

Polyisobutylene-Based Urethane Foams. II. Synthesis and Properties of Novel Polyisobutylene-Based Flexible Polyurethane Foams

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Synopsis

Novel polyisobutylene-based flexible polyurethane foams (PIB-PUF) have been prepared manually by the prepolymer method using three-arm star hydroxyl-terminated polyisobutylenes (PIB-triols) and toluene diisocyanate (TDI). Solvent extraction and IR spectroscopy of PIB-PUFs indicated essentially complete crosslinking. Conventional polyether-based polyurethane foams (PE-PUFs) and polybutadiene-based polyurethane foams (PBD-PUFs) have also been prepared by the same method and select physical-mechanical properties of all these urethane foams, such as tensile strength, elongation, resilience, water permeability, hot air stability, and hydrolytic stability, have been examined and compared. Although the density of PIB-PUF is lower than that of PE-PUF, its tensile strength is superior to the latter. Elongation of PIB-PUF is almost the same as those of the other foams. The PIB-PUF exhibits low resilience which indicates good damping properties. Due to the hydrophobicity of the soft segment, PIB-PUF exhibits very low water permeability. The hydrolytic and hot air stability of PIB-PUFs are outstanding. Attempts have been made to determine gas permeabilities; however, due to the open-cell nature of the foams, these studies could not be completed. The new PIB-based urethane foams combine excellent thermal, environmental, barrier, and mechanical properties, unmatched by conventional PUFs.

INTRODUCTION

Flexible polyurethane foams are important for the insulation, furniture, bedding, transportation, etc. industries. The soft segments of commercial flexible polyurethane foams are exclusively of polyether or polyester polyols, which, on account of their inherently low moisture and chemical resistance, exhibit rather poor environmental stability. Hydroxyl-terminated polyisobutylenes have recently been used as soft segments in polyurethane elastomers on account of their excellent damping and barrier properties, oxidative and hydrolytic stability, and low moisture permeability.¹⁻⁵ Thus hydroxyl-terminated PIBs are expected to impart a desirable combination of properties of flexible urethane foams. On the negative side, hydroxyl-terminated PIBs are expected to exhibit poor miscibility with water (i.e., the conventional blowing agent) and high viscosity during flexible urethane foam synthesis. Experiments have therefore been carried out to substantiate the expectations and to overcome the potential problems. The kinetics of the reaction between hydroxyl-terminated PIB and isocyanates have been studied during the first phase of these investigations, and conditions were found under which this reaction proceeds with a sufficiently high rate for the synthesis of foams.⁶

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This paper concerns the synthesis and characterization of PIB-based flexible polyurethane foams and a comparison of select chemical-physical-mechanical properties of these new PIB-PUFs with conventional polyoxypropylene-based polyurethane foams and a polybutadiene diol-based foam.

EXPERIMENTAL

Materials

Three-arm star hydroxyl-terminated polyisobutylene (Akron Cationic Polymer Development Co.) has been synthesized by living carbocationic polymerization of isobutylene.⁷⁻⁹ The polyoxypropylene triol (Vorarol 3010, Dow Chemical Co.)¹⁰ and the hydroxyl-terminated polybutadiene (R-45HT, ARCO)¹¹ have been used as received. Material characteristics are shown in Table I. Toluene diisocyanate (Mondur TD-80, Mobay, 80/20 2,4- and 2,6-TDI isomer mixture)¹² was vacuum-distilled before use. Triethylene diamine (33% in dipropylene glycol, DABCO-33LV, Air Products and Chemicals),¹³ stannous octoate (25% in dioctyl phthalate, FOMREZ C-7, Witco Chemical Co.)¹⁴ catalysts and silicone surfactant (5043, Dow-Corning)¹⁵ were used as received. Methylene chloride and tetrahydrofuran (THF) were stored over molecular sieves (4 Å). Chlorobenzene, anhydrous (Aldrich), and di-*n*-butylamine (Aldrich) were used as received. The reagents to determine the NCO content of the prepolymers were prepared as follows: A ~ 0.1*N* di-*n*-butylamine solution in chlorobenzene was prepared. Standard 0.1*N* HCl was prepared by diluting a Fisher certified HCl solution in a volumetric flask with distilled water. Indicator solution (0.1%) was prepared by dissolving bromophenol blue (Aldrich) in methanol.

Foam Preparation

Flexible polyurethane foams were prepared by the isocyanate-terminated prepolymer method as follows: Polyol and excess TDI were added to a 250-mL three-neck round-bottom flask equipped with magnetic stirrer, condenser, and thermometer under dry N₂. The amounts of the starting materials were calculated, and the target NCO content of the prepolymers was selected to be 6%, because orienting experiments showed too violent reaction with 9% NCO of the PIB prepolymers. The synthesis conditions for the three polyols were somewhat different as dictated by the viscosity and reactivity differences of these starting materials. In the case of the PIB-triol, methylene chloride (about the same amount as the PIB-triol) was added to reduce viscosity and FOMREZ C-7 (1% on PIB-triol) catalyst was added. The NCO content of the prepolymer was determined as follows: A small amount of carefully weighed prepolymer (~ 0.2 g) was placed in a stoppered 250-mL Erlenmeyer flask and 20-mL di-*n*-butylamine in chlorobenzene solution (~ 0.1*N*) were added immediately by a pipet. The sample was completely dissolved by shaking, and it was stored at room temperature for 1 h to insure complete reaction of the isocyanate with the di-*n*-butylamine. After adding 60 mL methanol and 5 drops of indicator solution, the excess di-*n*-butylamine was back-titrated with 0.1*N* HCl. According to ASTM D1638, the NCO content of the prepolymer is

TABLE I
 Characteristics of Polyols Used for the Synthesis of Prepolymer

Trade name and manufacturer	Main chain structure	\bar{M}_n^a	\bar{F}^b	Synthetic conditions			NCO content (%)
				Solvent used	Temp (°C)	Time (h)	
Polyisobutylene triol (PIB-triol, Akron Cationic Polymer Dev. Co.)	$\left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array} \right)_n$	7000 $\bar{M}_w/\bar{M}_n = 2.1$	3.0 ^c	CH ₂ Cl ₂	45	19	5.7
Polyether triol (Voranol 3010, Dow)	$\left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2\text{CHO}- \\ \\ \text{H} \end{array} \right)_n$	3650 $\bar{M}_w/\bar{M}_n = 1.7$	3.0 ^c	CH ₂ Cl ₂	55	17	5.6
Hydroxyl-terminated polybutadiene (R-45HT, ARCO)	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-$	3000	3.0	—	55	18	5.6
		2800	2.3	—	50	2	5.7

^a By VPO.

^b \bar{F} = number average end functionality calculated from \bar{M}_n values (by VPO) and OH no. values provided by company pamphlets.^{10,11}

^c By IR.

TABLE II
 Polyurethane Foam Formulation

Raw materials	Polyisobutylene-based PUF		Polyether-based PUF	Polybutadiene-based PUF
	$\bar{M}_n = 7000$	$\bar{M}_n = 3650$		
	(parts by weight)			
Prepolymer	100	100	100	100
Silicone surfactant ^a	0.2	1.5	1.8	1.0
Triethylene diamine ^b	3.0	3.0	2.5	2.0
Water	1.16	1.14	1.15	1.16
CH ₂ Cl ₂	5.0 ^d	4.6 ^d	3.0	5.0
THF	5.6	3.5	—	—
TDI index ^c	105	105	105	105
Mixing time (s)	7-9	10	10	10
Curing	10 min	8 min	5 min	5 min
	room temp and 10 min 55°C	room temp and 10 min 55°C	room temp and 3 min 55°C	room temp and 3 min 55°C
Mold preheat (°C)	55	55	55	55

^aDow Corning 5043.

^bAir Products and Chemicals DABCO 33LV.

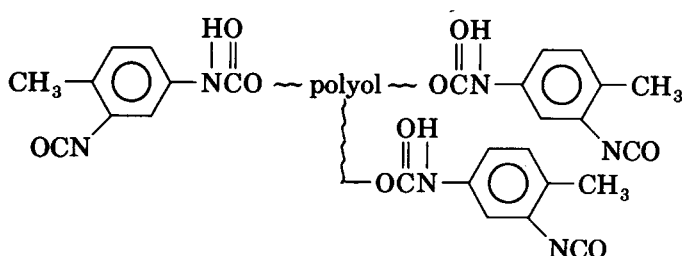
^cTDI index = (the amount of TDI/theoretical required amount of TDI) × 100; TDI index of conventional polyether-based PUF = 103-107.

^dThe total amount of CH₂Cl₂ includes CH₂Cl₂ of prepolymer.

given by

$$\text{NCO (\%)} = \frac{[(B - S) \times N \times 4.202]}{W} \quad (1)$$

where B = HCl (mL) required for titration of the blank, S = HCl (mL) required for titration of the sample, N = normality of the HCl, and W = weight of sample (g) used. The results are shown in Table I. The NCO contents of the prepolymers were less than 6%, evidently every OH end group has reacted with TDI:



In case of the PIB prepolymer, most of the solvent was evaporated by blowing dry N₂ into the system. The final solvent content was less than 5%. The foam cells may collapse and become undesirably coarse, if the prepolymer contains sizable quantities of solvent. Table II shows the formulations used. The foams were synthesized manually as follows: Six grams prepolymer were poured in a small aluminum dish (diameter 4.5 cm, depth 1.8 cm) and predetermined amounts of solvent (THF and CH₂Cl₂ with PIB-PUF and CH₂Cl₂ with PE-PUF and PBD-PUF) were added to reduce viscosity. The system was mixed by a glass rod. In experiments with PE-PUF and PBD-PUF first the silicon surfactant was added and mixed by a glass rod, and then a mixture of

DABCO-33LV/water was added by a microsyringe. In experiments with PIB-PUF, first the catalyst and the silicon surfactant were added and mixed by a glass rod, then a 2/1 mixture of water/THF was added by a microsyringe. The THF was used to effect the miscibility between water and the PIB-triol. The difference in the raw materials' addition was dictated by the character of the polyols, i.e., miscibility and viscosity. Finally, the systems were mixed by a high speed (~ 5000 rpm) stirrer for ~ 10 s at room temperature and poured on a Teflon-coated glass plate ($20 \times 20 \times 0.15$ cm). Another identical glass plate was placed on this "cream" as soon as feasible. The thickness of the foam was controlled by spacers. Before use, the glass plates were heated in an oven at 55°C to avoid skin formation on the cream. The foams were cured at room temperature until they almost set and were then further cured in an oven at 55°C . Curing times are shown in Table II. Finally the glass plates were removed, and the foams cured at room temperature for at least 1 week before characterization studies.

Foam Characterization Methods

IR spectra were run on a Beckman Model FT 2100 instrument equipped with a Spectra Tech Model 300 ATR (attenuated total reflectance) attachment. Extraction studies were carried out with THF. Samples were dried in a vacuum oven at room temperature overnight. Preweighed samples (1–2 g) were Soxhlet extracted with THF (24 h). After extraction the samples were dried at room temperature in a vacuum oven and weighed. Resilience (ball rebound) was determined by a ball rebound tester. This tester consists of a 11 mm inside-diameter vertical clear glass tube in which a 8 mm diameter (2.0 g) steel ball is released from a height of 500 mm. The top of the ball was at 508 mm above the surface of the foam (it is most convenient to note the position of the top of the ball on rebound). Samples were 5 mm thick, and they were placed on a steel plate. Five specimens per sample were tested, and the average of five drops was calculated. The water permeation test was carried out by using a device shown schematically in Figure 1. The foam samples ($2 \times 1 \times 0.5$ cm) were placed at the bottom part between two parallel flat glass plates ($7.5 \times 2.5 \times 0.1$ cm). The glass plates and the foam sample were assembled tight by a silicone sealer. The gap between the two glass plates was 0.2 cm (spacer). In the upright position, water (dyed blue by bromophenol blue to facilitate observation) was poured into the device 5 cm above the surface of the foam. The time (in seconds) for the first drop of water to pass through the foams was determined at room temperature. Tensile strength was measured by an Instron tabletop model instrument at 25°C and microdumbbells ($5 \times 0.25 \times 0.5$ cm) at a strain rate of 5 cm/min. The averages of 10 specimens per sample are reported. Air oven aging and hydrolytic stability were determined according to ASTM D3574. Specifically, air oven aging was determined by suspending samples in air oven for 22 h at 140°C , then cooling to room temperature and measuring the tensile properties. The percent change in physical property was calculated. The experimental and control specimens were stamped out from the same samples. Hydrolytic stability was determined by suspending samples in steam (100°C) for 3 h, then drying them for 3 h in an air oven at 70°C , and then cooling to room temperature and measuring the tensile properties.

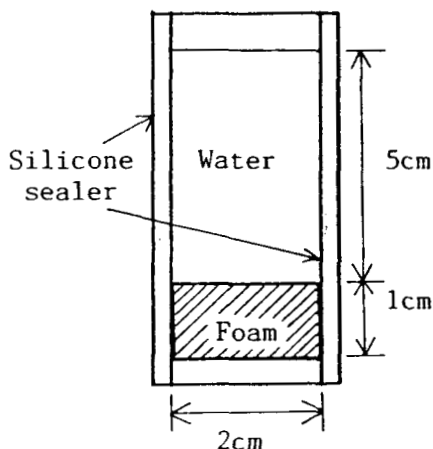


Fig. 1. The device for water permeation test.

The satisfactory dispersion of water and prepolymer is of paramount importance for good foams. Initial difficulties created by the relatively high viscosity and hydrophobicity of the PIB prepolymer have been overcome, and good foams were obtained. Initially THF, which is miscible with water and is a good solvent for the PIB prepolymer, was only used to reduce the viscosity of the system and to improve dispersion. However, when sufficient amounts of THF were added to reduce the viscosity, it was difficult to remove this solvent rapidly because of its relatively high boiling point ($bp_{760} = 66^{\circ}\text{C}$), and due to residual THF in the PU gel the cells collapsed before the foam could set. In contrast, CH_2Cl_2 ($bp_{760} = 39.8^{\circ}\text{C}$) gave good viscosity reduction, but it is a poor solvent for water. Thus THF/ CH_2Cl_2 mixtures were used to reduce the viscosity and to improve dispersion. The required amount of water in this system is so small (~ 1.2 parts by weight), compared with those of conventional urethane foams (3–4 parts by weight), that even the mixed solvent can bring about satisfactory viscosity reduction and dispersion.

The extent of crosslinking was checked by infrared spectroscopy and extraction. Figure 2 shows the ATR-IR spectrum of a representative foam. The absence of absorptions at 3640 and $2270\text{--}2240\text{ cm}^{-1}$ characteristic of OH and NCO groups and the presence of absorptions at 1640 and 1700 cm^{-1} (CO

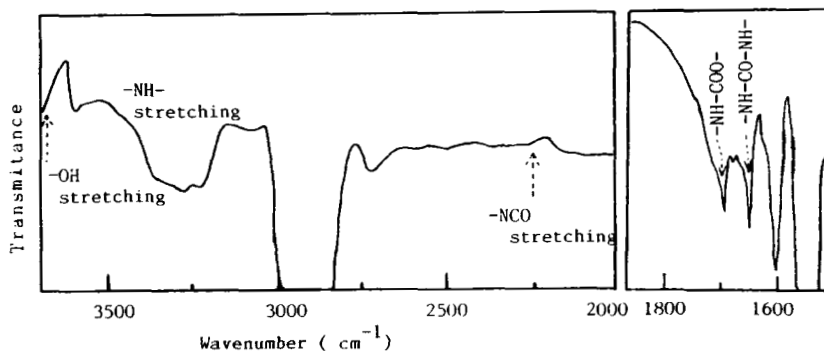


Fig. 2. Infrared spectrum of polyisobutylene-based polyurethane foam (by ATR).

TABLE III
 Properties of Polyurethane Foams

Properties	Polyisobutylene-based PUF		Polyether-based PUF	Polybutadiene-based PUF
	$\bar{M}_n = 7000$	$\bar{M}_n = 3650$		
Density (kg/m ³)	92	98	124	119
Cell size (no./in.)	40-50	40-50	50-60	40-50
Extractables by THF (%) ^a	1.5	5.6	0.1	3.7
Tensile strength (kPa)	117	243	84	222
Elongation (%)	124	106	130	124
Resilience (ball rebound) (%)	3.9	8.3	12.5	34.7
Water permeability (s)	13,300	57,900	55	170
Hydrolytic stability ^b				
Deterioration of tensile strength (%)	-1.7	-5.4	-9.5	-15.3
Deterioration of elongation (%)	-0.8	-3.3	-8.1	-13.8
Hot air stability ^c				
Deterioration of tensile strength (%)	-3.4	-2.4	-2.4	-64.9
Deterioration of elongation (%)	-5.6	-5.6	-4.8	-79.2

^a Extractables exclusive additives, such as catalyst and surfactant.

^b Aging at 100°C at 100% RH for 3 h (ASTM D3574).

^c Aging at 140°C for 22 h (ASTM D3574).

groups) characteristic of urea and urethane groups, respectively, indicates polyurethane and polyurea formation.¹⁶

The results of extraction studies are shown in Table III. The low extractables indicate essentially complete crosslinking.

Urethane Foam Characterization

Density and Cell Size. The data are shown in Table III. The densities are much higher than those of commercial urethane foams (15-35 kg/m³) because of the small amount of water used in foaming. The cell sizes are small enough (40-60 cells/in.) to obtain meaningful physical property data. However, cell distributions are less uniform than those exhibited by machine-made foams.

Stress-Strain Properties. Stress-strain properties of foams are compiled in Table III, and Figure 3 shows the stress-strain curves. These properties are markedly dependent upon foam density and somewhat affected by cell size. Generally tensile strength and elongation increase with increasing density and decreasing cell dimension.¹⁷ While it is very difficult to compare tensile strengths and elongations of the foams having different densities, some cautious generalizations can be made. Thus while the density of PIB-PUF is much lower than that of PE-PUF, the former is still much stronger than the latter. Evidently the stress-strain properties of PIB-PUF are much superior to those of the conventional PE-PUF. In contrast, the tensile strength of

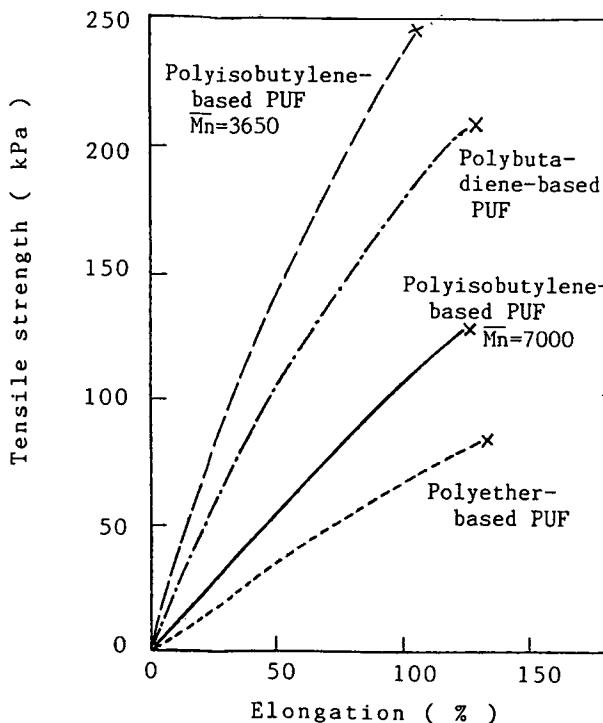


Fig. 3. Stress-strain curves of polyurethane foams.

PIB-PUF is somewhat lower than that of PBD-PUF in view of the difference of densities.

In regard to molecular weights, the \bar{M}_n of PIB-triol ($\bar{M}_n = 7000$) was much higher than those of the other polyols used ($\bar{M}_n = 2800, 3000$). Generally tensile strengths increase with decreasing molecular weights of PIB-triols in polyurethane elastomers.⁵ Thus, had we used a lower molecular weight PIB-triol, we would have obtained much higher tensile strengths. The elongation of the PIB-PUF is almost the same as those of the other foams. Tensile strengths and elongations of these foams seem to be less than those of commercial polyurethane foams. Considering that these foams were hand-made and commercial polyurethane foams are machine-made, their lower tensile properties becomes understandable.

Resilience (Ball Rebound). Resilience data are shown in Table III. The resilience of PIB-PUF is much lower than those of the other polyurethane foams. The low resilience of PIB-PUF is due to the polyisobutylene moiety. It is well known that the PIB chain has a strongly delayed elastic response to deformation.¹⁸ These good damping characteristics would render PIB-PUFs promising shock absorbers.

Water Permeability. Water permeability characteristics are compared in Table III. The time required to pass water through PIB-PUF is very much longer than those for the other foams. This extremely low rate of water permeation is caused by the highly hydrophobic nature of PIB. Machine-made

more uniform cell size materials would be expected to exhibit even lower permeability, and could yield interesting insulators and sealants.

Hot Air Stability. Thermal stabilities of the foams were compared by ASTM D3574 using a circulating air oven at 140°C for 22 h, and the results are summarized in Table III. The retention of mechanical properties of PIB-PUF after hot air exposure is very good. The hot air stability of PIB-PUF is virtually the same as that of PE-PUF and is far superior to PBD-PUF. In view of the saturated structure and good chemical resistance of polyisobutylene, the good hot air stability of PIB-PUF is not surprising.

Hydrolytic Stability. Hydrolytic stabilities of the foams were determined, and the results are shown in Table III. In contrast to the other foams, after exposure to wet steam for 3 h the change in tensile properties of PIB-PUF is negligible. Such a high hydrolytic stability is due to the highly hydrophobic nature of the PIB chain, which protects the urethane linkages from attack by moisture. Interestingly, the hydrolytic stability of PBD-PUF is much lower than that of PIB-PUF in spite of the hydrophobic nature of the PBD chain. This low hydrolytic stability of PBD-PUF is likely caused by its low thermal stability even at 100°C.

Gas Permeability. Attempts have been made to determine the gas permeabilities of our foams (ASTM D 1434); however, due to the open-cell nature of our samples, satisfactory vacuum could not be maintained, and these studies remained unsuccessful. We anticipate very low gas permeability of closed-cell rigid PIB-PUFs or high density PIB-based sponges; after all IIR (butyl

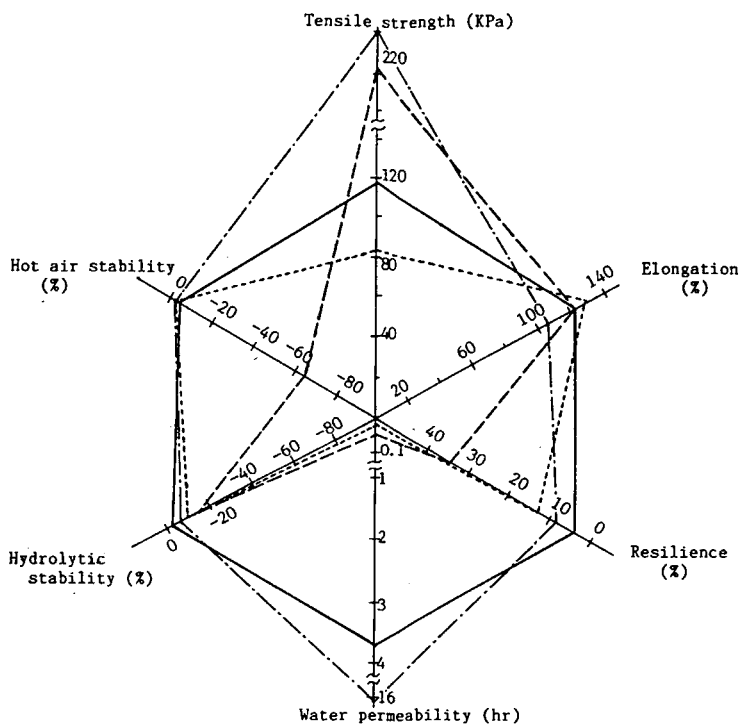


Fig. 4. The physical properties of urethane foams: (—) PIB-PUF, $\bar{M}_n = 7000$; (---) PIB-PUF, $\bar{M}_n = 3650$; (···) PE-PUF; (-·-·) PBD-PUF.

rubber, a copolymer of isobutylene, and a very small amount of isoprene) is one of the best barrier rubbers known.

CONCLUSIONS

The results of physical property evaluations of three foams are pictorially combined in Figure 4. This figure shows at a glance the characteristics of PIB-PUF compared with the other foams. The combination of outstanding barrier, thermal, oxidative, and hydrolytic properties together with the good mechanical properties of PIB-PUF may render this material useful for a variety of applications as sealants, insulators, shock-and-vibration absorbers, etc.

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