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Copolymer Production From Poly(Vinyl Alcohol)

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Abstract

The treatment of PVA with concentrated hydrochloric acid using a reflex technique for several days to transfer some of PVA to PVC as co-polmer. Black material formed with very high ability to absorb water (approximately 220%) which indicates large voids formed in the new structure which confirmed by many tests. The new structure is a good water storage which is interested in agriculture applications

Keywords: Copolymer, Poly vinyl alcohol, Poly vinyl chloride, Absorb, Storage.

الخلاصة

علاج بولي فنيل الكحول مع حمض الهيدروكلوريك المركزة باستخدام تقنية رد الفعل لعدة أيام لتحويل بعض بولي فنيل الكحول إلى بولي فينيل كلوريد كبوليمر مشارك. حيث تكون مادة سوداء لها قدرة عالية جدا على امتصاص الماء (حوالي 220٪) مما يدل على الفراغات الكبيرة التي تشكلت في الهيكل الجديد الذي أكده العديد من الاختبارات. الهيكل الجديد يحزن الماء بشكل جيد وهذا مثير للاهتمام في تطبيقات الزراعة.

الكلمات المفتاحية: بوليمر مشترك، بولي فنيل الكحول، بولي فنيل كلوريد، امتصاص، خزان.

1.Introduction

Graft copolymers have been widely used for compatibilization of immiscible polymer blends as well as the improvement of interfacial adhesion in composites. Poly(vinyl alcohol) with varying physical properties can be obtained from poly(vinyl acetate) by varying the solvent and temperature used in the vinyl acetate polymerization (Matsumura, 2005). It has been widely utilized in polymer modifications as it is readily available, it is inexpensive and it has hydroxyl groups present. Graft copolymers of poly(vinyl alcohol) have been prepared especially by irradiation techniques. PVA with grafted methyl methacrylate has been studied as membrane for hemodialysis (Finch, 1992). Graft copolymers consisting of 50 % PVA, 25 % poly(vinyl acetate) and 25% grafted ethylene oxide units have been used to prepare capsules for drugs which do not require any additional plasticizers (Nozakura, *et.al.*, 1973). Crosslinked PVA derivatives have been reported by reacting their hydroxylic groups with dianhydrides and diisocyanates (Yuki *et.al.*, 1969).

PVOH polymers with no color and odor, melt at around 180-228°C, and display glass to rubber transition at 75-85°C. As the degree of vinyl acetate hydrolysis to vinyl alcohol increases, the polymer structure becomes more crystallized, which is associated with increased in intermolecular forces, melting and glass transition temperatures, and enhanced solubility in water (Marten, 2002). Hydrochloric acid is prepared by dissolving hydrogen chloride in water. Hydrogen chloride can be generated in many ways, and thus several precursors to hydrochloric acid exist. The large-scale production of hydrochloric acid is almost always integrated with the industrial scale production of other chemicals. Hydrochloric acid is used for a large number of small-scale applications, such as leather processing, purification of common salt, household cleaning, (Simhon & Rachel, 2003) and building construction(Norman & Earnshaw, 1997). Oil production may be stimulated by injecting hydrochloric acid into the rock formation of an oil well, dissolving a portion of the rock, and creating a large-pore structure. Oil well acidizing is a common process in the North Sea oil production industry. Physical properties of hydrochloric acid, such as boiling and melting points, density, and pH, depend on the concentration or molarity of HCl in the aqueous solution. They range from those of water at very low concentrations approaching 0% HCl to values for fuming hydrochloric acid at over 40% HCl. [Perry, et al., 1984]. The aim of this work preparation of copolymer from PVA and concentrated hydrochloric by convert some of PVA to Poly vinyl chloride (PVC) by reflux technique copolymers.

2. Experimental part

2.1 Materials

Poly (vinyl alcohol) was purchased from Verdean house, Daryaganj, New Delhi-110002 (India) with the degree of hydrolysis (86.0 -89.0 %) and molecular weight of 85,000 g / mole.

Hydrochloric acid purchased from with Al- Ghadir Company melting point is 48 °C, PH=6.3

2.2 Preparation of PVA/HCl

PVA/HCl films were prepared by reflex method by mixing PVA solution with HCl. PVA solution was prepared by dissolving (5g) PVA powder in 150 ml distilled water (DW) with continuous stirring for 30min in 70 ℃. The solution is then placed in a glass flask located in the reflex and the hydrochloric acid is added in a gradient. It stays in the reflex for 38 hours. Note the color change. The solution is placed in a glass tube on the heater to remove the HCl and leave until a layer appears on the surface after the layer appears clearly. Washing with distilled water. In order to neutralize the solution, NaCl was added gradually until pH be 7. The resulting polymer from this process dark red, squishyand insoluble in distilled water is formed. The procedure of preparing and testing PVA / HCl pastes was shown in figure (1).

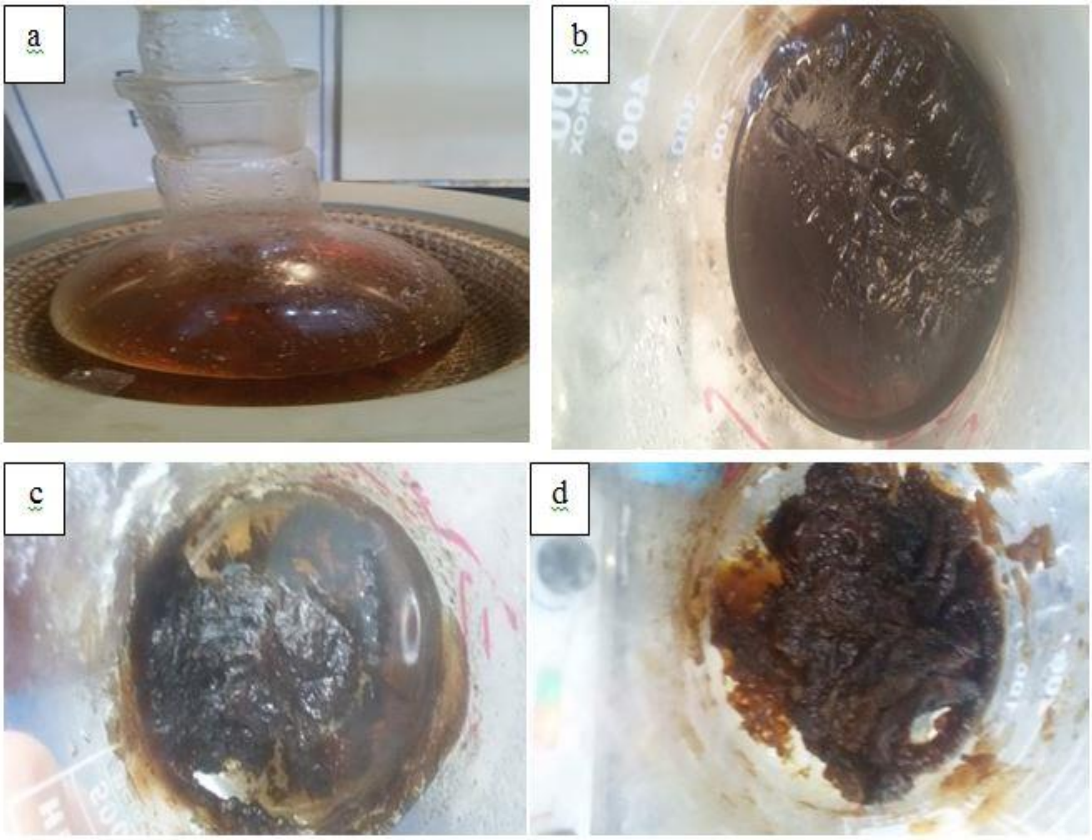


Figure (1): Images for PVA / HCl paste preparation a- PVA/HCl mixture in reflex for 38 hr b- heating to remove HCl at 75℃ for 24 c- Washing by DW and NaCl for neutralizing d- formed PVA/HCl Paste.

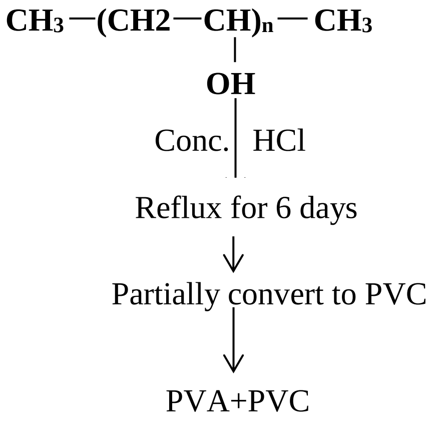
2.3 Tests

Fourier transform infrared spectra technique is used for the characterization of very complex mixtures by FTIR analysis instrument type(IR Affinity-1) made in (Kyoto Japan). UV-Visible –CECIL 2700 computerized spectrophotometer is used to determine the absorption of light from a sample. The sample is placed in a specific position of UV / VIS. Analytical Scanning Electron Microscope (SEM), model (JEOL 6400 F) used to examine the morphology of prepared flims. The sample used in the testing was cut into small pieces (1x1 cm) to fit into the device. The surface morphologies of the prepared films were characterized on a NanoScope IIIA MultiMode AFM instrument in air at ambient conditions using tapping mode probes with constant amplitude (200 mV). The rotated tapping mode etched silicone probe with a resonance frequency of 250 kHz was used. The test was performed according" to ASTM D3418-03 using SH1MADZ-4 DSC-60 device. The sample of PVA and PVA / HCl mixtures in the powder form was tested under nitrogen gas and heating rate of 10 ˚C/min with heating range from RT to 350 ˚C. The water absorption test was performed according to ASTM D570 .Dry SAP sample (W_o= 0.1g) is put in the tea-bag, immersed in the DW for 60 minutes. Absorbency under load (AUL) was measured in the prepared samples that previously absorbed 0.9% NaCl solution under pressure of 2.068 kPa. AUL tool consists of a perforated plate with height =0.7 cm, and diameter = 8 cm putted inside the Petri dish (height =1.2 cm, diameter =11.8 cm).

2.4. Results and Discussion

2.4.1 FTIR result

Figure (2) shows the FTIR spectra for PVA/HCl mixture. It is clear that there is a new band in the 682cm^{-1} position which means that there is a chemical reaction between PVA matrix and HCl (C-Cl bond). Also, the intensity of C-H (at 1424.58 cm^{-1} position, increased.



$$CH_3-(CH_2-\underset{\displaystyle OH}{\underset{|}{CH}})_n-CH_3$$

Conc. HCl

Reflux for 6 days

Partially convert to PVC

PVA+PVC

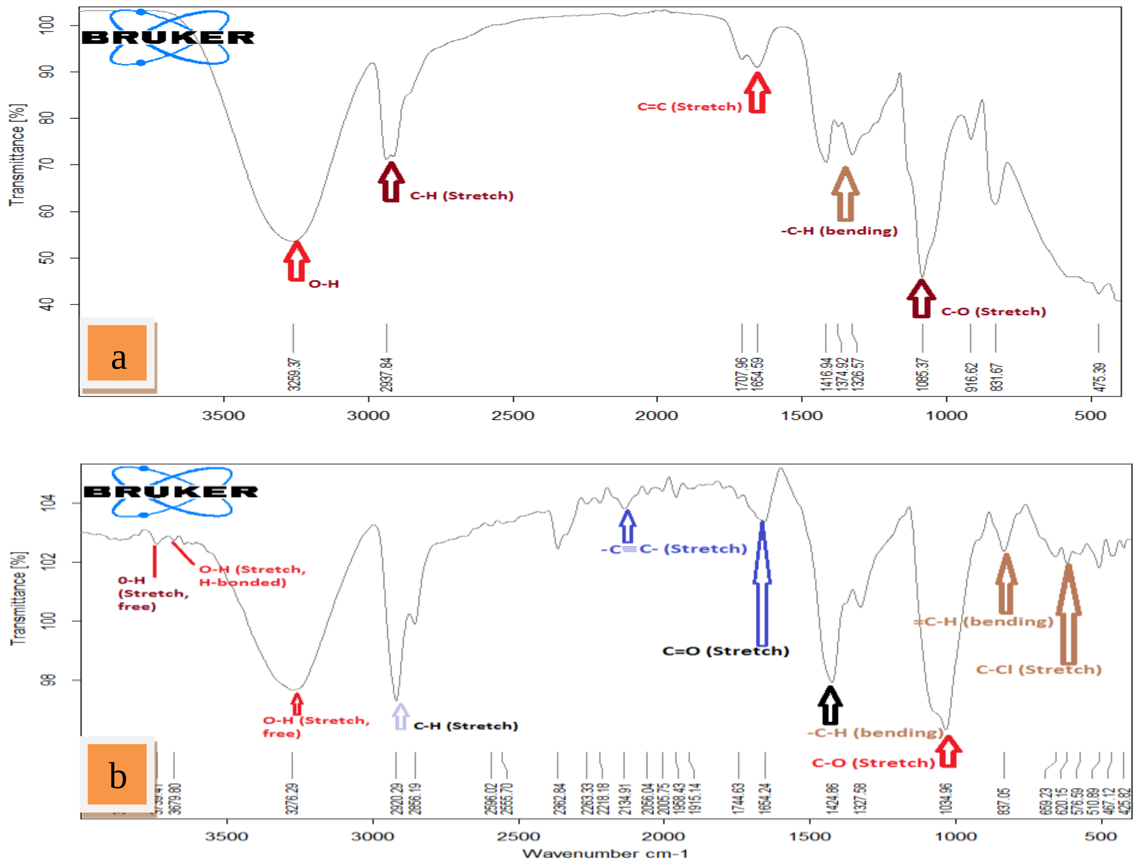


Figure (2): FTIR spectra for (a) pure PVA(b) (PVA / HCl) mixtures

2.4.2 UV-Visible result

The spectrum of UV-visible for pure PVA (figure 3) shows the absorption of n→ π after treatment of PVA with concentration HCl result in reaction to PVC and change the structure of PVA.

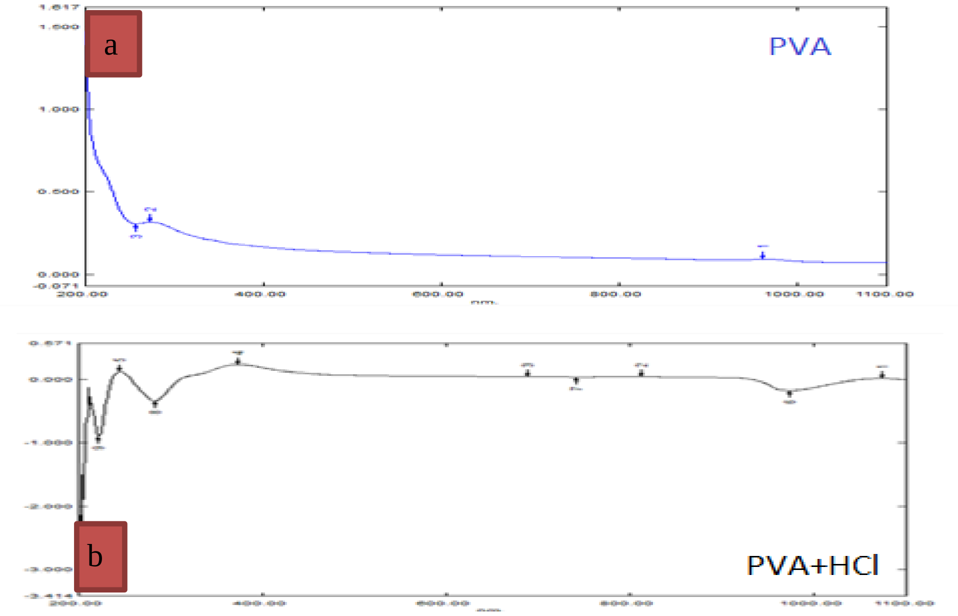


Figure (3): UV-Visible for (a) PVA (b) PVA/HC mixture

2.4.3 Morphology Test

2.4.3.1 SEM result

Figure (4) shows that the treatment of PVA with HCl change it from smooth surface to rough surface due to C-Cl bond which appeared at (682) cm^{-1}. This make a good interactions between two polar polymers (PVA+PVC) through hydrogen bonding making a structure voides or rooms to storage water up to 220% which is useful in agriculture application.

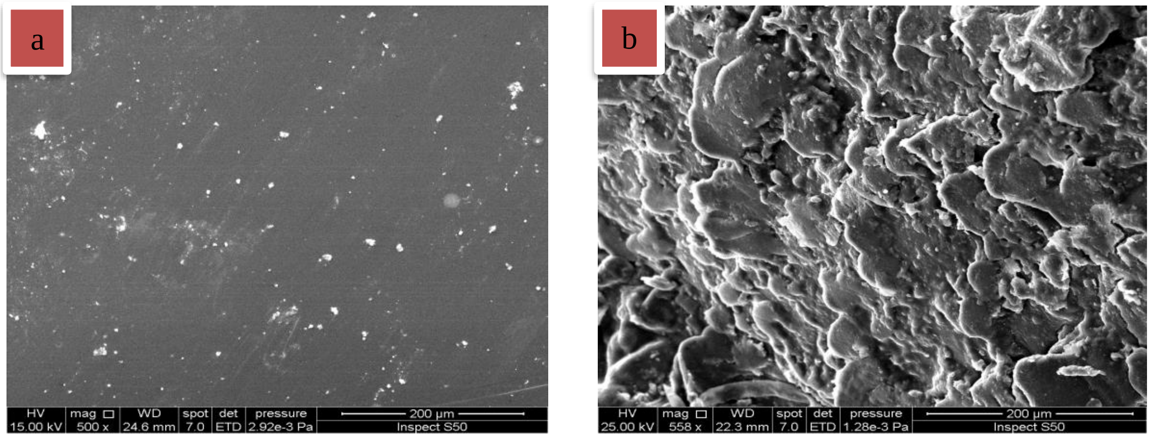


Figure (4): SEM images of (a) PVA (b) PVA/HCl mixture

2.4.3.2 AFM result

Figure(5) shows the AFM images of the PVA/HCl. It is noted that the average diameter of particles (69.85nm) and that the largest percentage of volume (15.92%) have 55nm size and there is 96.58% have 100 nm size or less as shown in table 1.

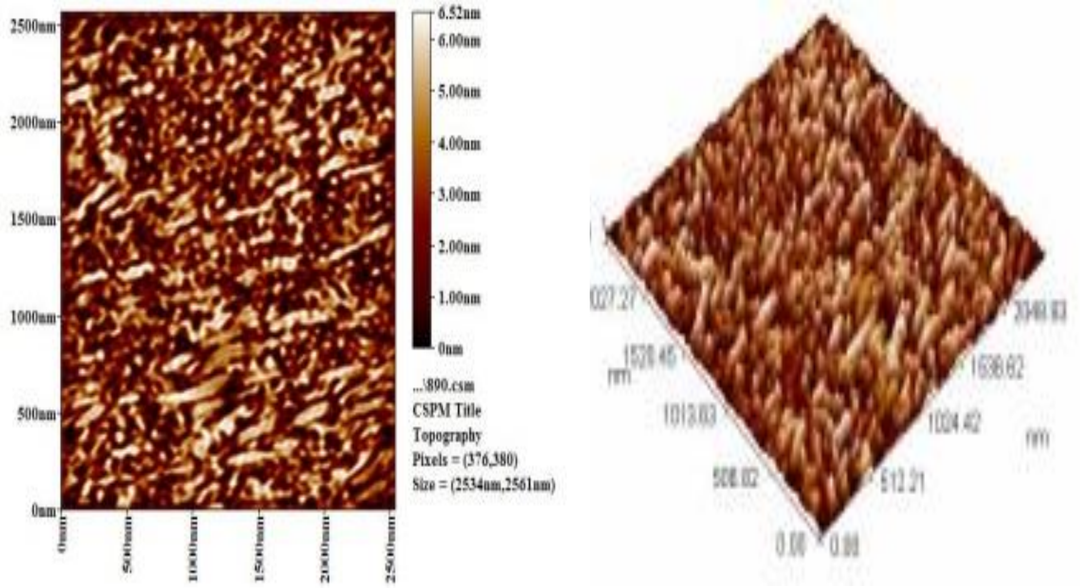


Figure (5): AFM images for PVA/ HCl sample

Table(1): AFM parameters of PVA/HCl

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	0.17	0.17	80.00	9.93	76.88	110.00	1.03	98.97
55.00	15.92	16.10	85.00	8.05	84.93	115.00	0.68	99.66
60.00	15.07	31.16	90.00	5.31	90.24	135.00	0.17	99.83
65.00	11.99	43.15	95.00	4.45	94.69	145.00	0.17	100.00
70.00	13.18	56.34	100.00	1.88	96.58			
75.00	10.62	66.95	105.00	1.37	97.95			

2.4.4 DSC result

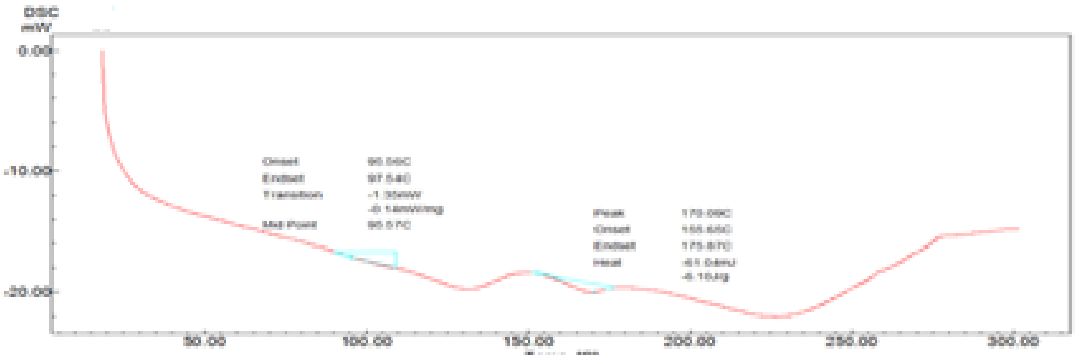


Figure (6) : DSC curve for pure PVA

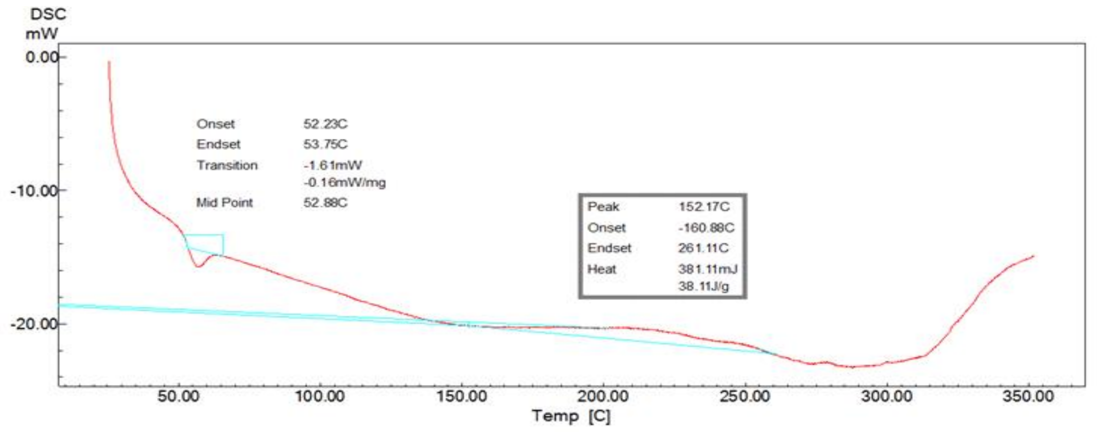


Figure (7): DSC curves for PVA/HCl

Figures (6) and (7) show the DCS analysis of pure PVA and (PVA/HCl) mixtures. The activation can be calculated as follows:

$$E_a = \Delta H^{\ddagger} + RT$$

Where :

E_a: activation energy (kJ mol^{-1}), $\Delta H^{\ddagger}$: activation enthalpy (kJ mol^{-1}),

RT: thermal energy (work); RT= P dV (kJ mol^{-1}).

According to molecular models (the activation energy for chain rupture is about 60 k Cal/mol (251 kJ mol^{-1}), so that at room temperature the value of the decisive factor for chain rupture as a thermal fluctuation process is about 101.

$$\therefore E_a = \Delta H^{\ddagger} + RT = RT\, D_f$$

Where:

R : the gas constant (0.0083 kJ K^{-1} mol^{-1})

T: the absolute temperature (K)

D_f : decisive factor E_a at R.T=251 kJ mol^{-1}

$$E_a = \Delta H^{\ddagger} + RT = 251$$

Since RT value small at room temperature which is equal to 2.47 kJ

mol^{-1} comparing with $\Delta H^{\ddagger}$:

$$\because\ \Delta H^{\ddagger} \gg RT$$

$$\therefore E_a = \Delta H^{\ddagger} = RT\, D_f$$

$$E_a = 0.0083 \text{ kJ K}^{-1} \text{ mol}^{-1} \ast 298.15$$

$$\text{K} \ast D_f = 251 \text{ kJ mol}^{-1}$$

$$D_f = 101.43$$

Each unit of $D_f = \frac{251}{101.43} = 2.475$ kJ mol^{-1}

1. Pure PVA

T_g of pure PVA= 95.57 ℃ (from fig 5)

$$E_a = RT\,D_f$$

$251 = 0.0083 * 368.57 * D_f \quad \rightarrow \quad D_f = 82.049$

$\Delta D_f = D_f$ at R.T$-$ D_f at 95.57 ℃

$= 101.43 - 82.049 = 19.38$

Addition E_a from different temperatures (25 to 95.57°C):

$= \Delta D_f *$ Each unit of $D_f = 19.38 * 2.475 = 47.718$ kJ mol^{-1}

E_a (at 95.57°C) $= 251 - 47.718 = 203$ kJ mol^{-1}

$\Delta T = 95.57 - 25 = 70.57$ ℃

$$1℃ = \frac{addition\ Ea}{\Delta T} = \frac{203}{70.57} = 2.8766 \text{ kJ mol}^{-1}$$

2- For PVA/HCl

The temperature of chain rupture falls to 53.75℃ due to addition HCl to the PVA

$\therefore T_g = 53.75$ ℃ (Figure 5)

$$E_a = RT\,D_f$$

$$251 = 0.0083 * 326.75 * D_f \quad \rightarrow \quad D_f = 92.55$$

$$\Delta T = 53.75 - 25 = 28.75 ℃$$

Addition E_a from different temperatures from 25 to 60.9 ℃ :

$= 28.75℃ * 0.679$ kJmol^{-1}℃ = 19.52125

Given energy by HCl addition = 47.718$-$ 19.52125

= 28.5907 kJ mol^{-1} (this given by HCl

E_a (at 53.75 °C) = 203-28.5907 = 174.4993 kJ mol^{-1}

Table (2): Effect of HCl on PVA at R.T& E_a (251 kJ mol^{-1}) with D_f = 101.43

Sample	T_g (°C)	D_f	E_a at T_g (kJ mol^{-1})	Addition E_a (kJ mol^{-1})
Pure PVA	95.57	82.049	203	47.718
PVA/HCl	53.75	92.55	174.4993	19.52152

Table (3): Expected destroyed secondary bond by HCl in PVA.

Sample	Given energy by addition pigment (kJ mol^{-1})	Secondary bond energy (kJ mol^{-1})	Expected type of destroyed bond
HCl	28.5907	0.08 – 40	(Van der Waals bonds) Dispersion (London) forces

4.2.5 The Absorbency

Using tea-bag method, the dried PVA/HCl powders were submmerged in water, and its swelling ratios (water absorbing capacities; WAC) was recorded over time until maximum swelling degree was reached according to the following equation.

$$\text{WAC} = (W_1 - W_o)/W_o$$

Where W_o: dry weight (g) and W_1 wet weight (g).

$$\text{WAC} = \frac{3.2-1}{1} \times 100\% = 220\% \left(\frac{g}{g}\right)$$

the absorbency under the load applied (AUL) was used by measuring the absorption capacity in (0.9% NaCl) saline solution under load 2.068 according to Equation.

$$\text{AUL} = (W_2 - W_1) / W_1$$

Where, W_2 and W_1 are weights of swollen and dry samples respectively.

$$\text{AUL} = \frac{1.24-1}{1} \times 100\% = 24\ \% \left(\frac{g}{g}\right)$$

2.5 Conclusion :

It seems that with copolymer formation from PVA a new structure formed with high ability to absorb water up to 220%, this is due to formation of large voids in the structure between PVA and PVC as many tests show that.

2.6 References

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