Synthesis and Characterization of IPNs for Electrochemical Actuators


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Abstract. Interpenetrating polymer networks (IPNs) have been developed for many years leading to materials with controlled properties. When an electronic conducting polymer (ECP) is incorporated into an IPN, this one becomes a conducting IPN (CIPN). The synthetic pathway ensures a non homogeneous dispersion of the ECP through the IPN thickness of the material. The system is thus similar to a layered one with the advantage that the intimate combination of the three polymers needs no adhesive interface. The last step in making the CIPN into an actuator is to ensure the ionic conductivity by incorporation of an ionic salt. The highest ionic conductivity through the IPN matrix is necessary in order to ensure the best actuation. The chosen salt is an ionic liquid, i.e. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI). Based on IPN architectures electrochemical actuators have been designed and actuation in open air has been characterized.

Introduction

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymer networks synthesized in juxtaposition. The presence of entangled cross-links strongly increases the miscibility of the polymers compared to usual blends and leads to a material with good dimensional stability. The aim of these types of polymer associations in general is to obtain materials with better mechanical properties and a possibly improved combination of the properties of their components although this last point cannot be considered as being always true. The semi-IPNs differ from IPNs in that they are composed of a linear polymer entrapped into another polymer network [1].

Electronic Conducting polymers (CPs) have attracted attention notably because of possible dimensional changes due to the ion expulsion/inclusion during oxidation or reduction process. CPs thus can be used as the active material in actuators or artificial muscles and lead to interesting potential applications (robotics, prosthetics, microvalves...)[2, 3, 4, 5, 6, 7]. Among electronic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has received much attention because of its particularly high stability in the doped state and the high structural regularity due to exclusive 2-5 linkage. Thus, this polymer is potentially very attractive for applications involving electrochemical actuators [8]. Actuators working in open air are generally built in a configuration where the internal layer is a Solid Polymer Electrolyte (SPE) sandwiched between two CP layers (CP//SPE//CP) and the relative differential expansion between conducting polymer layers results in
bending [9]. Such actuators could present a main drawback [10], indeed a delamination process which limits the actuator’s lifetime was reported when a conductive polymer film was deposited on a flexible polymer film sputtered with a thin layer of metal. This delamination is due to the poor cohesion between the CP film, the metal layer and the flexible SPE. The delamination problem can be overcome if the actuator is designed as a three-component, conducting semi-interpenetrating polymer network [11] (CIPN) where a linear electronic conducting polymer is embedded within an IPN SPE matrix. Here the matrix is composed of two polymers, with at least a poly(ethylene oxide) polymer as the SPE partner. The actuator-synthetic pathway that we developed ensures an inhomogeneous dispersion of the electronic conducting polymer through the thickness of the IPN host matrix, i.e. the quantity of CP decreases from the outside towards the center of the film. The system is thus similar to a layered actuator but for the fact that it is a one-piece device instead of being a three-layered device (Fig. 1).

![Figure 1: Beam shaped CIPN actuator](image)

Solid polymer electrolytes (SPEs) based on poly(ethylene oxide) (PEO) have been investigated extensively as ionic conducting materials [12]. The oxygen atoms in PEO can coordinate metal cations (usually Li\(^+\)) and improve ion-pair separation which favors increased ionic conductivity. One of the main drawbacks of PEO based SPEs is the often significant degree of crystallization at ambient temperature. Indeed ion migration mainly takes place in the amorphous part of the polymer and the crystalline regions decrease ion mobility both by blocking the paths of ions and by reducing the overall polymer flexibility. In order to decrease the crystallinity of PEO, the preparation of single networks or else interpenetrating polymer networks constitutes one of the most interesting approaches. However the low diffusion coefficient of ion species in the SPE leads to an intrinsically weak ionic conductivity. When the SPE is swollen into an electrolyte solution, the ionic conductivity can be increased. However, the evaporation of the solvent must be minimized which is not an easy matter. In order to solve the problem of ion conduction, several authors have shown that room temperature ionic liquids (RTIL) can be successfully used as novel electrolytes because notably of their high ionic conductivity, good electrochemical stability and non-volatility [13, 14]. Many polar polymers have been used as polymer matrices for ionic liquid electrolytes such as poly(ethylene oxide) or poly(vinylidenefluoride-co-hexafluoropropylene) [15].

In this paper, we report the synthesis of two kinds of PEO based IPN SPEs. The first one is synthesized from poly(ethylene glycol) dimethacrylate and diethylene glycol bis(allyl carbonate) leading to a poly(ethylene oxide) / polycarbonate IPN (PEO/PC IPN). The second one is composed of polybutadiene (PB) and PEO (PEO/PB IPN). In each case i.e. IPN SPEs, PEO networks act as the solid electrolyte partner and the second network in the IPN (polycarbonate or polybutadiene) will ensure convenient mechanical properties. CIPNs have been synthesized from poly(3,4-ethylenedioxythiophene) (PEDOT) and the two above mentioned SPEs. The presence of ethylene oxide units both in the PEO network and the ethylenedioxy function of PEDOT, will ensure a compatibilizing effect and should help the formation of the interpenetrating polymer network [16]. Applications to actuators working in open air for a long time have been studied. The obtained device is a one-piece actuator having bending deformation. For robotics applications, it is obvious
that a bending type deformation is of limited interest. Thus, the transformation of this initial actuator into a device exhibiting a linear deformation has been demonstrated.

Experimental

Materials
Methoxy poly(ethylene glycol) methacrylate (PEGM, Mw=300 g mol\(^{-1}\)), poly(ethylene glycol) dimethacrylate (PEGDM, Mw=875 g mol\(^{-1}\)), hydroxyl end-functionalized polybutadiene (HTPB, \(M_n = 2800\) g mol\(^{-1}\), alcohol functionality \(f_{OH} = 2.4\)) (Cray Valley), and dibutyltin dilaurate (DBTDL 95%) were obtained from Aldrich and used without further purification. Diethyleneglycol bis(allyl carbonate) (CR39\(^{\circledR}\)) (Aldrich) was used as received; 3,4-ethylenedioxythiophene (EDOT) (Bayer) was distilled under reduced pressure prior to use. Acetonitrile (HPLC grade from Acros), dichloromethane (Carlo-Erba), propylene carbonate (HPLC grade from Carlo-Erba) methanol (Carlo-Erba), anhydrous iron III chloride (Acros), lithium perchlorate (Aldrich), dicyclohexylperoxidicarbonate (DCPD) (Groupe Arnaud) and Desmodur\(^{\circledR}\) N3300 (pluri-NCO cross-linker, \(5.2 \times 10^{-3}\) mol of NCO per gram of Desmodur\(^{\circledR}\)) (Bayer) were used as received. Benzoyl peroxide (BPO) (Acros) was dried under vacuum at room temperature. Azobisisobutyronitrile (AIBN) (Acros) was recrystallized from methanol and dried under vacuum at room temperature. The synthesis of the room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (EMITFSI), was carried out according to the procedure described by Grätzel et al. [17] for subsequent use as an electrolyte in the conducting IPN.

Preparation of Poly(ethylene oxide) / Polycarbonate (PEO/PC) IPN SPE
The CR39\(^{\circledR}\) (20 wt%) and PEGDM (80 wt%) and the initiator mixture (DCPD 1 wt% with respect to PEGDM weight and BPO 5 wt% with respect to CR39\(^{\circledR}\) weight) were stirred together and poured into a glass mould to yield 250 µm thick film. The mixture is heated at 35°C for 3 hours in order to promote the formation of the PEO network. The reaction temperature is then raised to 80°C for 3 hours, allowing the PC network and thus the IPN formation. The IPN is post-cured for 3 hour at 100°C.

Preparation of Poly(ethylenedioxide) / Polybutadiene (PEO/PB) IPN SPE
DCPD was used for methacrylate radical initiation of PEGDM and PEGM methacrylate functions, while Desmodur\(^{\circledR}\) N3300 was the cross-linker for HTPB and DBTDL was the catalyst for the reaction between NCO and OH functions. The given amounts of PEGDM, PEGM, HTPB were poured as such into a flask. In all IPN preparations reported in this study, PEGM and PEGDM were introduced in a 1:3 weight ratio corresponding to 75 wt% PEGM and 25 wt% PEGDM into the PEO network. Desmodur\(^{\circledR}\) was then added to the mixture ([NCO]/[OH] = 1:1) as well as the DCPD initiator (2.2 wt% with respect to the sum of methacrylate oligomers weight). The minimum volume of toluene (typically 1 mL for a total weight of 1 g of PEGDM, PEGM and HTPB) is then added to ensure the homogeneity of the mixture. The obtained solution was stirred under argon atmosphere for 30 min, and DBTDL catalyst was then added ([DBTDL]/[OH] = 0.06). The mixture was poured into a mould made from two glass plates clamped together and sealed with a 250 thick Teflon\(^{\circledR}\) gasket. This mould was then kept at 50°C for 3 h. The sample was then postcured for 1 h at 80°C and dried for 8 h at 50°C under vacuum.

Preparation of CIPN actuator
The SPE films were soaked into pure EDOT for given lengths of time and their surface was wiped off with filter paper afterwards. The swollen films were then immersed into a FeCl\(_3\) aqueous solution (1.5 mol.L\(^{-1}\)). The film is then washed several times with methanol until the color disappears completely, i.e. excess of FeCl\(_3\) is removed. The film surface is then wiped off with filter
paper. The conducting material is dried at 60°C under vacuum for 24 h.

**Preparation of CIPN actuator with linear deformation**

The SPE films were soaked into pure EDOT for given lengths of time and their surface was wiped off with filter paper afterwards. FeCl$_3$ soaked filter paper is directly put in contact with the EDOT swollen PEO/PB IPN for 8 h. The EDOT polymerization is repeated once more. The film is then washed several time with methanol until the color disappears completely, i.e., excess of FeCl$_3$ is removed. The film surface was then wiped with filter paper. The conducting material was then dried at 60 °C under vacuum for 24 h.

**Characterizations**

The two probe-technique with gold pressure contact was used for the room temperature electrical resistance measurements on conducting IPNs. Electrical resistance measurements were performed along the surface (Rs) and across the thickness or bulk (Rb) with a KEITHLEY 197 autoranging microvolt DMM. For the measurement of Rs, the interspacing of electrodes (area of 1.8 mm$^2$) was 1 cm. The bulk conductivity was measured after cutting the film edges in order to suppress the electrical conductivity contribution through the edges along the surface.

**Actuation testing**

After the edges were cut out, the CIPNs (approximate dimensions 10x30x0.250 mm$^3$ or 10x30x0.10 mm$^3$) were immersed in a chosen electrolyte solution for a given time at room temperature. The conducting IPNs were then maintained horizontal with steel clamps. The deformation response was obtained by applying a voltage between ±2 and ±5 V. The relative deformation of the film was recorded with a laser displacement sensor (ILD 1401-5, Micro-Epsilon).

**Results and discussion**

**I. PEO/PC/PEDOT CIPN Actuator**

**PEO/PC IPN BASED SPE**

IPN SPEs based on a combination of one PEO network (80 wt%) and one PC network (20 wt%) were prepared from poly(ethylene glycol) dimethacrylate (PEGDM) and diethyleneglycol bis(allyl carbonate) (CR39®). These IPNs are synthesized via a two step in-situ method. In this method all reactants are mixed together prior to initiation, but the reaction mechanisms leading to the two network partners must be different; otherwise a single copolymer network forms through crossed reactions. However copolymerization can be prevented even in the case of a single polymerization mechanism providing the two monomers have quite different reactivity towards for instance free radicals as it will be the case here [18]. Indeed in this work, the in-situ sequential IPN strategy was chosen because the terminal methacrylate double bonds of PEGDM are more reactive than the allylic double bonds of CR39®. Thus two different initiators, each specific to one system and which decompose at two different temperatures were chosen. The monomer (PEGDM and CR39®) and initiator mixture is first heated at 35°C for 3 hours, leading to the formation of the PEO network. The temperature is then raised and kept at 80°C for additional 3 hours leading the formation of PC network through the allyloxicarbonate functions. Finally, the IPN is post-cured for 3 hours at 100°C.
Conducting IPNs were prepared by dipping the 3,4-ethylenedioxythiophene (EDOT) swollen SPE films into 1.5 mol L\(^{-1}\) iron III chloride (FeCl\(_3\)) aqueous solution. The conductivity value along the film surface is around 1 S.cm\(^{-1}\). Furthermore, the bulk conductivity, \(\sigma_b\), is at least 100 times lower than the electrical conductivity along the surface (\(\sigma_s\)). This result implies that there is an inhomogeneous distribution of PEDOT across the sample thickness, i.e. the concentration decreases from the outside towards the center, leading to a very poor connectivity of PEDOT inside the bulk of the matrix. This inhomogeneity can be taken advantage of. Indeed this type of non symmetric dispersion of the conducting polymer is precisely the characteristic in which the actuation capacity originates.

Before actuation testing, the conducting semi-IPN is swollen in a LiClO\(_4\) aqueous solution (10\(^{-1}\) mol.L\(^{-1}\)) for 24 hours. A bending deformation is observed when a voltage is applied between the two electrodes. The response time is quite slow and ranges from 5 s to 3 min depending on the applied voltages. Furthermore the working lifetime in air is limited to about 20 cycles due to the evaporation of water but the actuating capacity can be restored after immersion in LiClO\(_4\) aqueous solution. Nevertheless, the main drawback of this device is that cracking quickly develops during successive deformations.

II. PEO/PB/PEDOT semi-IPN Based Actuator

PB/PEO IPN BASED SPE

Owing to the drawbacks of the above mentioned actuator, a new conducting IPN was designed. In order to improve the bending rate, short poly(ethylene oxide) side chains into the PEO networks as dangling chains were introduced in the SPE structure through the design of a “branched PEO network” [19]. The flexibility of the chains is thus expected to be less restricted than in an unbranched network and the amount of volume available for the migration of ions would be much higher. In addition, Room Temperature Ionic Liquids (RTIL) can advantageously substitute for LiClO\(_4\) aqueous solution as mentioned previously [13, 14]. Finally, crack formation can be prevented if polybutadiene elastomer is used instead of polycarbonate in the SPE matrix.

The SPE IPN is composed of two polymers, PEO and PB in 80/20 relative weight proportion. The PEO network is obtained from polymerization /cross-linking of poly(ethylene glycol) methacrylate (75 wt%) and dimethacrylate (25 wt%) in the presence of DCPD as initiator. The PB network is obtained through cross-linking reactions between hydroxy telechelic polybutadiene (HTPB) and Desmodur\(^\circledR\) in the presence of DBTDL as catalyst. The synthesis of IPNs requires toluene as solvent since HTPB and PEGDM/PEGM are not miscible. The mixture is heated at 50°C for 3 hours, leading to the formation of the IPN. Finally, the IPN is post-cured for 1 hour at 80°C.

First, we have measured the ionic conductivity of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) “saturated state” in a single PEO or PEO/PB IPNs. Fig. 2 shows the increase in the ionic conductivity when the temperature increases from 30°C to 85°C. Ionic conductivity could not be measured in the case of PB network because conductivity values are too low, lower than 10\(^{-8}\) S.cm\(^{-1}\). The conductivity values for the single PEO networks are in the same order of magnitude than the 80/20 IPN and the values are quite high, 10\(^{-3}\) S.cm\(^{-1}\) at 30°C and increases up to 10\(^{-2}\) S.cm\(^{-1}\) at 80°C. This result can be understood since the EMITFSI uptake for the single PEO network and IPN are almost similar, i.e. 180wt% and 220wt% respectively. Ionic conductivities for both networks are lower than the conductivity of the neat EMITFSI (8.10\(^{-3}\) S.cm\(^{-1}\) at 25°C) only by less than one order of magnitude. It should be pointed out that the ionic conductivity is not affected by the presence of 20wt% PB which prevents the crack formation during
bending deformations in working actuator. These results indicate that IPN architecture appears to be, as expected, a very efficient way for designing SPE with particular mechanical properties.

![Figure 2](image)

**Figure 2**: Ionic conductivity of EMITFSI swollen networks as a function of the temperature. △: (PEO/PB) IPN (EMITFSI uptake: 220wt%); ○: PEO single network (EMITFSI uptake: 180wt%)

**PEO/PB/PEDOT CIPN ACTUATOR**

**Actuator elaboration**

CIPNs were prepared by dipping the EDOT swollen PEO/PB IPN films into a 1.5 mol L⁻¹ FeCl₃ aqueous solution for x hours leading to the formation of PEDOT inside the IPN. For all prepared samples, the electrical resistances were measured along the surface (Rs) and across the thickness or bulk (Rb) of the film. The ratio Rb/Rs, are plotted on Figure 3 as a function of the polymerization time (x hours) in FeCl₃ aqueous solution. The ratio Rb/Rs decreases as the polymerization time increases. For example, the bulk resistance is about 10 times higher than the resistance along the surface for an EDOT polymerization time of 18 hours. This result implies that there is an inhomogeneous distribution of PEDOT across the sample thickness, i.e. the concentration decreases from the outside towards the centre, leading to a very poor connectivity of PEDOT inside the bulk of the matrix. By increasing the polymerization time, the concentration of PEDOT in the center of the film should increases. Therefore the probability of PEDOT connectivity inside the bulk of the matrix increases and for a polymerization time higher than 22 hours the CIPN is not an actuator anymore. When the polymerization time is less than 16 hours not enough PEDOT has formed in order for the IPN to become conducting and thus able to perform actuating.
Figure 3. Variation of Rb/Rs ratio as a function of the polymerization time of EDOT. EDOT swollen PEO/PB IPNs (uptake: 110wt%) are dipped for x hours into a FeCl$_3$/water solution (1.5 mol.L$^{-1}$)

**Actuator characteristics**

Before actuation testing, the CIPN was swollen either in LiClO$_4$ / propylene carbonate electrolyte (LiClO$_4$/propylene carbonate) or in EMITFSI. Then, a 2V potential difference was applied between the two sides of a strip of the above CIPN and polarity inversions were applied. A bending deformation is observed. Higher potential values can be applied providing that a cycling frequency higher than 1 Hz is used. For a 10 Hz square cycling frequency, the EMITFSI swollen actuator can be cycled for $3.5\times 10^6$ times at a potential up to 4 V with no degradation.

We have determined the spectral response of CIPN actuator using a laser beam equipped device (which can respond at vibration frequencies up to 500 Hz). The test setup is shown in Fig. 4 where the actuator works under an applied voltage of ± 2V at various frequencies. An actuator (swollen in LiClO$_4$/propylene carbonate)(dimensions: 16x8x0.1-mm$^3$) is first tested at p=13 mm away from sample mount (see Fig. 4). In Fig. 5 a low peak of vibration amplitude is observed around 3 Hz and the amplitude decreases due to insufficient time for ion mobility. Then a resonance frequency is found at 10Hz and it is assigned to the sample length and mechanical properties of the CIPN. By decreasing sample dimensions (11x2x0.1-mm$^3$, tested at p=8 mm), the resonance frequency can be increased up to 15Hz.
However, as interesting as can be a bending CIPN actuator, it is probably more interesting to realize a polymer actuator endowed with a linear actuating ability in air and exhibiting displacement amplitude as high as possible because it would suit more applications including robotic and biomedical fields. The principle for building up a one-piece linear actuator using the previously described CIPN system is to promote two alternate types of areas in the CIPN: a first kind in which polymerization of EDOT will be able to occur inside the SPE and a second type of area in which no polymerization will be possible (Fig. 6). The fabrication has been performed using a masking technique in order to prevent EDOT polymerization in the central part of the SPE film [20]. This new type of film, where a precisely controlled area is completely devoid of PEDOT, was then immersed in LiClO$_4$/propylene carbonate (1 mol L$^{-1}$) before being connected through its conducting zones to a generator as shown in Fig. 6. If a low alternative voltage is applied, a linear deformation is clearly observed.

Linear displacements were measured using the laser displacement sensor. The almost full amplitude (1.9 mm) is reached after 8 seconds when a 0.05 Hz continuous square wave pulse of 3.5V is applied. Furthermore, the linear displacement increases linearly with increasing applied voltage at least for applied voltage lower than ±3V (Fig. 7).

Figure 4: Illustration of experimental setup.

Figure 5: Tip displacement of actuator with frequency. Actuator dimensions: □16x8x0.1-mm, p= 13 mm. △11x2x0.1-mm, p= 8 mm. (LiClO$_4$/propylene carbonate: 1 mol. L$^{-1}$). Applied voltage : 2V

Figure 6: Representation of the linear actuator device.
Figure 7: Linear actuator. Applied voltage dependence of the linear displacement using LiClO₄/propylene carbonate as electrolyte.

Conclusion

In summary, an interpenetrating polymer network three component system based on a non-homogeneous dispersion of PEDOT through the thickness of the PEO/PC and PEO/PB IPNs matrix was prepared as an actuator. Cracking problems were solved by introducing PB in the CIPN actuator matrix. Concerning SPE performances, ionic conductivity has been measured on a EMITFSI swollen (PEO/PB) SPE IPN and reaches a value as high as $1.6 \times 10^{-3}$ S.cm⁻¹ at 20°C. The CIPN structure exhibits advantages compared to a three-layer actuator since the adhesive interfaces between the PEDOT and SPE are suppressed by construction and replaced by a much larger interaction surface. Applying a low voltage between the two edges of the CIPN in the presence of RTIL electrolyte the actuator operates in air for a long period at 1-10Hz frequency. Linear movements in open air have been also demonstrated through precise control of PEDOT devoid areas alternating with conducting areas and the performances in linear actuation were measured.
References