

Radiation Crosslinking of Polyurethanes

INTRODUCTION

Polyurethanes owe many of their useful thermomechanical properties to their segregation into hard and soft microphases.¹⁻⁴ The three contributions to phase formation are (1) a drive to reduce the surface area between phases leading to larger domains, (2) a limit to domain size imposed by the finite length of the hard and soft segments, and (3) the drive to increase entropy by phase mixing.⁵ When the temperature is changed, the relative effects of these contributions lead to a new equilibrium phase structure. The material tends towards this equilibrium state if its soft phase is above its glass transition temperature. Crosslinking is expected to impair the ability of a polyurethane to approach a new equilibrium state and thus affect the polyurethane's thermal behavior.

Previous studies dealt with the crosslinking of a polyurethane with various amounts of a peroxide crosslinking agent.⁶⁻⁸ Since this process was carried out at an elevated temperature, the phases were fixed in the relatively mixed state characteristic of that temperature. As a result, its mechanical properties such as modulus were reduced. In this paper, radiation was used to crosslink a polyurethane at room temperature. Crosslinking a polyurethane when its phases were relatively well segregated was expected to increase the stability of its phase structure. The purpose of this study was to determine if this increase in stability was significant and if it could extend the presence of the hard phase component to higher temperatures. Although the crosslinked material exhibited a higher modulus and better high temperature properties, these results were interpreted to be analogous to the increase in modulus observed when a conventional single phase polymer is crosslinked. No evidence for an increase in phase stability was observed.

EXPERIMENTAL

Instrumentation

The proton free induction decay measurements were made on a Bruker SXP broadband spectrometer operating at 100 MHz in the phase-sensitive detection mode. The external field was that imposed by a Varian V-3800-1 high resolution magnet stabilized by a ¹⁹F external lock. The decays were captured by a Biomation 610 transient recorder at a 1-MHz digitation rate. A PDP-11/34 computer was used to accumulate and numerically analyze the decays.

The moduli of the radiation crosslinked samples were measured at a crosshead speed of 0.21 cm/s using samples with a 0.065×0.465 cm² cross section. The annealing studies were performed on a Rheovibron Dynamic Viscoelastometer DDV-II (Toyo Measuring Instruments, Tokyo, Japan) at 11 Hz using samples 2.0 cm long and a 0.32×0.07 cm² cross section.

Materials

The materials used in this study were based on a single linear polyester polyurethane. The hard segments contained *p,p'*-diphenylmethyl diisocyanate and 1,4-butanediol. The soft segment was poly(tetramethylene adipate) glycol (MW ca. 1100). The diisocyanate, diol, and glycol were mixed and "melt-reacted" randomly to yield a polyurethane containing 30 wt % hard segments (30 wt % diisocyanate and diol). Samples were then exposed under vacuum to a cobalt-60 source at a dose rate of 550 krad/h. The exposure times were chosen such that their degree of crosslinking as determined by their swelling in dimethylformamide (DMF) corresponded to that exhibited by samples of a previous study crosslinked with 0.5, 1.0, and 2.0 wt % peroxides.^{6,7} The exact nature of radiation crosslinking in polyurethanes is not known. Crosslinking is believed to be most efficient in the soft phase, although both phases may participate in the reaction process.

Samples used in the annealing studies were heated at 120°C for 10 min, quenched in liquid nitrogen, and then brought rapidly to room temperature in a water bath.

TABLE I
Important Characterization Parameters for Radiatively and Chemically
Crosslinked Polyurethanes

<i>Radiatively crosslinked polyurethanes</i>				
Radiation dose (Mrad)	0.0	21.5	80	210
Swelling in DMF (%)	Soluble	275	205	165
Young's modulus (MPa)	11.3 ± 0.7	10.6 ± 0.4	11.1 ± 0.4	14.0 ± 0.7
<i>Chemically crosslinked polyurethanes</i> ^{6,7}				
Peroxide level (wt %)	0.0	0.5	1.0	2.0
Swelling in DMF (%)	Soluble	275	205	165
Young's modulus (MPa)	12.8	11.5	10.3	7.2

Analysis

Free induction decays were collected as described in a previous study.⁸ A nonlinear fit of the form

$$M(t) = M_f e^{-t/T_{2f}} + M_s e^{-t/T_{2s}}$$

was then applied to the decay, where $M(t)$ is the magnetization as a function of time, M_f and M_s are the initial magnetization of the fast and slow components respectively, and T_{2f} and T_{2s} are the spin-spin relaxation times of the fast and slow components, respectively. In previous studies all four fitting parameters M_f , M_s , T_{2f} and T_{2s} were allowed to vary independently in the fitting procedure. This created some difficulty in this study at high temperatures. When the rapid decay was a very small fraction of the total decay, T_{2f} would sometimes become nearly as large as T_{2s} , and M_f would begin to increase with temperature. The fitting program was effectively ignoring the very small contribution from the rapid decay and using two components to fit the much larger contributions from the slow decay. To prevent this artifact, the value of T_{2f} was fixed for each sample throughout its temperature range. The temperature chosen was 0°C, although T_{2f} was nearly independent of temperature from 0°C to 40°C, which covered much of the region of interest. The value of T_{2f} was 21 s. The theoretical justification for fixing T_{2f} is based on the fact that, at temperatures below that which motional narrowing is effective, the linewidth is independent of temperature.

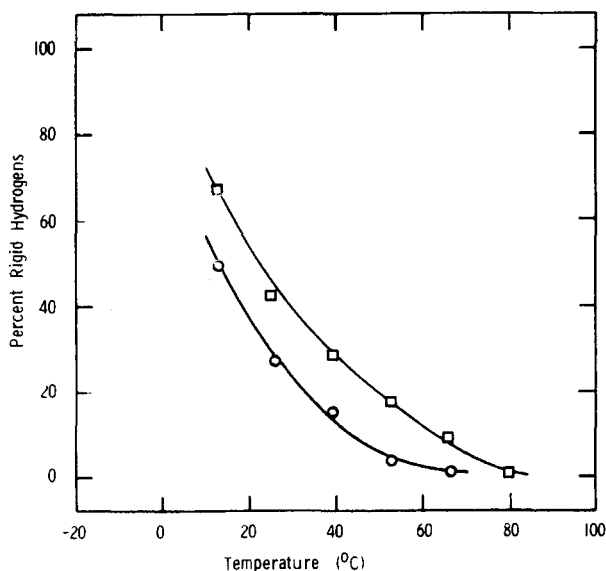


Fig. 1. The percent hard phase vs. temperature for the linear (○) and most heavily cross-linked (□) polyurethanes.

RESULTS AND DISCUSSION

The Young's moduli for polyurethanes crosslinked to various degrees by radiation or peroxide are shown in Table I. The difference in moduli of the uncrosslinked samples (radiation dose equal to 0.0 and peroxide level equal to 0.0) is due to experimental uncertainty. The two sets of measurements were performed in different laboratories using different sample configurations. The moduli of the peroxide crosslinked polyurethanes were found to decrease uniformly with peroxide concentration. Previous studies^{6,7} have shown that incomplete phase separation, caused by crosslinking the material in a mixed state, was responsible for this decrease. As expected, the moduli of the radiation crosslinked polyurethanes show no such decrease because they were crosslinked at room temperature in a segregated state. We believe that the increase in modulus at the highest radiation dose is analogous to the increase in modulus observed when a conventional single phase polymer is crosslinked. This interpretation is supported by additional experiments of this study.

The percent hard phase versus temperature is shown in Figure 1 for the linear and most heavily crosslinked polyurethanes. The phase behavior of the samples exposed for intermediate periods of time lie slightly to the right of that of the uncrosslinked sample and are not shown. The percent hard phase of the polyurethane crosslinked to 210 Mrad is approximately 15% greater than that of the linear polyurethane throughout the transition range. Since the additional hard phase is observed at the crosslinking temperature, it cannot be attributed to the "locking in" of the phase structures. The additional hard phase must be due to the immobilization of material which initially contributed to the soft phase component. This immobilization probably takes place near the phase boundaries where segmental freedom is already diminished.

Just as crosslinking at elevated temperatures caused the mixed state to persist to low temperature,⁸ we expected that crosslinking at room temperature would cause the segregated state to persist to higher temperatures. This effect is not evident from Figure 1, however. The hard phase contribution of the crosslinked polyurethane runs parallel to that of the linear polyurethane. As discussed in the previous paragraph, the offset is due to the immobilization of soft segments. Only if the offset increased with temperature, could we be confident that crosslinking is causing the phase segregation to persist to higher temperature.

The moduli of the linear and most heavily crosslinked polyurethanes are compared in Figure 2. Crosslinking leads to an increased modulus throughout the temperature range. The moduli and percent hard phase protons are closely related as can be seen by the similar temperature offsets between the linear and crosslinked materials for each property.

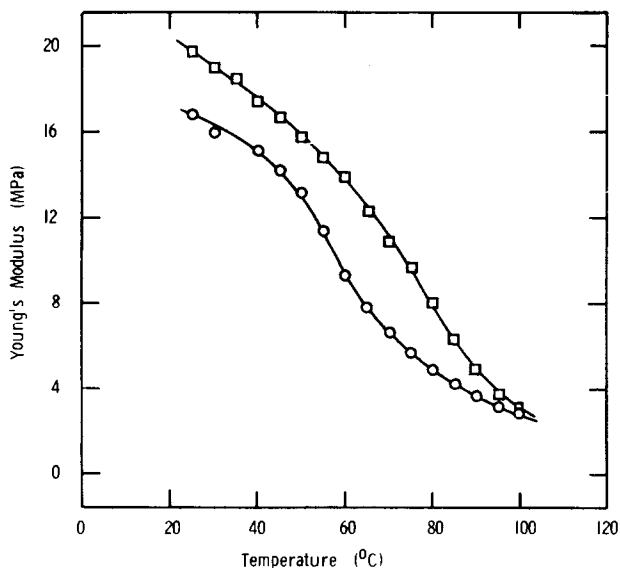


Fig. 2. The moduli vs. temperature for the linear (○) and most heavily crosslinked (□) polyurethanes.

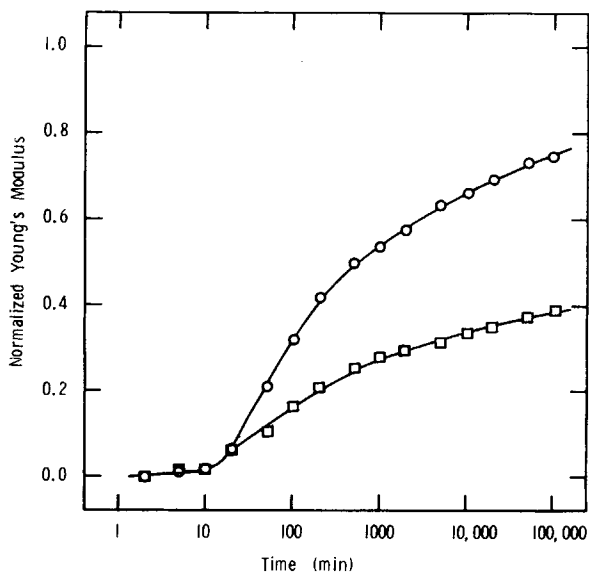


Fig. 3. Normalized moduli recovery curves for the linear (○) and most heavily crosslinked (□) polyurethanes after being subjected to a temperature pulse.

Annealing experiments were used to determine the effect of crosslinking on the kinetics of phase separation. Small angle x-ray scattering, differential scanning calorimetry, and mechanical and nuclear magnetic resonance methods⁹⁻¹² have been used to follow the degree of phase separation after a temperature pulse. In this study a dynamic viscoelastometer was used to follow the process. This technique offers the advantage of measuring Young's modulus, which is expected to be of the most value from an engineering point of view, as a function of time on a single sample. Previous mechanical methods required a separate sample for each measurement. Because the dynamic viscometer measurement could be repeated on the same sample, the recovery curve could be mapped in great detail.

Figure 3 shows the normalized modulus recovery curves for the linear and most heavily crosslinked polyurethanes. As was seen for chemical crosslinking, radiation crosslinking decreases the speed at which the material returns to its equilibrium phase structure.

CONCLUSIONS

Radiation crosslinking caused an increase in Young's modulus and an increase in the percent hard phase component at the highest dosage level studied. The increases were analogous to the increase in modulus observed when a conventional single phase polymer is crosslinked. Temperature studies revealed no evidence of the phase structure being locked in place by the crosslinking. Radiation crosslinking retards the rate of phase formation after a temperature pulse.

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ROGER A. ASSINK

Sandia National Laboratories
Albuquerque, New Mexico 87185

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