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Process Variability Effects on Tensile Response in Injection Molded, Fluorinated Thermoplastics

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KEYWORDS

copolymers, thermoplastics, mechanical properties, structure-property relationships, manufacturing, molding

ABSTRACT

The mechanical properties of fluorinated thermoplastics (i.e., tensile strength and elongation) can vary with changes in injection molding processing parameters. Four fluoropolymers are examined: poly(vinylidene fluoride) (PVDF) and random poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) with three CTFE concentrations. Dog bones were manufactured with various cylinder dwell times and mold cooling times to assess the manufacturing sensitivity to the tensile response. Dwell and cooling times increasingly impact mechanical performance as CTFE concentration increases. Specimens exhibit higher tensile strength as a function of injection order. The first injected specimen exhibits the lowest tensile strength and highest elongation in all copolymers. This trend becomes more pronounced among fluoropolymers with higher CTFE concentration and lower weight-averaged molecular weight. Parallel plate rheology was used to obtain the zero-shear viscosity as a function of material type, process, and injection order. We found that in the copolymers, the first injected sample exhibited a lower zero-shear viscosity than the next, which indicates a lower molecular weight in the first injected specimen. This phenomenon was not present for the PVDF homopolymer. Copolymer mechanical uncertainties are hypothesized to result from the shorter molecular weight chains extruding out of the specimens' sides as a flash due to higher mobility with CTFE segments.

1 | INTRODUCTION

Minimizing variations in injection-molded thermoplastics allow for reliable and consistent results when characterizing and manufacturing polymers and copolymers. Various parameters have been proven to affect the variations in injection-molded parts: cooling time, packing time, packing pressure, thermoplastic melt temperature, mold temperature, injection pressure, and injection speed.[1] Injection-molded part quality can be assessed quantitatively through part weight and thickness and qualitatively through defects such as shrinkage, warpage, sink marks, weld lines, burn marks, and textures.[2] Minimizing process variations and increasing quality in injection-molded thermoplastic parts results in mechanical consistency amongst various thermoplastic grades. PVDF-CTFE copolymer membranes in lithium batteries require mechanical strength, flexibility, and electromechanical stability.[3] Consistent manufacturing is necessary to achieve low variation in mechanical properties allowing investigation of structure-property relationships. Polarized thin sheets of PVDF are obtained through stretching and poling, which alters the alignment of molecular chains. These PVDF thin films have mechanical and electrical properties that vary with time, temperature, frequency, and stress.[4] Therefore, to maintain steady mechanical and electrical properties, it is essential for consistent and repeatable processing when manufacturing thin membranes and injection molding PVDF-CTFE for applications.

Poly(vinylidene fluoride) (PVDF) is a non-toxic, semi-crystalline thermoplastic fluoropolymer with high mechanical strength **(Figure 1a)**. It exhibits piezoelectric and pyroelectric properties and is resistive to ultraviolet radiation, chemical, and thermal reactions.[5] PVDF has many modern-day medical industry applications, including chemical processing, electronic components, nuclear waste management, and membrane separation technologies. PVDF can be processed into thin membranes and used as filters for water treatment plants, gas purification, food processing, and pharmaceuticals.[6] However, PVDF has disadvantages since it has poor alkali resistance, making it a poor material as a hydrophobic membrane.

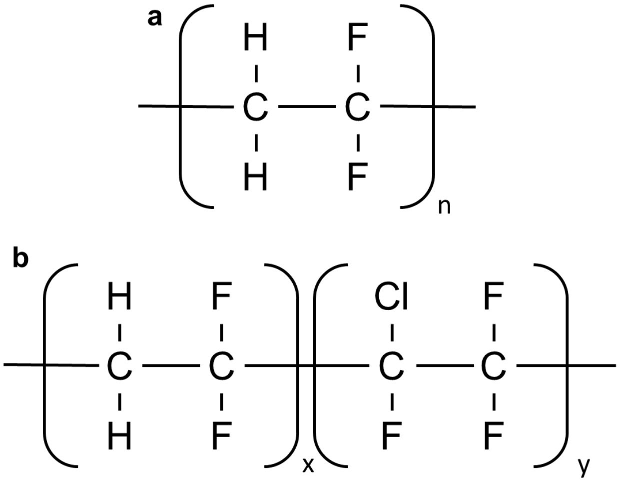

***Figure 1. (a)** PVDF and **(b)** PVDF-CTFE molecular structures.*

Poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) has a higher hydrophobicity and better alkali resistance than PVDF due to the CTFE chain segments, **(Figure 1b)**. The copolymer also has the advantage of being more processable than other PVDF additives.

In this work, we investigate the mechanical properties of PVDF and PVDF-CTFE thermoplastics produced by injection molding to assess the impact of dwell time on mechanical uncertainty. The injection molding process varied by changing the times the copolymer was heated in the cylinder (i.e., the dwell time) and the times the dog bones were allowed to cool before removing them from the mold (i.e., the cooling time). This work demonstrates CTFE's contribution to process sensitivity during injection molding on mechanical consistency.

2 | EXPERIMENTAL PROCEDURE

2.1 | MATERIALS AND METHODS

Three PVDF-CTFE concentrations were provided by 3M (Saint Paul, MN) in powdered form. Herein, the PVDF-CTFE materials will be referred to as Lots 17, 21, and 23, with CTFE molar percent concentrations of 73.7 %, 76.2 %, and 78.8 %, respectively. PVDF was provided by Arkema Innovative Chemistry (King of Prussia, PA). The grade used was Kynar 705 (referenced herein as K705) and arrived in pellet form. All materials were stored in a dark cabinet without any constant light source at 24 °C and 20 % humidity.

The pellets/powder of the four types of polymer/copolymers are packed into the 190 °C cylinder in stages to prevent bubbles in samples and allowed to rest before injection. This study examines tensile property sensitivity to injection molding parameters, specifically cylinder and mold dwell times. Five different resting and cooling processes are devised. Process A allows the material to rest in the cylinder for 15 minutes and cool in the mold after injection for 5 minutes. Process B rests for 15 minutes and cools for 15 minutes, Process C rests for 60 minutes and cools for 5 minutes, and Process D rests for 60 minutes and cools for 15 minutes. Process E is a duplicate of Process A but with an initial injection pressure of 700 bar for 15 seconds and no post pressure under the same cylinder/mold temperature conditions previously mentioned. Each procedure is summarized in **Table 1**.

Table 1. *Summary of cylinder and cooling times for Procedures A-E.*

Procedure	Cylinder (min)	Cooling (min)
A	15	5
B	15	15
C	60	5
D	60	15
E*	(Procedure A) 15 sec @ 700 Bar, no post pressure	

Figure 2. *The injection molder, cylinder, mold, and Type 3 dog bone specimen used in this study. In the upper right-hand side is a sample of K705 (left) and PVDF-CTFE (right).*

A Thermo Scientific HAAKE MiniJet Pro was used for injection molding Type 3 tensile dog bone specimens, as shown in **Figure 2**. The mold produced a sample with a cross-sectional gauge area of 1.6 x 5.0 mm and an overall length of 90.0 mm. Molds are coated with a PTFE lubricant (DuPont, Wilmington, DE) to minimize surface damage to the dog bones upon mold extraction. Each process uses one filled cylinder (yielding 6-

7 specimens), with the specimen number designations representing the order of specimen injection from the cylinder. The material is injected into a 90 °C mold with an initial pressure of 700 bar (i.e., 70 MPa) for 60 seconds and a post pressure of 200 bar (i.e., 20 MPa) for 10 seconds, excluding the pressure variation in Process E. The mold is extracted from the MiniJet Pro and cooled with a fan on a tabletop at approximately 24 °C.

Once cooled for the time specified by the process type (i.e., A-E), the specimens are extracted from the mold, with the flashes measured and flash/gates trimmed. Specimen length, width, height, and flash measurements are recorded. Each specimen is labeled with the injection order number and stored in a sealed container within a freezer to reduce crystallization and moisture exposure before testing.[7]

Tensile testing is performed with an Instron 5569 with oven at a constant 40 °C with a load cell of 2 kN and head speed of 500 mm/min. The oven has a testing strain limit of 178.50 mm or 521.47 % of the original specimen length before the grip collides with the inside oven ceiling, which automatically terminates the test. Testing was consistent with the American Society for Testing and Materials (ASTM) D638 standard. The fixture separation and the length from clamps are set to 27.19 mm and 34.23 mm, respectively. The specimen is inserted into the clamps within the oven and allowed to reach thermal equilibrium for 5 minutes before the stress/strain testing commences. Data is saved as a .csv file and processed through a custom MATLAB program for ultimate tensile strength, elongation at fracture, and modulus analysis. All corresponding moduli data can be found in **Figures S2** and **S3** in the supporting information.

2.2 | GEL PERMEATION CHROMATOGRAPHY

Molecular weights were determined with gel permeation chromatography implemented in two different laboratories. Samples were dissolved in tetrahydrofuran or ethyl acetate at 5 mg/mL and then filtered. Commercial columns with polystyrene-divinylbenzene packing were used for separation, and molecular weight parameters were determined relative to polystyrene standards using signals from the refractive index or evaporative light scattering detectors. A specific lot of FK-800 that had been measured with all the different method variations was used to standardize measurements taken by the different laboratories or in cases where the laboratory methods had to be modified due to column or solvent availability.

2.3 | PARALLEL PLATE RHEOLOGY

Rheology pucks were injection molded per Process A and Process D into disk molds (D = 30 mm, t = 1.5 mm). Due to expansion, puck thickness was nominally 1.75 mm upon retrieval. Here, we examined the first and second injected specimens for comparison. Pucks were then cut to size with an 18 mm die press. Rheology was performed on a HAAKE Mars parallel plate rheometer (Thermo Fisher Scientific) using 20 mm parallel plates and a stage heated to 210 °C. Pucks were placed on a preheated bottom plate, and the top plate was placed in contact with the puck (nominal plate gap of 1.75 mm). A heated hood enclosed the system, and the puck was allowed to heat for 5 minutes to ensure a homogeneous melt. The plate gap was then reduced to 1.5 mm before testing to ensure the molten polymer reached the edge of the 20 mm top plate. The procedure used was a constant deformation (τ_o = 1 Pa) frequency sweep (ω = 0.25 – 100 rad/s) where complex viscosity was monitored as a function of frequency.

2.4 | SPECIMEN AND TESTING

All injection-molded PVDF-CTFE Lots are observed to be almost entirely transparent with a slight, almost imperceptible brown tinting, indicating an amorphous morphology. All K705 specimens are white opaque, which indicates crystallization. The values in **Table 2** are the calculated mean values with a standard deviation of the specimens mechanically tensile tested for ultimate tensile strength in MPa, elongation at fracture as a percentage of original specimen length, and Young's Modulus in MPa. An attempt is made to produce a total of seven specimens for each of the processes and each of the materials. Data from specimens that slipped out of the grips during testing was rejected. Each process is detailed in the Supporting Information.

3 | RESULTS AND DISCUSSION

3.1 | AVERAGES AND STANDARD DEVIATIONS

Table 2 shows the average and one standard deviation for each material type and process. PVDF-CTFE Lots with higher CTFE concentrations demonstrate statistically significantly higher strength values than Lots with lower concentrations. As CTFE concentration increases, the standard deviation of tensile strength increases. The strength values for K705 experience the lowest standard deviations through each process compared with the average strength value. Specifically, for Process A, the deviation in strength is 0.65% (i.e., 0.32 MPa /48.52 MPa = 0.65%). For the PVDF-CTFE lots, this percentage is 9.2%, 16.3%, and 30.2% as CTFE concentration increases. Due to the increasingly high strength deviations, next, we examined the strength of each dog bone as a function of extrusion order.

Table 2. *Mean material ultimate tensile strengths, elongations, and modulus per process with one standard deviation.*

Material	Process	Strength [MPa]	Elongation [%]	Modulus [MPa]
K705 (0.0 %)	A	48.52 ± 0.32	50.82 ± 4.59	2.76 ± 0.05
	B	49.46 ± 0.32	50.52 ± 7.27	2.92 ± 0.16
	C	49.48 ± 1.00	50.65 ± 6.22	2.25 ± 0.14
	D	48.60 ± 0.53	51.40 ± 4.49	2.39 ± 0.31
	E	47.90 ± 1.13	49.77 ± 9.80	2.38 ± 0.10
Lot 17 (73.7 %)	A	2.72 ± 0.25	428.93 ± 143.71	0.12 ± 0.02
	B	2.44 ± 0.60	458.97 ± 101.95	0.13 ± 0.04
	C	2.62 ± 0.69	448.47 ± 91.01	0.12 ± 0.02
	D	2.65 ± 0.53	360.86 ± 115.31	0.13 ± 0.03
	E	2.93 ± 0.70	307.83 ± 134.24	0.13 ± 0.05
Lot 21 (76.2 %)	A	4.43 ± 0.72	205.91 ± 96.67	0.31 ± 0.05
	B	3.73 ± 0.90	305.59 ± 172.56	0.26 ± 0.08
	C	4.60 ± 1.23	234.02 ± 159.88	0.30 ± 0.09
	D	4.48 ± 1.19	242.61 ± 153.87	0.30 ± 0.08
	E	4.80 ± 1.02	214.26 ± 155.36	0.30 ± 0.08
Lot 23 (78.8 %)	A	5.26 ± 1.59	197.68 ± 147.66	0.34 ± 0.10
	B	6.16 ± 1.67	197.61 ± 121.19	0.54 ± 0.13
	C	5.57 ± 1.96	199.50 ± 144.28	0.37 ± 0.15
	D	5.43 ± 1.79	197.15 ± 146.67	0.36 ± 0.13
	E	7.95 ± 2.83	159.59 ± 133.36	0.61 ± 0.20

3.2 | ORDER OF CYLINDER INJECTION

The first extruded specimen for all the PVDF-CTFE Lots exhibits the lowest tensile strength of all specimens per cylinder. Tensile strength variability for Lot 17 Process A between the first and subsequent dog bones had the lowest deviation for all processes. Lot 17 Processes B-E exhibited more pronounced differences between the first injected specimen and its subsequent dog bones from each cylinder. However, some leveling off in strength increases as injection order increases can be observed (**Figure 3**). Overall, Lot 17 had the smallest strength deviations for all the PVDF-CTFE materials studied. Lot 17 also contains the lowest CTFE concentration.

Lot 21 Processes A-E result in more significant increases in tensile strength from the first specimen to the subsequent injected specimens. Some leveling off was also observed from the tensile strength values towards the later end of the extruded specimens. The strength deviations from the first injected dog bone on is highest for Lot 23 and decreases for Lots 21 and 17, thus corroborating the large variation observed in the strength standard deviation as noted above.

Lot 23 experienced the largest sensitivity to process variation and injection order. Lot 23 also contains the highest concentration of CTFE studied here. Process A strength increase levels off after specimen 4 with a final increase at specimen 7. A staircase-pattern increase in strength can be observed in Processes B and D. Process C has a similar increase as Process A but has a probable outlier with specimen 5. Process E is observed to be less consistent but still increases tensile strength for specimens 1-3, with specimens 4 and 7 breaking the staircase-pattern trend. However, specimens 5 and 6 still seem to follow the staircase pattern similar to Processes A-D.

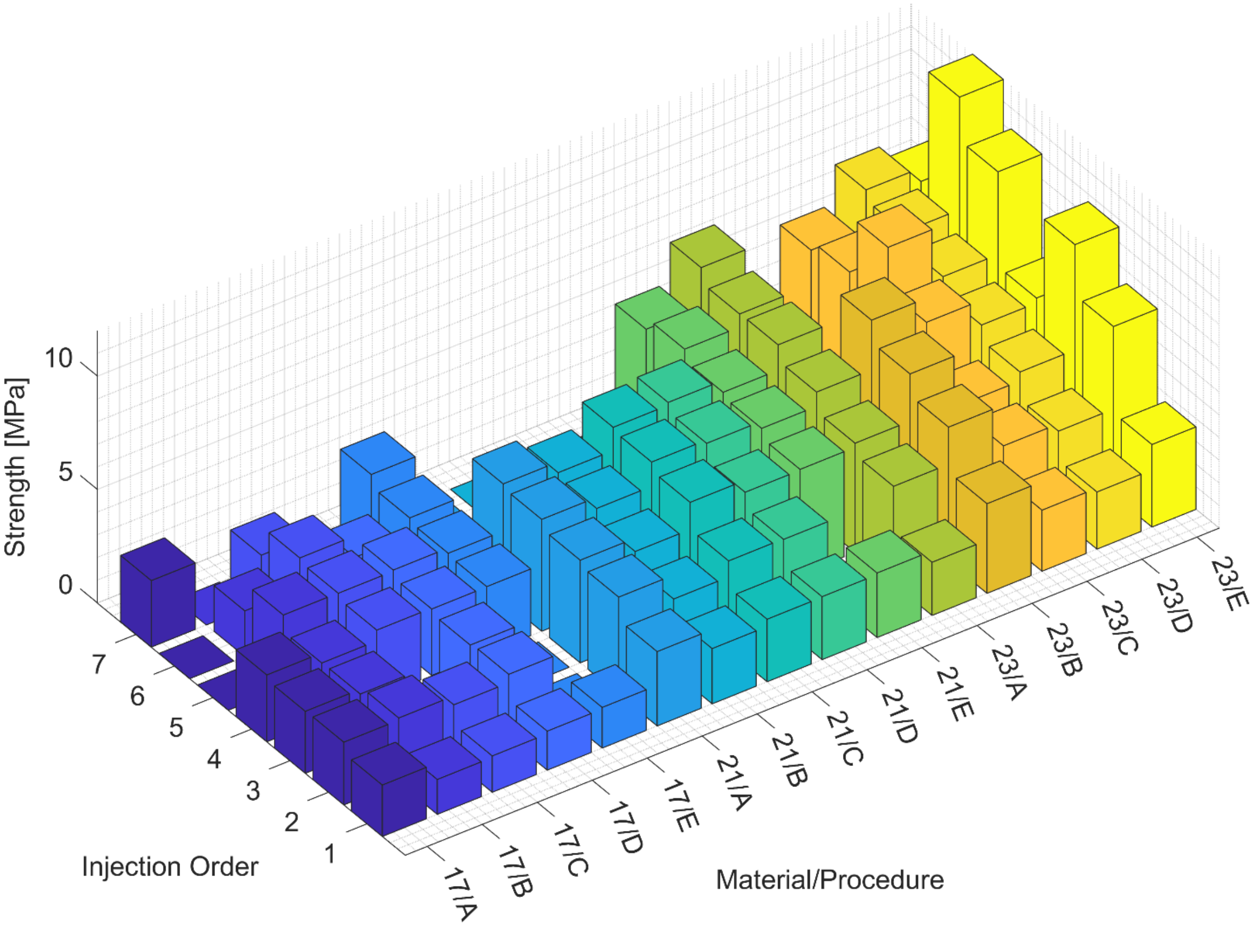

Figure 3. *Ultimate tensile strength by injection order for Processes A-E of PVDF-CTFE Lots.*

However, K705 did not result in any significant change in tensile strength from one extruded specimen to the next, **(Figure 4)**, suggesting that CTFE concentration significantly impacts the injection molding process. This postulation is further supported by the PVDF-CTFE Lots with lower percentages of CTFE, e.g., Lot 17, having a lesser impact on processing order versus the higher percentage CTFE Lot 23, except for the first injected specimen.

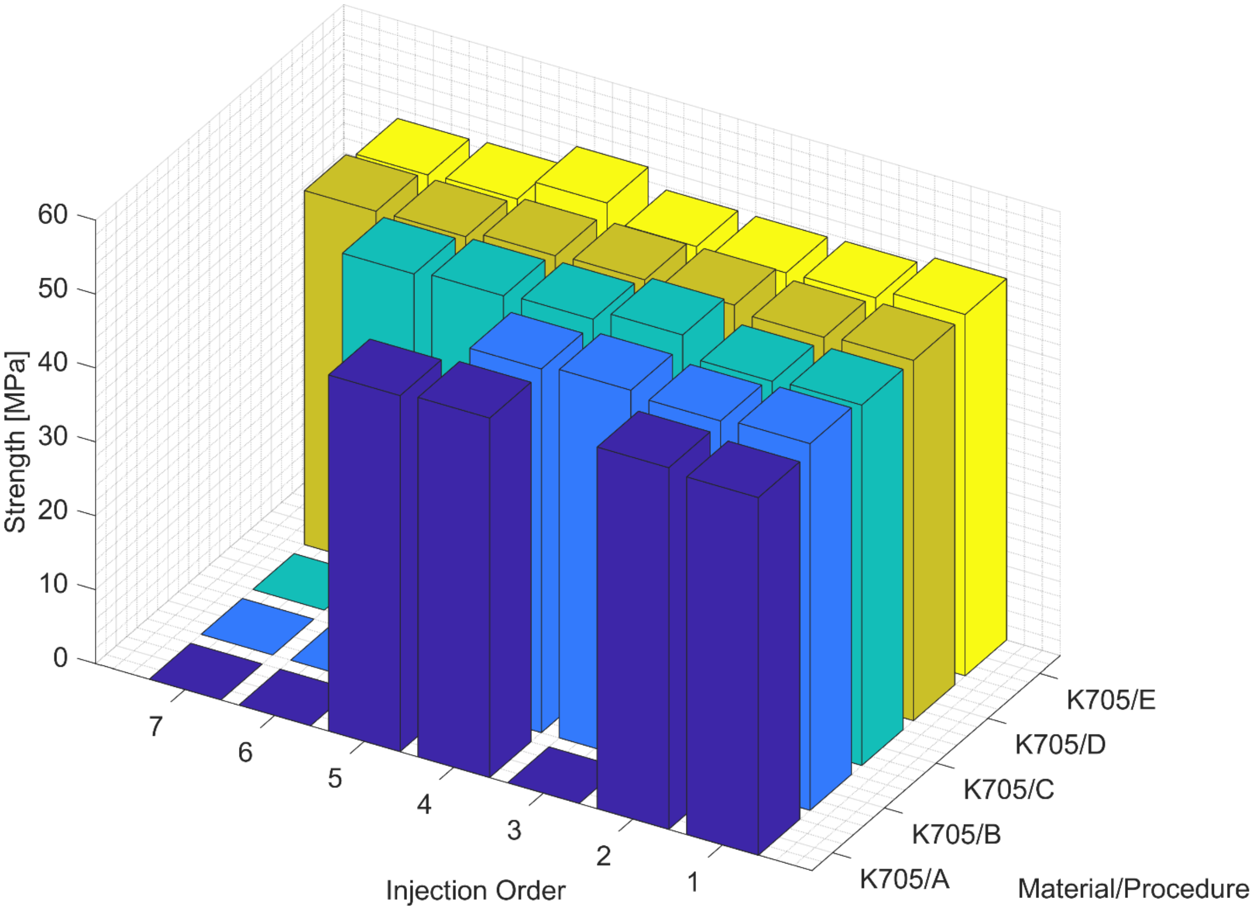

Figure 4. *Ultimate tensile strength by injection order for Processes A-E of K705.*

K705 does show some deviation in elongation between tested specimens for Processes A-E, **(Figure 5)**. Processes C and E may have the smallest elongations for the first injected specimens and the longest for the final injected specimen. However, this could be a coincidence considering there is no significant staircase pattern for Processes A, B, and D. This could result from normal elongation variability with stress/strain tensile testing versus other methods of determining copolymer mechanical properties.

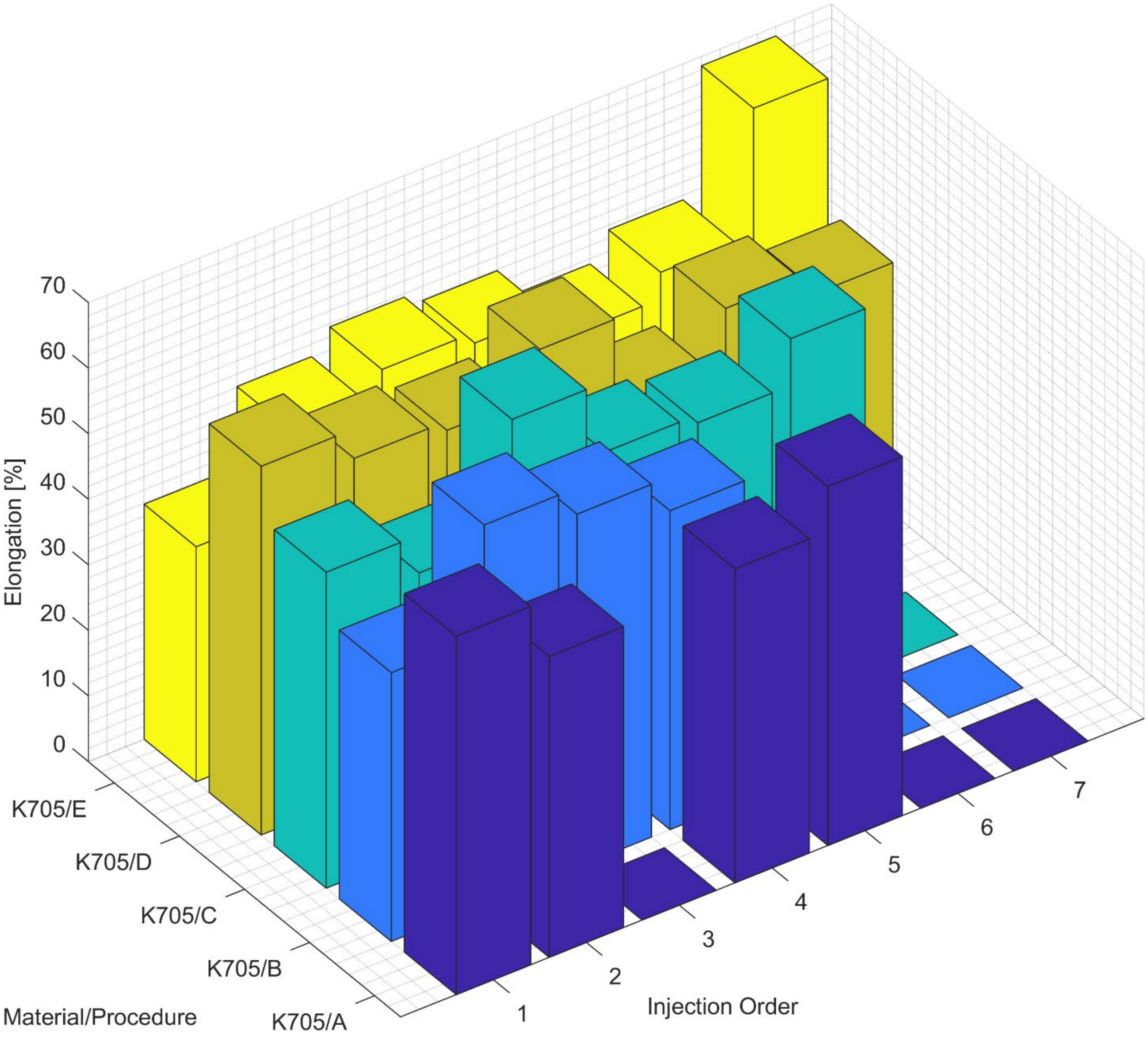

Figure 5. *Elongation at break by injection order for Processes A-E of K705.*

As with the tensile strength plots in **Figure 3**, there are noticeable trends in the elongation at fracture results for the first dog bone onward. The elongation results for Lot 17 are consistent with Process Lot 17 experiences the lowest elongation deviation compared with Lots 21 and 23 (with higher CTFE concentration).

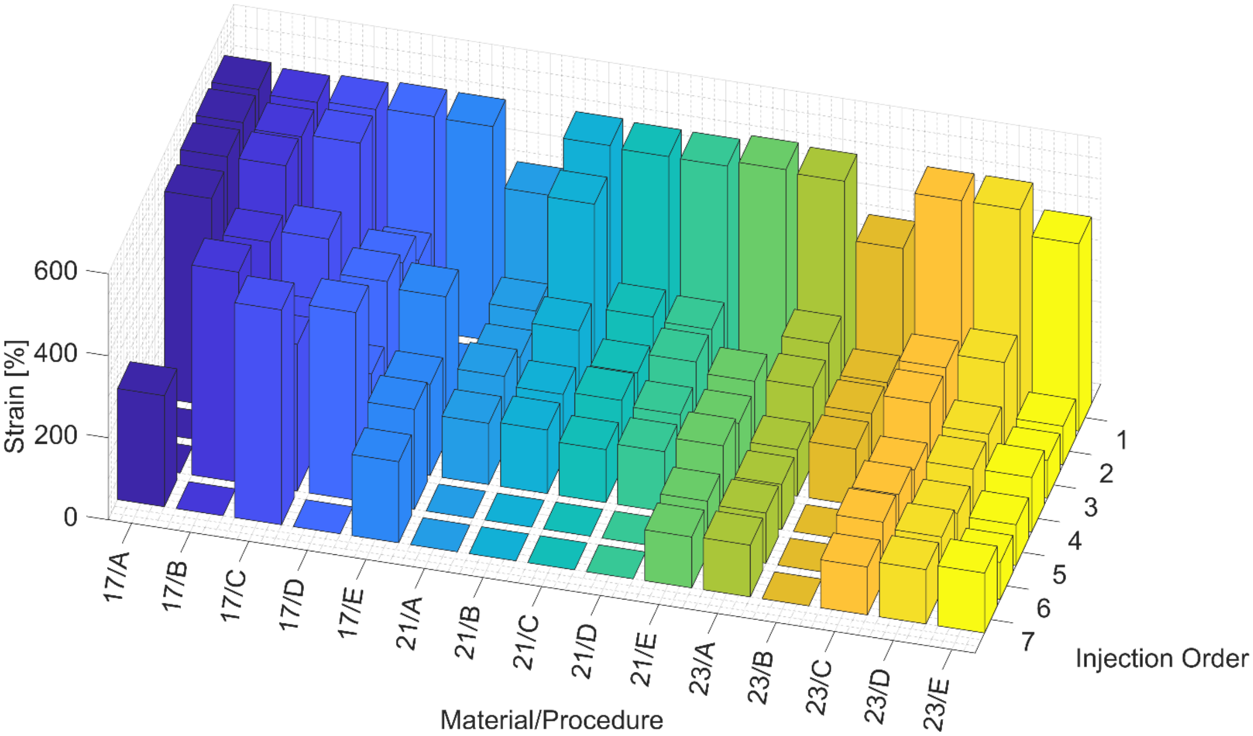

Figure 6. *Elongation at break by injection order for Processes A-E of PVDF-CTFE Lots.*

No discernable patterns in elongations are observed for K705, refer back to **Figure 5**, compared with the PVDF-CTFE Lots, (**Figure 6**). Again, the data suggests that CTFE concentration significantly impacts the injection molding process. Higher CTFE concentrations e.g., Lots 21 and 23, exhibit a noticeable trend, with the first extruded specimens elongating significantly more than the subsequent specimens. In contrast, CTFE absent and lower CTFE concentrations, e.g., K705 and Lot 17, do not have a discernable trend.

3.3 | INVESTIGATION OF AGGREGATE EFFECTS IN STRENGTH DEVIATIONS

To determine the key driver for mechanical deviations, we examine the strength deviation as a function of the molar percent CTFE concentrations (CTFE %), molecular weight (M_w), and polydispersity index (PDI) for each material (see **Table 3**). The molecular weight and dispersity values are reported from GPC experiments. Here, we discuss the impact of M_w on strength in reference to (1) the aggregate effects with respect to the M_w of each material (shown in **Table 3**) and (2) individual effects in each injected dog bone (discussed with the rheology below). The M_w referenced in **Figure 7** is determined from **Table 3** and assumed to be constant for each material since we consider the deviations of all processes simultaneously for each material. The strength deviations are taken from **Table 2**. The marker on each plot represents the average of each process deviation per material. For example, from **Table 2** for K705, this would be the average of 0.32 MPa (Process A), 0.32 MPa (Process B), 1.00 MPa (Process C), 0.53 MPa (Process D), and 1.13 MPa (Process E). The error bars represent one standard deviation of each of these values. The goal of this figure is to numerically visualize strength deviation across all processes for each material to determine if the molecular weight, dispersity, CTFE%, or a combination thereof is a driving factor for the observed variance.

The PDI values calculated are the ratio between weight-average molecular weight (M_w) and number-average molecular weight (M_n) (i.e., M_w/M_n). Chauvenet's criterion was used to calculate the outliers from the **Table 2** data and removed before generating Plots A-D in **Figure 7**. **Figure 7A-7C** plot the strength deviation as a function of M_w, PDI, and CTFE%. (The same plot for elongation is shown in **Figure S4**.) Subplot A displays the strength deviation as a function of M_w. There is a generally decreasing correlation between strength deviation and molecular weight. Upon examining strength deviation as a function of dispersity, no obvious trend emerges. For CTFE concentration, it appears that strength deviation correlates positively with CTFE%. However, in each case, there is no statistical significance due to the overlap in error bars. Since the same deviation values are used in each case, none of the variations can be considered statistically significant when taken as a whole. This means that to assess what is happening mechanistically, we must consider injection order rather than aggregate effects

***Table 3**. Sample PVDF and PVDF-CTFE percent concentrations, number-average molecular weights, weight-average molecular weights, and polydispersity.*

Material	CTFE %	M_n	M_w	PDI
K705	0	43800	83100	1.90
Lot 17	73.7	71446	108651	1.52
Lot 21	76.2	54519	90706	1.66
Lot 23	78.8	39564	78281	1.98

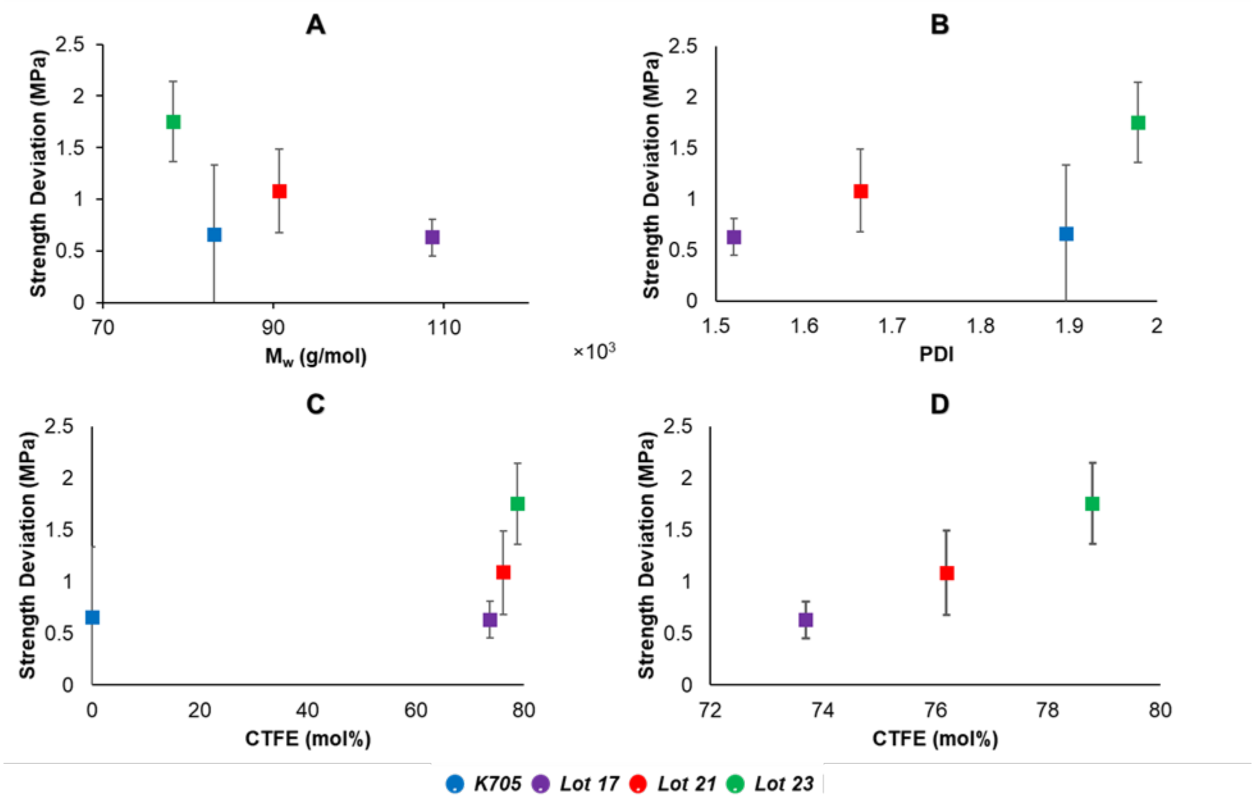

Figure 7. *Plots A-D represents one standard deviation of all process variances in tensile strengths for K705 (blue) and Lots 17 (purple), 21 (red), and 23 (green) taken for all process types (i.e., the standard deviation of tensile strength for Processes A-E). Plot A compares the sample deviations to the weight-average molecular weight (M_w). Plot B compares the sample deviations to the polydispersity index (M_w/M_n). Plot C compares the sample deviations to the CTFE molar concentrations. Plot D is a truncated view of Plot C.*

In general, we know that mechanical strength of a material is positively correlated with the size of its molecular chains, especially when the chains grow beyond the critical molecular weight for entanglement. This relationship is influenced by the degree of entanglement, which limits chain diffusivity, increasing their overall strength. However, other factors affecting polymer or copolymer tensile strengths include composition and arrangement, morphology and crystallinity, and processing conditions.[8]

3.5 | INJECTION ORDER EFFECTS AND MOLECULAR WEIGHT

In polymer melts and solutions, M_w can be ascertained using Equation 1, where η_o is the zero-shear viscosity and k and α are material and temperature-dependent parameters.

$$\eta_o = kM_w{}^{\alpha}$$

Injection-molded pucks followed Process A and Process D, where the first and second pucks were retrieved and tested via parallel plate melt rheology to assess η_o.

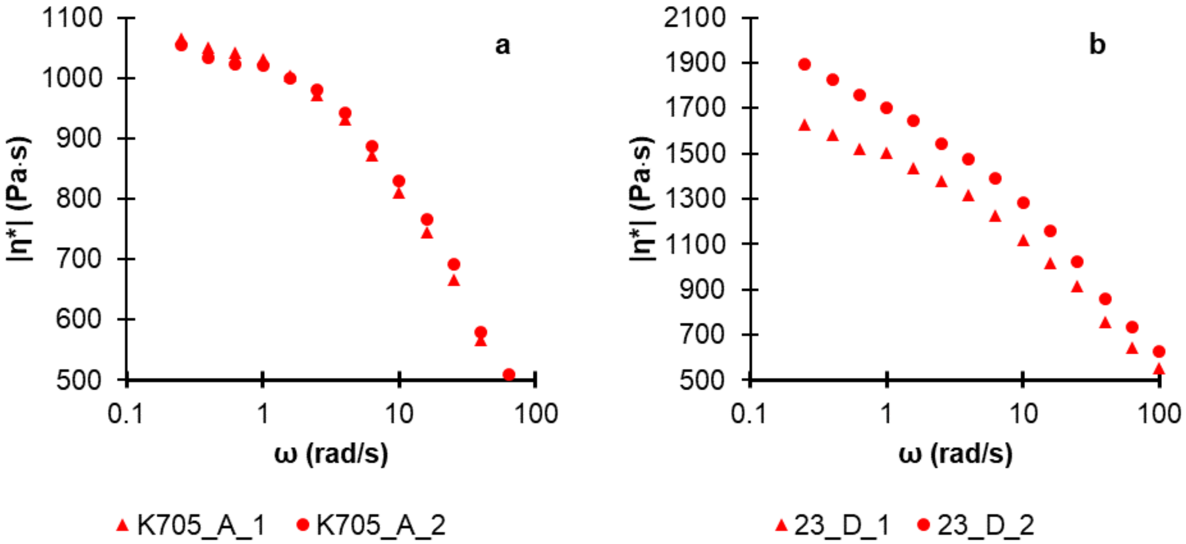

Figure 8. *Viscosity as a function of oscillation frequency for (a) K705 Process A (lowest strength deviation) and (b) Lot 23 Process D (highest strength deviation). The triangles represent the first injected sample, and the circles represent the second injected sample.*

Table 4. *Zero-shear viscosity for each material injection molded via Process A and Process D.*

Material	Process	Injection Order	η_o (Pa·s)	%difference
K705	A	1	1065	-1%
		2	1055	
	D	1	1056	-2%
		2	1040	
Lot 17	A	1	2135	15%
		2	2462	
	D	1	3017	24%
		2	3749	
Lot 21	A	1	2645	2%
		2	2695	
	D	1	2094	14%
		2	2393	
Lot 23	A	1	1909	7%

		2	2047	
	D	1	1626	16%
		2	1894	

Figure 8 shows viscosity plots for samples with the highest (Lot 23 Process D) and lowest (K705 Process A) strength deviations. Viscosity plots for all other samples are shown in **Figures S5-S8**. The viscosity evaluated at the lowest frequency (i.e., 0.25 rad/s) for each material, process, and injection order is shown in **Table 4**. In each case of the PVDF-CTFE copolymers (Lots 17, 21, and 23), the first injected puck exhibits a lower zero-shear viscosity than the second. This confirms that the M_w of the first injected component is lower than subsequentially injected pucks. Molecular weight variation is more prevalent in Process D than Process A, which is likely caused by the higher chain mobility because the polymer is exposed to a higher temperature for a longer period of time. The cylinder temperature is not sufficiently high to onset decomposition. The decomposition temperatures for Lot 17, Lot 21, and Lot 23 are 403 °C, 397 °C, and 386 °C, respectively. In the PVDF homopolymer (K705), the zero-shear viscosity is the same regardless of injection order. These findings are consistent with tensile strength findings, as decreasing M_w would also decrease tensile strength and increase elongation.

3.5 | FLASH LENGTHS

The flash lengths are measured from the longest point, usually closest to the gauge, of each specimen and displayed in **Table 5**. Flash occurrence was always found on either of the sample top corners with the gauge located between them. Additionally, smaller flash occurrences extended around the edges of all the PVDF-CTFE samples but were no more than a millimeter. All amounts of flash were removed from the perimeter of the samples before storage. Again, the cause of flash on Lots 17, 21, and 23 is thought to result from small chain mobility due to the high pressure of injection molding (e.g., 700 bar), which results in a smaller M_w for the first injected specimen. The flash length decreases with injection order, while tensile strengths and zero-shear viscosity increase. None of the K705 specimens generated flash during the injection molding. Lots 17, 21, and 23 experience flash when injection molded due to CTFE segments increasing chain mobility under high pressure.

Table 5. *Longest flash lengths (mm) of each specimen by order of injection molding out of the cylinder of K705 and Lots 17, 21, and 23.*

	K705					Lot 17				
Order	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**
1	0.0	0.0	0.0	0.0	0.0	6.1	3.8	4.3	5.0	4.9
2	0.0	0.0	0.0	0.0	0.0	3.8	2.0	2.6	1.1	1.4
3	0.0	0.0	0.0	0.0	0.0	4.4	2.4	2.6	1.7	1.2
4	0.0	0.0	0.0	0.0	0.0	4.2	1.9	2.8	2.0	2.9
5	0.0	-	0.0	0.0	0.0	3.8	2.9	3.7	2.7	1.2
6	-	-	0.0	0.0	0.0	2.1	2.1	3.9	-	1.1
7	-	-	0.0	0.0	0.0	1.9	-	-	-	0.4
8	-	-	-	-	-	-	-	-	-	-
	Lot 21					**Lot 23**				
Order	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**
1	5.0	6.6	4.1	4.3	2.4	4.8	6.7	4.3	6.0	4.5
2	4.7	3.0	2.5	3.8	1.2	3.1	2.0	1.8	3.5	1.4
3	3.1	2.9	3.0	1.9	1.3	2.3	1.9	1.9	2.2	0.9
4	3.1	2.4	2.8	2.5	1.5	2.1	2.1	1.8	1.8	2.4
5	3.3	2.6	2.8	2.3	1.4	1.8	-	1.7	2.4	0.9
6	-	-	-	1.7	1.4	3.1	-	1.6	2.0	0.8

7	-	-	-	-	1.4	3.0	-	2.2	1.5	2.4
8	-	-	-	-		2.7	-	-	-	-

4 | CONCLUSION

Various fluorinated thermoplastics were injection molded using different specifications for cylinder dwell time and mold cooling time, and their mechanical property variance was assessed. Thermoplastics with higher CTFE concentrations exhibited the most sensitivity to process parameter variation, as shown by their heightened deviations in tensile strength. Upon further investigation, we found that the injection order played a large role in mechanical properties. Specifically, in the PVDF-CTFE samples, the first dog bone was consistently the weakest with high elongation. The extent of this variation was increased with CTFE concentration and longer cylinder dwell times. Conversely, PVDF homopolymers did not experience the same injection order dependency. Higher CTFE concentration in the copolymer implies greater sensitivity to processing variabilities, as seen by the deviations in their mechanical responses.

Through rheological investigation, we assessed injection order dependency on the zero-shear viscosity, which relates to a thermoplastic's weight-average molecular weight (M_w). Results showed that the first injected specimen of each material and process exhibited a lower zero-shear viscosity than the subsequent specimen, strengthening the argument that the first specimen contains a lower M_w than the subsequent specimen.

No flash was created for PVDF K705 specimens during the injection molding, while Lots 17, 21, and 23 experienced flash. The first specimens in each process had the largest flashes, with decreasing flash length as the specimens were injected from a singularly filled cylinder. The pressurized injection molding process and/or the higher mobility of the heterogenous PVDF-CTFE chains may force out lower molecular weight chains during the earlier specimens, which accounts for the formation of larger flashes observed. This could also explain increasing strength and decreasing elongation with specimen order.

SUPPORTING INFORMATION

Supporting Information is available from the Wiley Online Library or from the author.

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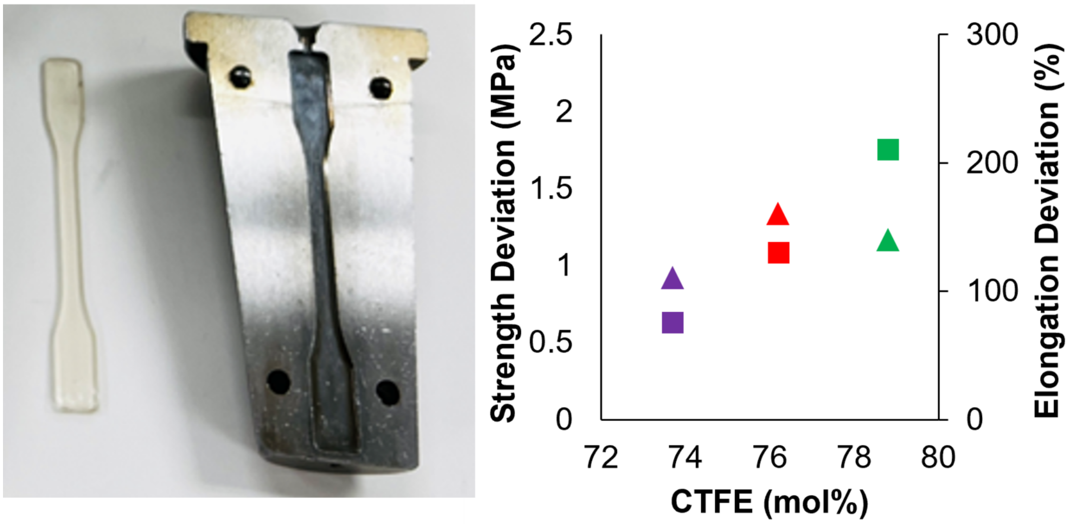

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