

Preparation of Polypyrrole–Polyurethane Composite Foam by Vapor Phase Oxidative Polymerization

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SYNOPSIS

Conductive polypyrrole–polyurethane composite foam was prepared by vapor phase polymerization of pyrrole on polyurethane foam using mixtures of FeCl₂ and FeCl₃ as oxidants. With increase in the FeCl₂/FeCl₃ ratio, the conductivity of the composite foam increased in spite of the decrease in polypyrrole content in the composite foam. Both conductivity and polypyrrole content increased with increase in the oxidant content in polyurethane. The conductivity of the composite foam is also a function of reaction temperature, and lower reaction temperatures were preferable for higher conductivity. The composite foam exhibited tensile strength and elongation comparable to those of pristine polyurethane foam. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

There is a rapidly growing interest in electrically conductive polymers. Among these, polypyrrole (PPy) is one of the promising materials due to its easy preparation and relatively high stability in the air. However, PPy is, like many other conductive polymers, insoluble in any of ordinary solvents, and this limits its characterization and processing by conventional methods. The difficulty in processing PPy is also associated with its poor mechanical properties, and this strictly restricts its practical application as a conductive plastic or elastomer.

In order to improve mechanical properties and processibility of PPy, a number of composite materials of PPy have been prepared, especially the composites with other polymer materials such as poly(vinyl chloride)^{1–4} or polyamide.⁵ In the previous study, we reported the preparation of conductive composite foam by vapor phase polymerization of pyrrole on polyurethane (PUr) foam.⁶ Conductive PUr has been commercially produced by mixing carbon powder with PUr, and it has been used as antistatic plastic or elastomer. However, the content

of carbon in PUr should be high in order to obtain conductivity of 10⁻³–10⁻⁴ S/cm, which causes considerable decrease in mechanical strength of PUr. In contrast, it was found that the vapor phase polymerization of pyrrole on PUr foam containing iron (III) chloride gives conductive elastic composite of excellent mechanical properties comparable to the pristine PUr foam.⁶ In this study, we report the details of the effect of reaction conditions, especially the amount and composition of iron chlorides as oxidants, on the electrical and mechanical properties of PPy–PUr composite foam.

EXPERIMENTAL

Materials

Pyrrole was purchased from Tokyo Kasei Kogyo Co. Anhydrous iron (III) chloride (FeCl₃) and iron (II) chloride (FeCl₂) tetrahydrate were purchased from Wako Pure Chemical Industries, Ltd. These were used without further purification. Open cell PUr foam (CF-40, density 0.020 g cm⁻³) was a commercially available product of INOAC Co. which was composed mainly of a copolymer of poly(propylene oxide) (average molecular weight 3000) and toluene diisocyanate.

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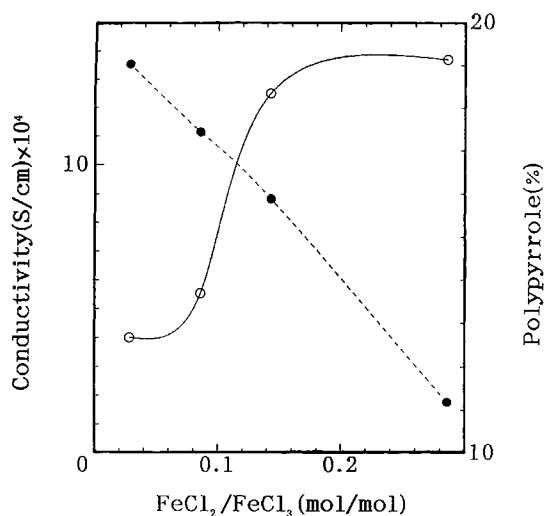


Figure 1 Effect of FeCl_2 - FeCl_3 ratio on the conductivity and PPy content in PPy-PUR composite foam. FeCl_3 33 wt %, reaction temp. 20°C , reaction time 24 h: (O) conductivity, (●) PPy content.

Method

A piece of PUR foam was impregnated with a solution of iron chloride in methanol and then dried in vacuum. The content of iron chloride and the ratio of FeCl_2 to FeCl_3 in PUR foam was changed by changing the concentration of iron chloride and FeCl_2 - FeCl_3 ratio in the solution. Then, the foam was exposed to saturated pyrrole vapor in a sealed glass vessel at a constant temperature. After the reaction, the composite foam was washed with acetone and dried in vacuum. The contents of iron chloride before the reaction and of PPy after the reaction in the foam are expressed as weight percent based on the original weight of PUR foam.

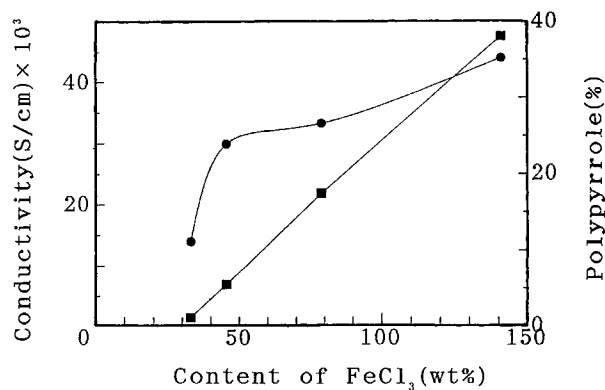


Figure 2 Effect of FeCl_3 content on the conductivity and PPy content in PPy-PUR composite foam. FeCl_2 - $\text{FeCl}_3 = 1/3.5$ (mol/mol), reaction temp. 20°C , reaction time 24 h: (■) conductivity, (●) PPy content.

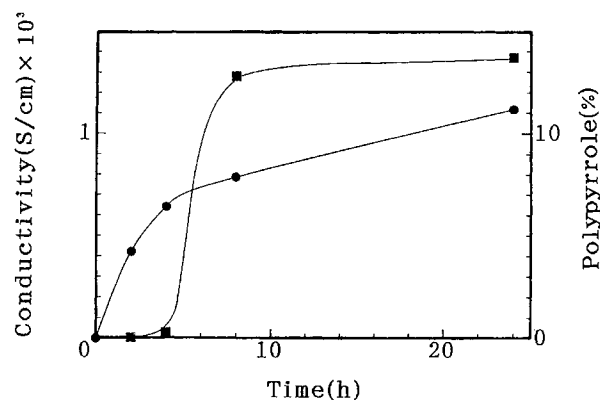


Figure 3 Change in conductivity and PPy content in PPy-PUR composite foam with reaction time. FeCl_3 33 wt %, FeCl_2 - $\text{FeCl}_3 = 1/3.5$ (mol/mol), reaction temp. 20°C : (■) conductivity, (●) PPy content.

Measurement

The electrical conductivity of PPy-PUR composite foam was measured by four-point method at room temperature. Thermal gravimetric analysis was performed with a Seiko SSC-5200 instrument. Scanning electron micrographs (SEM) were taken with a JEOL JXA-6100P instrument.

RESULTS AND DISCUSSION

Effect of Oxidant Composition

The vapor phase polymerization of pyrrole has been utilized for the preparation of composites of PPy

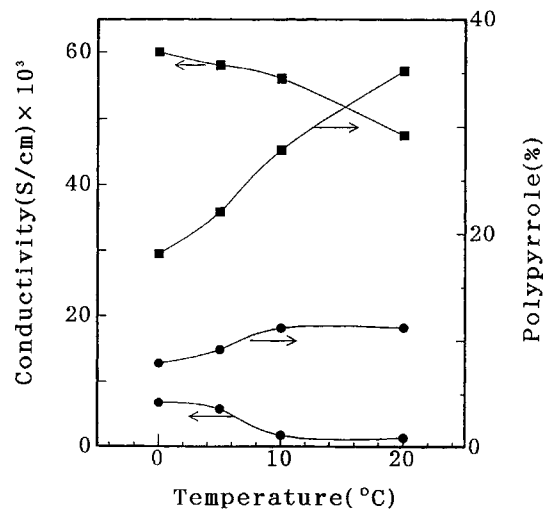
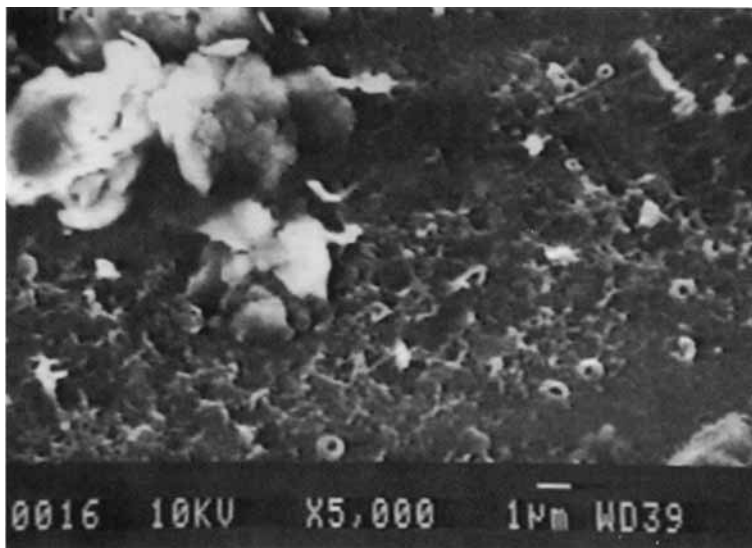


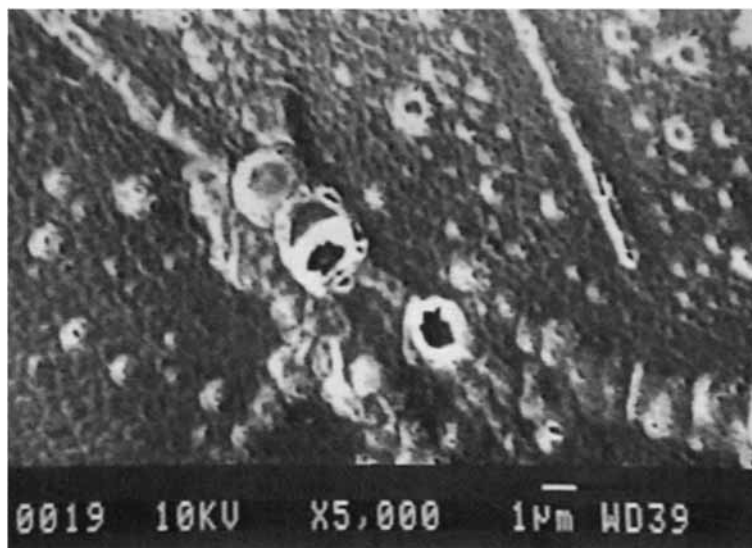
Figure 4 Effect of reaction temperature on the conductivity and PPy content in PPy-PUR composite foam. FeCl_2 - $\text{FeCl}_3 = 1/3.5$ (mol/mol), reaction time 24 h: (●) FeCl_3 33 wt %, (■) FeCl_3 140 wt %.

and other polymer materials such as poly(vinyl chloride),⁷ poly(vinyl alcohol),⁸⁻¹⁰ and polyacrylonitrile.¹¹ FeCl_3 is the oxidant that has been utilized most extensively. We prepared PPy-PUr composite foam by oxidative polymerization of pyrrole vapor on PUr foam containing FeCl_3 .⁶ It was found that the rate of polymerization and the conductivity of

the resultant PPy-PUr composites were strongly dependent on the concentration of FeCl_3 in the solutions that were used for impregnation of the oxidant into the PUr foam. The polymerization temperature of pyrrole also strongly affected the conductivity of the PPy-PUr composites. The results seem to suggest that the content of the oxidant in



A



B

Figure 5 Scanning electron micrographs of the surface of PPy-PUr composite foam. FeCl_3 33 wt %, FeCl_2 - $\text{FeCl}_3 = 1/3.5$ (mol/mol), reaction time 24 h. (A) reaction temp. 0°C , (B) reaction temp. 20°C .

PUr and its oxidation potential are important factors for controlling the electrical conductivity of the PPy-PUr composites.

The effect of oxidation potential of the oxidants on the conductivity of PPy has been reported for solution polymerization of pyrrole.¹² The oxidation potential of FeCl₃ was optimized by changing the nature of the solvent or by mixing FeCl₂. Therefore, we first investigated the effect of addition of FeCl₂ to FeCl₃ as an oxidant for vapor phase polymerization of pyrrole on PUr foam. The result is shown in Figure 1. It can be seen that the conductivity of PPy-PUr composite foam increased with increase in the molar ratio of FeCl₂ to FeCl₃ at a constant content of FeCl₃ in PUr. However, the conductivity became constant at the molar ratio higher than about 0.2. In contrast to conductivity, the content of PPy in the composite foam decreased almost linearly with increase in the molar ratio of FeCl₂ to FeCl₃. Thus, the mixtures of the two iron chlorides are preferable to FeCl₃ as oxidants for preparation of highly conductive composite foam. The result may indicate the formation of PPy of higher density or structurally different from those obtained by FeCl₃ alone. The low contents of PPy in the composite may be advantageous for the mechanical properties of the composite as will be described later.

Figure 2 shows conductivity and PPy content in PPy-PUr composites as a function of FeCl₃ content in PUr foam. The molar ratio of FeCl₂ to FeCl₃ was kept constant at 1/3.5. It can be seen that both conductivity and PPy content in the composite foam increased with increase in the oxidant content. In particular, the former increased linearly with the oxidant content within the range of oxidant content investigated.

The time course of the PPy formation is illustrated in Figure 3. It may be assumed that poly-

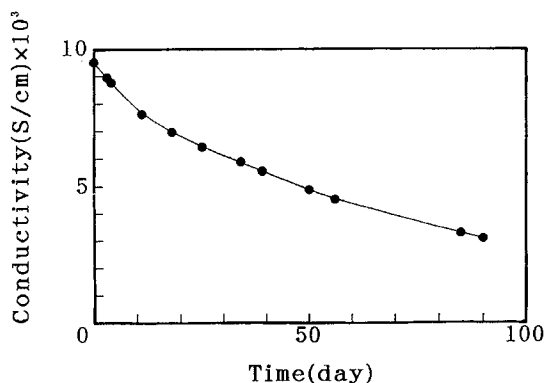


Figure 6 Change in conductivity of PPy-PUr foam with time in the air at 25°C.

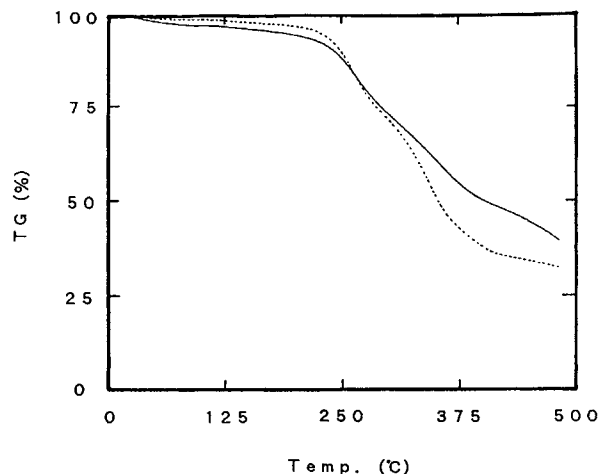


Figure 7 TG analysis of PPy-PUr composite foam. FeCl₃ 40 wt %: (—), without FeCl₂; (---) FeCl₂-FeCl₃ = 1/3.5 (mol/mol).

merization of pyrrole occurs initially at separate spots on the surface of PUr. As shown in Figure 3, induction period and the following rapid increase in conductivity at 4–8 h reaction seem to indicate the initial formation of separate PPy spots and then consecutive PPy on or in the PUr foam. Then, after the coverage of the surface of the PUr by PPy layer, conductivity will be almost constant with slow increase in PPy content in the composite foam.

Effect of Reaction Temperature

The conductivity and PPy content are also the function of polymerization temperature, as illustrated in Figure 4. It is obvious that lower reaction temperatures are preferable for higher conductivity in spite of lower PPy content in the composites. Similar results were obtained for polymerization of pyrrole by FeCl₃ in solutions.¹³ This may be attributed to suppression of undesirable side reactions such as oxidation of pyrrole ring or crosslinking of the polymer chains, which decrease the length of conjugated double bonds.

The formation of dense surface structures of PPy may be an alternative reason for higher conductivities at lower temperatures. The surface structure of the composite foam was observed by SEM. As shown in Figure 5, the composites have relatively fine surface structures, but there seems to be some difference between the composites prepared at 0 and 20°C. A more comprehensive study is required before reaching a conclusion with respect to temperature effect on conductivity.

Table I Properties of the Composite Foam^a

Property Composite Foam	Conductivity × 10 ³ (S/cm)	Polypyrrole Content (wt %)	Tensile (kg/cm ²)	Elongation (%)
FeCl ₃ composite	0.87	9.13	1.31	294
FeCl ₂ -FeCl ₃ composite ^b	1.21	4.25	1.31	446
PU foam	< 10 ⁻⁹	0	1.41	463

^a Reaction was carried out at 20°C for 24 h.

^b FeCl₂-FeCl₃ (mol/mol) = 1/3.5.

Stability and Mechanical Properties of PPy-PUr Foam

It is known that many of conductive polymers are sensitive to air oxidation, and therefore, the stability of conductivity is an important factor for practical application of the conductive polymers. The change in the conductivity of PPy-PUr foam in the air is shown in Figure 6. The conductivity decreased gradually, but after 3 months it had still about 30% of the original conductivity. The thermal stability of PPy-PUr foam was estimated by thermogravimetric (TG) analysis (Fig. 7). Below 250°C, there are only small differences in weight loss for the composites prepared by FeCl₃ with or without FeCl₂.

The tensile strength and elongation of the composites were measured and the results are listed in Table I. Comparing the composite foams prepared by FeCl₃ and a mixture of two iron chlorides, the latter exhibits much higher elongation that is comparable to that of pristine PUr. This may be attributed to lower PPy content in the composite prepared by FeCl₂/FeCl₃ as described above. The excellent mechanical properties, coupled with higher conductivity and lower PPy content, of the composite foam indicate that FeCl₂-FeCl₃ mixtures are preferable to FeCl₃ alone as oxidants for preparation of high-performance composite foam of PPy and PUr.

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