

Carboxylated Polyurethane Anionomers and Their Composites with Polypyrrole

GABRIELA ROBILĂ, I. DIACONU, TINCA BURUIANĂ, E. BURUIANĂ, P. COMAN

Romanian Academy, Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 6600 Iași, România

Received 5 March 1999; 6 June 1999

ABSTRACT: Some polyurethane anionomers synthesized by a two-step substitution postreaction of urethane hydrogen atoms with CH_2COONa groups were studied. The influence of ionic structures on the mechanical and electrical properties of polymers was followed. The carboxylated polyurethane anionomers were used to obtain electroconductive composites with polypyrrole, by immersion of polyurethane films in aqueous solution of pyrrole and oxidative chemical polymerization of the heterocyclic monomer with FeCl_3 . The proportion of polypyrrole in the composites increased by introduction of ionic groups. Stress-strain behavior and electrical conductivity of composites were compared with those of the anionomers. Incorporation of polypyrrole significantly enhanced the electrical conductivity but diminished mechanical properties. Some composites possess both satisfactory conductivity and mechanical properties. The results were explained by the morphological changes induced by ionic group and polypyrrole presence. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1385–1392, 2000

Key words: polyurethane ionomers; polypyrrole; electroconductive composites

INTRODUCTION

A growing research and development effort has been directed in recent years toward polyurethane ionomers, one of the most complex groups of all ionomers presently known. The nature, length, and location of all building blocks can be varied widely, and this variation will be reflected in the structure, morphology, and properties of the resulting polymers.¹ Among the polyurethane ionomers those with carboxylate groups were considered to be very attractive compounds especially for application as aqueous dispersions.²

Some recent studies were focused on polyurethane anionomers with ionic groups incorporated into the hard segments, mostly by using dimeth-

ylolpropionic acid as chain extender.^{3–7} Previously we synthesized some polyesterpolyurethane anionomers with carboxylate groups on urethane nitrogen atoms⁸ by a two-step modification of a nonionic polymer,⁹ and some properties of these anionomers were reported.⁸ Here we describe more mechanical and electrical properties of above the polymers and their testing for synthesis of some composites with polypyrrole.

To develop polypyrrole-based conductive materials for commercial applications,¹⁰ much attention has been given to preparation of conductive polypyrrole-polymer composites, which have good enough conductivity, processability, and improved mechanical properties.¹¹ Several approaches have been developed, based on electrochemical or chemical polymerization of pyrrole. By coating an anode with polymer film and immersion in a solution containing both electrolyte and pyrrole, composites with poly(vinyl alcohol),¹² poly(tetrafluoroethylene),¹³ poly(vinyl chloride),¹⁴ or polyurethanes¹⁵ were electrochem-

Correspondence to: G. Robilă.

Contract grant sponsor: Roumanian Academy; contract grant number: GAR 2714/1997.

Journal of Applied Polymer Science, Vol. 75, 1385–1392 (2000)

© 2000 John Wiley & Sons, Inc.

CCC 0021-8995/00/111385-08

ically synthesized. Different soluble anionic polymers were used as macromolecular electrolytes and dopants to prepare conductive composites by anodic polymerization of pyrrole,¹¹ and recently we presented a sulfonated polyurethane anionomer/polypyrrole composite obtained by this method.^{16,17} Latex particles with anionic surfaces together with electrochemical polymerized polypyrrole were precipitated on an anode to generate composite films.¹⁸ In both previous cases, the anionic groups of polymers interact with positively charged polypyrrole, and the resulting materials are considered conductive molecular composites.

The electrochemical method is expensive, and the yields of the composite are restricted by the area of the electrode. Chemical polymerization can overcome these disadvantages. Polyurethane/polypyrrole composites were prepared by an emulsion pathway, from the mixture of two polymers.¹⁹ Conductive films poly(vinyl alcohol)/polypyrrole resulted when poly(vinyl alcohol) containing FeCl_3 were exposed to pyrrole vapor.²⁰ Also by using pyrrole vapor, polymerization conductive polyurethane foams,^{21,22} electroconductive films based on poly(vinyl pyridine),²³ or crosslinked flexible matrices of styrene-acrylate copolymers^{24,25} were produced. When a solution of pyrrole and poly(methyl methacrylate) was sprayed on the surface of an aqueous solution of oxidant, films of polypyrrole/poly(methyl methacrylate) were obtained.^{26,27} A diaphragmatic procedure gave conducting polypyrrole-Nafion composite films through chemical polymerization of pyrrole.²⁸

Conductive molecular composites were prepared by immersion of pyrrole-swollen films of poly(ethylene terephthalate)²⁹ or sulfonated polystyrene³⁰ in aqueous FeCl_3 . In the present research the latter chemical method of *in situ* polymerization of pyrrole was used to obtain conductive polyurethane anionomer/polypyrrole composites. The effect of polypyrrole incorporation on the ionomer film properties also was studied.

EXPERIMENTAL

Synthesis

The ionomers with carboxylate groups were obtained as previously,⁸ by two-step modification of a linear polyesterurethane, based on poly(ethylene adipate)diol ($M_n = 2000$), 4,4'-methylenebis(phenyl isocyanate) and 1,4-butane diol (molar

ratios of 1 : 6 : 5). In the first step, the reaction of neutral polyurethane with sodium hydride in dimethylformamide (DMF) was performed. In a second step, the solution of sodium-substituted polyurethane, obtained as above, was reacted with an equivalent quantity of sodium chloroacetate. To obtain a certain content of ionic groups, stoichiometric quantities of hydride and, respectively, chloroacetate were used, based on urethane groups content. Ionic polymers were separated by precipitation with ethyl ether from the filtered reaction mixture and washed many times with the same nonsolvent. The substitution degree of urethane hydrogen atoms with chloroacetate groups was evidenced in infrared spectra and was determined quantitatively from elemental analysis, by determining the loss of nitrogen.⁸

Pyrrole (Aldrich Chemical Co., Milwaukee, WI) was purified immediately before use by passing it through activated alumina. The procedure was repeated until a colorless liquid was obtained.

Ionic polyurethane films were obtained from 1% solution in DMF. The solutions were poured onto horizontal glass plates and placed at 60°C under air atmosphere for 48 h. The final film was peeled away from the glass, and preparation of conductive composite films was carried out using the procedure described by De Jesus et al.³⁰ Anionomer films were first immersed in aqueous solution of pyrrole (0.5 M) for various times (4–72 h), at room temperature. Then they were removed from pyrrole solution and dried with a tissue. Polymerization of pyrrole was initiated by immersion in aqueous solution of FeCl_3 (1.0 M) for 24 h, also at room temperature, washed several times with distilled water, and finally dried at 50°C for 48 h.

The conductive polymer content in the films was calculated gravimetrically, weighting the dried films before and after pyrrole polymerization.

Characterization

Hydrophilicity was as previously measured⁸ on polymer sheets, at 85% relative humidity.

Mechanical properties of the anionomer films and composites were determined at room temperature with a crosshead speed of 9.0 mm/min, using a laboratory-built device that also included a data acquisition system and an IBM PC-compatible computer. Dumbbell samples were used, 10 mm wide at two ends and 4.5 mm wide and 10 mm long at the neck.

Table I Characteristics of Polyurethane Anionomers

Polymer	Substitution Degree of Urethane Hydrogen (%)	Stress at Break (MPa)	Elongation at Break (%)	σ (S cm ⁻¹)
PU	0	44.0	660	4.7×10^{-11}
PUA-1	100	10.0	400	2.96×10^{-10}
PUA-2	50	0.5	55	2.10×10^{-9}
PUA-3	25	23.0	535	8.83×10^{-11}
PUA-4	14	35.0	650	5.63×10^{-11}

Electrical conductivity measurements were performed on anionomer or composite films, (about 0.1 cm thick), provided with vacuum-evaporated silver electrodes of circular form, symmetrically arranged on both sides of the film. The dc conductivity values were calculated from the steady values of the transient charge currents, measured at room temperature and normal pressure.

Thermal analysis of the polyurethanes was carried out on a derivatograph (MOM, Budapest). Thermogravimetry (TG) and DTG curves were recorded between 20 and 600°C, with a heating rate of 12°/min, under air atmosphere. Sample weight was 50 mg, and reference material was α -Al₂O₃.

RESULTS AND DISCUSSION

Polyurethane Anionomers

For the studied polyurethane ionomers, the substitution degree of urethane hydrogen atoms by ionic groups was between 100 and 14% (PUA-1 to PUA-4). Some of their characteristics are listed in Table I. As can be seen, introduction of ionic structures on polymer backbone exerts considerable influence on the physical properties of the polyurethane. Stress at break progressively decreased when about 25% of urethane hydrogen are substituted with $-\text{CH}_2\text{COO}^-$ anionic groups and dramatically dropped for polymer with 50% substitution (PUA-2). PUA-1 anionomer, with total substitution at urethane structures, shows a slight increase of stress at break and a significant enhancement of ultimate elongation.

As seen in Figure 1, stress versus strain curves indicate an elastomer-type behavior for PUA-3

and PUA-4, while PUA-1 presents a characteristic deformation for a plastic behavior, when elongation increases at about constant stress.

These findings are in disharmony with those previously reported for other polyurethane anionomers with carboxylic groups,^{7,31} when an improvement of mechanical properties by introduction of ionic groups was seen. Besides usual interactions between molecular segments of neutral polyurethanes, the case of ionomers must take in account ion-ion, ion-dipole, anion dipole-H bridge interactions,³² and steric effects induced by substituents. The initial nonionic polyurethane used in this investigation presents long hard segments and a high phase separation promoted by hydrogen bonding. As a result, tensile strength and elongation also are high. When ionic groups were introduced, although electrostatic ion-ion interactions and ion-hydrogen bonds are

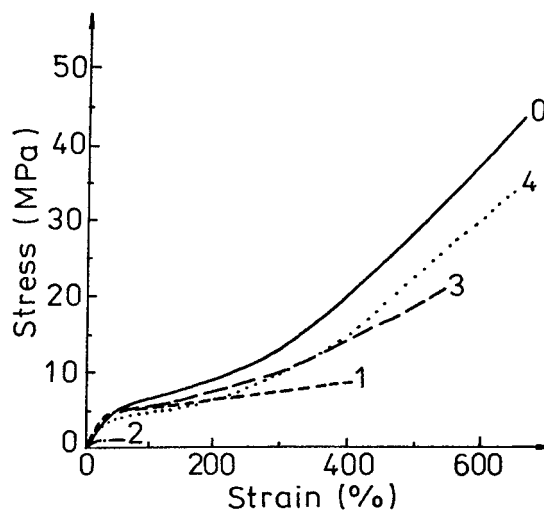


Figure 1 Stress-strain curves for nonionic polyurethane (0) and for PUA-1-PUA-4 anionomers (1-4).

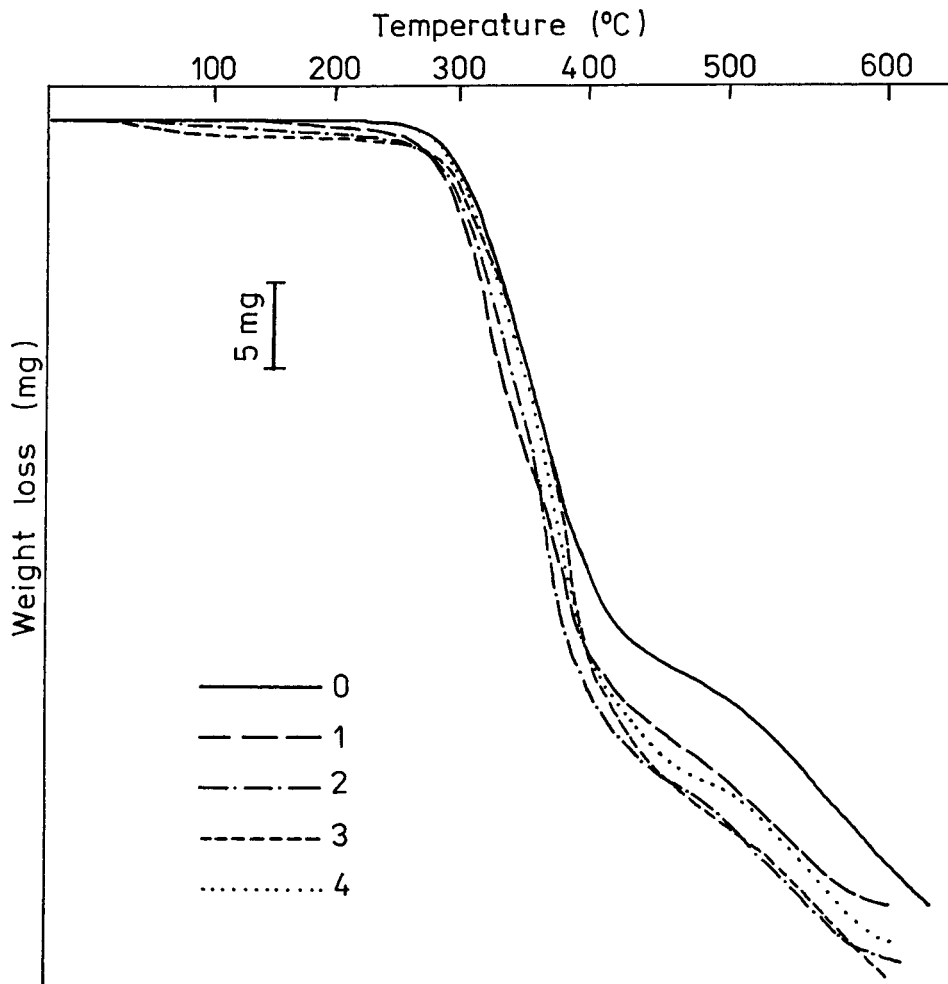


Figure 2 Thermal behavior of nonionic and ionic polyurethanes PU (0) and PUA-1–PUA-4 (1–4).

stronger than are ordinary hydrogen bonds,⁷ macromolecular chains are distanced by introduction of $-\text{CH}_2\text{COO}^-$ side groups, and interchain cohesivity is reduced. The possibility of hydrogen bonding diminished and affected physical properties. In Figure 1, stress crystallization of PU and PUA-4 can be observed, suggesting a similar phase-separated structure. Segregation of phase diminishes at 25% substitution. When substitution degree increased to 50% (PUA-2), hard segment structure was completely inadequate to allow a close packing of chains, as suggested by dramatic lowering of mechanical properties. Some electrostatic interactions between ions or dipoles of the same hard segment could favor a specific arrangement of macromolecules. At total substitution of urethane hydrogen atoms with sodium acetate groups (PUA-1), the polymer is in-

capable of hydrogen bonding (substitution of hydrogen atoms from $-\text{OCONH}-$ was checked by IR spectroscopy⁸), but an increased number of electrostatic interactions tends to restore hard domain order and improves mechanical response. Side groups act as interchain spacers and so stress at break is low enough.

Electrical conductivity is increased by introduction of ionic groups, as data from Table I show. Again, for 50% substitution of urethane hydrogen atoms with ionic groups, a specific behavior is observed, the higher conductivity suggesting that a specific and uniform distribution of electrons in sample exists.

TG curves presented in Figure 2 do not show major differences in thermal stability of studied anionomers. Below 400°C the weight loss of sample PUA-4 with very low content of ionic groups

Table II Polyurethane Anionomers and Their Composites

Polyurethane	Relative Hydrophilicity	Meq Ionic Groups/100 g Anionomer	Time of Immersion in Pyrrole (h)	Pyrrole Content in Composite (%)
PU	1	0	4	0.70
			24	1.93
			72	6.54
PUA-1	1.85	252	4	12.08
			24	14.60
			72	17.91
PUA-2	1.52	157	4	9.65
			24	13.68
			72	10.41
PUA-3	1.13	73	4	3.61
			24	14.07
			72	19.59
PUA-4	1.48	41	4	2.85
			24	11.01
			72	20.00

and of nonionic polyurethane are the same (about 60%). A small increase of weight loss and a decrease in initial degradation temperature was observed for PUA-1–PUA-3 compared with the original polyurethane sample, and this may indicate that ionization can disrupt the order in the hard domains. This result agrees with previous finding for some polyurethane cationomers.³³

Electroconductive Composites with Polypyrrole

To obtain composites with polypyrrole, the polyurethane anionomer films were immersed in aqueous solution of pyrrole for various times (Table II). The time of contact with oxidant solution was held constant (24 h). Data from Table II show that generally, the percentage of polypyrrole from composites increases with time of immersion in pyrrole solution, suggesting that diffusion of monomer in polyurethane controls polymerization.

The presence of ionic groups in polyurethanes produced a significant increase of the electroconductive polymer ratio in composites, due to the higher hydrophilic nature of the ionomers, which provides a more favorable environment for diffusion of pyrrole and FeCl₃ aqueous solutions. It is known that to initiate pyrrole polymerization, the oxidative potential of FeCl₃ must be high enough, and this is the case in aqueous solutions. Here is the contribution of ionic groups, which determined a low swelling of polymers in water, allowing diffusion of monomer and ferric chloride.

There is a direct relationship between the increase of polypyrrole proportion in composites and the content of ionic groups in ionomers only for the samples obtained by 4 h immersion in pyrrole solution. For higher immersion times, the quantity of heterocyclic polymer was practically the same for all ionomer composites, independently of ionic group content. Only samples obtained from PUA-2 showed a lower content of polypyrrole, and presently we do not understand the origin of this behavior.

The behavior of the polyurethane anionomers/polypyrrole composites under uniaxial stress is presented in Table III and in Figures 3–5. As can be seen, the presence of pyrrole results in a dramatic modification of mechanical properties of anionomers. Initial modulus increased for all composites comparatively with polyurethane films, due to rigidity of polypyrrole chains. Elongation at break of composites decreased for all immersion times in the case of anionomers with a low content of ionic groups, but slightly increased for the samples with 50 or 100% substitution of urethane hydrogen. In this last case, the reinforcement effect of polypyrrole macromolecules may be observed, due to fragility of support ionomer films.

The composites exhibit an increase of elongation when substitution degree with ionic groups in polyurethane support increased from 0 to 25%. For 50% substitution, a fast decrease was observed, and then elongation increased again for

Table III Mechanical Characteristics of Polyurethane Anionomers/Polypyrrole Composites

Anionomer Support	Immersion Time					
	4 h		24 h		72 h	
	<i>R</i> (MPa)	$\Delta l/l_0$ (%)	<i>R</i> (MPa)	$\Delta l/l_0$ (%)	<i>R</i> (MPa)	l/l_0 (%)
PUA-1	10	120	5.8	80	2	8
PUA-2	4.5	50	4.7	50	7.4	32
PUA-3	23	510	6.7	275	5.2	42
PUA-4	22.5	480	15	400	5.8	41
PU	20	475	12.3	300	—	15

all samples, except those with 72-h polymerization time. The low mechanical strength of these last composites could be explained by the large quantity of conductive polymer as well as by long action time of aqueous medium on the polyurethane matrix. Some hydrolytic degradation could appear.

For the composites based on ionomers with lower ionic content and obtained by 4- to 24-h immersion in pyrrole solution, the mechanical properties have reasonable values.

Electrical conductivity of the anionomers/polypyrrole composites is listed in Table IV, and they are in the range of 10^{-9} – 10^{-4} S cm^{-1} . When the time of immersion of polyurethane films in monomer solution increased, the conductivity of composites also increased. Electrical conductivity is

affected not only by polypyrrole quantity from composite but also by polymer support structure. By polymerization of pyrrole in an ionomer matrix, formation of a polypyrrole–polyurethane polyanion complex takes place, when the anionomer plays a role as a polymer dopant as well as a supporting material. Previously, this was proposed and demonstrated for other polymers with ionic groups.^{11,28,30,34}

Table IV results show that conductivity of synthesized composites increased generally with anion content in the ionomer matrix. The composites with 72-h polymerization time display practically an identical conductivity for all polyurethane ionomers used and also for neutral polyurethane. An explanation could be formed of a polypyrrole layer on surface, where polymer an-

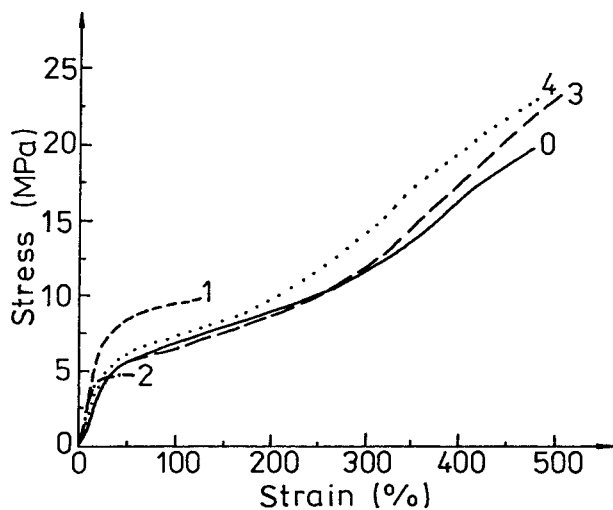


Figure 3 Stress–strain curves for the polyurethane/polypyrrole composites obtained by 4-h immersion in monomer solution [polyurethane supports: PU, 0; PUA-1–PUA-4, curves 1–4, respectively].

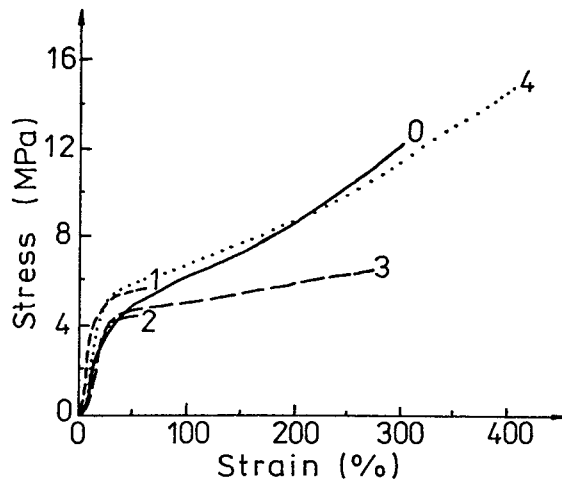


Figure 4 Stress–strain curves for the polyurethane/polypyrrole composites synthesized by 24-h immersion in monomer solution (polyurethane supports: 0, non-ionic polyurethane; 1–4, PUA-1–PUA-4 ionomers, respectively).

ions are not implied. Thus, the structure of the conductive layer will be the same for all support polymers, and it will determine the conductivity rather than the thickness of the layer.

The composites based on the anionomer with all urethane hydrogen atoms substituted by carboxylate groups show a lower conductivity. The domain-ordered structure of this ionomer and a high level of ionic content could lead to the loss of regularity in the polypyrrole structure. The large sizes of dopant anions could generate distortion of the conjugate planes in the polymer chains, and these distortions could be responsible for lower conductivity.³⁵

One might expect that transmission electron microscopy would provide some helpful data about morphology of studied anionomers and composites, and so their properties would be better understood. Such works are in progress now in our laboratory.

CONCLUSIONS

The ionomers synthesized by introduction of sodium carboxylate groups on urethane nitrogen atoms of a polyurethane with long, rigid segments exhibit modified mechanical and electrical properties, determined by ionic group content. Modification of phase separation by cooperation of electrostatic interactions, hydrogen bonds, and steric

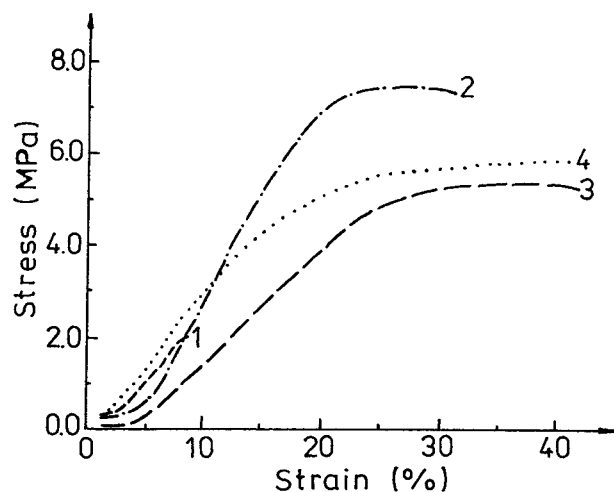


Figure 5 Stress-strain curves for the polyurethane/polypyrrole composites synthesized by 72-h immersion in monomer solution (polyurethane supports: 0, non-ionic polyurethane; 1–4, PUA-1–PUA-4 ionomers, respectively).

Table IV Electrical Conductivity of Polyurethane Anionomer/Polypyrrole Composites

Anionomer Support	Immersion Times		
	4 h (S cm ⁻¹)	24 h (S cm ⁻¹)	72 h (S cm ⁻¹)
PUA-1	8.19×10^{-9}	1.85×10^{-6}	7.71×10^{-5}
PUA-2	1.75×10^{-5}	1.97×10^{-4}	3.00×10^{-4}
PUA-3	6.39×10^{-6}	8.35×10^{-5}	2.41×10^{-4}
PUA-4	6.70×10^{-9}	1.82×10^{-5}	1.87×10^{-4}
PU	7.26×10^{-9}	8.31×10^{-7}	2.36×10^{-4}

effects of the substituents was considered to explain the results.

Electroconductive molecular composites with polypyrrole can be successfully prepared by immersion of polyurethane films in aqueous solution of pyrrole and oxidative polymerization of the heterocyclic monomer by FeCl₃. The presence of polypyrrole significantly enhanced electrical conductivity but diminished mechanical properties. Composites with good electrical conductivity and satisfactory mechanical behavior were obtained when anionomers with lower content of ionic groups were immersed for short times in aqueous pyrrole solution, and these could be considered to be the most attractive candidates for the development.

REFERENCES

- Xiao, H.; Frish, K. *Advances in Urethane Ionomers*, Technomic: Lancaster, PA, 1995.
- Reiff, H.; Dieterich, D. In *Ionomers*; Tant, M.; Mauritz, G. Wilkes), Blackie: London, pp. 444–476 (1997).
- Yang, C.; Grassel, T.; Bell, J.; Register, R.; Cooper, S. *J Polym Sci Part B Phys* 1991, 29, 581.
- Chen, S.; Hsu, J. *Polymer* 1993, 34, 2769.
- Chen, S.; Hsu, J. *Polymer* 1993, 34, 2776.
- Hourston, D.; Williams, G.; Satguru, R.; Padget, J.; Pears, D. *J Appl Polym Sci* 1997, 66, 2035.
- Hourston, D.; Williams, G.; Satguru, R.; Padget, J.; Pears, D. *J Appl Polym Sci* 1998, 67, 1437.
- Robilă, G.; Buruiană, T.; Buruiană, E. *Eur Polym J* 1999, 35, 1305.
- Ding, S.; Register, R.; Yang, C.; Cooper, S. *Polymer* 1989, 30, 1204.
- Skotheim, T. A. *Handbook of Conducting Polymers*, Marcel Dekker: New York, 1986.
- Bidan, G. *J Chim Phys* 1989, 86, 45.

12. Lindsey, S.; Street, G. *Synth Met* 1984, 10, 67.
13. Penner, R.; Martin, C. *J Electrochem Soc* 1986, 33, 310.
14. Niwa, O.; Kakuchi, M.; Tamamura, T. *Synth Met* 1987, 18, 310.
15. Bi, X.; Pei, Q. *Synth Met* 1987, 22, 145.
16. Robilă, G.; Ivănoiu, M.; Buruiană, T.; Buruiană, E. *J Appl Polym Sci* 1993, 49, 2025.
17. Robilă, G.; Ivănoiu, M.; Buruiană, T.; Buruiană, E. *J Appl Polym Sci* 1997, 66, 591.
18. Jasne, S.; Chiklis, C. *Synth Met* 1986, 15, 175.
19. Ruckenstein, E.; Chen, J. *Polymer* 1991, 32, 1231.
20. Ojio, T.; Miyata, S. *Polym J* 1986, 18, 95.
21. He, F.; Omoto, M.; Yamamoto, T.; Kise, H. *J Appl Polym Sci* 1995, 55, 283.
22. Fu, Y.; Paolo, D.; Erkey, C.; Weiss, R. *Polym Prepr* 1997, 38(2), 430.
23. Mohammadi, A.; Lundstrom, I.; Inganas, O.; Salanek, W. *Polymer* 1990, 31, 395.
24. Yin, W.; Lin, H.; Li, J.; Li, Y.; Gu, T. *J Appl Polym Sci* 1997, 64, 2293.
25. Yin, W.; Li, J.; Wu, J.; Gu, T. *J Appl Polym Sci* 1997, 63, 13.
26. Moreta, M.; Hashida, I.; Mishimura, M. *J Appl Polym Sci* 1988, 36, 1639.
27. Chan, H.; Hor, T.; Ho, P.; Tan, K.; Tan, B. *J Macromol Sci A Chem* 1990, 27, 1081.
28. Yioda, T.; Ohtani, A.; Honda, K.; Shimidzu, T. *Macromolecules* 1990, 23, 1971.
29. Li, C.; Song, Z. *Synth Met* 1991, 40, 23.
30. De Jesus, C.; Weiss, R.; Chen, Y. *J Polym Sci Part B Polym Phys* 1997, 35, 34.
31. Al Salah, H.; Frish, K.; Xiao, H.; Mc Lean Jr, J. *J Polym Sci Part A Polym Chem* 1987, 25, 2727.
32. Dieterich, D. In *Advances in Urethane Ionomers*; Technomic: Lancaster, PA, 1985; p. 1–21.
33. Chen, S.; Chan, W. *J Polym Sci Part B Polym Phys* 1990, 28, 1499.
34. Lee, Y.; Shin, D.; Cho, J.; Park, Y.; Son, Y.; Baic, D. *J Appl Polym Sci* 1998, 69, 2641.
35. Ruckenstein, E.; Hong, L. *Synth Meth* 1994, 66, 249.