shifted towards lower frequency with an increase in temperature. Hydrogen bonding, both interurethane and hard-soft segment, decreases with temperature. The structural properties of estane, therefore, change with temperature. Two-dimensional cross-correlatin analysis will next be applied to the spectra to resolve overlapped bands and to view related changes with temperature.

ACKNOWLEDGMENTS

Funding for this experiment was provided through a Laboratory Directed Research and Development project at Los Alamos National Laboratory on polymer aging.

REFERENCES

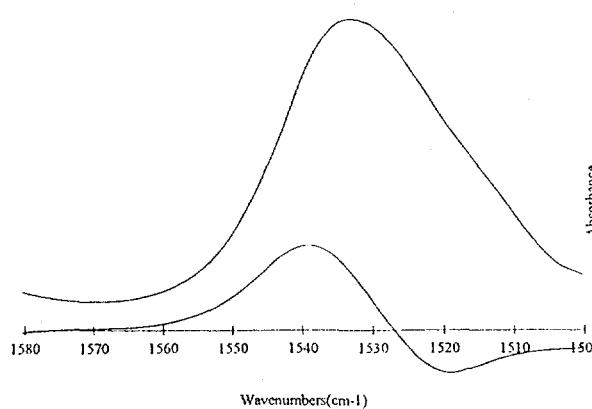


FIGURE 4. Relative band change in higher-frequency N-H bending and C-N stretching region at 100.0 °C.

1. Paik Sung, C. S.; Schneider, N. S., *Macromolecules*, **8**, 68-73, 1975.
2. Paik Sung, C. S.; Schneider, N. S., *Macromolecules*, **10**, 452-458, 1977.
3. Srichatrapimuk, V. W.; Cooper, S. L., *J. Macromol. Sci., Phys.*, **B15**, 267-311, 1978.
4. Senich, G. A.; MacKnight, W. J., *Macromolecules*, **13**, 106-110, 1980.
5. Brunett, C. M.; Hsu, S. L.; MacKnight, W. J., *Macromolecules*, **15**, 71-77, 1982.
6. Christenson, C. P.; Harthcock, M. A.; Meadows, M. D.; Spell, H. L.; Howard, W. L.; Creswick, M. W.; Guerra, R. E.; Turner, R. B., *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1401-1439, 1986.
7. Koberstein, J. T.; Gancurz, I.; Clarke, T. C., *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 2487-2498, 1986.
8. Lee, H. S.; Wang, Y. K.; Hsu, S. L., *Macromolecules*, **20**, 2089-2095, 1987.

9. Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C., *Macromolecules*, **21**, 59-65, 1988.
10. Meuse, C. W.; Yang, X.; Yang, D.; Hsu, S. L., *Macromolecules*, **25**, 925-932, 1992.
11. Hong, J. L.; Lillya, C. P.; Chien, J. C. W., *Polymer*, **33**, 4347-4351, 1992.
12. Wang, F. C.; Feve, M.; Lam, T. M.; Pascault, J. P., *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 1305-1313, 1994.
13. Lee, H. S.; Hsu, S. L., *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 2085-2098, 1994.
14. Reynolds, N.; Spiess, H. W.; Hayen, H.; Nefzger, H.; Eisenbach, C. D., *Macromol. Chem. Phys.*, **195**, 2855-2873, 1994.
15. Goddard, R. J.; Cooper, S. L., *Macromolecules*, **28**, 1390-1400, 1995.
16. Siesler, H. W., *Polym. Bull.*, **9**, 471-478, 1983.
17. Bummer, P. M.; Knutson, K., *Macromolecules*, **23**, 4357-4362, 1990.
18. Teo, L. S.; Chen, C. Y.; Kuo, J. F., *Macromolecules*, **30**, 1793-1799, 1997.
19. Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C., *Macromolecules*, **19**, 2149-2157, 1986.