

# Preparation and characterization of some physical properties of new copolymers containing azo linked

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**Abstract** - A five new types of PVA copolymers containing azo groups were synthesized using Cold – Warm esterification of PVA with 4,4-Azo dibenzoic acid, which was synthesized by air oxidation of P-nitro benzoic acid. The structures of the synthesized compounds were identified by FT- IR spectroscopy. Copolymerization of PVA with 4,4-Azo dibenzoic acid was target to obtain new polymeric materials with original physical and chemical properties adaptable to specific uses. Swelling, crosslinking and mechanical testing studies will be conducted simultaneously. The azo polymers having high molecular weight range above  $72,000 \text{ g mol}^{-1}$  were soluble in most of the polar solvents like N,N-dimethyl formaldehyde, dimethylsulfoxide, and dichloromethane but they were all insoluble in xylene. The swelling behavior of these hydrogels was related to the degree of cross linking. DSC analysis showed good thermals by the range  $160.5 - 279.6^\circ\text{C}$  for five copolymers.

**Index Terms** - Esterification, polyvinyl alcohol 72000, 4,4-Azo dibenzoic acid, crosslinking, swelling behavior ,DSC, and tensile.

## 1 INTRODUCTION

Polyvinyl alcohol (often abbreviated as PVOH) is a water-soluble synthetic material used as an emulsifier and adhesive. PVA can be modified by reaction of pendant –OH groups with various reagents to form new polymers with novel surfactant properties (Greg, et al .2010). Linear PVA is synthesized from vinyl acetate and available with various molecular weights (Martins, et al, 2000). PVA have high hydrophilicity, good film-forming properties and outstanding physical and chemical stability, (PVA) is an excellent membrane material for preparation of hydrophilic ultra filtration (UF) and nano filtration membranes (yang, et.al. 2008). The tissue-like high water content and elastic properties make hydro gels advantageous for many biological applications, including contact lenses, controlled release matrices, and bio adhesives ( Peppas, et al, 1987 & Muhebach, 1997). Chemical modification is a powerful tool for obtaining polymers with new properties and therefore for increasing the scope of their applications (zhang, et al, 2005).

Azo compounds have a great biological activity as well as industrial importance because of their mutagenic and carcinogenic effects (Patai, 1975). They are capable of oxidizing many compounds bearing the functional groups R-N=N-R' (Azo-dyes), in which R and R' can be either aryl or alkyl groups. These compounds are widely used and discarded in worker collections. Additionally, azo-dyes can cause biological alteration (Houk, 1992. & Chung, 1992).

The purpose of this study was to prepare hydrogels membrane from (PVA) With 4,4-azodibenzoic acid. The physical properties of prepared polymers was studied.

## 2 Material Instrumental and Methods:

Poly (vinyl alcohol) with a molecular weight of 72000 g/mol (Fluka), and were used without purification. P-nitro benzoic acid and other solvents. Infrared spectra of the azo compounds and its copolymer were recorded on (shimadzu, FTIR.8400s) in the range  $(4000-400) \text{ cm}^{-1}$  using KBr pellets. Molar conductance of the copolymer was determined in ethanol ( $10^{-3}$ ) at room temperature using (Philips PW-Digital Conduct meter).

### 2.1 Synthesis of PVA- 4,4-azodibenzoic acid copolymers:

#### 2.1.1 Synthesis of 4,4-azodibenzoic acid:

Synthesis of 4,4-azodibenzoic acid was obtained by condensation of P-Nitro benzoic acid with itself under air oxidation, (Khalil, at el., 2007). As shown in scheme (1).

#### 2.1.2 synthesis of copolymers:

(10 gm, 0.159 mmol) of PVA was added In 250 ml of 2-necked round bottom flask containing magnetic bar and dissolve with 100ml of distill water fitted with thermometer. the mixture was stirred, heated at  $50^\circ\text{C}$  till a clear solution was obtained, few drops (2-3 drops) of Conc.  $\text{H}_2\text{SO}_4$  was added and the reaction mixture was stirred for 2hr., cool with ice water bath to  $10^\circ\text{C}$  for 30 min, then (2.16 gm, 0.008mmol) of 4,4-azodibenzoic acid was added and another (2-3 drops) of Conc.  $\text{H}_2\text{SO}_4$  was added. The reaction mixture was heated for another 2 hours at  $40-50^\circ\text{C}$ , Until light orange color of azo polymer was obtained. Then poured on a glass mould and left to dry slowly at room temperature in a dark place for 2 days. The dried sample was then washed with distilled water to remove the un reacted PVA materials and re-dried again in an oven at  $30^\circ\text{C}$  for 2 hours and stored in a dry and dark glass box. The experiment was repeated with 20%, 30%, 40% and 50%.of PVA and 4,4-azodibenzoic acid compound, as shown in table (1), scheme (1).

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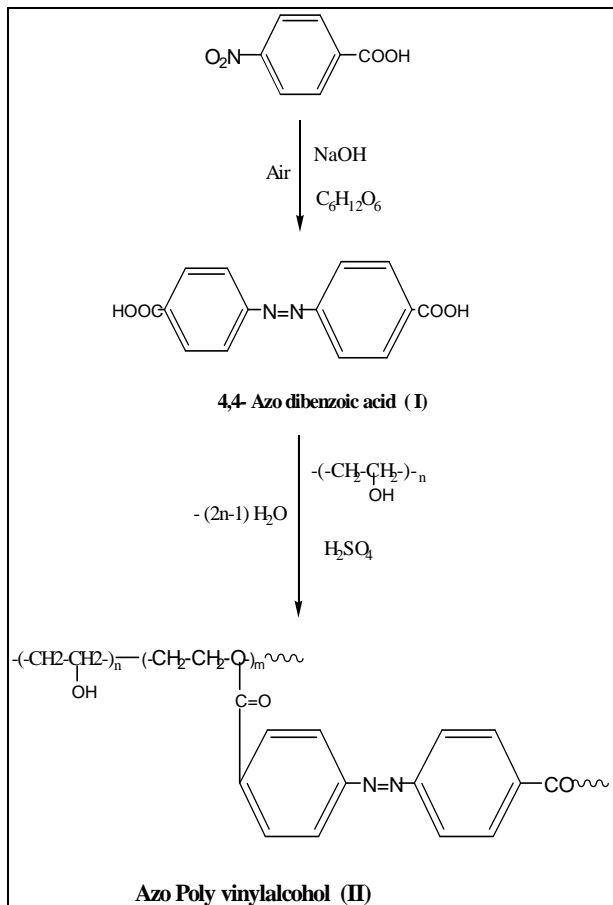
TABLE 1

**The percentage of polyvinyl alcohol reacts with 4, 4-Azodibenzoic aci**

**SCHEME 1**

Sample No.	PEG	4,4-Azodibenzoic acid	color
I	10%	2.16	Light orange
II	20%	4.32	Light Orange
III	30%	6.48	orange
IV	40%	8.64	Reddish orange
V	50%	10.80	Reddish orange

**Synthesis Of Copolymers (Azo poly vinyl alcohol)**



**2.3 DSC Analysis:**

Thermal behaviors of the modified PEG-AZO and its modified compounds with different percentage were studied using differential scanning calorimeter (DSC- 60 Shimadzu) to identify whether the modification leads to produce cross linked or/and grafted structures. Each 10 mg sample was weighed into an aluminum crimped pan which gave an air tight seal and the reference was empty pan. The instrument was calibrated using indium of known melting point and heat of fusion, and the scanning rate of 10 °C /min.

**2.4 Solubility:**

0.2 gm (M1) of each compound under investigation was dissolved in different solvents (see Table 2) at 25°C with continuous shaking for 12 hours and left to stand overnight. The solution was then filtrated through pre weighed filter paper No.41, and then the filter paper was re-weighed after a complete drying. The difference in weight gives the mass of the dissolved sample (M2). The percentage of solubility (S %) can be calculate from the following relation (Finch, 1973) :

$$S \% = M2 / M1 \times 100 \dots\dots\dots (1)$$

**2.5 Copolymer Swelling:**

Swelling of copolymer was carried out in water at 25°C using film samples with an average mass in the range of 0.17-0.130gm. The sample mass –to – water volume ratio was 1-30. The samples were removed from water at the predetermined time intervals, wiped gently with filter paper and weighed using an analytical balance. The sample mass change resulting from the water uptake expressed in percent was calculated according to the formula:

$$\Delta m = (m_t - m_0) / m_0 * 100 \dots\dots (2)$$

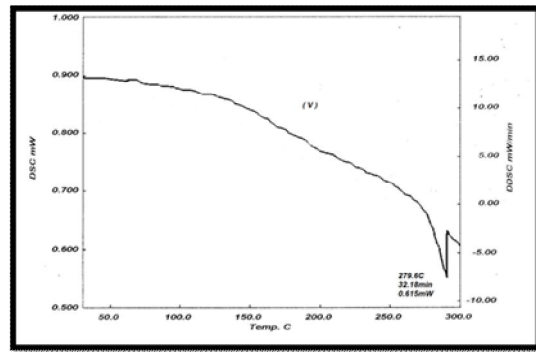
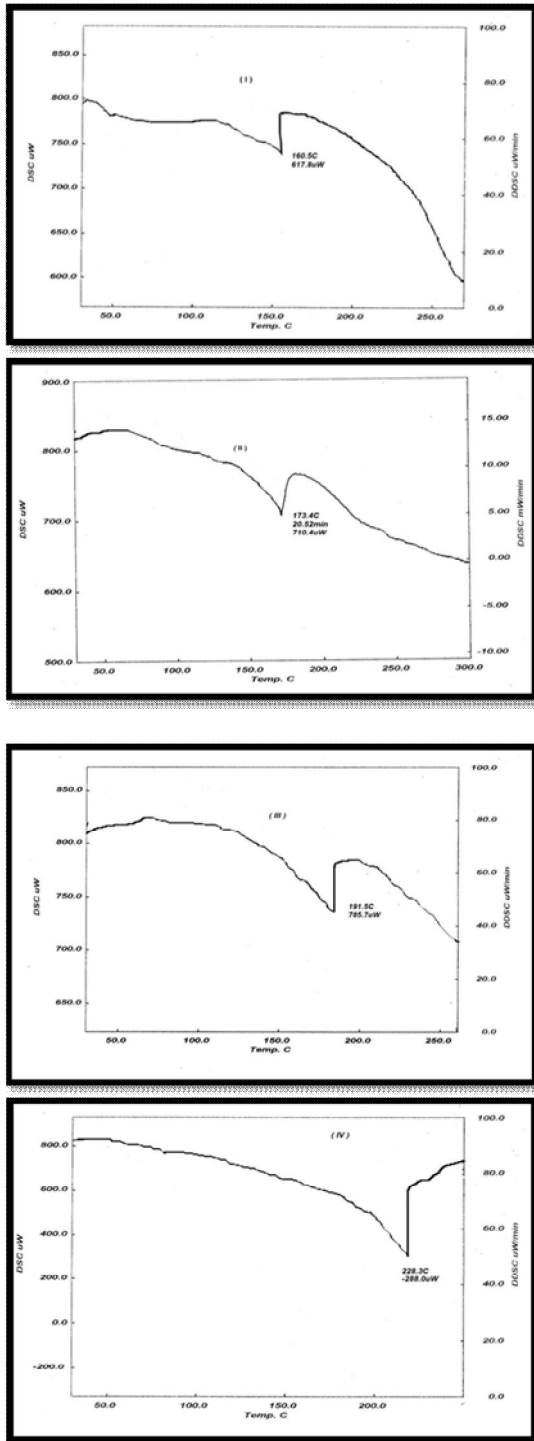
Where m<sub>0</sub> and m<sub>t</sub> are the masses of dry and wet samples, respectively. (Katazyna, et al., 2002. & Jatuphorn, et al., 2007).

**3 Result and discuses :**

The structure of the polymer was confirmed by spectral analysis (FT-IR) which show a stretching absorption of –OH at (3456-2890cm<sup>-1</sup>), (C=O) =1730cm<sup>-1</sup>, azo group (N=N) = 1590cm<sup>-1</sup>,and C-O-C single of esteric group at 1095cm<sup>-1</sup>. The polymer Azo - PVA is composed of pendant azobenzene groups through ester linkages.

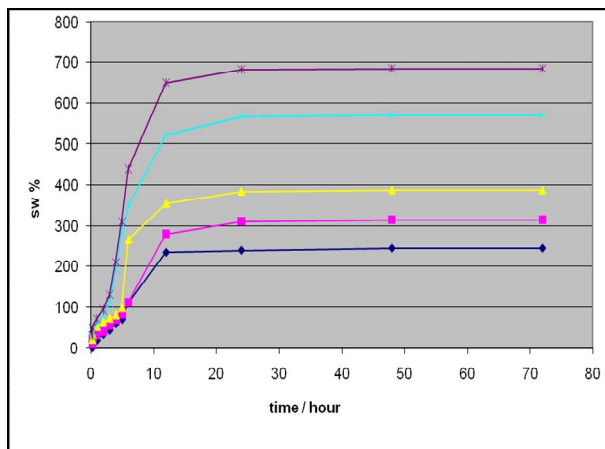
Differential scanning calorimetry (DSC) was used to study the thermal properties and kinetic parameters involved in the cross linking processes, we find that the azo poly vinyl alcohol is good thermal properties specially when mixed the 50% of PVA with 50% of 4,4- azo dibenzoic acid by range (160.5 - 279.6°C) and the result for all copolymers obtained in table (2). fig.(1).

**Fig. (1): DSC Curves of Azopolymers (I), (II), (III), (IV) and (V) of 10°C / min.**



The experiments of swelling were carried out at room temperature (25°C). The samples were weighed at different time intervals until the hydrated weight was constant. Absorbency was calculated as grams of water per gram of dry polymer. In the second procedure a polymer sample that had been weighed accurately was immersed in distilled water at room temperature and left until equilibrium was attained table(2), fig (2). All copolymers obtained in the study swelled in distilled water. The amount of absorbed water was dependent on the material composition. The most hydrophobic polymers based on poly vinyl alcohol and azo dibenzoic acid absorbed ( 223-678% ).The same increase of the PVA hydro gels obtained by freezing-thawing processes at -20°C/20°C has been evidenced by other researchers, corresponding to the relative swelling decrease ( Pat,achial, 2009).

**Fig. 2. Swelling behaviors as a function of time for copolymers (I), (II), (III), (IV), and (V) in 25°C.**



polymers was studied by differential scanning calorimetry (DSC) experiments, The polymers showed initial crosslinking temperature in the range of 160–279°C.

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The synthesized AZO-PVA derivatives were soluble in organic solvents such as DMF, DMSO, but they were all week soluble in THF and pyridine and insoluble in ethanol...etc, table (3). While the modified PVA as different percentage were observed lower solubility than the pure PVA at the same conditions and that could be copolymer leads to decrease the number of inter molecules hydrogen bonds of the copolymers.

Tensile strength is important for a material that is going to be stretched or under tension, therefore, fiber have need good tensile strength to improve the tensile of a polymer sample. We take the sample which is stretched by a machine such as an instron, then using Zewigle machine and continue to increase the amount of force, on the sample until it breaks. The stress needed to break the sample represents the tensile strength of the material. Since tensile stress is the force placed on the sample divided by the cross-sectional area of the sample, tensile stress and tensile strength as well as both measured I unit of fore divided by units of area and it is usually N/m<sup>2</sup> (Jang, 1994). The reinforcing order can be written as follows :-

Azo polyvinylalcohol (V) > Azo polyvinylalcohol (IV) > Azo polyvinylalcohol (III) > Azo polyvinylalcohol (II) > Azo polyvinylalcohol (I) . See table (2).

**TABLE 2**  
 Some properties of azo poly vinyl alcohol.

Sample No.	Tensile strength MPa	DSC	Swelling degree %
I	2.68	160.5	244
II	17.50	173.4	315
III	26.45	191.5	388
VI	50.13	228.3	570
V	90.6	279.6	685

**4 CONCLUSION**

PVA polymer was modified via esterfaction of some – OH groups with 4,4- di Azo Benzoic Acid group, to obtain half esters with carboxylic acid groups, physical proparteis of PVA-Azo copolymer membrane was studied and. Water absorption was determined gravimetrically as a function of time at room temperature. The thermal behavior of the

**TABLE 3**

**Solubility of copolymers in different solvents at 25°C.**

Samp le No.	DMSO	DMF	DMAC	pyridin e	TH F	xylene	hexanol	Chloroform	Aceton e	Toluen e	benzen e
I	S	S	S	W	W	N.S	N.S	N.S	N.S	N.S	N.S
II	S	S	S	W	W	N.S	N.S	N.S	N.S	N.S	N.S
III	S	S	S	W	W	N.S	N.S	N.S	N.S	N.S	N.S
IV	w	w	w	W	W	N.S	N.S	N.S	N.S	N.S	N.S
V	w	w	w	W	W	N.S	N.S	N.S	N.S	N.S	N.S

-V.S= very strong when the percentage reached >80%, S= strong when reached 70%, W= slightly soluble weak when reached 50% and N.S = not soluble when less than 50%.

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