Assessment of Applicability of Carreau, Ellis, and Cross Models to the Viscosity Data of Resin Solutions*

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SYNOPSIS

In this study, three popular rheological models, which fit adequately well to viscosity data of polymeric materials, are chosen for making a comparative assessment of their applicability to practical data. The resulting nonlinear equations of the three models are solved by using Levenberg Marquardt's algorithm. The assessment of their applicability to practical viscosity data of 66 solutions of two resins in 11 solvent systems and reported data of other polymers has been analyzed. The Carreau and Ellis models have yielded unique global estimates for various rheological parameters, whereas the Cross model yielded local solutions. However, both Carreau and Cross models yielded parameter estimates with low overall residual error. The three models are found to have good applicability to viscosity data of resin solutions in good and moderate solvents; however, some deviation is observed when they are tested for solvents in which the resin has poor solubility. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The knowledge about rheological flow behavior of polymer melts or solutions and the orientation of molecules in the course of processing applications helps in assessing the durability and performance of finished products. The data on such parameters are essential in predicting the life cycle of the material from its synthesis to processing, and, of course, to the end uses. Viscosity and normal stresses of polymer melts and solutions have been the subject of extensive studies in which usually the non-Newtonian changes induced by the steady shearing flow are attributed to the degree of chain entanglement. The viscosity coefficient depends on the rate of deformation of entanglements in systems that possess certain elastic properties. At sufficiently low or zero shear rate, the viscosity coefficient (η_0) is almost constant and it continues to decrease to a constant value of (η_∞) at increasingly high or infinite shear rates. The flow behavior of a non-Newtonian fluid can be practically characterized in terms of these parameters.

The elastic storage energy associated with a polymer fluid generates stresses when it is subjected to flow under shear. A good number of rheological models that take into account such conditions and describe the flow behavior of polymers,[1-3] melts,[4,5] suspended solids,[6] and biological fluids[7] under shear are available in the literature.[8,9] Some of them have theoretical foundations[10] but lack flexibility to accommodate viscosity data for a large class of non-Newtonian fluids. There are empirical models that correlate adequate viscosity data of various fluids through a number of meaningful parameters. A flow equation that meets the following requirements is likely to have wide range of applications:

(a) It should accommodate experimental data over a wide range of shear rates.

(b) It should have a minimum number of independent constants.

(c) The appropriate constants could be readily evaluated.

(d) The constants should have a real physical significance.

Carreau and Kee[11] presented an uniform notation of some of the successful models. They evaluated them in terms of their ability to simultaneously de-

scribe some or most of the rheological functions such as the non-Newtonian viscosity, the normal stress difference functions, the components of the complex viscosity, stress growth, and stress relaxation. They recommended the multiple parameter models proposed by Chen and Bogue,[12] Meister,[13] Carreau,[14] Acieino et al.,[15] Thien and Tanner,[16] and Macdonald[17] for describing adequately viscoelastic fluids under shear growth experiments.

In this study, the following three popular rheological models, which fit adequately well to viscosity data of polymeric materials, are chosen for assessing their applicability to practical data.

Carreau model[14]:

$$\frac{\eta}{\eta_0} = \frac{1}{[1 + (t_1 D)^2]^S} \tag{1}$$

Ellis model[8]:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (\tau_{12}/\tau_{1/2})^{\beta-1}} \tag{2}$$

Cross model[19]:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{[1 + \alpha D^{2/3}]} \tag{3}$$

Here, η is apparent viscosity, whereas η_0 and η_∞ are the viscosities at zero and infinite shear rates; D, the shear rate; t_1, a time constant; α, a constant associated with rupture of linkages; and S and β, dimensionless parameters. S is positive but less than 1, whereas β is greater than 1; $\tau_{1/2}$ is the shear stress at $\eta = \eta_0/2$, τ_{12} is the shear stress, and n is an adjustable exponent, which is taken as $\frac{2}{3}$.

In case one wants to use these models for graphical reproduction, they can be simplified further by considering their applicability under the following conditions:

1. At Fairly Low Shear Rates

The factor $(t_1 D)^2 \ll 1$ and eq. (1) becomes[18]

$$\eta = \eta_0 - \eta_0 S(t_1 D)^2 \tag{4}$$

where η is a linear function of D^2 with intercept η_0. Similarly, in eq. (2), $\tau_{12} \approx -\eta_0 D$ and it could be rewritten as[18]

$$\eta = \eta_0 - \eta_0 \left[\frac{\eta_0 D}{\tau_{1/2}}\right]^{\beta-1} \tag{5}$$

Here, η is a linear function of $D^{\beta-1}$ and η_0 can be obtained from the intercept when β is more than 1. The factor $[(\eta_\infty \alpha D^{2/3})]/\eta_0 \ll 1$ and eq. (3) takes the following form[19]:

$$\frac{1}{\eta} = \frac{1}{\eta_0} + \frac{\alpha D^{2/3}}{\eta_0} \tag{6}$$

in which $1/\eta$ is a linear function of $D^{2/3}$ with intercept $1/\eta_0$ and slope α/η_0.

2. At Very High Shear Rates

With increasing shear rates, apparent viscosity as predicted by eqs. (1) and (2) decreases and tends to zero; however, the models could be corrected by the inclusion of a term η_∞, infinite shear viscosity, to the following forms:

$$\frac{(\eta - \eta_\infty)}{(\eta_0 - \eta_\infty)} = \frac{1}{[1 + (t_1 D)^2]^S} \tag{7}$$

$$\frac{(\eta - \eta_\infty)}{(\eta_0 - \eta_\infty)} = \frac{1}{[1 + (\tau_{12}/\tau_{1/2})^{\beta-1}]} \tag{8}$$

The Cross model already includes the term η_∞ and it reduces to the following form at high shear rates[19]:

$$\eta = \eta_\infty + \frac{[\eta_0 - \eta_\infty]}{\alpha} D^{-2/3} \tag{9}$$

with η being a linear function of $D^{-2/3}$ and intercept η_∞.

The above three are well-established models and their applicability to practical data has been studied by those who proposed them as well as by others. The review of a part of the reported literature on these models projects the scope of their general applicability.

In their analysis of rheological equations, Carreau et al.[18] are of the opinion that the Ellis and Carreau models are more flexible and capable of characterizing non-Newtonian fluids. They further asserted that with the accessibility to computers the above models can conveniently replace the use of power-law expression. Rudin and Chee[20] used the well-known extrapolation methods of Ferry[21] and Cross[22] for linearizing the experimental non-Newtonian data. They found that the Cross model yielded linear plots because of the adjustable exponent n in the Cross equation. When n is $\frac{2}{3}$, Cross[22] found that his

model could be applied successfully to the published data. Narender[23] found that the Cross extrapolation model yielded linear plots when it was applied to polyamide resin solutions and to paint dispersions. Cross,[24,25] while discussing the applicability of his model in the light of molecular weight and polydispersibility of polymers, reported that the exponent n was dependent on molecular weight distribution and degree of dispersity of the polymer molecules. He found that n tends to a value of 1 when his model is applied to monodispersed linear polymers. However, when he applied his model to experimental data for a wide range of pseudoplastic systems including polymer dispersions, polymer systems, and molten polymers the exponent n had a value of $\frac{2}{3}$.

The Cross model that has been analyzed in this paper was used earlier[26,27] to study the rheological behavior of alkyd resins in different solvents to establish a relationship between rheological parameters of resins and solubility parameter of solvents. The results produced a good relationship between rheological parameters of the resin and the solubility parameters of solvents in which it was dissolved. The graphical extrapolation of the relationship was used as an indirect method for deriving the solubility parameter value for the resin.

EVALUATION OF RHEOLOGICAL MODELS

The resulting nonlinear equations obtained in all the three models could be solved by Gauss–Newton, steepest descent, or the Marquardt's method.[11] The Gauss–Newton converges only for very good initial guess values and the steepest descent may require a prohibitive amount of computer time. Hence, Levenberg Marquardt's algorithm[28] (a variation of gradient method) is chosen to solve the system of nonlinear equations. In this model, the partial derivatives of errors with respect to the variables to be evaluated are estimated to create a Jacobian matrix, J. For each variable, the Gauss–Newton step "s" is calculated and then the next current estimate x is calculated. In the matrix notation, this is equivalent to solving

$$J \cdot s = -f(x) \qquad (10)$$

In the first step, x is the vector of initial guesses; at each subsequent step, the new x is old x plus "s." This requires the evaluation of the inverse of the Jacobian matrix.

However, this inversion fails sometimes, especially when there are more constraints than the variables to be solved. In such situations, an additional condition that

$$\sum_j d_j^2 s_j^2 \qquad (11)$$

be reduced to a minimum has been added. Here, d is the vector of weight factors computed from the norms of the columns of the Jacobian matrix. In this situation, "s" is computed to satisfy the minimization criterion as well as solving Newton equation with the Jacobian.

EXPERIMENTAL

Polymers

Semipolymerised 52% linseed oil–glycerol–phthalate polyester resin having an acid value of 10 mg of KOH/g and weight-average molecular weight of 8870 and polyamide resin, a reaction product of dilinoleic acid and ethylene diamine, having the weight-average molecular weight of 41,620 were used for studying their flow behavior. Certain characteristics of these resins are reported below:

Solvents

The following seven solvents, which have good, medium or poor solvency for the polyester resin, were selected.

Solvent	Solubility Parameter, δ (cal/cc)$^{1/2}$
1. Isobutyl butyrate	8.04
2. Cyclohexane	8.18
3. Butyl acetate	8.46
4. Ethyl acetate	9.10
5. Methyl ethyl ketone	9.27
6. Cyclohexanone	9.88
7. Butyl cellosolve	10.24

In the case of polyamide resin,[27] which has its δ = 9.90 (cal/cc)$^{1/2}$, the solubility parameter of the cosolvent systems was so adjusted[29] that it is almost equal to that of the resin:

Solvent Blends	Proportion of Solvents by Weight	Solubility Parameter, δ $(cal/cc)^{1/2}$
1. Butanol : toluene	(4.0 : 6.0)	9.90
2. Butanol : cyclohexane	(5.5 : 4.5)	9.92
3. Cyclohexanol : cyclohexane	(4.5 : 5.5)	9.90
4. Cyclohexanol : toluene	(4.0 : 6.0)	9.85

PROCEDURE

A solution was prepared by dissolving a certain amount of the resin in a solvent or in a cosolvent system. The homogeneous resin solution was passed through a closed fritted-glass-filtering unit to make it free from any suspending particles or undissolved material (resin/polymer). The weight fraction of resin in the solution was estimated after filtration. The solutions were stored in a room conditioned at $25 \pm 1°C$ for at least 24 h before conducting viscosity measurements at $25 \pm 0.1°C$ by using a Haake Rotovisco RV-12 Searyl-type rotational viscometer with M-500 measuring head and NV sensor system (double gap sensor) at different shear rates. The apparent viscosity and the shear rate data were calculated by using the methods given in the manual[30,31] supplied along with the viscometer.

RESULTS AND DISCUSSION

The viscosity–shear relationship is found to have an important bearing on the technological requirements of non-Newtonian fluids that exhibit pseudoplastic flow. There are many rheological models that describe this relationship; however, the selection of the most useful one for its application to practical data has no basic criterion. The models, i.e., eqs. (1)–(3), which describe the non-Newtonian viscosity–shear relationship well and appear to be the useful ones in yielding important fluid parameters for material characterization, are discussed below:

The functional dependence of models (1) and (3) is shear rate, whereas model (2) depends on shear stress, which is also indirectly related to the shear rate.

These models have been tested by analyzing the practical data with the help of a computer program. The output parameter, zero shear viscosity, η_0, being common in the three models, has been chosen as the basis of criterion for assessing their applicability to viscosity data.

The concept of η_0 is often used without an explicit definition; however, current theories attribute η_0 to an estimated Newtonian viscosity as it has zero shear history or when the material is subjected to vanishingly small stresses. Apparent viscosity data of polyester and polyamide resins in various solvents were fed to the computer program and parameters like η_0, η_∞, τ_1, S, τ_{12}, α, and β were obtained as output data. The values of these parameters reported in Tables I–IV and plotted in Figures 1–7 illustrate the relative applicability of these models to practical data.

Data in Tables I and II indicate a continuous increase in η_0 values with the concentration of polyester resin in different solvents as well as that of polyamide resin in solvent systems. The graphical representation of η_0 as a function of concentration for polyester resin solutions in Figure 1 shows that these models have good applicability to viscosity data of a resin solution in good solvents, whereas similar plots in Figure 2 exhibit slight (some) deviation among the plots when these models are tested for the resin solution in solvents in which the resin has poor solubility. The plots in Figures 3 and 4 represent η_0 vs. concentration data for polyamide resin show more or less similar features as observed in the case of polyester resin.

A careful analysis of η_0 data obtained by the three models indicates that the Carreau and Cross models have better applicability to apparent viscosity data of the resins in comparison to the Ellis model. These models are expected to be applicable to viscosity data of resin solutions over a wide range of concentration and shear rate. It is observed that these models have good applicability to systems below critical concentration limits. In an earlier publication,[32] the critical concentrations of these resins in various solvents or solvent systems have been reported. However, the viscosity data of concentrated resin solutions tested show that the Carreau and Cross models have better agreement in the output data in comparison to the Ellis model.

The error listed in Tables I and II is of much lower order when the data are analyzed by using the Carreau and Cross models compared to that of the Ellis model. In the case of resin solutions in different solvents, similar variations in η_0 and error are observed.

The values of η_0 obtained from the three models for the low and high concentration of the resin in individual solvents are plotted in the form of a bar chart in Figures 5 and 6 for polyester resin and in Figure 7 for polyamide resin. These plots project a representative illustration of the applicability of the three rheological models to the viscosity data of 66 solutions of the two resins in 11 solvent systems. All three models are found to describe well the vis-

Table I Results of the Carreau, Ellis, and Cross Models

Concn	Carreau Model		Ellis Model		Cross Model	
	η_0	Error	η_0	Error	η_0	Error
Ethyl acetate						
0.2510	14.096	1.195	12.492	2.047	14.293	0.495
0.2872	17.461	1.968	16.061	3.263	19.089	1.698
0.3564	15.357	0.731	16.659	0.889	15.153	0.571
0.4029	29.057	3.212	27.889	4.233	28.882	3.339
0.4563	40.289	2.075	40.363	2.488	39.492	2.156
0.5036	67.985	5.569	68.039	3.643	67.497	3.111
Cyclohexane						
0.2238	10.705	1.190	10.045	1.529	11.740	0.684
0.2370	13.880	0.646	13.258	1.084	14.873	0.594
0.2632	15.207	2.529	16.470	5.615	23.354	3.117
0.3091	24.107	1.546	28.090	2.615	26.686	2.107
0.3409	43.284	3.353	43.764	3.185	43.633	2.662
0.3770	81.050	2.197	95.151	2.352	86.419	2.398
Methyl ethyl ketone						
0.1606	4.845	0.206	4.825	0.286	5.185	0.186
0.2464	8.824	0.376	9.005	0.624	8.690	0.428
0.2591	9.754	0.492	10.081	0.758	10.553	0.448
0.3717	17.554	1.084	18.181	1.542	17.198	0.823
0.4097	21.231	0.664	21.617	0.754	21.713	0.487
Butyl cellosolve						
0.0515	14.440	1.736	13.528	2.074	16.291	0.793
0.1039	22.109	3.965	19.833	2.131	26.389	1.618
0.1531	22.898	1.925	21.915	1.831	23.437	1.917
0.2011	24.410	2.475	23.739	1.700	24.192	2.571
0.2501	37.132	4.227	35.635	1.746	37.196	4.348
0.3003	49.758	1.917	51.915	1.410	48.019	2.326
Butyl acetate						
0.0485	3.318	0.040	3.377	0.045	3.829	0.033
0.0943	5.119	0.283	4.770	0.424	5.154	0.307
0.1359	9.364	0.129	11.994	0.329	9.570	0.180
0.1721	9.824	1.443	8.963	1.707	11.201	0.934
0.2025	15.097	1.227	14.505	2.135	15.448	1.213
0.2368	21.901	3.789	19.478	5.280	24.803	3.315
0.2729	31.773	3.092	31.243	4.041	31.372	3.286
Isobutyl-n-butyrate						
0.0506	2.991	0.014	2.951	0.013	3.748	0.057
0.1050	5.011	0.124	5.592	0.216	5.894	0.106
0.1558	6.178	0.083	7.013	0.116	6.885	0.085
0.2010	10.754	0.691	11.486	1.196	12.376	0.596
0.2505	16.083	1.399	15.657	2.642	17.387	1.247
0.2942	27.531	2.642	26.914	1.874	27.663	2.722
0.3477	30.367	1.874	31.143	0.740	29.749	2.114
0.4067	104.740	0.740	109.854	0.890	103.075	0.919

Table I (Continued)

Concn	Carreau Model		Ellis Model		Cross Model	
	η_0	Error	η_0	Error	η_0	Error
Cyclohexanone						
0.0520	13.681	1.375	11.882	2.490	15.639	1.170
0.0957	13.739	0.513	14.781	1.021	12.978	0.699
0.1442	23.503	2.485	21.702	4.094	25.722	2.204
0.2005	29.615	1.005	32.121	1.725	28.650	1.249
0.2571	41.409	1.677	43.036	2.316	39.449	2.110
0.2959	59.927	1.404	66.762	2.228	56.549	2.108

Table II Results of the Carreau, Ellis, and Cross Models for Polyamide Solutions in Cosolvent

Concn	Carreau Model		Ellis Model		Cross Model	
	η_0	Error	η_0	Error	η_0	Error
Butanol : toluene (4 : 6)						
0.1106	15.433	3.181	13.217	4.320	18.529	2.682
0.1235	17.591	3.708	15.422	4.961	20.707	3.187
0.1361	20.486	4.826	16.943	6.748	21.270	3.138
0.1521	23.233	1.896	24.515	4.762	24.049	1.802
0.1680	26.233	3.555	24.515	4.762	27.559	3.380
0.1849	31.942	3.585	30.495	4.798	32.320	3.632
Butanol : cyclohexane (5.5 : 4.5)						
0.1160	21.103	3.309	19.104	4.529	23.238	2.995
0.1239	23.433	3.025	21.803	4.236	25.301	2.749
0.1330	26.242	2.353	25.488	3.204	26.140	2.463
0.1486	25.808	2.862	25.007	3.491	25.769	2.949
0.1573	33.403	4.604	31.312	5.815	34.319	4.557
0.1687	38.293	4.863	36.782	6.059	38.490	4.949
Cyclohexanol : Cyclohexane (4.5 : 5.5)						
0.0910	39.719	2.898	38.905	3.485	39.244	3.005
0.1027	47.345	3.419	47.582	4.143	46.441	3.738
0.1070	47.574	3.986	47.115	4.569	46.661	4.248
0.1111	53.964	1.210	57.539	1.574	51.907	1.629
0.1176	59.150	1.423	62.070	1.779	57.478	1.721
0.1250	71.145	1.492	80.115	2.348	68.584	2.066
Cyclohexanol : Toluene (4 : 6)						
0.1005	22.417	3.759	19.603	3.485	23.296	6.177
0.1178	25.954	3.317	24.303	4.610	25.623	3.571
0.1396	34.983	3.237	34.287	4.426	34.753	3.460
0.1605	43.892	1.577	46.251	2.165	42.347	1.936
0.1984	54.912	0.396	58.257	0.380	55.312	0.434
0.2257	83.185	1.742	88.656	2.229	81.158	2.130

Table III Results of the Carreau, Ellis, and Cross Models

	Carreau Model		Ellis Model		Cross Model	
Concn	t_1	S	τ_{12} ($\times 10^4$)	β	η_∞ ($\times 10^4$)	α
Ethyl acetate						
0.2510	0.004	0.165	1.89	2.303	0.358	0.007
0.2872	0.005	0.129	2.92	1.983	0.541	0.007
0.3564	0.006	0.035	75.54	1.378	0.297	0.001
0.4029	0.006	0.069	18.95	1.752	0.688	0.003
0.4563	0.006	0.041	77.95	1.594	0.923	0.001
0.5036	0.007	0.041	103.20	1.608	1.637	0.002
Cyclohexane						
0.2238	0.003	0.110	3.75	2.081	0.278	0.004
0.2370	0.004	0.126	3.06	1.986	0.397	0.005
0.2632	0.002	0.108	4.33	2.299	0.486	0.008
0.3091	0.002	0.044	32.86	1.522	0.619	0.002
0.3409	0.005	0.044	71.11	1.636	0.961	0.002
0.3770	0.001	0.029	1418.00	1.315	2.157	0.001
Methyl ethyl ketone						
0.1606	0.003	0.096	2.10	1.948	0.094	0.003
0.2464	0.005	0.091	2.65	1.681	0.232	0.003
0.2591	0.003	0.115	2.37	1.883	0.146	0.004
0.3717	0.005	0.072	9.85	1.598	0.686	0.002
0.4097	0.007	0.023	401.00	1.482	11.441	0.002
Butyl cellosolve						
0.0515	0.004	0.150	1.95	2.074	0.330	0.008
0.1039	0.006	0.161	2.15	2.131	0.880	0.012
0.1531	0.006	0.114	4.02	1.831	0.860	0.006
0.2011	0.006	0.072	14.30	1.700	1.424	0.003
0.2501	0.006	0.071	22.89	1.746	1.099	0.003
0.3003	0.009	0.036	178.80	1.410	13.752	0.002
Butyl acetate						
0.0485	0.001	0.128	1.96	2.395	0.168	0.002
0.0943	0.003	0.127	1.29	2.159	0.001	0.003
0.1359	0.006	0.129	0.54	1.627	0.891	0.007
0.1721	0.003	0.121	2.66	2.310	0.441	0.005
0.2025	0.006	0.116	2.50	1.836	0.487	0.006
0.2368	0.004	0.119	5.31	2.137	1.322	0.007
0.2729	0.006	0.057	32.96	1.635	2.947	0.002
Isobutyl-n-butyrate						
0.0506	0.001	0.417	1.09	3.695	0.085	0.003
0.1050	0.002	0.137	1.06	1.916	0.294	0.005
0.1558	0.002	0.107	2.15	1.754	0.318	0.003
0.2010	0.004	0.134	1.60	1.905	0.777	0.007
0.2505	0.005	0.126	2.44	1.886	0.408	0.007
0.2942	0.006	0.078	12.98	1.703	2.211	0.003
0.3477	0.006	0.051	39.60	1.530	2.294	0.002
0.4067	0.011	0.015	11,580.00	1.287	54.948	0.001

Table III (*Continued*)

	Carreau Model		Ellis Model		Cross Model	
Concn	t_1	S	τ_{12} ($\times 10^4$)	β	η_∞ ($\times 10^4$)	α
Cyclohexanone						
0.0520	0.006	0.166	1.28	2.209	0.088	0.010
0.0957	0.009	0.097	2.01	1.588	0.875	0.005
0.1442	0.006	0.126	3.85	1.969	1.858	0.008
0.2005	0.009	0.065	12.82	1.464	8.370	0.004
0.2571	0.009	0.041	98.84	1.424	8.882	0.002
0.2955	0.012	0.041	113.50	1.325	18.607	0.002

Table IV Results of the Carreau, Ellis, and Cross Models for Polyamide Solutions in Cosolvent

|	Carreau Model		Ellis Model		Cross Model	
Concn	t_1	S	τ_{12} ($\times 10^4$)	β	η_∞ ($\times 10^4$)	α
Butanol : Toluene (4 : 6)						
0.1106	0.004	0.137	3.138	2.394	0.086	0.007
0.1235	0.004	0.125	4.154	2.296	0.749	0.007
0.1361	0.004	0.150	4.037	2.489	1.225	0.008
0.1521	0.005	0.084	5.952	1.771	1.811	0.005
0.1680	0.005	0.084	11.870	1.886	3.931	0.004
0.1849	0.005	0.076	16.270	1.801	2.095	0.005
Butanol : Cyclohexane (5.5 : 4.5)						
0.1160	0.005	0.107	6.016	2.060	1.196	0.005
0.1239	0.005	0.096	7.635	1.912	4.077	0.006
0.1330	0.006	0.069	15.700	1.713	3.593	0.003
0.1486	0.005	0.052	31.220	1.717	3.867	0.002
0.1573	0.005	0.074	18.440	1.908	1.820	0.003
0.1687	0.005	0.058	38.960	1.739	3.853	0.002
Cyclohexanol : Cyclohexane (4.5 : 5.5)						
0.0910	0.006	0.048	49.540	1.696	6.685	0.002
0.1027	0.006	0.032	253.500	1.500	9.333	0.001
0.1070	0.007	0.027	303.200	1.570	2.210	0.001
0.1111	0.013	0.022	2281.000	1.272	22.880	0.001
0.1176	0.011	0.022	1667.000	1.314	32.640	0.002
0.1250	0.010	0.041	140.700	1.325	29.500	0.003
Cyclohexanol : Toluene (4 : 6)						
0.1005	0.004	0.154	3.585	2.282	0.027	0.004
0.1178	0.005	0.093	8.938	1.899	0.015	0.003
0.1396	0.006	0.067	23.640	1.679	6.917	0.003
0.1605	0.009	0.037	156.300	1.387	15.780	0.002
0.1984	0.004	0.020	2212.000	1.352	29.510	0.001
0.2257	0.013	0.019	6798.000	1.258	56.870	0.003

Ethyl Acetate
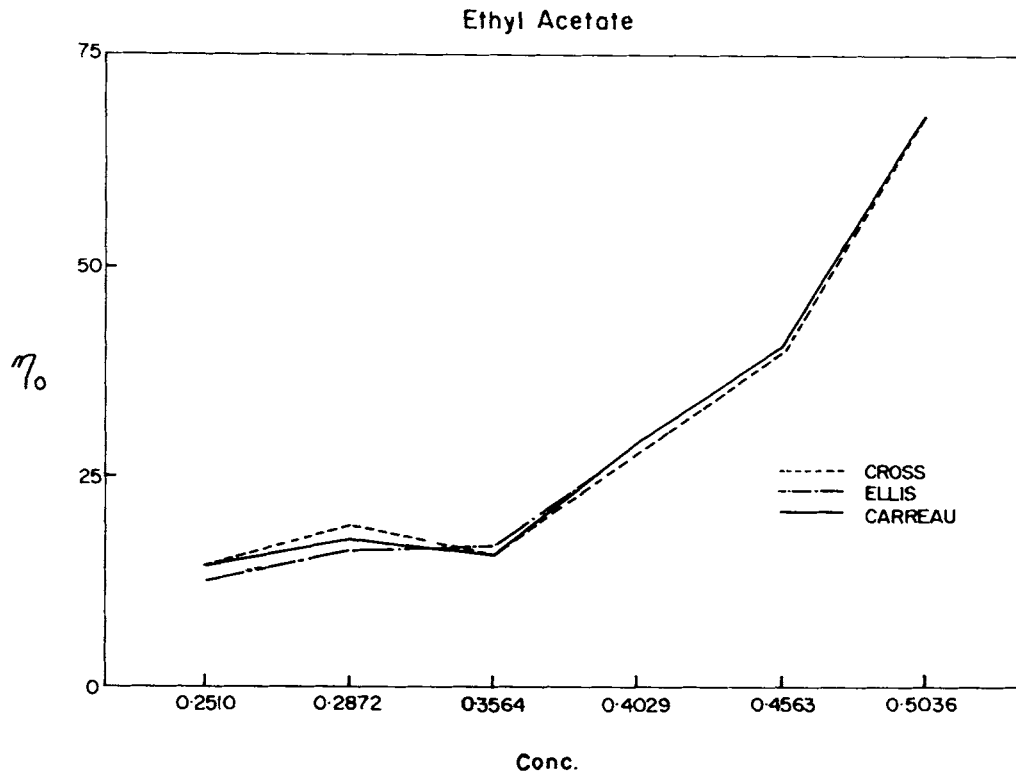
Figure 1   Graphical representation of η_0 data of polyester resin in a good solvent obtained from the three models as a function of concentration.
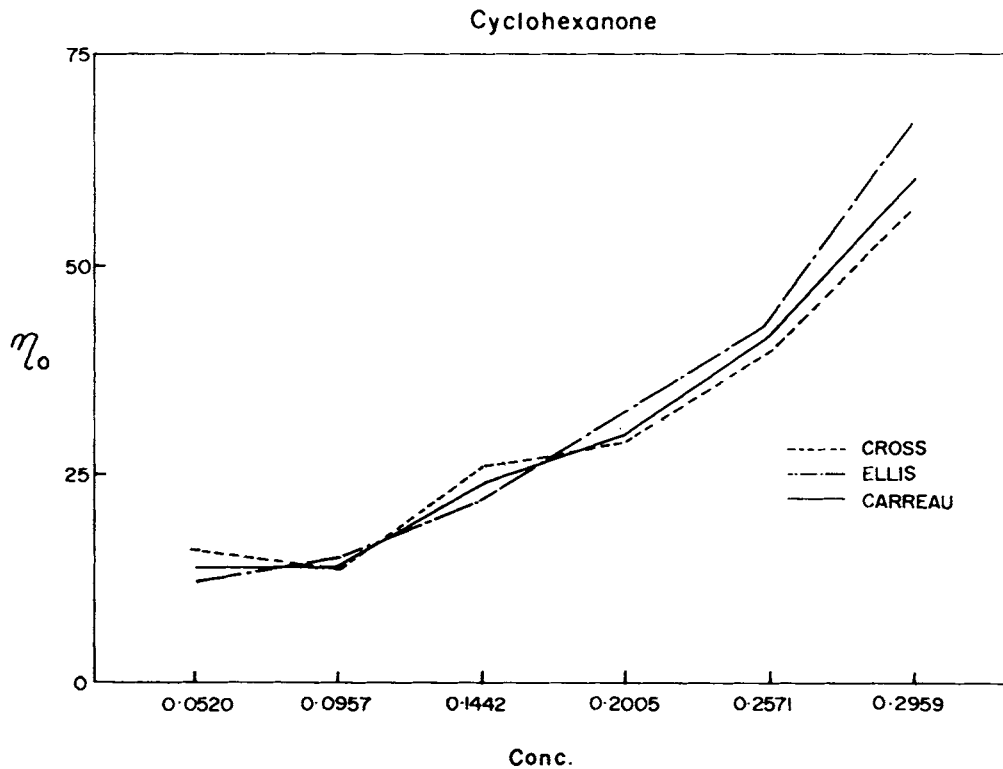
Cyclohexanone

Figure 2   Graphical representation of η_0 data of polyester resin in a poor solvent obtained from the three models as a function of concentration.
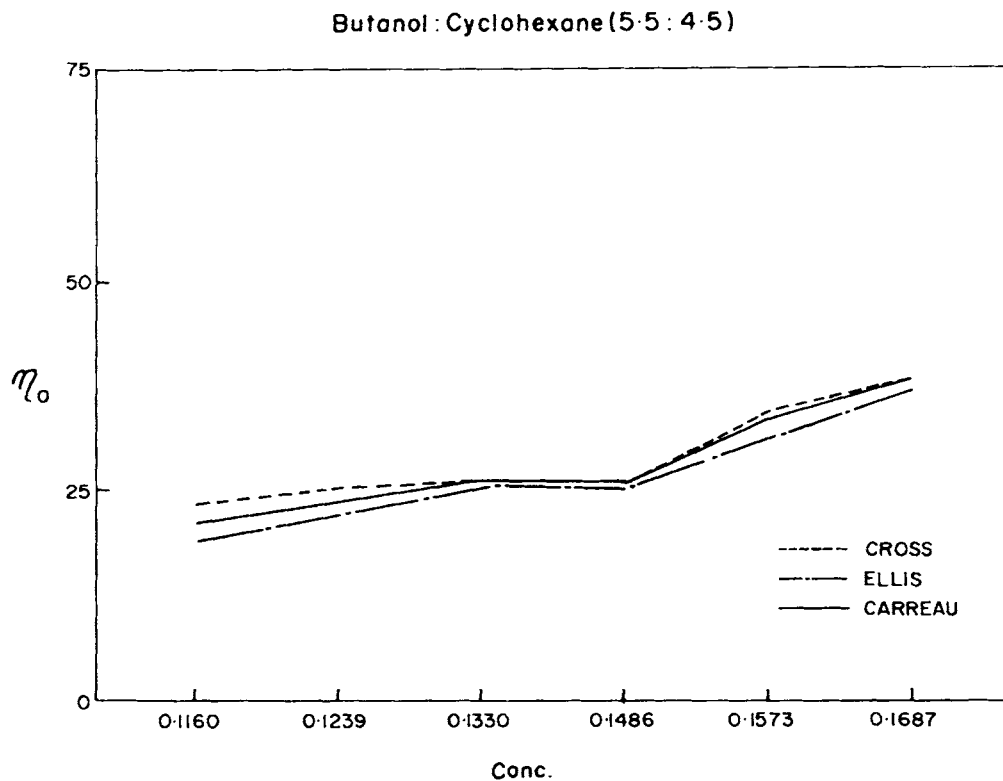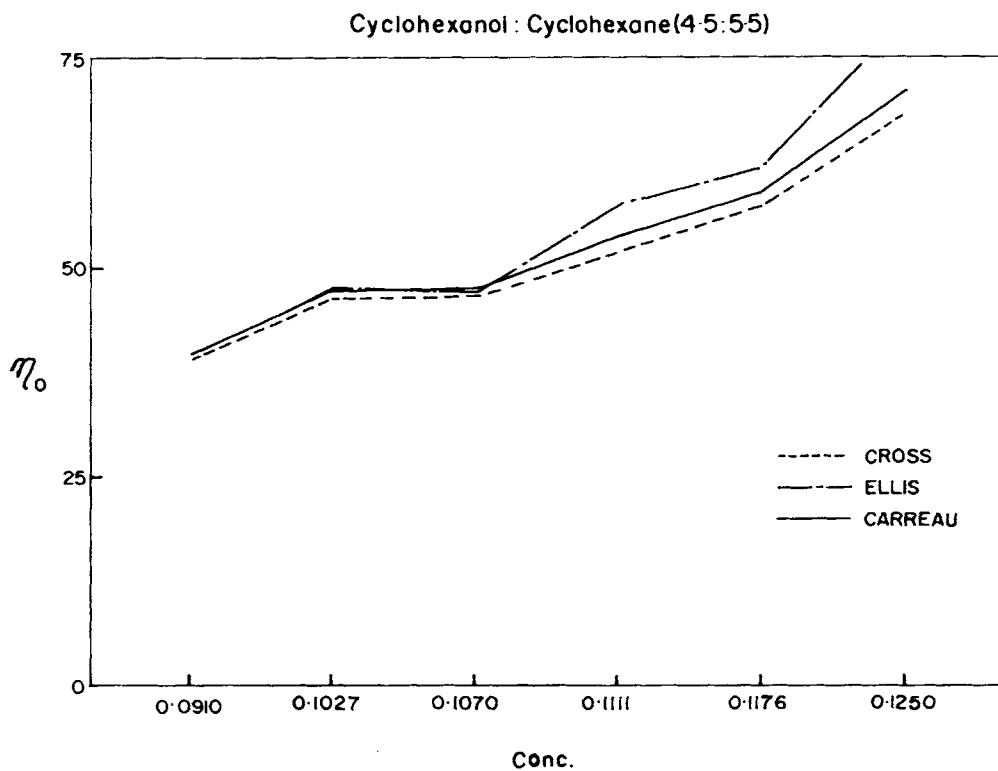
Butanol : Cyclohexane (5·5 : 4·5)

Figure 3   Graphical representation of η_0 data of polyamide resin in a good solvent system obtained from the three models as a function of concentration.

Cyclohexanol : Cyclohexane (4·5 : 5·5)

Figure 4   Graphical representation of η_0 data of polyamide in a poor solvent system obtained from the three models as a function of concentration.
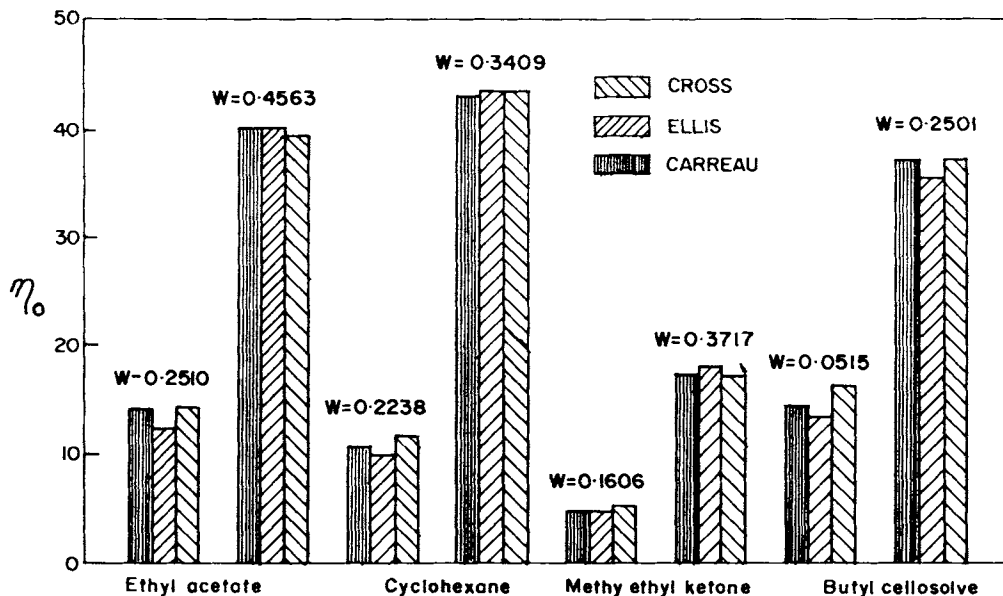
Figure 5   Comparisons of three models for low- and high-weight fractions (w) of polyester resin in different solvents.

cosity data in the form of output parameter, η_0. A careful overview of the illustration of η_0 data indicates that Carreau model has a little edge over the Ellis and Cross models.

Rheological Parameters Other Than η_0

Like η_0 in Tables I and II, parameters in Tables III and IV could not be used for direct comparison of the three models. However, the time constant, t_1,

obtained from the Carreau model, is closely related to the elastic time constant for most polymeric materials[14] and it is similar in magnitude to the Cross model's rupture constant, α, a parameter associated with the rupture of linkages. The shear stress, τ_{12}, of the Ellis model and η_∞ of the Cross model may be considered for indirect comparison as τ_{12} and η_∞ increase with concentration of the resin in the solution. S and β are associated with the power-law behavior of pseudoplastic materials. The
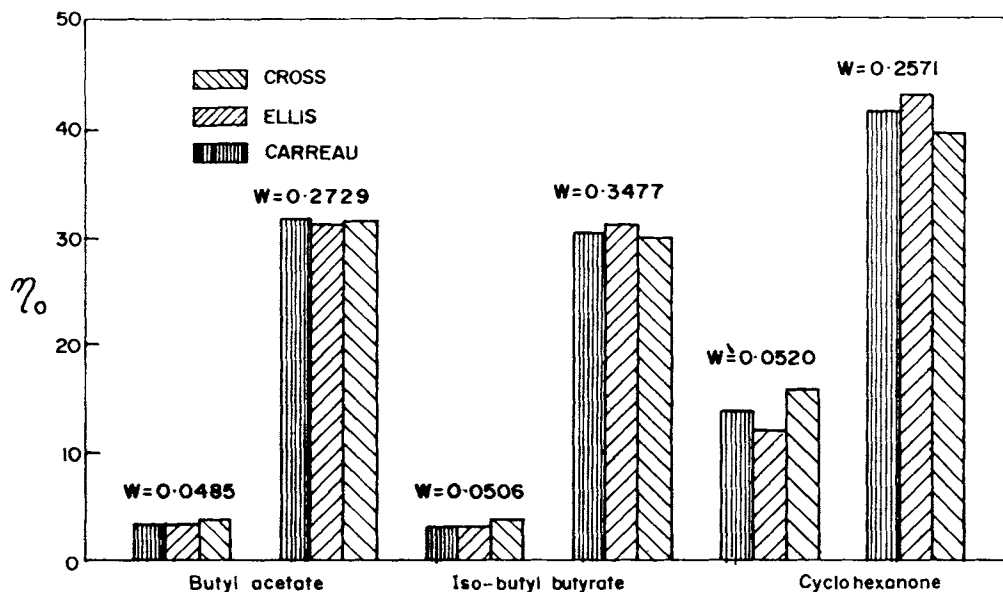

Figure 6   Comparisons of three models for low- and high-weight fractions (w) of polyester resin in different solvents.
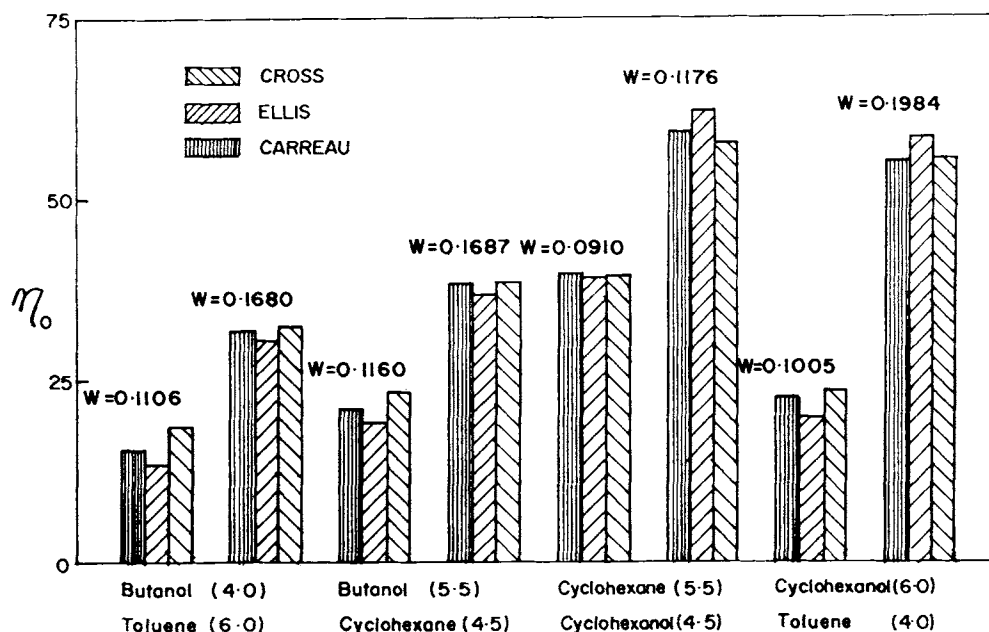
Figure 7   Comparisons of three models for low- and high-weight fractions (w) of polyamide resin in different solvents.

two parameters τ_{12} and $\tau_{1/2}$ of the Ellis model are related to the shear stress buildup in the system during the processing operation.

Infinite shear viscosity, η_∞, in the Cross model is a significant physical parameter. It has its importance in terms of shear thinning of a polymer solution when the viscosity becomes independent of shear rates. From the engineering application point of view, its importance arises when a polymer melt or solution is stirred to the extent that it becomes free from entanglement and the molecules become oriented to impart optimum physical strength to the finished product.

Applicability of These Models to the Reported Data of Polymers

The applicability of these models was also tested by using reported practical data[33] on solutions of three polymers, i.e., poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) in toluene at room temperature obtained by using a rotational viscometer.

Since the authors did not report the experimental data on viscosity at different shear rates, they were derived from the viscosity vs. shear rate plots. The logarithmic values of viscosity were used, to reduce the scale and the problem of overflow, while doing the computations of data for applying the models to

solutions of the first two polymers. The parameter estimates obtained for the three models are presented in Table V.

A careful assessment of data reveals that all the three models have given reliable parameter estimates, though there are some variations in the η_0 estimates. This is because of the likely variation in

Table V   Results of Carreau, Ellis, and Cross Models for Different Polymers

Carreau Model	Ellis Model	Cross Model
Poly(methyl methacrylate)		
$\eta_0 = 2.715$	$\eta_0 = 1.868$	$\eta_0 = 2.698$
$t_1 = 0.0008$	$\tau_{12} = 5.434 \times 10^3$	$\eta_\infty = 0.107$
$S = 0.305$	$\beta = 8.178$	$\alpha = 0.032$
Error = 0.028	Error = 0.801	Error = 0.032
Polystyrene		
$\eta_0 = 1.761$	$\eta_0 = 1.638$	$\eta_0 = 1.234$
$t_1 = 0.066$	$\tau_{12} = 1.352 \times 10^5$	$\eta_\infty = 0.504$
$S = 0.087$	$\beta = 9.688$	$\alpha = 0.011$
Error = 0.850	Error = 0.827	Error = 0.009
Poly(vinyl acetate)		
$\eta_0 = 0.094$	$\eta_0 = 0.094$	$\eta_0 = 0.099$
$t_1 = 5.26 \times 10^{-7}$	$\tau_{12} = 9.582 \times 10^{-4}$	$\eta_\infty = 1.177 \times 10^{-6}$
$S = 0.015$	$\beta = 0.205$	$\alpha = 0.004$
Error = 0.003	Error = 0.003	Error = 0.003

Table VI   Cross-validation Results of Carreau, Ellis, and Cross Models for Different Solvents

Solvent	Carreau	Ellis	Cross
Ethyl acetate	−1.190	−1.549	0.611
Cyclohexane	0.031	−0.546	0.326
Methyl ethyl ketone	−0.275	−0.281	0.393
Butyl cellosolve	−0.491	−1.577	0.201
Butyl acetate	−0.159	−0.262	0.325
Isobutyl-n-butyrate	−0.117	−0.109	0.108
Cyclohexanone	−0.108	−0.398	−0.010
Butanol : Toluene (4 : 6)	−0.020	−0.717	0.350
Butanol : Cyclohexane (5.5 : 4.5)	−0.147	−1.179	0.972
Cyclohexanol : Cyclohexane (4.5 : 5.5)	0.465	0.074	−0.006
Cyclohexanol : Toluene (4 : 6)	−0.793	−1.806	2.871

the values of basic data on viscosities, shear stress, and shear rates that were derived from plots in the reported literature. The η_0 estimates for the solutions of the third polymer derived by these models are identical and the error is also the least. In the case of the solution of this polymer, the basic data required for testing applicability of the models were available.

Cross Validation

The three models have also been cross-validated with some test data and the results of these cross-validations are presented in Table VI for various solvents. This test gives the error that is obtained as a difference between the observed and predicted values, which were calculated for resin solutions in different solvents using the parameters estimated from the three models. The data in the table reveal that these models have predicted the results quite accurately.

CONCLUSIONS

It was observed that among the three models both the Carreau and Ellis models have yielded unique global estimates for the parameters, whereas the Cross model has yielded several different local solutions. Hence, in the case of the Cross model, the nearest solution to the Carreau and Ellis model solution was considered. This, in turn, means that both the Carreau and Ellis models appear to be more robust compared to the Cross model.

Among the three models considered in this study, both the Carreau and Cross models have yielded parameter estimates with low overall residual error.

However, since the Cross model has yielded only a local solution and not a global one, there is a need to improve the functional form of the model, which may give a unique global solution.

NOMENCLATURE

η	apparent viscosity
η_0	zero-shear viscosity
η_∞	infinite-shear viscosity
t_1	time constant in eq. (1)
D	shear rate
S	dimensionless parameter in eq. (1)
τ_{12}	shear stress
$\tau_{1/2}$	characteristic shear stress in eq. (2)
β	dimensionless parameter in eq. (2)
α	rupture constant in eq. (3)
J	Jacobian matrix
s	Gauss–Newton step
d	vector of weight factors
δ	solubility parameter

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