The Thermal Aging of Filled Polyurethane

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SYNOPSIS

Thermal aging and strain endurance experiments on a filled rubber were performed at several temperatures. The rubber was polyurethane (PU) made from hydroxyl-terminated polybutadiene (HTPB) with 4,4'-diphenyl methane diisocyanate (MDI). The filler was sodium chloride. The mechanical properties, glass transition temperature, dynamic viscoelasticity, and chemical structures were investigated for filled and unfilled PU under an aging period at 60 and 80°C and 50% relative humidity. We found that at 60°C the chemical structures of the filled and unfilled rubbers had no changes in 30 days during aging. But moisture had some effects on the filled PU and changed its mechanical properties. At 80°C, the chemical structures of the filled and unfilled PU had changed due to the thermal oxidation of polybutadiene in aging. The deterioration was more apparent for the filled rubber than for the unfilled. The prestraining would dewet the filler from the samples and it increased the voids.

INTRODUCTION

The structure-property relationship of polyurethane elastomers derived from liquid hydroxyl-terminated polybutadiene (HTPB) and diisocyanate systems have been studied extensively.[1-4] The characteristics of polyurethane (PU) are, first, a superior hydrolytic stability arising from the nonpolar main chain of HTPB, and, second, the ability of being compounded with a large amount of filler. In this paper, we examined the thermal aging behavior of the filled and unfilled PU made from HTPB and 4,4'-diphenyl methane diisocyanate (MDI). When an elastomer was in the aging process, some physical and/or chemical changes might occur that resulted in changes in its mechanical properties. Christiansen et al.[5] studied the aging of HTPB propellant and found that both the tensile strength and gel content increased with aging time. They ascribed this phenomenon to the chemical reactions at the sites of unsaturation in the polymer chain, as also found in the PBAN and CTAN propellants by Layton.[6] Lay-

ton used iodimetric titration and NMR to determine the total unsaturation in the polymer and concluded that the double bonds were disappearing with aging and more rapidly at the elevated temperature.

All the earlier studies showed that the polybutadiene (PB) was the least stable component of polybutadiene containing polymers and was susceptable to O_2 attack even at room temperature. Also, this reaction was accelerated by heat and UV radiation.[7-10] In all the above studies, the absorbance in the O—H and C=O region in the IR spectrum increased and the butadiene absorbance decreased. The systematic examination of PB oxidation was done by Rabek et al.[11,12]

The other component of PU we studied was aromatic isocyanate. It turned yellow on exposure to sunlight or by thermal aging.[13-16] In this paper, we show the thermal aging behavior of HTPB-based PU and investigate the effect of prestraining on the mechanical properties of the samples.

EXPERIMENTAL

Material

Liquid hydroxyl-terminated polybutadiene (HTPB) from ARCO Chemical having a molecular weight

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Figure 1 Prestraining apparatus.

Figure 2 The variation of mechanical properties of PU aging at 60°C: (△,□) natural state; (▲,■) prestrained to 10%.
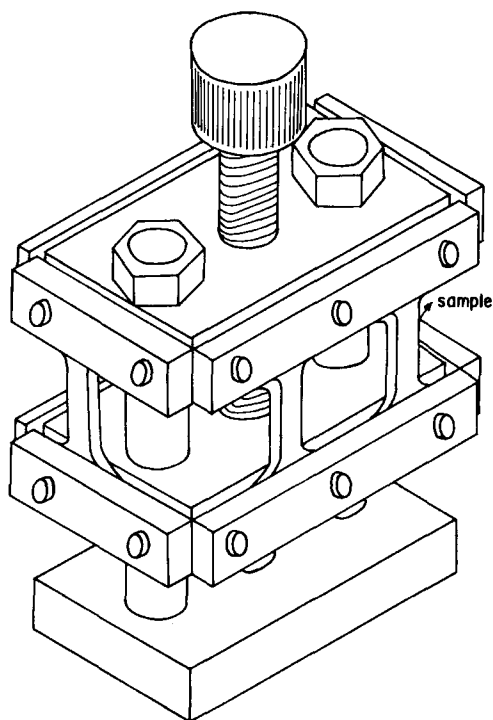
2800 consisted of about 60 wt % *trans-*, 20 wt % *cis-*, and 20 wt % vinyl content. The average hydroxyl functionality was 2.2. 4,4'-Diphenyl methane diisocyanate (MDI) from Bayer was stored at 60°C for 30 min before use. The catalyst for the urethane reaction was dibutyltin dilaurate (T12) and was used without further purification. The sodium chloride provided by Taiwan Salt Works was dried and ground. We chose the salt of 88–105 μm (#170) by sieving and reserved it in the oven.

Synthesis of PU

The HTPB was dried and degassed at 90°C for 1 day and then mixed with T12 (.018 wt %) and salt (50 wt %) with a high-speed stirrer for a further 30 min under reduced pressure (5 mmHg). Then we added the liquid MDI to the blend (NCO/OH = 1/1) and continuously stirred and degassed it for 1 min. It was poured quickly into a preheated mold and placed on a hot press at 90°C for 24 h. The sample was then postcured at room temperature for 1 week.

Aging and Tests

The samples were divided into two groups: One was in its natural state and the other was prestrained to
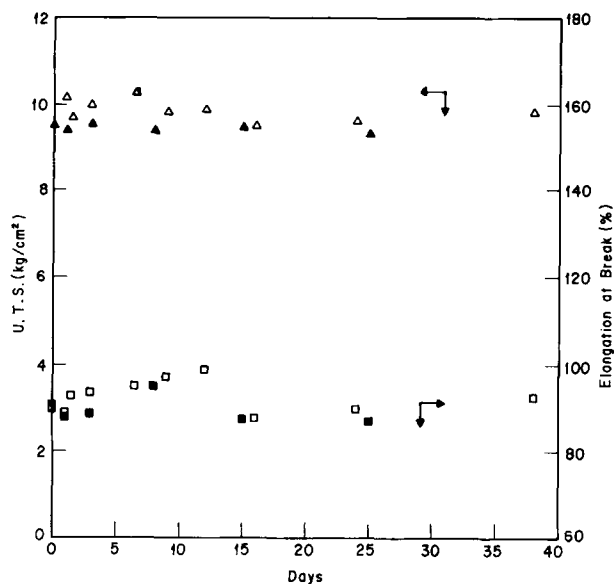
10% of its initial length ($\Delta L/L_0 = 10\%$) using the simple apparatus shown in Figure 1. The samples were put into the chamber with constant temperature (60 or 80°C) and constant humidity (R.H. = 50%) for 30–45 days.

After a period of aging, the samples were taken into the desiccator at room temperature and 50%
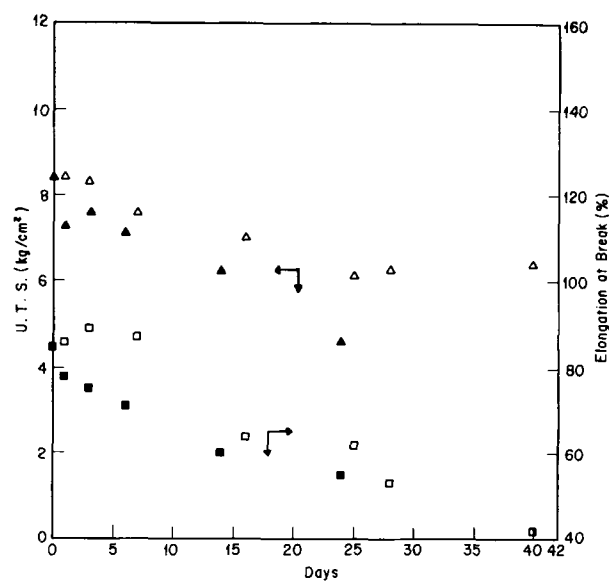

Figure 3 The variation of mechanical properties of PU aging at 80°C: (△,□) natural state; (▲,■), prestrained to 10%.
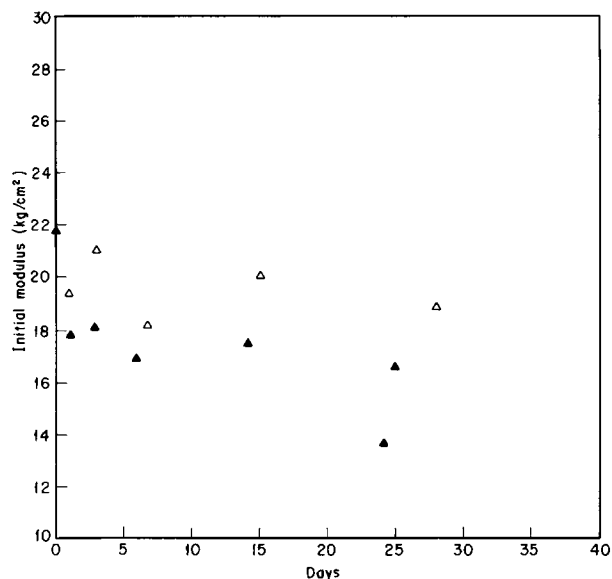
Figure 4 The variation of initial modulus of PU aging at 80°C: (△) natural state; (▲) prestrained to 10%.
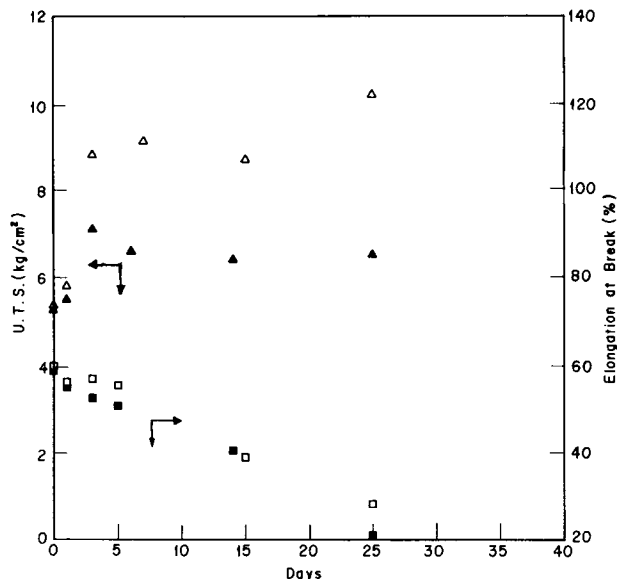

Figure 6 The variation of mechanical properties of filled PU aging at 80°C: (△,□) natural state; (▲,■) prestrained to 10%.

R.H. for 3 h. Mechanical properties were measured by an Instron. The dumbbell specimens had a thickness of about 2 mm. The crosshead speed was 1 cm/min.

Dynamic mechanical measurements were performed on compression-molded film, which had a thickness of 0.3–0.5 mm, with a Rheovibron Model

DDV-II-C (Toyo Baldwin) at a frequency of 110 Hz, ranging in temperature from −125°C to 60°C at a rate of about 1.5–2.0°C/min.

Infrared absorption spectra (from 4000 to 400 cm⁻¹) were recorded with an infrared spectrophotometer (Hitachi) on compression-molded films (80–100 μm).
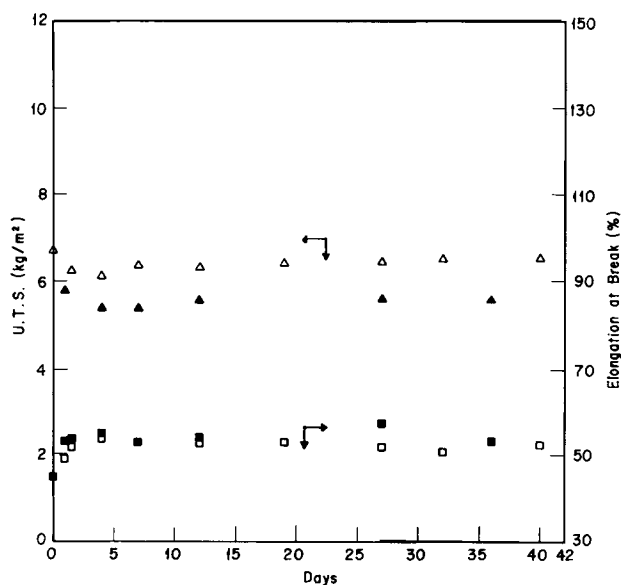

Figure 5 The variation of mechanical properties of filled PU aging at 60°C: (△,□) natural state; (▲,■) prestrained to 10%.
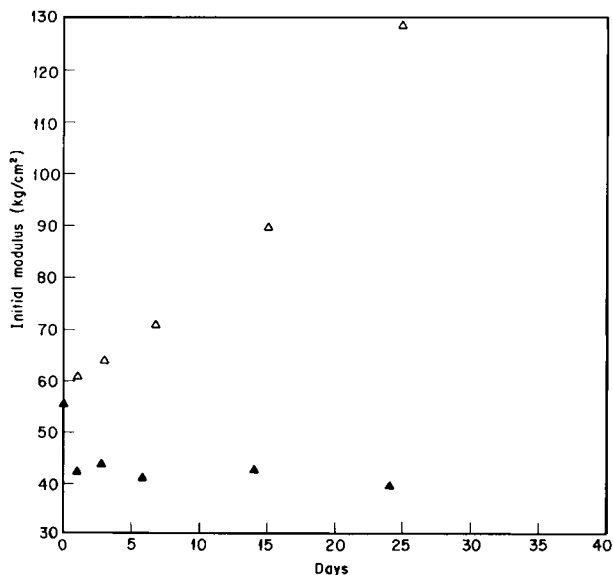

Figure 7 The variation of initial modulus of filled PU aging at 80°C: (△) natural state; (▲) prestrained to 10%.
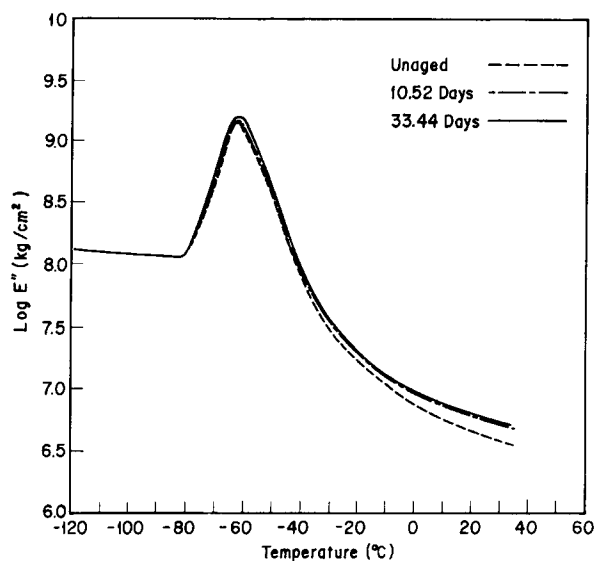
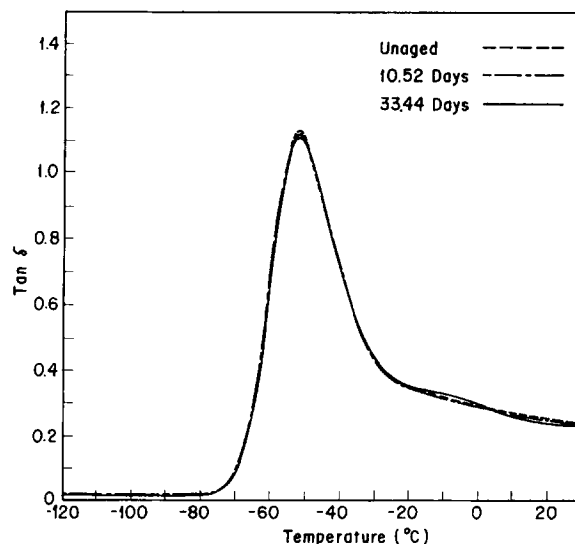**Figure 8**   The variation of loss modulus of PU aging at 60°C.

Figure 10   The variation of loss tangent of PU aging at 60°C.

RESULTS AND DISCUSSION

Mechanical Properties

From Figure 2, we know that the mechanical properties of the unfilled PU aging at 60°C, whether it was strained to 10% or unstrained, had no changes for 40 days. The prestraining had little effect on the PU rubber. But at 80°C, the tensile strength and initial modulus of PU decreased with the aging time,

but all the changes slowing at later times, as seen in Figures 3 and 4.

For the filled PU aging at 60°C, as shown in Figure 5, the tensile strength continuously decreased to a steady value in the first 2 days. The decrease of tensile strength was caused by diffusion of moisture into the samples, and the sodium chloride was deliquesed. Therefore, it resulted in poorer adhesion and the loss of rigidity of the salt.
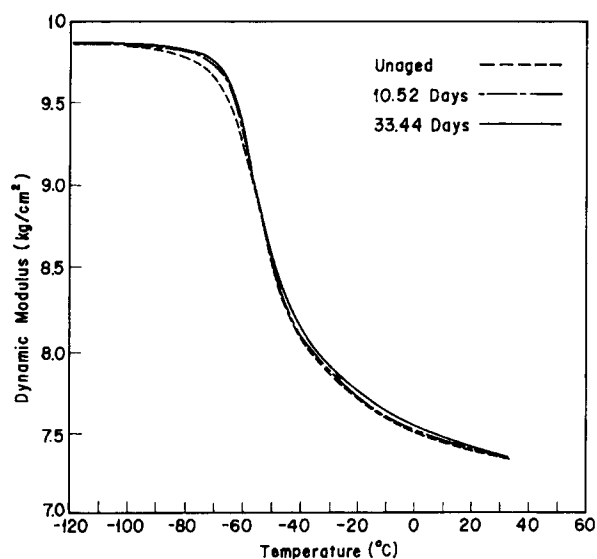
Under aging at 80°C in Figure 6, the tensile

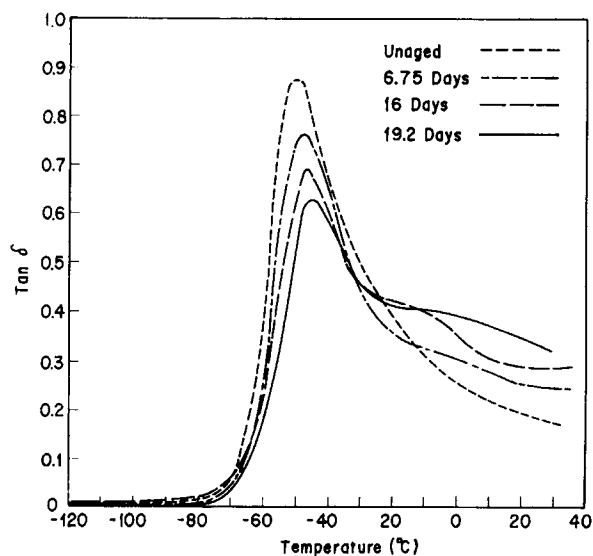**Figure 9**   The variation of dynamic modulus of PU aging at 60°C.

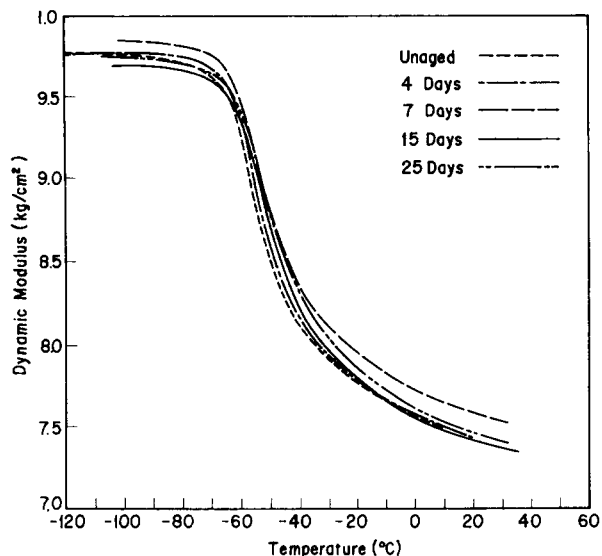**Figure 11**   The variation of loss tangent of filled PU aging at 60°C.

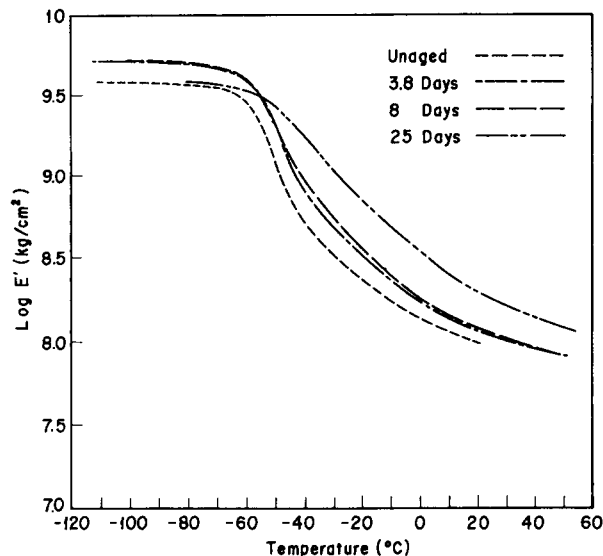**Figure 12** The variation of dynamic modulus of PU aging at 80°C.

Figure 14 The variation of dynamic modulus of filled PU aging at 80°C.

strength of filled PU increased apparently after 2 days. The initial modulus also increased with aging time, as shown in Figure 7. The increases of tensile strength and initial modulus of the samples might be caused by cross-linking.[17] Also, Oberth[18] found that the tensile strength and initial modulus of PU filled with glass bead increased and the elongation at break decreased as the cross-linking density increased.

From the above figures, we also determined that the tensile strength of the prestrained filled rubber was less than that of the samples without strain. This could be due to the dewetting of the fillers by prestraining and, thus, the increasing of the voids.

Dynamic Mechanical Measurements

From the peak of loss modulus (Fig. 8), we know that the glass transition temperature of PU was at −61°C and that of filled PU was at −55°C. The higher value of the filled PU was because the segmental motion was restricted by the fillers.
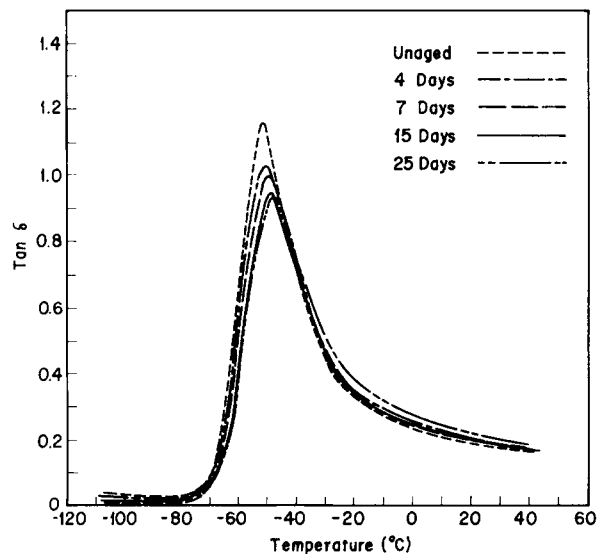

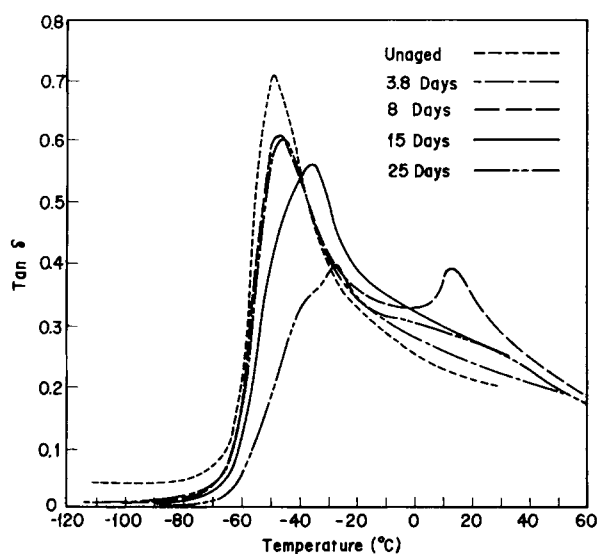**Figure 13** The variation of loss tangent of PU aging at 80°C.

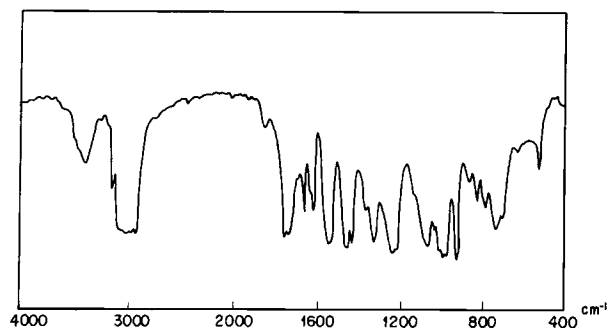**Figure 15** The variation of loss tangent of filled PU aging at 80°C.

Figure 16 IR spectrum of PU.

Under aging at 60°C, the dynamic modulus and tan δ of PU did not change significantly for 35 days, as seen in Figures 9 and 10. But the damping peak value of filled PU aging at 60°C decreased as the aging proceeded, as shown in Figure 11. It was caused by the absorbed moisture that was frozen into ice at such a low temperature to increase the effective volume and rigidity of the fillers. Also, we found another small damping peak appearing near 0°C, possibly related to the change of the state of H₂O.

Under aging at 80°C, the dynamic modulus and tan δ of PU all decreased, as shown in Figures 12 and 13. Besides the effect of moisture, the chemical structure of PU had changed as indicated by IR spectra. As regards the filled PU, the increase of the T_g, the increasing broadness of the transition zone, and the increase of dynamic modulus above T_g were obvious, as shown in Figures 14 and 15. The T_g increased to −41°C after 25 days of aging. The cross-linking reaction increased with increased aging temperature.[17]

Infrared Spectra

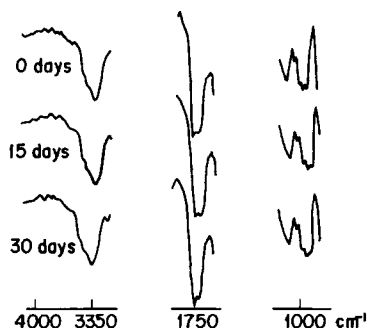Figure 16 shows the infrared (IR) spectrum of the cast unaging PU film. The absorption peak due to
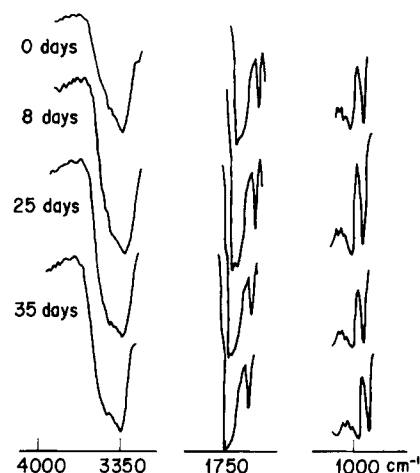

Figure 18 IR spectrum of filled PU aging at 60°C.

the NCO isocyanate groups at 2250 cm⁻¹ was not observed, indicating that the isocyanate groups had reacted completely. The band at 3352 cm⁻¹ had some shoulders that indicated that the N—H groups were somewhat hydrogen-bonded.[19] The absorption band between 1710 and 1750 cm⁻¹ were due to the free and hydrogen-bonded carbonyl groups.[19,20] The butadiene contents were to be trans-1,4 form at 972 cm⁻¹, 1,2 form at 912 cm⁻¹, and cis-1,4 form at 685 cm⁻¹, having a little overlap with the phenyl group or the terminal vinyl group.

Figure 17 shows the IR spectra of unfilled PU aging at 60°C. There were no changes in 30 days. The IR spectra of the filled PU aging at 60°C (Fig. 18) also did not show any changes in 30 days.
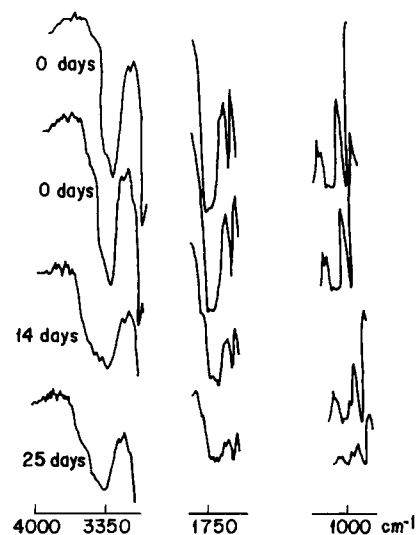

Figure 17 IR spectrum of PU aging at 60°C.

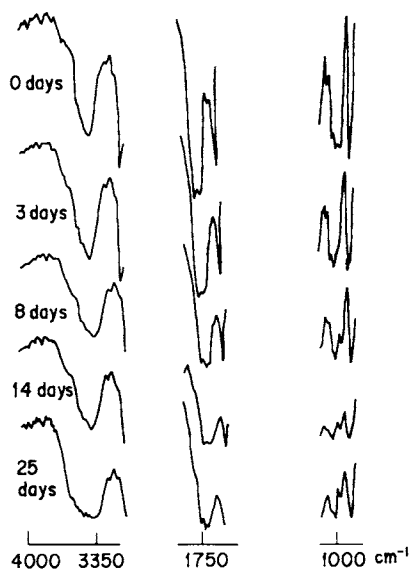**Figure 19** IR spectrum of PU aging at 80°C.

Figure 20   IR spectrum of filled PU aging at 80°C.

When aging at higher temperature, 80°C, especially for the filled PU, the IR spectra showed some changes (Figs. 19 and 20). We found that the absorption bands at 3400–3600 cm^{-1} (—OH) and 1710–1750 cm^{-1} (—C=O) became broader with aging time. Also, the C=O absorbance was increasing at the lower wavenumber (around 1700 cm^{-1}), due to the thermal oxidation of polybutadiene,[8] which would produce hydroxyl and carbonyl groups. The probability of hydrogen bonding, thus, might have increased to some extent.

Also, the aging of polybutadiene might introduce both the chain scission and cross-linking to the sample. From Figures 19–20, we could see the butadiene content decreasing with aging time as we examined the peaks at 972, 912, and 685 cm^{-1}. Especially for the peak at 972 cm^{-1}, the trans-1,4 form decreased more obviously than did the other two forms.

CONCLUSIONS

The unfilled and filled PU aging at 60°C had no changes in chemical structure at least for 30 days. But the moisture could diffuse into the filled samples through the voids. Consequently, the tensile strength of filled PU decreased to a steady value as the moisture content arrived at an equilibrium value. Under aging at 80°C, the carbonyl and hydroxyl groups increased and the butadiene content decreased. The cross-linking reaction appeared to be dominating the

aging behavior of filled PU at 80°C as the initial modulus, tensile strength, and T_g increased with aging time. But the chain scission reaction appeared to be dominating the aging behavior of PU at 80°C as the initial modulus and tensile strength decreased with aging time. However, this requires more evidence. Also, the prestraining would decrease the tensile strength of the filled PU.

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