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Gas Permeability, Water Absorption, Hydrolytic Stability and Air-Oven Aging of Polyisobutylene-Based Polyurethane Networks

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SUMMARY

Polyisobutylene-based polyurethane networks have been synthesized by crosslinking polyisobutylene glycols with triphenylmethane triisocyanate and their gas permeability, water absorption, hydrolytic stability, and air oven aging characteristics was examined by ASTM methods. The preparation of the polyurethane sheets is described. The oxygen permeability of polyisobutylene-based polyurethanes is lower than that of vulcanized butyl rubber and their water absorption is negligible. The hydrolytic stability of these new polyurethanes is outstanding and their mechanical properties (tensile strength, modulus, elongation) remain practically unchanged after four days of exposure to 85° steam. Similarly, air aging for two days at 128° affects little mechanical properties.

INTRODUCTION

Recent research in our laboratories led to the synthesis of new liquid α,ω-di(hydroxy)polyisobutylenes (PIBDO) (IVAN et al. 1980) which when reacted with suitable di- or triisocyanates gave rise to new polyisobutylene-based polyurethanes (KENNEDY et al. 1981) containing rubbery polyisobutylene (PIB) soft segments. These unique polyurethanes are expected to combine the excellent physical and processing characteristics of polyurethanes with the outstanding barrier properties and chemical/hydrolytic/weathering/environmental stability of PIB. On account of its very low gas permeability, vulcanized butyl rubber is used for inner tubes, inner liners in tubeless tires, air cushions, pneumatic springs, accumulator bags, air bellows, etc. (POLYSAR BUTYL HANDBOOK, 1966). Since PIB is a saturated polyhydrocarbon that contains only primary and secondary hydrogens, it is insoluble in water and exhibits excellent thermal and chemical resistance. The commercial success of crosslinked PIB (butyl rubber) is mainly based on the combination of these desirable physical-chemical-mechanical properties. Conventional polyurethanes contain polar polyether or polyester soft segments and as a consequence are inherently less resistant toward moisture and chemicals (DOYLE, 1971).

In view of these considerations it was of interest to examine our polyisobutylene-based polyurethanes in regard to gas-barrier properties (possible foam applications) and moisture resistance. This paper concerns experiments (mainly ASTM tests) carried out toward this end and demonstrates some

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of the outstanding characteristics of these new materials.

EXPERIMENTAL

Materials. The synthesis and purification of α,ω-di(hydroxy)polyisobutylene has been described (IVAN et al, 1980). n-Pentane (Fisher Scientific) was distilled over calcium hydride before use. Tetrahydrofuran (Fisher Scientific) was first distilled over lithium aluminum hydride under dry nitrogen, then freshly redistilled over sodium under dry nitrogen before use. Triphenylmethane triisocyanate (Desmodur R, Mobay Chemical) was obtained as 20% solution in methylene chloride. It was purified in a dry box by precipitating in dry n-pentane to remove insoluble oligomer, then fractionally distilled on a high vacuum line (only middle fraction was collected). The distillate was a light yellow viscous liquid, which crystallized upon storage under dry nitrogen. The yield after purification was 14% and the purity of the triphenylmethane triisocyanate was found to be 99.99% by the di-n-butylamine - HCl titration method (ASTM D1638).

Network Synthesis. Under a dry nitrogen atmosphere in a stainless steel enclosure, α,ω-di(hydroxy)polyisobutylene was dissolved in dry tetrahydrofuran (40%, w/v), mixed with a stoichiometric amount of triphenylmethane triisocyanate, then poured onto an open Teflon pan(12 x 12 x 0.5 cm). The mixture was allowed to cure at 45°C for two weeks while the solvent was slowly evaporated, subsequently the polyurethane pad was placed in a vacuum oven and curing was completed at 85-90°C for three days under vacuum.

Physical Testing Methods. Oxygen gas permeation rates of polyurethane sheets were determined according to ASTM D1434 method using 5 cm^2 discs at 30°C (89 hours O_2 purge). The tests were carried out courtesy of the Goodyear Tire and Rubber Company.

Hydrolytic stabilities were determined according to ASTM D3137 method. Samples (microdumbbells) were suspended in a closed jar containing 100 ml distilled water and heated to 85 ± 5°C for 4 days, then cooled to room temperature. After exposure the tensile properties were measured and the percent changes relative to that exhibited by the original sample were calculated. The microdumbbells were 0.254 cm wide, 5 cm long cut from an ∿0.6 mm thick sheet. Tensile strength was measured at 24°C on an Instron Model 1130 tensile tester equipped with pneumatic clamps. The strain rate was 25 min^{-1}.

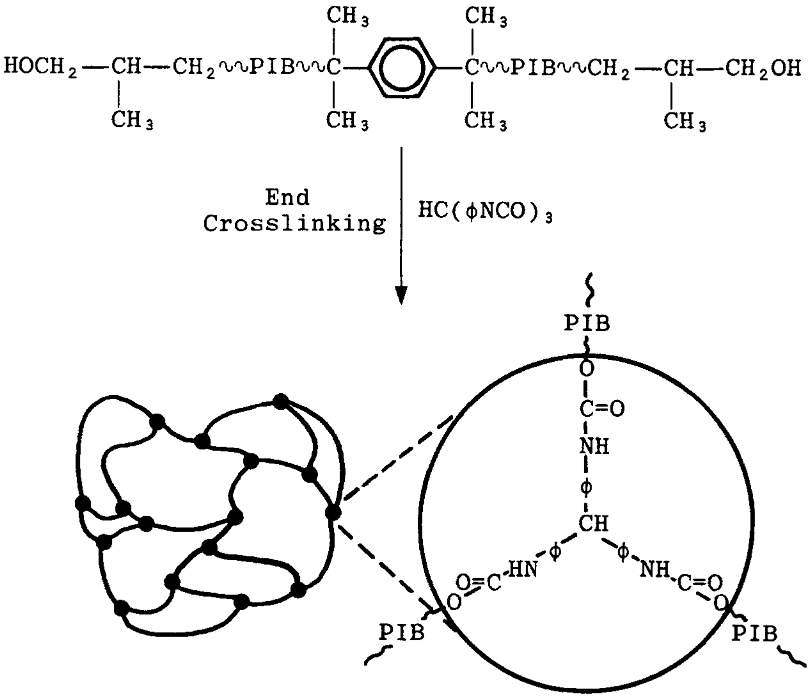
Air-oven aging was tested by ASTM D537 method. Samples (microdumbbells) were suspended in a circulating air oven for two days at 128°C. The dimensions of the microdumbbells and the tensile test were the same as used for the hydrolytic stability test.

Water absorption was determined according to ASTM D570 method using 5 cm long 2 cm wide ∿0.6 mm thick sheets. The specimens were placed in a test tube containing distilled water and maintained at 75 ± 1°C for 48 hr. Then the samples were removed from the water, the surface water was wiped off with a dry cloth, and the weight increase was determined immediately. Percentage of water absorbed = [(wet wt.-original wt.)/original wt.] x 100.

Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer using 15 mil thick films.

RESULTS AND DISCUSSION

Preparation of PIB-Based Polyurethane Sheets. Polyisobutylene-based polyurethane pads were synthesized by crosslinking α,ω-di(hydroxy)polyisobutylene (PIBDO) with stoichiometric amounts of triphenylmethane triisocyanate (TTI):



The completion of crosslinking was checked by infrared analysis. Figure 1 shows the IR spectrum of a thin polyurethane film made with a PIBDO of $\bar{M}_n = 3,400$. The absence of absorptions at 3640 cm^{-1} or 2250 cm^{-1} (characteristic bands for free hydroxyl and isocyanate groups, respectively) indicates that crosslinking was complete. The strong broad absorption between 3100 cm^{-1} and 3400 cm^{-1} was assigned to the NH stretching of the urethane linkages.

Oxygen Permeability. Two thin polyurethane films were examined for oxygen gas permeability and the results are summarized in Table I.

TABLE I

Oxygen Gas Permeability of Polyisobutylene-based Polyurethane Networks

PIBDO $\overline{M}_n$	Thickness mil	O_2 Permeability Coefficient, $\overline{P}$* $\frac{cm^3 \times mil}{100\ in^2 \times 24\ h \times atm}$
3,400	15	202.5
11,500	20	202

* at 30°C, 89 hr O_2 purge, 100% humidity

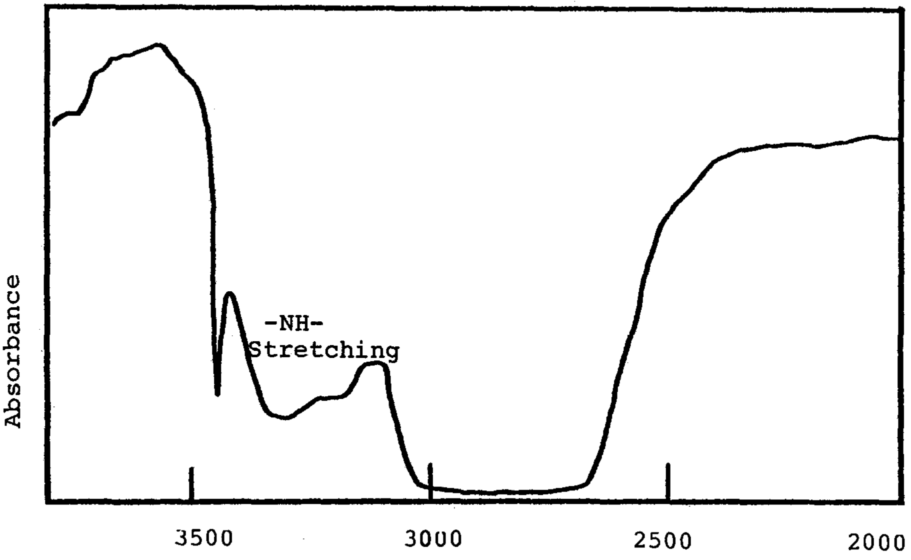


Figure 1. Infrared Spectrum of Polyisobutylene-Based Polyurethane Film. (PIBDO $\overline{M}_n$ = 3,400, Thickness = 15 mil)

As a point of reference, the permeability coefficient $\overline{P}$ of butyl rubber vulcanizates containing 50 parts of SRF carbon black at 30°C is in the range of 650 - 4750 cm^3 x mil/(100 in^2 x 24 hr x atm) (POLYSAR BUTYL HANDBOOK, 1966). Evidently the oxygen permeability of PIB-based polyurethane is much lower than that of butyl rubber (exact comparisons cannot be made because we are unaware of $\overline{P}$ values of unfilled butyl rubber gums). It is of interest that PIB-containing polyurethanes exhibit low $\overline{P}$'s in the absence of fillers or extenders (the urethane linkages represent only 2 and 6.7% w/w of the total composition, depending on the $\overline{M}_n$ of the PIB segment shown in Table I, respectively).

<u>Water Absorption</u>. The water absorption of PIB-based polyurethanes was determined by ASTM D570 method. Results are summarized in Table II.

TABLE II

Water Absorption of Polyisobutylene-based Polyurethane Networks

PIBDO $\bar{M}_n$	Percentage of Water Absorbed* %
3,400	0.016
11,500	0.01

* 50 x 20 x 0.6 mm^3 sheets immersed in distilled water at 75 ± 1°C for 48 hr; averages of two samples

The extremely low moisture absorptions are not too surprising in view of the nonpolar hydrocarbon nature of the telechelic PIB-diol.

Hydrolytic Stability. The hydrolytic stability of the new PIB-based polyurethanes has been determined by the ASTM D3137 method (steam treatment at 85°C for 4 days). Results are summarized in Table III.

TABLE III

Hydrolytic Stability of Polyisobutylene-Based Polyurethanes*

Polyurethane	Tensile strength, σ_b KPa	Modulus E(300%) KPa	Elongation ε_b %
PIBDO-1, $\bar{M}_n$=3,400			
Untreated	3834	831	1020
Treated*	3650	819	960
Percent Change,%	-4.8	-1.4	-5.9
PIBDO-2, $\bar{M}_n$=11,500			
Untreated	2280	487	1100
Treated*	2270	479	1040
Percent Change,%	-0.4	-1.6	-5.5

*ASTM D3137: Steam treatment at 85 ± 5°C, 96h; average of three samples

The tensile strength and elongation of the polyurethane made with the lower molecular weight PIB-diol ($\bar{M}_n$ = 3,400) diminished ∿5% upon treatment with 85°C steam for four days. In contrast, the tensile strength of the polyurethane containing the higher molecular weight PIB-diol ($\bar{M}_n$ = 11,500) did not change to any significant degree. In general, the change in physical properties is negligible as a result of the rather severe hydrolysis test employed. The high hydrolytic stability of our polyurethanes is due to the low moisture permeability and low water absorption of PIB domains that effectively protect the urethane linkages from the influence of water

Air-Oven Aging. The aging in air of PIB-based polyurethanes was tested by ASTM D573 method (air-oven at 128° for 48 hr). Results are shown in Table IV. In view of the saturated structure and well-known chemical resistance of PIB, the generally good retention of mechanical properties of the new PIB-based polyurethanes after aging in air for 48 hr at 128°C is not too surprising.

TABLE IV

Air-Oven Aging of Polyisobutylene-Based Polyurethanes*

Polyurethane	Tensile strength, σ_b KPa	Modulus E(300%) KPa	Elongation ε_b %
PIBDO-1, $\bar{M}_n$=3,400			
Untreated	3834	831	1020
Treated*	3554	826	925
Percent Change,%	-7.3	-0.6	-9.3
PIBDO-2, $\bar{M}_n$=11,500			
Untreated	2280	487	1100
Treated*	2132	485	1026
Percent Change,%	-6.5	-0.4	-6.7

*ASTM D513: Circulating air-oven at 128°C, 48h; average of three samples

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