New Conductive Thermoplastic Elastomers. Part II. Physical and Chemical-Physical Characterization

E. Carone, L. D'Ilario, A. Martinelli

Dipartimento di Chimica, Università di Roma "La Sapienza," P.O. Box 34–Roma 62, Roma, Italy

ABSTRACT: To overcome the problems relevant to the low processbility and scarce mechanical properties of polyaniline, in a previous work we have proposed the synthesis of elastomeric conducting copolymers prepared by grafting polyaniline (EB) or sulfonated polyaniline (SPAN) chains to the backbone of a carboxylated segmented polyurethane (PEUA). In the present work the physical and chemical-physical properties of the copolymers are investigated. As evidenced by thermal (DSC) and dynamo-mechanical (DMTA) characterization, the introduction of EB or SPAN in the matrix enhances the hard-soft phase segregation effect, because of the strong tendency of the conductive polymer chains to aggregate. Moreover, the EB and SPAN chains, grafted to the polyurethane backbone, acting as reinforcing filler, give rise, compared with the mechanical properties of the insulating matrix, to an increase of the Young modulus and a decrease of the tensile set. When the copolymers are HCl doped their electrical conductivity increases many orders of magnitude, reaching values of about $10^{-3} \, \Omega^{-1} \, cm^{-1}$. The conductivity, measured along the deformation direction, may be further increased by stretching the copolymer films. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1259–1264, 2002

Key words: polyurethanes; elastomers; conducting polymers

INTRODUCTION

Much interest has been focused in the last years in solving the processability problems of the conducting polymers. As far as polyaniline is concerned, a great advance was made, from both the theoretical and practical point of view, by Cao and coworkers.[1] By using functionalized sulfonic acid as a dopant, these authors made the polymer soluble in many solvents, allowing the production of self-standing films. After this discovery a number of works were addressed to study the structural, mechanical, and electrical properties of the films and their modification upon the deformation and orientation process.[2,3] In general, by stretching or wet-spinning polyaniline,[4] an increase in the sample conductivity along the orientation axis was observed. For 120–180% extension the conductivity enhances about two- or threefold, compared with the unoriented material.[3]

To further improve the processability and mechanical properties of polyaniline, mainly towards the elastomeric behavior, two precesses were followed: (1) the swelling of EB film in a solution of perfluoroacetic acid in acetonitrile,[5] and (2) the production of composites materials containing the conductive polymer as filler dispersed in an elastomeric insulating matrix, like EPDM,[6] SBS,[7] nitrilic rubber,[8] or polyurethane.[9]

Recently we reported[10] a third method, consisting of the synthesis of copolymers prepared by grafting polyaniline (EB) or sulfonated polyaniline (SPAN) chains to the backbone of a carboxylated segmented polyurethane (PEUA) by means of an amidation reaction. From the chemical characterization of the new conducting materials[10] (PEUAPAN and PEUASPAN), the presence of an average number of one SPAN aromatic ring and three EB aromatic rings per PEUA repetitive unit was found, which cannot be assumed as amidation degree being at this moment unavailable the molecular weight of the inserted EB and SPAN chains.

In the present study the thermal, mechanical, dynamo-mechanical, and electrical properties of these polymers are reported, and the effect of the sample deformation on the electrical conductivity is analyzed.

EXPERIMENTAL

Polymer synthesis

The synthesis of the conducting polymers, Emeraldine (EB), and sulfonated Emeraldine (SPAN), and their grafting on carboxylated polyurethane (PEUA), based on methylene-bis-4,4'-phenyl isocyanate (MDI), poly(propylene oxide) (PPO), and 2,2'-hydroxymethyl propionic acid (DHMPA) was reported in a previous article.[10]
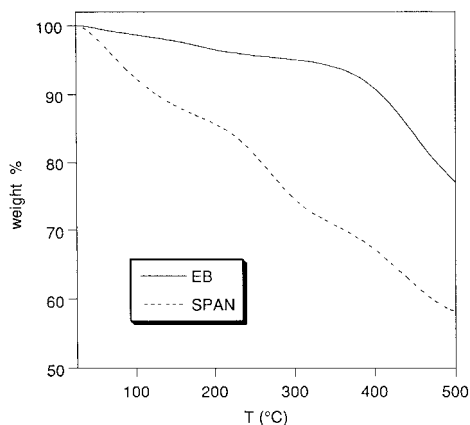
Figure 1 Thermogravimetric curves for EB and SPAN.

Thermal analysis

Differential scanning calorimetry (DSC) analysis were carried out under N_2 using a Mettler TA-3000 DSC apparatus. The scan rate used for the experiments was 20 K/min, and the sample weight about 8–9 mg.

The thermal stability of the polymers was followed by thermogravimetric analysis (TGA) using a Mettler TG50 thermogravimetric analyzer in a temperature range 25–500°C.

TGA experiments were recorded under N_2 at an heating rate of 10 K/min.

Dynamic mechanical analysis (DMA)

The temperature dependence of dynamic mechanical properties was studied by means of a Rheometrics Solid Analyzer RSA II, over the temperature range −150–10°C. The test frequency was 1 Hz, and the heating rate 5 K/min.

Mechanical testing

To evaluate the tensile properties of the polymers the standard test method ASTM D 412-92 was followed. Stress–strain curves were recorded by means of an Instron 4502 apparatus using a crosshead speed of 500 mm/min and a 10-N cell. The polyurethane test samples were previously compression molded at 80°C under a pressure of 1 MPa to obtain rectangular-shaped films.

Electrical characterization

All the materials were doped by exposure to the gas phase of 37% HCl aqueous solution for 24 h. The samples were then dried under vacuum at room temperature for 2 h. Electrical conductivity was measured by means of the four-probe technique on pressed pellets of EB or SPAN and polyurethane films prepared as described in the mechanical test procedure. To fol-

low the conductivity variation as a function of the deformation of PEUAPAN and PEUASPAN, two electrodes were placed at the either ends of the sample, inside the Instron measuring cell grips. Great care was done to avoid any electrical contact between the grips and the electrodes. The sample was extended with a rate of 50 mm/min. The conduction values recorded during the test were normalized by the actual dimensions of the polymer films, assuming the volume change to be negligible, to take into account the sample section reduction during the deformation.

RESULTS AND DISCUSSION

In Figure 1 the thermogravimetric results for EB and SPAN heated under N_2 are reported.

For the EB and SPAN samples the weight loss (about 5% for EB and 13% for SPAN) in the lower temperature range (25–200°C) was attributed to water or solvents trapped within the polymer.[11]

At higher temperature the SPAN weight loss in the range from 200 to 320°C is due to the elimination of the sulfonic acid groups.[12] The observed 20% decrease of the sample weight corresponds to the 25% sulfonation degree, that is one sulfonic group per four aniline rings. The second weight loss at about 400°C can be assigned to the decomposition of the polymers.

From the thermogravimetric curves of Figure 2 we can observe the different weight loss behavior of our polyurethane samples.

Pure PEUA shows two distinct weight losses at 280 and 350°C, attributed to decarboxylation and decomposition of the polymer, respectively. Because of the high amidation degree the first process in not observable in the PEUAPAN.[10] In the PEUASPAN sample the two processes due to the decarboxylation and to the desulfonation merge in a large weight loss between 200 to 330°C. The temperature of the maximum decomposition rate is located for both the amidated
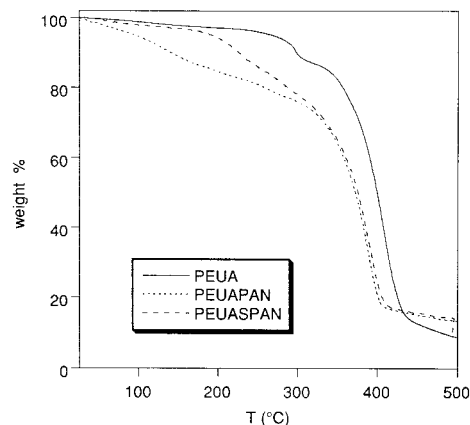

Figure 2 Thermogravimetric curves for PEUA and for the grafted copolymers PEUAPAN and PEUASPAN.
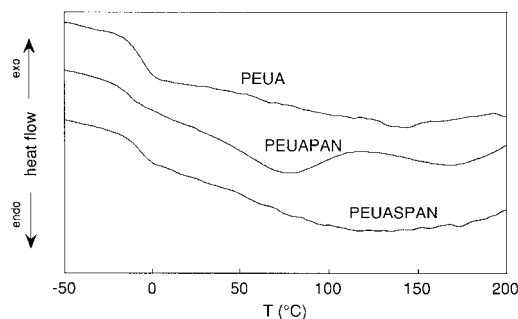
Figure 3 DSC thermograms for PEUA, PEUAPAN, and PEUASPAN.

polymers at 380°C, at a slightly lower temperature than that of PEUA. The higher residual weight at 450°C for PEUAPAN and PEUASPAN samples compared to PEUA is due to the presence of Emeraldine chains, being the aromatic rings more stable than the other components of the polymeric material.

DSC curves for polyurethanes are shown in Figure 3 and the thermal analysis data are summarized in Table I. T_g was taken at the midpoint of the transition.

In the explored temperature range all the analyzed polymers undergo the soft segment glass transition, whose position, as displayed in the thermograms, does not show a marked variation. The largest modification in the thermal behavior of the samples resides in the heat capacity change (ΔC_p) at the T_g. The introduction of EB enhances the hard–soft phase segregation effects within the polymeric material because of the strong tendency of the conductive polymer chains to aggregate. This is demonstrated by both the decrease of the T_g value and ΔC_p. In the case of PEUA, in fact, there is a partial stiffening of the soft segments due to the possible weak H-bond interaction involving the ether oxygen, which explains the higher ΔC_p value. As far as PEUASPAN is concerned, it must emphasized that the lower conductive polymer content of the material reduces the segregation, thus explaining the intermediate values of T_g and ΔC_p.

As the temperature rises, the broad endothermic peaks are associated with the disorganization process of long-range order in the hard segment domains.[13]

The temperature dependence of the dynamic mechanical properties of the polymers are shown in Figures 4(A) and (B) and 5, where the in-phase (G') and quadrature (G'') components of the complex tensile

TABLE I
Thermal Analysis Data of PEUA, PEUAPAN and PEUASPAN

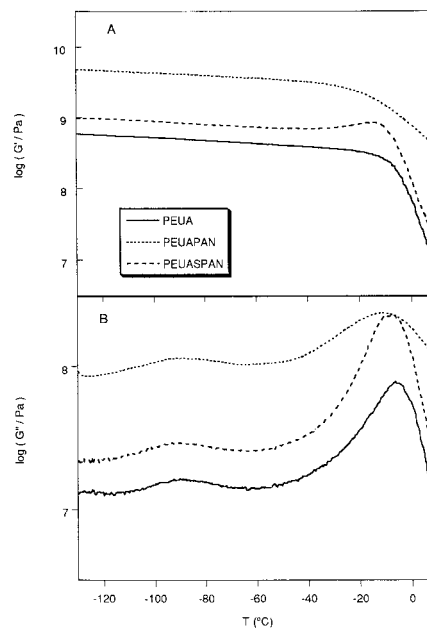| Sample	T_g(°C)	ΔC_p(J g^{-1} K^{-1})
PEUA	−7	0.45
PEUAPAN	−13	0.16
PEUASPAN	−8	0.24

Figure 4 Storage (G') and loss (G'') modulus temperature dependence of PEUA, PEUAPAN, and PEUASPAN.

modulus and their ratio (G''/G' = tan δ) are reported. The transition temperature determined from the maximum of the loss modulus G'' are listed in Table II.

In the temperature range explored, two peaks are observed—the α peak, taken as the glass transition of the polymers, and the β peak, attributed to either the relaxation of the aromatic rings[14] or to the relaxation of water molecules linked to the polymer chains by means of the hydrogen bonds.[15,16]

The α transition data are consistent with those obtained by the DSC technique. The introduction of EB and SPAN in the PEUA chain induces a decrease in the T_g value and, as the major consequence, a large decrease of the viscous component involved in the transition, being the height of the tan δ related to the mobile amorphous material (Fig. 5). A polymer stiffness increase as a function of the amount of conduc-
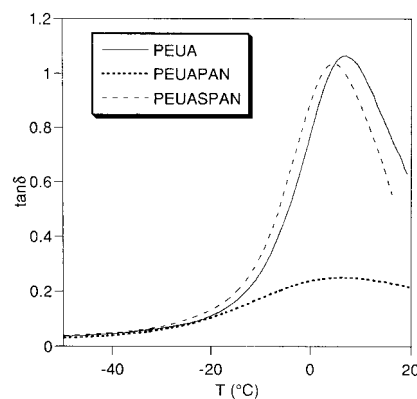

Figure 5 Loss factor (tan δ) temperature dependence of PEUA, PEUAPAN, and PEUASPAN.

TABLE II
Dynamo-mechanical Thermal Analysis Data
of PEUA, PEUAPAN, and PEUASPAN

Samples	T_α(°C)	T_β(°C)	tanδ magnitude
PEUA	−6	−89	1.07
PEUAPAN	−10	−90	0.25
PEUASPAN	−8	−89	1.03

TABLE III
Tensile Properties of PEUA, PEUAPAN and PEUASPAN

	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile set (%)
PEUA	1.1	4.6	2650	6
PEUAPAN	9.8	2.5	60	3
PEUASPAN	3.5	0.9	300	3

tive polymer linked to the polyurethane backbone is revealed by the increase of the moduli value in the glassy plateau region from −130 to −20°C and by the absence in PEUAPAN of the G'' abrupt drop during the glass transition.

The stress–strain curves of the three polymers are displayed in Figure 6, and the Young modulus, tensile strength, elongation at break, and the tensile set are reported in Table III. In the inset of Figure 6 the mechanical behavior of PEUA is reported up to the break point.

The results for the PEUA sample are comparable with the data obtained for other polyurethanes of this kind.[17] Because of a poor phase separation, due to the interaction between the carboxylic and ether groups that weakens the cohesion in the hard segment, the PEUA sample shows a low initial modulus, a high elongation at break, and a yield point at about 200% elongation. Moreover, after a 10% deformation, a tensile set of 6% indicates the presence of a partial viscous flow of the polymer chains. The EB chains, grafted to the polyurethane backbone, act as reinforcing filler, making the materials harder and less deformable. Despite this, the tensile set decreases, and the polymer films tend to be flexible and self-supported. In the PEUASPAN sample, the minor quantity of inserted conducting polymer produces an increase in the Young modulus but does not prevent the chain viscous flow at high deformation (>100%). The tensile strength, in fact, remains low.
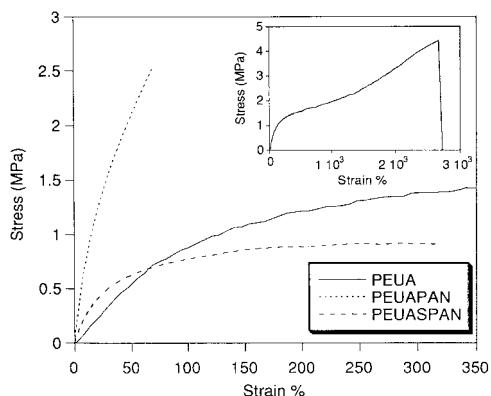
In Table IV, the electrical conductivity (σ), measured using the four-probe technique, of the pressed samples of conducting polymer and of the synthesized polyurethane films, are reported.

The conductivity of HCl-doped EB and SPAN synthesized by us are in agreement with the value reported in literature.[18,19]

PEUA, as well as undoped grafted copolymers, show a very low conductivity, typical of a good insulator. When PEUAPAN and PEUASPAN are doped, their electrical conductivity increases by many orders of magnitude, reaching values that may be suitable for many practical applications, like protection shields against electromagnetic field.

Because of the original method we have employed to prepare the conducting elastomeric polymers, it is difficult to compare our results with those presented in other works, where the blending process is used to increase the conductivity of insulating materials. Moreover, the electrical properties of these composites strongly depend on the polymer used as matrix, on the polyaniline synthesis, on doping agents, on the sample preparation method and, of course, on the concentration of the conductive filler. From the analysis reported in our previous article,[10] it was possible to estimate that the grafted conducting polymer concentration was about 13 and 5 wt % for PEUAPAN and PEUASPAN, respectively. Elastomeric conductors based on polyaniline blend, with comparable conducting filler content and neat EB conductivity, show a σ value lower[6,20] or similar[7] to that we have measured in our samples.

During extension deformation the conducting polymer films we have synthetized increase their conductivity measured along the stretch direction. Figure 7

Figure 6 Stress–strain curves for PEUA, PEUAPAN, and PEUASPAN. The figure inset shows the PEUA mechanical behavior to the break point.

TABLE IV
Electrical Conductivity of Undoped
and HCl Doped Polymers

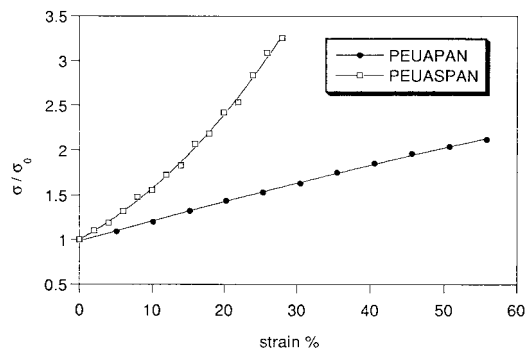| Samples	Undoped conductivity (Ω^{-1} cm^{-1})	Doped conductivity (Ω^{-1} cm^{-1})
EB	$(7.6 \pm 0.6) \times 10^{-5}$	$(3.0 \pm 0.5) \times 10^{-1}$
SPAN	$(8.1 \pm 0.6) \times 10^{-5}$	$(2.0 \pm 0.5) \times 10^{-1}$
PEUA	$<10^{-14}$	$<10^{-14}$
PEUAPAN	$<10^{-14}$	$(6.1 \pm 0.6) \times 10^{-3}$
PEUASPAN	$<10^{-14}$	$(1.5 \pm 0.6) \times 10^{-3}$

Figure 7 Relative conductivity (σ/σ_0) change of PEUA-PAN and PEUASPAN as a function of the sample deformation.

shows the conductivity ratio value σ/σ_0 as a function of the strain, where σ_0 is the conductivity of the undeformed PEUAPAN and PEUASPAN films, and σ is the conductivity in the stretching direction.

Such a behavior was also observed for composites prepared mixing polyaniline with plastic[21] or elastomeric[7] polymers. Dodecylbenzensulfonic acid doped polyaniline (PANI-DBSA) blended with ultrahigh molecular weight polyethylene shows a conductivity increase of two orders of magnitude when drawn at 105°C to a draw ratio of 40.[21] The phenomenon was associated with the high degree of orientation of the polyaniline chains along the stretch direction, as evidenced by near-infrared dichroism and wide-angle X-ray diffraction experiments.

The variation in the contact probability among the conductive PANI–DBSA aggregates, dispersed in a styrene–butadiene–styrene copolymer (SBS) matrix (polyaniline content of 11%), was, on the other hand, invoked to explain the conductivity increase during sample extension.[7] Xie and Ma found a $\sigma/\sigma_0 = 15.6$ for an elongation of 450% of the blend and, for purposes of comparison with our samples, a σ/σ_0 of about 2 for a strain of 50%. An orientation effect on the conductivity of such a material was hypothesized only for the m-cresol treated blend, in which the polyaniline chains are in a more expanded conformation.

Despite the lower concentration of the conducting component, the PEUASPAN conductivity variation due to the sample stretching is higher than that found for PEUAPAN (Fig. 7). Such a behavior may be explained in the light of a possible higher and more homogenous SPAN dispersion in the insulating matrix. This could both facilitate the orientation of the SPAN chains and increase the contact probability among conducting aggregates upon extension. Moreover, a substantial contribution to this process may be brought by the previuously described lower phase segregation of PEUASPAN, which causes a partial chain viscous flow during polymer deformation.

Because of the complexity of the system we are dealing with, a more detailed morphologic and struc-

tural analysis, which is corrently in progress, should be necessary to suggest a model explaining our phenomenological observations.

CONCLUSIONS

The physical and chemical-physical properties of elastomeric thermoplastic conducting polymers (PEUA-PAN, PEUASPAN), obtained by grafting polyaniline (EB) and sulfonated polyaniline (SPAN) on a carboxylated segmented polyurethanes (PEUA), are investigated.

The introduction of the conducting polymer in the matrix gives rise, as evidenced by thermal (DSC) and dynamo-mechanical (DMTA) characterization, to an increase of the hard–soft phase segregation of the material, because of the tendency of the conductive polymer chains to aggregate. In fact, in the DSC experiments carried out on the conducting copolymers, the heat capacity change at the T_g results to be smaller than that recorded for the PEUA, and the glass transition shifts at lower temperature.

The dynamo-mechanical thermal analysis (DMTA) confirms such a behavior, as evidenced by the reduction of the height of the loss factor peak involved in the conducting copolymers glass transition.

Moreover, the EB and SPAN chains, grafted to the polyurethane backbone, acting as reinforcing filler, partially prevent the viscous flow phenomena during the deformation of the conducting materials in stress–strain experiments and give rise, compared with the mechanical properties of the pristine matrix, to an increase of the Young modulus and a decrease of the tensile set. Copolymer films result to be flexible and self-supported.

When PEUAPAN and PEUASPAN are HCl doped their electrical conductivity σ increases many orders of magnitude, reaching values of about $10^{-3}\ \Omega^{-1}\ cm^{-1}$, which may be suitable for many practical applications. By stretching the polymer films the conductivity, measured along the deformation direction, may be further increased. At a strain of 30% the σ value is 1.5-fold, for PEUAPAN, and threefold, for PEUASPAN, greater than that of the undeformed material.

References

1. Li, S.; Dong, H.; Cao, Y. Synth Met 1989, 29, E329.
2. Adams, P. N.; Pomfret, S. J.; Monkman, A. P. Synth Met 1999, 101, 776.
3. Abell, L.; Pomfret, S. J.; Adams, P. N.; Middleton, A. C.; Monkman, A. P. Synth Met 1997, 84, 803.
4. Pomfret, S. J.; Adams, P. N.; Comfort, N. P.; Monkman, A. P. Polymer 2000, 41, 2265.

5. Kitani, A.; Yoshioka, K.; Maitani, S.; Ito, S. Synth Met 1997, 84, 83.
6. Faez, R.; De Paoli, M.-A. Eur Polym J 2001, 37, 1139.
7. Xie, H.-Q.; Ma, Y.-M. J Appl Polym Sci 2000, 77, 2156.
8. Tassi, E. L.; De Paoli, M.-A. J Chem Soc Chem Commun 1990, 155.
9. Ho, K. S.; Hsieh, K. H.; Huang, S. K.; Hsie, T. H. Synth Met 1999, 107, 65.
10. Carone, C.; D'Ilario, L.; Martinelli, A. J Appl Polym Sci, to appear.
11. Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K. Synth Met 1991, 41–43, 765.
12. Chen, S. A.; Hwang, G. W. Polymer 1997, 38, 333.
13. Grasel, T. G.; Cooper, S. L. J Biomed Mater Res 1989, 23, 311.
14. Kajiyama, T.; Macknight, W. J. Trans Soc Rheol 1969, 13, 527.
15. Varlet, J.; Cavaillè, J. Y.; Perez, J. J Polym Sci Part B Polym Phys 1990, 28, 2691.
16. Pacella, C. Ph.D. thesis, 1999.
17. Yang, C. Z.; Grasel, T. G.; Bell, J. L.; Register, R. A.; Cooper, S. L. J Polym Sci Part B Polym Phys 1991, 29, 581.
18. Armes, S. P.; Aldissi, M. Polymer 1991, 32, 2043.
19. Yue, J.; Epstein, A. J. J Am Chem Soc 1990, 112, 2800.
20. Spirkova, M.; Stejskal, J.; Quadrat, O. Synth Met 1999, 102, 1264.
21. Valenciano, G. R.; Job, A. E.; Mattoso, L. H. Polymer 2000, 41, 4757.