

Polyurethane–Polyaniline Conducting Graft Copolymer with Improved Mechanical Properties

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ABSTRACT: The crosslinking effects on the mechanical and electrical properties of a conducting copolymer obtained by grafting polyaniline on a carboxylated polyurethane were investigated. The synthesis and characterization of the polyurethane–polyaniline copolymer (PEUAPAN) were previously reported. The crosslinking process was carried out by reacting ethylenediamine with those polyurethane residual carboxylic groups not involved in the amide binding to the conducting chains. The insoluble material obtained (PEUAPANc) shows a marked elastomeric feature,

as evidenced in stress–strain and stress–relaxation measurements. Although the crosslinked graft copolymer conductivity is lower than that of the pristine material, its variation during deformation cycles is reversible because the chain relaxation and viscous flow phenomena are drastically suppressed by the crosslinks. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2516–2521, 2003

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INTRODUCTION

In previous papers, we described the synthesis¹ and the physical and chemical physical characterization² of new elastomeric copolymers obtained by grafting polyaniline or sulfonated polyaniline on a carboxylated, segmented polyurethane (PEUA). These materials show electronic conductivity when doped with hydrochloride acid and elastomeric behavior when a tensile deformation is applied. In fact, the conductive polymer inserted, acting as filler, partially prevents the viscous flow of the polyurethane chains that constitute the insulating matrix. Conductivity values reached by the graft copolymers ($\sim 10^{-3} \Omega^{-1} \text{ cm}^{-1}$) make the copolymers suitable for many practical applications; for example, protection shields against electromagnetic fields. Furthermore, the possibility of increasing the conductivity of the polymer films by stretching seems to us to be a peculiar characteristic that may have practical applications; for example, the production of strain-gauge devices. In light of such observations, we have tried to increase the elastomeric properties of the material by crosslinking the graft copolymer polyurethane–polyaniline (PEUAPAN) with ethylenediamine (EDA). The residual carboxylic functions of the polymer (i.e., those not involved in the amide bound to the conducting chains) were used. The one-pot reaction utilized the same acid group

activation system (i.e., *N,N'*-dicyclohexylcarbodiimide and *N*-hydroxysuccinimide) as that used to insert the conducting polymers by the formation of an amidic bond with the terminal NH group of the conducting polymer. The so-obtained material was insoluble and characterized by a marked elastomeric feature, as evidenced by the results of the stress–relaxation experiments.

Although the crosslinked graft copolymer conductivity was lower than that of PEUAPAN, its variation during deformation cycles was reversible because the chain relaxation and viscous flow phenomena were drastically suppressed by the crosslinks.

EXPERIMENTAL

Polymer synthesis

The syntheses of the conducting polymer (emeraldine, EB) and of the carboxylated polyurethane (PEUA), based on methylene-bis-4,4'-phenyl isocyanate (MDI), poly(propylene oxide) (PPO), and 2,2'-hydroxymethyl propionic acid (DHMPA), were reported in a previous paper.¹ The reaction leading to the crosslinked conducting graft copolymer (PEUAPANc) was carried out in three steps:

1. PEUA carboxylic groups activation with *N,N'*-dicyclohexylcarbodiimide (DCC) and *N*-hydroxysuccinimide (HSI);
2. partial amidation of activated acid functions with the terminal NH₂ of EB;
3. crosslinking of the polymer with EDA that reacts with the remaining activated carboxylic functions.

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The first two steps were described in a previous paper. As far as the third step is concerned, EDA (in 30 % molar ratio with respect to the PEUA carboxylic groups) was added in the reaction vessel before the PEUAPAN purification procedure. During the reaction, which proceeds for 24 h at room temperature under constant stirring, the solution viscosity increased until the formation of a gel occurs. PEUAPANc was purified from unreacted DCC, HSI, EDA, and dicyclohexylurea (DCU), a secondary product of the reaction, by Soxhlet extraction in methyl and ethyl alcohol. The polymer was then washed with a plenty of *N*-methyl-2-pyrrolidone (NMP; Fluka puriss. p.a.), to eliminate the unreacted EB. High-temperature boiling NMP was removed with water, and the polymer was dried under vacuum at 30°C for 24 h. The resultant PEUAPANc was insoluble in all the usual organic solvents tested.

Thermal analysis

Differential scanning calorimetry (DSC) analysis was carried out under N₂ using a Mettler TA-3000 DSC apparatus. The scan rate used for the experiments was 20 K/min, and the sample weight was ~8–9 mg.

Mechanical testing

Stress–strain curves were recorded with 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 homogeneous rectangular-shaped films. The standard test method ASTM D 412-92 was followed to evaluate the tensile properties of the polymers.

The tensile stress–relaxation experiments were carried out at 10% constant elongation, so chosen to obtain an accurate force measurement while remaining in the linear stress–strain region.³ The stress–relaxation behavior was monitored at room temperature over a time period of 1200 s after the deformation was imposed.

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 the four-probe technique on polyurethane films prepared as described in the mechanical test procedure. To follow the conductivity variation as a function of the deformation of PEUAPAN and PEUAPANc, two electrodes were placed at the ends of the sample, inside the Instron measuring cell grips. Great care was

taken 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, thereby taking into account the sample section reduction during the deformation, assuming negligible volume change.

RESULTS

The synthetic procedure adopted allows the same EB content in the two graft copolymers PEUAPAN and PEUAPANc, as evidenced by Fourier transform infrared (FTIR) measurements. Other than a weak absorption at 1640 cm⁻¹, due to the aliphatic amide bond between EDA and the carboxylic function, and a small variation in the CH₂ peaks intensity, the spectra of the two polymers are identical. In our previous paper,¹ the grafted conducting polymer concentration was reported to be ~13 wt % for PEUAPAN.

As observed in a previous paper,² the process of grafting EB on carboxylated polyurethane (PEUA) gives rise to substantial modifications of the thermal and mechanical properties of the copolymer. Indeed, the introduction of EB enhances the hard–soft phase segregation effects within the graft copolymer (PEUAPAN) because of the strong tendency of the conductive polymer chains to aggregate. This result is demonstrated by both the decrease of the glass-transition temperature (T_g) value and heat capacity change (ΔC_p) observed for PEUAPAN. Moreover, the EB chains, grafted to the polyurethane backbone act as reinforcing filler, making the materials harder and less deformable.

Because of the formation of chemical bonds between the hard segments, the effect of the crosslinking was, as expected, to further increase the phase segregation of PEUAPAN.

The thermal, mechanical, and electrical properties of the crosslinked material may be explained in the light of the new morphology of PEUAPANc. In fact, as a consequence of the decreased interaction between hard and soft segments, the greater mobility achieved by the polyether chains is reflected in the decrease of T_g to -15°C. Such a value is 2 and 8°C lower than those of PEUPAN and PEUA, respectively.

Moreover, the soft segments in a segregated state can move and orient themselves more freely when subjected to a tensile stress. The mechanical behavior change of the conducting graft copolymer due to the crosslinking reaction is shown in Figure 1. The mechanical behavior of PEUA up to the break point is shown in the inset of Figure 1.

The Young's modulus, tensile strength, elongation at break, and the tensile set of PEUA, PEUAPAN, and PEUAPANc are reported in Table I. The reduction of

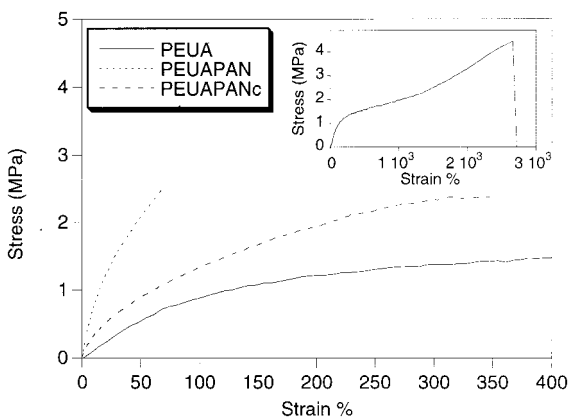


Figure 1 Stress–strain curves of PEUA, PEUAPAN, and PEUAPANc. The figure inset shows the PEUA mechanical behavior up to the break point.

the rigidity and the improvement of the elastomeric properties of the PEUAPAN were the main effects observed. In fact, a great increase of the elongation at break was found together with the lowering of the Young's modulus value. Indeed, the strong hard–hard interaction in PEUAPANc, which is due to the coexistence of the hydrogen and covalent crosslinking bonds, inhibits the viscous flow of the polymer chains at the highest strain values. After the removal of the stress, the sample entirely recovered its dimension, as evidenced by the very low value of the tensile set.

To study the progressive reduction of the plastic properties as the chemical modifications on pristine polyurethane PEUA occur, the stress–relaxation behavior of the polymers was followed. The stress variation, normalized with respect to the initial stress, f_0 , as a function of time, is shown in Figure 2. The experimental data were properly fitted with the stretched exponential law;^{4–6} that is:

$$f(t)/f_0 = f_\infty/f_0 + (1 - f_\infty/f_0)\exp[-(t/\tau)^\beta] \quad (1)$$

where f_∞/f_0 is the normalized residual stress at $t = \infty$, τ is the relaxation time, and β is a shape parameter related to the breadth of the relaxation curve and indicates the non-exponentiality of the viscoelastic responses. The parameter β (which is equal to 1 for a single exponential and decreases as the relaxation pro-

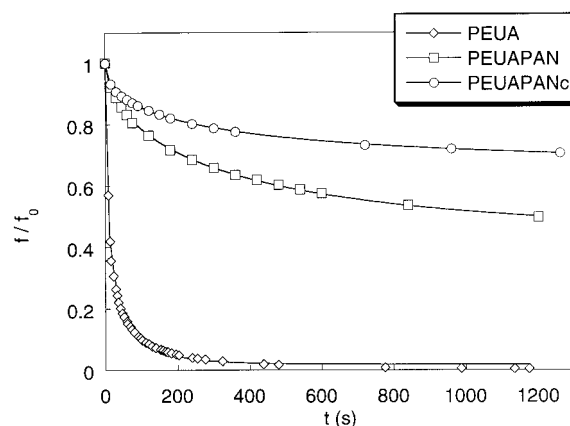


Figure 2 Stress–relaxation behavior of PEUA, PEUAPAN, and PEUAPANc.

cess stretches over different time scales) may be considered as a measure of the system nonhomogeneity.

The values of the parameters employed in eq. 1, obtained by performing a least-square fitting procedure on the experimental data, are reported in Table II. In general, the relaxation behavior of all the materials examined may not be reduced to a single exponential relaxation process; rather the behavior involves a large distribution of relaxation times, as evidenced by the low value of the parameter β .

The PEUA relaxation phenomena are very large and fast. In fact, only 1.6% of the initial stress was maintained by the polymer that undergoes a rapid reorganization of the soft segment chains toward the maximum entropic content. Soon after applying the deformation, the viscous flow took place because it was not prevented by the poor phase segregation of the material. Such a phenomenon was partially suppressed and slowed down by the introduction of the EB chains by direct linking to the hard segments. This direct linking, as pointed out in the previous paper,² enhanced the hard–soft phase segregation within the polymeric material because of the strong tendency of the conductive polymer chains to aggregate. The progressive breakdown of such structures takes place during the stress decay. The driving force of the process may indeed be found in the oriented soft chains tendency to regain a random distribution of their configuration state. Moreover, the covalent network in

TABLE I
Tensile Properties of PEUA, PEUAPAN, and PEUAPANc

Sample	Youngs modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile set (%)
PEUA	1.1	4.6	2650	6
PEUAPAN	9.8	2.5	60	3
PEUAPANc	4	2.4	350	1

TABLE II
Stress-Relaxation Parameters Calculated with Equation 1

Sample	f_{∞}/f_0	τ (s)	β
PEUA	0.016	16	0.51
PEUAPAN	0.42	358	0.59
PEUAPANc	0.61	534	0.44

PEUAPANc has the effect of stopping or slowing down the slippage of the chains and partially suppressing the hard domain disruption, as shown by the increase of relaxation time τ and f_{∞}/f_0 value. The stress decay rate decreased and, after 20 min, 70% of the initial strain was maintained.

The electrical conductivity values of our synthesized polyurethane films, measured by the four-probe technique, are shown in Table III. As previously mentioned, PEUAPAN and PEUAPANc are characterized by the same amount of conducting polymer. The lower conductivity value found for the crosslinked graft copolymer may be attributed to two distinct reasons. The first one is related to the lower HCl diffusivity inside the more compact three-dimensional structure of the material, which may result in being partially doped. The other reason is related to the different morphology assumed by the polymer. In fact, the forced phase segregation of PEUAPANc hard segments, involved in the crosslinks and in the EB amide bonds, decreases the EB dispersion in the insulating matrix and, accordingly, the contact probability among conducting aggregates.

The conductivity drop, which is a consequence of the PEUAPAN crosslinking process, represents a drawback. This drawback is overcome by the better mechanical behavior and, as will be seen later, by the outstanding electrical properties realized upon polymer deformation of the PEUAPANc compared with the non-crosslinked material.

By straining PEUAPAN and PEUAPANc films, their conductivity measured along the stretch direction increases. The conductivity ratio σ/σ_0 as a function of the strain in two consecutive deformation cycles, where σ_0 is the conductivity of the non-deformed PEUAPAN and PEUAPANc films, are shown in Figures 3A and 3B.

TABLE III
Electrical Conductivity of Undoped and HCl Doped Polymers

Sample	Undoped conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	Doped conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
PEUA	$<10^{-14}$	$<10^{-14}$
PEUAPAN	$<10^{-14}$	$(6.1 \pm 0.6) \cdot 10^{-3}$
PEUAPANc	$<10^{-14}$	$(6 \pm 2) \cdot 10^{-4}$

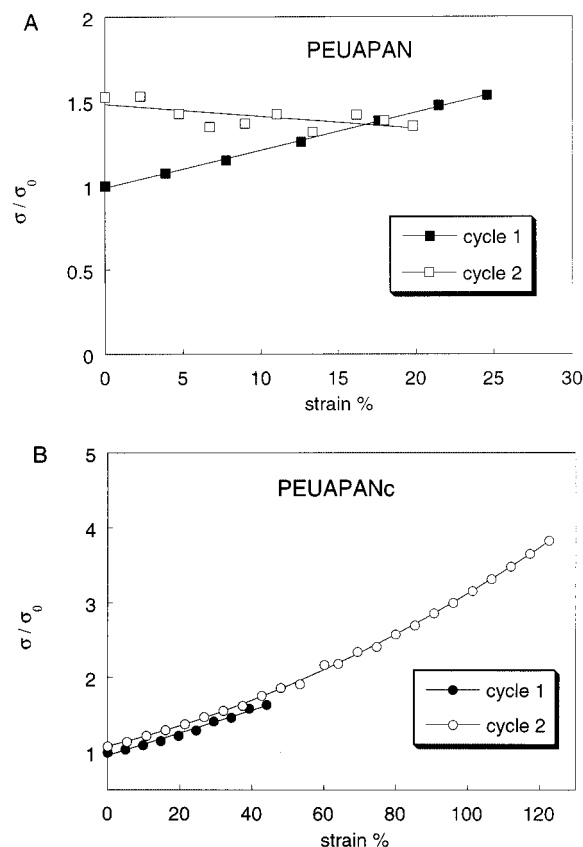


Figure 3 Relative conductivity (σ/σ_0) change of (A) PEUAPAN and (B) PEUAPANc as a function of the sample deformation for the first and second cycle.

The conductivity increase, recorded for both the polymers, may be attributed to the orientation of the polyaniline chains along the stretch direction or to the variation of the contact probability among the conductive EB aggregates. The relative conductivity variation of PEUAPAN was only slightly greater than that of PEUAPANc, whereas substantial differences between the behavior of the two polymers may be found during a second extension process carried out after the stress was removed. By applying a deformation of $<10\%$, the electrical behavior of PEUAPAN due to the applied strain is reversible. On the contrary, after a strain of 25% is applied, the PEUAPAN conductivity variation as a function of strain is irreversible (Fig. 3A). The starting σ/σ_0 value of the second cycle is approximately the same as the final value measured during the first cycle and does not substantially vary in the second deformation cycle, although a small decrease may be observed. As far as the PEUAPANc is concerned, its higher elastomeric feature allows a greater extension in both cycles. After a strain of 45% and after the nearly total recovery of the sample dimension, the conductivity data of the second cycle overlap the first cycle ones (Fig. 3B). This result indi-

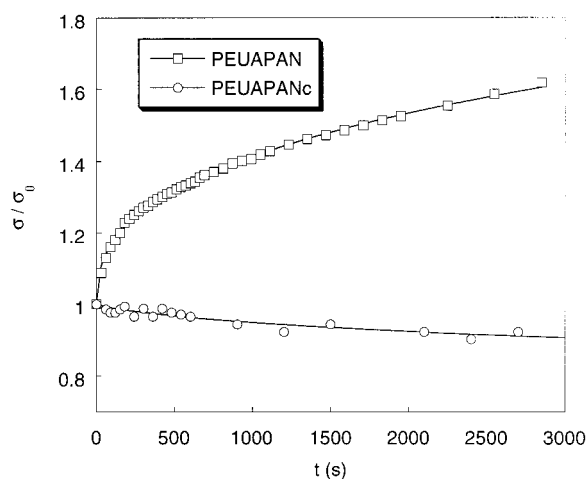


Figure 4 Relative conductivity (σ/σ_0) relaxation of PEUAPAN and PEUAPANc as a function of time.

cates that the structural and morphological changes responsible of the electrical behavior of PEUAPAN, are reversible in the experimental conditions employed.

The phenomena just described, like those of the stress–relaxation experiments, may be better understood by analyzing the sample conductivity change as a function of time after the polymer films are rapidly deformed at a fixed strain of 20%. These conductivity “relaxation” curves for the two polymers are shown in Figure 4. The σ/σ_0 value reported on the abscissa represents the conductivity variation normalized with respect to the starting value and recorded soon after the deformation was applied. The behavior of the two polymers appears to be very different: the conductivity of the PEUAPAN film drastically increased, whereas the PEUAPANc sample showed a small conductivity decrease as a function of time. As for the mechanical relaxation experiments, a phenomenological stretched exponential model was used to interpolate the data. The values of the function parameters are reported in Table IV. The relaxation time, τ , for both materials is higher than that found in the mechanical experiments. This difference may be related to the fact that the polyurethane chain portions that are not directly involved in the link with EB, like the segregated soft segments, may more freely relax. On the other hand, the fraction of the material responsible for the electrical behavior (i.e., the EB chains or polyurethane segments directly connected or interacting with the hard domains or the phase mixed soft segments of the conducting polymer), approaches the equilibrium conditions more slowly because of its lower mobility. In the non-crosslinked material, the variation of the electrical properties is strictly related to the chain viscous flow that takes place after deformation. The conducting polymer orientation and ag-

gregate disruption phenomena, which allow a more homogeneous dispersion of EB in the insulating matrix and were previously invoked to explain the conductivity increase during deformation, remain during the chain relaxation period. Such structural and morphological evolution is substantially hampered in PEUAPANc, which, as expected, relaxes to a very small extent. The data recorded in the conductivity “relaxation” experiments are consistent with those regarding the electrical behavior of our films as a function of the deformation cycles.

In conclusion, the crosslinked material, although characterized by a lower conductivity, shows marked elastomeric properties, and the electrical behavior during extension deformation is reversible. In fact, the conductivity increase with the sample stretch is observed in consecutive deformation cycles because the relaxation phenomena are nearly totally suppressed by the crosslinks.

CONCLUSIONS

We investigated crosslinking effects on the mechanical and electrical properties of a polyaniline/polyurethane conducting graft copolymer. The relaxation behaviors of the pristine (PEUAPAN) and crosslinked (PEUAPANc) material were also studied by analyzing the sample stress and conductivity changes as a function of time after the polymers films were rapidly deformed at a fixed strain. The results show that the crosslinking reaction increases the elastomeric properties of PEUAPANc, as evidenced by the great increase of the elongation at break and by the decrease of the Young’s modulus and the tensile set. This result suggests that the strong hard–hard interaction, due to the coexistence of the hydrogen and covalent crosslinking bonds, also inhibits the viscous flow of the polymer chains at the highest strain values. The viscous flow inhibition positively affects the electrical properties of the polymer; that is, the crosslinked material, although characterized by a lower conductivity compared with that of PEUAPAN, shows reversible electrical behavior during extension deformation. In fact, the conductivity increase with the sample stretch is observed in consecutive deformation cycles. The PEUAPAN conductivity variation as a function of strain is irreversible.

TABLE IV
Conductivity Relaxation Parameters
Calculated with Equation 1

Sample	σ_∞/σ_0	τ (s)	β
PEUAPAN	3.7	83000	0.4
PEUAPANc	0.8	3700	0.7

With regard to polymer relaxation behavior, the experimental data are properly fitted with the stretched exponential law. The mechanical and conductivity relaxation process of all the material examined is characterized by a large distribution of relaxation times, as evidenced by the low value of the parameter β and the very different behavior of the two polymers. In particular, after the polymers films are rapidly deformed at a fixed strain, the conductivity of PEUAPAN drastically increased during the relaxation period because of the chain viscous flow. In contrast, PEUAPANc showed a small conductivity decrease because it is substantially hampered by structural and morphological evolution.

The modification of our graft semiconducting copolymers described herein could extend their possible

future applicability in the field of electromechanical devices.

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