

Hybrid Electrically Conductive Polyaniline/Polyurethane Foams

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Received 12 May 2000; accepted 3 August 2000

ABSTRACT: Electrically conductive polyaniline/polyurethane foams were prepared. The DC conductivity of the composite prepared at pH = 0.505 is about 0.9 S/cm. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 893–897, 2001

Key words: polyaniline/polyurethane foams; conductive composite

INTRODUCTION

This note concerns the DC conductivities of polyaniline salt (PANI) in the pores of two kinds of open-cell polyurethane foams. Some of these PANI-filled samples were good electrical conductors. Synthesized PANI¹ is a dark blue/black powder with little mechanical strength. The foams that are the carriers of PANI possess considerably better mechanical properties. The room-temperature DC conductivities of our samples of PANI/foam were determined for two kinds of foams, various sizes of the foams, and samples prepared at various polymerization conditions (change of H⁺ concentration).

EXPERIMENTAL

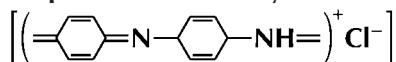
Preparation of Flexible Foam

The materials used are listed in Table I.

Procedure

The four components (Pluracol 1156, Voranol 3010, Niax Silicone L-620, and water) were weighed in a 1-L cup and were stirred for a few seconds until the foam formed a homogeneous mixture. The two catalysts, Dabco 33LV and Dabco T-9, were weighed, added to the mixture, and stirred until a homogeneous mixture was achieved. This mixture was component B. TDI was weighed in a separate cup (component A). Components A and B were mixed and stirred immediately for 6–8 s and the mixture was poured into a cake box. The cream time (15 s), the rise time (75 s), and the tack-free time (19 min) were recorded, after which the foam was placed in an oven at 100°C for 1 h.

Preparation of the Polyaniline Salt



in the Flexible Foam

Materials

Aniline and ammonium persulfate ((NH₄)₂ S₂O₈) were purchased from Aldrich Chemicals (Milwaukee, WI). Hydrochloric acid was purchased from

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Contract grant sponsor: National Science Foundation; contract grant number: DMR 9628224.

Journal of Applied Polymer Science, Vol. 80, 893–897 (2001)
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Table I Materials Used in the Preparation of Flexible Foam

Trade Name	Chemical Composition	Manufacturer	Parts by Weight
Pluracol 1156	Graft polyether polyol ^a	BASF	25.00
Voranol 3010	Polyether polyol ^b	Dow Chemical Co.	75.00
Niax Silicone L-620	Silicone surfactant ^c	OSi Witco	1.00
Dabco 33LV	Dipropylene glycol (67%) Triethylenediamine (33%)	Air Products and Chemicals, Inc.	0.30
Dabco T-9	Stannous octoate (97%) 2-Ethylhexanoic acid (3%)	Air Products and Chemicals, Inc.	0.25
Lupranate T-80	80/20 mixture of 2,4- and 2,6-toluene diisocyanate	BASF	57.56
Water			5.00

^a Graft (styrene/acrylonitrile) polyoxypropylene adduct of a triol.

^b Polyoxypropylene adduct of 1,2,3-propanetriol.

^c Polyalkyleneoxidedimethylsiloxane.

Pharmco (Brookfield, CT). Aniline was vacuum distilled under 20 mm pressure. Ammonium persulfate and hydrochloric acid were used without further purification.

Procedure

The basic procedure in Enzel and Bein¹ was followed. The flexible foam was immersed in aniline until the foam completely absorbed aniline. The foam samples were immersed in a mixture of hydrochloric acid of various concentrations and ultrapure water at 0°C, and an aqueous solution of ammonium persulfate was added to the stirred solution at a ratio of 1 : 4 oxidant to aniline. The solution was stirred for 2 h at 0°C and then allowed to warm up to 23°C for 12 h. The PANI/foam was washed with ultrapure water, then

dried at 80°C for 2 days. Samples of different sizes and different acid concentrations (1–5M) were prepared.

Preparation of Rigid Foam

The materials used are listed in Table II.

Procedure

Voranol 360 (100 g) was placed in a paper cup. DABCO DC-193 (2.8 g) was added and mixed with a drill mixer using a steel stirrer. The required amounts of catalysts (DABCO 33LV and DABCO T-12) and Ortegol 501 (surfactant) were added and blended with this mixture. Forane 141B (51 g) was added and mixed thoroughly. Immediately thereafter PAPI 27 (72 g) was added to the above system and mixed for 15 s.

Table II Materials Used in the Preparation of Rigid Foams

Trade Name	Chemical Composition	Manufacturer	Parts by Weight
Voranol 360	Propoxylated glycerol and propoxylated sucrose	Dow Chemical Co.	100
DABCO DC-193	Poly(oxyalkylene dimethylsiloxane) copolymer	Air Products and Chemicals, Inc.	2.8
Ortegol 501	Surfactant, cell opener	Goldschmidt Chemical Corp.	2.0
DABCO 33LV	Triethylenediamine in dipropylene glycol	Air Products and Chemicals, Inc.	2.0
DABCO T-12	Dibutyltin dilaurate	Air Products and Chemicals, Inc.	0.6
Forane 141B	1,1-Dichloro-1-fluoroethane	Elf-Atochem	51
PAPI 27	Poly(methylene) poly(phenylisocyanate)	Dow Chemical Co.	72

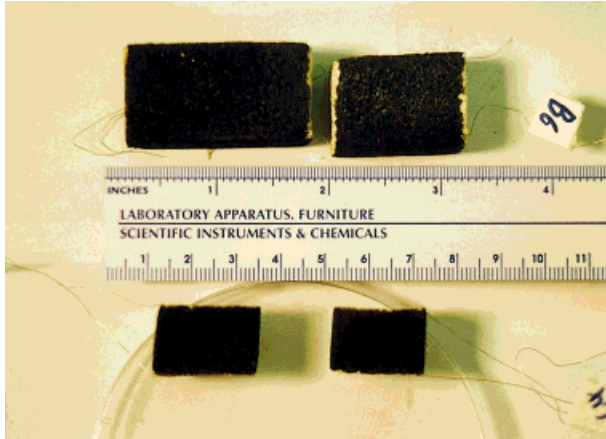


Figure 1 Photograph of PANI/flexible foam.

Preparation of the Polyaniline Salt in the Rigid Foam

The same materials and experimental procedure were used as in the preparation of the polyaniline salt in the flexible foam. Samples of different sizes were prepared.

RESULTS AND DISCUSSION

Phase Morphological Characteristics

The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens were mounted on stubs with silver paint. All the specimens for SEM were coated with platinum in a Hummer V

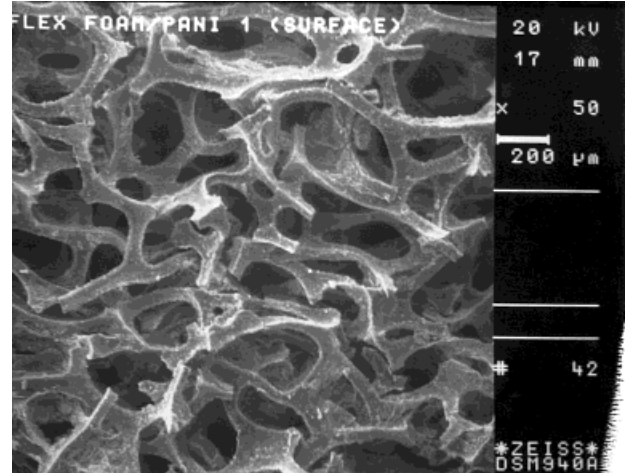


Figure 3 SEM micrograph of PANI/flexible foam.



Figure 4 Photograph of half-cut PANI/rigid foam.

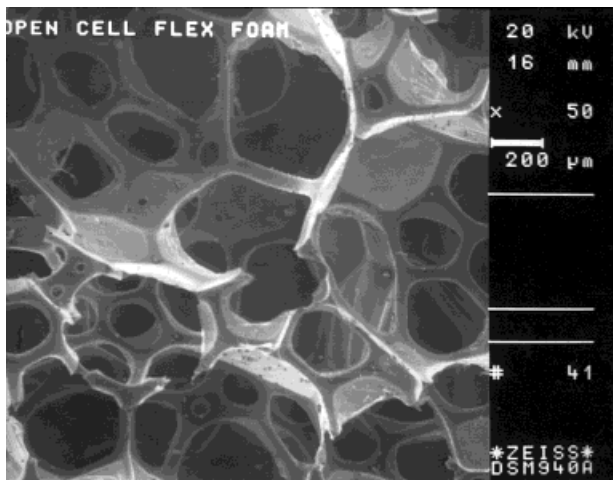


Figure 2 SEM micrograph of flexible foam.

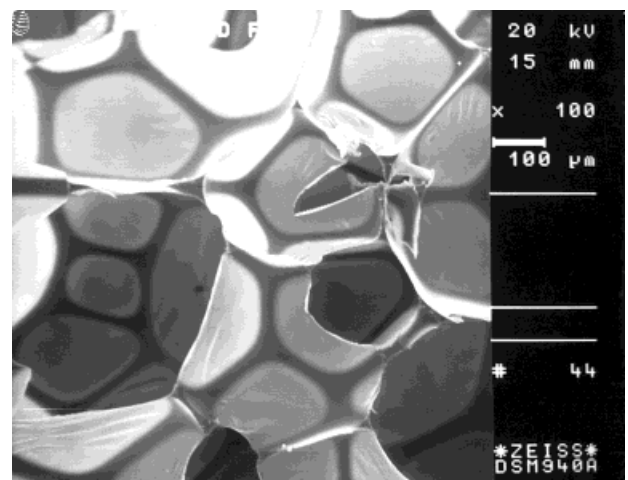


Figure 5 SEM micrograph of rigid foam.

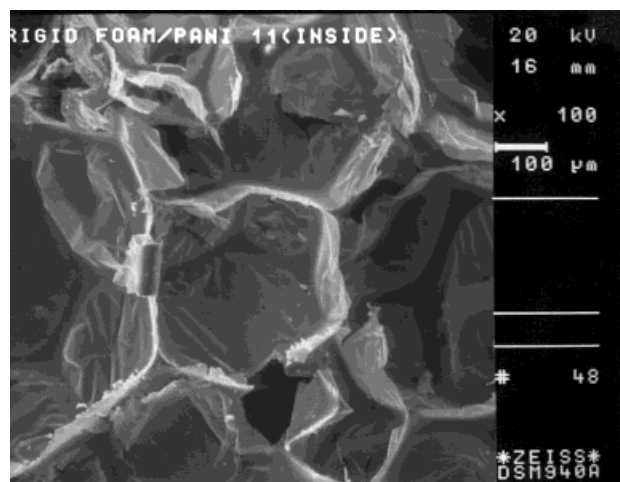


Figure 6 SEM micrograph of PANI/rigid foam (section taken from the inside of the sample).

sputter coater. They were then observed with a digital scanning microscope (DSM 940; Zeiss, Oberkochen, Germany) operating at a voltage of 20 kV. The electron images were recorded directly from the cathode ray tube on Polaroid 55 film. Figures 1–3 show that PANI could go through the pores of the flexible foam, forming a well-distributed layer inside the pores. On the other hand,

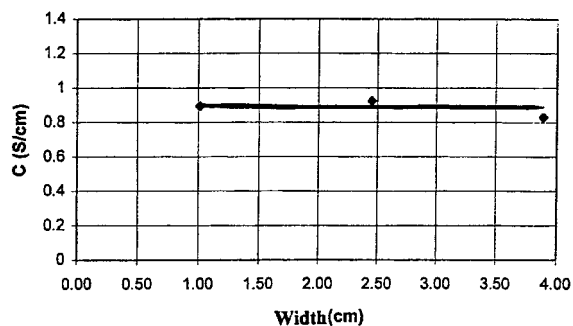


Figure 7 DC conductivity: width of PANI/flexible foam with the same area (3.23cm^2).

Figures 4–6 show that PANI did not fully percolate through all the pores of the rigid foam. Only a surface layer contained a high concentration of PANI. The interior of the samples had negligible amounts of PANI.

DC Conductivity

The two opposite sides of the foam with the same area were painted with silver paint purchased from Ernest F. Fullam (Latham, NY). Two pieces of copper wire were attached on each of the painted sides. The paint was dried at room tem-

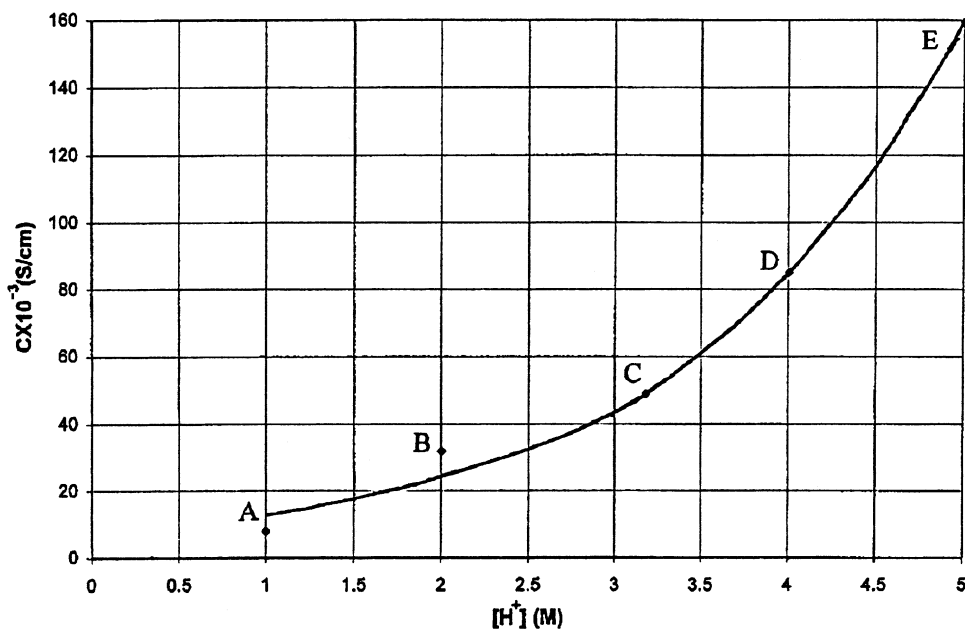


Figure 8 DC conductivity of PANI/flexible foam: acid concentration $[\text{H}^+]$. Point A: PANI/foam = 5.731 : 1 (wt); point B: PANI/foam = 1.575 : 1 (wt); point C: PANI/foam = 0.422 : 1 (wt); point D: PANI/foam = 0.484 : 1 (wt); point E: PANI/foam = 1.105 : 1 (wt)

Table III DC Conductivities of the PANI/Rigid Foam with the Same Area (6.74 cm²)

Sample No.	Width (cm)	PANI : Foam (wt)	σ (S/cm)
1	0.55	15.2 : 1	9.1×10^{-3}
2	0.62	16.0 : 1	6.8×10^{-3}
3	1.43	18.6 : 1	7.8×10^{-5}
4	1.71	16.8 : 1	3.2×10^{-6}
5	2.61	12.0 : 1	1.48×10^{-6}

perature for 2 h. A Fluka 70 series II multimeter (Fluka, Milwaukee, WI) was used to test the resistance between the two sides by touching only the two pieces of wire for each sample. The time lag between each measurement and the next one on the same sample was 5 min.

The DC conductivity of the PANI/flexible foam with the same area (3.23 cm²) and different widths is shown in Figure 7. This shows that the DC conductivities of the samples did not change appreciably with the size of the sample. The DC conductivities of the same size (2.00 × 1.00 × 2.20 cm) PANI/flexible foam with different HCl acid concentrations during polymerization are shown in Figure 8. The DC conductivities of the samples increased rapidly with increase of the acid con-

centration. We speculate that the acid concentration during polymerization influences the molecular weight of PANI. The weight-average molecular weight of the pure PANI was about 462,100. PANI could not percolate freely through the rigid foam. Thus, the DC conductivities that were measured (only the conductivities on the surface layer of the rigid foam samples) depended on the thickness of the conductive layer and the size of the sample (see Table III).

CONCLUSIONS

Clearly conductive hybrids of flexible polyurethane foams and PANI, which are much stronger than pure PANI films, can be prepared. A potential application for these hybrids is for packaging materials for electronic components because the static charges on the components can be conducted away. The pore system of the rigid foams does not allow for free percolation of the PANI through the samples.

This work was supported by NSF grant DMR 9628224.

REFERENCE

1. Enzel, P.; Bein, T. *J Phys Chem* 1989, 93, 6270.