POLYM.–PLAST. TECHNOL. ENG., 37(1), 103-113 (1998)

# PREPARATION AND EVALUATION OF POLYURETHANE FOAM/RUBBER MEMBRANE-BASED SAMPLERS FOR USE IN ISOCYANATE SAMPLING

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**Abstract**

In order to collect isocyanate in both aerosol and vapor forms, we have developed a dual-membrane sampler which features a moist porous bed, backed up by an impermeable membrane. A polyester–polyurethane foam (PUF) was selected to function as the porous bed, and it was evaluated for its ability to resist solvent

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degradation and swelling while permitting rapid air penetration. Natural rubber (NR) and styrene-butadience rubber (SBR) membranes were prepared to serve as backup membranes. These were also evaluated for their solvent compatibility and air-penetration characteristics. A polyester–polyurethane foam backed up by a NR membrane prepared by an efficient vulcanization procedure was selected as the best combination for development of the isocyanate sampler. Recovery studies using the hexamethylene-based polyisocyanate, biuret, indicate better than 80% recovery of polyisocyanate after application to the PUF.

## INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) has been looking for alternative sampling methods to collect isocyanate monomer and oligomers generated during polyurethane spray-painting operations. The presently accepted analytical methods use an impinger filled with either 1-(2-methoxyphenyl) piperazine in toluene [1], tryptamine in dimethylsulfoxide [2], or a new method which employs 1-(9-anthracenyl methyl) piperazine as the derivatizing reagent [3]. An alternative dry-sampling method has also been developed which uses a dual-filter cassette consisting of a 5-μm PTFE filter backed up by a glass-fiber filter impregnated with 9-(methylaminomethyl) anthracene [4]. The latter method has been approved for use in Quebec since 1987, although it has the potential to give a low recovery of derivatized isocyanate if the isocyanate reacts before the derivatizing reagent can be added to the 5-μm PTFE filter.

In an effort to devise a convenient method which alleviates the spilling problems associated with an impinger, yet allow for an accurate determination of the polyisocyanate aerosol, we have developed a novel solid-sorbent sampler which consists of a microporous polyester–polyurethane foam (PUF) backed up by an ultrathin (0.2 mm) elastomer membrane supported on an aluminum mesh screen. This assemblage is similar to other prototype asymmetric composite membranes [5,6]. The polyurethane is mechanically stable, resistant to solvent, and penetrable to air, and is an efficient trap for isocyanate aerosol; whereas the backup membrane allows air to flow with a sufficient linear velocity (at least 0.5 L/min) in order to capture particles in the respirable range (up to 10 μm) while remaining impermeable to solvent, derivatizing

reagent, and isocyanate vapor swept from the support bed. The aluminum mesh provides the membrane assembly with a support in order to prevent collapse. The assembly is similar to the ORBO 1000 PUF cartridge and filter cartridge assembly [7].

## EXPERIMENTAL

### Materials

All polyurethane sponges were obtained from Polyplastics (Austin, TX). The polyester-type polyurethane (PUF) sponge (4#CE) chosen for further evaluation was in the form of a 2-in.-thick, 12-in. × 12-in. block. The natural rubber (NR) was ISNR-5 grade (M.W. = $10^5$) obtained from the Rubber Research Institute of India (Kottayam, India). Styrene-butadiene rubber (SBR) with a bound styrene content of 21.5–25.5% (M.W. = $10^4$) and a polydispersity index of 1.4 was obtained from Synthetics and Chemicals (Bareilly, UP, India). The same lots of NR or SBR were used throughout. Viton was obtained from DuPont (courtesy of Bill Stahl) and membranes were fabricated as previously described [8]. Viton membranes were used as gasket materials. The aluminum mesh screen (1 $mm^2$ openings) was obtained at Ace Hardware and cut to fit. Asbestos samplers were obtained from Nucleopore (Pleasanton, CA).

### Sponge Evaluation

Ten open-celled, porous PUF sponges were cut into cylinders and then soaked overnight in 2-propanol, dioxane, dimethylsulfoxide (EM Science), acetonitrile [high-performance liquid chromatographic (HPLC) grade, EM Science], butylbenzoate (Fluka), and tributylphosphate (Aldrich). All of these solvents were at least reagent grade. Only those sponges which maintained their mechanical rigidity and did not react with solvent were deemed suitable for further study.

### Membrane Fabrication

Four formulations which differ in the amount and type of vulcanizing agent were used. These formulations have been designated as (1) "conventional," which uses about 1.5–2.0% sulfur, (2) "efficient," which uses about 0.6% sulfur and 1% tetramethylthiuram disulfide, (3) "per-

oxide," which uses about 4% dicumyl peroxide, and (4) "mixed," which incorporates both sulfur and peroxide. Weights of additives are based on the dry rubber content and were incorporated into the dry rubber matrix by a two-roll mixing mill (friction ratio 1:1:4). The formulations for the NR and SBR membranes are given in Table 1.

All the membranes were prepared by a compression-molding technique which involved vulcanization at 160°C under a pressure of 30 tons in a hydraulic press with electrically heated plates. The membranes were heated until cured, as determined by an oscillating disk rheometer (Monsanto Rheometer R-100). The surface tack was eliminated by pressing the sample at 120°C for 2 min between two sheets of aluminum foil in a hydraulic press.

**TABLE 1**
**Composition in Parts per Hundred of NR and SBR membranes**

| Ingredients | Method type | | | |
|---|---|---|---|---|
| | Conventional | Efficient | Peroxide | Mixed |
| | Natural Rubber | | | |
| Natural rubber (ISNR-5 grade) | 100 | 100 | 100 | 100 |
| Stearic acid | 1.5 | 1.5 | — | 1.5 |
| Zinc oxide | 5 | 5 | — | 5 |
| Sulfur | 2 | 0.6 | — | 1.5 |
| Dicumyl peroxide | — | — | 4 | 1.5 |
| Tetramethylthiuram disulfide | — | 1 | — | — |
| *N*-Cyclohexyl-2-benzothiazyl sulfenamide | — | 1.5 | — | — |
| Morpholinebenzothiazyl sulfenamide | 0.6 | — | — | 0.6 |
| | Styrene-Butadiene Rubber | | | |
| SBR-1502 | 100 | 100 | 100 | 100 |
| Stearic acid | 2 | 2 | 100 | 100 |
| Zinc oxide | 5 | 5 | — | 5 |
| *N*-Cyclohexyl-2-benzothiazyl sulfenamide | 1 | 2 | — | 1 |
| Dicumyl peroxide | — | — | 4 | 2 |
| Sulfur | 2.2 | 0.5 | — | 1.5 |

A total of 53, 4-in. × 6-in. membrane sheets were prepared for testing purposes. Mill shrinkage of the membranes was determined on a piece of compounded sheet as per ASTM standard method D-1917-89. Film thicknesses were determined using a micrometer (Welch Scientific, Chicago, IL) with a range of 0–25 mm and 0.01-mm precision.

### Solvent Diffusion into NR and SBR Membranes

The solvent resistivity for NR and SBR membranes, prepared by the efficient technique (AB1 to AB6 membranes, P1 and P2), was determined by calculating diffusion coefficients based on data obtained using a solvent uptake method [8].

### Sampler Preparation

The PUF sponge was cut into cylinders (2.5 cm in diameter by 5.0 cm in height) using a sharp-edged carbon-tipped die (hole saw, $1\frac{1}{8}$ in., Fort Worth, IN). The cylinders were cut to a height of 2.5 cm, soaked overnight in a solution of acetonitrile in order to remove impurities, dried in air, soaked in acetonitrile or tributylphosphate, then squeezed repeatedly until just moist.

The NR and SBR backup membranes, aluminum mesh screen, and Viton membranes were also cut to a diameter of 2.5 cm with the same die. The inside of the Viton membrane was cut out to an inner diameter of 1.5 cm with a pair of scissors so that it could function as a gasket.

The cellulose acetate filter was removed from the Nucleopore asbestos sampler, the membrane was positioned on the aluminum mesh screen, secured with the Viton gasket, and then the entire assembly was mounted within the Nucleopore cassette. The PUF sponge was then positioned on top of the gasket. The cassette halves were adjusted for maximum airflow without puckering of the membrane, and the halves firmly secured with Teflon tape.

### Air-Penetration Studies

A simple experimental apparatus was constructed consisting of a mercury manometer attached to the sampler, which was then attached to the ALPHA-1 constant-flow pump. After the pump was turned on, the mercury level was allowed to rise in the manometer. Those membranes in which the mercury level was the same (within 10%) both in the

presence and in the absence of a membrane were deemed to have sufficient air penetration through the cassette to undergo further evaluation. Twenty-four out of 53 membranes after installation into a Nucleopore cassette passed the initial screening and were further evaluated for their ability to allow airflow.

An ALPHA-1 constant-flow pump (Dupont Nemours) operable between 5 and 5000 $cm^3$/min was set to 1000 $cm^3$/min and then calibrated to 1.0 L/min (±0.1 L/min) using a Buck calibrator (A.P. Buck, Inc., Orlando, FL). The instrument provides true constant-flow operation within 5% over its entire flow-rate range. The pump was set to turn off after 2 min of restricted flow. Relative airflow penetration (efficiency) was measured with the Buck calibrator by determining the ratio of airflow after and before attachment of the modified Nucleopore sampler into the sampling train. Measurements were repeated and fell within a 2% relative standard deviation from the mean.

## Reagents and Instrumentation Used for Recovery Studies

1-(2-Methoxyphenyl)piperazine (MOP) was obtained from Fluka. Desmodur N-75, which is 75% hexamethylene-based polyisocyanate in xylene and which contains 35–40% biuret trimer of HDI (Material Safety Data Sheet), was obtained from Bayer (Pittsburgh, PA). All other chemicals and solvents were reagent grade or better.

The HPLC system consisted of a Beckman 110B solvent delivery system, an Altex 210A sample injector, and a Beckman 160 absorbance detector operated at 254 nm. A LC-8-DB 3 μ (7.5 cm × 4.6 mm) column (Supelco, Bellefontane, PA) and 40/60 acetonitrile/methanolic buffer (pH = 6.0) mobile phase were used for analyzing the MOP derivatives. The injection volume of sample was consistently 5 μl.

## Preparation of Standards for the Recovery Studies

A standard 833–1100-μg/ml stock solution of the polyisocyanate was prepared by mixing about 0.025 g of Desmodur N-75 in 25 ml of toluene with 0.050 g of MOP derivatizing reagent in 25 ml of toluene. The two reagents were allowed to react overnight. Then, 70 μl of acetic anhydride were added the next day in order to acetylate any excess derivatizing reagent. The solution was evaporated to dryness and reconstituted to 5.0 ml with acetonitrile. Working standards were prepared by serial dilution from the stock and ranged from 2 to 1000 μg/ml.

### Recovery Studies

The polyester–polyurethane sponge (#4 CE) was soaked in a derivatizing reagent solution made by dissolving 4.3–12.0 mg of MOP in 100 ml of acetonitrile or tributylphosphate. The sponge was squeezed until just moist, which corresponds to approximately 800–1100 μl of the derivatizing solution in the sponge. The sponge was then positioned within either a 1-dram vial or within the sampler after assembly of the cassette (*vide supra*).

Variable amounts of polyisocyanate (ranging from 40 to 560 μg of Desmodur N-75) were added to the sponge. After 15–120 min, the sponge was soaked with 0.0, 4.3, or 12.0 mg of MOP in 100 ml of acetonitrile, massaged repeatedly, and an aliquot then removed from the saturated sponge. Then 25–60 μl of acetic anhydride was added, the solution was filtered through a 0.45-μ Nylon filter to remove any particulates, and concentrated to a final volume of 2–14 ml. The final theoretical concentration of polyisocyanate ranged from 10 to 40 μg/ml.

## RESULTS AND DISCUSSION

None of the dry polyurethane sponges impeded airflow. Of 10 polyurethane sponges, only 3 maintained their mechanical integrity after soaking in dimethylsulfoxide or toluene. Of these three, the polyester–polyurethane sponge (#4CE) was the most resilient and had a solvent uptake of three to five times the weight of sponge; it was therefore chosen for all subsequent studies. This sponge was further evaluated for its stability in other solvents (i.e., 2-propanol, dioxane, tributylphosphate, and butylbenzoate). In each case, the sponge remained intact and did not impede airflow when moist.

We found that 16 of our 53 membranes did not impede airflow substantially or turn off the pump. The results are given in Table 2.

Six natural rubber membranes AB1, AB2, AB3, AB4, AB5, and AB6, vulcanized by the efficient technique for ½h and dried for 24 h, produced good airflow rates after insertion into the sampler. Although the mixing composition of these membranes did not vary, they did vary in thickness within a narrow range (0.22 ± 0.03 mm). The AB5 membrane exhibited the highest airflow rate efficiency of 90%, whereas AB3 and AB6 had the lowest (about 72%). The airflow rates decrease by less than 5% when the PUF sponge is inserted in front.

**TABLE 2**
**Airflow Test Results and Solvent Diffusion Coefficients for Select Membranes**

| Membrane | Thickness (mm) | Flow rate[a] (L/min) | Efficiency (%) | Diffusion coefficient ($\times 10^7$ cm$^2$/sec) DMSO | *t*-Butyl-benzene | Toluene | DMF |
|---|---|---|---|---|---|---|---|
| *AB1 | 0.25 | 829(±23) | 82 | 1.82 | 2.12 | 2.68 | 1.99 |
| AB2 | 0.19 | 811(±17) | 80 | 1.78 | 2.02 | 2.61 | 1.97 |
| AB3 | 0.22 | 690(±10) | 71 | 1.79 | 2.00 | 2.56 | 1.92 |
| AB4 | 0.24 | 859 | 87 | 1.78 | 1.95 | 2.50 | 1.88 |
| AB5 | 0.24 | 890 | 90 | 1.76 | 1.96 | 2.48 | 1.85 |
| AB6 | 0.20 | 773(±15) | 72 | 1.75 | 1.90 | 2.42 | 1.81 |
| P2 | 0.15 | 770(±90) | 83 | 2.04 | 3.42 | 3.64 | 2.21 |
| P3 | 0.22 | 890(±40) | 84 | 2.01 | 3.35 | 3.60 | 2.12 |
| P4 | 0.16 | 644 | 63 | — | — | — | — |
| R1 | 0.22 | 977 | 87 | | | | |
| S3 | 0.15 | 854 | 86 | | | | |
| S4 | 0.22 | 705 | 71 | | | | |
| Q1 | 0.17 | 508 | 51 | | | | |
| Q2 | 0.17 | 806(±14) | 80 | | | | |
| Q4 | 0.21 | 784(±06) | 78 | | | | |
| Q5 | 0.14 | 937 | 90 | | | | |

[a] The value in parentheses indicates the absolute variation in flow rate observed for each backup membrane.

Unfortunately, none of the NR membranes prepared by conventional, peroxide, or mixed techniques, even for the thinnest membranes, allowed at least a 50% airflow efficiency.

Some of the SBR membranes, vulcanized by the efficient technique for 1 h and then dried for 24 h, worked well: P2, P3 and P4 (see Table 2). The average airflow rate efficiency for the P2 and P3 membranes was 84%, whereas for P4, the efficiency was 63%.

Four out of five SBR membranes prepared by the conventional technique and designated as Q1, Q2, Q4, and Q5 gave airflow rate efficiencies ranging from 90% to 51%. Of the peroxide-cured SBR membranes,

only R1 exhibited a high efficiency of 87%. Of the five SBR latex membranes prepared by the mixed method, S3 and S4 gave efficiencies of 86% and 71%, respectively.

Diffusion coefficients for several solvents into NR and SBR membranes prepared by the efficient technique (AB1 to AB6 and P1 and P2) are reported in Table 2. Diffusion coefficient data were not obtained for the other membranes. The diffusion coefficient values are low, ranging from about $1.8 \times 10^{-7}$ cm²/sec for DMSO in NR up to a high of $3.6 \times 10^{-7}$ cm²/sec for toluene into SBR. Within the sampling interval of 15 min, DMSO and DMF did not break through the nominal 0.2-mm membranes, whereas toluene was observed to swell both the NR and SBR membranes.

Recovery studies using a sampler sponge (#4 CE) moistened with a solution of 43 mg/L of MOP in acetonitrile yielded 62.2% (standard deviation = 2.8%, $n = 3$) of the theoretical amount of Desmodur N-75 added to the sponge (167 μg). Varying the amount of Desmodur N-75 added to the sponge so that the final concentration was in the range

**TABLE 3**
**Biuret Recoveries from Polyester–Polyurethane Foam/Natural Rubber (ABI) Dual Membrane Sampler**

| Concentration (μg/ml) | Integrated peak area[a] | Percent recovery (%) |
|---|---|---|
| 10 | 987 ± 46 | 98 |
| 10 | 834[b] | 82 |
| 20 | 884 ± 144 | 60[c] |
| 20 | 1325 ± 39 | 91 |
| 30 | 1494 ± 110 | 71 |
| 30 | 1675 ± 65 | 80 |
| 40 | 2028 ± 59 | 86 |
| 40 | 2767 ± 21 | 117 |

*Note*: PUF has been moistened with a solution of 120 mg/L of MOP in tributylphosphate. The sample is extracted with 120 mg/L of MOP in acetonitrile.

[a] Integrated peak area is the average of three runs.
[b] Single run.
[c] Sample leaked.

10.0–34.4 μg/ml yielded percent recoveries which varied from 83.0% to 112.4% ($n$ = 4). For the second set of samples, the sponge was soaked after 15 min with a solution of MOP in acetonitrile. This step is critical for improving the recovery, as it promotes a better reaction between the polyisocyanate and the derivatizing reagent and limits the possibility that the polyisocyanate will react with atmospheric moisture and other interferents. If soaking of the sponge is delayed, the recovery decreases gradually by about 15% over a period of 2 h. An analogous step which involves soaking a PTFE membrane after collection of the isocyanate is also used by Lesage et al. [4] in their sampling protocol.

Recovery studies were also performed using the PUF/AB1 backup membrane in a Nucleopore cassette sampler. The PUF was moistened with a solution of 120 mg/L of MOP in tributylphosphate Table 3 gives the results of this recovery study. Tributylphosphate is less volatile than acetonitrile and therefore keeps the sponge moist at airflow rates on the order of 1 L/min. As can be seen from Table 3, the results range from a low of 71% (excluding the sample that leaked) to a high of 117%. The average percent recovery is 86%, with a standard deviation of 17% (relative standard deviation of 20%).

## CONCLUSIONS

A polyester–polyurethane membrane (#4 CE obtained from Polyplastics) moistened with 1-(2-methoxyphenyl) piperazine in acetonitrile or tributylphosphate is suitable for the derivatization and subsequent recovery of reactive isocyanate. Natural rubber membranes prepared by an efficient vulcanization technique, and styrene-butadiene rubber membranes which are thin can be positioned within a polypropylene cassette and allow sufficient airflow, yet prevent solvent breakthrough so that they can function efficiently as backup membranes. The combination of polyurethane sponge followed by a thin elastomer membrane shows some promise as an effective dual-membrane combination for the entrapment and subsequent recovery of isocyanate. Although the PUF is viable and all the membranes are resistant to solvent, which is extremely important for their application as barrier materials, more work needs to be done in order to increase the percent recovery and improve the air penetration through and not around the backup membrane. Further investigations on improving the properties of the PUF bed and the development of new backup membranes are now in progress.

## ACKNOWLEDGMENTS

WER and TMA would like to thank the National Institute for Occupational Safety and Health (Grant No. R01OHO329501) for its support of this project.

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