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Toward transparent composite films with selective solar spectral, flame retardant and thermal insulation functions

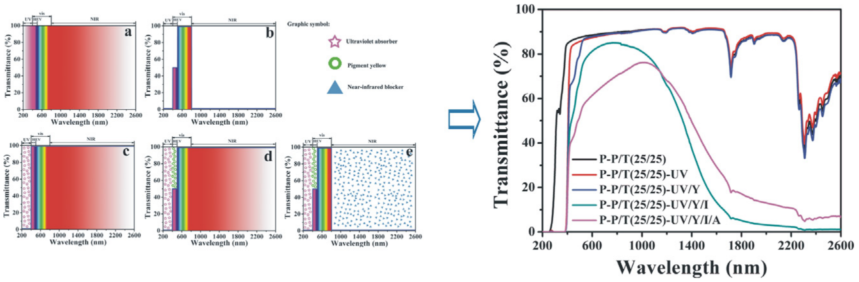
Xiuping Yin[a,b], Zhen Zhang[a], Miao Wu[a], Jun Zhang[a,b,*], Guozhong Xu[c]

[a] College of Materials Science and Engineering, Nanjing Tech University, Nanjing, 210009, China
[b] Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, Nanjing, 210009, China
[c] Nanjing Huage Electric Plastic Co., Ltd., Nanjing, 210009, China

HIGHLIGHTS

- The prepared transparent film blocked different wavelength light in solar spectrum.
- Simultaneous increase in the thermal insulation and flame retardancy was achieved.
- The mechanism of the selective blocking different wavelength light was elucidated.

GRAPHICAL ABSTRACT



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ABSTRACT

Optical films with high visible (vis) wavelength transparency as well as high ultraviolet (UV) light/high-energy visible (HEV) light/near-infrared (NIR) blocking properties are desired for applications as glass films in building/automotive, and protective films for color printing or culture relics. Herein, the above multi-functions were achieved by preparing the PVC with plasticizer, UV absorbers, pigment yellow and NIR blockers. The prepared transparent films keep high transmittance in visible region (74.53%) and low transmittance in UV region (0.35%), HEV region (52.80%) and NIR region (28.11%). Meanwhile, the flame retardancy was considerably high as verified by its high limiting oxygen index (LOI) value (31%). Moreover, a decrease of about 14.1 °C can also be observed in temperature test using a solar simulator, indicating their outstanding heat insulation/cooling properties. No loss in mechanical performance was observed with the addition of functional additives. All these suggest the potential of using PVC films for outdoor heat-insulation applications.

1. Introduction

Optical films with high visible (vis) wavelength transparency as well as high ultraviolet (UV) light/high-energy visible (HEV) light/near-infrared (NIR) blocking properties are needed for applications as glass films in building or automotive, and protective films for color printing or culture relics [1]. Recently, multi-layer nanocomposite films using inorganic nanoparticles with special selective solar properties have been well studied [2–4]. Nanocomposite films using organic polymers and inorganic/organic nanoparticles have attracted significant attention because their potential to be used in optical applications requires high visible transparency [5]. The properties of the composite films can be achieved through selection of nanoparticles, functional additives and mixed them with certain polymeric matrix. Among the wide variety of polymers, poly (vinyl chloride) (PVC) represents a class of thermoplastic polymeric materials with extensive industrial applications, such

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[*] Corresponding author. College of Materials Science and Engineering, Nanjing Tech University; Nanjing, 210009, China.
E-mail address: zhangjun@njtech.edu.cn (J. Zhang).

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as bill boards, optical devices, and packaging [6]. PVC films can be divided into soft and rigid films, depending upon the content of plasticizer [7]. Plasticized PVC does not block UV light, but it can be modified to block UV, HEV or NIR light via addition of appropriate inorganic and organic nanoparticles. UV absorbers that can transform the incoming radiation into low energy thermal dissipation are good choice for UV protection of the organic polymers [8–10]. Therefore, UV-shielding materials have been prepared by adding a slight amount of UV absorbers. HEV light can been blocked by adding pigment yellow, which served as the complement color of blue (the main part of HEV), can absorb blue light [11,12]. Moreover, near-infrared blocker such as metal oxides (indium tin oxide (ITO), antimony tin oxide (ATO)) with wide band gap are ideal candidates for NIR blocking [13].

Besides the optical performance, flame retardancy and thermal stability are another two factors that should be considered in real applications. PVC itself is non-flammable because of relatively high chlorine content (56.8%) [14]. However, the addition of relatively high amounts of plasticizers greatly dilutes the flame retardent effect of chloride and therefore largely reduces the flame retardancy of pristine PVC [7]. Therefore, flame retardants are usually added in plasticized PVC in order to reduce the possible fire hazard. On the other hand, PVC is of low thermal stability. In some cases, the added flame retardents even exert a catalysis effect of dehydrochlorination of PVC during thermal degradation, which lowers the thermal stability.

In our previous work [5], high transparent plasticized PVC films with selective optical properties and cooling performance were prepared with the assistance of UV absorber, yellow pigment, ATO/ITO. However, the prepared film is lack of flame retardancy [5]. While replacing the polyester plasticizer with flame-retardant plasticizer (tris (1-chloropropan-2-yl) phosphate, TCPP) and further addition of antimony trioxide (Sb_2O_3) did help to improve its flame retardancy [15]. However, the improvement was based on the sacrifice of thermal stability and transparency [15]. Therefore, we herein aimed to prepare plasticized PVC composite that not only has great flame retardancy, but also exhibits good thermal, optical and heat-insulation properties. As the best of our knowledge, preparing plasticized PVC transparent films that possess multi-functions (flame retardant, thermal insulation functions) without any loss in transparency and other properties has not been reported yet, although transparent optical films in other polymeric systems that has thermal-insulation [16] and/or flame-retardancy [17] have been investigated. To achieve these goals, polyester plasticizer (PEP) and flame-retardant plasticizer (tris (1-chloropropan-2-yl) phosphate, TCPP) with different ratios were firstly investigated regarding the flame retardancy and thermal stability. It was found that TCPP can increase the flame retardancy but greatly lower the thermal stability. So a volume ratio of PEP/TCPP (25/25) which has a balance between these two was selected and the functional additives such as UV absorbers, pigment yellow, ITO and ATO were added to improve the optical and heat-insulation properties. Limiting oxygen index (LOI), thermogravimetric analysis (TGA), mechanical properties, ultraviolet-visible-near-infrared spectrophotometer (UVPC) and temperature testing were used to evaluate the performance of the composites.

2. Experimental

2.1. Materials

PVC resin (Type: S-1000) that has a polymerization degree of 970–1070 was provided by China Petrochemical Co. Ltd., Qilu Branch. PEP was from Dainippon Ink AND Chemical Co. Ltd., Japan. Organotin stabilizer (T-137, butyl type with around 14 wt% tin) was purchased from Arkema Beijing Chemical Co. Ltd., China. Liquid paraffin was produced by Jinling Petrochemical Co. Ltd., Switzerland. TCPP was obtained from Jiangsu Jacques Chemical Co., Ltd., China. 2-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-5-chlorobenzotriazole (UV326) was produced by BASF Chemicals (China) Ltd., China. Pigment Yellow was obtained from Clariant Chemicals (China) Ltd, and its specific information (i.e., molecular structure) can be referred in our published work [18]. ITO and ATO were supplied by Nanjing Haitai Nano-materials Co. Ltd., China.

Table 1
Formulation of samples filled with different additives.

Sample code[a,b]	Composition (phr)					
	PEP	TCPP	UV326	Pigment yellow	ITO	ATO
P-P/T(50/0)	56.5	0	–	–	–	–
P-P/T(45/5)	50.9	6.4	–	–	–	–
P-P/T(35/15)	39.6	19.2	–	–	–	–
P-P/T(25/25)	28.3	32.0	–	–	–	–
P-P/T(15/35)	17.0	44.8	–	–	–	–
P-P/T(5/45)	5.7	57.6	–	–	–	–
P-P/T(0/50)	0	64.0	–	–	–	–
P-P/T(25/25)-UV	28.3	32.0	0.5	–	–	–
P-P/T(25/25)-UV/Y	28.3	32.0	0.5	0.006	–	–
P-P/T(25/25)-UV/Y/I	28.3	32.0	0.5	0.006	1	–
P-P/T(25/25)-UV/Y/I/A	28.3	32.0	0.5	0.006	0.5	0.5

[a] The ratio in the bracket refers the volume ratio between PEP and TCPP; while the value in the column of "Composition" refers the weigh as the reference of hundred parts of PVC resin.

[b] For simplifying purpose, the 1st and 2nd P, T, UV, Y, I and A represents PVC, PEP, TCPP, UV326, pigment yellow, ITO and ATO, respectively.

2.2. Sample preparation

The 100 phr PVC was mixed with PEP and/or TCPP, 1.5 phr organtion (thermal stabilizer) and 0.6 phr liquid paraffin (lubricant). The volume ratio between PEP and TCPP utilized for mixing was varied as 50/0, 45/5, 35/15, 25/25, 15/35, 5/45, 0/50, respectively. The mixture was firstly mixed using an electric blast drying oven (HG 101-1A, Nanjing Experimental Instrument Factory, China) at 120 °C for 20 min in order to pre-plasticize the PVC. Then, different dosages of UV326, pigment yellow and ITO were added into pre-plasticized PVC that has the volume ratio of 25/25 between PEP and TCPP. The specific formulation can be referred in Table 1. Then, the mixture of additives and pre-plasticized PVC were roll-milled (Shanghai Rubber Machinery Works, China) at 150 ± 5 °C for 5 min to give rise to PVC compounds. The obtained PVC compounds were further compression molded and machined to prepare standard specimens for further characterizations. None of solvents were used during the sample preparation.

2.3. Limiting oxygen index (LOI)

LOI values were determined by an oxygen index instrument (HC-2, Jiangyin County Analysis Instrument Factory, China) on bars of $80 \times 10 \times 4\,mm^3$ in dimension according to ISO 4589–2:1996.

2.4. Thermogravimetric analysis (TGA)

The thermal stability of samples was determined by a thermogravimetric analyzer (Q500, TA instruments, America) under the flow of nitrogen. The heating rate was 20 °C/min and the scan was from room temperature to 800 °C.

2.5. Ultraviolet-visible-near-infrared spectrophotometer (UVPC)

The transmittance spectra of the PVC films with approximate 0.3 mm thickness were recorded by UV-vis-NIR spectrophotometer (UV-3100PC, Shimadzu, Japan) at room temperature using air as the reference. The spectrum range is measured from 200 to 2600 nm. Detailed information and the calculation method of irradiance-weighted transmittance value could be referred in our previous work