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Effect of Sorption, Repeated Sorption and Desorption on Solubility and Swelling of the Poly(vinyl alcohol) Esters

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Series of polyesters prepared by partially esterification of poly(vinyl alcohol) and with different acid chloride *viz.*, anthranilic acid, amino acetic acid and *p*-amino benzoic acid chloride. Solubility and swelling of these products in water have been evaluated. To study how the solubility and swelling of polyesters were affected by sorption, repeated sorption and desorption of the product of each series used for sorption once were carried out. The solubility (g/mL) and swelling degree (g/g) were calculated. When polyester resin dissolves in water every time the swelling degree of the undissolved polyester resin varies over a narrow range.

Key Words: Poly(vinyl alcohol), Anthranilic acid, Amino acetic acid, *p*-Amino benzoic acid, Swelling degree.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is commercially available in various grades depending on its degree of hydrolysis and degree of polymerization[1]. Its solubility in water depends on its degree of hydrolysis, degree of polymerization, tacticity, cross linking *etc*. Its hydroxyl groups cause its high affinity for water with strong H-bonding between intra and intermolecular (chain) hydroxyl groups. Previous reported works of PVA have remarkable effect on its swelling[2]. Its hydroxyls have been studied as swollen elastic networks and as water sorbents[3-5]. Various polyesters have been prepared from PVA and studied their solubility and degree of swelling to correlate them with various structural factors[6-10]. Its hydrolysis has been studied as having swollen elastic nature of water sorption.

When PVA is partially esterified with different mono and dibasic acids, ester content increases. OH group content decreases cross-links get introduced and hence relative changes in hydrophilic, hydrophobic groups and chain lengths affect solubility and swelling. Sorption properties of the

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chelating ion-exchange resin towards various divalent metal ions are studied by static equilibration technique as a function of pH and time of equilibration[10]. The functional PVA was copolymerized and/or cross-linked with acrylic acid or its partially neutralized form to give cross linked polyacrylates that could swell in water[11]. Various polymers have been prepared from PVA and studied for solubility and swelling[12-15]. The super absorbent polyacrylate polymers were prepared[16,17]. Biodegradable polyacrylates using functionalized PVA as a cross-linking agent were studied[18,19].

EXPERIMENTAL

The series of polyester-resins were prepared using different acid chloride such as anthranilic acid (ANA), amino acetic acid (AAA) and *p*-amino benzoic acid (4-AB) chloride and varying proportions of PVA as 1:1, 1:2, 1:3, 1:5, 1:10 (having degree of polymerization 1640 and degree of hydrolysis 97 % of Koch-Light make, England) with thionyl chloride in dimethyl formamide in presence of pyridine. These products were studied for sorption, resorption and desorption. The process were recycled. The result are presented in Table-1. The solubility and swelling degree for repeated sorption are compared with increase in number of hydroxyl groups (X). From the study of solubility and swelling degree of the sample in water, evaluated the number of moles of water required to cause maximum swelling of 1 g mole of resin, also minimum number of moles of water required to solubilize 1 g mole of the polyester sample.

TABLE-1
WATER RESORPTION

Product	Water sorption (I)		Water resorption (II)		Water desorption (II)	
	Solubility (g/mL)	Degree of Swelling (g/g)	Solubility (g/mL)	Degree of Swelling (g/g)	Solubility (g/mL)	Degree of Swelling (g/g)
K-P-ANA(3)	0.020	2.20	0.073	3.08	0.009	3.15
K-P-ANA(5)	0.024	3.95	0.093	5.69	0.032	6.10
K-P-ANA(10)	0.021	2.56	0.011	2.21	0.006	2.18
K-P-AAA(3)	0.030	2.45	0.072	1.45	0.005	1.66
K-P-AAA(5)	0.024	2.36	0.023	1.90	0.014	1.84
K-P-AAA(10)	0.025	3.34	0.058	2.93	0.004	2.67
K-P-4-AB(3)	0.022	2.39	0.013	2.73	0.012	2.79
K-P-4-AB(5)	0.032	2.94	0.097	3.84	0.004	3.99
K-P-4-AB(10)	0.023	2.19	0.045	2.47	0.004	2.48

RESULTS AND DISCUSSION

When water comes in contact with porous hydrophilic resin, the small mobile water molecules from water phase readily diffuse through water-resin interface and to the porous hydrophilic groups of the resin in the resin phase. Sorption of water by polyester takes place upto a certain limit. When further sorption takes place beyond the limit, the substance was solubilize. It was found that the products dissolve to some extent, exhibiting the possibility and need studying swelling an solubility simultaneously. Hence, determined (1) weight of the sample before sorption (W_{BS}), (2) weight of the sample after sorption in water (W_{AS}), (3) weight of the drying the sorbed sample (W_{DS}), (4) volume of the water used initially for sorption (V_{BS}) and (5) volume of water after sorption (V_{AS}). Usually, the degree of swelling is determined as:

$$\text{Degree of swelling (DS)} = \frac{W_{AS} - W_{BS}}{W_{BS}}$$

Because, a part of sample gets solubilized during sorption, the degree of swelling (DS) dry basis is better evaluated as (equation):

$$(\text{DS}) = \frac{W_{AS} - W_{BS} - \dfrac{qW_{DS}}{W_{BS}(1-q)}}{W_{DS}}$$

where q represents the water content (g/g) of the sample. Solubility (g/mL) of the sample is evaluated as:

$$\text{Solubility (Sol)} = \frac{W_{BS}(1-q) - W_{DS}}{W_{BS} - V_{AS}}$$

where V_{AS} can be approximated for water as:

$$V_{AS} = W_{AS} - W_{DS} = \frac{q - W_{DS}}{W_{BS}(1-q)}$$

It has been observed that the values of degree of swelling and solubility show gradation in series in general.

To study how the solubility and swelling of the resin are affected by repeated sorption (recycling), we carried out sorption and desorption of the resins of each series used for sorption once. The result have been utilized to calculate solubility of the resin, degree of swelling of the resin. The solubility (g/mL) of the resin is calculated as:

$$\text{Solubility (I) (g/mL)} = \frac{W_{DS} - W_{DR}(\text{I})}{W_{BS} - V_{AS}}$$

The results for 1:1 and 1:2 proportions of PVA and acid chlorides were unsatisfactory. Hence are not mentioned in Table-1.

$$\text{Solubility R (I) (g/mL)} = \frac{W_{DS} - W_{DR}(I)}{W_{BS} - V_{AS}}$$

$$\text{Solubility R (II) (g/mL)} = \frac{W_{DR}(I) - W_{DR}(II)}{W_{BS} - V_{AS}}$$

$$\text{Solubility R (III) (g/mL)} = \frac{W_{DR}(II) - W_{DR}(III)}{W_{BS} - V_{AS}}$$

where $W_{DR}(I)$, $W_{DR}(II)$ and $W_{DR}(III)$ are weights of the dried samples after first, second and third resorption, respectively, and V_{BS} is volume of the water used initially for sorption at every time. V_{AS} is volume of water after sorption and resorption at every time. It has been shown above that how it can be approximated for water.

Degree of swelling (g/g) of the resins is evaluated as:

$$\text{Degree of swelling R(I) (g/g)} = \frac{W_{AR}(I) - W_{DR}(I)}{W_{DR}(I)}$$

$$\text{Degree of swelling R(II) (g/g)} = \frac{W_{AR}(II) - W_{DR}(II)}{W_{DR}(II)}$$

$$\text{Degree of swelling R (III) (g/g)} = \frac{W_{AR}(III) - W_{DR}(III)}{W_{DR}(III)}$$

where $W_{AR}(I)$, $W_{AR}(II)$ and $W_{AR}(III)$ are weights of the samples after first, second and third resorption, respectively.

When the resin was subjected to repeated sorption and desorption, a part of resin dissolve in water every time. The solubility of the resin in first sorption experiment decreases considerably in subsequent sorption experiments. Similarly the swelling degree of undissolved resin varies a very narrow range.

From the studies of the solubility and swelling of the sample in water, we can evaluate (1)A: number of moles of water required to cause maximum swelling of 1 g mol of the and (2) B: minimum number of moles of water required to solubilize 1 g mol of sample.

$$A = \frac{DS \times W_F(a)}{18} \quad \text{(Sorption capacity)}$$

$$B = \frac{W_F(a)}{\text{Solubility} \times 18}$$

where $W_F(a)$ represents the formula weight of the sample in anhydrous form. The formulae are suggested in agreement with C-H analysis ester content and water content of the resins. The values of X and formulae are presented in Table-2.

TABLE-2
WATER SORPTION

Product	m.f.	X	Solubility (g/mL)	Degree of swelling (g/g)	A	B
K-P-ANA(1)	$C_{10}H_{12}NO_3$	0.50	0.037	1.82	19.62	219.29
K-P-ANA(2)	$C_{13}H_{18}NO_8$	2.00	0.041	3.53	61.97	428.18
K-P-ANA(3)	$C_{19}H_{31}NO_8$	5.00	0.039	3.08	68.62	571.23
K-P-ANA(5)	$C_{27}H_{47}NO_{12}$	9.00	0.038	3.42	109.63	843.57
K-P-ANA(10)	$C_{49}H_{93}NO_{24}$	20.00	0.038	4.13	247.57	1577.49
K-P-AAA(1)	$C_5H_{9.5}N_{1.5}O_3$	0.50	0.063	6.49	49.94	121.69
K-P-AAA(2)	$C_{4.5}H_9NO_{2.75}$	0.25	0.049	3.06	20.57	137.19
K-P-AAA(3)	$C_5H_{10}NO_3$	0.50	0.051	3.16	23.17	143.79
K-P-AAA(5)	$C_8H_{16}NO_{4.5}$	2.00	0.041	3.03	33.33	268.29
K-P-AAA(10)	$C_{16}H_{31}NO_{8.5}$	6.00	0.044	3.36	69.63	470.29
K-P-4-AB(1)	$C_{10}H_{12}NO_3$	0.50	0.038	1.79	19.29	283.60
K-P-4-AB(2)	$C_{16}H_{24}NO_6$	3.50	0.043	2.96	49.66	390.18
K-P-4-AB(3)	$C_{19}H_{31}NO_8$	5.00	0.038	2.87	63.94	586.26
K-P-4-AB(5)	$C_{27}H_{47}NO_{12}$	9.00	0.041	2.16	69.24	781.84
K-P-4-AB(10)	$C_{49}H_{93}NO_{24}$	20.00	0.034	2.03	121.69	1763.10

The above results imply that the swelling capacity of the resin is practically unaffected by the dissolution of the fraction of the resin dissolved in water would not have higher swelling capacity than the fraction remaining undissolved.

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