

Rheology of nylon 6 containing metal halides

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Addition of metal halides to nylons has been shown to be advantageous in a number of ways. The decrease in melting temperature, increase in glass transition temperature and melt viscosity by such additions have allowed more convenient processing of low molecular weight polymers and thermally unstable polymers. Rheological data depicting the variation of melt viscosity with shear rate at temperatures relevant to processing are necessary in optimizing and trouble-shooting plastics processing operations. In the present paper, a method has been proposed to estimate, complete flow curves or rheograms of nylon–metal halide systems with the use of a master curve knowing the melt flow index and glass transition temperature of the system. The validity of the approach has been verified for the nylon 6–lithium chloride system and shown to hold good for any nylon–metal halide combination.

1. Introduction

A variety of inorganic salts, mainly metal halides, have been used for modifying the structure and properties of nylon 6 and has been the subject of a number of recent publications [1–18]. Metal halides cannot be termed as fillers or diluents because their effects are much more pronounced than those expected of the fillers or diluents. They could be better described as reactive additives because of their capability of interacting with the active amide-group sites along the nylon chain. Besides the interest in the detailed mechanism of polymer–salt interaction, there is growing awareness about the influence of the metal halides on the processibility of nylons [19, 20]. The melting temperature of the pure polyamide could be depressed by use of salt additives so as to allow processing well below the conventional processing temperature [17]. The use of salt additives would thus be advantageous for processing very high melting or thermally unstable polymers [20]. The strong interaction between the salt and the polar nylon chains leads to a substantial increase in the polymer glass transition temperature, a decrease in the crystallization temperature and rate, and an increase in the melt viscosity. The enhanced melt viscosity, achieved through salt addition, would allow more convenient processing of a low mol-

ecular weight polymer and would help in raising the melt viscosity of nylon 6 to an appropriate value for optimum processing [21]. A knowledge of the complete flow curve depicting the variation of melt viscosity of the salt-modified polymers with shear rate and temperature is essential for assessing material processibility, process design/optimization and trouble-shooting (i.e. the correction and elimination of defects encountered during polymer processing).

2. Background information

Melt flow data on nylon 6 metal halide mixtures have been obtained by Acierno *et al.* [12, 15]. In the first case [12], lithium and potassium halides were mixed with the polymerized caprolactam and in the second case [15], lithium chloride was added during the anionic polymerization of caprolactam in order to avoid the mixing step which often becomes a severe hindrance in large scale continuous processes. Consistent results were found in both cases. Their melt viscosity experiments included the use of a capillary viscometer operating at a constant force for obtaining the pressure drop against flow rate curves. Different capillaries were used in order to get different shear rate conditions. The tests were carried out at different temperatures so as to generate a series

of curves showing the variation of viscosity with shear rate and temperature. The variables influencing the viscosity are shear rate, temperature, the type and the amount of metal halide. Generation of the rheograms thus involves time-consuming parametric studies. The metal halides used to date for modifying the structure and properties of nylon 6 include lithium chloride, lithium bromide, potassium chloride, ferric chloride, calcium chloride, magnesium chloride, copper chloride, cobalt chloride and cobalt thiocyanate, though only the first three have received attention from a rheological point of view.

Melt viscosity data necessary for generating flow curves of polymers are generally obtained on sophisticated instruments such as the Weissenberg Rheogoniometer, Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer, etc which are beyond the financial means and technical capabilities of most small-scale processors. It is thus desirable to find an alternative route to obtain the estimated flow curves which could eliminate the existing expensive and time-consuming methods. Such a procedure has been successfully developed by Shenoy *et al.* [22] for engineering thermoplastics including nylons. Their method gives an estimate of the flow curve at the required temperature from a knowledge of the glass transition temperature and the melt flow index of the polymer. The melt flow index (MFI) is often used as an alternative measure of viscosity for comparative purposes. It is a single point measurement defined as the amount of polymer in grams extruded in ten minutes through a capillary of standard dimensions, under specified conditions as in ASTM D1238-73 (see Appendix I for details).

In the present paper it is shown that all the rheograms generated by Acierno *et al.* [15] for the nylons containing metal halides can be unified into one master curve independent of the temperature and the amount of metal halide. This master curve could then be used for estimating the rheograms in the case of undiluted polymer-salt mixtures merely from the knowledge of the MFI and the glass transition temperature of the system.

3. Data analysis

The melt flow index is a flow parameter obtained from an extrusion rheometer. The expressions for shear stress τ and shear rate $\dot{\gamma}$ conventionally used for flow through a capillary tube can be used to determine the relationship between MFI, viscosity

and shear rate:

$$\tau = \frac{R_N F}{2\pi R_p^2 l} \quad (1)$$

$$\dot{\gamma} = \frac{4Q}{\pi R_N^3} \quad (2)$$

where R_p is the piston radius (0.4737 cm), R_N is the nozzle radius (0.105 cm), l is the length (0.8 cm), F is the test load L in $\text{kg} \times 9.807 \times 10^5$ (dynes), Q is the flow rate = $\text{MFI}/(600\rho)$ (cc sec^{-1}) and ρ is the polymer melt density (g cc^{-1}). The geometric parameters are all fixed as in ASTM D1238-73 given in Appendix I.

On substituting the values of the geometric parameters of the melt flow apparatus, Equations 1 and 2 can be simplified to give

$$\tau = 9.13 \times 10^4 L \quad (3)$$

$$\dot{\gamma} = \frac{1.83 \text{ MFI}}{\rho} \quad (4)$$

As per the fixed temperature and load conditions of the MFI measurement, a point on the shear stress against shear rate curve at that temperature can be obtained using Equations 3 and 4. This fact can be put to use for estimating the MFI from a known shear stress against shear rate curve in cases when the MFI of the polymer is not supplied by the manufacturer or is too low to measure on the melt flow indexer. This method has been successfully employed by Shenoy *et al.* [22, 23] and Rideal and Padget [24]. In the present case, this procedure for determining MFI was resorted to, for analysing the data of Acierno *et al.* [15] (see Table I).

Using the fact that $\eta = \tau/\dot{\gamma}$, Equations 3 and 4 can be modified to give

$$(\text{MFI})\eta = 4.98 \times 10^4 \rho L \quad (5)$$

$$\frac{\dot{\gamma}}{\text{MFI}} = \frac{1.83}{\rho} \quad (6)$$

For a given polymer, since the density and MFI load condition is fixed, the right hand side of Equations 5 and 6 are both constant. This suggests that a master curve can be obtained by plotting $(\text{MFI})\eta$ against $\dot{\gamma}/(\text{MFI})$ on a log-log scale at the temperature of MFI measurement as found by Shenoy *et al.* [22, 23].

In order to determine the effective MFI at temperatures other than the ASTM temperature a modified WLF (Williams-Landel-Ferry) type equation can be used [22].

TABLE I Details of nylon 6–lithium chloride systems used in Fig. 1

Lithium chloride	MFI* (Temperature (° C)/ Load condition, (kg))	Data Temperature (° C)	Number of data points [Shear rate range (sec ⁻¹)]	Source
—	9.8(230/2.16)	230	3(1–100)	[12]
—	20.0(250/2.16)	250	3(1–100)	[12]
—	70.0(270/2.16)	270	3(1–100)	[12]
1.8	5.0(230/2.16)	230	3(1–100)	[12]
1.8	19.0(250/2.16)	250	3(1–100)	[12]
1.8	37.2(270/2.16)	270	3(1–100)	[12]
3.7	3.6(230/2.16)	230	3(0.3–10)	[12]
3.7	8.0(250/2.16)	250	3(0.3–10)	[12]
3.7	20.0(270/2.16)	270	3(1–20)	[12]

*MFI value read out from τ against $\dot{\gamma}$ curve using Equations 3 and 4.

$$\log \frac{\text{MFI}(T_2)}{\text{MFI}(T_1)} = \frac{8.86(T_2 - T_s)}{101.6 + (T_2 - T_s)} - \frac{8.86(T_1 - T_s)}{101.6 + (T_1 - T_s)} \quad (7)$$

where T_1 is the temperature of MFI measurement in K, T_2 is the temperature at which MFI is desired, T_s is the standard reference temperature taken as $T_g + 50$ K and T_g is the glass transition temperature of the polymer.

It is important to note here that the glass transition temperature of nylon is affected by the addition of salt and varies substantially with salt concentration as can be seen from Fig. 1 reproduced from Acierno *et al.* [15]. It is essential to use the glass transition temperature of the polymer–salt mixture under consideration rather than of the nylon when Equation 7 is used for estimating the MFI at the temperature of interest.

From Appendix I, it is evident that there is more than one test load condition under which MFI can be determined. At different load conditions, the single-point measurement of MFI is merely shifted in the non-Newtonian (shear thinning) portion of the shear stress against shear rate curve. Every load condition corresponds to a fixed shear stress as per Equation 3. In cases when the MFI value is required at a load condition different from the determined one, the following equation can be used [22]:

$$\frac{\text{MFI}(L_2)}{\text{MFI}(L_1)} = \left(\frac{L_2}{L_1}\right)^{1/n} \quad (8)$$

Where L_1, L_2 are the test loads at conditions 1 and 2 and n is the pseudoplasticity index given by the slope of the shear stress against shear rate curve on a log–log scale taken within the limits of shear stresses corresponding to loads L_1 and L_2 .

4. Results and discussion

Fig. 2 gives the master curve for the variation of melt viscosity with shear rate for nylon 6 with and without LiCl. It is seen that a single curve is obtained which is independent of the temperature of viscosity measurement and quantity of LiCl, when $\eta(\text{MFI})$ against $\dot{\gamma}/\text{MFI}$ is plotted on a log–log scale. Fig. 3 depicts the data for nylon 6, nylon 66, nylon 610 and a copolymer of nylon [22] along with the present data points of Fig. 2 superimposed on it (for details of nylons see Table II). Fig. 4 shows the result of superimposing Fig. 2 on the curve given by Shenoy *et al.* [23] for filled nylon (for details of filled nylons see Table III). It has been shown [23] that irrespective of the type, amount and shape of the filler as well as the type and amount of the coupling agent used, a single curve could be obtained. Since

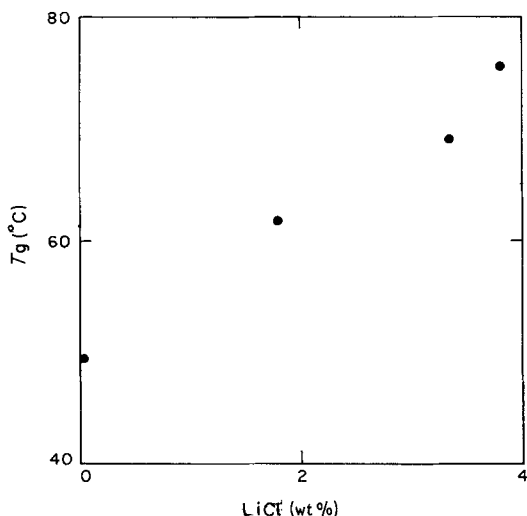


Figure 1 T_g against salt concentration from [12].

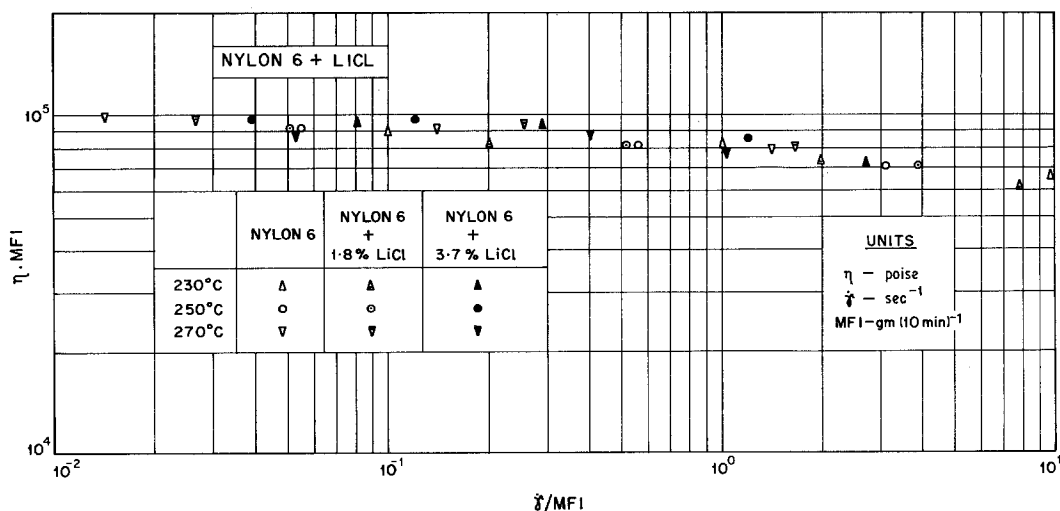


Figure 2 Master curve for nylon 6–lithium chloride systems for test load condition of 2.16 kg.

TABLE II Details of nylon grades used in Fig. 3

Nylon grades	MFI* (Temperature (° C)/ Load condition (kg))	Data temperature (° C)	Number of data points (shear rate range (sec ⁻¹))	Source
Plaskon 8201	5.0(231/2.16)	231	4(10–4000)	[25]
Plaskon 8201	13.7(260/2.16)	260	4(10–10000)	[25]
Plaskon 8201	29.5(288/2.16)	288	4(10–10000)	[25]
Plaskon 8205	1.9(260/2.16)	260	4(10–2000)	[25]
Plaskon 8205	2.5(268/2.16)	268	4(10–2000)	[25]
Plaskon 8205	4.0(288/2.16)	288	4(10–2000)	[25]
Nylon 6	8.2(230/2.16)	230	3(1–100)	[26]
Nylon 6	16.7(250/2.16)	250	2(10–100)	[26]
Nylon 6	30.6(270/2.16)	270	2(10–100)	[26]
Nylon 6	33.0(230/2.16)	230	4(10–4000)	[27]
Zytel 42NC10	4.0(280/2.16)	280	5(1–10000)	[25]
Zytel 42NC10	6.3(295/2.16)	295	5(1–10000)	[25]
Zytel 101NC10	49(280/2.16)	280	4(10–1000)	[25]
Zytel 101NC10	63(290/2.16)	290	4(10–10000)	[25]
Zytel 101NC10	80(300/2.16)	300	4(10–10000)	[25]
Nylon 66	45(288/2.16)	288	4(10–10000)	[27]
Nylon 66	49(291/2.16)	291	4(10–10000)	[27]
Maranyl A-100	113(280/2.16)	280	5(10–10000)	[28]
Nylon 610	235(280/2.16)	280	4(10–10000)	[27]
Nylon copolymer	79(280/2.16)	280	4(10–10000)	[27]
Nylon 6	9.8(230/2.16)	230	3(1–100)	[15]
Nylon 6	20.0(250/2.16)	250	3(1–100)	[15]
Nylon 6	70.0(270/2.16)	270	3(1–100)	[15]
Nylon 6 + 1.8 lithium chloride	5.0(230/2.16)	230	3(1–100)	[15]
Nylon 6 + 1.8 lithium chloride	19.0(250/2.16)	250	3(1–100)	[15]
Nylon 6 + 1.8 lithium chloride	37.2(270/2.16)	270	3(1–100)	[15]
Nylon 6 + 3.7 lithium chloride	3.6(230/2.16)	230	3(0.3–10)	[15]
Nylon 6 + 3.7 lithium chloride	8.0(250/2.16)	250	3(0.3–10)	[15]
Nylon 6 + 3.7 lithium chloride	20.0(270/2.16)	270	3(1–20)	[15]

*MFI values read out from τ against $\dot{\gamma}$ curve using Equations 3 and 4.

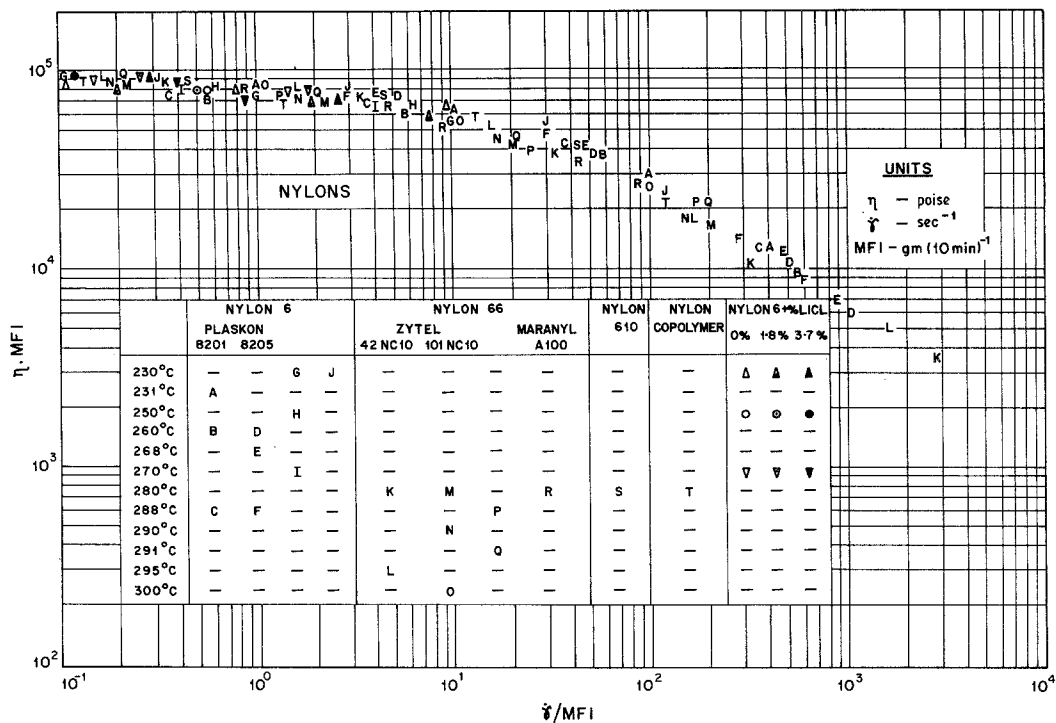


Figure 3 Master curve for nylons from [22] for test load condition of 2.16 kg with nylon 6–lithium chloride system data superimposed on it.

TABLE III Details of filled nylons used in Fig. 4

Nylon grades	Filler type, amount	MF1* (Temperature (° C)/ load conditions (kg))	Data temperature (° C)	Number of data points (shear rate range, sec ⁻¹)	Source
Zytel	—	40(288/2.16)	288	3(50–6700)	[27]
Zytel	—	49(291/2.16)	291	4(10–10000)	[27]
Zytel	Glass fibres 15 phr	29.4(291/2.16)	291	4(10–10000)	[27]
Zytel	Glass fibres, 50 phr	12.8(288/2.16)	288	3(10–4400)	[27]
Zytel	Glass fibres, 50 phr	15.7(291/2.16)	291	4(10–10000)	[27]
Maranyl A 100	—	113(280/2.16)	280	5(100–10000)	[28]
Maranyl A 190	Glass fibres, 50 phr	22(280/2.16)	280	5(100–1000)	[28]
Nylon	—	9.8(230/2.16)	230	3(1–100)	[15]
Nylon	—	20.0(250/2.16)	250	3(1–100)	[15]
Nylon	—	70.0(270/2.16)	270	3(1–100)	[15]
Nylon	Lithium chloride, 1.8 phr	5.0(230/2.16)	230	3(1–100)	[15]
Nylon	Lithium chloride, 1.8 phr	19.0(250/2.16)	250	3(1–100)	[15]
Nylon	Lithium chloride, 1.8 phr	37.2(270/2.16)	270	3(1–100)	[15]
Nylon 6	Lithium chloride	3.6(230/2.16)	230	3(0.3–10)	[15]
Nylon 6	Lithium chloride	8.0(250/2.16)	250	3(0.3–10)	[15]
Nylon 6	Lithium chloride	20.0(270/2.16)	270	3(1–20)	[15]

*MF1 values read out from τ against $\dot{\gamma}$ curve using Equations 3 and 4.

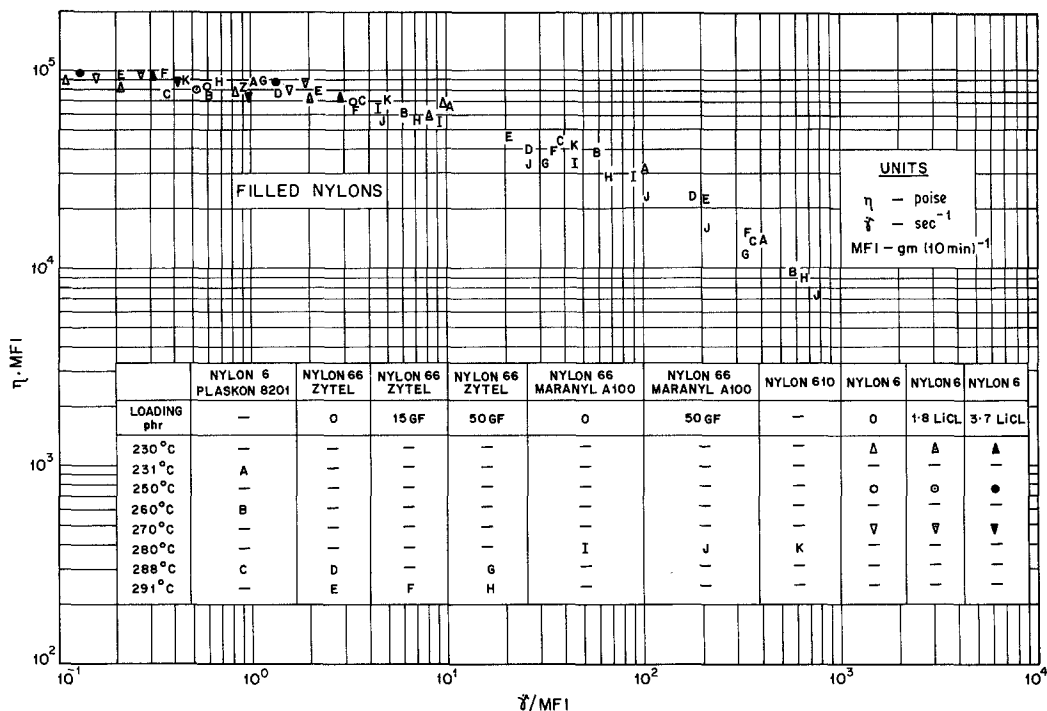


Figure 4 Master curve for filled nylons from [23] for test load condition of 2.16 kg with nylon 6–lithium chloride system data superimposed on it (GF – glass fibres, LiCl – lithium chloride).

metal halides would fall in the category of additives with coupling ability, it is reasonable to expect the same master curve given in [23] for filled nylon to hold good for nylon–LiCl mixtures as evident in Fig. 4. In view of the general validity shown through superimposition of Fig. 2 on the master curve of all nylons in Fig. 3 and also on the master curve for filled nylons in Fig. 4, it can be concluded that the master curve in Figs. 2, 3 or 4 should be applicable to other nylon–salt systems containing other types of metal salts and also at different loading levels.

The master curves can be used for generating the rheograms at any required temperature using the following steps:

1. Obtain MFI for the polymer–salt mixture under temperature and loading conditions specified in ASTM D1238-73.

2. In cases when the loading condition is different from 2.16 kg as specified in the master curve, obtain a new value of MFI using Equation 8 at the loading condition of the master curve.

3. When the specified temperature is different from the condition at which the rheogram is desired, obtain an effective value of MFI using Equation 7.

4. Using the correct value of effective MFI, obtain the viscosity against shear rate curve by mere substitution in the master curve.

5. Conclusion

The unifying approach has been successfully demonstrated to coalesce rheograms of nylon 6 containing amounts of lithium chloride when expressed in terms of a modified viscosity function, $\eta(\text{MFI})$, and a modified shear rate $\dot{\gamma}/\text{MFI}$. The master curve so generated has been shown to coalesce with the master curve for pure nylons of different grades and also with the master curve for filled nylons with different fillers. It can thus be concluded that the unified curve of nylon 6–lithium chloride would, in general, be valid for all nylon–metal halide systems and the rheograms for these systems can then be generated from merely the knowledge of MFI and the glass transition temperature of the system.

Appendix I

Tables AI and AII.

TABLE AI Standard testing conditions of temperature and load as per ASTM D1238-73 for nylons

Polymer	Temperature (° C)	Load (piston + weight) (kg)	Approximate pressure	
			(kg cm ⁻²)	(psi)
Nylon	275	0.325	0.46	6.50
	235	1.000	1.41	20.05
	235	2.160	3.04	43.25
	235	5.000	7.03	100.00

TABLE AII ASTM specifications for piston and die dimensions

	Diameter		Length	
	(mm)	(inch)	(mm)	(inch)
Piston	9.474 ± 0.007	0.3730 ± 0.0003	6.35 ± 0.13	0.250 ± 0.005
Die	2.095 ± 0.005	0.0825 ± 0.0002	8.00 ± 0.02	0.315 ± 0.0008

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