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Articles

Solid Thermoplastic Laminable Electrochromic Film

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A new kind of solid plastic electrochromic (EC) film, prepared by introducing EC molecules, belonging to a class of bipyridinium salts (viologens), and plasticizers into preformed solid thermoplastic polymers, is presented. The particularly easy preparation of this EC device makes it suitable for large-scale applications, by simple lamination of the film between conductive glasses. In this way it is possible to eliminate the disadvantages of fast EC films, due to the variation of the solvent organization around the EC molecules and to the onset of the hydrostatic pressure of the fluid layer which can break or separate from the glass supports. The electrochromic cells based on our solid films have undergone up to 10^5 operational cycles in which coloring, bleaching processes, and stationary state conditions have been adjusted by applying suitable electric pulse sequences.

Introduction

Electrochromic (EC) technology and EC devices are drawing attention for their high potentiality in relation to solar control and display applications. The working principle of EC systems is very simple and is linked to the use of EC molecules which exhibits new optical absorption bands when an electron is gained or lost in a redox process.[1,2] In the most simple EC devices, EC active molecules are dissolved in some medium interposed, as a single thin film, between the conductive inner surfaces of two transparent supports (generally glass slabs). The first examples of these EC films are those obtained by dissolving anodic and cathodic EC molecules in a fluid electrolyte solvent. In this case the performance of the system is controlled by the molecular diffusion of the EC molecules. During the coloration step, when a potential difference between the electrode layers is applied, the EC molecules need to diffuse toward the conductive electrodes, where they are reduced (cathodic process) and oxidized (anodic process). Color across the film is generated by the change of the optical absorption of the cathodic or anodic (or both of these) species.[3−5] When the electric potential is removed, anodic and cathodic molecules diffuse across the medium and the electron-transfer process, between the oxidized and reduced species, takes place. EC molecules will then return to their zero-potential equilibrium state, and the color will disappear. The electrochromic fluid film has the advantage of being reasonably fast (operational time less than 1 second) but cannot be used in large solar control window or large display for several reasons. First of all, it must be mentioned that materials forming the fluid film are subjected to natural convection or a process known as aggregation[6] or segregation,[7] due to variation of the solvent organization around the EC molecules when they undergo redox processes. Near the anode the solution density increases with respect to the bulk, owing to the oxidation of the anodic material. Polar organic solvents used in EC devices in fact yield a better solvatation of cations and oxidized species. The motion of the solvation sphere surrounding the anodic material toward the newly formed oxidized species allows the solution to become more dense. At the cathode the effect is reversed. In this way very severe color inhomogeneity in large area devices can occur. Other drawback phenomena encountered in large EC devices where fluid films are sandwiched between glass slabs are due to the onset of the hydrostatic pressure of the fluid layer which can break or separate from the glass supports.

To eliminate the disadvantages of the fluid film EC devices, polymer thickeners have been introduced into the EC fluid solution. Examples of these systems are those described by Tsutsumi et al.[8−10] which contain organic EC redox materials, solvents, and some percentage of a cross-

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linked polymer, formed by in situ polymerization of some fluid monomers added to the formulation. It is difficult to say which kinds of charge transport mechanism are acting in such gelled system. Depending on degree of thickening, an electron may be exchanged by the following: (1) mass transport to the electrode; (2) redox electron hopping and/or (3) polaron hopping; (4) combination of the above mechanisms. Other kinds of EC devices involve conducting polymers in which redox molecules are immobilized by providing reactant pendants.[11−13] In such systems electron transfer proceeds by redox hopping or by electronic conductivity of the polymer itself. Our research work different from EC gelled mobile systems and EC immobilized systems was devoted to the development of an easy technology based on self-standing materials where redox centers mobility is reduced but not suppressed.

We here present a new kind of solid plastic EC film,[14] prepared by introducing EC molecules and plasticizers into preformed solid thermoplastic polymers. These substances are exposed to a simple thermal blending process, consisting of mixing and warming the mixture to a temperature higher than the thermoplastic polymer T_g, but lower than the degradation temperature of the EC molecules. After the mixture is cooled at room temperature, a homogeneous solid film, with EC properties and great adhesion ability to a glassy support, is obtained. Thus, the preparation of the EC film does not require any solvent evaporation or UV polymerization process. This has allowed a particularly easy preparation of EC devices suitable for large-scale applications, by simple lamination of the film between conductive glasses.

Experimental Section

Preparation of the EC Device. A mixture of 40 wt % of poly(vinyl formal) (Aldrich, Italy), 4 wt % of ethyl viologen diperchlorate (Aldrich, Italy), 1 wt % of hydroquinone (Aldrich, Italy), and 55 wt % of propylene carbonate (Aldrich, Italy) was warmed to a temperature of 100 °C. After this mixture was cooled to room temperature, a homogeneous plastic mixture, with EC properties, was obtained. The EC film was prepared simply by pressing the plastic mixture using a homemade laboratory press. The thickness of the film was 200 μm. A device EC cell was prepared by laminating the film between two glass supports coated with indium tin oxide. The thickness was set to about 100 μm by means of glass spheres.

UV/Visible Spectroscopy. The electro-optical properties of ECD were measured with a YASCO V550 UV−Vis spectrometer.

The light intensity with no sample in place was assumed to be the full-scale intensity.

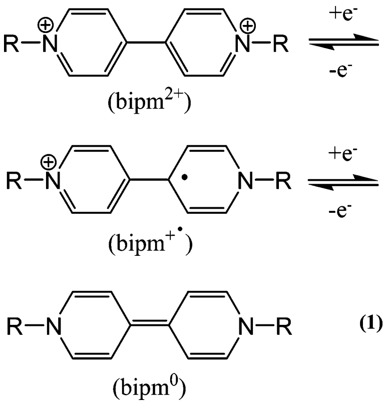
Measurements were performed at 25 °C.

Scanning Electron Microscopy. Morphology analysis was performed on cross sections of ECD, cut after immersion in liquid nitrogen, left under vacuum for several hours to extract any liquid component, gold-coated, and finally examined in a Leica LEO 420 scanning electron microscope.

Results

We obtained EC self-supported plastic film by using different thermoplastic polymers such as poly(methylmethacrylate) (PMMA), polycarbonate, thermoplastic polyurethane (TPPU), poly(vinylbutyral) (PVB), and poly(vinyl formal) (PVF), but we will present in detail only the results obtained for PVF since this polymer is a very strong adhesive for glass. On the other hand, the amount of polymer matrix exceeds 50 wt %, without severe decrease of the EC operational time. In such conditions, plastic EC film with good mechanical properties can be produced by extrusion or similar processes, independently from the presence of the supports.

Many of the cathodic EC molecules that have been used in the past in fluid films can be used as EC cathodic components, but we will report only examples of EC film obtained by using an EC cathodic component belonging to a class of bipyridinium salts (viologens), which are a well-known class of EC compounds displaying different colors dependent on their oxidation state and the nature of the substituents at the nitrogen atoms.[15−20]



(1)

For example, with simple alkyl groups the dication species are colorless while the radical cations are blue/violet. The neutral, di-reduced compounds, formed by one-electron reduction of the radical cations or by direct two-electron reduction of the dications, show a weak color intensity since no optical charge transfer or internal transition corresponding to visible wavelength is accessible.[2,15]

The introduction of anodic compounds that can act as donors shorten the operational time of the presented EC films, as was expected. Moreover, we have found that when particular anodic molecules, such as hydroquinone, are introduced, a marked shortening of the bleaching time occurs. Even if the role of these substances has to be elucidated, it

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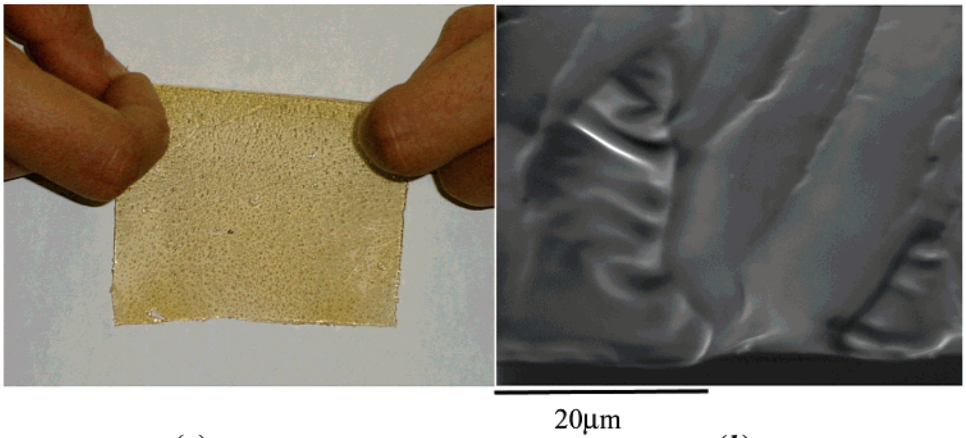


(*a*) (*b*)

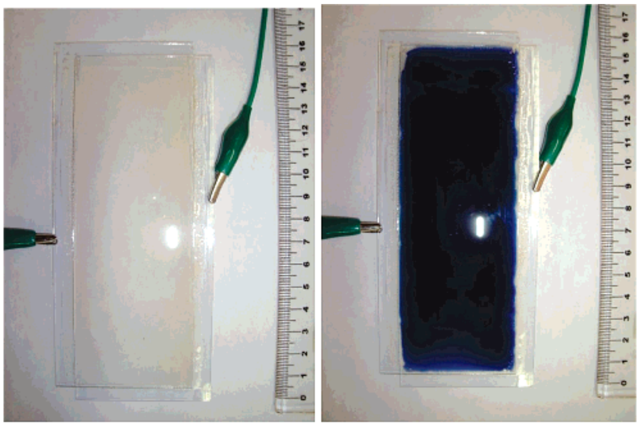
Figure 1. (a,b) SEM image of the solid EC film. Morphology of a 40 wt % PVF, 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone, and 55 wt % propylene carbonate electrochromic plastic film.

seems reasonable to expect that their great tendency to form charge-transfer complexes with viologens[21−28] can assist electron-transfer processes in EC plastic films.

To favor the dissolution of the EC molecules into the PVF polymer matrix, we have used propylene carbonate (PC) which is also a good plasticizer for this polymer. PC also has the advantage of having a high-boiling point so that no evaporation of this component occurs, during the thermal blending process.

Figure 1a shows an example of self-supported film containing 40 wt % PVF, 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone (H_2Q), and 55 wt % propylene carbonate (see the Methods section for details).

The film has been prepared only by pressing the plastic formulation (mixed by hand at the temperature of 100 °C) by a laboratory homemade press (this simple procedure of film preparation did not avoid the formation of some air bubbles inside the film). The thickness of the film shown in Figure 1a is 200 μm. Figure 1b shows a picture taken with the electron microscope of a transverse section of the same film. It can be seen that the inner structure of the film appears to be very compact. No phase separation of liquid components inside the polymer matrix are detected within a spatial resolution of the order of 2 μm. An EC cell, prepared by laminating the film presented in Figure 1 between two glass supports having ITO-coated inner surfaces, is shown in Figure 2.



(*a*) (*b*)

Figure 2. (a,b) Coloration of a laminated cell. Visual response of a 40 wt % of PVF, 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone, and 55 wt % propylene carbonate electrochromic film.

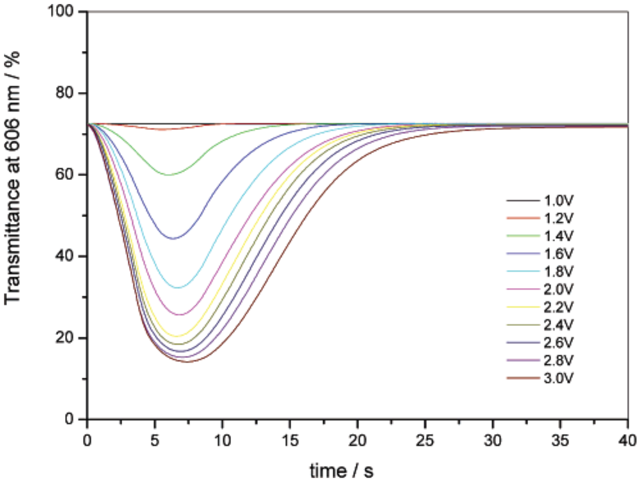


Figure 3. EC response to different pulse voltages. Transmittance of the EC cell shown in Figure 3 at 606 nm, as a function of time and applied voltage. dc pulses of 5 s have been applied to the cell.

In Figures 2a and 2b the nonoperating and operating (by 2.0 V dc current) devices are reported for comparison. The lamination has been performed by pressing the plastic film between the glass supports by means of a vacuum press at the temperature of 100 °C. The two glass supports remained strongly glued together. Any effort to delaminate the cell at room temperature without breaking the cell was unsuccessful. The system could be delaminated only at 80 °C. The thickness of the plastic electrochromic film after lamination was 100 μm. The visible spectrum of the cell shown in Figure

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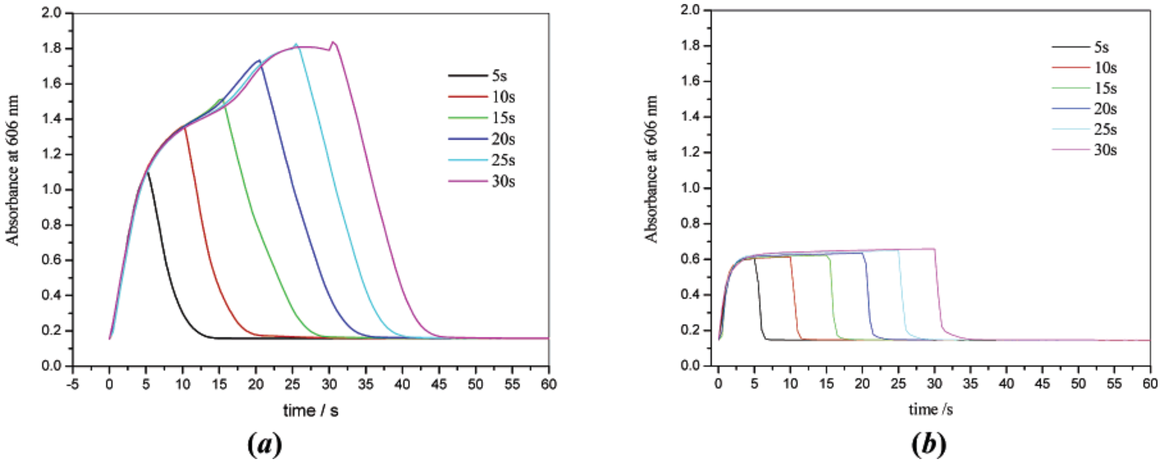


Figure 4. Electrochromic response of solid and liquid films. Comparison of the electrochromic response at 606 nm and 2.2 V of a solid plastic film containing 40 wt % PVF, 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone, and 55 wt % propylene carbonate (a) with that of a fluid film containing 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone, and 95 wt % propylene carbonate (b), for increasing driving time.

2b is characterized by an intense peak at 606 nm.

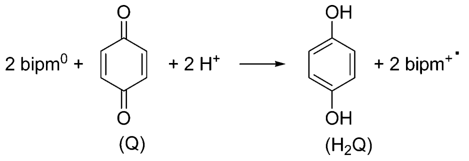
Discussion

We have chosen to follow the absorption band centered at 606 nm as a function of applied voltages and as a function of time to characterize the response of the EC. A dc square pulse has been applied to the cell. Some results are reported in Figure 3 where the transmittance of the film has been graphed as a function of the applied pulse voltage.

An EC response appears for voltages around 1.4 V and becomes more and more enhanced by increasing the voltage. The transmittance decreases during the dc pulse application since the population of the radical bipm$^{+\bullet}$ cation gradually increases, during the electrode charge injection. The absorption does not decrease immediately after the removal of the pulse, but keeps increasing for a little while. The explanation for this behavior is straightforward. At the applied voltages, the process shown in eq 1 occurs, so the bipm^0 noncolored species also starts to form. This clearly reduces the population of the red-absorbing bipm$^{+\bullet}$. Once the pulse is removed, two processes must be taken into account: the conversion of the neutral back into the monocation species and the conversion of the latter into the dication form. If the rate of the first reaction is greater than the second one, the population of the absorbing monocation species keeps increasing for a while, after removal of the dc electric pulse and then it decreases. The decay of neutral species into the monocation form, after the voltage removal, can actually occur by different chemical processes. One of these processes is the comproportionation reaction.[29,30]

$$\text{bipm}^{++} + \text{bipm}^{0} = 2\ \text{bipm}^{+\bullet} \qquad (2)$$

Another possible process for the conversion of bipm^0 into bipm$^{+\bullet}$ is given by the reaction with the oxidized form of the anodic compound, that is to say,



(3)

To show the substantial differences existing between the electrochromic response of the film presented in this paper with respect to that of a fluid film obtained by dissolving analogous percentages of the same anodic and cathodic compounds into propylene carbonate, Figure 4a and 4b are reported.

Here several absorption curves obtained by using progressively longer driving times at 2.2 V are shown. In the case of the fluid film (Figure 4b), the variation of driving time has an easy effect on the typical response of the film: the absorption curves reach a constant limit value in about 3 s. Variations of the driving time simply increase the extent of

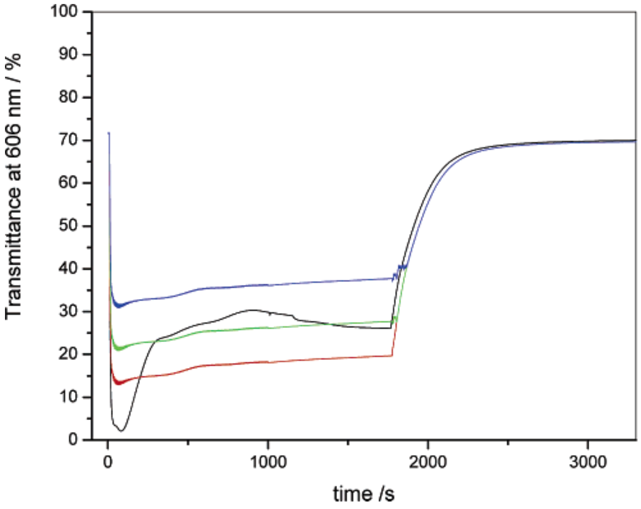


Figure 5. Electrochromic response to different electric driving modes. Long time electrochromic response of a plastic solid film containing 40 wt % PVF, 4 wt % ethyl viologen diperchlorate, 1 wt % hydroquinone, and 55 wt % propylene carbonate for two different electric driving modes. Black curve: continuous driving at 2.2 V. Red curve: modulated driving (2.2 V, 2 s ON alternated with 1 s OFF starting from 20% transmission). Green curve: modulated driving (1.8 V, 2 s ON alternated with 1 s OFF starting from 30% transmission). Blue curve: modulated driving (1.6 V, 2 s ON alternated with 1 s OFF starting from 40% transmission).

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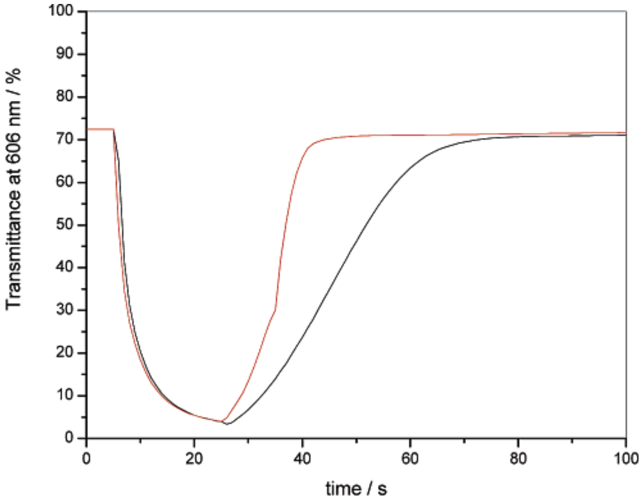

Figure 6. Bleaching time. Bleaching time shortening by application of a bleaching voltage. Black curve: bleaching is spontaneously achieved (driving voltage is shut off at 25 s). Red curve: bleaching is achieved under a bleaching voltage (2.2 V with opposite polarity with respect to coloring voltage) applied at 25 s.

this steady-state region with constant absorption. The bleaching time is also about 3 s and remains constant with variation of the driving time. The trend of the absorption curves both in the coloring and bleaching regions resembles that of a monoexponential function.

In the case of the solid film (Figure 4a) the behavior is much more complex. No stationary region appears, even during longer coloring processes. Up to 25 s of driving time, the absorption keeps increasing with increasing of the charging time. Only for driving times longer than 25 s the curves show a plateau region, where a negative slop starts to appear. For charging time above 15 s, the coloring curves also exhibit a flex. As stated before, the absorption increases for a short while after the voltage is removed. The behavior of the responses observed in both solid and fluid films is the object of another study currently in progress, where the kinetic equations related to the coloring and bleaching processes are derived and the evolution time of each species present at the electrodes is calculated. Nevertheless, we can say that the differences observed in the electrochromic response of the solid film with respect to the behavior of the fluid one must be ascribed to differences in the chemical kinetics of the redox process occurring in the film and at the interface between film and electrodes. These differences can arise from the slowing down of the molecular translation diffusion in the solid film, with respect to that of the fluid system. In the fluid film the fast translation diffusion assists the rapid establishment of a stationary state, where the concentration of the monocation species does not change during the voltage application to the cell. In a liquid-like

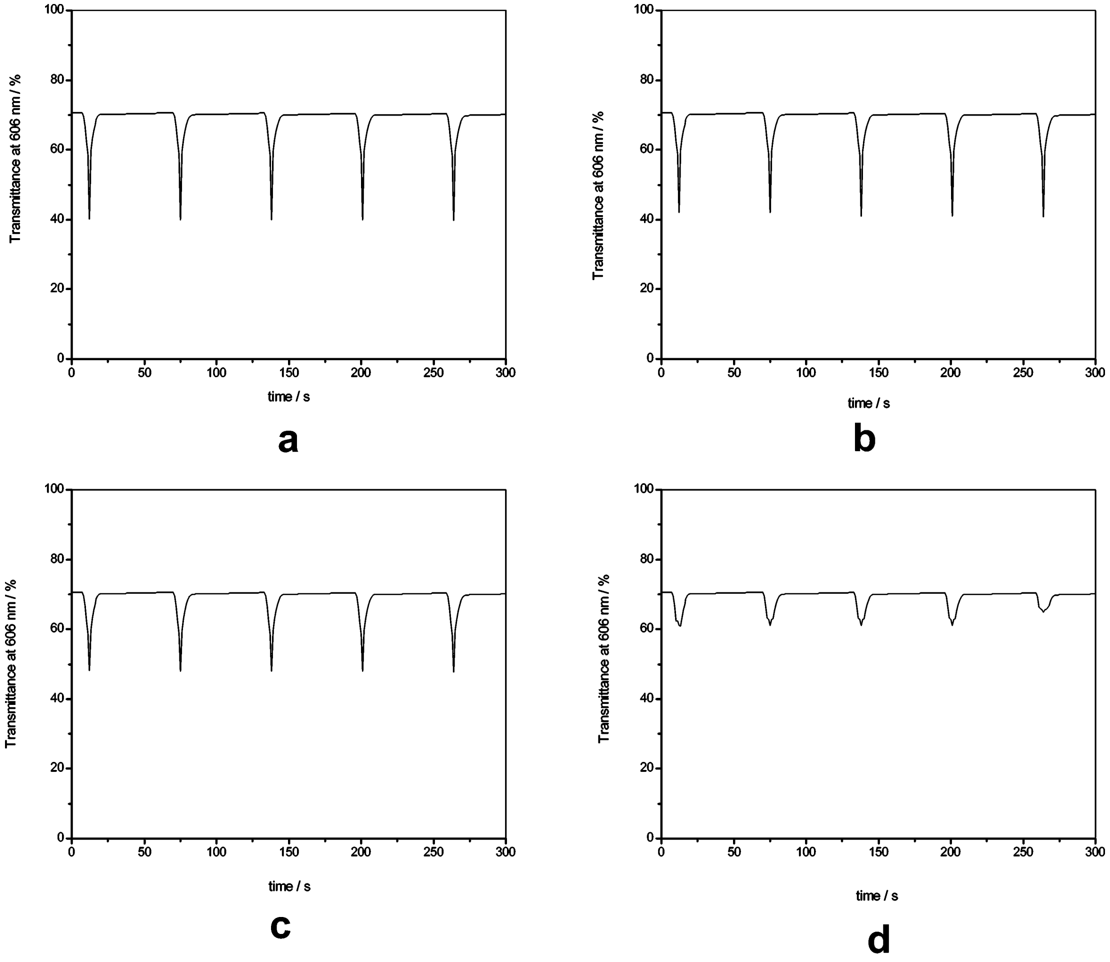

Figure 7. Operational life. Profile of some selected coloring bleaching responses at various stages of the cycling life: (a) cycles 10−14; (b) cycles 1000−1004; (c) cycles 50000−50004; (d) cycles 99996−100000. Pulse amplitude: 1.8 V. Pulse length: 5 s. Waiting time between neighboring cycles: 40 s.

environment the absorption curves abruptly drop immediately after removal of the electric power supply since the concentration of the neutral viologen remains very small in the system. In fact, fast translation diffusion leads to very efficient oxidation of the neutral viologen species, probably by both reactions (2) and (3). This effect is not observed in the solid film because the most important contribution to charge transport is given by redox hopping. Bounded translation diffusion, occurring in limited space length, cannot be excluded of course, according to the observation that coloring and bleaching times tend to increase with increasing of the polymer matrix concentration. For long electric power supplying times the population of the neutral viologen uncolored form becomes gradually important and makes the absorption curves decrease. Even if at short driving times a more intense contrast when compared to that of the fluid systems is observed, nevertheless it seems that the solid film cannot be exploited for usages in which a strong absorbing state needs to be kept constant for a long time. This problem could be solved by using electrochromic molecules having a single colored oxidized (anodic type) or reduced (cathodic type) state. We will show that the solid film presented here can be kept in an almost constant high-absorbing level, by applying appropriate time-modulated electric driving pulses. The application of potentiostatically controlled current pulses instead of continuous current has been shown to be a very useful method for producing the enhancement of the rate of coloration and the durability of electrochromic devices.[31] The enhancement of the durability of electrochromic devices produced by the periodic interruption of the applied current can be ascribed in this case to the minimization of the excess concentration of the bipm$^{+\bullet}$ species and the consequent decrease of the rate of the viologen second reduction. This is shown in Figure 5, which reports the data in transmittance units (100% is the transmittance of air) at 606 nm.

The black curve shows the transmission of the solid film as a function of time for a driving voltage kept constant at 2.2 V. The graph highlights more evidently than Figure 4a the decreasing of film absorption (increasing of transmittance) after a maximum absorption (minimum transmittance). The curve does not converge to any stationary state transmittance, at longer time, but keeps oscillating around 25% transmittance (this behavior can be better shown when a longer time scale is used). If a pulsed (2 s ON followed by 1 s OFF) driving mode is applied, using a constant driving voltage until the transmittance reaches the value of 15%, the transmittance remains almost constant in time (variation of about 3%). Of course, more stable values of absorbance could be obtained by applying tailor-made driving pulse sequences. A deep investigation with regard to this point was beyond the aim of the present work and is currently in progress Another interesting feature of the electrochromic response of the presented solid film is that the bleaching time can be shortened by applying to the film an off voltage having an opposite polarity to that applied during the coloring step. This effect is shown in Figure 6.

The black curve reported in Figure 6 was obtained from the plastic solid film, by applying a voltage of 2.2 V for 25 s. The probe light going through the sample is almost decreased to about 3%. Once the driving voltage is cut out, almost 50 s is required to bring back the transmission to the predriving level. On the other hand, when a counter voltage of −2.2 V is applied (red curve), after having colored the film for 25 s with 2.2 V, the bleaching time reduces to about 10 s.

It is very important to conclude by highlighting that the electrochromic cells based on our solid films have undergone up to 10^5 operational cycles without any damage to the systems (Figure 7).

Conclusion

We have presented here a novel electrochromic plastic self-supported film made by a solid polymer matrix where electrochromic molecules and appropriate plasticizer have been dissolved. The concentration of the polymer matrix can reach 50%, giving reasonable coloring and bleaching time. The operational times required for maximum optical contrast are of the order of 10−20 s, considerably longer than those required by most applications (1−2 s). The plastic film can be produced by extrusion and can be used in the lamination process to produce electrochromic devices, such us composite glass or plastic intelligent windows. Coloring, bleaching processes, and stationary state conditions can be adjusted by applying suitable electric pulse sequences. The laminated cells appear to be very stable up to 10^5 operational cycles.

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