Chemical and physical changes in a hydrolyzed poly(ester urethane)

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Introduction

Hydrolytic degradation has been shown to be a significant problem for poly(ester urethane) elastomers exposed to high humidity environments. The ester group in the soft segment is particularly susceptible to hydrolysis. One of the products of this reaction is a carboxylic acid group that catalyses further hydrolysis.[1] The resulting reduction in molecular weight leads to deterioration of the elastomer's mechanical properties. In this paper we have measured the extent of the hydrolysis reaction by ^{13}C NMR spectroscopy. In addition we have measured the spin-spin relaxation time of the soft phase and followed the increase in mobility of these segments. Both measurements were performed on the solid polymer. These measurements provide an excellent monitoring tool of the chemical and physical state of polymer during the aging process.

Experimental

Materials. The poly(ester urethane) was obtained from B. F. Goodrich Company. This material, Estane® 5703,[2] has hard segments based on 4,4'-methylenediphenyl 1,1'-diisocyanate, soft segments based on poly(butylene adipate) and a 1,4 butanediol chain extender. The samples were aged from 2 to 8 weeks at 80°C and 95°C under 100% relative humidity.

Instrumentation. The ^{13}C and ^{1}H NMR spectra were collected on a Bruker AMX400 spectrometer at 100.6 and 400.2 MHz respectively. The ^{13}C spectra were acquired using direct polarization, high power ^{1}H decoupling, a delay time of 4 s and static conditions. A Carr-Purcell experiment (90°- τ - 180°- τ - acq) was used to measure the ^{1}H spin-spin, T_2, relaxation time. A total of 20 delay times, τ, ranging from 2 μs to 10 ms were used.

Results and Discussion

The polyester-polyurethane was aged under 100% relative humidity at 80°C and 95°C. The unaged sample consists of semi-rigid pellets and converts to a viscous, tacky substance during the aging process. The ^{13}C spectra of the unaged and 95°C aged polyester-polyurethane are shown in Figure 1.
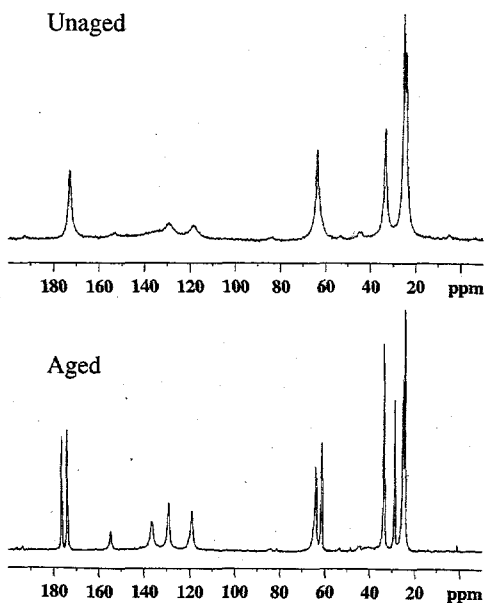
Analysis of the spectra shows that the primary aging mechanism is hydrolysis of the ester linkage.[3] The ester carbon resonates at 173 ppm, while the methoxy carbon adjacent to the ester group resonates at 63 ppm. The spectrum of the aged sample contains two additional resonances. A new resonance at 178 ppm corresponds to a carboxylic acid and a new resonance at 65 ppm corresponds to an alcohol. In addition, the narrowing of the ^{13}C linewidths in the aged sample implies that the segmental chain motion has increased significantly.

To quantitatively measure changes in the chain dynamics, ^{1}H relaxation experiments were performed. Figure 2 shows the intensity of the ^{1}H spin-echo as a function of twice the delay time (2τ) for the unaged sample and for samples aged 2, 4 and 8 weeks at 95°C. The relaxation rates of the aged
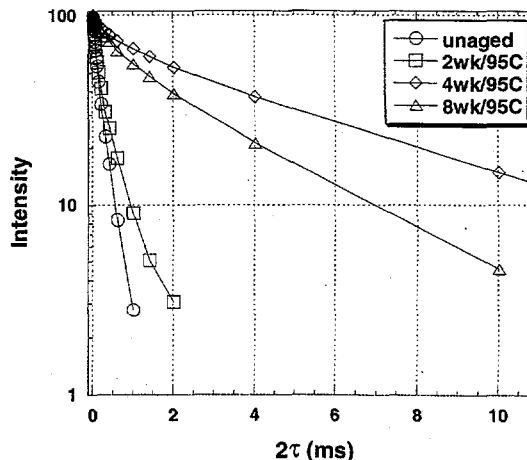
Figure 2. Log of the intensity of the ^{1}H spin-echo as a function of the dephasing time, 2τ.

samples decrease with aging time, indicating that the mobility of the aged samples increases. This increase in mobility is consistent with the narrowing of the ^{13}C linewidths. Increased mobility is a direct result of hydrolytic chain scission of the ester linkage. The solid lines are least squares fits of the experimental data using two component fitting functions. Both the fraction of hydrogen associated with the faster relaxing component and the relaxation rate of this component decrease with increasing aging time. In addition, the slower relaxation rate decreases with increasing aging time.

In order to quantify the increase in mobility with aging time, we have defined T_{2eff} as the time it takes for the spin-echo to decay to 1/e of its initial value. $1/T_{2eff}$ for the 80°C and 95°C aged samples are shown in Figure 3 as a function of aging time. The lines are smooth curves drawn to guide the eye.
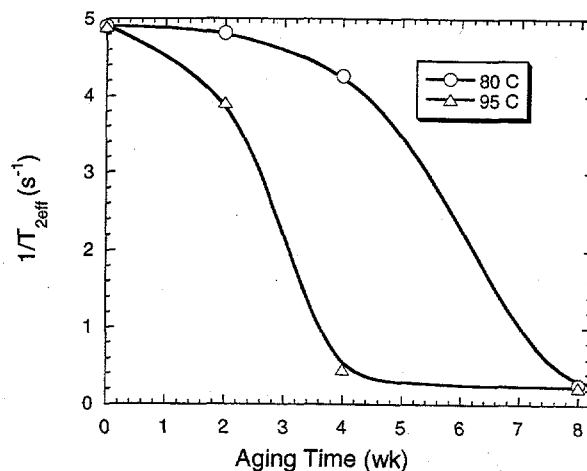
Figure 1. ^{13}C direct polarization NMR spectra of the aged (8wks at 95°C) and unaged poly(ester urethane).

Figure 3. Decay time of T_{2eff} to 1/e of its initial value for the 80°C and 95°C aged poly(ester urethane) samples.

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Changes in $1/T_{2eff}$ are modest until the aging times reach 4 and 2 weeks for the 80°C and 95°C temperatures, respectively. T_{2eff} of the 80°C sample undergoes a significant reduction between 4 and 8 weeks, while the T_{2eff} of the 95°C sample undergoes a significant reduction between 2 and 4 weeks. This behavior suggests an autocatalytic response due to production of carboxylic acid by the hydrolysis reaction. The T_{2eff} of both samples approach the same limiting value for long aging times.

Conclusions

^{13}C and ^{1}H NMR spectroscopies were used to characterize the hydrolytic degradation of a poly(ester urethane) elastomer. Both chemical and physical properties related to the degradation process could be measured in the solid polymer. Formation of carboxylic acid and alcohols is related to a marked increase in segmental mobility of the polymer. The induction time for increased mobility implies an autocatlytic degradation mechanism.

References

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