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IR Reflectivity Change from Electroactive IPN

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A promising alternative of multi-layered devices showing electrochromic properties results from the design of a self-supported semi-interpenetrating polymer network (semi-IPN) including an electronic conductive polymer (ECP). The formation of the ECP in the network has already been described by oxidative polymerization using iron trichloride as an oxidant and leading to conducting semi-IPN with mixed electronic and ionic conductivities as well as convenient mechanical properties. This work relates to the elaboration of such semi-IPN using a PEO/NBR (Nitrile Butadiene Rubber) IPN in which a linear poly (3, 4-ethylenedioxythiophene) (PEDOT) is formed symmetrically and selectively as thin layers on the two sides of the film matrix. PEO/NBR/PEDOT semi-IPNs lead to interesting optical reflective properties in the IR between 0.8 and 25 μm. Reflectance contrasts up to 35% are observed when, after swelling in an ionic liquid, a low voltage is applied between the two sides of the film. The PEO/NBR IPN as a thin film possesses both a good flexibility and a good resistance against thermal ageing compared with a single PEO network previously employed. Moreover, the combination of NBR and PEO in an IPN leads to materials possessing a good ionic conductivity at 25°C. Finally, NBR/PEO/PEDOT semi-IPNs allow observing comparable reflectance contrast in the IR range than those previously shown by PEO/PEDOT semi-IPNs.

Keywords Interpenetrating polymer network; nitrile butadiene rubber; poly(3,4-ethylenedioxythiophene); poly(ethylene oxide); reflective device

Introduction

The development of Electronic Conducting Polymers (ECP) since the last forty years results from their promising electronic, optical and electrochemical properties [1]. Among the numerous ECP applications the spectral electro-modulation in the visible and infrared region opens interesting possibilities to develop electrochromic devices (ECD) in the visible range [2–4] or electro-reflective devices (ERD) in the infrared [5,6]. However, a major drawback to develop sustainable applications results from the multilayered architecture of such devices. In order to favor the manufacturing of ECD or ERD, we have developed new devices with a monobloc architecture [7–10] taking advantage of Interpenetrating

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Polymer Network (IPN) macromolecular architecture. An IPN is usually defined [7] as a combination of two polymer networks synthesized in the presence of each other. An IPN presents the advantages of combining the properties of each polymer network component and leads to a far better morphological stability than corresponding polymers blends [8]. When a linear polymer replaces a polymer network inside an IPN, the architecture is called a semi-IPN.

Associations of optoelectronic properties of ECPs formed exclusively on each side of the film of the IPN lead to promising self-supported films whose optical properties change after a low voltage is applied between the two sides of the film. This device is self-supported because it does not need electronic collectors such as ITO glasses as it is the case in multilayered device. Beyond the electrochromic applications, these IPNs combining electronic and mechanical properties are also attractive for actuators [9–12].

The elaboration of these devices implies an oxidative polymerization of the conjugated monomer within the pre-formed matrix (polymer network or IPN). We have developed such a protocol with 3,4-ethylenedioxithiophene (EDOT) and $FeCl_3$ as oxidizing agent in order to obtain the corresponding polymer (PEDOT) inside a polyethylene oxide (PEO) matrix. The PEDOT embedded in the matrix was chosen because of the reversibility of the electrochemical doping-dedoping process [13,14]. The electrochromic behavior depends on the amount of PEDOT within the matrix. When the PEDOT content is low—usually <0.3 wt%—the PEO/PEDOT semi-IPN is transparent and leads to electrochromic changes in the visible range [15,16]. For higher weight contents, the semi-IPN is opaque and can be used in a device possessing interesting tunable reflectivity in the IR [17].

First we will described the elaboration of the PEO/PEDOT semi-IPN–leading to a full electroreflective device (ERD) possessing tunable reflective properties in the IR after swelling by an ionic liquid, 1-ethyl-3 methylimidazolium bis (trifluoromethylsulfonyl) imide (EMImTFSI) as electrolyte. The optical contrast was then measured as well as in the 0.8–2.5 μm range and in the middle IR, notably the band II (3–5 μm) and band III (8–12 μm). However, owing to the fact that a degradation of the PEO matrix occurs when the semi-IPN is exposed in air at 80°C [16] PEO matrix was advantageously replaced by an IPN associating PEO network and nitrile butadiene rubber (NBR) network. NBR is a polyacrylonitrile-polybutadiene copolymer [18] presenting mechanically, thermally and chemically resistant and a glassy temperature (T_g) spanning between −50°C and −15°C depending on the acrylonitrile content [19]. We will show that the optical contrast of these new NBR/PEO/PEDOT self-supported devices is as high as the one measured for PEO/PEDOT semi-IPN while the mechanical properties, notably the elongation at break of the host matrix is improved.

2. Experimental Section

The monomer 3,4-ethylenedioxythiophene (EDOT) was purified by distillation under vacuum before use. Nitrile butadiene rubber with 44 wt% acrylonitrile content (NBR, Perbunan 4456F Lanxess), bis(dimethyl benzyl) peroxide/dicumyl peroxide 98% (DCP, Aldrich), poly(ethylene glycol) dimethacrylate (PEGDM, M_n = 750 g.mol^{-1}) (Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGM, M_n = 475 g.mol^{-1}) (Aldrich), hydroquinone (Aldrich) were used without further purification. Cyclohexanone (Acros), dichloromethane (VWR), propylene carbonate (Acros, 99.5%), acetonitrile

(ACN, Acros 99.9%), bis(trifluoromethane)sulfonamide lithium salt (LiTFSI, Aldrich), N-ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide 99% (EMImTFSI, Solvionic), were used as received. 2,2′-Azobisisobutyronitrile (AIBN, initiator) (Aldrich) was recrystallized from methanol and dried under vacuum prior to use. Hydrazine solution (25% in water, Aldrich), nitrosyl tetrafluoroborate ($NOBF_4$, Aldrich, 95%) were used as received.

PEO networks were prepared as follows: 0.5 g PEGM, 0.5 g PEGDM, 1 wt% AIBN and 50 mg EDOT were stirred together under argon at room temperature [15]. The mixture was poured into a mould made from two glasses plates clamped and sealed with 500 μm thick Teflon gaskets. The mould was then held at 50°C during 4h and post-cured for 1h at 80°C. Finally after cooling at room temperature and Teflon removal, a free-standing EDOT-swollen PEO network was obtained. The EDOT-swollen PEO films are immersed in a $FeCl_3$ saturated chloroform solution in order to promote the oxidative polymerization of EDOT. The time and temperature conditions are adjusted until a homogeneous dark blue coloration is obtained.

NBR single networks were prepared [20] as follows: 48g NBR were introduced in the mixing chamber of a Haake PolyLab OS with roller-rotors speed of 50 rpm at 100°C for 10 min. 0.96g DCP was added and the blend was mixed for 10 additional minutes. The blend was compression molded and cross-linked in a hydraulic-heated press at 180°C and a pressure of 285 $kg.cm^{-2}$ for 30 min. Finally, NBR films were washed by dichloromethane in Soxhlet® during one week to extract additives and dried at 50°C under vacuum. The extractible content is close to 4%. NBR single networks are 110 μm thick. NBR/PEO IPNs were prepared by a two-step process. PEGM, PEGDM (50/50 wt/wt) and cyclohexanone (PEO precursors/cyclohexanone weight ratio = 75/25) were stirred together under vacuum during 45 min at room temperature. AIBN (3wt% with respect to the total weight of methacrylate oligomers) was introduced and the mixture was stirred 30 additional minutes under vacuum. NBR single network films, were swollen in the cyclohexanone solution of PEO precursors during 3h, wiped carefully with filter paper and laid between two glass plates. Samples were kept 1h at 70°C and 1 h at 100°C. NBR/PEO IPNs were then dried 24 h at 70°C under vacuum. The thickness of the resulting films was about 140 μm. The NBR/PEO films were soaked into pure EDOT for given intervals of time. The swollen films were then immersed into a $FeCl_3$ aqueous solution (1.5 $mol.L^{-1}$) for given intervals of time. The time and temperature conditions are adjusted until a homogeneous dark blue coloration is obtained

The morphology of the NBR/PEO/PEDOT film was imaged with a SEM model CARLZEISS AG-ULTRA 55 GEMINI, connected to an X-ray analysis system (Energy Disperse X-ray analysis, EDAX). The NIR optical characterizations were performed in reflectance mode using an integrated sphere (60mm diameter) mounted onto a JASCO V-570 spectrophotometer. The scan rate was set to 1000 $nm.min^{-1}$ between 800nm and 2500nm. For characterization in the middle infrared (MIR), a Fourier Transform Infrared spectrophotometer (Nicolet-Magnar IR) fitted to a hemispheric reflectometer SOC100 extension IR was used to record spectra between 2.5 μm and 25 μm.

The ionic conductivity of electrolyte containing semi-IPNs was measured by complex impedance method using impedance analyzer Autolab Frequency Response Analyser System. The experiments were performed in the [0.01Hz–100 kHz] frequency range at 25°C. The real component of the impedance was plotted versus the imaginary component, the resistance and, the conductivity of the film was determined at the frequency which produced the lowest imaginary response.

3. Results and Discussion

3.1. Synthesis, Characterization and Reflectance Behaviour in the IR of the PEO/PEDOT Semi-IPN

Previous work described the synthesis and characterization of the PEO/PEDOT semi-IPN first from the radical copolymerization of PEGDM and PEGM–with an equivalent PEGM/PEGDM proportion in the presence of EDOT using AIBN as initiator [17]. Then PEO/PEDOT semi-IPNs were prepared by dipping the EDOT swollen PEO films at room temperature into a $FeCl_3$ solution. These experimental conditions lead to a preferential polymerization just under the PEO network surface rather than in the bulk [11]. The self-supported and conducting PEO/PEDOT semi-IPN films can be handled easily and remain slightly flexible. The distribution of PEDOT in the conducting semi-IPN was determined at the micrometer level using AFM imaging technique, running in current-sensitive mode [17]. It clearly appears that doped PEDOT, consistent with the chemical oxidative method, is mainly located in equivalent thicknesses (few μm) depending on the polymerization time just under the surface of the semi-IPN film. For example, the penetration's depth was about 3 μm for a PEDOT content of about 1% (the PEDOT content was determined from the elemental analysis of sulfur atom).

The reflectance spectra in the 0.8 to 2.5 μm NIR range were determined according to the doping level of PEDOT. Therefore the reflectance contrast at 2.5 μm was measured between the most doped PEDOT (after treatment with $NOBF_4$) and the most dedoped state (after treatment with hydrazine). In the oxidized state (most reflective state in the near IR), the% reflectance (%R) can reach 33% at 2.5 μm, while %R is only 8% in the reduced state of PEDOT. Therefore the reflectance contrast is about 25% at 2.5 μm. The spectroelectrochemical reflective behaviour of the semi-IPN containing 1 wt% PEDOT and after swelling with EMImTFSI was carried out in the infrared between 2.5 and 25 μm. The change of the optical reflectance was studied as a function of the applied voltage. The extreme reflectance change was observed for applied voltages of -1.2 to $+$ 1.2 V corresponding respectively to the most reduced and the most oxidized PEDOT in the semi-IPN. The integrated reflectance contrasts are 30% and 37% in band II and III respectively. These values are only slightly lower than literature reported values of parent multilayered devices [5,6,21,22].

Despite satisfactory switching time and memory effect the main drawback of this device is the occurrence of a degradation process in air when the temperature is increased above 60°C [16]. This ageing mainly results from the thermal degradation of PEO leading to the formation of hydroxyl radicals which induces a degradation of PEDOT itself. For example, the electroactivity loss reaches 10% after 20000 cycles at 25°C, after 10000 at 60°C and after only 2000 at 100°C [17]. In order to improve the life time of such device when the working temperature increases and also to make film more flexible and thinner, the PEO matrix has been replaced with a new matrix containing Nitrile Butadiene Rubber (NBR) which is commercially available and possesses interesting mechanical and thermal properties [19].

3.2. Synthesis and Characterization of the NBR/PEO/PEDOT Semi-IPN

NBR single network was first prepared by using as cross-linker dicumyl peroxide (DCP) in order to further prepare NBR/PEDOT semi-IPNs. Unfortunately, when NBR single network is swollen with EMImTFSI, the resulting ionic conductivity is very low (about

Table 1. Strain and Stress at break and ionic conductivity of the two single networks and NBR/PEO IPN swollen by 40 wt% EMImTFSI

Samples	Strain at break (%)	Stress at break (MPa)	Ionic conductivity ($S.cm^{-1}$) at 20°C	Ionic conductivity ($S.cm^{-1}$) at 80°C
NBR	340	2.2	1.3×10^{-5}	1.8×10^{-4}
PEO	<10	0.5	4.9×10^{-4}	4.7×10^{-3}
NBR/PEO	110	1.2	3.4×10^{-4}	1.1×10^{-3}

10^{-6} $S.cm^{-1}$) at 25°C, a value which is three orders of magnitude lower than that of a PEO network swollen with EMImTFI [20]. As the ERD device requires high ionic conductivity in order to obtain satisfactory switching time (less than a few minutes at 25°C), NBR/PEO IPNs were synthesized.

Then the challenge was to synthesize NBR/PEO IPN presenting a convenient compromise between satisfactory mechanical properties and high ionic conductivity. Typically these characteristics were obtained for a NBR/PEO IPN with a 1/1 weight ratio in each polymer network, the PEO network requiring a cross-linking content of 50 wt% of PEGDM. Table 1 shows that the elongation at break of NBR/PEO IPN (about 110%) is intermediary between those of single PEO network and single NBR network, 10% and 350% respectively.On the other hand the stress at break of NBR/PEO IPN and PEO network is similar (about 1.2 MPa) and lower than that of NBR network (2.2 MPa). After swelling by EMImTFSI the ionic conductivities of NBR/PEO IPNs and of PEO network have the same order of magnitude (10^{-4} $S.cm^{-1}$) at 20°C and are much higher than those of single NBR networks (see Table 1).

Then the NBR/PEO/PEDOT semi-IPN was prepared by dipping the EDOT swollen PEO/NBR IPNs into $FeCl_3$ aqueous solution in order to promote EDOT polymerization. The PEDOT content within the IPN depends on the polymerization time as showed in Fig. 1.

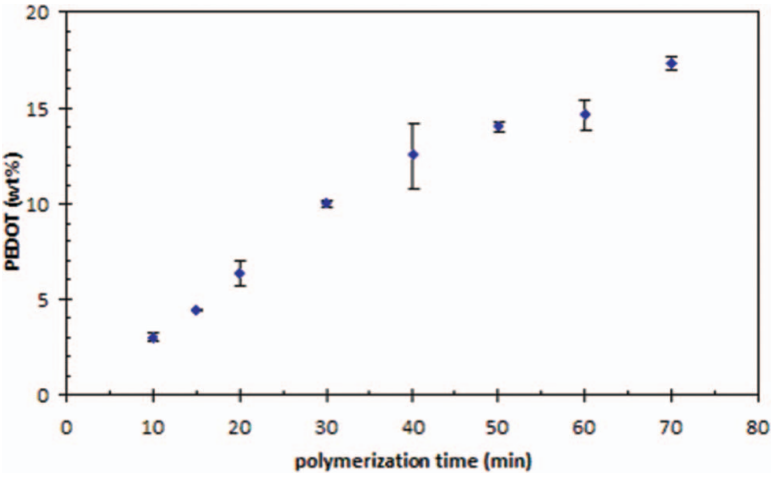

Figure 1. Effect of EDOT polymerization time at 40°C on the PEDOT content in NBR/PEO IPN.

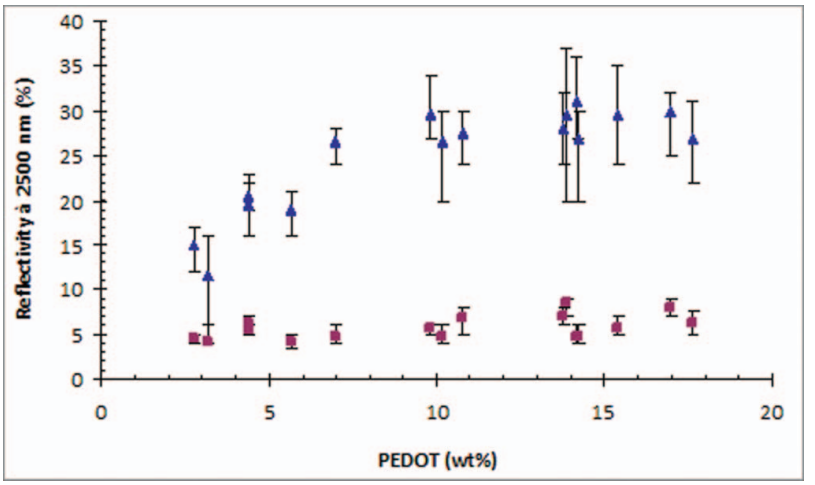

Figure 2. Dependence of the%Reflectivity at 2500 nm of NBR/PEO/PEDOT semi-IPN after dedoping step (■) and re-doping step (▲).

The PEDOT content is less than 5 wt% for a polymerization time lower than 20 minutes and reaches about 15 wt% for a polymerization time longer than 50 minutes. We have showed by SEM measurements and EDX mapping that the sulphur content is higher on each side of the film than in the centre of the sample indicating the preferential localisation of PEDOT in the IPN film [20]. For example the thickness of the PEDOT-rich phase is between 15 and 20 μm for a PEDOT content of 15 wt% for a film 140 μm thick.

We have determined the optical reflectivity at 2500 nm for NBR/PEO/PEDOT semi-IPN after a dedoping step by hydrazine and full re-doping by tetrafluoroborate nitrosyle (0.2M.of $NOBF_4$ in ACN). Figure 2 shows the evolution of%R versus the PEDOT content for both doped and de-doped steps. While%R is quite constant (average value close to 5%) when PEDOT is dedoped, a maximum value up 25% was reached when PEDOT content is above 7% in the semi–IPN. Therefore the maximum optical contrast is for PEDOT content higher than 7%.

3.3. Change of Reflectivity in the Infrared of the NBR/PEO/PEDOT Semi-IPN Self-Supported Device

The NBR/PEO/PEDOT semi-IPN becomes a flexible and soft operational device when swollen with EMImTFSI. We have shown [24] that the change of the reflectivity after applying a voltage of -1.5 or $+1.5$ V between 2.5 and 25 μm is similar to that observed for PEO/PEDOT semi-IPN. The reflectance (%R) varies from about 10% to 50% between 2.5 and 7.5 μm under the two extreme states. In the 10 to 25 μm range, the%R varies from 25 to 55% for the same applied voltage variation.

Table 2 gathers the optical contrasts observed between 2.5 and 25 μm. They are slightly higher for PEO/PEDOT semi–IPN than for NBR/PEO/PEDOT semi–IPN. The main reason is probably that the optimization carried out for PEO/PEDOT semi-IPN has not been done for NBR/PEO/PEDOT one, the optimization of both the PEDOT and the EMImTFSI content are still under investigation.

Table 2. Optical contrasts (%R) for PEO/PEDOT and NBR/PEO/PEDOT semi-IPN devices

	PEO/PEDOT semi-IPN	NBR/PEO/PEDOT semi-IPN
Optical contrast at 2.5 μm	25%	22%
Optical contrast at 7.5 μm	35%	30%
Optical contrast between 10 to 25 μm	40%	30%

Experiments are in progress demonstrating that the thermal aging of NBR/PEO/PEDOT is drastically improved compared with POE/PEDOT semi-IPN, notably in the presence of EMImTFSI.

Conclusion

This work presents the elaboration of two kinds of semi-IPNs consisting in a-PEO network or NBR/PEO IPN- host matrix in which PEDOT is formed within the matrix and preferentially located near the surface of the film matrix. After swelling with EMImTFSI, these semi-IPNs become self-supported electro-emissive devices (ERD) in the IR between 2.5 and 25 μm when a low voltage is applied between the two sides of the film. The reflectivity contrasts between the extreme doped states of PEDOT are quite similar for each ERD despite the fact that the PEDOT thickness on each side of the film is higher for NBR/PEO/PEDOT semi-IPNs than for PEO/PEDOT semi-IPNs. Finally NBR/PEO/PEDOT semi-IPNs are more interesting than PEO/PEDOT semi-IPNs due to the fact that the first one is more flexible, soft and thinner than the second one.

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