

## Synthesis and characterization of some modified polyvinyl alcohol

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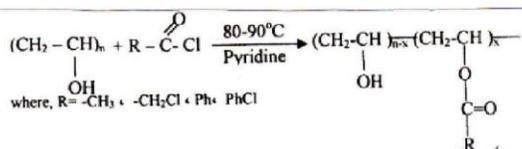
### Abstract

Some esters were prepared from reaction of different molecular weight of PVA with some acid chloride (prepared by reaction of acid with thionyl chloride or phosphorous pentachloride) in the presence of pyridine. The thermal and rheological properties were studied. The increasing of bulky groups decreasing stability of the thermal and rheological properties.

### Introduction

The modified polymers are formed from through a chemical reaction of the functional groups on the polymers chains. The modified polymers have a different physical, chemical, mechanical and thermal properties from the original polymers, and this will increase the technological application<sup>(1-7)</sup>. The chemistry of PVA is largely concerned with ester formation<sup>(7)</sup>. Polymer derived from polyvinyl alcohol can be expressed by the general equation.

The modified (PVA) has been studied intensively as a membrane<sup>(8)</sup>, such as reverse osmotic<sup>(9-14)</sup> dialysis<sup>(15,16)</sup> release of water soluble drugs<sup>(17-20)</sup>. The effect pH and the ionic strength on the swelling behavior of copolymers containing PVA hydrogel are described by several authors<sup>(21)</sup>. In this work we reported the reaction of PVA of different molecular weight with different acid chlorides which described by the above general equation. The modified (PVA) polymers studied thermally and rheologically.



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**Experimental**

**(I) Material**

The PVA used have a molecular weights of 20000, 72000, 113000, and were supplied from Merck CO.

**(II) Instruments**

- i. A Daven port melt flow rate indexer model 3180 used in the rheological measurements.
- ii. Du pont thermoanalyser model 990 with DSC unit (910) connected to microprocessor data was used in this study.

**(III) Synthesis of modified polymers**

The Acid chloride have been prepared from the reaction of acid with thionyl chloride<sup>(22)</sup> or with phosphorous pentachloide<sup>(32)</sup>. 1g of PVA have been dissolved in 100 ml of dimethylformamide (DMF). 10 ml of pyridine have been added then the acid chloide added drope by drope, heating cotinued at 80-90°C for 3-4 hours, the mixture was cooled and added to a 350 ml of distilled water, precipitate was formed , washed with 5% of hydrochloric acid and then redissolved in dioxane and repercipitated with distilled water. The prepared polymers were

The polymer	a b c
1- Poly vinyl acetate	IV, V, VI
2- Poly vinyl benzoat	VII, VIII, IX
3- Poly vinyl chloro acetat	X, XI, XIII
4- Poly vinyl chloro benzoat	XIII

Where (a) m.w molecular weight of 20000, (b) m.w molecular weight of 72000 (C) m.w molecular weight of 113000 (IV).

**(IV) Characterization of Modified polymers.**

The prepared polymers were characterized By IR Spectroscopy. The Maine functional groups are tabulated in Table (1).

The CHN analysis measurement were used to determine the molecular weight depending on the percent % of the reaction and the result shown in Table (2)

**Results and Discussion**

**(I) Thermal characterization<sup>(24, 25)</sup>**

The thermal characterization of the modified polymer were investigated on a Dupont thermal analyses on a heating a rate of 10°C/min in the presence of nitrogen. Typical TG thermogram are shown in Figure (1,2) the results are shown in Table (3). Table (3) showed that the stability of the modified polymers decreases with increasing the bulk of the groups. This result confirmed by R=CH<sub>3</sub> group which showed a high stability which decreases in order -ph,- CH<sub>2</sub>Cl and -phCl respectively.

Tm and Tg in Table (4) were calculated by DSC thermogram and the result approved the same above relation of the stability with bulky groups.

**(II) Rheometric characterization<sup>(25)</sup>**

The melt flowrate measurement (MFR) were carried out according to ASTM D-1238.

The measurement of modified polymer at different temperatures (190-200)°C indicates a linear relation between log MFR and the applied load which show in Fig (5). The energy input decreases as the bulky groups in ereases as shown in Table(3). The total energy input in the melting process was determined graphically from arhenius formula

$$\text{Lin MFR} = \text{LinA} - \text{ERT}$$

Where:

E= energy input of polymer melt

T= absolute temperature

R= gas constant frequency

A= frequency

Table (1) IR bands for some group in the modification polymers

Bands	group	Wave Number $cm^{-1}$
$\nu$ (O-H)	-OH	3250-3560
$\nu$ (C-H)	C-H	300-3100
$\nu$ (C-H)	C-H	2850-2950
$\nu$ C=C ester	C=C	1590-1600
$\nu$ C=C	C=O	1715-1750
$\delta$ (C-H)	C-H	1405-1430
$\nu$ (C-O) ester	C-O	1030-1130
$\nu$ (C-O)	C-O	1130-1170
$\delta$ (O-H)	O-H	1230-1405
$\nu$ (Ar-Cl)	Ar-Cl	1025
$\nu$ (R-Cl)	R-Cl	750

Table [2] C. H. analysis of polymers.

Sample	Calculated		measurements	
	C%	H%	C%	H%
IV	55.428	07.6184	54.31	07.65
V	55.4188	07.656	54.365	08.68
VI	55.3355	07.613	53.0215	07.6977
(VII)	42.618	05.0846	41.82	05.34
VIII	42.909	05.1822	41.97	05.1426
(IX)	44.243	05.6202	43.84	05.5203
X	68.75	06.125	67.32	06.134
XI	68.405	06.330	67.821	06.231
XII	67.717	06.447	63.58	06.43
XIII	58.518	04.13	58.92618	03.455

Table [3] Thermal stability parameter of some polymers and prepared modified polymers

NO. Sample	Rate of decompositions %/min	Activation energy	% weight loss at temp	Decomposition end	Start Decomposition tem
I		43.95			
II	1.43		304	374	282
(III)	0.3083	46.2	317	319	263
(IV)	0.441	9.09	300	392	246
(V)	0.3915	21.85	316.6	425	273
(VI)	0.7512	26.22	387	425	325
VII	0.325	14.01	237	337	112.4
VIII	0.714		197	339	162.5
X	0.1485	14.39	216.6	279.1	125
(XI)	0.216		246	282	200
(XII)	2.54		240.5	250	212

Table (4)  $T_g$  and  $T_m$  to some standard polymers and modified

$T_g$	$T_m$	Sample
94	176	I
96	194	II
102	202	III
86	-	V
96	-	VI
88	154	X

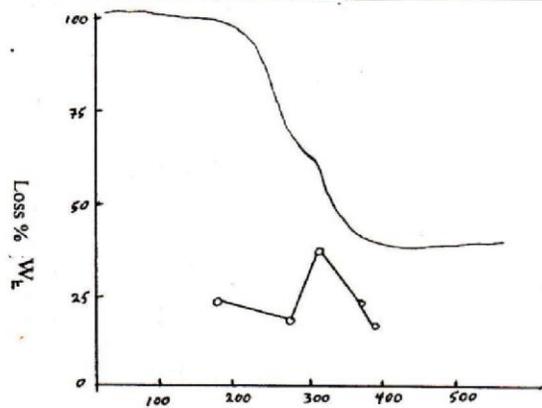


Fig (1) T.G.A of polymer (IV)

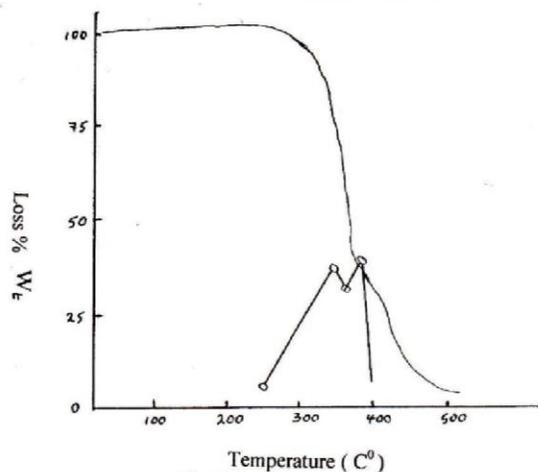


Fig (2) T.G.A of polymer (VI)

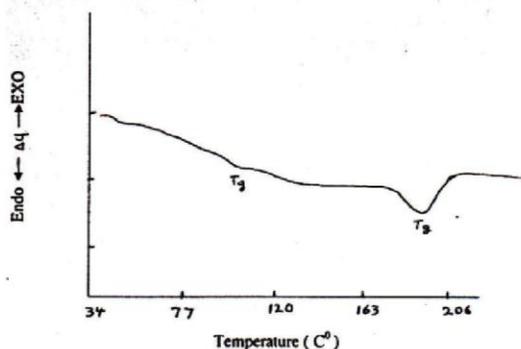


Fig (3) D.S.C of polymer (II)

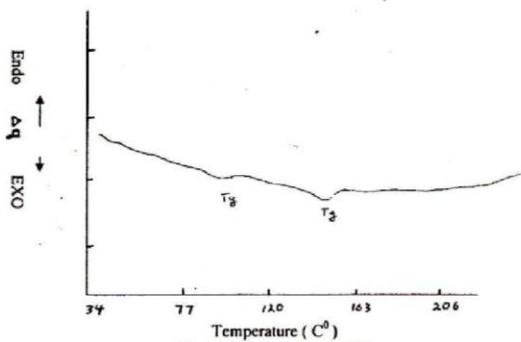


Fig (4) D.S.C of polymer (X)

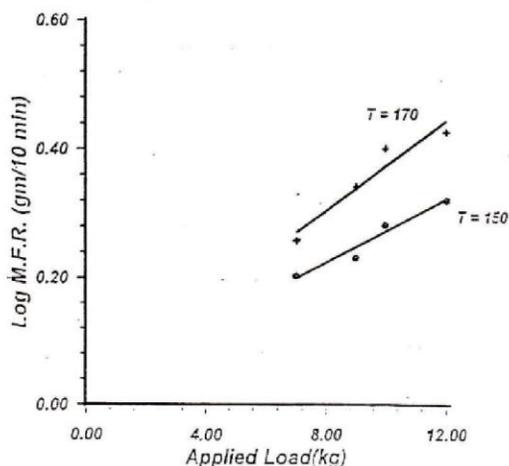


Fig (5) Effect of Applied load on M.F.R of polymer (XI)

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## تحضير ودراسة بعض خواص بولي فاينيل الكحول المحور

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### الخلاصة

تم تحضير بعض الاسترات من تفاعل PVA مع بعض كلوريدات الحوامض الكربوكسيلية باستخدام الثيونيل كلوريد وخامس كلوريد الفسفور بوجود البريدين، لاوزان وتمت دراستها من خلال الثبات الحراري DSC, TGA والخواص الانسيابية MFR. إن اختلاف النتائج يمكن أن يرجع إلى وجود بعض المجموعات المعاقة حيث انه كلما زاد حجم المجموعة قل الثبات الحراري لها و الخواص الانسيابية.