

## Homogeneous Photodegradation of PVC by Tungstophosphoric Acid

Kai Hua ZHANG, Jing Chang ZHANG, Wei Liang CAO\*

Faculty of Science, Beijing University of Chemical Technology, Box 32, Beijing 100029

**Abstract:** The photocatalytic degradation of polyvinyl chloride (PVC) films by tungstophosphoric acid (HPW) was investigated. The main reason for highly enhanced photodegradation of HPW-doped PVC film was studied and discussed.

**Keywords:** Homogeneous photodegradation, tungstophosphoric acid, PVC.

Recycling, abandon or incineration and degradation are ways for disposal of wasted PVC plastics. Most PVC products are one-off products with exceedingly low recovery value, and disposal of these wasted PVC through abandon or incineration causes serious environmental problems<sup>1-3</sup>. Therefore study and development of degradable PVC plastic have important meaning. Currently, biodegradable PVC plastics have been reported<sup>4-6</sup>. But these biodegradable PVC plastics have to add a great quantity of starch (about 30%), which affects the transparency and mechanical performance and do not suit to use for transparent PVC material. So study on transparent PVC packing material with photodegradable performance will overcome the above weakness of biodegradation and possess significant theory meaning and application worth. There are attempts on PVC photodegradation such as addition of nano-TiO<sub>2</sub><sup>7</sup>, but its effects on the transparency and the photodegradation efficiency are low.

This study achieved quick PVC photodegradation by adding heteropoly compound tungstophosphoric acid into PVC. This method not only kept PVC transparency, but also made the homogeneous catalysis degradation to be efficient, providing a completely new means for waste PVC disposal. Degradation of PVC by nano-TiO<sub>2</sub> and nano-CdS was also investigated for comparing with that by HPW, and the result show that the photocatalytic activities of nano-TiO<sub>2</sub> and nano-CdS are much lower than HPW's. Further study indicated that the high photocatalytic activity of HPW-doped PVC film was due to the redox property of HPW, rather than its acidity.

Tungstophosphoric acid (HPW, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O) (A. R.), purchased from Acros, was used without purification. TiO<sub>2</sub> and CdS nanoparticles were prepared according to references 8 and 9. The PVC powder is free from additives and the average degree of polymerization was among 1100~1000. The polymer stock solution was prepared by dissolving 50 g of PVC in 1 L of tetrahydrofuran (THF). 20 mg of different catalysts of

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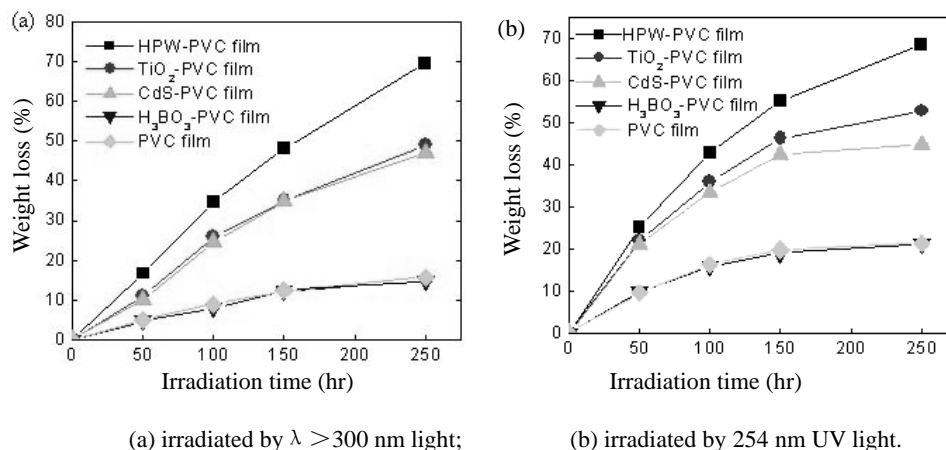
\* E-mail: caowl@mail.buct.edu.cn

HPW,  $\text{TiO}_2$ , CdS, and  $\text{H}_3\text{BO}_3$ , respectively, was suspended in 20 mL of PVC stock solution to give 2.0 wt. % of catalyst content with respect to the total mass of PVC. Among them HPW-PVC and  $\text{H}_3\text{BO}_3$ -PVC were both transparent, colourless and homogeneous solutions (each solution was added a thimbleful of water), while  $\text{TiO}_2$ -PVC and CdS-PVC were white and yellow opaque suspension, respectively. Catalyst-PVC solutions were evenly spread on slide glasses separately and dried for 2 days. The thickness of every resulting catalyst-PVC composite film was measured to be about 10  $\mu\text{m}$  by a micrometer.

Catalyst-PVC composite films with the catalysts concentration of 2.0 wt. % in PVC and pure PVC film were irradiated under the 250 W mercury lamp with 365 nm of main wavelength. In order to simulate solar light conditions, incident UV light onto samples passed through a Pyrex cover that cut-off light with the wavelength shorter than 300 nm. The light flux onto the samples was measured to be 2.0  $\text{mW}/\text{cm}^2$  ( $\lambda = 365\text{nm}$ ). PVC photodegradation by different catalysts was investigated under the irradiation of 20W UV lamp of wavelength 254 nm. The catalyst concentration of all the experiment was 1.5 wt. % and the light intensity was 1.0  $\text{mW}/\text{cm}^2$  ( $\lambda = 254\text{nm}$ ). Each sample was weighed before and after irradiation to monitor the weight loss as a result of photodegradation.

**Figure 1 (a)** displays the photoinduced weight loss of the pure PVC and catalyst-PVC films under irradiation of  $\lambda > 300$  nm light. The highest rate of weight loss was the HPW-PVC film rapidly decreased with irradiation and the weight reduced 69.6% in 250 h, while  $\text{TiO}_2$ -PVC and CdS-PVC films only showed 49.1% and 47.2% weight loss. The lowest weight loss was for  $\text{H}_3\text{BO}_3$ -PVC and pure PVC, which were of 14.9% and 15.7%, respectively. The fact that  $\text{H}_3\text{BO}_3$ -PVC film made little disparity from pure PVC film in weight loss and so did other acid catalysts such as phosphoric acid implied that the acidity of the catalysts could hardly photodegrade PVC and the high photocatalytic activity of HPW-doped PVC film was due to the redox property of HPW, rather than the acidity. **Figure 1 (b)** shows the same fact with **Figure 1 (a)**. In

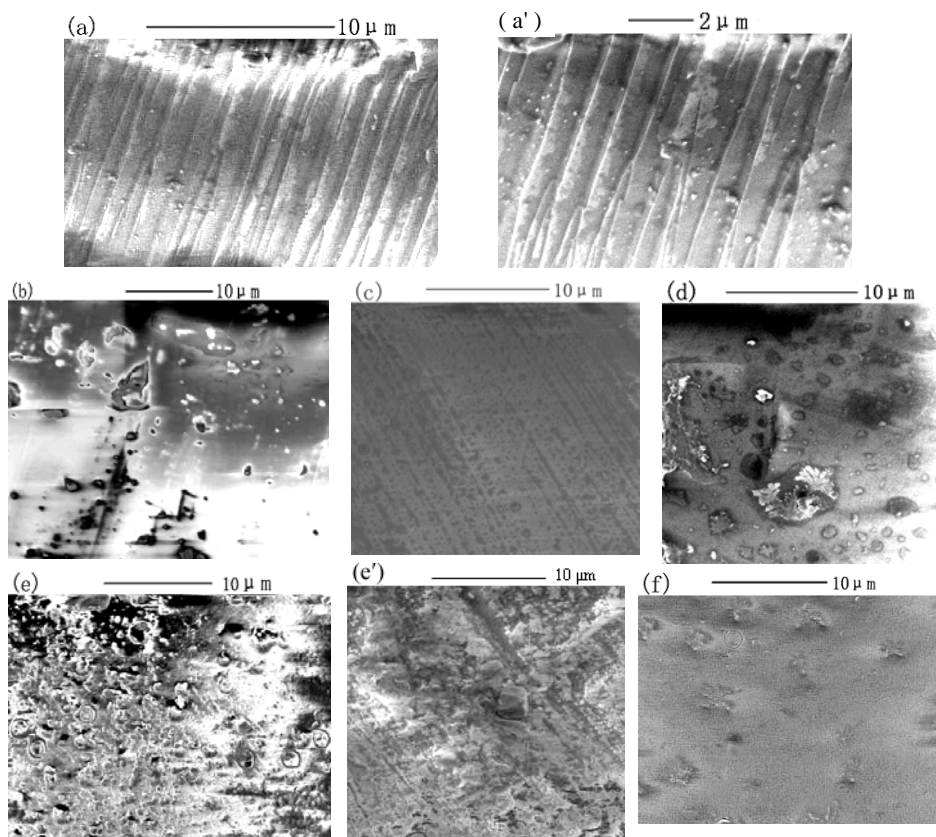
**Figure 1** Weight loss (%) of the catalyst-PVC and pure PVC films during irradiation.



addition, if without irradiation the weights of the catalyst-PVC composite films did not decrease, on the contrary it increased slightly after 250 h, indicating that all the catalysts can not make PVC degrade without light irradiation. The films gaining weight may be due to adsorbing water and other impurities in the air.

**Figure 2 (a), (b), (c)** show the scanning electron microscopic (SEM) images of the HPW-PVC (2.0 wt.%), TiO<sub>2</sub>-PVC (2.0 wt.%), and pure PVC before irradiation, respectively. The SEM images display that the surface of pure PVC was smooth and neat (**Figure 2 (c)**), and the catalyst clusters of HPW took on excellent uniform distribution in PVC film with the very small and evenly size of about some dozens nanometers. It can be seen more clearly in **Figure 2 (a')**, the enlarged view of **Figure 2 (a)**. However, TiO<sub>2</sub> particles showed very ununiform distribution in PVC film (**Figure 2 (b)**). Some parts of PVC film had TiO<sub>2</sub> while some parts had not, and the TiO<sub>2</sub> particles were incorporated into the polymer matrix in huge agglomerates, whose

**Figure 2** SEM images of catalyst-PVC (2.0 wt.%) and pure PVC films.



(a), (b), (c): HPW-PVC, TiO<sub>2</sub>-PVC, pure PVC films before irradiation; (a'): HPW-PVC film before irradiation (enlarged view); (d), (e), (f): HPW-PVC, TiO<sub>2</sub>-PVC and pure PVC films, 100 h irradiated by  $\lambda > 300$  nm light; (e'): TiO<sub>2</sub>-PVC film, 100 h irradiated by  $\lambda > 300$  nm light (worse degradation).

size extended up to a few micrometers. The SEM image of CdS was the same as that of TiO<sub>2</sub>. The above phenomena can be explained as follows: HPW can uniformly dissolve in PVC stock solution, that is, HPW and polymer PVC can be homogeneously dissolved in the solvent THF, while TiO<sub>2</sub> and CdS can not solve in the solvent and only got the suspension. After THF entirely evaporated, HPW was doped into PVC matrix homogeneously in clusters with fine dispersion and quite high doping rate, and such photodegradation seems belong to 'homogeneous catalysis' reaction, while TiO<sub>2</sub> and CdS were embedded into polymer matrixes ununiformly with far less doping rates, and the corresponding photodegradations belong to 'heterogeneous catalysis' reactions. This is the main reason why the photocatalytic activity of HPW is much higher than TiO<sub>2</sub> and CdS.

**Figure 2 (d), (e), (f)** show the SEM images of HPW-PVC, TiO<sub>2</sub>-PVC and pure PVC films irradiated by  $\lambda > 300$  nm light for 100 h. These images reveal that on the surface of HPW-PVC film existed photoinduced holes and the largest holes were 1  $\mu$  m in size (**Figure 2 (d)**). On the other hand, for TiO<sub>2</sub>-PVC film, each part got a different degradation due to the ununiform distribution of catalyst particles. On the parts with high degradation efficiency of films were gathered excess cavities (**Figure 2 (e)**), whereas there were only wrinkles or a little cavities on the parts with low degradation efficiency and the PVC films were not destroyed at all (**Figure 2 (e')**). Pure PVC film showed little sign of degradation and the photodegradation started from the accidented parts of the film surface (**Figure 2 (f)**). The SEM images of CdS-PVC showed the same fact as that of TiO<sub>2</sub>-PVC.

In conclusion, the present study demonstrates that the composite of PVC-heteropoly compound was expected to be used as a photodegradable product.

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