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Study The Effect Verifies of the Number of Moles of Acrylic Acid Monomer On Swelling of the New Prepared Modified Co-Polymer.

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ABSTRACT

In this work, modified polyester resin was prepared, by using pentarethrytol as material containing the four alcoholic groups, and reacted with phthalic anhydride as a first step, then added to the modified resin, which product, maleic anhydride as a second step. The product resin was identified by IR and 1HNMR spectroscopy. The acrylic acid monomer was added to the modified resin and in different number of moles (1.0, 1.5 & 2.0 mole). The hydroxyl content ratio was calculated, which has showed an increase the number of moles of the acrylic acid monomer due to increases the hydroxyl content ratio of the product copolymer thus lead to increase the swelling modified resin. The swelling measurement of the modified co-polymer by using three types of solvents water, ethyl alcohol and toluene in five different temperatures 298, 303, 308, 313 and 318 ^{o}K. The results showed increases the number moles of acrylic acid monomer, Leads to increase expansion, swelling ratio and volume fraction of the solvent of content in the sample, and decreased volume fraction of the specimen, the results also showed that the temperature significant impact on the swelling, as it is increasing the temperature, leads to increases of each of the solvent content in the sample, expansion ratio, swelling ratio and volume fraction of the solvent and decreased volume fraction of the specimen.

Keywords: Polyester resin, modified co-polymer, Acrylic co-polymer, Condensation polymerization, interpenetrating polymer network, Swelling, Swelling of co-polymer

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INTRODUCTION

The process of copolymerization is the joint polymerization of two or more monomer species. High–molecular mass compounds obtained by copolymerization are called copolymers [1]. The molecular chain of a copolymer is composed of different units, in accordance with the number of initial monomers [2]. If the reactants of a poly condensation have several different monomers, the result will be a copolymer [3]. The reaction of co-poly condensation has acquired great technical importance in recent years and is now widely used for the synthesis of various mixed polyesters and polyamides (e.g. containing ester and amide bonds simultaneously) and other copolymers. For instance, co-polycondensation of hexamethylenediamine, adipic acid and terephthalic acid [4]. Polymers may be classified as hydrophobic or hydrophilic, according to whether or not they dissolve or swell in water. The polymers which contain hydrophobic groups (e.g. C_2H_5) are water insoluble. The polymers which contain a hydrophilic group (e.g. OH), are water soluble, in the case of linear polymers or swell able in the case of cross linked polymers. In other words, the hydrogel can be defined as a polymeric material which will swell in solvent and it contains a significant fraction of water (usually more than 20%) within its structure. The term xerogel is given to the polymer network alone (dry state) **[5]**, thus,

Xerogel + Water → Hydrogel

Hydrogels, are some coherent system rich in water; they are made up of two principal components, a constant solid component consisting of a polymer network, and a variable liquid component, either water or an aqueous solution. The aqueous component can undergo exchange with the environment by diffusion or evaporation [6]. For getting materials combining biocompatibility with a good mechanical strength, two methods are used [7]. Copolymerization of hydrophilic monomers with hydrophobic monomers or with cross-linking agent or grafting of hydrophilic monomers on stronger polymer supports [8].

The swelling phenomena can be explained thermodynamically in terms of the chemical potential of water [9]. Before the equilibrium swelling is achieved, the chemical potential outside (water) the gel μ^0_1 is higher than that of (water) inside μ_1. Thus the water is absorbed by the gel. In other words, the water is imbibed osmotically into the gel network [10].

The effect of temperature on the equilibrium swelling of a hydrogel varies according to the nature of the xerogel [11]. The equilibrium water content decreases with increasing temperature, an exothermic process, while the increase of equilibrium water content with increasing temperature is an endothermic [12]. The effect of temperature on the equilibrium swelling is different from one solvent to another, depending on The interactions between the polymeric materials and the organic liquid [11]**.**

MATERIAL AND METHODS

Experimental

Preparation of modified polyester resin [13, 14]

In a 500 ml three-necked round bottom flask, (2.0 mole, 296 gm) of phthalic anhydride, and (1.0 mole, 136gm) of Pentaerythritol, were mixed together, this flask was equipped with a thermometer and a mechanical stirrer. The mixture warmed carefully with an electric heating mantle to 140 ^oC until a clear liquor is formed and then about 25 ml of Xylene was added carefully to the reaction flask, in the form of batch (two drops in each batch), Withdrawal of water formed in the esterification process, and the flask was gently heated. Heating was stopped after 40 min. at 160 ^oC, until no more water came off. The flask was allowed to cool to 50 ^oC. (0.5 mole, 49 gm) of Maleic anhydride was added carefully to the reaction flask, and the flask was gently rise heated, after melting material, added the drops of Xylene, until no more water came off 160 ^oC, after 2hr. The flask was allowed to cool to 70 ^oC, and (1.36×10^{-3} mole, 0.147gm) of Hydroquinone was added to the reaction flask, with stirred by mechanical stirrer, and (1.0, 1.5 and 2.0 mole) about (72, 108 and 144 gm), respectively of Acrylic acid monomer, was added to the modified polyester resin and stirred by mechanical stirrer, until a pourable syrup was formed. Figure (1), represents the stage-1 of the preparation of the modified resin and Figure (2), represents the stage-2 of the preparation of the modified resin. The negative test of $NaHCO_3$ solution proves that the prepared modified polyester resins don't contain any unreacted anhydride. Table (1), represents the physical properties of modified polyester resin.

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Table 1: Physical properties of the modified resins after addition of monomer

Physical properties	Value
Molecular Weight ($\overline{Mn}$)	Around 2100 gm/mole
Solid content	61 %
Viscosity	23 poise
Gel time	15-20 min at 25 °C
Acid Value	26
Density	1.5 (gm/cm3)

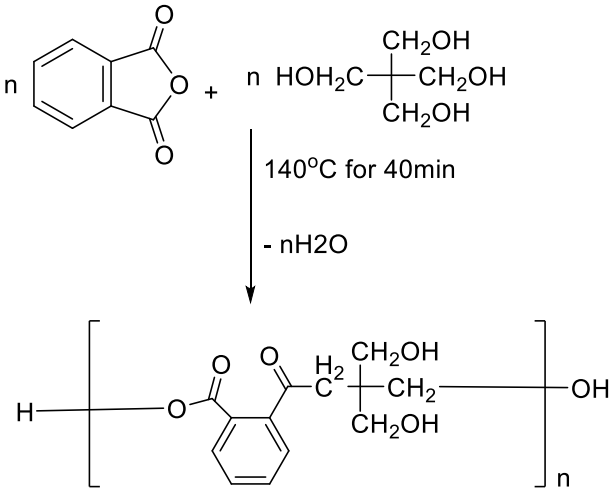

Figure 1: The stage-1 of the preparation of the modified resin.

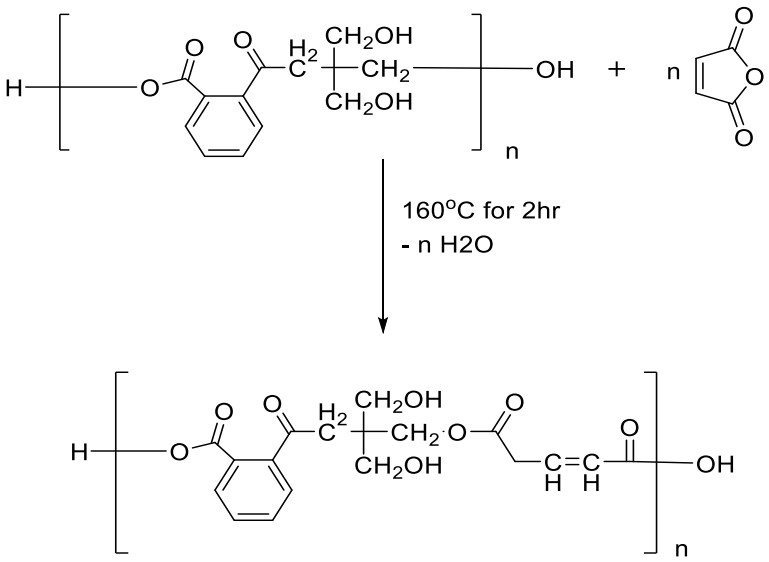

Figure 2: The stage-2 of the preparation of the modified resin.

Preparation of polymeric specimens

The specimens of polymeric material containing different number of moles of the acrylic acid monomer were prepared by using Methyl ethyl ketone peroxide (MEKP) as a hardener and cutting as a disc in dimensions (thickness = 3mm & diameter = 10mm) and the weighted of the xerogel discs was exactly 0.5 gm of all specimens were used in the swelling study.

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Swelling

The known weight and diameter of dried discs were put in sample vials. The swelling time was counted when the solvent was added into the sample vials. The diameter of the hydrogel and xerogel discs, were measured with calipers (Traveling Microscope Instrument) [10, 11]. The thickness of the hydrogel and xerogel discs was measured with a micrometer. The solvent contents of the hydrogels, were calculated according to the following equations [15].

$$\text{Solvent \%} = (\text{Wt. of hydrogel} - \text{Wt. of xerogel} / \text{Wt. of hydrogel}) \times 100$$

The extension ratios (ER) were calculated according to:

$$\text{ER \%} = d / d_0$$

Where, d and d_0 are respectively diameters of hydrogel and xerogel.

The swelling ratios (q) were calculated according to:

$$q \% = (ER)^3$$

The swelling of the discs was carried out at five different temperatures, (298, 303, 308, 313 and 318 k), by using three different solvents (Water, Ethanol and Toluene) in five different temperatures.

Hydroxyl Group Analysis [16, 17]

The hydroxyl values were evaluated according to ASTM: D-2849 (method A), the percentage of hydroxyl content in the prepared modified resin after addition different moles of Acrylic acid**.** The procedures commonly used for the determination of the hydroxyl group in alcohols include acetylation and phthalation.

RESUITS AND DISCUSSION

Preparation of modified polyester resin

The FT–IR, spectrum of the modified resin, Figure (3), showed the appearance of a strong broad band at about 3423 cm^{-1} for stretching alcoholic (-OH) with stretching (H–bond), and also showed a weak band at about 2902 cm^{-1} due to the -OH for carboxylic acid, the C-H sp^3 and sp^2 hybridization absorption at about 2544 cm^{-1}, 2654 cm^{-1} respectively, and the spectrum also showed a strong band at about1726 cm^{-1} assigned to a stretching band C=O for ester group. The spectrum appearance a weak sharp bands at about 1597 cm^{-1}, 1581 cm^{-1} due to C=C for conjugated system of benzene ring and also showed a bands at about 1284 – 1259 cm^{-1} assigned to C-O absorption band [18].

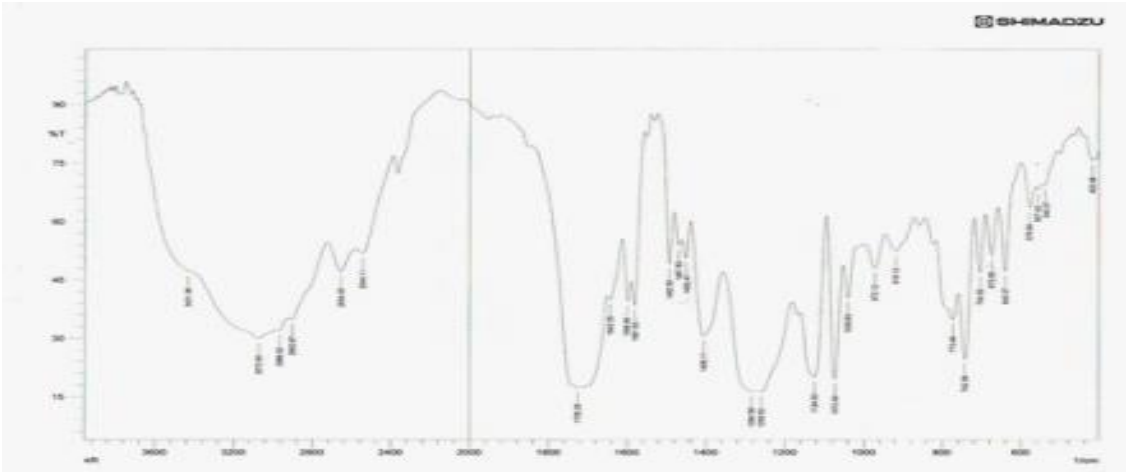

Figure 3: The FT-IR spectrum of the modified resin.

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Figure (4), showed the spectrum of 1HNMR, which explain the singlet signal at 13.24 ppm characteristic of proton in carboxylic acid group, furthermore the multiples in the region 7.53- 8.10 ppm back to all protons in aromatic ring, the signals at 6.27-6. 46 ppm for four protons of methylene in the structure of polymer, the multiples at 4.24- 4.50 ppm of methyl protons, but the triplet signal in 3.44- 3.62 ppm due to the proton of aliphatic alcohol so this spectrum was confirmed the structure of our target polymer [19].

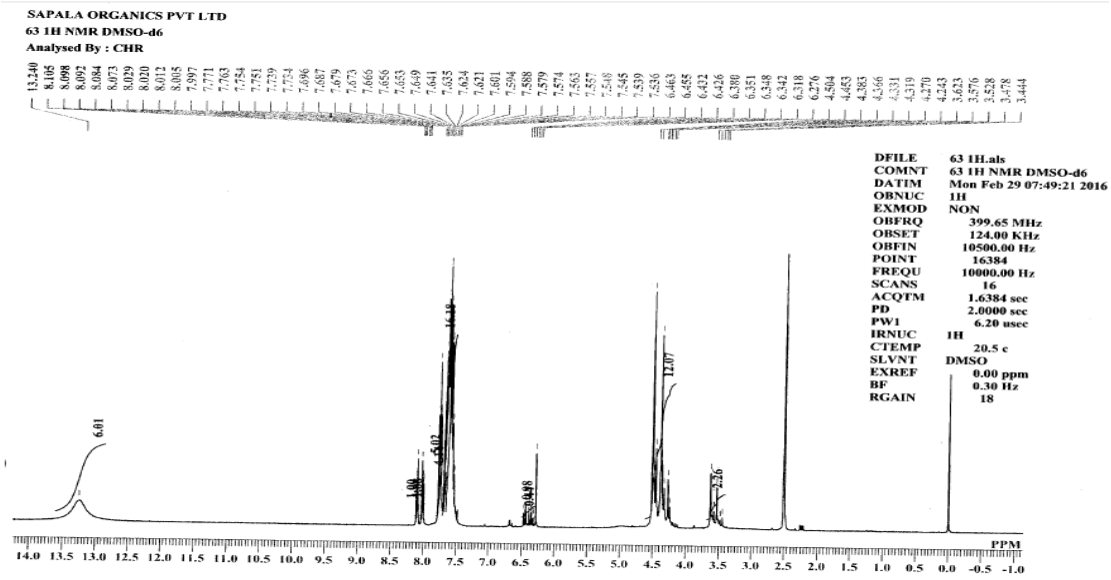

Figure 4: The 1HMNR spectrum of the modified resin.

Hydroxyl Group Analysis

The results obtained from these test indicate that, increases of %OH with increasing number of moles of the Acrylic acid monomer, as result to increase of the cross linked density between the copolymer chains, causing increasing the hydrophilic groups to increasing the swelling in the sample in solvents. Table (2), showed the percentage of hydroxyl content.

Table 2: The percentage of hydroxyl content

Types of Resin	Volume of NaOH (ml)	% OH
Modified resin (M.r)	30.1	47.835
(M.r) with 1.0 mole	37.4	61.004
(M.r) with 1.5 mole	42.7	75.320
(M.r) with 2.0 mole	56.3	89.103

Measured of swelling

The swelling curves of modified resin showed a plot of water, ethanol and toluene content for different compositions against swelling time (min.). The initial swelling rate was medium; the maximum being reached within the first few hours of the swelling. The shape of the swelling curves indicated that water–soluble molecules were being released from the xerogel upon swelling. The thicker discs required a longer time to attain maximum equilibrium [20].

A plot of solvent content versus time showed hydration curves of modified resin for three different numbers of moles from acrylic acid compositions ranging from 1.0, 1.5 and 2.0 mole, against swelling time (Min.) at different temperatures, as shown in Tables (3) to (8) and Figures (5) to (13) respectively.

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Table 3: Water Content (%) of modified resin with different number of moles of with acrylic acid monomer at five different temperatures

Time (min.)	Water content %			Temperature (°K)
	No. of moles of acrylic acids			
	1.0 mole	1.5 mole	2.0 mole	
60	1.9	2.85	3.89	298
	2.98	4.547	4.25	303
	4.49	5.983	6.876	308
	10.22	12.39	16.12	313
	14.24	14.95	19.3	318
120	6.68	4.87	8.655	298
	8.557	6.745	12.05	303
	10.4	8.6	14.88	308
	13.98	15.07	23.01	313
	16.44	17.03	25.12	318
180	10.4	10.43	15.82	298
	11.23	12.793	18.23	303
	14.33	15.7	19.41	308
	15.68	17.6	24.2	313
	17.09	18.51	27.65	318
240	10.65	14.5	19.73	298
	14.75	16.09	20.2	303
	16.6	18.84	22.52	308
	18.01	19.67	24.7	313
	18.7	22.53	31.46	318
300	13.87	18.78	21.61	298
	15.48	19.42	22.85	303
	17.98	21.63	25.13	308
	21.2	23.58	27.51	313
	21.4	24.8	32.26	318

Table 4: Ethanol Content (%) of modified resin with different number of moles of with acrylic acid monomer at five different temperatures

Time (Min.)	Ethanol content %			Temperature (°K)
	No. of moles of acrylic acids			
	1.0 mole	1.5 mole	2.0 mole	
60	16.48	16.55	16.9	298
	22.2	25.5	28.8	303
	25.743	30.65	37.1	308
	28.15	33.08	38.58	313
	30.98	36.99	42.3	318
120	17.58	18.42	24.5	298
	23.85	28.5	31.3	303
	26.876	33.39	38.15	308
	28.22	34.73	39	313
	31.39	37.8	42.5	318
180	19.5	20.45	30.3	298
	25.94	31.1	32.7	303
	29.18	34.01	38.4	308
	30.11	36.72	39.8	313
	34.05	38.65	43.2	318
240	25.12	25.82	31.6	298
	27.77	32.68	35.12	303
	30.47	36.53	38.6	308
	34.8	37.73	41	313
	37.08	39.89	43.8	318
	26.36	29.78	35.8	298
	27.96	34.79	37.432	303

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300	33.52	37.06	39.88	308
	36.6	38.52	41.96	313
	37.15	41.36	44.06	318

Table 5: Ethanol Content (%) of modified resin with different number of moles of with acrylic acid monomer at five different temperatures

Time (Min.)	Toluene content %			Temperature (°K)
	No. of moles of acrylic acids			
	1.0 mole	1.5 mole	2.0 mole	
60	1.01	1.49	1.98	298
	1.5	2.1	2.17	303
	2.654	3.04	5.26	308
	5.44	6.5	8.73	313
	7.6	8.02	10.38	318
120	2.27	4.26	6.79	298
	3.24	6.54	8.28	303
	4.512	7.85	9.75	308
	6.26	8.81	11.15	313
	8.6	10.44	13.27	318
180	6.945	11.64	13.36	298
	8.165	12.9	15.45	303
	9.3	13.67	17.17	308
	10.32	14.35	17.66	313
	13.7	16.07	18.97	318
240	8.98	13.8	15.75	298
	10.5	14.15	17.18	303
	12.3	15.47	17.76	308
	14.38	16.65	18.88	313
	15.72	17.64	19.8	318
300	11.53	14.29	17.11	298
	13.36	15.92	18.48	303
	15.87	18.73	19.79	308
	18.28	20.5	22.8	313
	19.566	21.26	24.1	318

Table 6: Parameters measured for the modified resin with different moles of the acrylic acid monomer in water at five different temperatures

Parameters / No. moles	Swelling Ratio (q)	Extension Ratio (ER)	Volume Fraction (Φ_2)	Volume Fraction (Φ_1)	Temperature (°K)
1.0 mole	1.0508	1.016	0.9516	0.0483	298
	1.1033	1.033	0.9063	0.0936	303
	1.12	1.04	0.8890	0.1109	308
	1.2079	1.065	0.827	0.1721	313
	1.2365	1.0733	0.8087	0.19126	318
1.5 Mole	1.103	1.033	0.9066	0.0933	298
	1.119	1.038	0.8936	0.1063	303
	1.1302	1.042	0.8847	0.1152	308
	1.219	1.068	0.8203	0.1796	313
	1.277	1.085	0.7830	0.2169	318
2.0 mole	1.1195	1.038	0.893	0.1067	298
	1.1302	1.042	0.8847	0.1152	303
	1.1412	1.045	0.8764	0.1235	308
	1.271	1.083	0.786	0.2132	313
	1.331	1.1	0.751	0.248	318

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Table 7: Parameters measured for the modified resin with different moles of the acrylic acid monomer in ethanol at five different temperatures

Parameters / No. moles	Swelling Ratio (q)	Extension Ratio (ER)	Volume Fraction (Φ_2)	Volume Fraction (Φ_1)	Temperature (^oK)
1.0 mole	1.27	1.083	0.787	0.212	298
	1.331	1.1	0.7513	0.249	303
	1.443	1.13	0.693	0.307	308
	1.561	1.16	0.667	0.333	313
	1.772	1.121	0.564	0.436	318
1.5 Mole	1.306	1.093	0.765	0.234	298
	1.4	1.12	0.714	0.286	303
	1.521	1.15	0.657	0.343	308
	1.643	1.18	0.609	0.391	313
	1.815	1.22	0.555	0.446	318
2.0 mole	1.4	1.12	0.714	0.285	298
	1.587	1.16	0.63	0.369	303
	1.728	1.2	0.579	0.421	308
	1.801	1.216	0.555	0.445	313
	1.876	1.233	0.533	0.467	318

Table 8: Parameters measured for the modified resin with different moles of the acrylic acid monomer in toluene at five different temperatures

Parameters / No. moles	Swelling Ratio (q)	Extension Ratio (ER)	Volume Fraction (Φ_2)	Volume Fraction (Φ_1)	Temperature (^oK)
1.0 mole	1.0252	1.0084	0.975	0.0246	298
	1.05	1.0167	0.952	0.0476	303
	1.061	1.02	0.943	0.0575	308
	1.1034	1.033	0.906	0.0937	313
	1.1195	1.038	0.893	0.1067	318
1.5 Mole	1.05	1.01667	0.952	0.0476	298
	1.061	1.02	0.943	0.0575	303
	1.0664	1.022	0.9377	0.0623	308
	1.1195	1.038	0.8933	0.1067	313
	1.1303	1.014	0.885	0.1153	318
2.0 mole	1.056	1.0183	0.947	0.053	298
	1.664	1.0216	0.9377	0.0623	303
	1.0716	1.0233	.9332	0.0668	308
	1.1357	1.0433	0.8805	0.1195	313
	1.1576	1.05	0.8638	0.1361	318

As clearly shown in these figures increasing time (min.) with increases of the solvent content (%). This behavior can be explained due to, the compound of solvent and the structure of polymer, i.e., present of the hydrophilic groups in the xerogel, concentration and nature of the solvent. All these factors will increase the solvent content (%) with the increased of time [21]. The low values of swelling process were affected by High chain flexibility and the degree of cross linking, i.e., in the modified polyester with 1.0 mole of acrylic acids, the values will be low comparing with the values in the modified polyester with 2.0 mole of acrylic acids.

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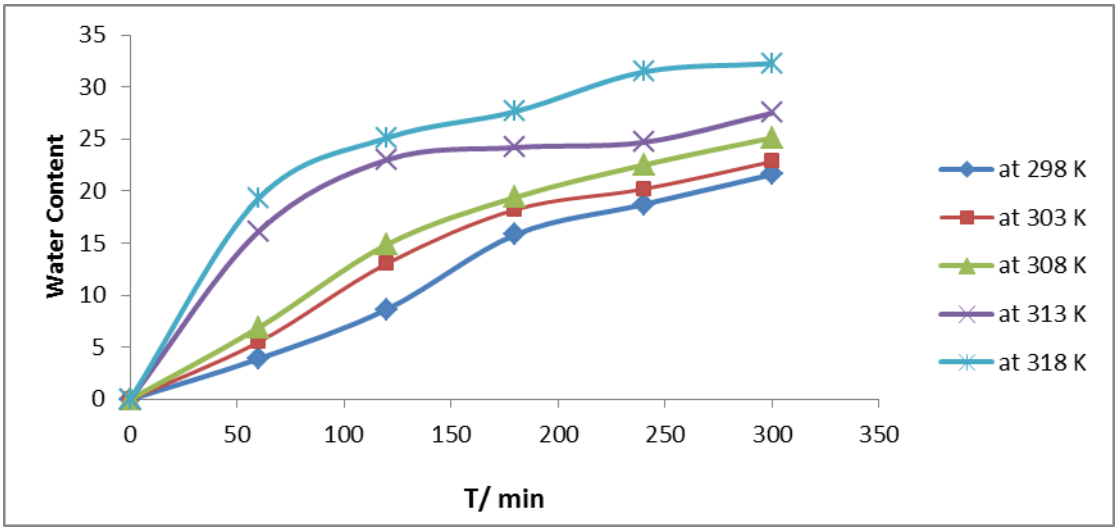

Figure 5: Water Content (%) curves of the modified resin with 2.0 mole of acrylic acid at different temperatures.

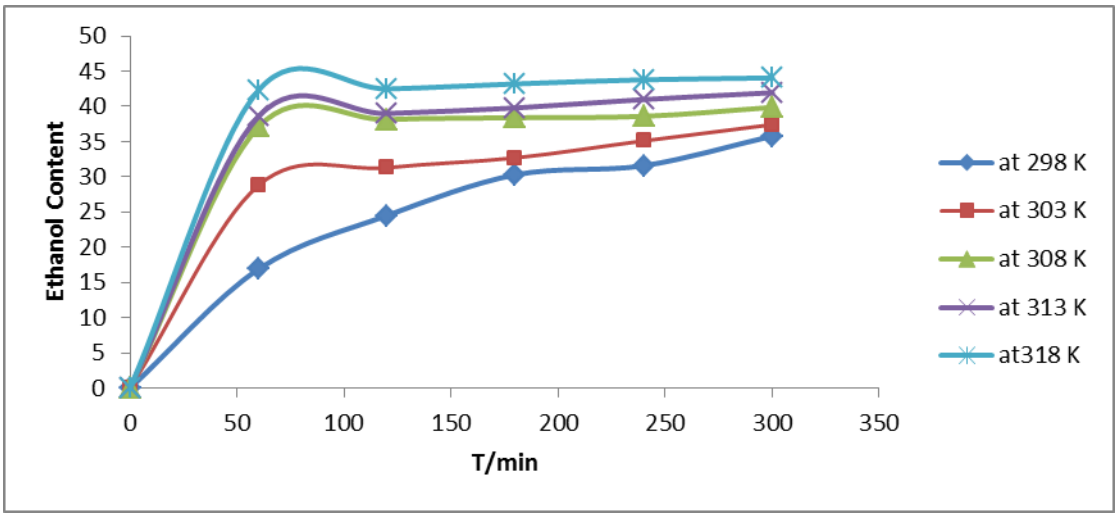

Figure 6: Ethanol Content (%) curves of the modified resin with 2.0 mole of acrylic acid at different temperatures.

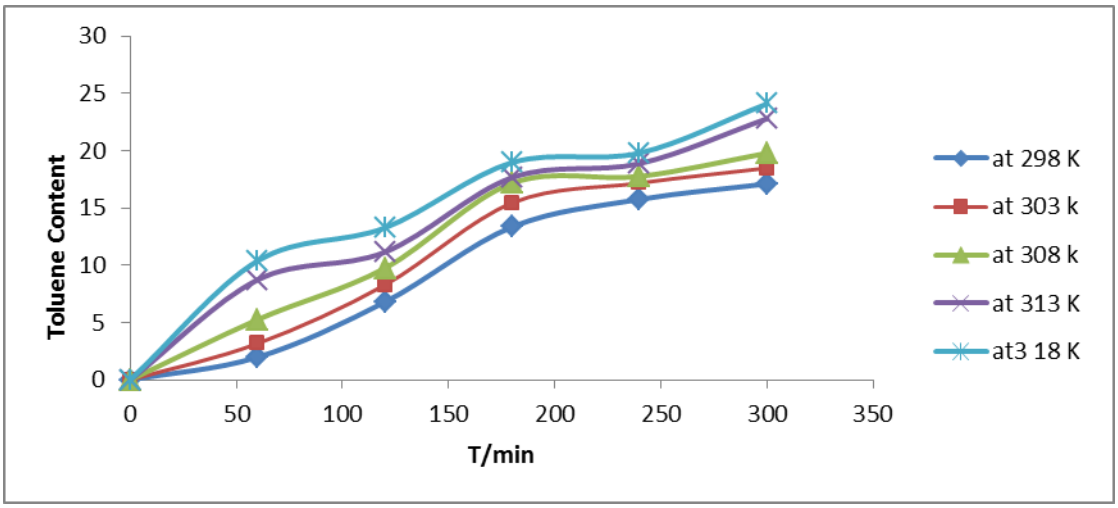

Figure 7: Toluene Content (%) curves of the modified resin with 2.0 mole of acrylic acid at different temperatures.

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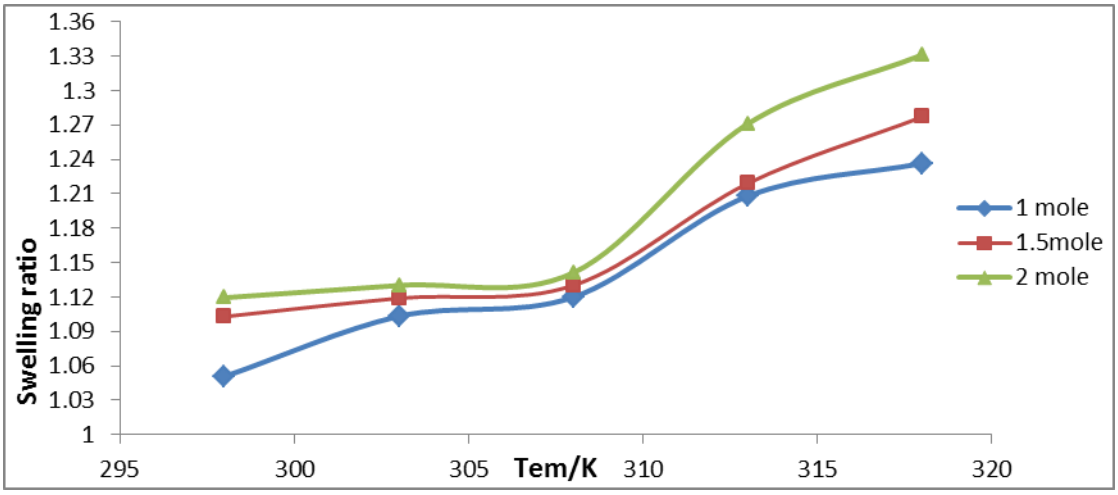

Figure 8: Swelling ratio (q) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in water

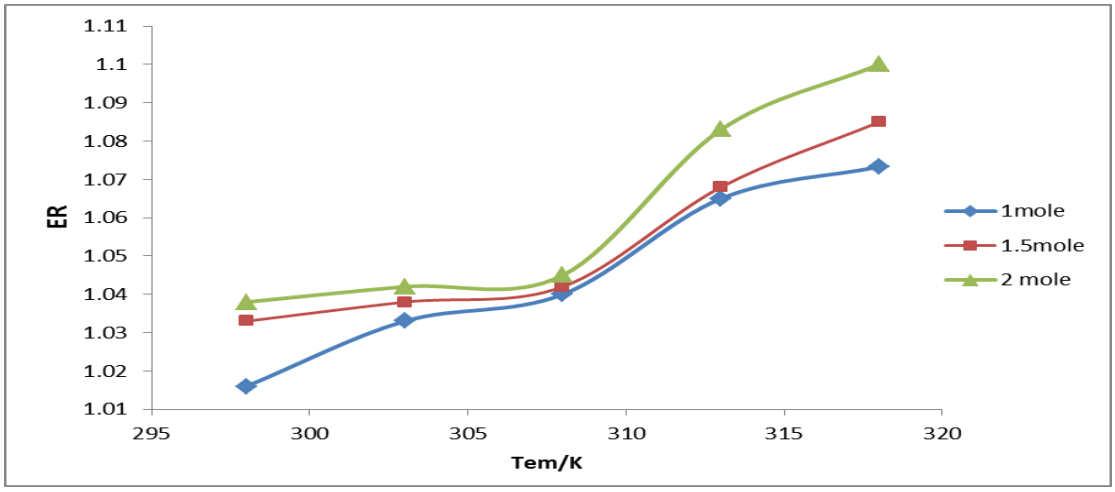

Figure 9: Extension ratio percent (ER%) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in water

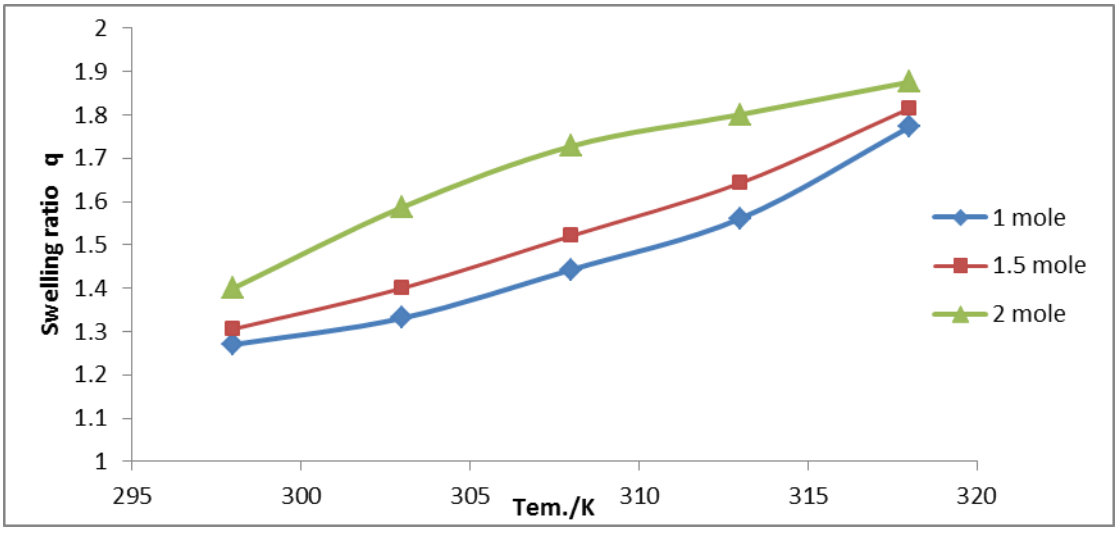

Figure 10: Swelling ratio (q) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in ethanol

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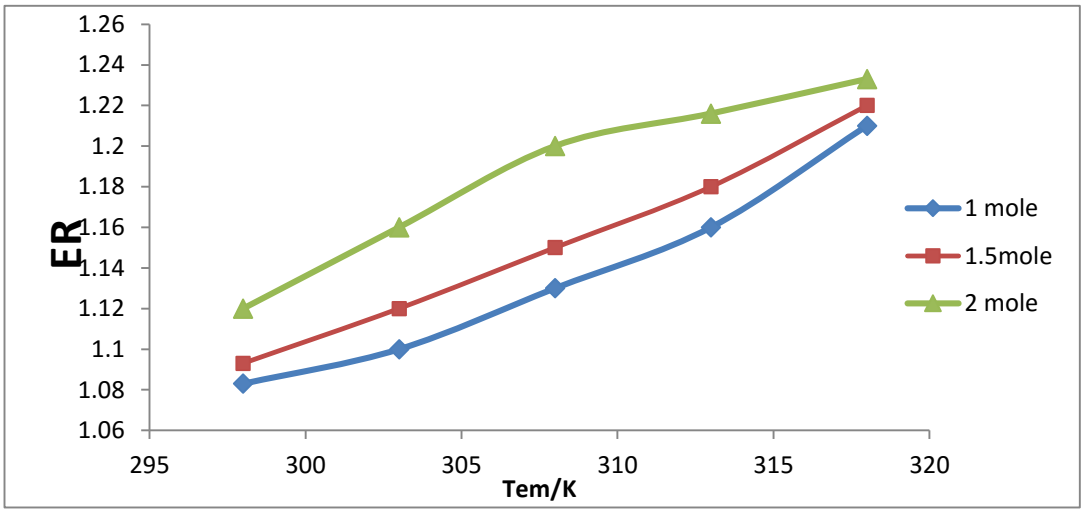

Figure 11: Extension ratio percent (ER%) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in ethanol

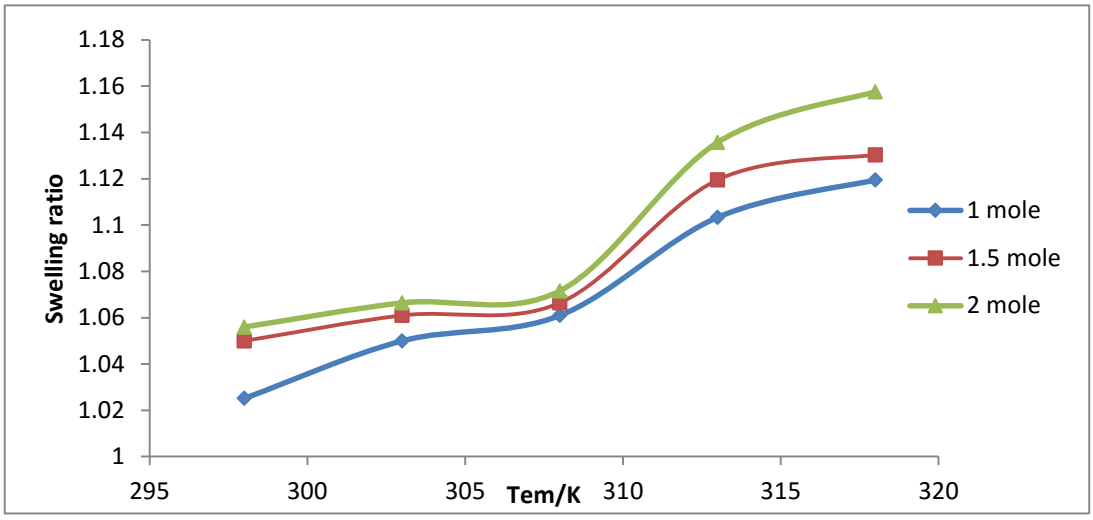

Figure 12: Swelling ratio (q) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in Toluene

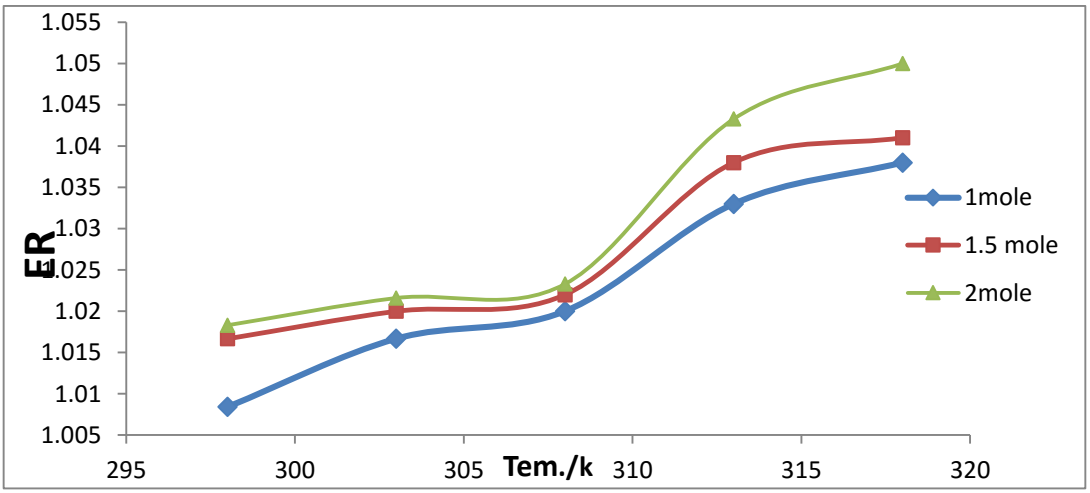

Figure 13: Extension ratio percent (ER%) curves of the modified resin containing different number of moles of acrylic acid monomer at different temperatures in toluene

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CONCLUSION

Increasing the number of moles of the acrylic acid monomer due to, increases the hydroxyl content ratio of the product copolymer, and thus leads to increases the swelling modified resin, and the increases of number of moles of the acrylic acid monomer, leads to increase of all of the parameters were measured (solvent content in the sample, expansion and swelling ratio, volume fraction of the solvent and decreased volume fraction of the specimen), the results also showed that the effect of the temperature on the swelling, as it is increasing the temperature, leads to increases of each of the solvent content in the sample, expansion ratio, swelling ratio and volume fraction of the solvent and decreased volume fraction of the specimen.

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