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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.[1] The resulting reduction in molecular weight (MW) leads to deterioration of the elastomer's mechanical properties. In our experiments we have:

① measured the extent of the hydrolysis reaction by ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

② measured the ^{1}H spin-spin relaxation time of the soft phase and followed the increase in mobility of these segments, and

③ used ^{1}H direct polarization experiments to measure the phase separation between the hard and soft components under aging. The increased mobility results in better phase separation between the hard and soft components.

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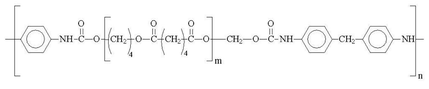
Experimental

Materials. The poly(ester urethane) was obtained from B.F. Goodrich Co. This material, Estane® 5703[2] has hard segments based on 4,4'-methylenediphenyl 1,1'-diisocyanate and soft segments based on poly(butylene adipiate) 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. ^{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 and high-power ^{1}H decoupling under magic-angle spinning conditions. Proton data was acquired under static conditions in a 4mm proton-free NMR probe. A Carr-Purcell experiment (90°- τ -180°- τ - acq) was used to quantify the chain dynamics by measuring the ^{1}H spin-spin, T_2, relaxation time. Direct polarization experiments were used to measure phase separation between the hard and soft components.

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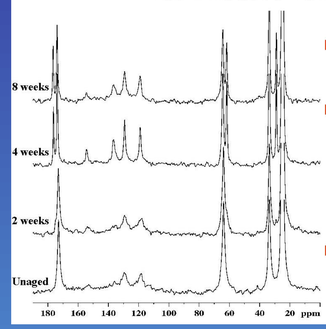
Aging of Poly(Ester Urethane) at 95°C and 100% Relative Humidity



- The unaged sample consists of semi-rigid pellets and converts to a viscous, tacky substance during the aging process.
- ^{13}C direct polarization NMR spectra of the unaged poly(ester urethane) shows two resonances due to the ester linkage:

  ester carbon ~173 ppm
  methoxy carbon ~ 64 ppm

  (The intensity of each spectrum has been cut-off in order to better display the regions of interest).
- The spectra of the aged sample show additional resonances at ~62 and ~176 ppm.

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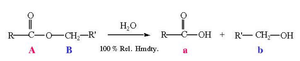
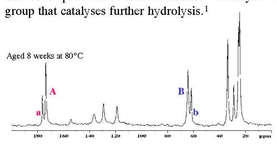
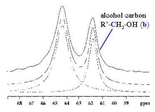
Investigating the Ester Linkage Degradation using ^{13}C NMR

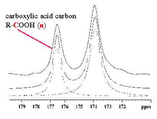
- Degradation due to hydrolysis reduces the MW.
- Products formed by the hydrolysis of the ester linkage in humid settings were monitored using ^{13}C NMR



- One of the products of this reaction is a carboxylic acid group that catalyses further hydrolysis.[1]







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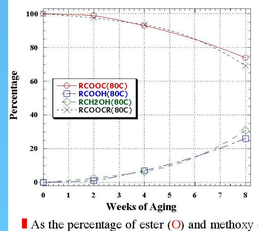
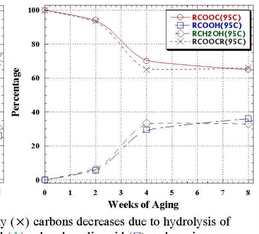
Percentage of Degradation Products





- As the percentage of ester (O) and methoxy (×) carbons decreases due to hydrolysis of the ester linkage, the percentage of alcohol (◇)and carboxylic acid (□) carbons increases, proportionally.
- After 8 weeks in a 100% relative humidity environment at 80°C, the percentage of carboxylic acid and alcohol groups (O and □) formed is roughly equivalent to those produced after 4 weeks in a 95°C setting (◇ and ×). (The smooth curves are drawn in the Figure to guide the eye.)

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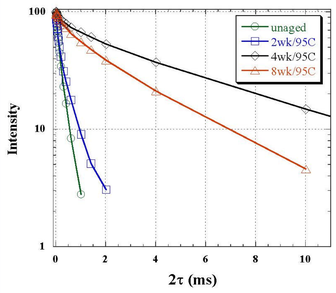
Measuring Changes in Poly(Ester Urethane) Chain Dynamics using ^{1}H NMR



- Figure showing the 'Log' of 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 solid lines are least squares fits of the experimental data using twocomponent fitting functions.
- The relaxation rates of the aged samples decrease with aging time, indicating that the mobility of the soft phase in the aged samples increases. This increase in mobility is consistent with the narrowing of the ^{13}C linewidths.

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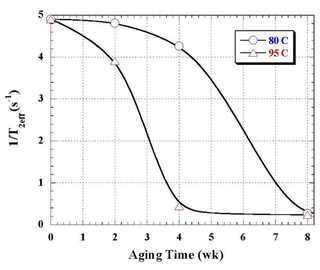
Quantifying the Increased Mobility in the Soft Phase using ^{1}H NMR



- T_{2eff} is the time it takes for the ^{1}H spin-echo to decay to 1/*e* of its initial value
- 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.
- The large reduction in T_{2eff} between 4 and 8 weeks for the 80°C aged sample, and between 2 and 4 weeks for the 95°C aged sample, suggests an autocatalytic response due to the creation of carboxylic acid in the hydrolysis reaction.[1]

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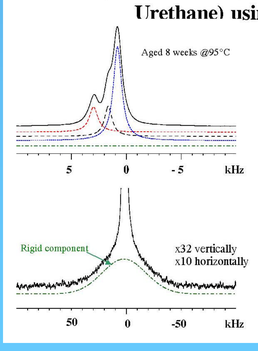
Analyzing Phase Separation in Poly(Ester Urethane) using ^{1}H NMR



- ^{1}H NMR is an effective tool for analyzing phase separation of the rigid and flexible segments into hard and soft components.
- Phase separation increases with aging. Rigid segments trapped within the soft amorphous phase are freed as the system become more mobile. These rigid segments then coalesce with the hard phase. Deconvolution of the ^{1}H NMR spectra for aged and unaged poly(ester urethane) reveals this increase. The percentages of the hard phase are:

  Unaged ~12%
  Aged 8 weeks @95°C ~25%
- This effect is analogous to chemi-crystallization.

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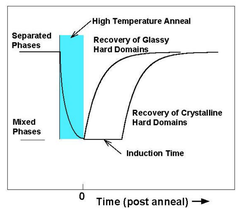
Hard Phase Morphology

Soft phases are composed primarily of amorphous segments above their T_g while the hard phases are composed primarily of rigid segments below their T_g or crystalline segments below their T_m.

Hard phase morphology (crystalline or amorphous) can be characterized by annealing experiments. After annealing, we measure the time dependence of phase formation:

a) glassy domains begin to reform at t = 0

b) formation of crystalline domains involves an induction time



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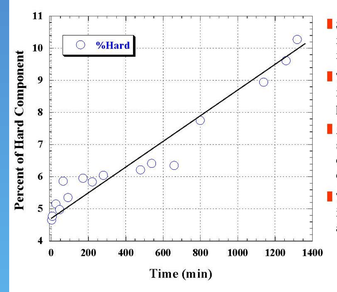
Estane Phase Formation after Annealing



- Sample annealed at 170°C for 5 minutes and quenched in liquid nitrogen.
- The 'hard' component accounts for ~12% of the unaged poly(ester urethane)
- Annealing mixes the hard and soft phases. After the quench, only ~4.5% of the sample exists in the hard phase.
- The lack of an induction period indicates that our system is amorphous and not crystalline

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Conclusions

^{13}C and ^{1}H NMR spectroscopies were used to characterize the chemical and physical changes occurring during the hydrolytic degradation of a poly(ester urethane) elastomer.

- ^{13}C MAS was used to measure the extent of hydrolytic degradation as a function of aging time at 80°C and 95°C
- ^{1}H spin-echo experiments showed that the mobility of the soft phase increased with aging time.
- ^{1}H wideline spectra showed that the hard phase was amorphous and increased in size during the aging process.

References:

(1) Brown, D.W.; Lowry, R.E.; Smith, L.E. *Macromolecules* **1980**, *13*, 248.
(2) Orler, E.B.; Wrobleski, D.A.; Smith, M.E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 763.
(3) Pegoretti, A.; Kolarik, J.; Penati, A. *Die Angewandte Makromolekulare Chemie* **1994**, *220*, 49.