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# STUDY ON SURFACE HYDROLYTIC KINETICS | OF POLY(VINYL ACETATE) GRAFTED ONTO POLYURETHANE FILM[1]

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**Abstract**—Alkali catalytic hydrolysis of poly(vinyl acetate) (PVAc) grafting onto polyurethane film surface was a heterogeneous reaction. The hydrolysis was carried on the PVAc particle surface, and the concentration of the alkali in the system was tested by titration method. The kinetics of PVAc surface hydrolytic reaction was studied by simple second-order reaction model. From linear regression analysis of experimental data, we inferred that the activation energy ($E_a$) and pre-exponential factor ($A$) of PVAc surface hydrolytic reaction were $70.7 \pm 0.2$ kJ mol$^{-1}$ and $(5.7 \pm 0.5) \times 10^{12}$ kg mol$^{-1}$ s$^{-1}$, respectively. The results of transmission electron microscopy stated that the apparent hydrolytic degree was 2.1% when the surface of PVAc particle hydrolyzed absolutely.

## INTRODUCTION

Polyurethane (PU) elastomer, widely used in many fields, has not only good wearability but also high hardness, intensity and considerable tenacity [1]. However, its surface resistivity ranges from $10^{11}$ to $10^{13}$ Ω and its volume resistivity from $10^{10}$ to $10^{12}$ Ω cm [2]. Because of friction, it often produces static electricity which will cause a series of disasters. At present, methods of avoiding or suppressing static electricity in PU elastomer mainly include: (1) blending antistatic agent or conductivity additive into PU; (2) changing the PU structure to make it have electric conductivity [3, 4]. In the first method, the antistatic durability of PU is unavoidable poor, as the antistatic agent is simply blending with the substrate of PU. In view of this question, we made the surface antistatic performance of the PU elastomer better by grafting with antistatic agent. Considering that there is few functional groups on the surface of PU, it is very difficult to graft antistatic agent by crosslinking reaction. Therefore, using benzoyl peroxide as photoinitiator, vinyl acetate (VAc) was grafted onto PU elastomer under UV light. After surface hydrolysis reaction, hydroscopic hydroxyl group was formed on the surface of the PU. Under the catalysis of $MgCl_2$, the antistatic agent was combined with hydroxyl by chemical linkage which improved the antistatic durability of PU. Researches about surface antistatic of PU had been reported [5, 6]. The investigation focused on the surface hydrolytic kinetics of PVAc grafting on PU film (PU-*g*-PVAc film) for further study the surface antistatic modification of PU in theory.

## EXPERIMENTAL

### *Materials*

PU-*g*-PVAc membrane (5 cm × 5 cm × 0.3 mm) was prepared in our group and according to the reference (or briefly describe the synthetic route ) and cut into pieces before use. Iodine, methyl alcohol, and hydrochloric acid were used without further purification.

### *Hydrolysis of PU-g-PVAc Film*

To a 100 ml three-necked flask which was fitted with a mechanical stirrer, funnel and thermometer, some PU-*g*-PVAc films and methanol-water (the ratio of methanol and water) solution were added. The mixture was placed in a water bath under rapid stirring (300 rpm) at a certain temperature. 10 minutes later, the quantificational sodium hydroxide aqueous solution (equal to the original molar concentration of hydroxide ion) was added. Some time (i.e., 1 minute, 5 minutes, 10 minutes, 15 minutes, 20 minutes, 30 minutes, etc., respectively) later, quantified solution was taken out, weighed, and titrated by standard hydrochloride acid, and phenolphthalein was used as indicator. The molar concentration of remain alkali ($[OH^-]$) in reaction system was calculated by using Eq. (1):

$$[OH^-] = \frac{(V_1 - V_2) \times C}{W \times (M_1/M_2)} \text{ (mol kg}^{-1}\text{)}, \qquad (1)$$

where $V_1$ and $V_2$ denote the volume (litre) of HCl before and after titration, respectively. $C$ denotes the concentration (mol l$^{-1}$) of HCl. $M_1$ and $M_2$ denote mass of sample, gross mass of sodium hydroxide and

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[1] Статья печатается в представленном авторами виде.

methanol aqueous solution, respectively. $W$ denotes mass of the reaction system which includes PU-*g*-PVAc film, sodium hydroxide and methanol aqueous solution.

### *Observation of the Shape of PU-g-PVAc Film after Hydrolysis*

The shape of the PU-*g*-PVAc films which were hydrolyzed in different concentration of sodium hydroxide aqueous solution and dyed by phosphotungstic acid, was observed by transmission electron microscope (TEM JEM-100SX; JEOL. Ltd., Tokyo, Japan).

### *Qualitative Test of Hydrolytic Degree of PU-g-PVAc Film*

The hydrolyzed PU-*g*-PVAc films were immersed in 1% (wt%) iodine alcohol solution and washed absolutely after ten minutes. The color changes of PU-*g*-PVAc films were observed after vacuum dryness. If the PU-*g*-PVAc film entirely hydrolyzed, it would display blue color. If the film partly hydrolyzed, it would turn red, and the hydrolytic degree of the PU-*g*-PVAc film was lower as the film getting deep red [7].

### *Apparent Hydrolytic Degree of PU-g-PVAc Film*

The apparent hydrolytic degree ($A_h$) was calculated by using Eq. (2):

$$A_h = 100(W_0 - W_1)/W_0 \ (\%), \tag{2}$$

where $W_0$ and $W_1$ denote the weights of PU-*g*-PVAc film before and after hydrolysis, respectively.

### *Calculation of Correlation Coefficient of Fitting Line*

The correlation coefficient ($r$) of fitting line was calculated by using Eq. (3) [8]:

$$r = \frac{n\Sigma xy - \Sigma x\Sigma y}{\sqrt{n\Sigma x^2 - (\Sigma x)^2}\sqrt{n\Sigma y^2 - (\Sigma y)^2}}, \tag{3}$$

where $r$ denotes correlation coefficient of fitting line, $n$ denotes group number of experimental data used by the fitting line, $x$ and $y$ denote abscissa data and ordinate data used by the fitting line, respectively.

## RESULTS AND DISCUSSION

### *Hydrolytic Reaction Kinetics Model of PU-g-PVAc Film Surface*

In the hydrolysis experiment, we found that the hydrolysis carried on extremely rapidly in the first stage and it would slow down through qualitative test of the hydrolytic degree of PU-*g*-PVAc film. The hydrolysis increased obviously when some methanol was added later, thus we conceived that the hydrolysis of PU-*g*-PVAc film was carried on two stages. Firstly, the hydrolysis reaction mainly occurred on the PVAc particle surface, as the ester group ($-OCOCH_3$) on the PVAc surface is accessible for hydroxyl ion ($OH^-$) to initiate hydrolysis reaction. Therefore, the hydrolysis in this stage carried on quickly. We named the first stage as surface hydrolysis reaction stage. After the ester group on the PVAc surface hydrolyzed completely, $OH^-$ started to diffuse inside the PVAc particle and react with interior ester group. The diffusing speed of $OH^-$ inside the PVAc particle was slow, the hydrolysis speed decreased in this stage. After adding methanol, the surface area of the PVAc particle increased as the methanol's swelling action, and the methanol also improved the diffusion performance of $OH^-$ in the interior of PVAc particle. As a result, the speed of hydrolysis increased. This stage was named as interior hydrolysis reaction stage. Based on these hypothesis [9, 10], we thought that the base-catalyzed hydrolysis of PVAc-g-PU was a heterogeneous reaction. In order to determine the hydrolysis kinetics of PVAc, diffusional disturbance of $OH^-$ inside and outside PVAc particles should be excluded. In this paper, the kinetics of hydrolysis is only aimed at the surface of PVAc particle, the influence of internal diffusion need not be considered. The influence of external diffusion can be eliminated by increasing the speed of stirring [11]. In our previous study, the results showed that the surface hydrolysis rate of PVAc-*g*-PU had nothing to do with stirring speed when the speed exceeded 250 rpm. So we chose 300 rpm in the hydrolysis experiment. The surface hydrolysis kinetics of PVAc particle could be disposed by the second-order reaction model, and its reaction velocity was mainly controlled by the concentration of alkali in the system and the concentration of ester group on the surface of PVAc particle [12, 13], that is:

$$R = -d[OH^-]/dt = -d[OAc]/dt = k[OH^-][OAc] \tag{4}$$

In the formula, $R$, $[OH^-]$ and $[OAc]$ denote PVAc surface hydrolysis reaction speed on PU-*g*-PVAc film, molar concentration of hydroxyl ion in the reaction, molar concentration of ester group on the surface of PVAc particle at the moment of $t$, respectively. $k$ denotes the surface hydrolysis speed constant of PVAc.

If $a$ denotes requirement molar concentration of alkali that one gram (1 g) PVAc grafted onto PU-*g*-PVAc film hydrolyzed absolutely, then [OAc] can be defined as:

$$[OAc] = a - \left([OH^-]_0 - [OH^-]\right) \tag{5}$$

In the formula, $[OH^-]_0$ denotes molar concentration of alkali in the original reaction system.

**Table 1.** $A_h$ and linear regression equations correspond to fitting lines

| No. | $[\mathrm{OH}^-]_0$, $10^{-3}$ mol kg$^{-1}$ | $A_h$, % | Linear regression equation | $r$ |
|---|---|---|---|---|
| A | 13.25 | 2.05 | $1/[\mathrm{OH}^-] = 41.67t + 73.16$ | 0.9998 |
| B | 48.25 | 2.64 | $1/[\mathrm{OH}^-] = 9.44t + 14.36$ | 0.9896 |
| C | 57.45 | 3.28 | $1/[\mathrm{OH}^-] = 5.05t - 6.44$ | 0.9855 |
| D | 62.25 | 3.97 | $1/[\mathrm{OH}^-] = 5.48t - 46.47$ | 0.9628 |

Note: The hydrolysis temperature ($T$) was 333.15 K.

Put Eq. (5) into Eq. (4), and then got surface hydrolysis kinetics equation of PU-*g*-PVAc as follows:

$$d[\mathrm{OH}^-]/dt = k[\mathrm{OH}^-]\left([\mathrm{OH}^-]_0 - a - [\mathrm{OH}^-]\right) \qquad (6)$$

When $[\mathrm{OH}^-]_0 = a$, then Eq. (6) can be changed into Eq. (7) by definite integral.

$$1/[\mathrm{OH}^-] = kt + 1/[\mathrm{OH}^-]_0 = kt + 1/a \qquad (7)$$

To PU-*g*-PVAc film, the content of PVAc is a definite value, also $a$ is a constant. Therefore, when $[\mathrm{OH}-]_0 = a$, $1/[\mathrm{OH}^-]$ is ordinate and $t$ is abscissa, a fitting line can be obtained. The slope and intercept of the line are $k$ and $1/a$, respectively.

When $[\mathrm{OH}^-]_0 \neq a$, in the process of surface hydrolysis on the PU-*g*-PVAc film, $[\mathrm{OH}^-]_0$–$a$–$[\mathrm{OH}^-] < 0$. Therefore, Eq. (6) is changed into Eq. (8) by definite integral.

$$\ln\frac{a[\mathrm{OH}^-]}{[\mathrm{OH}^-]_0\left([\mathrm{OH}^-] + a - [\mathrm{OH}^-]_0\right)} = k\left([\mathrm{OH}^-]_0 - a\right)t \qquad (8)$$

Require $b = a/[\mathrm{OH}^-]_0$, Eq. (8) can be changed to:

$$\ln\frac{[\mathrm{OH}^-]}{[\mathrm{OH}^-] + (b-1)[\mathrm{OH}^-]_0} = k[\mathrm{OH}^-]_0(1-b)t - \ln b \qquad (9)$$

For certain reaction system, $a$ is a fixed value, but the value of $[\mathrm{OH}^-]_0$ can be determined by the quantity of the alkali added in the experiment. Therefore, $b$ is also a constant, and fitting line can be obtained by the left item of Eq. (9) vs. $t$. The slope and intercept of the line are $k\,[\mathrm{OH}^-]_0(1 - b)$ and $(-\ln b)$, respectively.

Thus, it can be seen that we can divide the stage of hydrolysis reaction when the value of $a$ is determined. The value of $a$ can be obtained by the two methods:

(1) PU-*g*-PVAc films with same weight are added into alkali solutions with different concentration, and PVAc hydrolysis kinetics data are determined. From Eq. (7) and Eq. (9), we know that $1/[\mathrm{OH}^-]$ vs. $t$ has linear relationship when $[\mathrm{OH}^-]_0 = a$. Thus, fitting lines can be obtained by $1/[\mathrm{OH}^-]$ vs. $t$ when the molar concentrations of alkali in the original reaction system are different, we may choose $[\mathrm{OH}^-]_0$ corresponding best linear correlation coefficient as the value of $a$.

(2) The shape of PU-*g*-PVAc film can be observed by TEM when the apparent hydrolytic degree ($A_h$) of PVAc is different. When the value of molar concentration of alkali solution exceeds $a$, the PVAc particle will bring endo-hydrolysis, this will make the interior shape of PVAc particle changed. Thus, we can choose maximum molar concentration of the alkali to calculate the value of $a$ when the interior shape of PVAc particle has no change. From the fitting line by ln$k$ vs. $1/T$ from the experimental data, we can get the reaction activation energy and pre-exponential factor of PU-*g*-PVAc hydrolysis reaction by the slope and intercept of the fitting line corresponds to the Arrhenius formula ($\ln k = -E_a/RT + \ln A$).

### *Determining the Value of a*

The molar concentration of hydroxyl ion ($[\mathrm{OH}^-]$) was determined by neutralization titration in the hydrolysis system. The reciprocal values of molar concentration of hydroxide ion ($1/[\mathrm{OH}^-]$) were calculated, and the results of $1/[\mathrm{OH}^-]$ vs. $t$ were disposed by linear regression method. The linear regression equations and apparent hydrolytic degree ($A_h$) were listed in Table 1.

In fact, it took 1–2 minutes from sampling to titration in the experiment, therefore, the molar concentration of hydroxyl ion ($[\mathrm{OH}^-]$) determined by neutralizing titration was smaller than the actual value of $[\mathrm{OH}^-]$ at the time while sampling. According to Eq. (7), the intercept ($1/a$) of fitting line was more than the intercept in theory ($1/[\mathrm{OH}^-]_0$). From Table 1, we may observe that the intercepts of fitting lines (B, C, D) are less than their intercepts in theory, and the intercepts of fitting lines (C, D) are negative, so the linear regression equations correspond to fitting lines (B, C, D) should be excluded as they are inconsistent with the actual situation. Although the intercept of fitting line A is less than its intercept in theory, there is only minor difference between them, and its correlation coefficient ($r$) is the highest. Thus, $[\mathrm{OH}^-]_0$

**Table 2.** $k$ and linear regression equations correspond to fitting lines

| $[OH^-]_0$, $10^{-3}$ mol kg$^{-1}$ | $T$, K | Linear regression equation | $r$ | $k$, kg mol$^{-1}$ min$^{-1}$ |
|---|---|---|---|---|
| 21.01 | 303.15 | $1/[OH^-] = 3.44t + 47.02$ | 0.9892 | 3.44 |
| 17.36 | 313.15 | $1/[OH^-] = 9.67t + 56.72$ | 0.9899 | 9.67 |
| 14.46 | 323.15 | $1/[OH^-] = 22.49t + 65.39$ | 0.9923 | 22.49 |
| 13.25 | 333.15 | $1/[OH^-] = 41.67t + 73.16$ | 0.9999 | 41.67 |
| 9.54 | 343.15 | $1/[OH^-] = 110.54t + 95.08$ | 0.9944 | 110.54 |
| 5.13 | 363.15 | $1/[OH^-] = 359.14t + 192.88$ | 0.9988 | 359.14 |

($13.25 \times 10^{-3}$ mol kg$^{-1}$) corresponds to fitting line A was used as the value of $a$, in another word, the surface hydrolysis of PU-*g*-PVAc film most completed when the apparent hydrolysis degree ($A_h$) was 2.05%. Figure 1a showed that the lamella of PVAc particle grafting on the PU film changed entirely when the hydrolysis temperature was 333.15 K and $A_h$ was 2.1%, while in Fig. 1b there was crackle emerge inside the particle except full changes of lamella of PVAc particle when $A_h$ was 3.4%, which indicated that the inner hydrolysis reaction of PVAc had carried on. Because the value of $A_h$ (2.05%) corresponding to fitting line A in Table 1 is as near as value of $A_h$ (2.1%) in Fig. 1a, the hypothesis conditions for determining the value of $a$ are consistent with the experimental results.

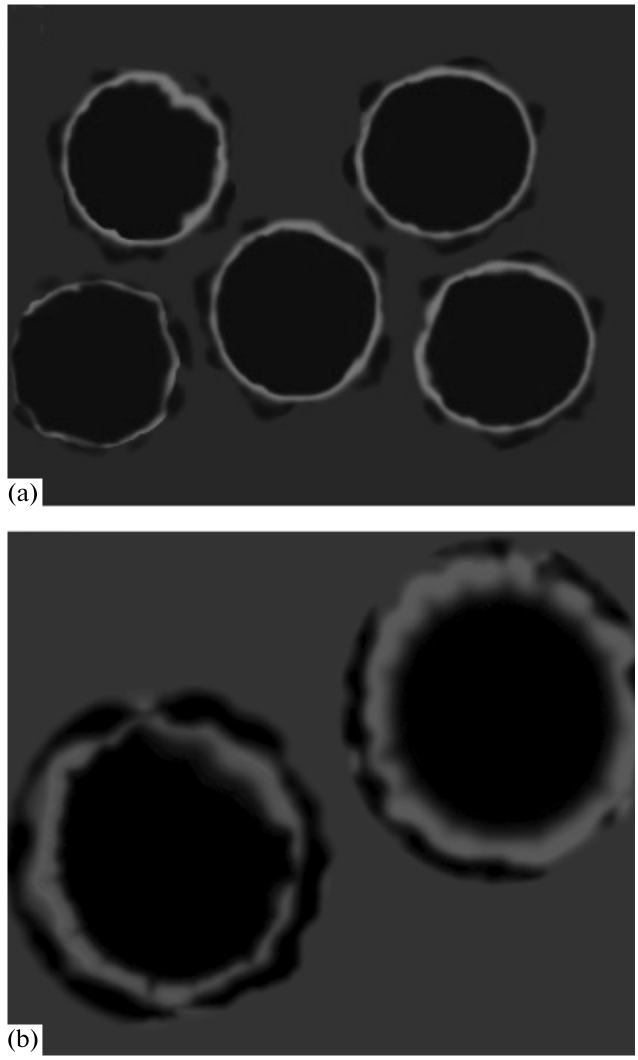

**Fig. 1.** TEM photos of PU-*g*-PVAc film after hydrolysis. (a) $A_h = 2.1\%$, $T = 333.15$ K (×7500), (b) $A_h = 3.4\%$, $T = 333.15$ K (×15000).

### *Surface Hydrolysis Kinetics Parameters of PU-g-PVAc Film*

The reciprocal values of molar concentration of hydroxide ion ($1/[OH^-]$) were calculated and the results of $1/[OH^-]$ vs. $t$ were disposed by linear regression method. The linear regression equation and rate constant ($k$) were listed in Table 2.

Table 2 states that linearity of fitting lines are good because their correlation coefficients ($r$) are all over 0.98. This demonstrated that Eq. (7) and its assumed condition are established when the hydrolysis temperature ranges from 303.15 K to 363.15 K. The linear regression equation corresponding to kinetic data (Table 2) is described as follows:

$$\ln k = -8.5079 \times 10^3/T + 29.3775 \qquad (10)$$

According to Arrhenius formula:

$$\ln k = -E_a/RT + \ln A \qquad (11)$$

From Eq. (10) and Eq. (11), we know that activation energy ($E_a$) and pre-exponential factor ($A$) of the surface hydrolysis of PVAc on the PU-*g*-PVAc film are $70.7 \pm 0.2$ kJ mol$^{-1}$ and $(5.7 \pm 0.5) \times 10^{12}$ kg mol$^{-1}$ s$^{-1}$, respectively.

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