폴리비닐알코올/$H_6P_2W_{18}O_{62}$ hybrid membranes의 광색 및 열적 특성

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Photochromic and thermal properties of poly (vinyl alcohol)/ $H_6P_2W_{18}O_{62}$ hybrid membranes

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1. Introduction

A new class of materials based on organic and inorganic species combined at a molecule level has obtained more attention recently[1]. HPA(heteropolyacid) shows unmatched applied perspective in terms of synthesis chemistry, analysis chemistry, biology, medicine and materials science[2]. As a potential photochemical material, the hybrid system of HPA and polymer has been investigated. However, the design and synthesis of heteropolyacid-based hybrids, which are at the forefront of the materials chemistry research, is still in its infancy. In order to modify the property of materials, here poly(vinyl alcohol)(PVA), as a polymer additive, is selected to combine with HPA, and some of the significant results, such as the photochromic behavior, conductivity and thermal stability etc., were showed.

2. Experiment

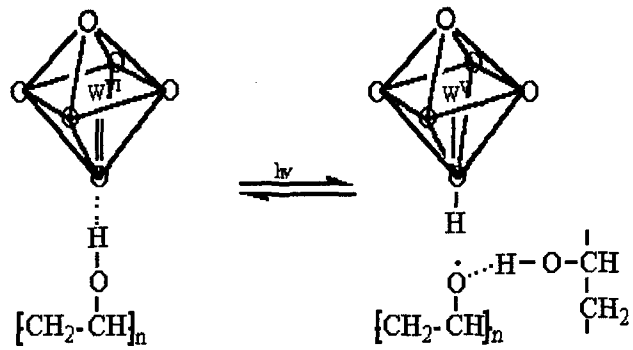
Aqueous PVA (20 wt%) was first prepared by dissolving polymer powder in distilled water and heating at 80℃ with stirring for 1h, then it was cooled to room temperature, stirred for 24h. The PVA solution of 20ml was added 10ml aqueous solution of P_2W_{18} (1, 2, 4, 8 and 16g respectively) with stirring for 24h at the ambient temperature. The HPA/PVA films were made by coating method, and then these films were dried under vacuum for 48h at 45℃ The films were calculated as 20, 33, 50, 66 and 80 wt% HPA respectively.

3. Results and discussion

The four characteristic bands of $P_2W_{18}O_{62}^{6-}$ appeared in the IR spectra. i.e.

vas(W-O_d): 953cm^{-1}; vas(W-O_b-W): 914cm^{-1}; vas(W-O_c-W): 798cm^{-1} and vas(P-O_a): 1090cm^{-1}. The band at ca. 3400cm^{-1}, which was the characteristic of O-H groups, increased with the increase of HPA content. These indicated that more intermolecular H-bonding formed between HPA and PVA with the increase of HPA content[3].

The thermal degradation steps and the melting point of PVA/HPA films were influenced by the difference of HPA content. The melting point of PVA decreased from 195 to 165 ℃ with the increase of HPA content from 20 to 80 wt%. The depression of the melting temperature indicated that the ordered association of the PVA molecules was decreased by the presence of HPA[4]. The films were reduced photochemically to yield a blue species under UV irradiation, and the color changed to deep blue with the increase of irradiation time and HPA content. For the photochromic mechanism of the films, we proposed that photoexcitation of the O=W ligand-to-metal charge transfer of WO_6 led to the transfer of one hydrogen from PVA to the oxygen atom at the photoreduced site in the edge-shared WO_6 octahedral lattice. At the same time the reduction of the polyoxometallates ($W^{6+} \longrightarrow W^{5+}$) happened. The photochromism of blue films was reversible, and the time from blue to colorless decreased with the increase of HPA content. We deduced that the extra hydroxy made the PVA oxidation state stable in the film containing less HPA content, and no extra hydroxy made the PVA oxidation state stable in the film containing more HPA content. So the more HPA content, the less the extra hydroxy was, the shorter the reversible time was. Eq.(1) denoted the oxidation-reduction process.



(1)

Notably, the conductivity of 8.33 ×10^{-6}× Scm^{-1} was observed when the HPA content was 80 wt%. It indicated that the crystalline water of the HPA, which was in the film-dried, was still kept because of the high hydrophilicity of PVA.

4. Reference

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