

Viscosity Correlation for Aqueous Polyvinylpyrrolidone (PVP) Solutions

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ABSTRACT: Polyvinylpyrrolidone (PVP) is characterized by its K -value, which is a function of the average molecular weight, the degree of polymerization, and the intrinsic viscosity. The viscosity was measured for aqueous PVP solutions with K -values ranging from 92.1 to 95.4 and with concentrations from 2 to 3 weight percent. A correlation was determined that relates solution viscosity to the K value and

weight percent PVP, which is particularly useful in its use as a photoresist in the manufacture of high resolution display screens. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1153–1155, 2003

Key words: polyvinylpyrrolidone (PVP); viscosity; photoresist

INTRODUCTION

Polyvinylpyrrolidone (PVP) polymers, $(C_6H_9NO)_n$, are used by a wide variety of industries, such as pharmaceutical, cosmetic, textile, adhesive, coating, and ceramic. This is due to the unique physical and chemical properties of PVP, particularly its good solubility in water and organic solvents, its chemical stability, its strong complexing ability with both hydrophobic and hydrophilic substances, and its non-toxic character.¹ PVP has been used as a photoresist system being activated with 4,4'-diazidostilbene-2,2'-disulfonic acid disodium salt (DAS).² It has been utilized to produce higher resolution cathode ray tube (CRT) displays than the traditional photoresist, polyvinyl alcohol (PVA) activated with ammonium dichromate (ADC).^{3,4} The PVP/DAS system has the additional benefit of being more environmentally acceptable, since it is free of chromium and other toxic metals. However, not much is known about PVP properties for this application, unlike the PVA/ADC photoresist, which has been studied for many decades.

PVP is characterized by the K -value, or the Fikentscher's viscosity coefficient, which is used mostly for polyvinylpyrrolidone and vinylpyrrolidone copolymers.⁵ The K -value is based on kinematic viscosity measurements, given by the Fikentscher equation⁶:

$$\frac{\log(c_{rel})}{c} = \frac{75K_0^2}{1 + 1.5K_0c} + K_0 \quad (1)$$

where c represents the concentration in g/100 mL; η_{rel} represents the relative viscosity as compared to the solvent; and K_0 represents $K/1000$. The K -value can be directly calculated by rearranging the Fikentscher equation:

$$K = \frac{\sqrt{300c \log(\eta_{rel}) + (c + 1.5c \log(\eta_{rel}))^2} + 1.5c \log(\eta_{rel}) - c}{0.15c + 0.003c^2} \quad (2)$$

However, the determination of the K -value depends upon measurement of the viscosity in a specific concentration with a particular viscometer.⁷ The concentration of anhydrous PVP is specified for each grade of the polymer: 0.1%, 1%, and 5% (w/v) for $K > 95$, $18 < K < 95$, and $K < 18$, respectively.

The viscosity-average molecular weight, M_v , can be calculated from the empirical equation³:

$$M_v = 22.22(K + 0.0075K^2)^{1.65} \quad (3)$$

These equations show that the higher the K -value, the higher the viscosity and the molecular weight. A PVP solution with a K -value between 80–100 has a molecular weight in the range of 900,000–1,500,000. In aqueous solutions, the effect of PVP concentration on the viscosity shows nearly a first-order relationship with a much greater influence at large K -values.^{5,7}

The PVP/DAS photoresist is a dilute aqueous solution of a high K -value PVP polymer and DAS activa-

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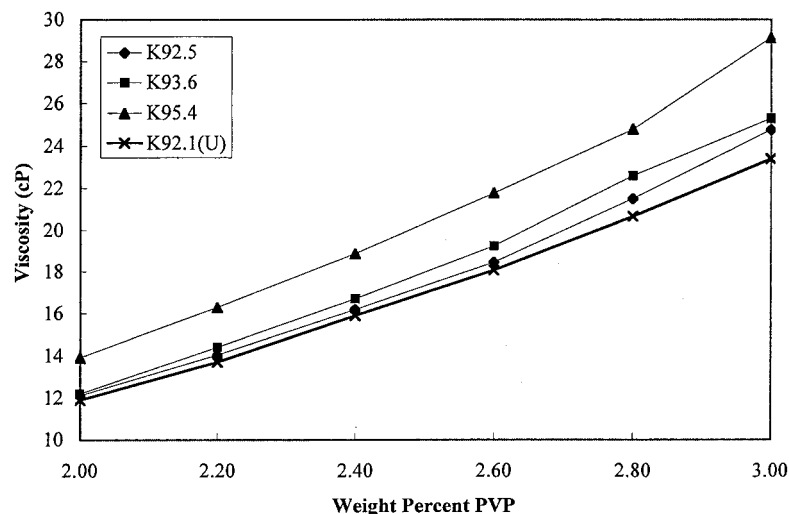


Figure 1 Viscosity versus weight percent PVP at room temperature ($\sim 23^{\circ}\text{C}$).

tor. Small amounts of surfactants are also sometimes added. PVP is the component of the photoresist that significantly contributes to the viscosity of the photoresist solution. The photoresist is applied to a display screen by spin coating and hence, the viscosity of the photoresist solution and the rotational rate of the panel control the thickness of the photoresist on the screen.^{3,8} Therefore, in order to get a consistent photoresist thickness, the viscosity of the PVP solution must be known and kept constant.

PVP obtained from a vendor with a nominal K -value actually has a wide range of K -values that fall within their specifications. For example, BASF sells PVP with a nominal K -value of 90, but the actual K -value can range anywhere between 90 and 98. Since the viscosity, weight percent of PVP, and K -value of a PVP solution are related, with each differing K -values, the weight percent of PVP in the photoresist solutions must be raised or lowered to compensate. In order to consistently control the viscosity of the PVP polymer solution more accurately, a correlation was required to relate the K -value, viscosity, and weight percent of PVP.

EXPERIMENTAL

The PVP solutions were obtained from BASF as pre-mixed solutions with about 20 wt % PVP solids dissolved in water. Four different K -values of PVP were used: 92.1 of an unpreserved PVP, 92.5, 93.6, and 95.4 of a preserved PVP. These K -values of PVP represent the range that is currently of interest for its use as a photoresist material. The preserved PVP solutions contained the biocide Cosmocil, which is used to increase shelf life. These PVP solutions were then further diluted with de-ionized water to produce solu-

amounts of original PVP solution and water were determined to produce the desired concentration of PVP in solution. A 100 mL beaker was placed on top of a balance and the desired amount of water was weighed, followed by the addition of the determined mass of PVP. This solution was then mixed with a magnetic stir bar until homogeneous (about 30 min).

A Brookfield Syncro-Lectric viscometer, model #LVT, with an ultra-low (UL) adapter was used to measure the viscosity of the solutions. To measure the viscosity, 16.5 mL of solution was placed into the capped UL adapter. The UL adapter was then placed around the spindle and attached to the viscometer. Once assembled, the viscometer was operated at the three highest possible spindle rotation rates (3, 6, 12, and 30 rpm depending on the viscosity of the solution) to increase the accuracy of the reading, and the viscosity was measured at each rate. The measurements at these three rates were then averaged to determine the viscosity of the solution. The accuracy of the measurements was ± 0.5 cP.

RESULTS AND DISCUSSION

The viscosity was measured at varying concentrations of PVP between 2 and 3 wt % at room temperature ($\sim 23^{\circ}\text{C}$). Figure 1 shows that the viscosity has a second-order polynomial dependence upon the weight percent of PVP for all K -values. The correlation for each K -value of PVP is listed in Table I. Figure 1 also shows that the viscosity increases for each weight percent of PVP as the K -value is increased.

With this data, a correlation relating the K -value, viscosity, and weight percent of a PVP solution was determined. The data were processed using a statisti-

correlation was determined (with the coefficients rounded off to four significant figures):

$$\mu = 38730W^2 - 9551W + 95.51WK - 32.17K + 0.1641K^2 + 1581 \quad (4)$$

where: μ is viscosity (cP), and W is the weight percent of PVP. Although this correlation is written to determine viscosity, it can be easily rearranged to determine the K -value. This equation is a second order polynomial in K -value and can be solved by using the quadratic equation as follows:

$$(0.1641)K^2 + (95.51W - 32.17)K + (38730W^2 - 9551W + 1581 - \mu) = 0 \quad (5)$$

$$K = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (6)$$

where $a = 0.1643$, $b = 95.51W - 32.17$, and $c = 38730W^2 - 9551W + 1581 - \mu$. The validity of this correlation was determined by measuring the viscosity of other PVP solutions with known K -values and weight percents of PVP. The data from these experiments are summarized in Table II.

The viscosity was calculated by using the correlation in eq. (3) for three different weight percents of PVP and then compared with the average measured viscosity. The average relative error for this correlation was approximately 1%. The viscosity was also calculated using the Fikentscher equation, which gave viscosities with an average relative error of about 58%. Equation (3) yields a much better prediction of the viscosity for the narrow range of conditions studied, which are of use for the photoresist application. However, by checking the predictions of both of these correlations with data available in the literature,^{5,7} neither was found to be a general correlation. Therefore, a correlation, such as given in eq. (3), would need

TABLE I
Correlations of Viscosity as a Function of Weight Percent PVP

K-Value	Correlation	R ²
92.5	$\mu = 45300W^2 - 1000W + 14.2$	0.9996
93.6	$\mu = 30200W^2 - 187W + 3.85$	0.9988
95.4	$\mu = 51500W^2 - 1080W + 15.0$	0.9988
92.1(U)	$\mu = 28000W^2 - 248W + 5.66$	0.9999

TABLE II
Viscosity Correlation Data

K-Value	PVP Concentration (Wt %)	Average Viscosity (cP)	Calculated Viscosity ^a (cP)	Fikentscher Viscosity ^b (cP)
92.5	2.22	14.4	14.2	19.7
	2.65	19.1	19.3	30.8
	2.93	23.4	23.3	40.5
93.6	2.13	13.6	13.9	18.9
	2.63	19.5	20.0	32.2
	2.88	23.5	23.8	41.4
95.4	2.18	15.9	16.1	22.0
	2.62	22.0	22.4	35.5
	2.95	27.8	28.0	49.8
92.1 (U)	2.15	13.3	13.5	17.9
	2.60	18.1	18.4	28.6
	2.97	23.6	23.6	41.0

^a Calculated from eq. (3).

^b Calculated from eq. (1).

to be developed for the particular range of conditions of interest.

CONCLUSIONS

A correlation between the viscosity, K -value of the PVP, and weight percent of the PVP was determined. Since an unconventional method of characterization, the K -value, is used for the PVP polymer, the K -value was related to more standard and convenient characterization method of viscosity measurement. With the K -value of the PVP, as given by a vendor, the correlation can be used to calculate the appropriate concentration of PVP needed to produce the desired viscosity, and thus allowing for the deposition of a uniform coating thickness of the photoresist.

References

1. Kroschwitz, J. I.; Howe-Grant, M., Eds. Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed.; Wiley: New York, 1989, Vol. 24.
2. Akagi, M.; Nonogaki, S.; Koshi, T.; Oba, Y.; Oikawa, M. Polym Eng Sci 1977, 17, 353.
3. Castellano, J. A. Handbook of Display Technology; Academic Press, Inc.: San Diego, 1992.
4. Ozawa, L. Cathodoluminescence: Theory and Applications; VCH Publishers: Weinheim, Germany, 1990.
5. Kroschwitz, J. I., Ed. Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1989, Vol. 17.
6. Kline, G. M. Modern Plastics 1945, Nov., 157.
7. Fusiak, F., Ed. PVP; In Polyvinylpyrrolidone Polymers; International Specialty Products: Wayne, NJ, 1999.
8. Castellano, J. A. Handbook of Display Technology; Academic Press, Inc.: San Diego, 1992.
9. Sasaki, K. Y.; Talbot, J. B. Adv Mater 1999, 11, 91.