

Mechanical Properties of Conducting H-Type Polysiloxane–Polypyrrole Graft Copolymers and Polytetrahydrofuran–Polypyrrole Block Copolymers

C. Biran,¹ L. Toppare,¹ T. Tinçer,¹ Y. Yağci,² V. Harabagiu³

¹Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

²Department of Chemistry, Istanbul Technical University, 80626 Istanbul, Turkey

³P. Poni' Institute of Macromolecular Chemistry, 6600 Jassy, Romania

Received 29 May 2001; accepted 17 January 2002

ABSTRACT: The mechanical properties of block copolymers of polypyrrole and pyrrolyl-ended azobis-polytetrahydrofuran (TPPy) and graft copolymers of pyrrolyl-ended H-type polydimethylsiloxane (SPPy) were investigated and compared with those of polypyrrole (PPy). Conducting films were prepared electrochemically at a constant potential and

doped with *p*-toluene sulfonate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1663–1666, 2002

Key words: polypyrroles; mechanical properties; conducting polymers; graft copolymers

INTRODUCTION

Conducting polymers have attracted great deal of attention because of their enormous potential applications, such as rechargeable batteries, nonlinear optics, gas separation membranes, gas sensors, and enzyme immobilization.^{1–9} Nevertheless, their applicability remains fairly limited because of their poor mechanical properties and lack of processability.

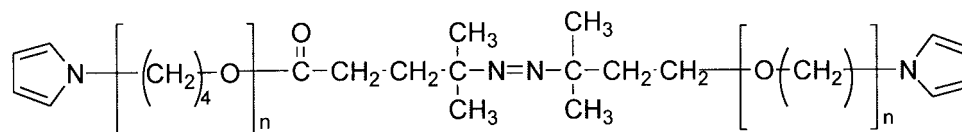
Polypyrrole (PPy) is a widely studied polymer because of its ease of synthesis. The main difficulty in the investigation of mechanical properties of conducting polymers arises from their irregular structure. The polymeric film is usually not only brittle but also fragile. The cauliflower-like appearance of PPy is the result of dendritic growth of polymer chains during electrochemical polymerization, which causes the presence of weak points within the polymer matrix. Noteworthy errors in most characterization studies inevitably stem from ill-measured thickness, which results in mechanical properties scattered in a rather broad range of values. The result is the same when one attempts to measure the electrical conductivity of the product.

Recently, many researchers have concentrated on the enhancement of the mechanical behavior of conducting polymers. Blending conducting polymers with thermoplastic polymers is one attempt to increase their processability.^{10–12} On the other hand,

synthesis of composite films through electrochemical polymerization of the conducting component on the electrode coated with insulating polymer yields rather homogeneous products compared to blends prepared as mechanical mixtures.^{13–17} Further, mechanical behavior can be improved by the synthesis of block or graft copolymers containing conventional and conducting sequences.^{18–20} This is achieved mostly by the use of polymeric initiators with functional groups within or at the end of the chain, which then is electropolymerized in the presence of the monomer of the conducting polymer. All these efforts may be successful to some extent, yet with some sacrifice of the polymers' conducting ability. Yin et al.²¹ proposed a composite film based on PPy and crosslinked poly(styrene–butyl acrylate–hydroxyethyl acrylate). However, their finding on the tensile strength of the product is at most 10.3 MPa. Zoppi and De Paoli²² prepared several types of blends of crosslinked polypyrrole/ethylene propylene diene monomer rubber, having tensile strength of about 50 MPa with very low conductivity, about 10^{-10} S/cm. Electrochemically prepared plasticized PPy films of BASF samples, referred to as LUTAMER P160, gave quite a wide range of tensile strength values between 26 and 42 MPa, with elongation percentage ranging from 3 to 8%.

In this study, the mechanical properties of the block copolymer of polypyrrole and pyrrolyl-terminated azobis-polytetrahydrofuran¹⁹ (TPPy) and the graft copolymer of pyrrolyl-ended H-type polydimethylsiloxane²⁰ (SPPy) were investigated and compared with those of PPy. Also, the differences in cross-sectional

Correspondence to: L. Toppare.



Scheme 1 Pyrrolyl-ended azobis-polytetrahydrofuran (TPPy precursor).

views were investigated by scanning electron microscopy (SEM).

EXPERIMENTAL

Pyrrole (Merck, Darmstadt, Germany) was distilled before use and stored at 4°C under nitrogen atmosphere. Dichloromethane (CH₂Cl₂) (Merck) and *p*-toluene sulfonic acid monohydrate (PTSA) (Aldrich, Steinheim, Germany) were used without further purification.

The synthesis and characterization of the two copolymers have been described previously.^{19,20} PPy and its block copolymer films, TPPy and SPPy, were prepared by potentiostatic electrochemical synthesis, which provides a constant oxidative potential at the anode. The chemical formulas of the two functionalized polymers, pyrrolyl-terminated azobis-polytetrahydrofuran (PTHF) and pyrrolyl-ended polydimethylsiloxane (PSi) are depicted in **Scheme I** and **Scheme II**, respectively. TPPy bears insulating sequences with a number-average molecular weight of 92,000; on the other hand, polysiloxane units in SPPy have an M_n of 1500.

Platinum foils (6 cm²), used as the working electrode, were coated with the given functionalized insulating polymer by dipping the electrode in a solution of polymer dissolved in CH₂Cl₂. The electrochemical polymerizations were done on a Wenking POS 73 (Göttingen, Germany) potentiostat, which was adjusted to supply a constant potential of 1.1 V versus Ag⁰/Ag⁺ reference electrode. Electrolyses were carried out with 0.125M PTSA as the supporting electrolyte and water as the solvent in the presence of 0.03M pyrrole for 60 min at room temperature under nitrogen atmosphere. From each type of copolymer, SPPy and TPPy, both washed (SPPy-W and TPPy-W) and unwashed (SPPy-U and TPPy-U) subtypes were prepared. To determine the grafting percentage of functionalized insulating polymers, series of simple gravimetric measurements were performed.

At least four samples were synthesized of a given type of polymer and only films that faced to the

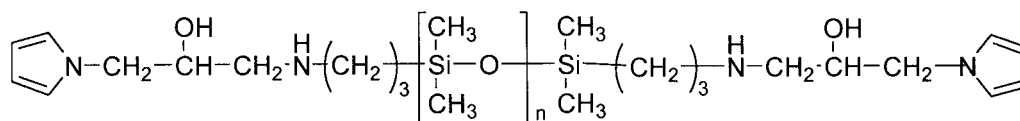
counter electrode were used for testing. Mechanical tests were performed by a Lloyd LS 500 (Fareham Lloyd, UK) computer-controlled tensile testing machine at room temperature with a draw rate 30 mm/min. The gauge length (L_0) was fixed at 26 mm and 100 N load cell was used for each run.

Conductivities of the samples were measured by a four-probe technique. SEM micrographs of the fractured surfaces of the mechanically tested films were taken by JEOL JSM-6400 (JEOL, Peabody, MA) SEM scanning microscopy.

RESULTS AND DISCUSSION

Three conducting polymer matrices were synthesized potentiostatically. Black, freestanding films, having a thickness of about 75, 60, and 30 μm, were obtained for PPy, TPPy, and SPPy, respectively. To wash the copolymers, the films were left in CH₂Cl₂ to dissolve and remove the ungrafted polymers. However, before rinsing with dichloromethane, films were immersed into acetonitrile to remove water. All washing processes were carried out at room temperature. It was determined gravimetrically that the grafting percentage for TPPy is 70%, whereas SPPy achieves 100% grafting.

Figure 1 represents the bar graphs of ultimate mechanical properties of the polymers. Both copolymers demonstrate higher tensile strength values [Fig. 1(a)] with respect to PPy, reaching 59 MPa, and the data were quite reproducible, with rather small standard deviation limits, as shown in the figure. Because of high grafting percentages, there was no appreciable difference between the ultimate strength of washed and unwashed samples of SPPy and TPPy. It was observed that, during washing, films were swollen and this was followed by shrinkage from the edges of rectangular specimens. This deformation directly affected the mechanical properties of the product. Both copolymers showed ultimate tensile strength values of more than 50 MPa, and upon washing they experienced a slight reduction. This value is apparently very



Scheme 2 Pyrrolyl-ended polydimethylsiloxane (SPPy precursor).

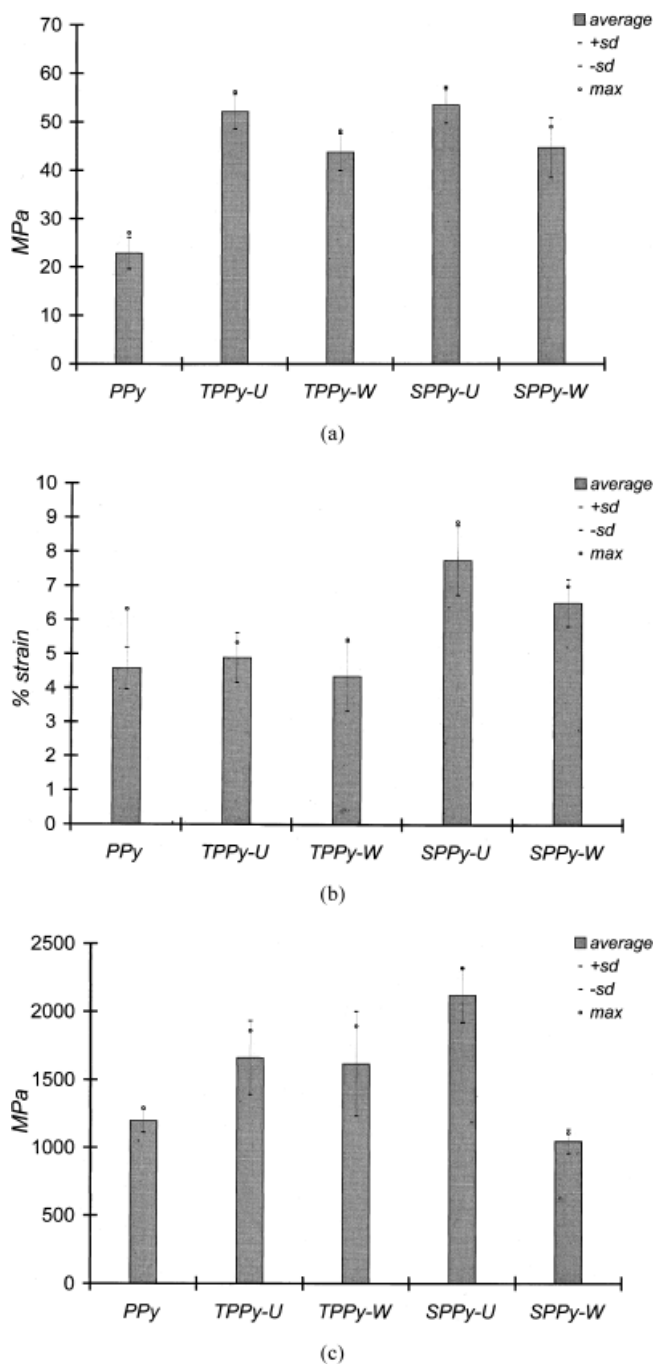


Figure 1 Ultimate mechanical properties of PPy and its copolymers TPPy and SPPy: (a) bar graphs of tensile strength values; (b) bar graphs of percent elongation values; (c) bar graphs of tensile moduli values.

promising when compared to that of the fragile and weak PPy.

Comparatively high elongation observed in SPPy samples is also noteworthy; they could be folded many times without any fracture. Indeed, this attractive feature was also verified by the strain values obtained [Fig. 1(b)]. No improvement in ultimate elongation was seen in TPPy. There were not many differ-

ences between PPy, TPPy-U, and TPPy-W having elongation of about 4.5%. However, SPPy-U and SPPy-W films surpassed them by reaching 9 and 7% elongation at break, which were 7.8 and 6.5% on average, respectively.

The variation in elastic modulus reflects both the rigidity and the flexibility of the samples. With the exception of SPPy-W, the tensile moduli [Fig. 1(c)] were found to be higher than that of pure PPy. However, these copolymers are not as brittle and fragile as PPy and are flexible.

The SEM micrographs (Fig. 2) of the cross-sectional view of the films give further information about the observed behavior. The typical dendritic growth in PPy was not observed for SPPy and TPPy. It can be stated that the copolymer products of PPy are rather homogeneous and the irregularity in the physical appearance has been overcome. In addition, it can be said that polysiloxane-containing copolymers of polypyrrole exhibit an interesting morphology [Fig. 2(d)]. The wormlike structure at the solution side of the copolymer is a specific feature of siloxanes. A similar appearance was observed previously in the copolymer of PPy with a different pyrrole-ended polysiloxane.²³ These wormlike projections most probably indicate the polysiloxane units, whose existence destroys the usual PPy morphology. If this is so, observation of the visible insulating polymer strengthens the theory that the pyrrole units added to the pyrrole moieties of the conventional polymer are comparably short compared with those of polypyrrole itself.

The uniform morphology of copolymers was also verified when the conductivities of the polymers were measured. There was no difference between the electrode and solution side electrical conductivities for washed SPPy (i.e., about 50 S/cm). The conductivity for TPPy-W was measured to be 10 S/cm. The latter copolymer has comparably low conductivity, which must be attributable to the long insulating polymer chains present in the matrix, although this deficiency is less than one order of magnitude.

CONCLUSIONS

Regardless of the presence of insulating sequences, there was no dramatic change in the conductivities of the copolymers compared with that of PPy synthesized at the same conditions. In addition, considerable improvement in mechanical properties was obtained for polypyrrole graft copolymers. The common difficulty in handling PPy and its copolymers because of their fragile nature does not exist in SPPy block copolymers. The tensile strength with a notable high elongation at break and modulus is obviously very surprising for low molecular weight silicon polymer; furthermore, the reproducibility in measured mechanical properties is axiomatically very good.

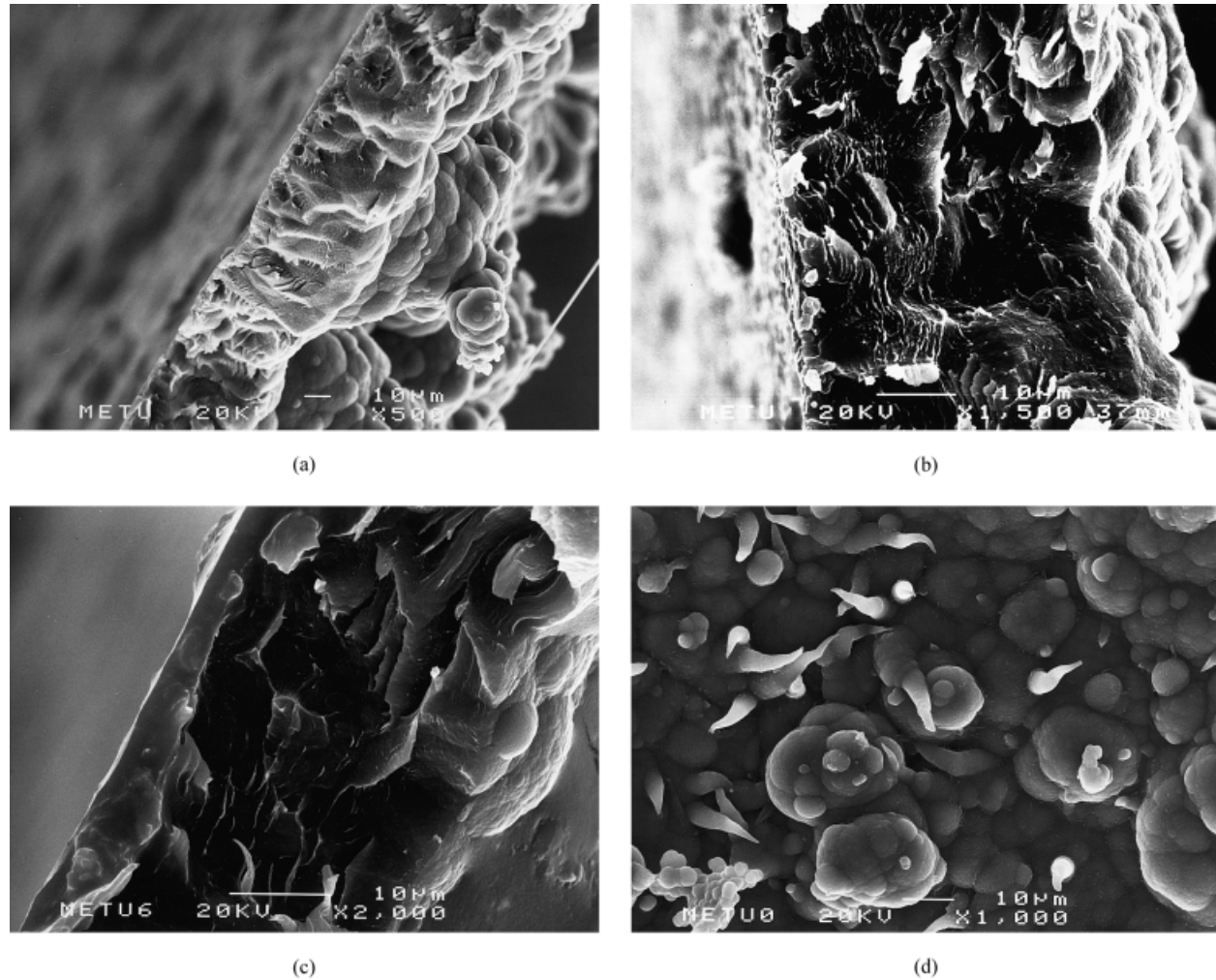


Figure 2 SEM films: (a) cross section of PPy; (b) cross section of Tppy; (c) cross section of SPPy; (d) solution side of SPPy.

References

- Peres, R. C. D.; DePaoli, M. A. *J Power Sources* 1992, 40, 299.
- Pellegrino, J.; Radebaugh, R.; Matters, B. R. *Macromolecules* 1996, 29, 4985.
- Anderson, M. R.; Matters, B. R.; Reis, H.; Kaner, R. B. *Science* 1991, 252, 1412.
- Sotzing, G. A.; Reynolds, J. R. *Chem Mater* 1996, 8, 882.
- Lindsey, S. E.; Street, G. B. *Synth Met* 1984, 10, 67.
- Chin, H. T.; Lin, S. J.; Huang, C. M. *J Appl Electrochem* 1992, 222, 358.
- Alkan, S.; Toppare, L.; Yagci, Y.; Hepuzer, Y. *J Biomater Sci Polym Ed* 1999, 10, 1223.
- Erginer, R.; Toppare, L.; Alkan, S.; Bakır, U. *React Funct Polym* 2000, 45, 227.
- Selampınar, F.; Toppare, L.; Akbulut, U.; Yalçın, T.; Süzer, Ş. *Synth Met* 1995, 68, 109.
- Stanke, D.; Hallensleben, M. L.; Toppare, L. *Synth Met* 1995, 72, 159.
- Aydınlı, B.; Toppare, L.; Tınçer, T. *J Appl Polym Sci* 1999, 72, 1843.
- Balçın, N.; Toppare, L.; Akbulut, U. *Composites* 1995, 26, 229.
- Wang, H. L.; Toppare, L.; Fernandez, J. E. *Macromolecules* 1990, 23, 1053.
- Selampınar, F.; Akbulut, U.; Yalçın, T.; Süzer, Ş.; Toppare, L. *Synth Met* 1994, 62, 201.
- Bozkurt, A.; Akbulut, U.; Toppare, L. *Synth Met* 1996, 82, 41.
- Kalaycıoğlu, E.; Akbulut, U.; Toppare, L. *J Appl Polym Sci* 1996, 61, 1067.
- Yılmaz, B. Y.; Akbulut, U.; Toppare, L. *J Macromol Sci Pure Appl Chem* 1998, A35, 261.
- Alkan, S.; Toppare, L.; Hepuzer, Y.; Yagci, Y. *J Polym Sci Part A: Polym Chem* 1999, 37, 4218.
- Öztemiz, S.; Toppare, L.; Önen, A.; Yağcı, Y. *J Macromol Sci Pure Appl Chem* 2000, A37, 277.
- Kalaycıoğlu, E.; Toppare, L.; Yağcı, Y.; Harabagi, V.; Pintela, M.; Ardelean, R.; Simionescu, B. C. *Synth Met* 1998, 97, 7.
- Yin, W.; Liu, H.; Li, J.; Li, Y.; Gu, T. *J Appl Polym Sci* 1997, 64, 2293.
- Zoppi, R. A.; De Paoli, M. A. *Polymer* 1996, 37, 1999.
- Günaydın, Ö.; Toppare, L.; Yağcı, Y.; Harabagi, V.; Pintela, M.; Simionescu, B. C. *Polym Bull* 2002, 47, 501.