

DRAWN FIBER: POLYMERS, PROCESS, AND PROPERTIES PRIMER

RESINATE

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INTRODUCTION

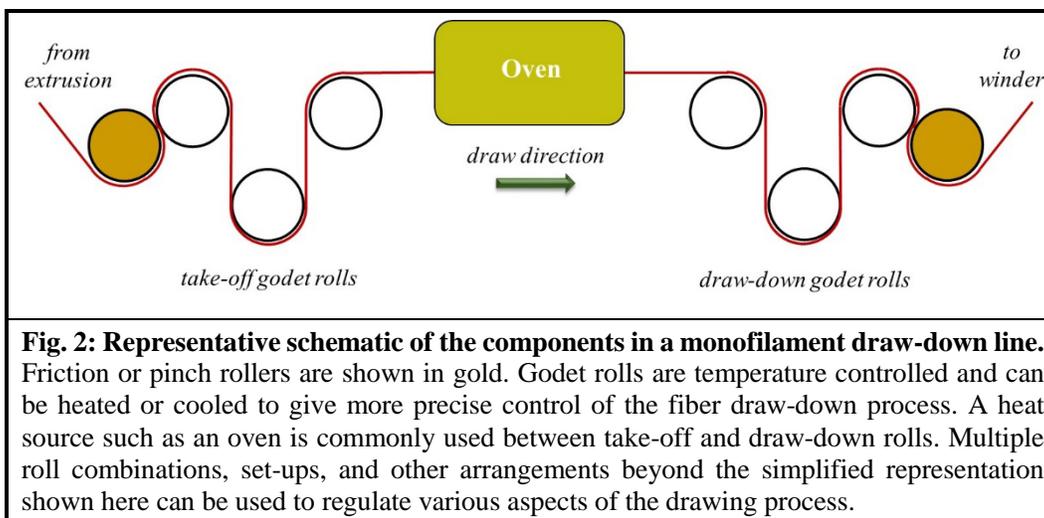
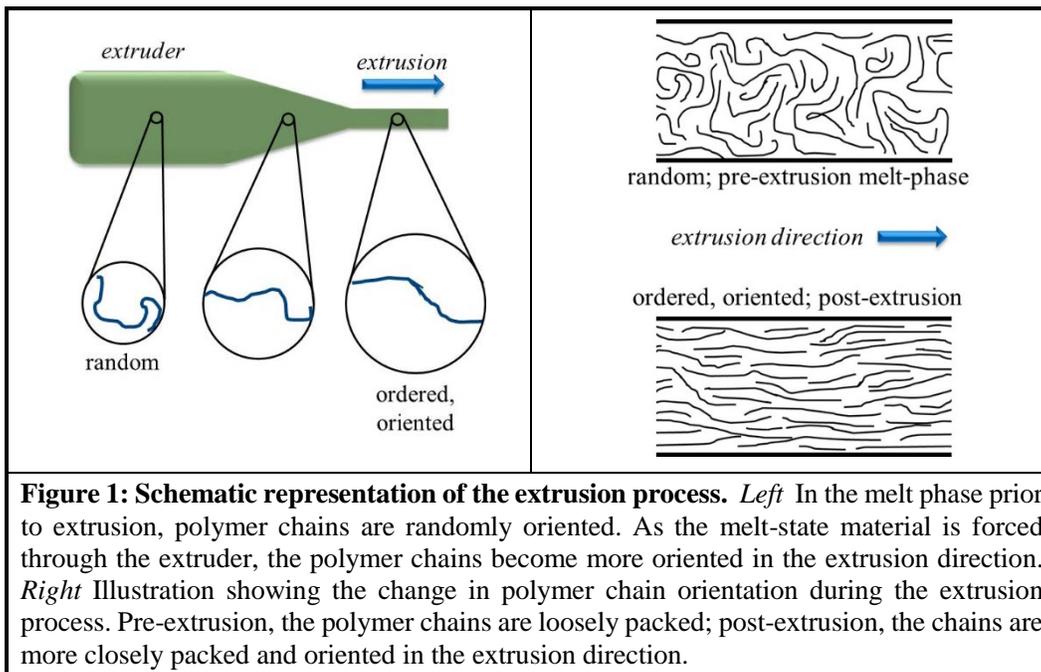
Drawn fiber is an improved performance monofilament based upon extrusion technology. Because of the added draw-down step during manufacturing to enhance performance, Zeus drawn fiber represents a superior monofilament compared to inexpensive and more commoditized monofilaments such as polyethylene terephthalate (PET) or nylon. Drawn fiber can be found in a broad spectrum of applications including over-braiding for hoses, weaves as mist eliminators, medical braiding, instrument and racquet strings, strengthening for industrial belting applications, and even bristles for brushes – including tooth brushes. Drawn fibers can exhibit a wide range of properties based on the particular polymer from which they are made and synthetic process specifics. While chemical attributes lie at the heart of much of the drawn fiber and polymer properties, for lay audiences this newsletter will principally discuss the macro-level attributes. Properties such as melting temperature, glass transition temperature, and several key mechanical traits of drawn fibers and the polymers from which they are created are described in overview. Other attributes such as crystallinity and polymer chain length and their relation to drawn fiber properties are presented. Altogether, these characteristics help explain much of the behavior of drawn fiber polymers. This issue of *RESINATE* we hope will serve as a gateway to learn the basics describing these fiber-based products and how this information can be used to suit specific application parameters.

THE DRAWING PROCESS

Drawn fiber is an industry term used to describe an enhanced monofilament extrusion that has been stretched, pulled, or *drawn down* post extrusion. This term refers to the characteristic that the fiber has been made thinner as a result of the drawing process; thus, it has been drawn down in size (diameter). Monofilament such as this are made from polymer resin materials that consist of very long polymer chain molecules. In the melt phase, the chains are arranged in a random or disordered state. The extrusion process initiates orientation of the chains in the extrusion direction (**Fig. 1 left**). Drawing or pulling on the extruded monofilament further orients the polymer chains in the machine direction resulting in more close packing polymer chains within the fiber (**Fig. 1 right**). The overall effect of the draw-down process is increased polymer chain density and strength. Therefore, drawn fiber typically possesses superior and often preferable mechanical attributes than simple extruded monofilament.

Stretching or drawing down of the extruded monofilament is a process (**Fig. 2**). Stretching is done at elevated temperature to facilitate mobility and greater alignment of the polymer chains. This is accomplished by passing the extruded monofilament through heat such as a water bath or oven. During the stretching process, the monofilament fibers are wound onto Godet rolls (also known as *stands* or *draw stands*), a series of multiple off-aligned rolls that are used to control stretching by turning at

different speeds. Godet rolls are usually heated to facilitate the stretching process. Godet rolls can be used in a wide range of combinations, set-ups, and other arrangements to precisely control phases of the drawing process. Godet rolls also provide a means to control slippage of the monofilaments. Maximum fiber strength is achieved in the drawing process when the polymer chains have reached maximum alignment in the same (machine) direction.

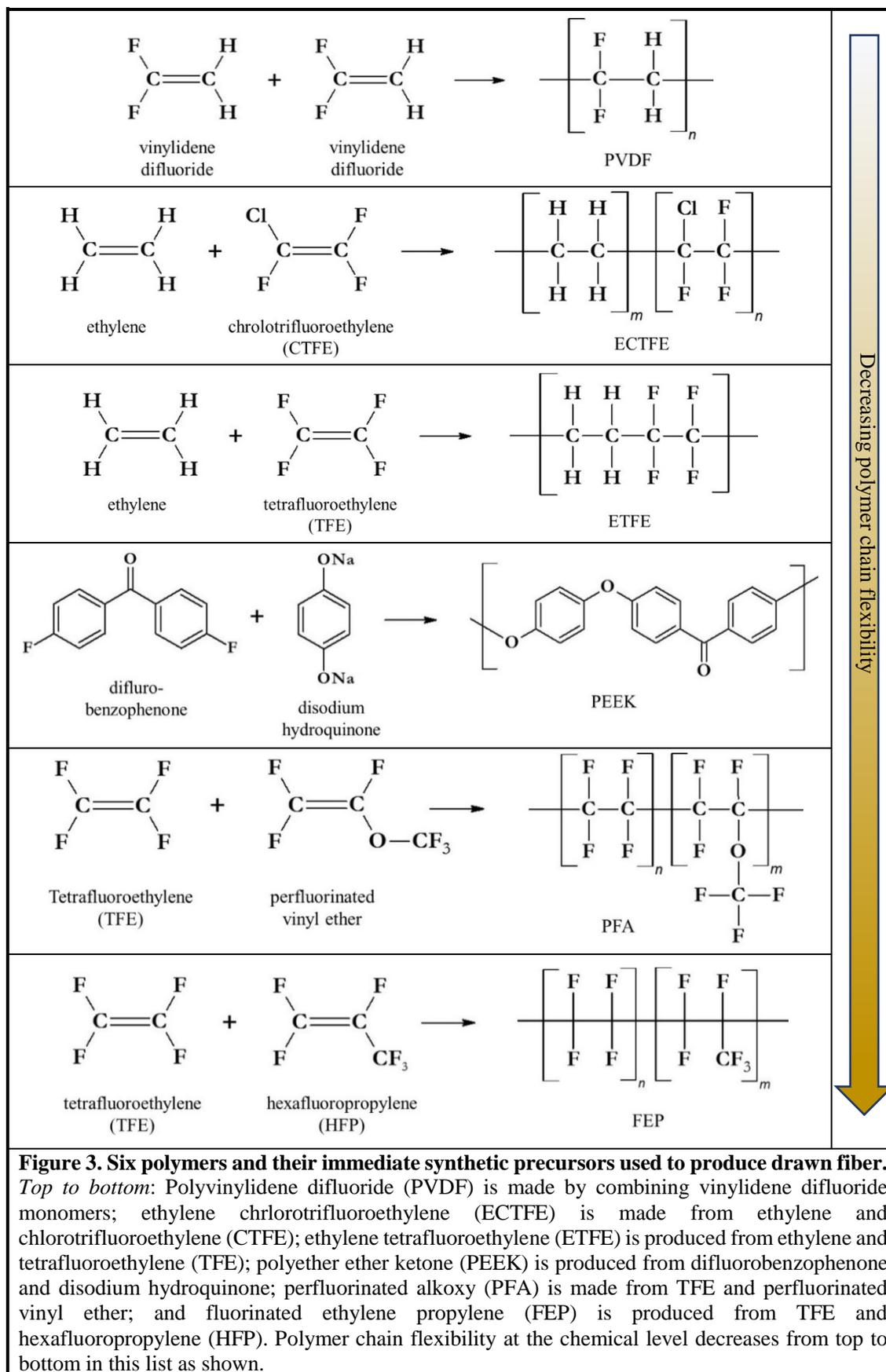


FACTORS AFFECTING DRAWN FIBER POLYMER PROPERTIES

Drawn fiber monofilament can be produced from many different kinds of polymer resins. Zeus Industrial Products, Inc., for example, features drawn fiber produced from (but not limited to) polyvinylidene difluoride (PVDF), polyfluoroalkoxy (PFA), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), ethylene chlorotrifluoroethylene (ECTFE), and polyether ether ketone (PEEK) (**Fig. 3**). These carbon chain backbone molecules are made from joining constituent monomers to form long-chain molecules (**Fig. 3**). As long-chain molecules, sometimes extending hundreds of carbons long, their properties are greatly altered from those of the monomers or even from shorter-chain homologs. This multiplicity of polymer formation together with their chemical structure forms the underpinning governing polymer properties. Resulting polymer attributes such as crystallinity, molecular weight, degree of polymerization, and molar volume become the basis for the final material properties at the macro level. These fundamentals provide a framework to explain properties of some of the polymers discussed here and used to produce high performance drawn fiber monofilament.

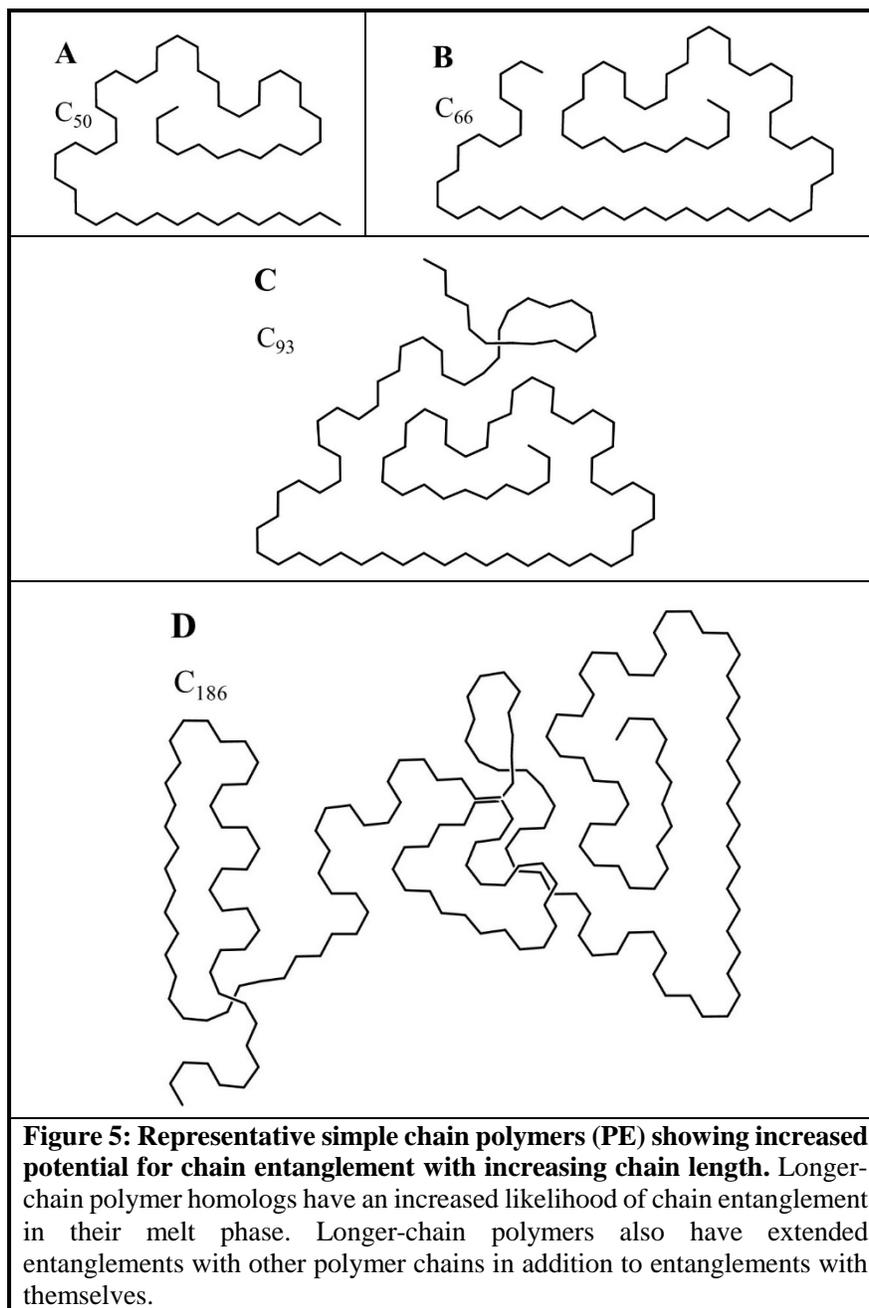
CHAIN LENGTH

Polymer chain length is a foundational attribute of these molecules. Chain length is the result of consecutive addition of monomers until the synthesis process is halted. During synthesis, polymer chain length can generally be controlled through the addition of reagents to terminate the synthetic chemical reaction. Or, the synthetic reaction can be allowed to terminate on its own upon exhaustion of the reactant monomers. Polymer chain length is a way of relating the average number of repeating units in the polymer material. C_{60} , for example, indicates that the average polymer molecule chain length for a material is 60 carbons long along its carbon backbone. It follows, too, that chain length can be inferred by molecular weight (and vice versa). Larger molecular weight polymers have more repeating units than their lower molecular weight homologs (**Fig. 4**). Many commercial polymers are generally described in this manner using the average molecular weight of the polymer for the polymer mass. PEG 5000, for example, refers to polyethylene glycol with an average molecular weight of 5000. Polymers such as these are not a uniform collection of identical molecular weights. They are, rather, a mixture with certain chain lengths predominating.



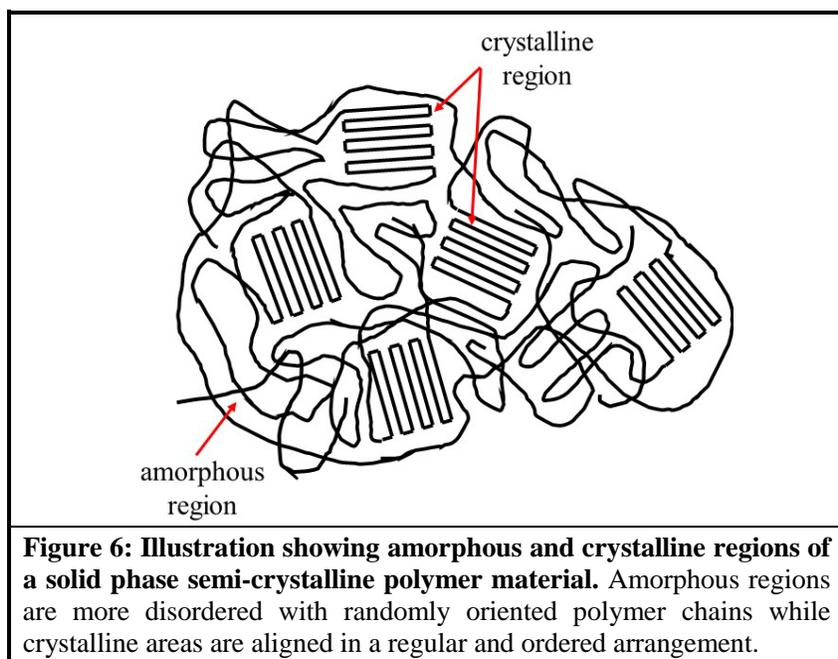
Polymer chain	Molecular formula and weight (MW)
	C ₁₀ H ₂₂ , 142
	C ₁₆ H ₃₄ , 226
	C ₂₄ H ₅₀ , 339
Figure 4: Relation of polymer chain length and molecular weight for the simple hydrocarbon polyethylene (PE). Molecular weight implicitly describes polymer chain length as molecular weight increases with addition of each C ₂ H ₄ - monomer. For PE and similar carbon-backbone analogs, chain length is indicated by the number of carbon atoms shown in the molecular formula.	

Polymer chain length is the root of many properties observed at the macro scale for these materials. Chemical nature aside, chain length affects such fundamental properties as molecular weight, melt temperature (T_m), and tensile strength. These aspects distinguish polymers from small molecules. Longer chain polymers experience greater chain entanglement than their shorter chain homologs (**Fig 5**). This greater entanglement contributes to greater chain-to-chain interaction which also translates into increased tensile strength (**Fig. 8A**). Long-chain polymers (with higher molecular weights) require more energy (such as from heat) to separate the polymer chains and shift the polymer mass from the solid to the melt phase. Thus, long-chain polymers exhibit higher melt temperatures, greater viscosity, and higher tensile strength than short-chain polymers with lower molecular weights.



CRYSTALLINITY

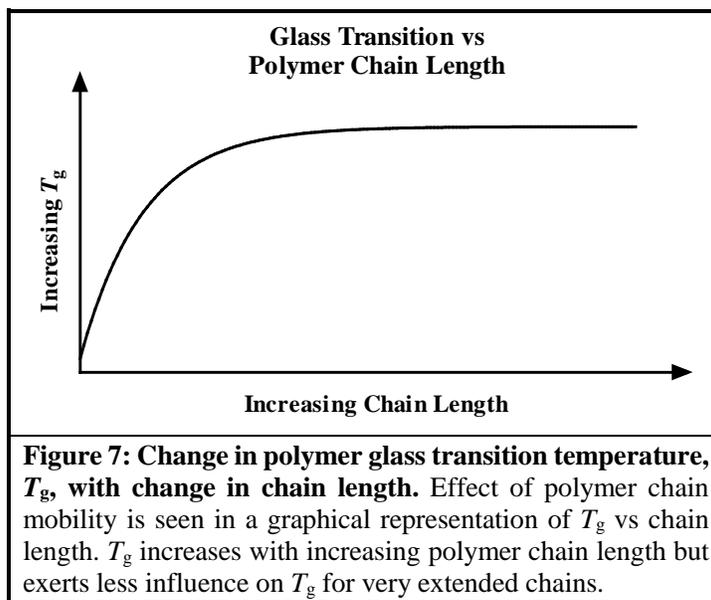
Crystallinity is another important feature of solid phase polymers. Crystallinity affects properties such as hardness, density, impact resistance, and melt temperature. While not directly correlated with molecular weight, crystallinity is related to molecular weight and chain length. More importantly, however, crystallinity is a function of the chemical topology of the molecular chain and conformational limitations stemming from its chemical features. Crystallinity is not uniform. Crystallinity can range from entirely amorphous (no crystallinity) to greater than 90% crystallinity for solid phase polymers, depending on the polymer (**Figs. 3 and 6**). Chain flexibility, including rotational capacity along atom-atom bonds, and intermolecular chain interactions, both attractive and repulsive, affect the way polymer chains can arrange themselves *in situ* leading to crystal formation. Slow cooling of the melt phase polymer can increase crystallinity while rapid cooling will reduce potential crystal formation. Simple chemical structure and greater linearity of the polymer chains favors crystal formation. Conversely, complex chain structure and more rigid (less flexible) molecules reduce the capacity for crystal formation. Solid phase polymers such as polystyrene with a high amorphous (less crystalline) character have lower melt temperatures and hardness while polymers such as polyethylene (PE) and polytetrafluoroethylene (PTFE) with greater crystalline (lower amorphous) character have higher melt temperatures and hardness.



GLASSY VS RUBBERY STATE

The degree of crystallinity or amorphous nature of polymers is also closely tied to the key polymer property of glass transition temperature, T_g . For solid phase polymer materials that contain both crystalline and amorphous regions, their molecules exist in different environments. Molecules in the amorphous region are highly restricted from movement but can vibrate to a small extent. This solid phase low temperature and limited vibrational state of the polymer comprises the *glassy state* of the material and is only relevant to the amorphous region. Glassy state polymers exhibit properties similar to crystals in that they are hard, brittle, and rigid. As the glassy state is heated, the polymer chains gain energy, become more mobile with increasing vibration, and gain in disorder. The polymer material then exhibits a *rubbery state* and takes on those properties that are typically associated with rubber. At this stage, the polymer still possesses amorphous as well crystalline regions. The temperature range or zone at which the amorphous region becomes rubbery is known as the *glass transition temperature*, T_g , and this occurs *only for the amorphous region*. Crystalline regions of the polymer exhibit a melting point or temperature, T_m , where the solid phase turns to a liquid phase. Semi-crystalline polymers – polymer materials that possess amorphous and crystalline regions – exhibit both a T_g and a T_m . These two temperatures are fundamental characteristics of the polymer and help to establish its global properties and behavior.

(There are other factors affecting polymer behavior and T_g and T_m including crosslinking of chains, pendant groups, plasticizers, but these shall not be discussed here, and this discussion will be concerned only with those characteristics with respect to the pure polymer).



Aside from mass, T_g is largely the result of chain mobility. Thus, factors which affect chain mobility must, too, affect T_g . Once again, chain length plays a vital role as more energy is required to energize – and mobilize – extended chain molecules. Chain length plays a diminishing role with respect to T_g , however, as the chain length increases (**Fig. 7**). Other critical characteristics surrounding chain mobility, including chain flexibility (at the atom level) and chain interactions (which include both repulsive and attractive forces), affect T_g . Polymer chains with a high degree of chain flexibility can more easily be changed into a rubbery state from the glassy state. In other words, this change or transition can occur with less input of energy – such as heat – for these molecules. Likewise, chains that exhibit a high degree of attractive forces between them require more energy to be moved from the glassy to rubbery state. Thus, chain flexibility, chain-chain interactions, and chain length play critical roles in determining T_g and the behavior of these polymers.

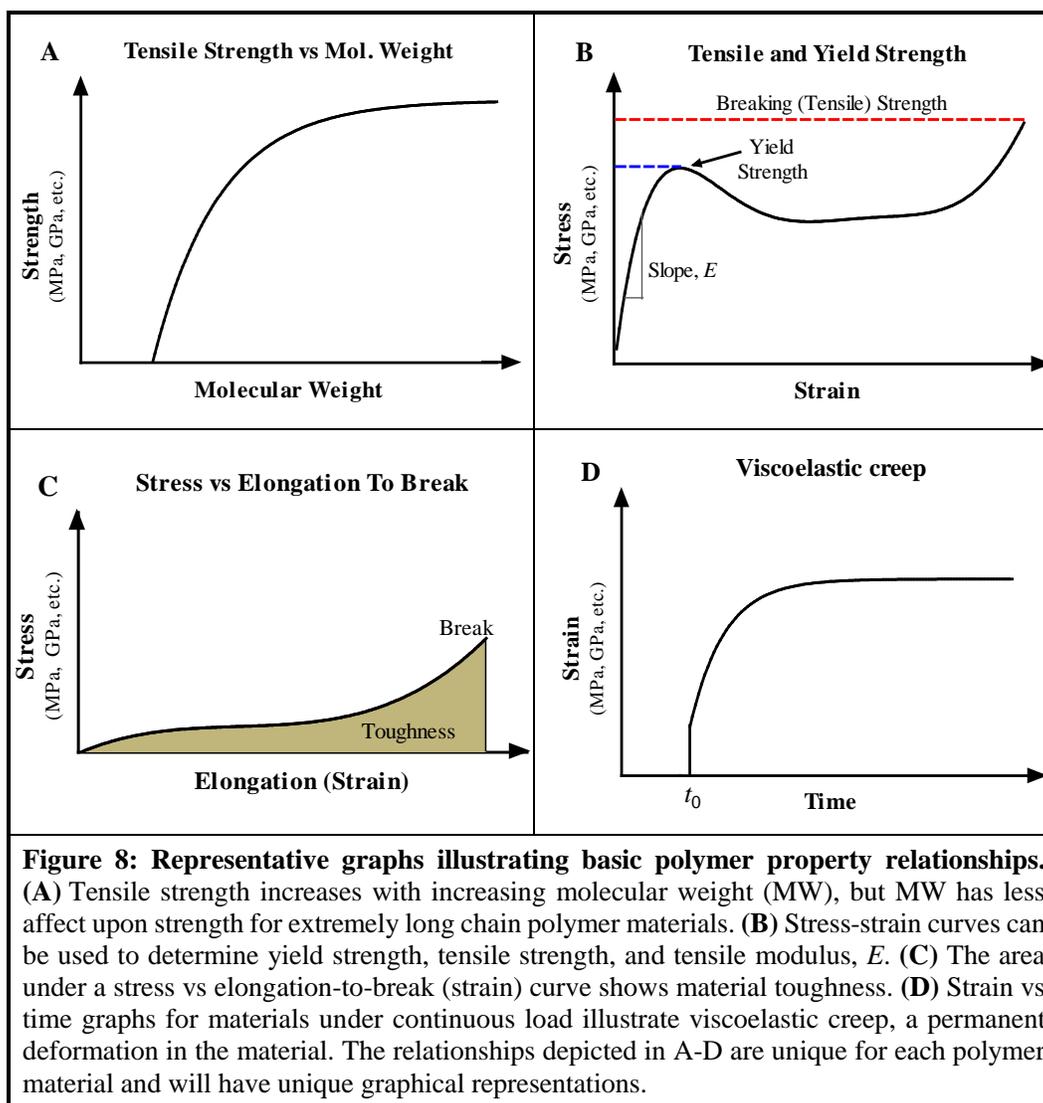
STRESS-STRAIN RELATIONSHIPS

The majority of polymer mechanical properties – and particularly those of most popular interest – can largely be grouped under stress-strain relationships. These relationships are unique for each material. Taking tensile strength as a first example, in its simplest terms, tensile strength is the maximum force that a material can support without breaking. For a drawn fiber, this force is applied in a linear direction and is therefore distributed in cross section over the diameter of the fiber. Such force applied through

an area is termed *stress*, σ (or mechanical stress), expressed as force per unit of area: $\frac{F}{A}$. Stress applied to a material often causes the material to deform. Such deformation is defined as *strain*, ε . Mathematically, strain is the amount of deformation in the applied force direction divided by the initial length of the material. For example, if the deformation of a material is measured in length: strain = $\frac{\text{elongation (change in length)}}{\text{initial length}} = \frac{\Delta L}{L_0}$. Plotting stress vs strain graphically can be used to reveal several fundamental characteristics of the fiber (**Fig. 8B**). *Tensile strength* shows the applied stress upon fracture of the fiber. *Yield strength*, on the other hand, shows the point where the linear elastic region of the stress-strain curve ends; this value illustrates where deformation begins to occur.

The stress-strain curve can be used to determine two other highly useful properties, *tensile modulus* and *toughness*. Tensile modulus, E (also known as Young's modulus), relates the stiffness of a material in the tensile direction. This characteristic could be viewed as the material's resistance to deformation. Tensile modulus is the ratio of stress (σ) to strain (ε): $E = \frac{\text{stress } (\sigma)}{\text{strain } (\varepsilon)}$. E is determined from the slope of the near-linear region of elasticity of the material from the stress-strain plot (**Fig. 8B**). This value gives an understanding into a material's proportional deformation under an applied stress. For a drawn fiber, this property can be viewed as somewhat similar to elongation with respect to the tension direction. The *area* under the stress-strain curve is also important; this reveals the material's *toughness* (**Fig. 8C**). Toughness relates the material's ability to absorb energy before fracture or breaking. The greater the area under the stress-strain curve, the greater the material's toughness.

After the application of a load or stress to a material and elongation appears to cease, the material may continue to deform though at a much slower rate. This time-dependent continued deformation under constant stress is called *creep*. This type of viscoelastic deformation is permanent and can be shown through a plot of strain vs time (**Fig. 8D**). The plot also shows how strain may become constant over time as the polymer material (or fiber) continues to deform. Here, too, molecular weight and chain flexibility play a role. Higher molecular weight polymers and those with less flexible chains result in increased resistance to creep. Thus, creep should be viewed as a long-term property when considering materials that will be used under significant load for an extended period.



(While there are many more mechanical properties and other graphical representations of the phenomena discussed here, we have chosen to limit our discussion to these basic properties and descriptions as a brief overview of those that are most relevant).

SUMMARY

Drawn fiber is an industry term used for ordinary monofilament that has been stretched and drawn down post extrusion. This added step in the creation of the monofilament further orients the polymer chains in the machine direction and results in increased density and tensile strength of the polymer material. Drawn fiber often possesses superior mechanical attributes overall than simple extruded monofilament due in large part to the draw-down step. Fiber characteristics can be controlled during the drawing process making drawn fiber a preferred material in the commercial monofilament fiber market. Zeus offers drawn fiber in multiple resins including (but not limited to) PVDF, PFA, FEP, ETFE, ECTFE, and PEEK.

A primary factor affecting drawn fiber traits is polymer chain length. This feature can be controlled during polymer synthesis. Polymer chain length is typically described by the average number of carbons contained in the chains or by the average molecular weight of the polymer chains. Longer polymer chains increase chain entanglement which in turn affects other critical polymer attributes including tensile strength. Chain length also affects characteristics associated with chain mobility including crystallinity, T_m , and T_g . Longer polymer chains result in higher T_g . Crystallinity, however, is more closely associated with the chemical nature and topology of the polymer chains including chain flexibility. Crystallinity describes the proportion of crystalline and amorphous regions within the polymer material and affects T_m and T_g . Thus, polymer chain length represents a basis of these properties which are ultimately responsible for the global characteristics of the polymer.

In addition to the physical properties of drawn fiber polymers, several popular mechanical attributes surrounding stress-strain relationships provide an instructive overview of these materials. A plot of stress vs strain illustrates key factors such as yield strength, the point at which it begins to deform, and tensile strength, where the polymer material begins to fracture. The stress-strain curve also shows the polymer's tensile modulus, or proportional deformation under load; and the area under this curve shows the material's toughness, or energy that the material can absorb before fracture. Time is consideration for materials that may be under load for sustained periods. In these instances, polymers may exhibit a permanent deformation known as creep, and this characteristic should be taken into account. Graphical plots illustrating these properties are unique to each polymer, and collectively they provide a convenient basis to characterize these materials for optimal practical use.

APPENDIX

Property	PEEK	ECTFE	ETFE	FEP	PFA	PVDF
Tensile Strength, 0.011" fiber (MPa)	638	256	367	97	261	783
Elongation at Break, 0.011" fiber (%)	30	30	23	44	25	31
Density (g/cm ³)	1.3	1.7	1.8	2.1	2.1	1.8
Crystallinity (%)	25 – 35	50	50	70	48 – 70	35 – 70
Coefficient of Friction	0.34	0.25	0.05 – 0.40	0.04 – 0.20	0.04 – 0.20	0.14 – 0.23
Flexural Modulus (GPa)	3.6 – 4.1	1.7	0.7 – 1.2	0.5 – 0.6	0.5 – 0.7	1.3 – 7.0
Tensile Modulus (GPa)	2.3 – 4.3	1.7	0.5 – 0.8	0.4 – 0.6	0.48	0.5 – 5.0
Working Temperature (°C / °F)	260 / 500	148 / 298	150 / 302	205 / 401	260 / 500	150 / 302
Melt Temperature (°C / °F)	343 / 649	242	250 / 482	260 / 500	310 / 590	210 / 410
Glass Transition Temperature, T_g (°C / °F)	150 / 302	85 / 185	40 – 130 / 104 – 266	80 / 176	90 / 194	-30 to -40 / -22 to -40
Chemical Resistance	Very Good	Moderate	Very Good	Excellent	Excellent	Excellent

Table 1: Properties overview of drawn fiber examples and polymers. Values for six of the polymers for which Zeus uses to produce drawn fiber. Tensile and elongation values are from 0.011" (0.279 mm) diameter fiber samples. Note that the properties shown are representative and may vary substantially based on proprietary processing methods, resin synthesis, and fiber manufacturer specifics.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,250 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

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MORE INFORMATION

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See also our free webinar series, “Zeus Drawn Fiber Essentials – Deciding Which Is Right For You.” This video presentation provides more in-depth discussion and insight on this topic. Part I of this two-part series, “PVDF and Introduction To Fluorine Chemistry” can be found [here](#); Part II, “Chemical Overview and Properties Comparison,” can be viewed [here](#). These free educational videos will complement the information in this issue of *RESINATE* and help guide you towards a best fiber product for you.