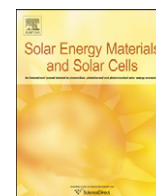




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Feasibility of conducting semi-IPN with variable electro-emissivity: A promising way for spacecraft thermal control

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ABSTRACT

This paper focuses on the performances of flexible all-polymer electroemissive devices as active materials for thermal control of satellites. These devices are made of a semi-interpenetrating network of poly(ethylene oxide) and poly(3,4-ethylenedioxythiophene) (PEO/PEDOT) where PEDOT is embedded within the PEO network and swollen with an ionic liquid. The reflectivity at 2.5 μm and the emissivity in the infrared region between 5 and 50 μm were measured at room temperature as well as the stability in vacuum. It was thus pointed out that these films exhibit interesting switching properties as notably a maximal emissivity contrast of 0.31 with a switching time less than 3 min. Moreover a low energy was required (473 J m^{-2}) to modulate the emissivity of the devices.

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1. Introduction

Thermal management of satellites is a key point for the protection of inner components such as batteries, optical instrumentation and individual payload against large temperature gradients. Spacecrafts in orbit may undergo temperature variations from -50 to $+100$ °C during exposure to cold space or sun, respectively. To keep the reliability of the components, the sensitivity of the detectors and of the pointing instruments, and also because of the limited mass and power available, it is necessary to design new systems for thermal regulation with low mass and low power consumption. Since no medium exists for conduction in the void of space, radiation is the only mode of heat transfer. Thermal control of satellites is mainly achieved using passive thermal coatings with constant thermo-optical properties, active heaters, thermostats and heat pipes. However their power consumption, their size and weight are less and less suitable with regard to future missions and economical challenge. Therefore thermal control to vary the heat rejection according to mission phase is not easily achieved and power consumption as well as the mass of the different components have to be reduced [1,2]. Some thermal louvers, which mechanically change their infrared emissivity (ϵ_{IR}) and solar absorptivity (α_{solar}), can be used today. Nevertheless this technology is costly, heavy and subject to failure since it includes mobile parts. New types of variable emissivity devices using various types of technologies are under

study, such as electrostatic radiators [3], louvers with micro-machined shutters (MEMSs) for the control of the radiator emissivity [4,5] or electrochromic devices (ECDs) [6–12]. ECDs present the advantage to be lighter, less expensive and adaptable to conventional systems and without moving parts so that micro-meteoritic impacts should have only localized effects on the system. Therefore this concept is more and more investigated by space thermal control community since the early 2000s even for future space suit temperature regulation [13].

Electrochromic devices have the ability to change their optical property such as absorbance or transmittance under the application of a low voltage [14,15]. The first electroactive materials were made of a metal oxide (such as tungsten oxide or nickel oxide) or of an organic molecule (viologen). They have been widely studied in the visible spectral region for applications such as solar glazing for buildings [16–22], windscreens and rear-views for cars [23] and optical displays [24,25]. However, few studies report their use in reflexion for infrared applications [26,27] such as camouflage coatings or thermal control of satellites. In this case, the devices are more specifically called electro-emissive devices (EEDs) [28–34]. Due to the fact that EEDs allow active control of emissivity of radiating surfaces, they are expected to lead to a significant reduction of on-board power budget and associated mass (thermal hardware, solar panel and batteries). One requirement for an external use of EEDs on satellites to avoid very high temperature when illuminated by the sun is a low solar absorptivity (< 0.3). This technology should lead to easier and more flexible design than the existing solutions for thermal control subsystem. Another advantage is that the variation of emissivity is tunable and can be programmed

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or controlled from the ground. Some commercial devices announced a tunable change in emissivity between 0.15 and 0.85 with a maximal variation of 0.53, which should allow an identical heat rejection capability to optical solar reflector (OSR) or second surface mirrors (SSMs) in hot phases of the mission [35]. In cold cases, such a variation of emissivity of radiating surfaces can reduce installed power needs for up to 70% with regard to classical solutions, depending on mission, orbit and thermal architecture of the spacecraft. More recently, electronic conducting polymers (ECPs) have been studied as electrochromic materials: the optical properties of ECP films from visible through IR range are also known to depend upon their oxidation/doping state [7,8,10,36–43]. Indeed, the application of a positive voltage on the active surface causes the layer to change its optical properties to a low emissive state (high reflective state) due to the p-doping of the ECP. On the other hand, the application of a negative voltage to the active surface causes the layer to change its optical properties to a high emissive state (low reflective state). Our laboratory recently developed an all polymer-based EED made of a semi-interpenetrating network of poly(ethylene oxide) and poly(3,4-ethylenedioxythiophene) (PEO/PEDOT) where PEDOT is embedded within the PEO network and filled with an electrolyte. This all polymer-based EED offers the advantage of being thin, flexible and resistant, while having the same components as common electroemissive materials (active layer, ion storage layer, counter-electrode and mechanical support) [44–46]. However we are confident on space durability issue of all-polymer EED since commercial samples based also on conducting polymer material have been successfully tested to gamma radiation, solar wind and UV [6,35]. This technology is considered by NASA to be experimented and used on future satellites programs [47].

In this article, the performances of PEO/PEDOT semi-IPNs were assessed for space applications. Optical measurements of the reflectivity variations between the reduced and oxidized states of the PEDOT were performed in the infrared range in ambient conditions and exhibit promising performances for spacecraft thermal control needs. In particular, contrast in emissivity, low consumption and low commutation time were confirmed. Moreover a series of thermal balance in high vacuum chamber have been performed on some samples to assess their behavior in partially space-like environment. Before going further in the evaluation and the improvement of such EED for space purpose, a brief overview of these first testing performances and results is presented in the paper.

2. Devices and experimental set-up

2.1. Materials

Poly(ethyleneglycol) dimethacrylate (PEGDM, $M_w=750 \text{ g mol}^{-1}$) (Aldrich), methoxy poly(ethyleneglycol) methacrylate (PEGM, $M_w=475 \text{ g mol}^{-1}$) (Aldrich), methanol (VWR > 99.5%), chloroform (VWR, 99.3%), anhydrous iron chloride III (FeCl_3) (ACROS, 98%) and 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide (EMITFSI) (Solvionic, 99%) were used as received. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under vacuum. 3,4-ethylenedioxythiophene (EDOT) from Bayer was distilled under reduced pressure prior to use.

2.2. Synthesis of PEO/PEDOT semi-IPN

As described in Refs. [46] and [48], PEO single networks are prepared as follows: 3 g PEGM, 3 g PEGDM, 60 mg AIBN (1 wt% with respect to the sum of methacrylate oligomers weight) and 0.3 g EDOT (5 wt%) are stirred together and outgazed under reduced pressure for 30 min at room temperature. The mixture

is then poured into a mold made of two glass plates clamped together and sealed with a 250 μm thick Teflon[®] gasket. The mold is kept at 50 °C for 4 h, then post-cured for 1 h at 80 °C. Finally after room temperature cooling, glass plates and Teflon[®] removal, a free standing EDOT-swollen PEO network is obtained.

The EDOT-swollen PEO films are immersed for 1 h in a FeCl_3 saturated chloroform solution at 50 °C in order to promote the oxidative polymerization of EDOT. The film is washed three times with methanol to remove the excess of FeCl_3 . Films are dried, edges are cut out, and then swollen with EMITFSI. The size of the sample is tailorable between 4 and 36 cm^2 and the swelling time varies with the surface of the sample (between 24 and 72 h). The thickness of the sample was about 250 μm .

2.3. Instrumentation and thermo-optical properties measurements

Electro-optical measurements were performed on a Jasco V-570 UV-VIS-NIR spectrophotometer to characterize the thermal and optical properties in the visible and near infrared range (250–2500 nm). A multi-channel VMP potentiostat (Biologic Scientific Instrument) was used additionally to the spectrophotometer to apply a bias voltage between -1.2 and $+1.2$ V. A TESA 2000 (AZ Technology) was used for emissivity measurements in the middle infrared range (5–50 μm) and also in the visible-near IR range (250–2500 nm) for absorptivity measurements at room temperature.

2.4. Thermal and vacuum testing

A prototype was developed to measure individually the emissivity modulation of each EED. It provides electrical and independent connections in order to apply the positive or negative bias to each sample: the samples are sandwiched between two aluminum plates preliminary covered with thin kapton[®] sheets (Fig. 1a). One plate serves as common counter-electrode for all samples while the other contains as many holes as samples. Then, one side of the sample is facing the environment (Fig. 1b). Electrical leads are appended to the samples to allow emissivity control and connected to a DC power supply. Thermocouples are fixed between the lower plate and each EED to measure the temperature of each sample at any time of the experiment. The objective is obviously to measure the impact of emissivity modulation during vacuum testing on the effective temperature of the surface (Fig. 1). To focus measurements on active EED effects, the prototype area located between samples was radiatively insulated from the environment with multi-layer insulation blanket (MLI) (Fig. 1c).

The rear side of the plate is heated by an electrical resistance heater in order to have a global control of the radiator thermal equilibrium and to fix reference temperature levels during test. Vacuum measurements were performed in a thermal vacuum chamber with a liquid nitrogen blackbody shroud to simulate space conditions (Fig. 2).

3. Results and discussion

3.1. Synthesis of the PEO/PEDOT semi-IPNs

The PEO network is obtained by free-radical copolymerization of poly(ethylene glycol) dimethacrylate and methoxypoly(ethylene glycol) methacrylate (50 wt%) in the presence of EDOT (5 wt%). Conducting semi-IPNs are prepared by dipping the 5 wt% EDOT-swollen PEO films at 50 °C into an iron chloride chloroform solution for 60 min in order to polymerize EDOT. The experimental conditions lead to a preferential polymerization

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