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Transparent and heat-insulation plasticized polyvinyl chloride (PVC) thin film with solar spectrally selective property

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ABSTRACT

In this work, we present the development and assessment of transparent and heat-insulation thin films that represent a new class of polyvinyl chloride (PVC) polymers. The addition of ultraviolet (UV) absorber, yellow pigment and indium tin oxide (ITO) or antimony tin oxide (ATO) showed significant improvement upon shielding effect against UV light, blue light and near-infrared (NIR) light, respectively. Particularly, environmentally friendly polyester plasticizer was applied. The optical and actual heat insulation properties were investigated by an Ultraviolet–Visible–Near infrared (UV–vis–NIR) spectrometer and a self-designed device, respectively. It was found that low transmittance (21.09% and 24.46% respectively) in NIR region (800–2600 nm) can be achieved with the addition of 2.0 phr ITO or ATO particles, and a decrease of 3 °C or 5 °C can also be observed in temperature test. Meanwhile, the thin films possessed a low UV transmittance performance (200–400 nm), accompanied with low transmittance in blue light range (400–500 nm) while maintained a high light transmittance in visible light range (400–800 nm). The shielding effectiveness provided by the materials fabricated in this study offer specificity and potency in next-generation transparent and heat-insulation thin film, with applications in protection of valuable antique, glasses, display screen and windows of automobiles.

1. Introduction

Sunlight is essential to the circulation of the living system as the main energy source. Sunlight mainly consists of three major parts: ultraviolet (UV) light, visible (Vis) light and near infrared (NIR) light. The lethal germicidal effect of UV light on bacteria has been used extensively as a high-efficiency way of sterilization [1]. Blue light, a high-energy light source in visible wavelength, is a clinically effective phototherapy in bacterial destruction [2] and plays a significant role in maintaining some groups of phytoplankton [3]. Additionally, NIR light has been used extensively in the treatment of ischemic and hypoxic wounds as a well-accepted therapeutic tool [4]. However, aforementioned lights are harmful in particular situations. The energy of UV light source is strongly centralized due to its short wavelength. Overexposure to UV irradiation will induce inflammation, sunburn and immunologic changes of skin [5,6]. UV exposure can also cause the degradation of encapsulant materials, resulting in the loss in the transparency and service life [7]. High levels of exposure to blue light may lead to ocular damage and are associated with the development of age-related macular degeneration [8]. Moreover, thermal effect of NIR may accumulate unexpected heat [9], and increase energy consumption targeted to cool inner temperature. Thus, materials with excellent optical and heat-insulation properties have great potential applications, such as glass film for building or automotive, and protective films for color printing or culture relics.

To address these problems, current researches have predominately focused on engineering transparent thin films with optical properties [10–12], yet most of them concentrate on conductivity. Indeed, the addition of inorganic functional particles into polymer matrix has promoted more satisfying properties [13–15]. Hence, some additives have been developed to block UV irradiation, blue light or NIR rays to prepare optical thin films, including ZnO [5], fluorine doped tin oxide (FTO) [16], indium tin oxide (ITO) [11,13], antimony tin oxide (ATO) [14], and cesium tungsten bronze ($Cs_{0.33}WO_3$) [17], etc. ITO and ATO are widely known as n-type oxide semiconductors, which are also good candidates for conductive fillers, transparent electrodes, solar cells and display devices because of their low resistivity and high transmittance in the visible light range [18]. ITO and ATO are known to be opaque in the NIR wavelength [19,20], because of the free carrier absorption within the conduction band [21,22]. Recently, polymer matrices have been used to produce transparent thin films in many fields, such as food packing [18], coke hoses [23], clothing fibers [24], and screen protection [25], etc. Several types of polymer matrices, like polyvinyl chloride (PVC),

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polyethylene terephthalate (PET) [18,26] and ethylene-vinyl acetate copolymer (EVA) [27], have been used in the transparent thin film industry for a long time. Around a specific temperature of 127 °C and 69 °C respectively [24,27], PET and EVA would crystallize and became opaque. PET and EVA are abandoned in this study due to their crystallization behavior under a specific temperature [24,27], whereas PVC exhibits no crystallization absolutely. Besides being durable, stable, strong and flame resistant [28,29], it can also be mixed with various additives to yield other necessary properties for more applications [30], such as toys, wall covering and flooring. Specifically, plasticizers are used widely to manufacture flexible PVC [30] thin films. However, toxic phthalate plasticizers have been used widely, which damage the environment and threat human health. In our consideration, environmentally friendly polyester plasticizer was applied and plasticized PVC was chosen to be the polymer matrix owing to its considerable transparent and excellent mechanical properties [28].

However, literatures published almost focused on shielding only one part of the harmful lights [5,6,8,12,20], or studied NIR-shielding property correlated to conductivity narrowly [12,16]. The optical and actual heat-insulation properties of transparent materials have barely been studied together. Therefore, it is of great interest to create transparent and heat-insulation materials with property of shielding all unexpected lights.

Traditionally, depositing upon a substrate is a proverbial way to fabricate optical thin films. The thin films are usually deposited by thermal evaporation method [31,32], ion beam sputtering [18], magnetron sputtering [12], and laser ablation [32]. Nevertheless, melt blending method is another efficient way to fabricate optical thin films [33]. In this study, melt blending method was applied. ITO or ATO particles can be dispersed into the polymer substrate mechanically by fluid shear force in melting process.

In this study, plasticized PVC was used for its considerable transparent and perfect mechanical properties and environment friendly polyester plasticizers were used for green concept particularly. UV absorber and yellow pigment were applied to block UV irradiation and blue light, respectively. ITO or ATO particles were also introduced to shield NIR light. Thus, plasticized PVC/ITO and plasticized PVC/ATO thin films showed improved optical and heat-insulation properties while remaining highly transparent. Herein, the influence of UV absorber, yellow pigment and different content of ITO or ATO on transmittance and mechanical properties were systematically investigated. Furthermore, the heat-insulation property was also evaluated by a self-designed device.

2. Experimental

2.1. Materials and sample preparation

PVC resin (Type: S-1000) was purchased from China Petrochemical Co. Ltd., Qilu Branch. ITO and ATO were supplied by Nanjing Haitai nano-materials Co. Ltd., China. Polyester plasticizer (2230) was from Dainippon Ink and Chemicals Inc., Japan. Organotin stabilizer (T-137) was provided by Arkema Beijing Chemical Co. Ltd., China. Liquid paraffin used as lubricant was produced by Jinling Petrochemical Co. Ltd., China. UV absorber (UV326) was obtained from Ciba Specialty Chemicals Co. Ltd., Switzerland. Yellow pigment (PY14) was supplied by Nanjing Huage Electronics and Automobile Plastic Industry Co. Ltd., China.

The synthesis formulation is defined in Table 1. The amount of additives is calculated by per hundred ratio (phr) to the mass of PVC resin. Plasticized PVC (100 phr PVC, 65 phr polyester plasticizer, 1.5 phr organotin, 0.6 phr liquid paraffin, 0.5 phr UV absorber (UV326) and 0.01 phr yellow pigment) was used as a control and was melt-blended with different content of ITO or ATO particles

Table 1
Synthesis formulation of specimens blended with different amount of additives.

PVC	Polyester plasticizer	Organotin	Liquid paraffin	UV absorber	Yellow pigment	ITO	ATO
100	65	1.5	0.6	0.5	0.01	–	–
100	65	1.5	0.6	0.5	0.01	0.5	–
100	65	1.5	0.6	0.5	0.01	1.0	–
100	65	1.5	0.6	0.5	0.01	1.5	–
100	65	1.5	0.6	0.5	0.01	2.0	–
100	65	1.5	0.6	0.5	0.01	–	0.5
100	65	1.5	0.6	0.5	0.01	–	1.0
100	65	1.5	0.6	0.5	0.01	–	1.5
100	65	1.5	0.6	0.5	0.01	–	2.0

for 5 min in a two-roll mill at 150 °C. The mixtures were subsequently compressed into 0.3 mm and 1 mm thickness thin films at 160 °C under a pressure of 10 MPa before further characterizations. 0.3 mm thickness thin films were used in transmittance spectra, light transmittance and haze measurement, while 1 mm thickness thin films were used for mechanical and heat-insulation properties test.

2.2. Characterization

Light transmittance and haze were measured by an automatic transmittance haze meter (WGT-S, Shanghai instrument physical optics instrument Co. LTD., China) according to ASTM D 1003 standard. Ultraviolet–Visible–Near infrared (UV–vis–NIR) spectrometer (UV3101PC, Shimadzu Co., Japan) was used to obtain transmittance spectra, ranging from 200 to 2600 nm. Transmittance (T) was proposed to evaluate the transmittance in different regions, which can be calculated by:

$$T = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda) d\lambda}{\lambda_2 - \lambda_1} \quad (1)$$

where $T(\lambda)$ is the transmittance value at the wavelength (λ); λ_1 and λ_2 are the minimum and maximum wavelength values of a solar region, respectively.

Actual heat-insulation property was assessed using a previous protocol [34], by a self-designed device [35]. The self-designed device is a high heat-insulation polymeric cylinder with a thermometer. The samples were all mounted on the glass surface of the device when the temperature test was conducted, on a sunny day. Another device without samples is also needed at the same time and the same place as a control. The internal temperatures are read during a certain time interval.

The tensile and tearing properties of the thin films were investigated by a universal testing machine (CMT 5254, Shenzhen SANS Testing Machine Co., Ltd., China) at a testing rate of 200 mm/min, according to GB/T 13022-1991 and GB/T 529-91, respectively.

3. Results and discussion

3.1. Light transmittance and haze

Table 2 demonstrates the light transmittance and haze of the mixtures. The light transmittance of the thin films is negatively correlated with increasing ITO or ATO content, and the increase in haze is accompanied simultaneously. With the addition of 0.5 phr ITO content, the light transmittance and haze are 85.47% and 6.57%, respectively. By adding 2.0 phr ITO content, the light transmittance declines to 76.34%, while the haze goes up to 16.08%. With regard to the plasticized PVC/ATO thin films, the addition of 2.0 phr ATO into the matrix decreases the light transmittance to 66.23%, and