

Flow Model Selection for Water Soluble Polymer Solutions

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Abstract

This research deals with the effect of type and concentration of different polymer solutions on rheological behavior and apparent viscosity. All polymers studied in this work are water soluble, which are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol. 55 experiments were performed with different polymer types and concentrations at 30 °C (± 1 °C). By using the Solver Add-in in Microsoft Excel®, the power law flow model was found to be the best fits the experimental results. The apparent viscosity of each polymer used at different concentrations was decreased with shear rates. It was found that XC-polymer solutions have higher shear stresses than other polymers. Also it was found that XC-polymer solutions have a higher viscosity, and its viscosity decreases much more than other polymer solutions used in this study.

Key words: *polymer, non-Newtonian fluids, Rheology*

1. Introduction

Viscosity is a principal parameter for any flow measurements of fluids, such as liquids, semi-solids, gases and even solids are made. There are many different techniques for measuring viscosity, each suitable to specific circumstances and materials. The selection of the right viscometer from the scores of instruments available to meet the need of any application is a difficult proposition. Today's instruments vary from the simple to the complex: from counting the seconds for a liquid to drain off a stick to very sophisticated automatic recording and controlling equipment [1].

In polymer solutions, polymer molecules are long chain molecules composed of many repeating units. The bonds along the polymer backbone are continually rotating, and as a result, the molecule itself is continually changing orientation and configuration on a length scale much smaller than the equilibrium size.

In dilute polymer solutions, the rheology of solution is dependant solely on the dynamics of an individual chain and the number of chains (i.e.

concentration) in the system. At high concentrations, interactions between polymer molecules impact the rheology in a significant way. As concentration further increases, polymer solutions exhibit a change from fluid-like to more elastic-like behavior [2].

Many flow models have been proposed, which are useful for the treatment of experimental data or for describing flow behavior [3]. Flow models range from the very simple to the very complex. Some of them merely involve the plotting of data on graph paper. Some are quite sophisticated and require use computers.

Once a correlation has been developed between rheological data and product behavior, the procedure can then be reversed and rheological data may be used to predict performance and behavior [1].

Flow Models

Many flow models (table 1) have been proposed, which are useful for the treatment of experimental data or for describing flow behavior. However, it is likely no given model fits the rheological behavior of a material over an extended shear rate range. Nevertheless, these models are useful for summarizing rheological data and are frequently encountered in the literature.

2. Experimental Work Polymers Used

Five polymers were used in this study, these are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol, as follow:

Sets of Experiments

55 experiments were performed to study the rheological properties of the aqueous solutions of polymers used in this study. Experiments were performed at 30 °C (± 1 °C). List of experiments is shown in Table (2). The instrument speed switched to 600, 300, 200, 100, 6 and 3 rpm and the dial reading was recorded

Table (1) Flow equations for flow models [3,7].

Flow model	Flow equation	Eqn. no.
Newtonian	$\tau = \eta \dot{\gamma}$...(1)
Bingham plastic	$\tau - \tau_o = \eta \dot{\gamma}$...(2)
Power law	$\tau = k \dot{\gamma}^n$...(3)
Modified power law	$\tau - \tau_o = k \dot{\gamma}^n$...(4)
Casson fluid	$\tau^{1/2} - \tau_o^{1/2} = \eta_\infty^{1/2} \dot{\gamma}^{1/2}$...(5)
Robertson - Stiff	$\tau = A (\dot{\gamma} + C)^B$...(6)
Modified Robertson - Stiff	$\tau - \tau_o = A' (\dot{\gamma} + C')^B$...(7)
Williamson	$\eta = \eta_\infty + \frac{(\eta_o - \eta_\infty)}{1 + \frac{ \tau }{\tau_m}}$...(8)
Cross	$\eta = \eta_\infty + \frac{(\eta_o - \eta_\infty)}{1 + \alpha \dot{\gamma}^n}$...(9)

Viscometer

The Fann viscometer model 35 is direct reading instrument which have six speeds: 600, 300, 200, 100, 6 and 3 rpm. It is a Couette coaxial cylinder rotational viscometer [7].

This instrument is a form of concentric cylinder viscometer that enables the variation of shearing stress with shear rate to be observed.

Preparation of Polymer Solution**Preparation of CMC, HEC and XC polymer solutions**

The method for preparing a sample of polymeric solution at a certain concentration was as follow:

A previously dried polymer powder was weighted to the nearest 0.001g using electronic balance, and added to 500 ml of distilled water in the Hamilton beach cup.

The polymer lightly sprinkled into the water and stirring continued for one hour to ensure completely polymer dissolution.

The prepared solution was kept at room temperature for 24 hr prior to conducting the rheological measurements.

Preparation of PVA solution

There are two methods for preparing aqueous solution of polyvinyl alcohol, the conventional

heating method and the microwave heating method.

The microwave oven method is the preferred method for preparing the PVA solution [8,9], so it was considered in this investigation as follow:

Dry PVA powder was weighted to the nearest 0.001g using electronic balance and added to 500 ml of distilled water in a Pyrex beaker with stirring.

The beaker placed in a microwave oven and turned on high for three minutes.

The prepared solution was kept at room temperature for 24 hr prior to conducting the rheological measurements

Rheological Measurements

The procedure for measuring the rheological properties of polymer solutions, using the Fann viscometer model 35 was as follow:

The sample cup was filled with polymer solution to the scribed line, and the rotor was immersed to the proper immersion depth. The instrument was operated at 300 rpm for three minutes to equalize the temperature of the bob, rotor and polymer solution. The instrument speed switched to 600, 300, 200, 100, 6 and 3 rpm and the dial reading was recorded.

Table 2:List of Experiments.

Exp.No.	Polymer	Conc.(g/l)
1	XC	4
2	XC	8
3	XC	12
4	XC	16
5	XC	20
6	XC	24
7	XC	32
8	XC	40
9	HEC	4
10	HEC	8
11	HEC	12
12	HEC	16
13	HEC	20
14	HEC	24
15	HEC	32
16	HEC	40
17	HEC	48
18	HEC	56
19	HEC	64
20	HEC	72
21	CMC	4
22	CMC	8
23	CMC	12
24	CMC	16
25	CMC	20
26	CMC	24
27	CMC	32
28	CMC	40

Exp.No.	Polymer	Conc.(g/l)
29	CMC	48
30	CMC	56
31	CMC	64
32	CMC	72
33	CMC-2	4
34	CMC-2	8
35	CMC-2	12
36	CMC-2	16
37	CMC-2	20
38	CMC-2	24
39	CMC-2	32
40	CMC-2	40
41	CMC-2	48
42	CMC-2	56
43	CMC-2	64
44	PVA	4
45	PVA	8
45	PVA	12
47	PVA	16
48	PVA	20
49	PVA	24
50	PVA	32
51	PVA	40
52	PVA	48
53	PVA	56
54	PVA	64
55	PVA	72

3. Results and Discussion

Flow Model Selection

The selection of the flow model that best fit the rheological behavior is useful for treating experimental data or for describing flow behavior.

In this work a new method, which is proposed by Morrison (2005) used [10]. This method uses the Solver Add-in in Microsoft Excel® to optimize the solution.

The basic outlines of this method include:

- ❖ The experimental data were arranged in the Excel spreadsheet. Two columns were used, one for shear rate and one for shear stress.
- ❖ A column was adopted to predict the value of shear stress which was calculated from a considered flow model. Since the values are unknown of the model parameters, therefore some guesses must be studied.

- ❖ A new column for the square of the deviation between the actual shear stress and the predicted value must be obtained. All the values in the error column must be placed in a cell.
- ❖ The Solver function in the Excel® is set up to minimize the error cell mentioned above. Solver will replace the initial guesses with optimized values.
- ❖ The Solver allows to put constrains on the ways in which it manipulate the cells to be changeable. For present work it is know that none of the model parameters may be negative, therefore this can be considered as constraint.

The results for using the Add-in in Microsoft Excel for the XC polymer solutions are shown in

Table (3). The results for other polymer solutions are shown in appendix (A).

From these tables, one can conclude that the power law model best fits the experimental results. So this model will be considered in the following sections.

The power law with yield model (equation 4) gives the same results as the power law model (equation 3), the Solver replace the guess value of the yield point and set it equal to zero, so this model became the same as the power law model.

Also the Robertson-Stiff model (equation 6) gives the same results, because the Solver set the parameter C equal to zero.

Figures (1) and (2) illustrate the results of using the Solver Add-in in Microsoft Excel for XC polymer solutions at 20 and 24 g/l respectively.

These figures show that the power law model is more representative to the experimental data, since these polymer solutions are shear thinning.

Table3 Model selection for XC Polymer solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g / l)	Sum of Square Error					
		Newtonian Eqn.(1)	Bingham Eqn.(2)	Power Law Eqn.(3)	With Yield Eqn.(4)	Casson Eqn.(5)	Robertson Eqn.(6)
1	4	0.997	0.331	0.130	0.130	0.252	0.130
2	8	1.248	0.253	0.063	0.063	0.163	0.063
3	12	1.705	0.476	0.081	0.081	0.301	0.081
4	16	2.087	0.597	0.106	0.106	0.376	0.106
5	20	2.226	0.453	0.048	0.048	0.248	0.048
6	24	2.641	0.523	0.065	0.065	0.286	0.065

The Power Law Model

The values of n and k , with the correlation coefficients of the best fit line (R^2) for all experiments are presented in Table (4). The

results for Experiments no. 7,8,19,20, 42 and 43 are ignored because the shear stress readings at high shear rates are out of the scale range for the Fann viscometer.

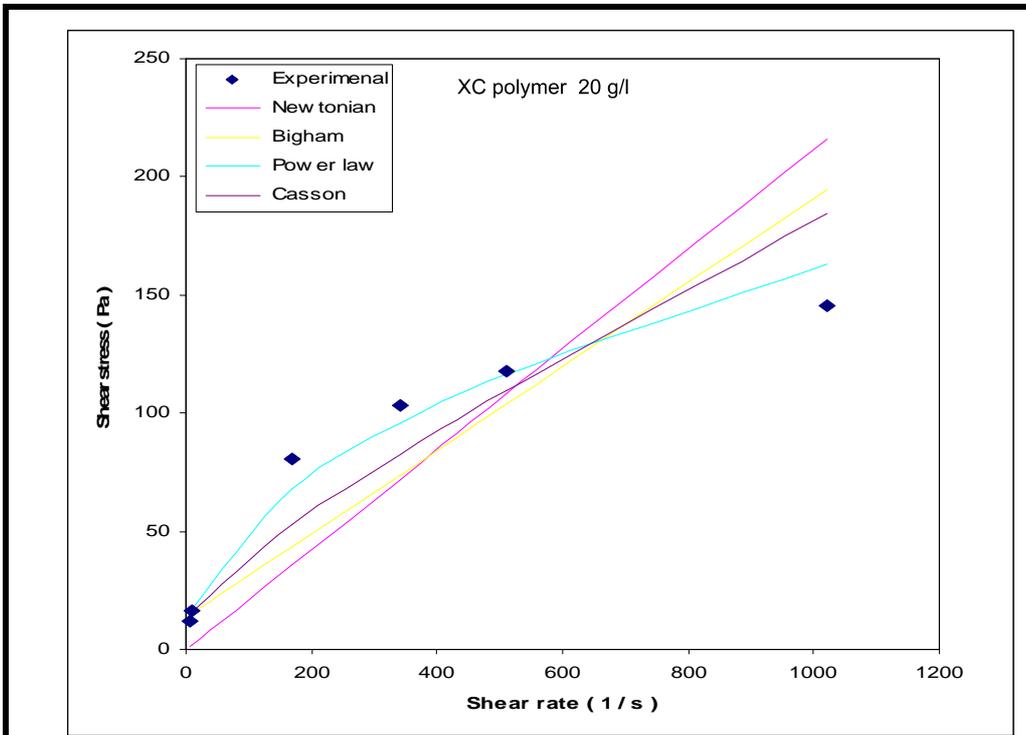


Figure (1) Experimental results and flow models representation for 20 g/l XC polymer solution.

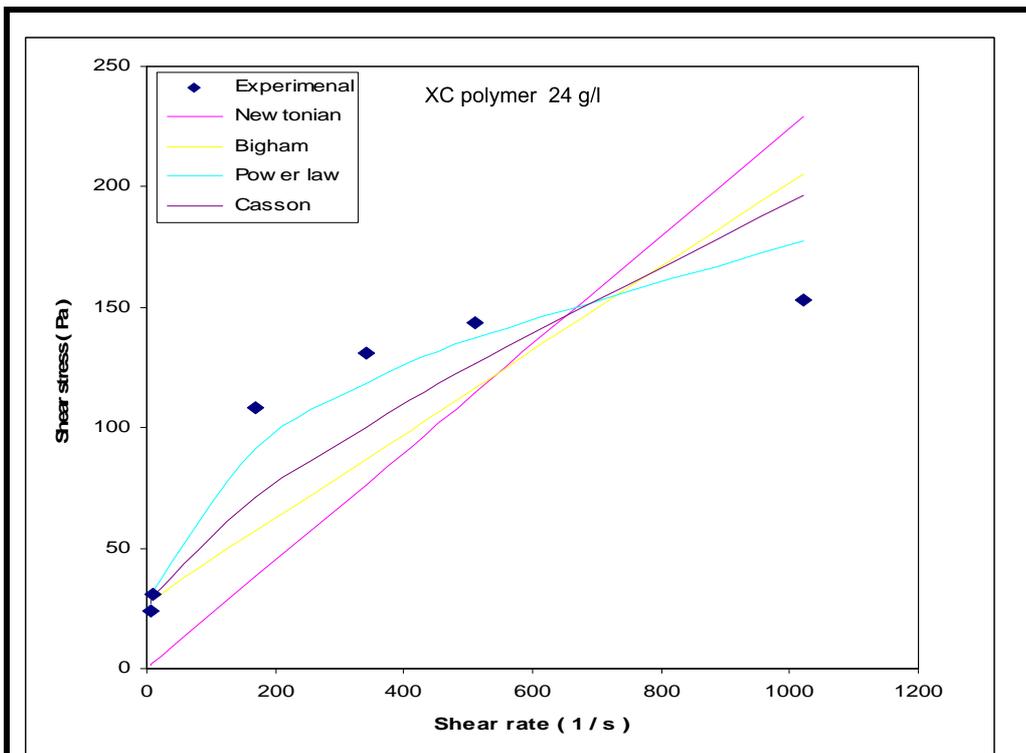


Figure (2) Experimental results and flow models representation for 24 g/l XC polymer solution

Table (4) Flow behavior index (n) and consistency index (k).

Exp.No.	n	k	R ²	Exp.No.	n	k	R ²
1	0.7930	0.0551	0.9917	29	0.7255	0.3024	0.9975
2	0.7113	0.2253	0.9949	30	0.7223	0.5366	0.9910
3	0.6479	0.7762	0.9923	31	0.7166	0.8617	0.9929
4	0.5684	2.6841	0.9857	32	0.7104	1.2530	0.9966
5	0.4904	5.5641	0.9913	33	0.7100	0.0169	0.9918
6	0.3774	13.364	0.9814	34	0.7032	0.0208	0.9791
7	-	-	-	35	0.6725	0.0363	0.9877
8	-	-	-	36	0.6387	0.096	0.9851
9	0.7127	0.022	0.9791	37	0.6556	0.182	0.9725
10	0.6272	0.0692	0.9817	38	0.6564	0.3520	0.9909
11	0.6334	0.0991	0.9825	39	0.6519	0.7558	0.9829
12	0.6273	0.1287	0.9906	40	0.6000	2.1249	0.9847
13	0.6260	0.2135	0.9639	41	0.5651	3.8227	0.9733
14	0.5973	0.3637	0.9841	42	-	-	-
15	0.5958	0.4924	0.985	43	-	-	-
16	0.5852	0.6978	0.9913	44	0.7100	0.0169	0.9918
17	0.5497	1.8832	0.9987	45	0.6645	0.0335	0.9991
18	0.5494	2.947	0.9575	45	0.6879	0.0316	0.9983
19	-	-	-	47	0.6835	0.0362	0.9954
20	-	-	-	48	0.6671	0.0605	0.9942
21	0.8242	0.0104	0.9896	49	0.6606	0.0930	0.9903
22	0.7807	0.0152	0.9982	50	0.6947	0.1199	0.9598
23	0.6904	0.0300	0.9848	51	0.6575	0.1867	0.9891
24	0.7362	0.0354	0.9868	52	0.6771	0.3470	0.9746
25	0.6679	0.0656	0.9776	53	0.6437	0.6234	0.9903
26	0.6935	0.086	0.9871	54	0.6196	1.4383	0.9809
27	0.7316	0.1192	0.9868	55	0.6311	1.6835	0.9886
28	0.7354	0.1584	0.9883				

Effect of Polymer Type on Flow Curves (shear stresses vs. shear rates)

Effect of polymer type on flow curves are shown on ordinary and logarithmic scales, at constant polymer concentrations of 4, 16 and 24 g/l, figures (3), (4) and (5) respectively.

From these figures one can conclude that, at low concentrations XC polymer solutions have a higher shear stresses than other polymer solutions

used in this work. At higher concentrations this phenomena is pronounced.

This is due to the molecular structure of XC polymer, which exists in disordered state in aqueous media that can be highly extended if it is subjected to shear rates.

PVA is less affected by shear rates than other polymers used

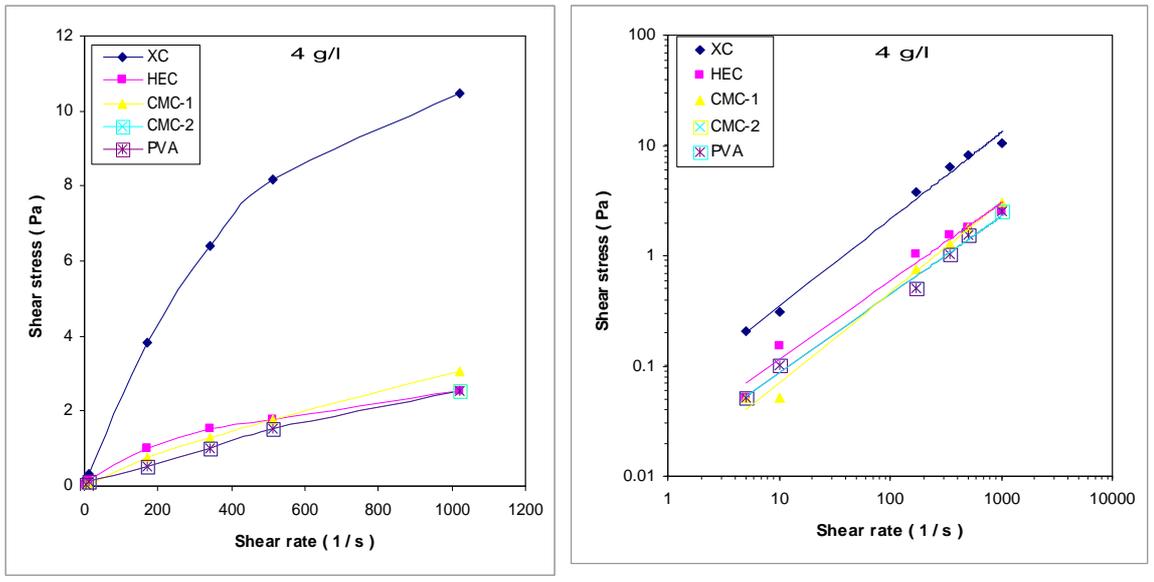


Figure (3) Effect of polymer type on flow curve (on ordinary and logarithmic scale), at polymer concentration of 4 g/l

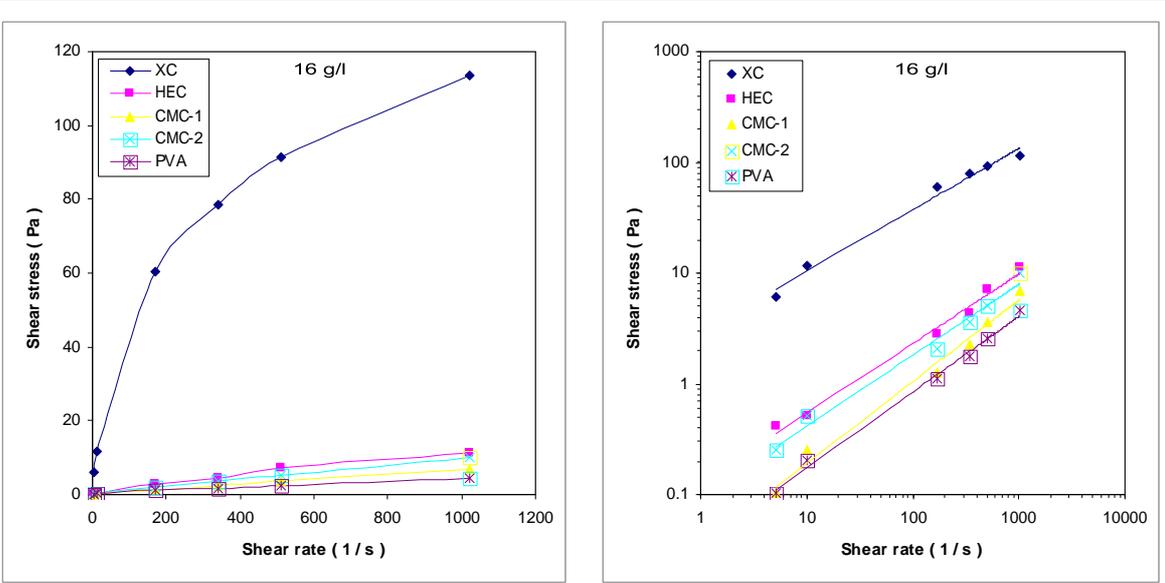
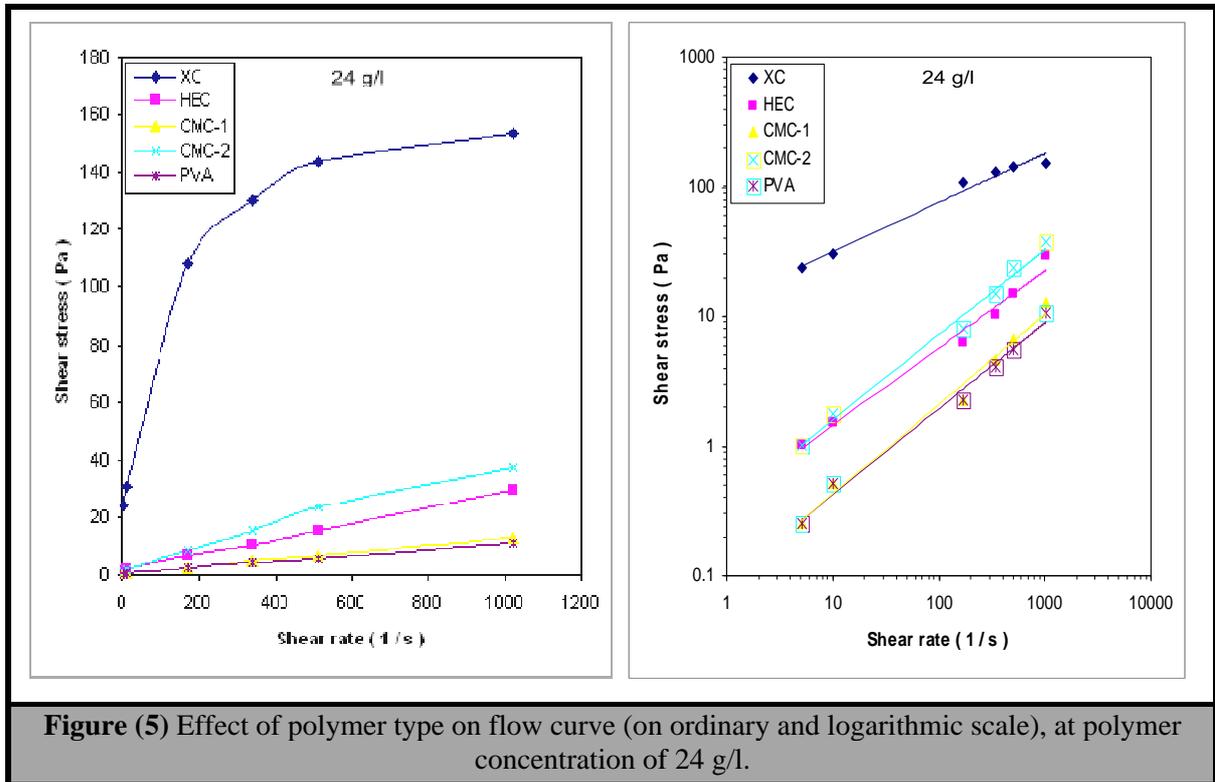


Figure (4) Effect of polymer type on flow curve (on ordinary and logarithmic scale), at polymer concentration of 16 g/l



Viscosity of Polymer Solutions

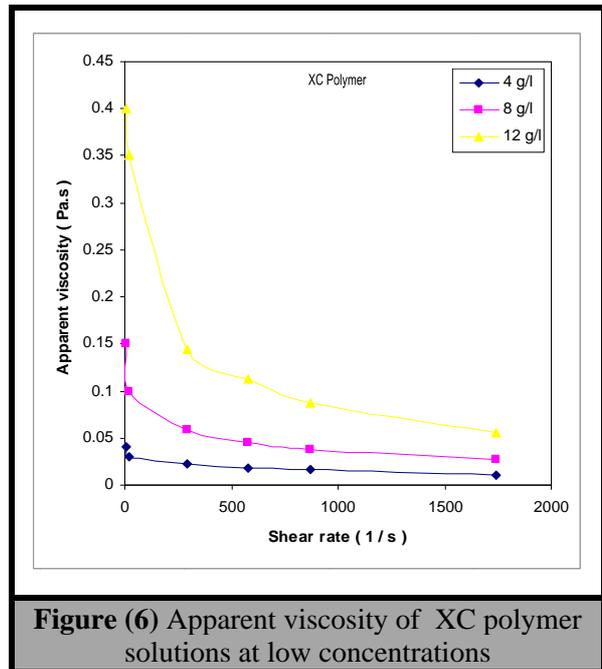
The effect of concentration of each polymer used on the apparent viscosity at low concentrations are shown in figures (6), (8), (10), (12) and (14), at high polymer concentrations are shown in figures (7), (9), (11), (13) and (15).

The apparent viscosity can be calculated from the power law mode, which takes the form [3]:

$$\eta_a = k \dot{\gamma}^{n-1} \dots \quad 10$$

In general, the apparent viscosity of all polymer solutions used in this work decreases as the shear rate is increased. This behavior occurs because as the shear rate is increased the polymer molecules orient and align with the flow direction, thus reducing the drag. As the shear rate is increased further, the alignment with flow becomes more complete, and the viscosity decreases further [5].

Also from the above mentioned figures, one can notice that as the polymer concentration is increased, the decreases in viscosity was found to be more pronounced at high shear rates.



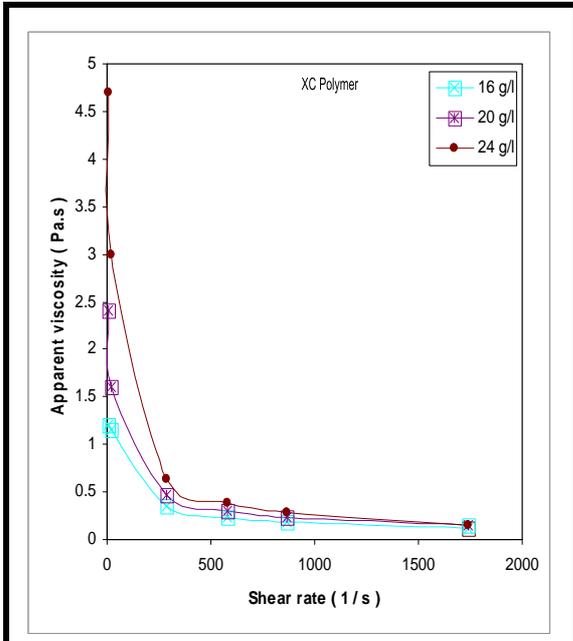


Figure (7) Apparent viscosity of XC polymer solutions at high concentrations

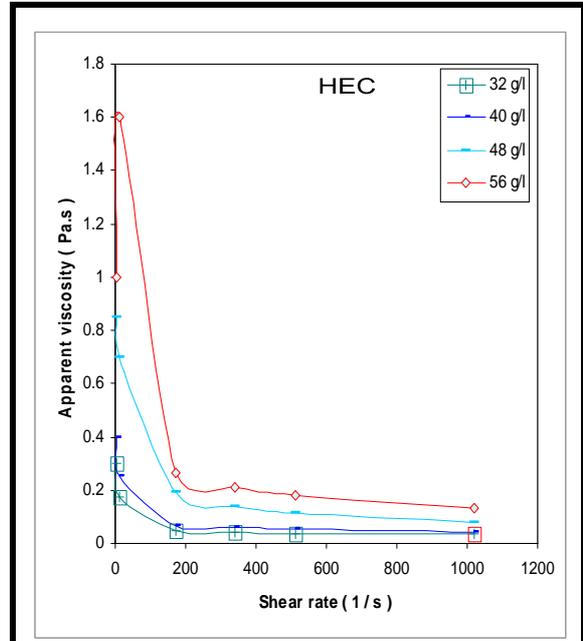


Figure (9) Apparent viscosity of HEC solutions at high concentrations

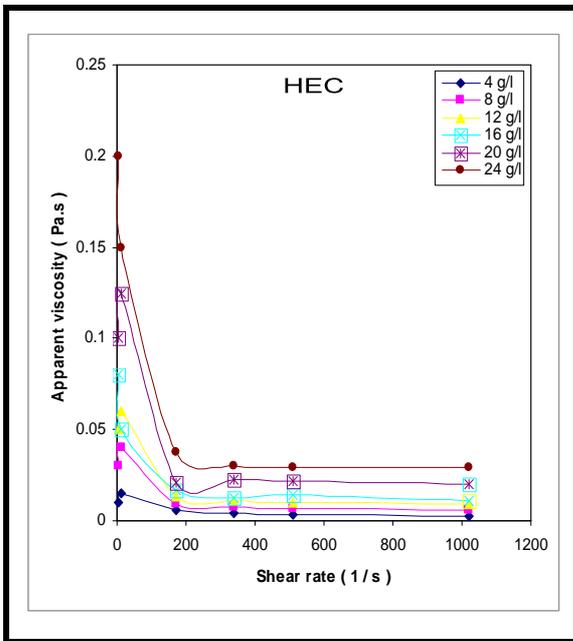


Figure (8) Apparent viscosity of HEC solutions at low concentrations

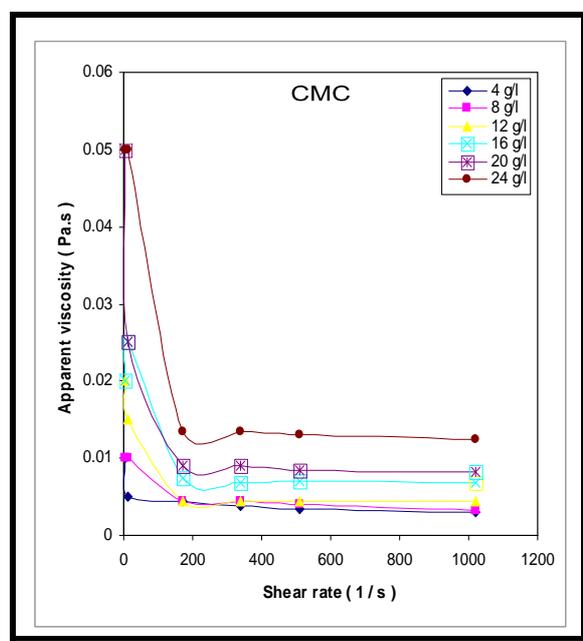


Figure (10) Apparent viscosity of CMC-1 solutions at low concentrations

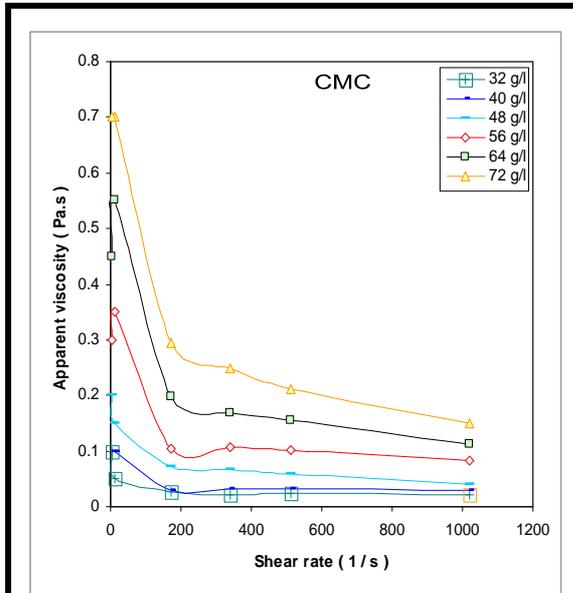


Figure (11) Apparent viscosity of CMC-1 solutions at high concentrations

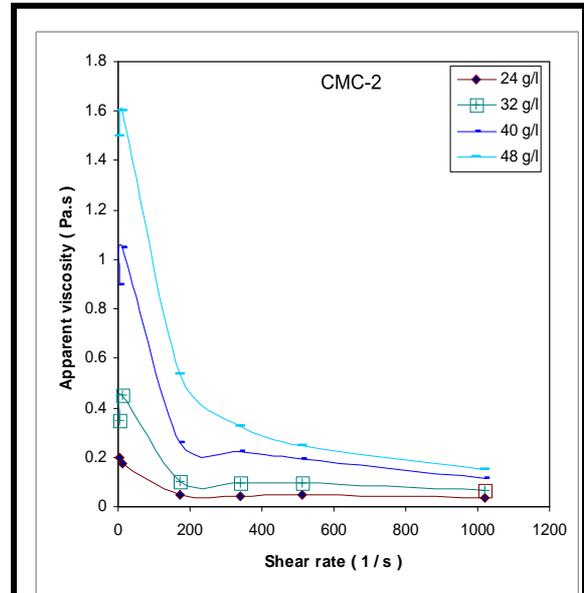


Figure (13) Apparent viscosity of CMC-2 solutions at high concentrations

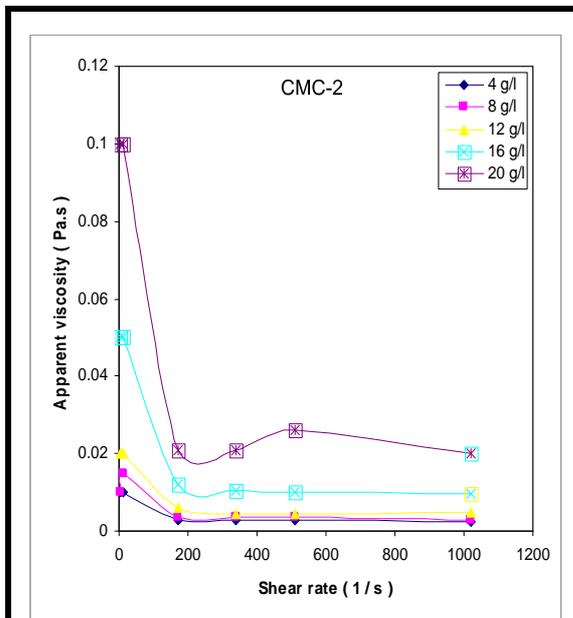


Figure (12) Apparent viscosity of CMC-2 solutions at low concentrations

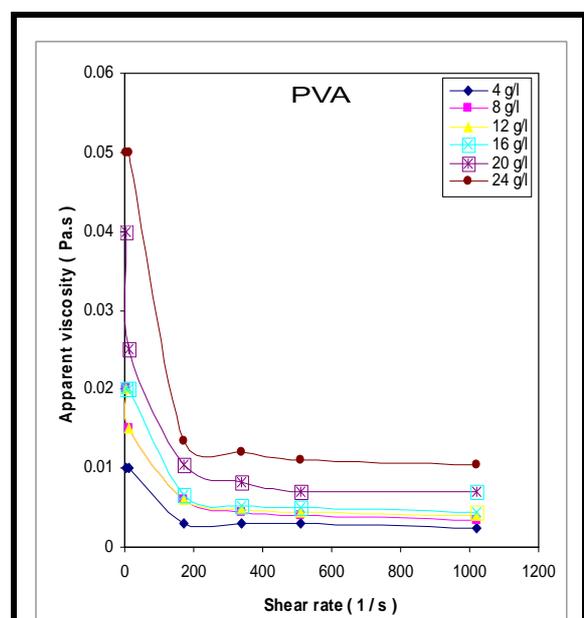


Figure (14) Apparent viscosity of PVA solutions at low concentrations

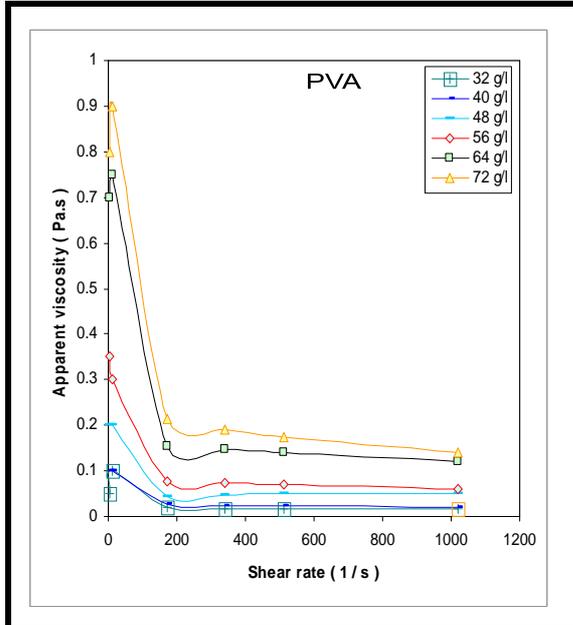


Figure (15) Apparent viscosity of PVA solutions at high concentrations

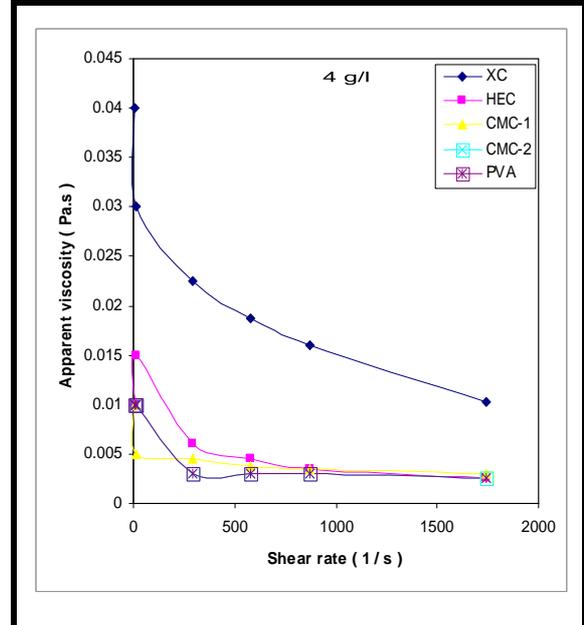


Figure (16) Effect of polymer type on viscosity at polymer concentration of 4 g/l

Effect of Polymer Type on Viscosity

The effect of polymer type on viscosity, at constant polymer concentrations of 4, 16 and 24 g/l, are shown in figures (16), (17) and (18) respectively.

From these figures one can notice that XC polymer solutions have higher viscosities than other polymer solutions used in this work, because of the molecular structure of the XC polymer, which has the disordered state.

Also it can be noticed that a decrease in viscosity is more pronounced in XC polymer solutions than other polymers.

It can be concluded that, in the range of polymer concentrations used in this study, the apparent viscosity can be ordered as:

$$\eta_{XC} > \eta_{HEC} > \eta_{CMC2} > \eta_{CMC1} > \eta_{PVA}$$

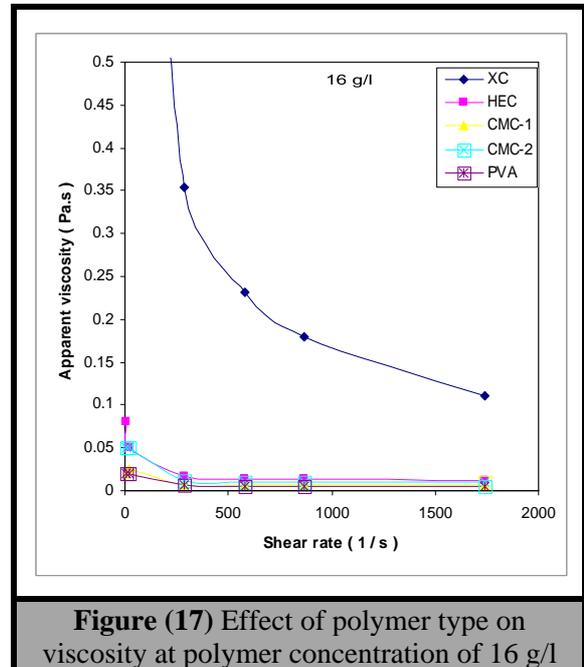


Figure (17) Effect of polymer type on viscosity at polymer concentration of 16 g/l

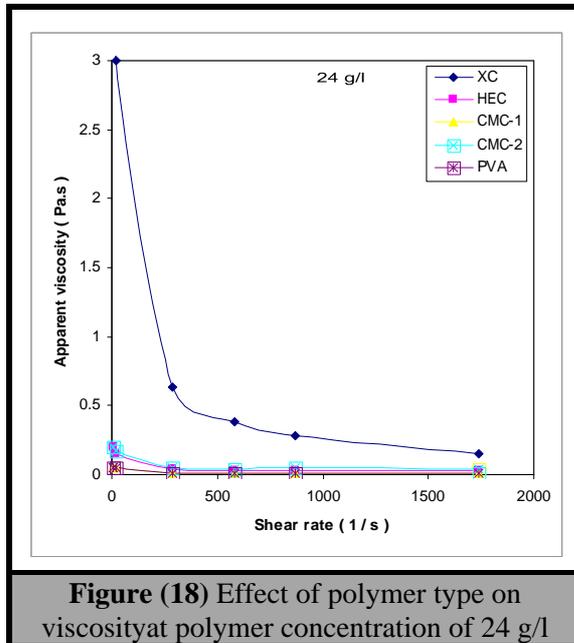


Figure (18) Effect of polymer type on viscosity at polymer concentration of 24 g/l

4. Conclusions

1. All polymer solutions used in this work (XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol) behave as shear-thinning fluid, in which the viscosity decreases as the shear rate increases, because the polymer molecules orient and align with the flow direction.
2. By using the Solver Add-in in Microsoft Excel®, the power law flow model was found to be the best fit to the experimental results.
3. XC-polymer solutions have a higher viscosity, and its viscosity decreases much more than other polymer solutions used in this study, because of the molecular structure of XC polymer, which exists in disordered state.

5. NOMENCLATURE

<u>Symbol</u>	<u>Meaning</u>	<u>Unit</u>
A, B, C	Parameters in Equation (6)	-
A', B', C'	Parameters in Equation (7)	-
k	Consistency index	-
<u>Greek letters</u>	<u>Meaning</u>	<u>Unit</u>
$\dot{\gamma}$	Shear rate	s^{-1}
ε	Strain or deformation	-
η	Viscosity	Pa. s
η_{∞}	Newtonian limiting viscosity	Pa.s
τ	Shear stress	Pa
τ_m	Shear stress at mean viscosity	Pa
τ_o	Yield stress	Pa

Abbreviations

CMC	<i>Carboxymethyl Cellulose</i>
PVA	<i>Polyvinyl Alcohol</i>
HEC	<i>Hydroxyethyl Cellulose</i>
XC	<i>Xanthomonas Campestris</i>

6. References

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http://www.chem.mtu.edu/~fmorriso/cm4650/Using_Solver_in_Excel.pdf

Appendix A

Flow Model Selection Using Add-in in Microsoft Excel

Table(A.1) Model selection for HEC solutions using Add-in in Microsoft Excel

Exp. No.	Conc. (g / l)	Sum of Square Error					
		Newtonian Eqn.(1)	Bingham Eqn.(2)	Power Law Eqn.(3)	With Yield Eqn.(4)	Casson Eqn.(5)	Robertson Eqn.(6)
9	4	1.376	0.616	0.243	0.243	0.731	0.243
10	8	1.386	0.342	0.144	0.144	0.226	0.144
11	12	1.371	0.256	0.138	0.138	0.165	0.138
12	16	1.306	0.048	0.017	0.016	0.017	0.017
13	20	1.293	0.246	0.245	0.243	0.229	0.245
14	24	1.368	0.051	0.038	0.038	0.028	0.038
15	32	1.374	0.027	0.018	0.011	0.013	0.018
16	40	1.436	0.048	0.003	0.002	0.004	0.003
17	48	1.823	0.316	0.010	0.010	0.150	0.010
18	56	1.731	0.551	0.235	0.235	0.389	0.235

Table(A.2) Model selection for CMC-1 solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g / l)	Sum of Square Error					
		Newtonian Eqn.(1)	Bingham Eqn.(2)	Power Law Eqn.(3)	With Yield Eqn.(4)	Casson Eqn.(5)	Robertson Eqn.(6)
21	4	0.543	0.128	0.166	0.148	0.702	0.166
22	8	0.763	0.138	0.025	0.025	0.462	0.025
23	12	1.055	0.031	0.030	0.030	0.044	0.030
24	16	0.907	0.189	0.155	0.150	0.140	0.155
25	20	1.083	0.015	0.028	0.014	0.062	0.028
26	24	1.057	0.114	0.102	0.102	0.084	0.102
27	32	0.866	0.044	0.043	0.043	0.069	0.043
28	40	0.912	0.108	0.104	0.104	0.089	0.104
29	48	1.122	0.197	0.031	0.031	0.111	0.031
30	56	0.988	0.195	0.109	0.108	0.127	0.109
31	64	1.142	0.332	0.082	0.082	0.215	0.082
32	72	1.237	0.316	0.042	0.042	0.190	0.042

Table(A.3) Model selection for CMC-2 solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g / l)	Sum of Square Error					
		Newtonian Eqn.(1)	Bingham Eqn.(2)	Power Law Eqn.(3)	With Yield Eqn.(4)	Casson Eqn.(5)	Robertson Eqn.(6)
33	4	1.013	0.123	0.107	0.108	0.076	0.107
34	8	1.085	0.332	0.210	0.210	0.252	0.210
35	12	1.170	0.150	0.109	0.109	0.096	0.109
36	16	1.250	0.135	0.105	0.105	0.087	0.105
37	20	1.239	0.174	0.173	0.173	0.171	0.173
38	24	1.209	0.100	0.060	0.060	0.052	0.060
39	32	1.337	0.340	0.154	0.154	0.229	0.154
40	40	1.776	0.528	0.127	0.127	0.339	0.127
41	48	2.181	0.754	0.202	0.202	0.520	0.202

Table(A.4) Model selection for PVA solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g / l)	Sum of Square Error					
		Newtonian Eqn.(1)	Bingham Eqn.(2)	Power Law Eqn.(3)	With Yield Eqn.(4)	Casson Eqn.(5)	Robertson Eqn.(6)
44	4	1.013	0.123	0.107	0.085	0.077	0.107
45	8	1.249	0.120	0.006	0.006	0.042	0.006
46	12	1.110	0.072	0.004	0.004	0.016	0.004
47	16	1.138	0.156	0.048	0.048	0.077	0.048
48	20	1.185	0.060	0.019	0.019	0.025	0.019
49	24	1.187	0.136	0.082	0.082	0.076	0.082
50	32	1.071	0.429	0.323	0.323	0.360	0.323
51	40	1.197	0.136	0.089	0.089	0.079	0.089
52	48	1.140	0.142	0.139	0.139	0.150	0.139
53	56	1.234	0.084	0.053	0.053	0.042	0.053
54	64	1.318	0.177	0.140	0.140	0.124	0.140
55	72	1.345	0.240	0.101	0.101	0.141	0.101

أختيار نموذج جريان محاليل البوليمرات المائية

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هذا البحث يهتم بدراسة تأثير نوع وتركيز البوليمر على الخواص الريولوجية للمحاليل المائية للبوليمرات وعلى اللزوجة الظاهرية. البوليمرات المستخدمة في البحث هي : XC - بوليمر ، كاربوكسي مثيل سيليلوز (نوعين) ، هايدروكسي مثيل سيليلوز ، بولي فنيل الكحول. تم دراسة الخواص الريولوجية باستخدام جهاز (Fann VG-35A) وذلك بقياس اجهاد القص (shear stress) المصاحب لكل معدل قص (shear rate). تم اجراء ٥٥ تجربة بتركيز مختلفة وعند درجة حرارة ٣٠ م° (± ١ م°). تم استخدام برنامج مايكروسوفت ايكسيل لايجاد افضل نموذج رياضي يمثل النتائج العملية . وقد وجد بان النموذج رياضي الاسي (Power law) هو الافضل . وجد بان اللزوجة الظاهرية لمحاليل البوليمرات تقل بزيادة معدلات القص. ايضا وجد بان محاليل XC بوليمر لها اجهاد قص اكثر من بقية محاليل البوليمرات. اخيرا وجد بان محاليل XC بوليمر لها لزوجة اكثر من بقية محاليل البوليمرات المستخدمة و بان محاليل XC بوليمر تقل لزوجتها اكثر عند تعرضها لمعدلات قص.

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