

Volume and Area Swelling of the Polyester-Polyols

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The product of partially esterifying poly (vinyl alcohol) and terephthalic acid, isophthalic acid, salicylic acid and *p*-hydroxy benzoic acid chlorides were polyester-polyols. Swelling of these products in water was studied. Relative and comparative studies of swelling and solubilities of polyester-polyols have been few from the determination of the density of the product before sorption and after sorption of water. Volume swelling per unit mass and volume swelling per unit volume were calculated. From the determination of the area of a square piece of the polyester-polyol before sorption and after sorption, area swelling per unit area, increase in length per unit length and increase in breadth per unit height (uncorrected for solubility) were calculated. Longitudinal swelling has also been recorded in relation to length, breadth and height. This can be related to rate of swelling in all directions.

Key Words: Swelling, Volume, Poly (vinyl alcohol), Terephthalic acid, Isophthalic acid; Salicylic acid, *p*-Hydroxy benzoic acid.

INTRODUCTION

Poly (vinyl alcohol) (PVA) is commercially available in various grades depending on its degree of hydrolysis and degree of polymerization. The solubility of poly (vinyl alcohol) in water depends on its degree of hydrolysis, degree of polymerization, tacticity, cross-linking¹ etc. When poly (vinyl alcohol) 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 hydrophobic, hydrophilic group and length affect solubility and swelling. The polymer characterized for sorption behaviour is being strong hydrogen bonding base^{2,3}; two separate modes of sorption can be distinguished. When the swelling of these products was studied it was found that the product dissolves to some extent exhibiting the possibility and need of studying swelling and solubility simultaneously. Determination of degree of swelling is used in practice for testing finished polymer articles intended for service in liquid and gaseous media. It also serves as a promising method of assessing the degree of cross lining, the degree of hydration, etc. Degree of swelling can be determined only for polymers with

limited swelling, because upon unlimited swelling, the polymer itself begins to dissolve. A wide range of PVA films were studied for their solubility and swelling and correlated with various structural factors⁴⁻¹⁰.

EXPERIMENTAL

The series of polyester-polyols were prepared using different acid chlorides and varying proportions of PVA. The acid-chlorides were prepared by treating the acid with thionyl chloride in dimethyl formamide (DMF) in presence of pyridine. The different amounts of reactants used, yield, colour, softening temperature of the products etc. are presented in Table-1. Volume swelling study of these products in water is carried out by using a cleaned, dried and previously weighed specific gravity bottle; then the bottle is filled with water and weighed at 298 K. The water was removed, the bottle was dried and weighed by known quantity of sample. The bottle with sample was filled with water and weighed first immediately and then after standing for 24 h. The density determination of the product before and after sorption (DBS and DAS respectively) was done. Volume swelling per unit mass and volume swelling per unit volume were calculated. Similarly, area-swelling study of these products was done by using travelling microscope. The sample of resin piece was cut into disc using diamond blade for the experiment. Its dimensions (length and breadth) were measured by using a travelling microscope. Then it was moistened with water and immediately its dimensions (length and breadth) were measured. Then it was kept in water for 24 h and again its dimensions (length and breadth) were measured. The results of volume swelling and area swelling are presented in Tables 2 and 3 respectively.

RESULTS AND DISCUSSION

From the determination of the density of the product before (DBS) and after sorption (DAS), volume swelling per unit mass and volume swelling per unit volumes were calculated as follows:

$$\text{Specific volume of the polymer before sorption (mL/g)} = \frac{1}{D_{BS}}$$

$$\text{Specific volume of the polymer after sorption (mL/g)} = \frac{1}{D_{AS}}$$

$$\text{Volume swelling (mL/g) (uncorrected for solubility)} = \frac{1}{D_{AS}} - \frac{1}{D_{BS}}$$

$$\text{Volume swelling (mL/mL)} = \frac{\frac{1}{D_{AS}} - \frac{1}{D_{BS}}}{\frac{1}{D_{BS}}}$$

The calculated values are presented in Table-2. The values of volume swelling

(mL/mL) lie between 5.76 and 14.38. Thus in some cases the volume increases as much as 14 times its original value; such large increases in volume on sorption can be used for various technological applications^{11, 12}.

TABLE-1
AMOUNT OF REACTANTS USED, YIELD, COLOUR, SOFTENING TEMPERATURE OF THE PRODUCTS

S. No.	Product	Poly (vinyl alcohol) (mmol)	Acid chloride (mmol)	Yield (%)	Melting/softening temp. (°C)	Colour
(a) Acid : terephthalic (TPA), temp. of reaction: 150°C time of reaction 6 h						
01	K-P-TPA(1)	22.7	4.9	67	d*	black
02	K-P-TPA(2)	45.5	4.9	100	d	brown
03	K-P-TPA(3)	68.2	4.9	100	d	brown
04	K-P-TPA(5)	113.6	4.9	100	d	brown
05	K-P-TPA(10)	227.0	4.9	100	d	brown
(b) Acid : isophthalic (IPTA), temp. of reaction: 150°C time of reaction 6 h						
06	K-P-IPTA(1)	22.7	4.9	67	d	black
07	K-P-IPTA(2)	45.5	4.9	100	d	brown
08	K-P-IPTA(3)	68.2	4.9	100	d	brown
09	K-P-IPTA(5)	113.6	4.9	100	d	brown
10	K-P-IPTA(10)	227.0	4.9	100	d	brown
(c) Acid : salicylic (SAA), temp. of reaction: 150°C time of reaction 6 h						
11	K-P-SAA(1)	22.7	6.4	68	122	black
12	K-P-SAA(2)	45.5	6.4	100	141	brown
13	K-P-SAA(3)	68.2	6.4	100	167	brown
14	K-P-SAA(5)	113.6	6.4	85	181	pink
15	K-P-SAA(10)	227.0	6.4	85	188	brown
(d) Acid : <i>p</i> -hydroxy benzoic acid (HbA), temp. of reaction: 150°C time of reaction 6 h						
16	K-P-HbA(1)	22.7	6.4	100	103	brown
17	K-P-HbA(2)	45.5	6.4	100	110	brown
18	K-P-HbA(3)	68.2	6.4	100	139	brown
19	K-P-HbA(5)	113.6	6.4	100	151	brown
20	K-P-HbA(10)	227.0	6.4	100	163	brown

* decomposition

From the determination of the area of a square piece of the product by using travelling microscope before sorption and after sorption, the swelling in area per unit area by water was calculated. Increase in length per unit length, increase in breadth per unit breadth and increase in height per unit height (uncorrected for solubility) were also calculated. All these values are presented in Table-3. It was found that the values of area swelling per unit area lie between 0.26 and 2.33.

TABLE-2
VOLUME SWELLING PER GRAM AND VOLUME SWELLING PER mL
OF POLYESTER-POLYOLS

S. No.	Product	Sp. volume of polymer (mL/g)	Sp. volume of polymer after 24 h (mL/g)	Volume swelling (mL/g)	Volume swelling (mL/mL)
1	K-P-TPA(1)	0.87	12.02	11.15	12.82
2	K-P-TPA(2)	1.05	12.15	11.10	10.57
3	K-P-TPA(3)	0.85	10.90	10.05	11.82
4	K-P-TPA(5)	0.90	10.07	9.80	10.19
5	K-P-TPA(10)	1.05	13.60	12.55	11.95
6	K-P-IPTA(1)	1.10	9.85	8.75	7.95
7	K-P-IPTA(2)	0.95	7.20	6.25	6.58
8	K-P-IPTA(3)	1.05	11.05	10.00	9.52
9	K-P-IPTA(5)	0.85	11.50	10.65	12.53
10	K-P-IPTA(10)	1.13	12.20	11.07	9.80
11	K-P-SAA(1)	0.87	10.50	9.63	11.07
12	K-P-SAA(2)	1.13	7.88	6.65	5.97
13	K-P-SAA(3)	0.85	6.80	5.95	7.00
14	K-P-SAA(5)	0.83	6.90	6.07	7.31
15	K-P-SAA(10)	1.050	7.10	6.05	5.76
16	K-P-HbA(1)	0.87	11.07	10.20	11.72
17	K-P-HbA(2)	0.95	13.00	12.05	11.84
18	K-P-HbA(3)	1.15	12.13	10.98	12.68
19	K-P-HbA(5)	0.80	12.30	11.50	14.38
20	K-P-HbA(10)	1.15	12.25	11.10	9.65

The results of swelling degree (g/g) of these products in water, NaCl, urea, Cu(II)¹³ are further compared with the volume swelling and area swelling and these are presented in Table-4.

Longitudinal swelling has been recorded in relation to length (LS_l), breadth (LS_b) and height (LS_h). It was observed that the values of LS_l are comparable to those of LS_b and much lower than that of LS_h . This can be related to the same rate of swelling in all directions, and to the fact that the length of the piece was comparable to its breadth but larger than its height and to the assumption that relative swelling obtained in any direction did not alter later.

TABLE-3
AREA SWELLING PER UNIT AREA AND HEIGHT PER UNIT HEIGHT
OF POLYESTER-POLYOLS

S. No.	Product	Area of polymer piece in presence of water		Area swelling per unit area (mm^2/mm^2)	Increase in		
		Immediately ($l \times b$) (mm^2)	After 24 h ($l \times b$) (mm^2)		Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	Height per unit height (mm/mm)
1	K-P-TPA(1)	4.80	8.38	0.75	0.31	0.33	6.89
2	K-P-TPA(2)	5.25	12.00	1.29	0.38	0.66	4.05
3	K-P-TPA(3)	4.95	11.20	1.29	0.74	0.30	4.67
4	K-P-TPA(5)	5.09	16.95	2.33	0.53	1.18	2.36
5	K-P-TPA(10)	4.05	9.63	1.38	0.52	0.59	4.41
6	K-P-IPTA(1)	5.88	12.10	1.06	0.48	0.39	3.34
7	K-P-IPTA(2)	7.92	15.05	0.90	0.41	0.35	2.99
8	K-P-IPTA(3)	5.40	10.54	0.95	0.41	0.38	4.39
9	K-P-IPTA(5)	8.61	17.26	1.00	0.36	0.47	5.77
10	K-P-IPTA(10)	6.08	13.69	1.25	0.50	0.50	3.80
11	K-P-SAA(1)	6.85	9.18	0.34	0.12	0.20	8.01
12	K-P-SAA(2)	8.69	22.40	2.15	1.01	0.56	1.21
13	K-P-SAA(3)	6.91	19.95	1.89	0.87	0.54	1.77
14	K-P-SAA(5)	6.63	17.11	1.58	0.79	0.44	2.22
15	K-P-SAA(10)	6.98	17.79	1.55	0.52	0.57	1.65
16	K-P-HbA(1)	4.84	7.37	0.52	0.24	0.23	7.37
17	K-P-HbA(2)	6.13	7.87	0.28	0.15	0.12	9.69
18	K-P-HbA(3)	4.62	6.68	0.45	0.20	0.20	6.28
19	K-P-HbA(5)	5.88	8.32	0.41	0.17	0.21	9.91
20	K-P-HbA(10)	8.43	10.62	0.26	0.11	0.13	7.45

TABLE-4

S. No.	Product	Swelling degree (g/g) of the resins in				Area swelling (mm ² /mm ²)	Volume swelling (mL/mL)
		Water	NaCl solution	Urea solution	Cu(II) solution		
1	K-P-TPA(1)	6.29	1.39	—	3.55	0.75	12.82
2	K-P-TPA(2)	6.15	2.46	—	3.75	1.29	10.57
3	K-P-TPA(3)	6.33	2.83	0.15	3.73	1.29	11.82
4	K-P-TPA(5)	6.13	9.39	7.71	3.11	2.33	10.19
5	K-P-TPA(10)	5.75	3.08	3.38	1.06	1.38	11.95
6	K-P-IPTA(1)	4.22	1.40	—	2.12	1.06	7.95
7	K-P-IPTA(2)	4.57	2.80	—	6.61	0.90	6.58
8	K-P-IPTA(3)	4.81	1.89	4.65	3.66	0.95	9.52
9	K-P-IPTA(5)	3.85	1.75	2.68	1.94	1.00	12.53
10	K-P-IPTA(10)	4.53	2.70	3.25	2.21	1.25	9.80
11	K-P-SAA(1)	2.20	1.57	—	4.34	0.34	11.07
12	K-P-SAA(2)	6.57	4.56	—	5.36	2.15	5.97
13	K-P-SAA(3)	5.80	3.34	4.32	5.40	1.89	7.00
14	K-P-SAA(5)	4.13	2.05	2.78	2.21	1.58	7.31
15	K-P-SAA(10)	3.38	3.67	3.80	1.38	1.55	5.76
16	K-P-HbA(1)	1.86	1.63	—	2.43	0.52	11.72
17	K-P-HbA(2)	2.51	1.73	—	2.00	0.28	12.68
18	K-P-HbA(3)	2.44	1.61	2.01	1.81	0.45	9.55
19	K-P-HbA(5)	2.34	1.66	2.26	1.79	0.41	14.38
20	K-P-HbA(10)	2.71	1.65	2.70	1.76	0.26	9.65

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