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# RHEOLOGICAL PROPERTIES & MOLECULAR WEIGHT DISTRIBUTIONS OF FOUR PERFLUORINATED THERMOPLASTIC POLYMERS<sup>†</sup>

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## Introduction

Dynamic viscosity measurements and molecular weight estimates have been made on four commercial, amorphous fluoropolymers with glass transitions ( $T_g$ ) above 100°C: Teflon AF 1600, Hyflon AD 60, Cytop A and Cytop M. These polymers are of interest as binders for the insensitive high explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) because of their high density and  $T_g$  above ambient, but within a suitable processing range of TATB.<sup>1-3</sup> As part of this effort, the rheological properties and molecular weight distributions of these polymers were evaluated.

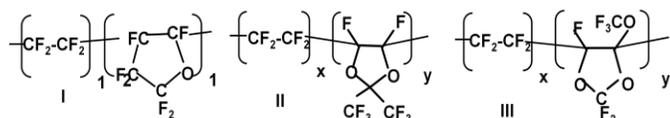
## Experimental

**Materials.** These fluoropolymers were purchased from their respective manufacturer or US affiliate. Teflon AF 1600 is manufactured by DuPont; Hyflon AD 60 is manufactured by Solvay-Solexus; and were used as received. The two Cytops are manufactured by Ashai Glass and distributed by Bellex Corporation as solutions in perfluorinated solvents and were dried at 110±5°C overnight prior to use. Flat disks were compression molded at approximately 20°C above  $T_g$ .

**Instrumentation.** All experiments were performed on a Rheometrics RMS 800 using 2.54 cm parallel plate fixturing under isothermal conditions with a frequency sweep from 0.1 to 100 rad/s. Five temperatures were scanned at 20°C increments from approximately 50 to 150°C above  $T_g$  starting at the highest temperature. Data from the five sets of curves was shifted in 2 dimensions using Rheometrics Orchestrator software version 6.5.4. No instrument expansion or Bagby corrections were made. Dynamic viscosity results, after time-temperature superposition, were fitted to Bueche, Carreau, and Ellis models using Orchestrator software. The extrapolated zero shear viscosity from these models is reported. The plateau modulus was estimated using  $G'$  at the minimum in  $G''$ .<sup>4,5</sup> Molecular weight distributions were estimated from the software using the Shultz distribution with a double reputation mixing rule, the plateau modulus estimated above, and an initial guess at polydispersity of 2.0.<sup>6,7</sup>

## Results and Discussion

**Chemical Structures** of Cytop (I), Teflon AF (II) and Hyflon AD (III) evaluated in this work are shown in **Figure 1**. As seen in the figure, these copolymers contain tetrafluoroethylene and cyclic perfluorofuran, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole,<sup>8</sup> or 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole rings,<sup>9</sup> respectively. To our knowledge, no rheological information has been published on the neat polymers. Because of their limited solubility, size exclusion chromatography (SEC) estimates of their molecular weight distributions are also unavailable.



**Figure 1.** Monomer repeat units of amorphous fluoropolymers Cytop (I), Teflon AF (II) and Hyflon AD contain 5 membered rings.

**Dynamic viscosity of amorphous fluoropolymers.** The dynamic viscosity of Teflon AF 1600 depicted in **Figure 2** was generated by time-temperature superposition of five sets of measurements from 0.1-100 rad/s from 200-300°C using 280°C as a reference temperature. Orchestrator software allows fitting  $\eta^*$  to several viscosity – frequency relationships including:

$$\eta^* = c_1 / \{1 + c_2 [c_3 \omega]^{c_4}\} \quad (\text{Beuche Eqn}) \quad (1)$$

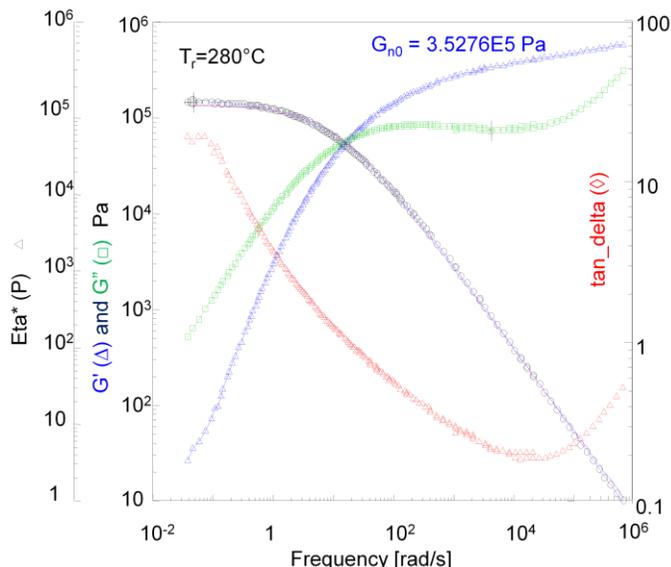
$$\eta^* = c_1 / \{1 + [\omega/c_2]^{c_3-1}\} \quad (\text{Ellis Eqn}) \quad (2)$$

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$$\eta^* = c_1 [1 + (c_2 \omega)^{c_3}]^{(c_4-1)/c_3} \quad (\text{Carreau Eqn}) \quad (3)$$

where  $c_1$  is the zero shear viscosity,  $c_2$ ,  $c_3$  and  $c_4$  are constants,  $\omega$  is the frequency in rad/s and  $\eta^*$  is the complex dynamic viscosity. Table 1 contains the results of fits to  $\eta^*$  for these four polymers and each of the 3 equations. All of the equations provide reasonable fits. Beuche and Ellis values of  $\eta_0$  were identical but Carreau was always higher. Reference temperatures for Hyflon and the two Cytop polymers were 240 and 210°C, respectively.



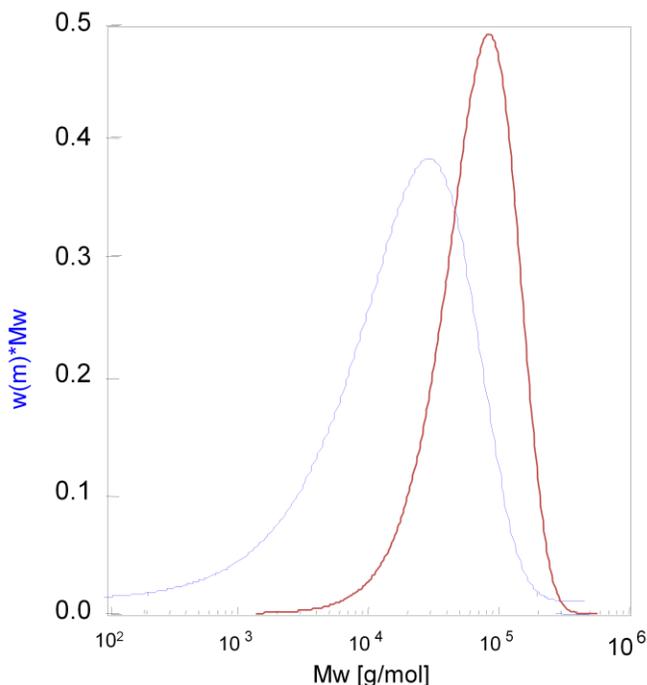
**Figure 2.** Teflon AF 1600 dynamic viscosity ( $\eta^*$ ), storage and loss moduli ( $G'$  and  $G''$ ) and tan delta as a function of frequency were compiled from two dimensional time-temperature superposition of measurements at 200-300°C.

**Table 1.** Similar  $\eta_0$  values were obtained from fitting various viscosity models to dynamic viscosity measurements on amorphous fluoropolymers.

Polymer	Eqn.	$c_1 = \eta_0$	$c_2$	$c_3$	$c_4$
Teflon AF	Beuche	1.43E+05	0.7422	0.15115	0.847
	Ellis	1.43E+05	9.4069	1.847	
	Carreau	1.65E+05	0.0870	0.62248	0.1129
Hyflon AD	Beuche	9503.42	1.0122	0.27362	0.7961
	Ellis	9503.46	3.5994	1.79614	
	Carreau	13136.8	0.2030	0.50225	0.1226
Cytop A	Beuche	1.33E+05	1.1381	0.38808	0.8195
	Ellis	1.33E+05	2.2003	1.81948	
	Carreau	1.87E+05	0.3388	0.50257	0.1019
Cytop M	Beuche	1.38E+04	2.1285	0.08366	0.7034
	Ellis	1.38E+04	4.0829	1.70338	
	Carreau	4.33E+04	0.0063	0.22694	-0.2082

**Molecular weight distributions** of these polymers were calculated using the synthesize molecular weight routine with the double reputation mixing rule assuming a Schultz distribution with an initial guess of  $M_w \sim 3 \times 10^4$ , polydispersity of 2 and a single Doi-Edwards term in the Orchestrator software. Initially, no Rouse term was used to fit the  $G'$  and  $G''$  data (see **Fig**

2 large squares and triangles). The plateau modulus ( $G_{\eta_0}$ ) was estimated as the value of  $G'(\omega)$  at the minimum in  $G''(\omega)$ , then adjusted slightly to minimize the residual error. Rouse terms were not used initially because when the entanglement molecular weight ( $M_e$ ) calculated from the plateau modulus and rubber elasticity theory were used, the results would not fit the data. Without Rouse terms, the best fits (least error) were from  $G_{\eta_0}$  greater than that calculated by Ferry's method because the Doi-Edwards behavior is only applicable to the plateau region of  $G'$ . As  $G_{\eta_0}$  is increased to improve the fit, the synthesized molecular weight distribution shifts to lower values (see **Figure 3** –blue trace) and polydispersity broadens well beyond that expected for free radical polymerizations.



**Figure 3.** Molecular weight distributions for Teflon AF 1600 calculated by (blue curve) varying  $G_{\eta_0}$  and minimizing the residual error without Rouse modes or (brown curve) using  $G_{\eta_0}$  from Ferry's method and minimizing residual error by adjusting the entanglement molecular weight.

Using Ferry's plateau modulus,  $G_{\eta_0}$ , but substantially lower entanglement molecular weight and reputation molecular weight narrows the distribution (red trace in **Figure 3**) and reduces the residual error. This brings the polydispersity closer to what one would expect for free radical polymerizations. The incorporation of Rouse modes also improves the fit to  $G''(\omega)$  vs  $\omega$  data in **Figure 2** (red curve). However the value for  $M_e$  calculated from rubber elasticity theory:

$$M_e = K\rho RT / G_{\eta_0} \quad (4)$$

where  $K=1$  or  $0.8$ ,  $\rho$  is the density,  $R$  is the gas constant and  $T$  is the temperature in degrees Kelvin is too high to produce good fits. For Teflon AF  $G_{\eta_0}$  of  $3.53E5$  Pa and  $K=0.8$  yields  $M_e$  of  $1.93E4$  Da. However  $M_e$  required for fitting  $G'$  and  $G''$  with Rouse modes in **Figure 2** was  $1.05E3$  Da. Fitting the  $G'$  and  $G''$  data without Rouse modes but requiring that  $G_{\eta_0}$  not change yields similar molecular weight distributions, but with errors as much as a factor of 8 higher than with Rouse modes. Table 2 lists molecular weight averages for Rouse mode fits for all 4 polymers. Entanglement molecular weights given in column 2 are for Rouse mode best fits to the data and were at least an order of magnitude lower than entanglement molecular weights from Equation 4 (shown in column 4). If these results can be believed, all of these polymers are relatively low molecular weight.

Polymer	$M_e / M_{rep}$	$M_n / G_{\eta_0}$	$M_w / M_e$	$M_z / PD$	Error / $T_{ref}$
Teflon AF	1050	9.50E3	3.47E4	4.39E4	4.36
w/ Rouse	2300	3.53E5	1.93E4	2.5	280
Hyflon AD	1260	9.60E3	3.94E4	6.97E4	13.9
w/ Rouse	2520	1.36E5	4.84E5	4.1	240
Cytop A	1700	1.39E4	4.86E4	8.36E4	6.1
w/ Rouse	3400	1.01E5	6.34E4	3.5	210
Cytop M	2100	3.93E3	2.77E4	5.23E4	24.74
w/ Rouse	4200	4.27E4	1.51E5	7.0	210

### Conclusions

The viscosity-frequency behavior of 4 amorphous fluoropolymers has been measured and fitted to 3 constitutive equations for viscosity. The molecular weights were calculated from the plateau modulus assuming a Schultz distribution and double reputation. The inclusion of Rouse modes in the molecular weight routine required about an order of magnitude lower values of  $M_e$  than predicted from rubber elasticity.

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