

# Evaluation of the Entanglement Molecular Weights of Maize Starches from Solution Rheological Measurements<sup>1</sup>

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## ABSTRACT

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The entanglement molecular weights of waxy maize (WM) and normal maize (NM) starches were calculated from solution rheological data. The viscoelastic behavior of both WM and NM starches were measured at several different concentrations and then shifted to produce a master curve for each of the materials. The theory of Doi and Edwards was used to calculate the plateau moduli from which values for the entanglement molecular weights for WM and NM starches were calculated. The entanglement molecular weights were  $100 \pm 15$  kg/mol for WM starch and  $96 \pm 8$  kg/mol for NM starch. These two values were within experimental error of one another and represent the entanglement molecular weight of

amylopectin, the major component of WM and NM starches. The entanglement degrees of polymerization for WM and NM starch, using a value of 162 g/mol for the monomer molecular weight of amylopectin, were  $617 \pm 92$  and  $592 \pm 49$ , respectively. The values for the entanglement molecular weight and the entanglement degrees of polymerization for WM and NM starch were markedly higher than those quoted for many commercial polymers. This finding indicates that molecular weights of  $>1$  million are required to produce starch-based materials with consistent physical properties.

Starch is a commodity polymer that is utilized today in a wide variety of commercial applications ranging from foods and adhesives to blends and composites. Increasingly, starch is being used in applications previously regarded as the realm of synthetic polymers because of the low cost and potential biodegradability of starch. In addition, starch is a renewable resource, and its potential to replace nonrenewable petrochemical-based polymers offers manufacturers a low-cost alternative to the increasing costs of many commercial synthetic polymeric materials.

Starch consists of (1–4) linked  $\alpha$ -D-glucopyranosyl units. Two major forms are found in natural starches: amylopectin and amylose. Amylopectin is a highly branched, very high molecular weight (typically 5,000–30,000 kg/mol) biopolymer. The branches in amylopectin are the result of the infrequent (1–6) bonds in the polymer. Amylose has a lower molecular weight (typically 20–800 kg/mol) and is essentially a linear-chain polysaccharide. In the United States, the major source of starch is maize. Waxy maize (WM) starch consists of nearly pure amylopectin. Normal maize (NM) starch consists of 20–25% amylose and 80–75% amylopectin. High-amylose starches also are known. In its native form, starch granules are  $\approx 10$   $\mu$ m in diameter. These granules can be dispersed in aqueous media at temperatures of 60–80°C (Whistler et al 1984).

Over the years, investigators have examined the rheological properties of starch in solution in either its native state (Steeneken 1989; Dintzis and Bagley 1995a; Dintzis et al 1995, 1996; Hansen et al 1991) or in transformed products (Evans and Haissman 1979, Eliasson 1986, Doublier et al 1987, Dintzis and Bagley 1995b). In addition, research was conducted on the rheological properties of starch during extrusion (Vergnes and Villemaire 1987; Vergnes et al 1987, 1993; Zheng and Wang 1994; Willett et al 1995; Della Valle et al 1996) and on the rheology and physical properties of starch and synthetic polymer blends (Seethamraju et al 1994, Bhattacharya et al 1995; Vaidya et al 1995; Yang et al 1996; Ram-

kumar et al 1997a,b). Rheological properties are important governing factors in control of the morphology developed during processing, including extrusion and jet-cooking processes.

Despite the numerous applications for starch, many unanswered questions remain regarding its basic rheological and physical performance properties. Although several studies have examined the average molecular weight for cross-linked WM starch (Gluck-Hirsh and Kokini 1997) and starch hydrogels (Kulicke et al 1989), an evaluation of the entanglement molecular weight of starch has yet to be reported.

The entanglement molecular weight is an important rheological parameter that governs many of the flow and final state physical properties of polymers. The original concept of entanglement molecular weights for high molecular weight polymers was based on experimental observations of a discontinuity in the slope of the log viscosity versus log molecular weight curve. Below the entanglement molecular weight, the slope has a value of unity; above the entanglement molecular weight, the slope has a value of 3.4 (Klein 1987). Polymers produced at molecular weights below the entanglement molecular weight exhibit brittle fracture and, in general, have low tensile strengths. To obtain the optimal mechanical properties from a polymer, the molecular weight must be 8–10 times that of the entanglement molecular weight. In this study, solution rheology data were used to obtain a value for the entanglement molecular weight of high-amylopectin maize starches.

## MATERIALS AND METHODS

### Materials

Two different starch materials were used in this study. NM starch (Buffalo 3401, CPC, Corn Products Div., Summit-Argo, IL) consisted of 25% amylose and 75% amylopectin. WM starch (Amioca, American Maize Products, Hammond, IN) consisted of 98% amylopectin and 2% amylose. The dimethyl sulfoxide (DMSO) solvent was obtained from Aldrich Chemical Company (Milwaukee, WI). All the materials were used as received.

### Solution Preparation

Solutions for the rheological measurements were prepared by adding the appropriate starch into a volumetric flask containing 10 mL of distilled water and stirring gently with a stirring bar at 30 rpm to wet and disperse the granules thoroughly. The stirring was continued and 60 mL of DMSO was added. The flask was then heated gradually for 20–30 min to 80°C, and held for 5 min at this temperature. As the starch dissolved, the dispersions which were originally opaque became clear with time. The solution was then

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cooled to room temperature and additional DMSO was added to bring the total final volume to 100 mL. Initially, solutions of the materials were made at a 5% (w/w) concentration. This stock solution was then diluted with DMSO and water (90:10) to the desired concentrations. For this study, solutions were produced at concentrations ranging from 0.02–0.05 g/mL.

### Rheological Measurements

Rheological properties of each of the solutions were measured using a controlled-stress rheometer (CSL<sup>2</sup> 500, CarriMed, Dorking, England) with a cone-and-plate fixture. All the rheological studies were conducted using a 4-cm diameter, 4° cone. The temperature of the sample was controlled using a Peltier plate which enabled the chamber of the rheometer to be controlled to within ±0.1°C. For each solution, a small-amplitude oscillatory shear experiment was conducted using frequencies of 0.01–10/sec. The oscillatory shear experiments were performed using a constant shear stress of 1,000 dyn/cm<sup>2</sup>. Before the oscillatory shear experiments, a torque sweep was conducted on each sample to ensure that the applied shear stress was within the linear viscoelastic regime of the material. The shear storage and loss moduli ( $G'$  and  $G''$ ) were measured from the oscillatory experiments.

### Intrinsic Viscosity Measurements

The intrinsic viscosities of the solutions were measured using a calibrated shear dilution viscometer (Cannon-Ubblohde series 150). For the solutions discussed in this work, the shear rates were all <100/sec. The measurements were performed in a circulating water bath at 25.0 ± 0.1°C. The stock solution was used for the first measurement and was then diluted in the viscometer. The resulting solution was mixed by gentle agitation before the next measurement. This process was continued until the flow time of the solution was within 5 sec of the flow time of the solvent. Flow times were measured a minimum of five times for each solution. The intrinsic viscosity was obtained for each of the materials by extrapolating the specific viscosity and concentration ( $\eta_{sp}/c$ ) where:

$$\eta_{sp} \frac{\eta - \eta_s}{\eta_s} \quad (1)$$

versus concentration, or

$$\frac{1}{c} \ln \left( \frac{\eta}{\eta_s} \right) \quad (2)$$

to zero concentration. In Eqs. 1 and 2,  $\eta$  is the viscosity of the polymer solution,  $\eta_s$  is the viscosity of the solvent, and  $c$  is the concentration.

## RESULTS AND DISCUSSION

### Evaluation of Coil Overlap Concentration

Stock starch solutions were diluted to concentrations of 0.02–0.05 g/mL. This concentration range places the samples in the semidilute regime where coil overlap can affect the conformational dynamics of the coils in solution. The transition from dilute solution to semidilute solution behavior is designated as  $c^*$  (Doi and Edwards 1988, Ferry 1980, Macosko 1994) and can be approximated by:

$$c^* \approx \frac{3}{[\eta]} \quad (3)$$

At concentrations significantly higher than  $c^*$ , the polymer chains become highly entangled and the conformational dynamics are governed largely by chain-chain interactions. The transition from

the semidilute to concentrated solution behavior is designated as  $c^{**}$  (Macosko 1994) and can be approximated crudely as:

$$c^{**} \approx \frac{10}{[\eta]} \quad (3)$$

For WM starch, the measured intrinsic viscosity was 209 ± 4 mL/g; for NM starch, the intrinsic viscosity was 178 ± 2 mL/g. Using Eqs. 3 and 4, the  $c^*$  value is 0.014 g/mL for WM starch and 0.017 g/mL for NM starch. The  $c^{**}$  value is 0.048 g/mL for WM starch and 0.056 g/mL for NM starch. The highest concentration used in this study for both WM and NM starch was 0.05 g/mL. Thus, the solutions studied are predominately in the semidilute regime, with only the highest concentration of the WM starch considered marginally concentrated.

### Oscillatory Shear Flow Experiments

Small-amplitude oscillatory shear experiments at 25°C were conducted on WM and NM starch solutions. The data for WM obtained at 80°C were shifted to 25°C using the time-temperature superposition procedure of Williams et al (1955). The data for WM and NM starch were then shifted, with respect to concentration, using the method of corresponding states as described by Ferry (1980). In this approach, a master curve is constructed using shifts in time and concentration in analogy to time-temperature superposition. Care must be taken when applying this approach as the concentration dependence of the various viscoelastic functions varies from the plateau to the terminal regimes as well as from the semidilute to dilute regimes. Several researchers (Ferry 1980) have used the following expressions with success:

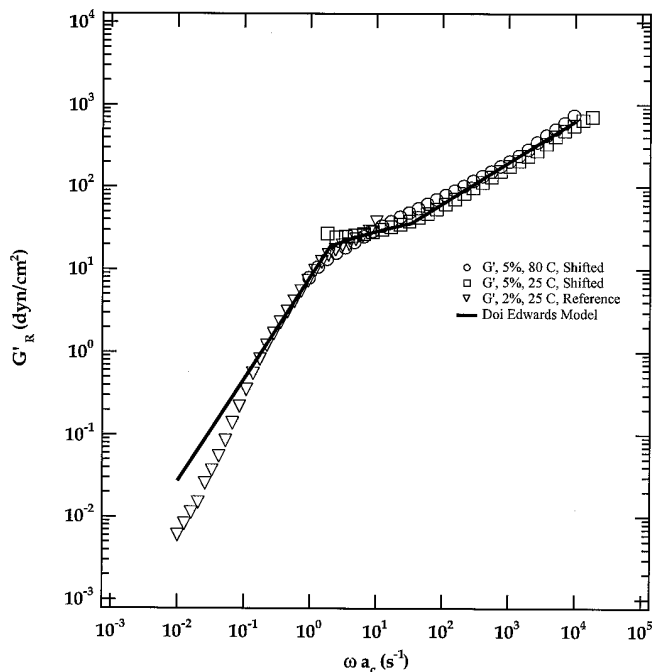
$$G'_R \equiv \left[ \frac{c_2}{c_1} \right]^2 G', \text{ versus } \omega a_c \quad (5)$$

where  $c_1$  and  $c_2$  are the reference and shifted concentrations, respectively, and  $a_c$  is the concentration shift factor. Thus, a plot of  $G'_R$  versus  $\omega a_c$  yields a master curve at the reference concentration.

The reference concentration selected for both materials was 0.02 g/mL, which will place the resulting master curves in the semidilute regime. The active shifting variable chosen was  $G'$ . The shifting was accomplished using software (Wavemetrics Igor Pro software, with an Apple Macintosh 8600/300 computer). Standard deviation of the fit was calculated as the difference between the log of the shifted storage moduli and the log of the reference storage moduli. The best overlap was chosen as the set of shift parameters that minimized the standard deviation. The results of the data shifts are illustrated in Figs. 1 and 2 for WM and NM starch, respectively. From Fig. 2, it is evident that the shifting routines applied to NM starch produced a master curve with more scatter in the data than they did for WM starch. This scatter might reflect the more complicated mixture of amylose and amylopectin that constitutes NM starch.

### Application of the Doi-Edwards Model

To obtain a value for the entanglement molecular weights for WM and NM starch, some kind of molecular or phenomenological models need to be applied to the data presented above. One approach to understanding the viscoelastic response of polymer chains in concentrated and semidilute solutions was advanced by Doi and Edwards (1978a–c, 1988), which is based on the concepts of reptation as formulated initially by DeGennes (1979). In reptation-based models, the polymer chains in a semidilute or concentrated solution are envisioned as moving predominately along their contour with the surrounding media behaving as a viscous liquid which can be characterized by a local viscosity or friction coefficient. Movements of the chain perpendicular to its contour are inhibited by the presence of a tube formed by the entangled network of the other chains in the solution. Within this framework,



**Fig. 1.** Master curve of the reduced storage modulus ( $G'_R$ ) versus reduced frequency for waxy maize (WM) starch at a reference temperature of 25°C and a reference concentration of 0.02 g/mL. Data were shifted in concentration according to the theory of reduced variables. Solid line denotes results of Doi-Edwards theory fitted to the experimental data using  $G_n = 30 \pm 3$  dyn/cm<sup>2</sup>,  $\tau_e = 0.030 \pm 0.002$  sec, and  $\tau_d = 50 \pm 4$  sec.  $a_c$  = concentration shift factor

the conformational dynamics of the chain can be characterized by a time constant ( $\tau_e$ ) that denotes the time when the effects of tube constraints on the viscoelastic functions are first observed. For a system with sufficiently high molecular weight at times shorter than  $\tau_e$ , the dynamics of the chains are given by the bead-spring model of Rouse (1953). At times longer than  $\tau_e$ , the dynamics of the chains are described by the reptation model up to the time when the chain disengages from the tube, designated as  $\tau_d$ .

For an oscillatory shear experiment, the storage modulus  $G'$  is predicted by the Doi and Edwards model as:

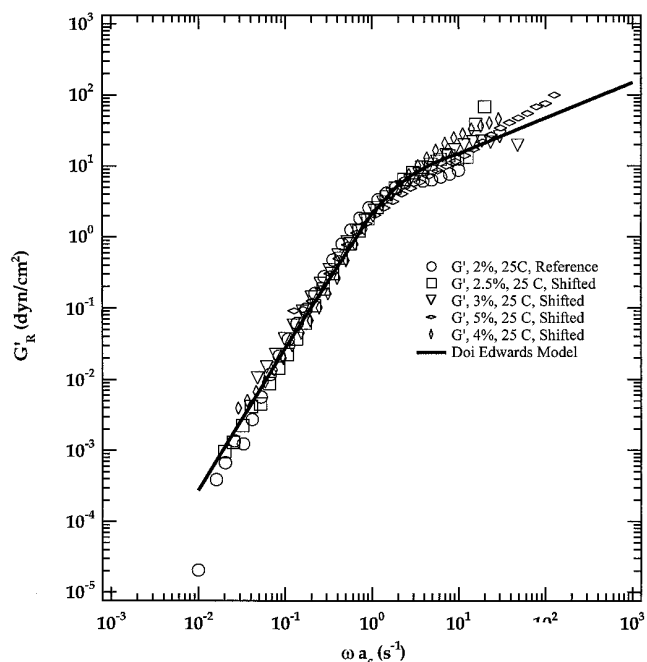
$$G'(\omega) = G_n \left( \frac{\pi}{2} \omega \tau_e \right)^{\frac{1}{2}} \text{ for } \omega \tau_e \geq 1 \quad (6)$$

and

$$G'(\omega) = G_n \sum_{p \text{ odd}} \frac{8}{\pi^2} \frac{1}{p^2} \frac{(\omega \tau_d / p^2)^2}{1 + (\omega \tau_d / p^2)^2} \text{ for } \omega \tau_e \leq 1 \quad (7)$$

where  $G_n$  is the plateau modulus and  $\omega$  is the oscillatory frequency in seconds.

Eqs. 6 and 7 were fitted to the experimental data of WM and NM starch using  $\tau_e$ ,  $\tau_d$ , and  $G_n$  as adjustable parameters. The fitting was accomplished using software (MathCad Pro with an Apple Macintosh 8600/300 computer). The standard deviation of the fit was calculated as the difference between the log of the experimental storage moduli and the log of the calculated storage moduli. The best overlap was chosen as the set of shift parameters that minimized the standard deviation. The results of the data fitting for WM and NM starch are illustrated in Figs. 1 and 2, respectively, and summarized in Table I. From the data presented in Table I, it is evident that both WM and NM starch exhibit a similar plateau modulus. However, the times for the entanglement and tube disengagement processes are quite different for the two materials. The shorter disengagement time for NM starch is probably due to the presence of the lower molecular weight amylose chains which are not present in WM starch.



**Fig. 2.** Master curve of the reduced storage modulus ( $G'_R$ ) versus reduced frequency for normal maize (NM) starch at a reference temperature of 25°C and a reference concentration of 0.02 g/mL. Data were shifted in concentration according to the theory of reduced variables. Solid line denotes results of Doi-Edwards theory fitted to the experimental data using  $G_n = 30 \pm 3$  dyn/cm<sup>2</sup>,  $\tau_e = 0.10 \pm 0.03$  sec, and  $\tau_d = 5 \pm 0.3$  sec.  $a_c$  = concentration shift factor

An estimate of the entanglement molecular weight can be obtained from the values of the plateau modulus using the Doi-Edwards theory. From the theory of elasticity (Treoar 1975), the relationship between  $G_n$  and the entanglement molecular weight ( $M_e$ ) is usually expressed as:

$$G_n = \frac{\rho RT}{M_e} \quad (8)$$

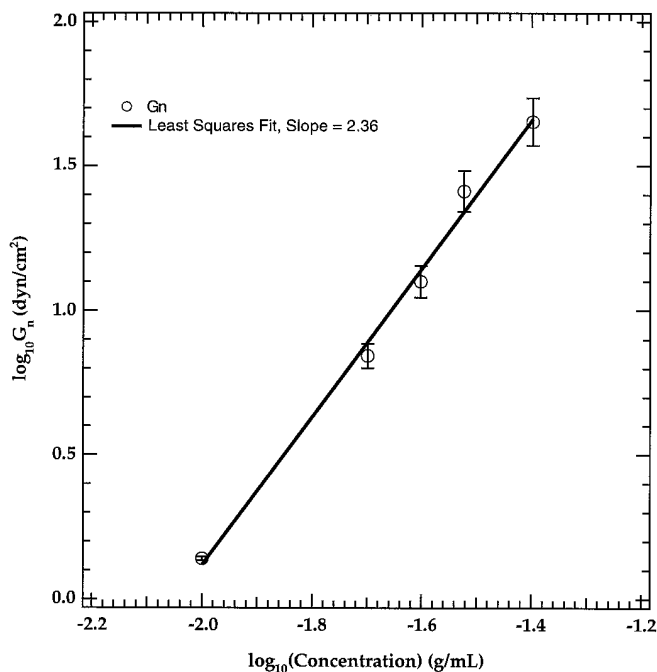
where  $\rho$  is the density,  $R$  is the gas constant, and  $T$  is the absolute temperature. The entanglement degree of polymerization ( $N_e$ ) is defined as:

$$N_e = \frac{M_e}{M_0} \quad (9)$$

where  $M_0$  is the monomer molecular weight. It is often useful to compare the entanglement degrees of polymerization of different materials instead of the entanglement molecular weight because the  $N_e$  value is independent of the size of the monomer unit. For many commercial synthetic materials, the transition to entangled flow behavior occurs at an  $N_e$  value of 200–300 (Klein 1987).

To utilize Eq. 8, we need to account for the effect of concentration. According to Ferry (1980),  $\rho$  in Eq. 8 needs to be replaced with  $c^2$ . This argument is forwarded based on the concentration dependence of density of the entangled chains. In contrast, De Gennes (1976a,b) has argued from scaling concepts that  $\rho$  should be replaced with  $c^{9/4}$ . Because we have utilized the theory of Doi and Edwards, which is based on De Gennes reptation concepts, the factor of 9/4 will be used in these calculations instead of 2. To corroborate this decision, the measured plateau moduli for NM starch are plotted against concentration as illustrated in Fig. 3. The slope of the fitted least squares line is 2.36, which is close to the value of 9/4 predicted by reptation theory.

Substituting  $c^{9/4}$  for  $\rho$  in Eq. 6 and using the values for  $G_n$  in Table I, the entanglement molecular weight of WM starch is  $100 \pm 15$  g/mol. For NM starch, the value for the entanglement molecu-



**Fig. 3.** Effect of concentration for the measured plateau modulus ( $G_n$ ) of normal maize (NM) starch at 25°C. Solid line represents best straight-line fit to experimental data. Slope of 2.36 is close to that predicted by reptation theory of 9/4.

lar weight is  $96 \pm 8$  kg/mol. The two values are within experimental error of one another and yield a value for the entanglement molecular weight of amylopectin. The entanglement degrees of polymerization for WM and NM starch, using a value of 162 g/mol for the monomer molecular weight of amylopectin, are  $617 \pm 92$  and  $592 \pm 49$ , respectively. A comparison of the entanglement molecular weights for WM and NM starch with common synthetic polymers is presented in Table II. The entanglement molecular weights and entanglement degrees of polymerization for WM and NM starch are higher than those quoted (Ferry 1980) for typical commercial synthetic polymers such as polystyrene (PS), polyethylene (PE), poly(methyl methacrylate) (PMMA), or poly(dimethyl siloxane) (PDMS), but they are comparable to that obtained for poly(*n*-octyl methacrylate). It is probable that the randomly branched structure of amylopectin contributes to the high value obtained for the entanglement molecular weight because bulky side groups are known to influence this molecular parameter. For instance, the entanglement molecular weight of polystyrene is 17–18 kg/mol, while the entanglement molecular weight of poly(vinyl cyclohexane), which is hydrogenated polystyrene, is 40 kg/mol. The difference in the entanglement molecular weight is attributed to the size difference in the benzene versus cyclohexane side groups.

## CONCLUSIONS

The entanglement molecular weights of WM and NM starch are calculated from solution rheological data. The viscoelastic behavior of both WM and NM starch are measured at several different concentrations and then shifted to produce a master curve for each of the materials. The theory of Doi and Edwards is used to calculate the plateau moduli from which values for the entanglement molecular weights for WM and NM starch are calculated. The entanglement molecular weight for WM starch is  $100 \pm 15$  kg/mol. For NM starch, the value for the entanglement molecular weight is  $96 \pm 8$  kg/mol. These two values are within experimental error of one another and represent the entanglement molecular weight of amylopectin, the major component of WM and NM starch. The entanglement degrees of polymerization for WM and NM starch,

**TABLE I**  
Summary of Model Parameters<sup>a</sup> from the Doi-Edwards Model as Applied to Waxy Maize (WM) and Normal Maize (NM) Starch<sup>b</sup>

Material	$G_n$ (dyn/cm <sup>2</sup> )	$\tau_c$ (sec)	$\tau_d$ (sec)
WM	$30 \pm 3$	$0.030 \pm 0.002$	$50 \pm 4$
NM	$30 \pm 3$	$0.1 \pm 0.03$	$5 \pm 0.3$

<sup>a</sup>  $G_n$  = plateau modulus;  $\tau_c$  = time when the effects of tube constraints on the viscoelastic functions are first observed;  $\tau_d$  = time when the chain disengages from the tube.

<sup>b</sup> Errors represent  $\pm 1$  standard deviation from the mean fit value.

**TABLE II**  
Comparison of Entanglement Molecular Weights ( $M_e$ ) and Entanglement Degrees of Polymerization ( $N_e$ ) for Waxy Maize (WM) and Normal Maize (NM) Starch and Several Commercial Synthetic Polymers<sup>a</sup>

Material	$M_e$ (kg/mol)	$N_e$	$M_0$ (g/mol)
WM	$100 \pm 15$	$617 \pm 92$	162
NM	$96 \pm 8$	$592 \pm 49$	162
PS	17–18	163–173	104
PE	1.25	45	28
PMMA	4.7	47	100
PDMS	12	162	74
Poly( <i>n</i> -octyl methacrylate)	87	439	198

<sup>a</sup> PS = polystyrene, PE = polyethylene, PMMA = poly(methyl methacrylate), PDMS = poly(dimethyl siloxane). Values for commercial polymers obtained from Ferry (1980).  $M_0$  = monomer molecular weight.

using a value of 162 g/mol for the monomer molecular weight of amylopectin, are  $617 \pm 92$  and  $592 \pm 49$ , respectively. The values for the entanglement molecular weight and the entanglement degrees of polymerization for WM and NM starch are markedly higher than those quoted for many commercial polymers. This finding indicates that in order for starch-based materials to have consistent physical properties, the minimum molecular weight is on the order of  $10^6$  g/mol. Materials produced with molecular weights  $<10^6$  g/mol will have physical properties such as tensile strength and fracture toughness which will depend strongly on the molecular weight of the sample.

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