Composites Science and Technology 167 (2018) 388–395

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

The effects of polybenzimidazole and polyacrylic acid modified carbon black on the anti-UV-weathering and thermal properties of polyvinyl chloride composites

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ARTICLE INFO

Keywords:
Polyvinyl chloride (PVC)
Polybenzimidazole
Modified carbon black
UV–vis spectra
Thermal properties

ABSTRACT

In this study, the effects of polybenzimidazole (PBI) and polyacrylic acid (PAA) modified carbon black (MCB) on the anti-UV-weathering and thermal properties of PVC composites were investigated. The optimal mass ratios of PBI and MCB to PVC are 0.1 wt% and 0.2 wt%, respectively, and the resultant 1PBI/2MCB/PVC composite membrane with a thickness of about 60 μm can block over 99% of UV light below 380 nm. The UV absorption mechanism was investigated by the optional band gap (Eg) and the fluorescence spectroscopy. The incorporation of PBI and MCB results in a decrease in Eg, from 4.96 eV for PVC membrane to 2.90 eV for 1PBI/2MCB/PVC composite membrane, and MCB can quench the fluorescence of PBI by photon-induced electron transfer to further protect PVC. The results of accelerated UV-weathering experiment indicate that the incorporation of PBI and MCB can improve the anti-UV-weathering property of PVC. The thermal degradation behaviors of PVC and its composite membranes in air and N_2 atmosphere were also investigated. The highest char residue (13.7 wt%) is obtained in 1PBI/2MCB/PVC composite membrane at 800 °C in N_2 atmosphere, with an increase of 73.4% compared with that of PVC membrane, which may be because PBI and MCB can synergistically accelerate the carbonization of PVC molecules to rapidly form stable char residue.

1. Introduction

Polyvinyl chloride (PVC) is a kind of general plastic extensively applied in electronic devices, construction, agriculture, packaging, etc., due to its good chemical resistance, mechanical properties, and flame retardancy. However, the exposure of PVC to ultraviolet (UV) light or heat, can cause the dehydrochlorination reaction and consequently the formation of conjugated polymers with poor physical properties. Therefore, there is a critical need to develop photo and thermal stabilizers capable of improving the anti-UV-weathering and thermal stability of PVC. Inorganic UV stabilizers, such as TiO_2 [1,2], ZnO [3], SiO_2 [4] and carbon black (CB) [5,6] can shield UV lights; while most organic UV absorbers, such as benzophenones and benzotriazoles can absorb UV protons. However, it is difficult for inorganic UV stabilizers to be uniformly distributed in the polymer matrix due to the large polarity difference between them; while organic UV stabilizers with a low molecular weight can be easily released from the polymer matrix by volatility and diffusion.

Many methods have been proposed to solve these problems, such as intercalating organic UV stabilizers into the inorganic layer for stabilization organic UV pigments [7–9], incorporating UV stabilizers into polymer chains to improve UV stabilization efficiency and to avoid the problems of compatibility and migration [10], and preparing polymers grafted inorganic particles [2]. Moreover, there is also a growing interest in preparing high molecular weight UV stabilizers [11,12].

Polybenzimidazole (PBI) is a fully aromatic heterocyclic polymer obtained from condensation polymerization between tetraamine and dicarboxylic acid. In our previous study, PBI was used as the proton exchange membrane, with high proton conductivity, chemical stability and mechanical properties [13–15]. Interestingly, it also shows high UV absorption and excellent thermal stability because of its benzene and imidazole ring [16,17], making it a promising photo and thermal stabilizer for PVC. CBs with a large polyaromatic system are widely used as a UV shielding reagent of polymer materials, and their photo stabilizing

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https://doi.org/10.1016/j.compscitech.2018.08.016
Received 7 May 2018; Received in revised form 13 August 2018; Accepted 16 August 2018
Available online 17 August 2018

efficiency is based on both the physical surface-area-dependent UV absorption and the photochemical activity. However, the structure and surface area of CBs differ considerably, and conductive CBs usually have higher surface areas and better structures compared with other CBs [18].

The combination of conductive CB and PBI may contribute to improving photon absorption and energy transfer [19]. Conductive CB chemically modified by PAA (MCB) can effectively induce the transfer of electrons and energy. Because the energy of PBI from UV photons is released by fluorescent light, MCB can be employed as a synergistic reagent to quench the fluorescence of PBI to further protect PVC.

In this study, PBI was synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, and the UV absorption, anti-UV-weathering property and thermal stability of PVC and its composite membranes with different concentrations of PBI and MCB were investigated. The mechanism of UV absorption and thermal stabilization of the PVC composite membranes were discussed. The findings of this study provide an efficient and simple approach to prepare PVC membranes with excellent anti-UV-weathering property and thermal stability.

2. Experimental

2.1. Materials

PVC resin (SG-5) (intrinsic viscosity: 112 mL/g) was purchased from Dongguan Dansheng Plastic Materials Co., Ltd. (Guangdong, China); 3,3′-Diaminobenzidine (DAB) was purchased from Shanghai DAB Chemical Co., Ltd. (China); 4,4′-oxybis (benzoic acid) (OBBA), methanesulfonic acid (MSA) and P_2O_5 were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China); and MCB was self-prepared by the irradiation of high-energy EB at 40 kGy in our previous study [20], and the grafting degree was 5.16 wt%. Other materials were used as received without further purification.

2.2. Synthesis of PBI

PBI was synthesized in phosphorus pentoxide/methansulfonic acid with a weight ratio of 1:10 [21]. Briefly, 2.14 g (10 mmol) of DAB and 2.58 g (10 mmol) of OBBA were added into a four-necked flask equipped with a mechanical stirrer, a drying tube, a thermo-couple and a vent of N_2, and then heated to 140 °C under stirring. The mixture was reacted at 140 °C for about 2.5 h until the appearance of Weissenberg effect. The resultant viscous solution was slowly poured into deionized water to obtain filamentous products. The polymer was washed several times with $NaHCO_3$ solution and deionized water, and then dried. PBI with a molecular weight of 1.03×10^5 g mol^{-1} was obtained.

2.3. Preparation of PVC and its composite membranes

PVC and its composite membranes were prepared by solvent casting. Briefly, 1 g of PVC and a certain amount of PBI and MCB were dissolved in 30 ml of DMF under vigorous stirring for 4 h, and then the solution was spread on a slide glass model and dried at 40 °C for 7 d in a vacuum oven to remove the solvent. The thickness of the resultant membranes ranged from 40 μm to 60 μm, and the formulas of the membranes are shown in Table 1.

2.4. Accelerated UV-weathering test

Accelerated artificial UV-weathering test was conducted on LUV-II accelerated weathering tester (Pushen, Shanghai) with an automated spray system and a heating equipment. All samples were exposed to a 60 W short wave UV lamp at 50 °C, and accelerated to weathering up to 1000 h.

Table 1
Formulas of samples.

Samples	Formula (wt%)		
	PBI	MCB	PVC
2PBI/1MCB/PVC	0.2	0.1	100
1.5PBI/1.5MCB/PVC	0.15	0.15	100
1PBI/2MCB/PVC	0.1	0.2	100
PBI/PVC	0.1	0	100
MCB/PVC	0	0.2	100

2.5. Characterization

The FTIR spectra of all samples were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) in the range of 400–4000 cm^{-1}. The molecular weight of PVC samples was measured by a gel permeation chromatography (GPC) (PL-GPC50) at a flow rate of 1 ml/min with DMF as the isocratic mobile phase. The UV–vis spectra of solutions and membranes were measured using a spectrophotometer (SP-1900, Shanghai). The fluorescence spectra were recorded on a PE LS-55 Lumine fluorescence spectrophotometer at an excitation wavelength of 345 nm and a slit of 1 nm at room temperature. The thermogravimetric analysis (TGA) was performed on STA 449 F3 Jupiter® (NETZSCH, Germany) in air and N_2 atmosphere, respectively. The samples were heated from 50 °C to 800 °C at a heating rate of 10 °C·min^{-1}. The morphology of PVC and its composite membranes before and after UV-weathering was observed using a S-4800 field emission scanning electron microscope (FESEM, Tokyo, Japan). The samples embedded in epoxy resin were cryogenically fractured in liquid nitrogen. Prior to SEM observation, all samples were coated with a thin gold layer. The mechanical properties of the membranes were measured on a MTS E43 equipment (USA) at 2 mm·min^{-1} in ambient atmosphere, and the average of at least 5 samples was obtained.

3. Results and discussion

3.1. Synthesis and characterization

PBI was successfully synthesized by the polycondensation of DAB and OBBA, and then characterized by FTIR, as shown in Fig. 1A. The peaks at 1663, 1471 and 1395 cm^{-1} can be attributed to C═N, C═C and C-N stretching of benzimidazole characteristic bands, respectively. The number average molecular weight (M_n), weight average molecular

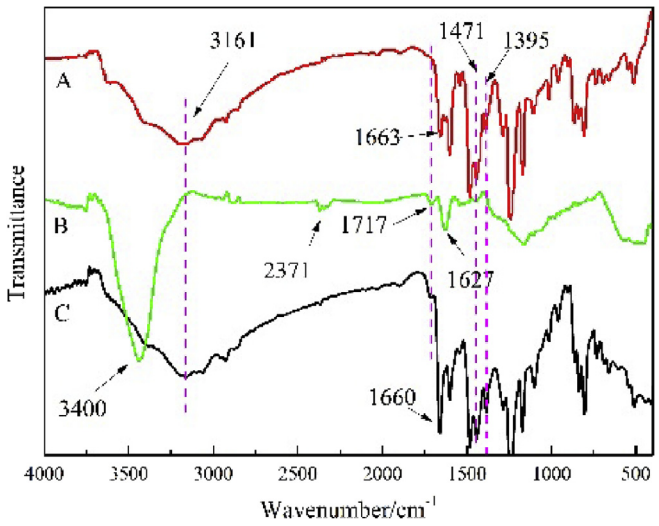

Fig. 1. FTIR spectra of PBI (A), MCB (B) and PBI/MCB (1/2) blend (C).