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Long-Life Air Working Semi-IPN/Ionic Liquid: New Precursor of Artificial Muscles

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Interpenetrating polymer networks (IPNs) containing an electronic conducting polymer (ECP) dispersed gradually into networks of two cross-linked polymers ensuring both ionic conductivity in a presence of a salt and mechanical properties perform interesting electrically stimulation. First, we will describe how is elaborated such an actuator and what is the influence of the ECP contents on the properties of the system. Then, we will show that if the salt incorporated in the IPN is a room temperature ionic liquid, this actuator can move for a very long time in air without significant decrease of its characteristics.

Keywords: actuator, electronic conductivity, interpenetrating polymer networks, ionic liquid, poly (3, 4-ethylenedioxythiophene), room temperature

INTRODUCTION

Electronic conducting polymers (ECPs) are now considered as a very important class of materials showing interesting electrical and optical properties. However, it is well-known that several among these polymers are insoluble in common solvents and usually decompose before melting [1]. In this case, the conventional methods of polymer processing cannot be used. One possibly promising solution is the combination of a conducting and an insulating polymer into an Interpenetrating Polymer Networks (IPNs) super structure. IPNs

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are defined as a combination of two or more polymer networks necessarily synthesized in the presence of each other [2,3]. The presence of cross-linked polymers in these architectures ensures both dimensional stability and the requested mechanical properties. In most reported cases, the measured volume percolation threshold for conductivity (generally below than 5%) is lower than that which is observed in statistical blends (e.g., 16 vol. %) [4–6].

ECPs have also attracted attention notably because of possible dimensional changes generated by the ion expulsion/inclusion migrations during oxidation or reduction processes [7–14]. ECPs thus can be used as the active material in actuators or artificial muscles and lead to interesting potential applications (robotics, prosthetics, microvalves...). Actuators working in air are generally built in a configuration where the internal layer is a Solid Polymer Electrolyte (SPE) sandwiched between two ECP layers (ECP//SPE//ECP) and the relative differential expansion between conducting polymer layers leads to a movement. Such actuators present as a main drawback, a delamination process which limits the actuator's lifetime due to the poor cohesion between the conducting polymer film and the flexible SPE [12].

Among electronic conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is now considered as one of the most interesting notably due to its particularly high stability in the doped state and the reversibility of the doping process. This polymer is thus potentially very attractive for applications involving electrochemical actuators [15].

In this study, we report the synthesis of SPE IPN which is composed of two networks: polybutadiene (PB) and poly(ethylene oxide) (PEO). The first network, i.e., PEO based, will act as the solid electrolyte partner and the second network in the IPN (PB) will ensure convenient mechanical properties (for example the flexibility). Conducting IPNs have been synthesized from poly(3,4-ethylenedioxythiophene) (PEDOT) and the above mentioned SPEs [16]. The presence of ethylene oxide units both in the PEO network and the ethylenedioxy function of PEDOT, would promote a compatibilizing effect, helping the formation of the IPN. We will describe the synthetic pathway of the two conducting partners and will show that the process leads to a gradual dispersion of the electronic conducting polymer through the thickness of the network, i.e., the amount of PEDOT decreases from the outside towards the centre of the film. The system is thus similar to a layered device with the advantage that the intimate combination of the three polymers needs no adhesive interface.

Furthermore in order to avoid the solvent evaporation which decreases the diffusion coefficient of the counter-ion species in the

SPE we have chosen to use a Room Temperature Ionic Liquids (RTIL) as electrolytesince they are non-volatile and non-flammable, and can be of interest for electrochemical devices [17–20].

EXPERIMENTAL

Materials

Methoxy poly(ethylene glycol) methacrylate (PEGM, $M_w = 300$ $g \cdot mol^{-1}$), poly(ethylene glycol) dimethacrylate (PEGDM,$M_w = 875$ $g \cdot mol^{-1}$), polybutadiene – α, ω di-hydroxy functionalized (HTPB, $M_w = 2800\,g \cdot mol^{-1}$), and dibutyltin dilaurate (DBTDL 95%) were obtained from Aldrich and used without further purification. 3,4-ethylenedioxythiophene (EDOT) (Bayer) was distilled under reduced pressure prior to be used. Toluene (Carlo-Erba), methanol (Carlo-Erba), anhydrous iron III chloride (Acros), dicyclohexylperoxydicarbonate (DCPD) (Groupe Arnaud) and Desmodur® N3300 (21.8×10^{-3} moles of NCO for 1 g of Desmodur) (Bayer) were used without further purification. 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].

Preparation of Polybutadiene/poly(ethylene oxide) IPN SPEs (PB/PEO IPN)

DCPD is used for methacrylate function initiation of PEGDM and PEGM. Desmodur® N3300 is the HTPB crosslinker and DBTDL is the catalyst of the reaction between NCO and OH functions. The mixture of PEGDM, PEGM and HTPB (0.2/0.6/0.2 weight proportions) were poured into a flask. Desmodur (1.1 eq/OH functions) and DCPD (3 wt% of the PEGDM-PEGM mass) are then added to the mixture. The minimum volume of toluene is then added to ensure the homogeneity of the mixture. The solution was stirred under argon atmosphere during 30 minutes. DBTDL was added (10 mol%/OH functions) and the mixture was poured into a glass mould to yield a 250 μm thick film. The mould was heated at 50°C for 3 hours and post-cured for 1 hour at 80°C. The film is then dried under vacuum before the preparation of the actuator.

Preparation of Conducting Polymer Based (semi) IPN Actuator

The SPE films were soaked into pure EDOT for given lengths of time from 5 to 60 minutes after which their surface was wiped off with filter paper. The swollen films were then immersed for 24 hours into a

$FeCl_3$ aqueous solution ($1.5\,mol \cdot L^{-1}$). The film is washed several times with methanol until the solvent remained colorless i.e., the $FeCl_3$ excess is removed. The film surface is then wiped off with filter paper. The conducting material is dried at 50°C under vacuum for 24 hours.

Characterizations

The electronic conductivity of the conducting IPN has been measured using a two gold pressure contact probes a room temperature. Electrical resistances were performed along the surface and across the thickness or bulk with a KEITHLEY 197 Autoranging microvolt DMM. For the electrical resistance on the surface, the interspacing of electrodes (area of $1.8\,mm^2$) was 1 cm. The bulk resistance was measured after cutting the film edges in order to suppress the electrical conductivity contribution through the edges along the surface.

Deformation Testing

After the edges were cut out, the conducting IPNs (dimensions $10\,mm \times 30\,mm \times 0.250\,mm$) were immersed in a EMImTFSI for two weeks at room temperature. The conducting IPNs were then maintained horizontal with steel clamps in order to ensure electrical contact with the potentiostat. The bending response was obtained by applying a square potential wave (from $\pm 2\,V$ to $\pm 5\,V$).

RESULTS AND DISCUSSION

PB/PEO IPN Based SPE

The SPE IPN is composed of two polymers, the poly(ethylene oxide) (PEO) and the polybutadiene, (PB) with the most convenient 80/20 relative weight proportion [16]. The PEO network is obtained from copolymerization of poly(ethylene glycol) methacrylate (75 wt%) and dimethacrylate (25 wt%) in the presence of DCPD as initiator. Short PEO side chains into the PEO networks as dangling chains were introduced to increase the flexibility of the chains and the amount of free volume available for the migration of ions. The PB network is obtained through cross-linking reactions between Hydroxy Telechelic Polybutadiene (HTPB) and Desmodur 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. The morphology of the resulting IPN

has been described elsewhere and typical dual phase morphology is observed [21].

PB/PEO/PEDOT Conducting IPN

Conducting IPNs were prepared by dipping the swollen EDOT IPN films into an iron III trichloride ($FeCl_3$) aqueous solution. Indeed due to the low EDOT solubility in water, i.e., 1.5×10^{-2} mol·L^{-1}, the polymerization rate and the diffusion of EDOT out of the film into the aqueous solution is slow and allows the penetration of $FeCl_3$ in the matrix before a significant amount of EDOT leaves the matrix. For different initial contents of EDOT, sulfur elemental analyses were performed on all prepared samples. Figure 1 shows the PEDOT final content in the IPNs as a function of the EDOT initial content. For a constant time of EDOT polymerization (16 hours) an increase of the initial weight proportion of EDOT loaded in the IPN (from 70 to 300 wt%) leads to an increase of the final PEDOT content. A maximum of 10% polymerization yield inside the matrix is then observed. These results mean that the main locus of EDOT polymerization is outside the film, either in the water or at the film surface.

The electrical resistance was measured along the surface (R_s) and across the thickness or bulk (R_b) of the film. These resistances are

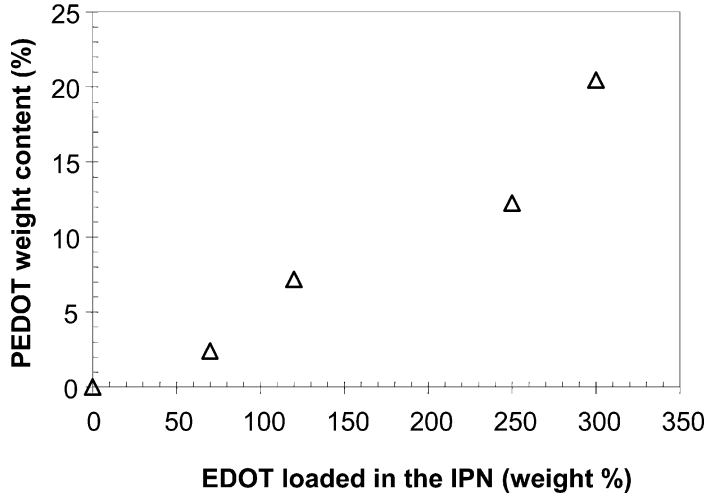

FIGURE 1 PEDOT weight content in the conducting IPN as a function of the EDOT weight proportion loaded in the PEO/PB IPN 80/20. (EDOT polymerization time: 16 hours).

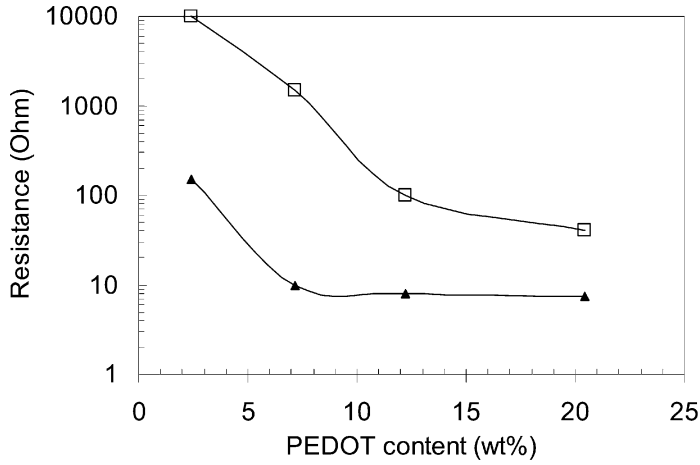

FIGURE 2 Variation of R_b (□) and R_s (▲) as a function of the weight PEDOT percent. Swollen PEO/PB IPNs with different EDOT contents are dipped for 16 hours into a $FeCl_3$/water solution ($1.5\,mol \cdot L^{-1}$).

plotted on Figure 2 as a function of the weight proportion of PEDOT. Theses curves show that for 7 weight % of PEDOT, the bulk resistance is at least 100 times higher than the resistance measured along the surface. This result implies that there is an inhomogeneous distribution

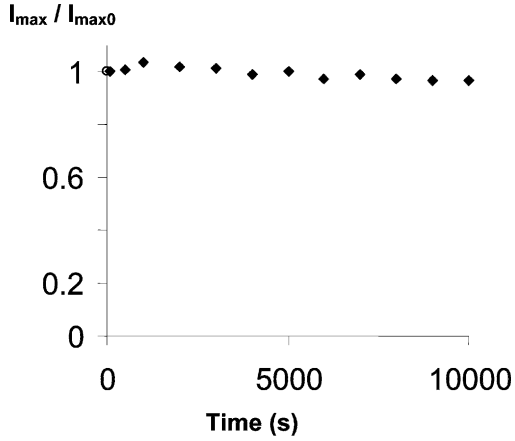

FIGURE 3 Normalized electric current versus time upon 2 V square potential pulse for EMImTFSI swollen conducting semi-IPN actuator. I_{max} represents the maximum of the current intensity and I_{max0} this maximum at $t = 0\,s$.

of PEDOT across the sample thickness, i.e., that the PEDOT concentration decreases from the outside towards the centre of the IPN sample, leading to a very poor connectivity of PEDOT inside the bulk of the matrix. This behaviour can be taken advantage of especially bearing in mind the fact the preparation of IPNs with a gradual dispersion of the conducting polymer throughout the thickness would be an asset for actuator applications. Therefore conducting IPNs were prepared according to this weight proportion (7 wt%) for actuator applications. Below this weight proportion of PEDOT, the resistance on the surface is too high, i.e., the electronic conductivity is not sufficient. For a PEDOT proportion higher than 7 wt%, the gradient tends towards to disappear.

Before actuation testing, the conducting IPN was swollen with EMImTFSI. A strip of the above conducting IPN was submitted to a potential of 2 V with a 1 Hz continuous square wave pulse. As shown on the Figure 3, the current intensity is very stable versus time and the actuator can be cycled for over 10000 times without delamination. Higher voltage can be applied providing that a cycling frequency higher than 1 Hz is used. For a 10 Hz square cycling frequency, the RTIL swollen actuator can be cycled for 3.5×10^6 times at potentials of up to 4 V with no degradation [16–21].

CONCLUSION

In this study conducting IPN based actuator architecture has been demonstrated. The device is made of PEDOT and a PEO/PB IPN. The dispersion of the conducting polymer in this device follows a symmetrical decrease from both outside faces towards the centre. The PEDOT mass quantity loaded in the conducting IPN was adjusted in order to get the electrical resistance along the surface at least 100 times higher than the in the bulk. In this case, the structure is similar to that of a typical three-layer actuator. The presence of RTIL (EMITFSI) allows the actuator be operated in open air for a very long time without significant loss of characteristics.

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