Research Article

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The regulatory effects of the number of VP(N-vinylpyrrolidone) function groups on macrostructure and photochromic properties of polyoxometalates/copolymer hybrid films

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Abstract: Nanocomposite films were synthesized by introducing phosphotungstic acid (PWA) into the poly (vinylpyrrolidone and methyl acrylate) (P (VP(N-vinylpyrrolidone)coMA(methyl acrylate))). FT-IR curves illustrated that non-covalent bond interaction was built between PWA particles and organic matrixes. In combination the results of SEM, TG-DTA and DSC, it was conducted that the ratio of functional groups of VP had a critical effect on the surface morphology, thermal stability of the hybrid films. Irradiated with ultraviolet light, the transparent thin hybrid films change from colorless to blue. Stored in air, the hybrid films could recover colorless gradually. The analysis of kinetics told us that higher VP content within the different systems always accompanied more superior photochromic performance, faster coloring and fading speed. Appearance of W^{5+} in ESR spectra indicated that the photo-reduction process between PWA and copolymer matrix occurred.

Keywords: photochromism; hybrid films; heteropolyoxometalate; pyrrolidone functional group; photoproduction electronic

1 Introduction

Photochromic material was one typical material, which can change color reversibly. In terms of its intriguing

structure and diverse properties, it is widely used in technological applications, such as information display, sensing, high-density recording and modified electrodes or holographic storage devices and so on (1-3). Polyoxometalates (POMs) is a series of multi-core inorganic metal-oxide clusters and can accept electrons or protons to reduce mixed-valency colored species (heteropolyblues or heteropolybrowns) without the substantial change of their structure. Considering of this, POMs always were used to form a donor-accepter embedded with organic polymers as electrons acceptor (4-6). Further, introducing the POMs into the functional side chain or main chain of the polymer, or in blends with polymers can develop a series of new composite materials with photochromic properties. The advantage of this combination lie in its not only improving machinability, but also broadening its range of possible application by greatly improving the structure of the polymer involved in the electron transfer and transport. Various of polymers with active functional groups, such as polyvinylpyrrolidone (PVPd) (7), polyacrylamide (PAM) (8), polyvinyl alcohol (PVA) (9) and polyether chains (PEs) (10) were already chosen as the polymer matrix to construct composites in terms of their good film-forming property, excellent optical quality and high reactivity of pyrrolidone group. There are two prevalent means to synthesize organic photochromic polymer materials. One is connecting the photochromic structural unit to the main chain or branch of the polymer by chemical copolymerization or grafting reaction to achieve coloration. In this case, the morphology of the polymer chains is of great significance of photochromic properties of the material. Henceforth, altering the molecular chain segments is an effective method to adjust the macrostructure and photochromic properties of this kind of material (11).

In previous study, we have successfully synthesized one excellent photochromic materials. In this paper,

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considering of MA monomer own none functional groups and was significant of photochromic properties of this kind of materials, a series of polymers with different amount of functional groups of VP were firstly composited using different mole ratio of VP/MA. Then corresponding photochromic materials were synthesized by entrapping PWA particles into these co-polys. To investigate the effect of the functional groups ratio of VP on the resulting composite films, multiple measurements were carried out, including scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric and different thermal analysis (TG-DTA), differential scanning calorimetric (DSC), ultraviolet-visible spectra (UV-vis) and electron spin resonance spectra (ESR). The results revealed that the functional group ratio can significantly influence the macrostructure and photochromic property of photochromic composite films.

2 Methods

N-vinylpyrrolidone (VP) monomer was provided by Aldrich and purified by fractional distillation twice before use. Methyl acrylate (MA) monomer was obtained from Aldrich and used as received. Phosphotungstic acid (PWA) were purchased from the Beijing Chemical Reagent and recrystallized twice before use. α , α -azobisisobutyronitrile (AIBN) came from Fluka recrystallized twice. All other chemical reagents were of analytical grade and used as received (12). Deionized water was used in all experiments.

Copolymer poly (vinylpyrrolidone and methyl acrylate) (P (VPcoMA)) was prepared according to the literature. The reaction equation and the structure of products are shown in Figure 1. The detail preparation process was as follows. Certain volume VP monomer and MA monomer (molecular ratio of VP/MA was 2:1, 1:1 and 1:2, respectively) were added to a three-neck flask, and then poured into relevant amount of ethanol as solvent.

Figure 1: The structure of P (VP-MA) copolymer.

Under N₂ atmosphere with 353 K, calculated amount of initiator AIBN (mole ratio of VP:AIBN was 1000:1) was dripped into the three-neck flask. The content was allowed to react with stirring under N₂ atmosphere for 2 h (12). Then, transparent copolymer ethanol solution was poured into methanol solution, and then the compound were dried in a degassed desiccator for 48 h to obtain the target product, white powder of P (VPcoMA) (denoted as P (2VPco1MA), P (1VPco1MA) and P (1VPco2MA), respectively). The e intrinsic viscositof copolymer P (VPcoMA) ethanol solution was measured at 298 K with a Ubbelodhe viscometer, and the molecular weight of the product was calculated by the Mark–Houwink equation (13), as follows:

$$[\eta] = 6.67 \times 10^{-2} M^{0.55} \quad (1)$$

In our experiments, the molecular weight of P (VPcoMA) was about 20,000. PWA and P (VPcoMA) with different VP/MA mole ratio were dissolved in ethanol with the different concentrations of 5 mg/mL and 40 mg/mL, respectively. Then 10 mL PWA solution was slowly added into the same volume P (VPcoMA) ethanol solution under vigorous stirring for 2 h at 333 K. The final transparent solution with different VP/MA mole ratio was obtained (denoted as PWA/P (2VPco1MA), PWA/P (1VPco1MA) and PWA/P (1VPco2MA), respectively) after cooled down to room temperature.

Composite film was prepared by using a 100 μ L syringe and dripping the transparent solution on various substrates such as silicon, KBr plates and quartz plates, which were used for SEM studies, FT-IR spectroscopy and UV-vis spectroscopy, respectively. All films were dried in a chamber with controlled air humidity that did not exceed 60%. The thickness of composite films was approximately 2.1 μ m, which was measured by a FCT-103 Film Thickness Measurement System (LCD) Lab, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science).

The scanning electron microscopy (SEM) images of samples were obtained on II itachi X-156 scanning electron microscopy operating at 25 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained with Nicolet Impact 410 FT-IR spectrometer in the range of 4000~400 cm^{-1} . The thermal stability of samples was measured with different thermal analysis (DTA) and simultaneous thermo-gravimetry (TG) from 50°C to 750°C in air, performed on NETZSCH STA 389 C thermal analyzer, with scanning rate of 20 min^{-1} . The thermal properties of the films were determined with a Mettler Toledo DSC 821e Differential scanning calorimetry in a nitrogen

atmosphere with a heating rate of 10 min^{-1} from 20°C to 180°C . Absorption spectra were measured on Shimadzu UV-1601PC ultraviolet-visible (UV-vis) spectrophotometer with 1 nm optical resolution in the range of $350\text{--}800\text{ nm}$. The electron spin resonance (ESR) spectra of samples were recorded at 85 k on an ER 200D-SRC spectrometer at X-band (12).

Photochromic experiments were carried out by a 300 W high-pressure mercury lamp as the light source. The distance between the lamp and samples was 15 cm . Films were exposed to air during irradiation. After irradiation for a certain time, in situ absorbance curve of films was obtained. The irradiation time was recorded until the curve was just the same as the before one. Films were sheltered from light under air conditions and absorption spectra were measured at regular intervals to monitor the bleaching process. All measurements were carried out at room temperature (12).

3 Results and discussion

Considering of the subtle nuances on the infrared spectra among the three ratio samples, one to one sample was the only one to be discussed here. FT-IR spectra of PWA/P (1VPco1MA) composite film before and after irradiation are presented in Figure 2. For comparison, PWA in KBr pellet and pure copolymer P (1VPco1MA) were also performed to confirm the structural feature in the final composite films. For pure copolymer film (curve *b*), there are four vibration bands at 1300 , 1427 , 1670 and 2927 cm^{-1} assigned to organic groups C–N stretching, CH_2 deformation, C=O stretching and CH_2

or CH stretching, respectively. Compared with curve *c*, the resulted composite film PWA/P (1VPco1MA) without irradiation, the characteristic bands assigned to organic groups are still preserved and only have a few shifts. As for pure PWA (curve *a*), there are four characteristic bands at 1080 , 982 , 890 and 802 cm^{-1} assigned to stretching vibration $\nu(\text{P-Oa})$, $\nu(\text{W-Od})$, $\nu(\text{W-Ob-W})$ and $\nu(\text{W-Oc-W})$, respectively, representing the Keggin geometry structure. Compared with curve *c*, the characteristic bands assigned to Keggin geometry unit are also still preserved except for a few cm^{-1} shifts and became weaker or stronger to some extent. More precisely, the W-Od band has a red shift and two of the others (W-Ob-W and W-Oc-W) of PWA exhibit blue shift. This phenomenon revealed that the non-covalent reaction happened between PWA particles and organic matrix. After irradiation for 5 min , PWA/P (1VPco1MA) composite film (curve *d*) changed from colorless to blue. Comparing with the original film, it was found that the W-Od asymmetrical stretching band had red shift, while stretching vibration for W-Oc-W and W-Ob-W band had blue shift by a few cm^{-1} , owing to the formation of heteropolyblues.

SEM images and size distribution of composite films were shown in Figure 3. It indicated that PWA particles exhibited spherical structure and pile together tightly, and the size distribution of the hybrid films decreased as the VP/MA mole ratio increased. More precisely, when the VP/MA mole ratio ranged from $2:1$ to $1:2$, the average particle size increased from 160 nm to 450 nm . Synchronously, the densification extent of the composite films became loose, which resulted in increasing of oxygen transmittance.

To study the thermal stability of the films and the effect of the perturbation of PWA particles, TG-DTA measurement was adopted and the resulting curves of three pure polymers and relevant composite films were depicted in Figure 4. Because the two of the rest composite films exhibited the similar tendency, only PWA/P(1VPco1MA) was inserted. Generally, orderly three-dimensional spatial structure accompanies high thermal stability. As shown in Figures 4a-c, for pure copolymer, thermal decomposition began at 350°C , 330°C and 325°C and accompanied exothermic peak at 488°C , 452.5°C and 425.5°C , respectively, which revealed that when reducing the mole ratio of VP/MA, the three-dimensional spatial structure of film followed chaotic. As for curve *d*, PWA/P (1VPco1MA), compared with P (1VPco1MA), the thermal decomposition temperature decreased to 250°C and exothermic peaks appeared at 350°C , verifying that the thermal stability of the hybrid films slipped down significantly after entrapping PWA particles into the copolymer films. It might be attributed to the entrapped

Figure 2: FT-IR spectra of: *a* – PWA particles, *b* – P (1VPco1MA), *c* – composite films PWA/P (1VPco1MA) without irradiation, *d* – composite films PWA/P(1VPco1MA) after irradiation with UV light.

Figure 3: SEM images and size distribution of PWA particles of composite films PWA/P (2VPco1MA) (a), PWA/P (1VPco1MA) (b), and PWA/P (1VPco2MA) (c).

PWA particles destroyed the three-dimension spatial structure of the copolymer.

The rigidity of pure copolymers and hybrid films were studied by DSC measurements, as shown in Figure 5. The results of DSC curves of pure copolymer followed the similar trend of TG-DTA curves: the glass transition temperature of P (2VPco1MA), P (1VPco1MA) and P (1VPco2MA) was 80°C, 70°C and 50°C, respectively, further revealing that the order of the three-dimension spatial structure decreased as the decline of the content of VP. And compared with P (1VPco1MA), the glass transition temperature of PWA/P (1VPco1MA) decrease by about 30°C. It was another proof for the entrapped PWA particles

Figure 4: TG-DTA curves of: *a* – pure copolymer P (2VPco1MA), *b* – P (1VPco1MA), *c* – P (1VPco2MA), *d* – composite film PWA/P (1VPco1MA).

Figure 5: DSC curves of: *a* – pure copolymer P (2VPco1MA), *b* – P (1VPco1MA), *c* – P (1VPco2MA), *d* – composite film PWA/P (1VPco1MA).

disturbing the three-dimension spatial structure of the copolymers.

In Figure 6, the absorbance change of PWA/P (1VPco1MA) composite film in photochromic process was shown as a function of the irradiation time. Before UV irradiation, there was no significant absorption from 400 to 800 nm. After UV irradiation, the color of the transparent films changed from colorless to blue gradually and two absorption bands at 490 nm and 700-750 nm appeared, which owing to intensity-enhanced d-d transition and metal-to-metal extra intervalence charge (TVCT) (W^{5+} to W^{6+}), respectively. After turning off the light, under air condition, the colored films began to bleach gradually. As shown in Figure 6b, the intensity of absorption bands decreased gradually with the bleaching time prolonged and no shift in maximum absorption was observed. But if stored in nitrogen, helium, argon or vacuum conditions, the color of films would remain for 2 days, which indicated

Figure 6: UV-vis spectra of PWA/P (1VPco1MA) with different times of irradiation time (a) and UV-vis spectra of PWA/P (1VPco1MA) with different times of bleaching time (b).

Figure 7: Kinetics of different conditions: (a) kinetics of: a – PWA/P (2VPco1MA), b – PWA/P (1VPco1MA), c – PWA/P (1VPco2MA), during coloration process; (b) kinetics of: a – PWA/P (2VPco1MA), b – PWA/P (1VPco1MA), c – PWA/P (1VPco2MA), during bleaching process.

that oxygen was a non-negligible factor during the bleaching process.

In order to describe the photochromic performance more detail, referring to the photochromic kinetics of former papers (14,15), the kinetics of the coloration process and bleaching process were explored using the following formula:

$$-\ln(A_{\infty} - A_t) = kt + b \quad (2)$$

where k is rate constant, A_{∞} , A_t represented for the observed reflection data measured at the end and time t of the reaction. And the results were inserted in Figure 7. Figure 7a shows the speed of coloration process where the rate constant k of PWA/P (2VP-co-1MA) was 1.202, which was almost twice of PWA/P (1VP-co-1MA) and more than

Figure 8: ESR spectra of: a – PWA/P (2VPco1MA), b – PWA/P (1VPco1MA), c – PWA/P (1VPco2MA).

Figure 9: Schematic shows interfacial interactions between PWA particles and organic matrix during the composite process.

triple of PWA/P (1VP-co-2MA). The result was in line with the change of VP content, to be accurate, the change of amount of functional groups of VP. As for the speed of bleaching, the rate constant k of PWA/P (1VP-co-2MA), PWA/P (1VP-co-2MA) and PWA/P (1VP-co-2MA) were -0.973 , -0.525 and -0.315 , respectively, which was relevant with the quantity of oxygen through the composite hybrid films.

ESR measurement was conducted to investigate the variation of electronic structure of hybrid films during photochromic process (as shown in Figure 8). The typical ESR signals were detected in irradiated films at 84 K. The signal with $g = 1.838$ was ascribed to W^{5+} , which was in agreement with reports in relevant papers (16-18). It indicated that small amounts of electric charge transferring happened between copolymer matrix and PWA particles (W^{6+} to W^{5+}) during the photoreduction process, converting heteropolyanions to heteropolyblues accompanied with simultaneous oxidation of copolymer matrixes. Using integral operation calculating half height of peaks, the results showed that the hybrid film with highest VP/MA mole ratio exhibited the biggest W^{5+} content, which was 1.25 times of PWA/P (1VPco1MA) and 1.92 times of PWA/P (1VPco2MA). These indicated that higher VP content in composite films always accompanied stronger photochromic response. Generally, interaction between different components had a significant impact on microstructure and physical and chemical properties of hybrid materials, especially which were formed by non-covalent bond. Apart from the oxidation-reduction reaction, the non-covalent interaction in the composite process also was a crucial factors acting on macrostructure and photochromic properties of the films. The original linear polymer chain was extended structure but it would be destroyed after introducing the PWA particles into the chains, which directly leading to the reduction of the thermal stability. As shown in Figure 9, after changing the ratio of introduced MA monomer, the amount and distribution of active groups in VP chains would follow. Larger amount

of functional groups of VP always accompanied bigger chance of participating in composite reaction and at the same time, the capability of participating in photo oxidation-reduction was enhanced and the response speed of coloring quicken.

The bleaching process was a chemical one and related to the presence and diffusion of oxygen in system. Generally, the surface of the thin films is too dense to get more difficult to pass through the oxygen. Therefore, the densification extent of copolymer films became a decisive factor on reversibility of photochromic properties. Considering of the results of SEM, it was easily to know that as the VP content decline, the oxygen permeability became better. Simultaneously, the bleaching speed quickened, which was coordinated with the kinetics results.

4 Conclusions

A series of composite films were synthesized by introducing PWA particles into the co-polymer matrixes copolymerized with different mole ratio of VP/MA. Multiple characterization methods were carried out and it was found that the macrostructure, thermal stability and photochromic properties of the resulting hybrid films could be controlled by changing the amount of functional groups of VP in the system. Using this method, composite photochromic materials exhibiting different coloration and bleaching speed can be synthesized by adjusting the quantity of functional groups.

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