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# Thermomechanical depolymerization of dextran[☆]

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## Abstract

Native, high-molecular weight dextran was subjected to ultrasonication at 20 kHz and 1.5 MHz, jet-cooking with high pressure steam and twin-screw extrusion under a variety of conditions. The extent of depolymerization was measured by size-exclusion chromatography and viscometry. All methods reduced the molecular weight and solution viscosity of dextran. The greatest degree of depolymerization occurred with 20 kHz ultrasonication. With extrusion, increasing amounts of specific mechanical energy input resulted in greater degrees of depolymerization. Each of these methods has advantages and drawbacks for the production of reduced-molecular weight dextrans. Sonication was more effective at depolymerizing dextran, but is currently too expensive to be amenable to large-scale manufacture. Extrusion is relatively inexpensive and scalable, but produces some undesirable dark-colored side products. Jet cooking is inexpensive and scalable, and does not produce the colored side products, but requires dissolution of the sample in water, followed by drying. Considering all of these factors, jet-cooking may show the most promise for production of low-viscosity dextran fractions. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Dextran; High pressure steam; Jet-cooking; Sonication; Twin-screw extrusion

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## 1. Introduction

Low-molecular weight dextrans are used for such clinical applications as blood plasma extenders and as starting materials for dextran sulfates (Alsop, 1993; DeBelder, 1993). Related low-molecular weight glucans were proposed as food ingredients (Cote et al., 1997). Normally, dextrans are synthesized from sucrose as high-molecular weight polymers which are unsuitable for certain applications. Strategies for producing materials of lower molecular size include acid hydrolysis (Alsop, 1993; DeBelder, 1993), enzymolysis (Corman and Tsuchiya, 1957), ultrasonication (Watson and Wolff, 1955; Basedow and Ebert, 1977; Szu et al., 1986; Lorimer et al., 1995 and shear degradation (Basedow et al., 1979); Carrasco et al., 1987). Biosynthesis in the presence of acceptors (polymerization terminators) is another possibility (Tsuchiya et al., 1955). Each of these methods has advantages and drawbacks.

Extrusion (Lai and Kokini, 1991; Millard et al., 1997; Willett et al., 1997) and jet-cooking (Dintzis and Bagley, 1995; Lawton, 1995; Dintzis and Fanta, 1996; Millard et al., 1997) was reported to affect the viscosity of starch polysaccharides, but little is known about depolymerization of other polysaccharides by these methods. Extrusion especially represents a relatively low-cost, high-throughput method well suited for industrial scale-up. Development of a low-cost method for production of low-viscosity dextran and other polysaccharides will likely lead to new markets for these products.

## 2. Experimental

High molecular weight industrial grade dextran (Dextran 2P, advertised weight-average molecular weight ($\bar{M}_{\bar{w}}$ range $5 \times 10^6 \pm 2 \times 10^6$) was purchased from Pharmachem Corp., Bethelehem, PA. Nitrogen content as measured by the Kjeldahl method was 0.14%, which corresponds to a protein content of approximately 0.88%.

Dextran powder was extruded in a Werner and Pfleiderer ZSK-30 corotating twin screw extruder, with a 25/1 L/D

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Table 1
Dextran extrusion parameters

| Sample | Dextran feed rate (g/min)[a] | Water feed (g/min) | Moisture content (%) | Screw speed (rpm) | Torque fraction | SME (J/g)[b] | Melt temperature (°C) |
|---|---|---|---|---|---|---|---|
| 1 | 148 | 48 | 28 | 135 | 0.44 | 453 | 109 |
| 2 | 182 | 39 | 21 | 135 | 0.62 | 519 | 115 |
| 3 | 204 | 31 | 17 | 175 | 0.71 | 684 | 126 |
| 4 | 238 | 27 | 14 | 240 | 0.79 | 891 | 140 |
| 5 | 261 | 27 | 13 | 275 | 0.77 | 916 | 149 |
| 6 | 261 | 20 | 11 | 275 | 0.92 | 1098 | 160 |

[a] Dextran moisture content = 4.0%.
[b] Specific Mechanical Energy; calculated on dry basis.

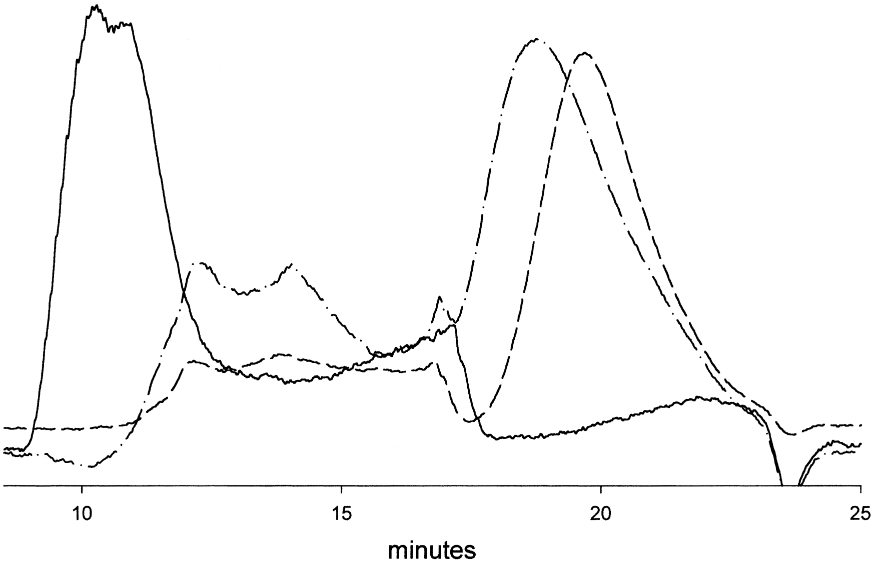

Fig. 1. HPSEC analysis of native, high-molecular weight dextran (—), dextran sonicated at 1.5 MHz (– · –), and dextran sonicated at 20 kHz (– – –). Conditions: Shodex KB-806 M column, eluted at 23°C with $H_2O$ at 0.5 ml/min. Detection by optical rotation with Shodex OR-1 detector. Vertical scale is relative detector response in mV, normalized to bring all samples to the same scale.

barrel. Dextran powder was metered into the feed throat in the first barrel section and transported by a series of conveying elements. Distilled water was injected via a triple-piston pump at approximately 16 L/D downstream from the feed throat. The next 9 L/D consisted of a series of kneading sections as follows: 45/5/14, 45/5/14 LH; 45/5/14, 45/5/14 LH; 90/5/28, 45/5/14 LH; 90/5/28, 20/10 LH. In this nomenclature, the first number is the stagger angle in degrees between individual blocks in a kneading element. The second number gives the number of blocks per element and the final number is the length of an individual block in mm. Elements with the LH designation are left handed blocks, which increase pressure and retention time. The kneading sections were separated by a single conveying element of 28 mm pitch. The thermoplastic dextran was then conveyed to the die section and extruded through a die plate with 2 holes of 4 mm diameter each.

Table 1 summarizes the extrusion parameters used in this work. Extrusion was begun using the mildest conditions (Sample 1). After the extruder had stabilized with this set of parameters, extrusion was continued for approximately 10 min before sampling. After sampling, the extrusion conditions were changed to increase the severity, as measured by specific mechanical energy, and allowed to stabilize again before sampling. Moisture contents ranged from 28% (Sample 1) to 11% (Sample 6).

The specific mechanical energy (SME) imparted to the dextran during extrusion was calculated using the following expression:

$$\mathrm{SME} = \frac{2\pi^{*}2T_{\mathrm{s}}^{*}f_{\mathrm{T}}^{*}N}{m}$$

where $T_s$ is the maximum torque per shaft (86 N m), $f_T$ is the fraction of maximum torque experienced during extrusion, $N$ is the screw speed in rpm, and $m$ is the feed rate in g/min. The units of SME are J/g.

Jet cooking was done on 2% aqueous dextran samples using a high-pressure steam jet cooker as described by Lawton (1995) and by Dintzis and Fanta (1996). Two different sets of conditions were employed during jet cooking. The milder set of conditions employed a temperature of 158° and inlet and outlet steam pressures of 70 and 40 psig, respectively. The more severe conditions were 176° and inlet and outlet pressures of 120 and 40 psig. Details of the jet-cooking process and apparatus was described (Dintzis and Fanta, 1996).

Dextran solutions were sonicated at 1.5 MHz using a UES Model 1.5-660 sonicator with an attached 500 ml glass chamber (Ultrasonic Energy Systems, Panama City, FL). The chamber was cooled by immersion in an ice-water bath during sonication. Sonication at 20 kHz was performed as previously described (Cote, 1992).

Viscosity determinations were performed at 20°C, using a Brookfield LVTDV-I viscometer (Brookfield Engineering Laboratories, Stoughton, MA) equipped with either a small sample adapter or a UL adapter. Both of these use a rotating cylinder within a cylindrical chamber, and the choice of adapter depended on the viscosity range. High performance size-exclusion chromatography (HPSEC) was performed using a Waters 625 LC system equipped with a Shodex KB-806 M gel permeation column, eluted at ambient temperature (23°C) with water at a flow rate of 0.5 ml/min. Detection was by either refractive index (Waters 401 detector) or optical rotation (Shodex OR-1 detector).

Colorimetric measurements of solid powdered materials

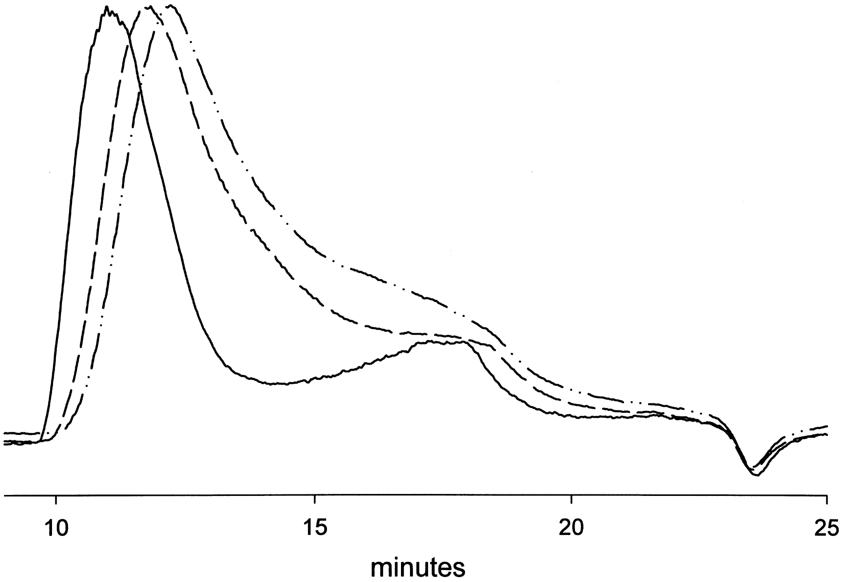

Fig. 2. HPSEC analysis of native, high-molecular weight dextran (—), dextran jet-cooked at 120/40 psig, 176° (– – –), and dextran jet-cooked at 70/40 psig, 158° (– · · –). See Fig. 1 for details.

were accomplished by use of a Hunterlab Colorimeter Model D25-3 (Hunter Associates Laboratory, Riston, VA). The parameter *L* is a measure of sample lightness (100 = lightest, 0 = darkest), *a* is a measure of red (positive) or green (negative) color, and *b* is a measure of yellow (positive) or blue (negative) color.

## 3. Results and discussion

It is clear from our prior work (Cote, 1992) and previous work done by others (Watson and Wolff, 1955; Basedow and Ebert, 1977; Szu et al., 1986; Lorimer et al., 1995) that ultrasonication will depolymerize dextran and other polysaccharides to give a lower $\bar{M}_{\bar{w}}$, low-viscosity product. The products are very clean and uniform, and yields are virtually 100%. However, the required treatment times are long, on the order of several hours or more for relatively small samples, and the equipment is expensive and not amenable to scale-up. Most prior work utilized sonicators designed for cell disruption, which operate at 20 kHz. The effect of sonication at higher frequency (1.5 MHz) was also investigated in the present study. Fig. 1 shows HPSEC analysis of dextrans extensively sonicated at 20 kHz and 1.5 MHz. The sonication process was monitored chromatographically and when significant changes in $\bar{M}_{\bar{w}}$ had ceased, the process was judged to be complete. As Fig. 1 shows, sonication at either frequency dramatically lowered the $\bar{M}_{\bar{w}}$ distribution of dextran, as expected. However, treatment at 20 kHz resulted in a significantly lower final $\bar{M}_{\bar{w}}$ distribution relative to the material treated at 1.5 MHz. We can currently provide no explanation for this difference, but it should be pointed out that, unlike light radiation, the energy of sonic irradiation is not related to frequency. The mechanism of ultrasonic depolymerization of dextran was investigated in detail by previous workers, who have found that temperature, time, intensity (i.e., amplitude or power), and solution concentration are the most important factors (Lorimer et al., 1995). It has also been found that sonication breaks bonds near the middle of the chain, resulting in two molecules of roughly equal size, each approximately half the length of the original chain (Basedow and Ebert, 1977) It is generally believed that the effect of ultrasonication is due mainly to the high temperature and shear produced by sonically-induced cavitation (Basedow and Ebert, 1977). That is, alternating compression and rarefaction causes bubbles to rapidly form and collapse within the solution. Temperatures within the bubbles can be quite high, and shear at the liquid–vapor interface is likewise high (Basedow and Ebert, 1977). This combination of high temperature and high shear is probably the cause of dextran depolymerization by ultrasonicaion. The frequency of the applied ultrasound is apparently important only in so far as relates to its ability to induce cavitation in a given solvent. Typically, sonochemistry is performed at 20 kHz. Higher frequencies may lead to less efficient cavitation. For example, medical ultrasound imaging is performed at 5–10 MHz. These higher frequencies are not known to cause physical changes in fragile biological structures.

Jet cooking of dextran also caused depolymerization, as seen in Fig. 2. Dextran jet-cooked under conditions of higher pressure and temperature was more extensively degraded, but both sets of conditions caused significant decreases in molecular size and viscosity. This is essentially a shear induced phenomenon, as suggested by the shift in the elution time of the higher $\bar{M}_{\bar{w}}$ peak in Fig. 2. This peak, representing the highest $\bar{M}_{\bar{w}}$ chains, shifts from approximately 11 min to approximately 13 min, with no

Table 2
Hunter $L^*a^*b$ color index values for dextran samples in solid form ($L$ = Lightness; $a$ = red ( + )/green ( − ); $b$ = yellow ( + )/blue( − ))

| Sample | *L* ± s.d. | *a* ± s.d. | *b* ± s.d. |
|---|---|---|---|
| Dextran | 92.6 ± 0.2 | −1.4 ± 0.1 | 8.6 ± 0.1 |
| Sonicated[a] dextran | 91.89 ± 0.05 | −0.99 ± 0.03 | 4.38 ± 0.02 |
| Jet-cooked[b] dextran | 88.9 ± 0.7 | −0.83 ± 0.05 | 6.4 ± 0.1 |
| Extruded dextran 1 | 80.9 ± 0.8 | 0.6 ± 0.3 | 17.1 ± 0.6 |
| Extruded dextran 2 | 80.8 ± 1.7 | 0.7 ± 0.1 | 18.4 ± 1.5 |
| Extruded dextran 3 | 75.8 ± 3.0 | 2.3 ± 0.9 | 21.2 ± 1.9 |
| Extruded dextran 4 | 80.2 ± 1.0 | 1.5 ± 0.3 | 17.9 ± 0.6 |
| Extruded dextran 5 | 78.9 ± 1.1 | 2.0 ± 0.3 | 18.6 ± 0.3 |
| Extruded dextran 6 | 79.07 ± 0.07 | 1.9 ± 0.3 | 20.2 ± 0.2 |

[a] Sonicated at 1.5 MHz.

[b] Jet cooked at 120/40 psig, 176°.

corresponding shift in the elution time of the smaller peak at approximately 18 min. This indicates that jet-cooking chiefly affects longer chains.

Extrusion led to noticeable changes in the appearance of the dextran samples. The conditions of high SME and temperature led to highly colored products which had a distinct odor of caramel or slightly burnt sugar. Color changes in extruded dextrans are shown in Table 2. The extruded dextrans were all significantly more colored than the original dextran, as indicated by the decrease in factor *L* (lightness) values. Sonicated dextran was virtually identical to untreated dextran in color, and jet-cooked dextran was only slightly more colored. Extruded dextran samples contained more reddish and yellowish hues (factors *a* and *b*), indicating an increase in brownish-amber coloration. Solutions of the extruded dextrans tended to be less turbid than native dextran, suggesting a decrease in molecular size, although the extruded samples did contain higher levels of unfilterable particulate matter. The effect of extrusion on molecular weight is illustrated by HPSEC analysis. As Fig. 3 indicates, there is a successive decrease in $\bar{M}_{\bar{w}}$ with increasing SME. Lack of reliable molecular weight standards in this range prevents us from obtaining good estimates of the molecular masses of these compounds.

Depolymerization is also indicated by the viscosity behavior of the extruded dextran samples. Fig. 4 demonstrates the relationship between mechanical energy input during extrusion and solution viscosity of the resultant products. In addition to exhibiting lower viscosities, samples with greater SME displayed less shear thinning (Fig. 5). A similar relationship between SME and $\bar{M}_{\bar{w}}$ was observed for extruded waxy maize starch (Willett et al., 1997).

Many factors influence the effects of extrusion on polymers, including temperature, shear rates, and moisture levels. In turn, these factors are influenced by such parameters as screw design, feed rates, heating or cooling rates. These factors all impact the changes in polymer molecular size through SME.

The three physical methods of dextran depolymerization are compared in Fig. 6. Ultrasonication obviously resulted in the greatest degree of breakdown, leading to a much lower viscosity than the other two methods. The sample shown here is that produced by sonication at 1.5 MHz. The material produced at 20 kHz is even lower in viscosity, and is comparable to gum arabic in its rheological properties (Cote, 1992).

Jet-cooking under high steam pressure and extrusion under the harshest conditions described here led to materials with similar viscosities (Fig. 6). Milder extrusion conditions led to less depolymerization; for the sake of clarity, only Sample 6 is shown in Fig. 6.

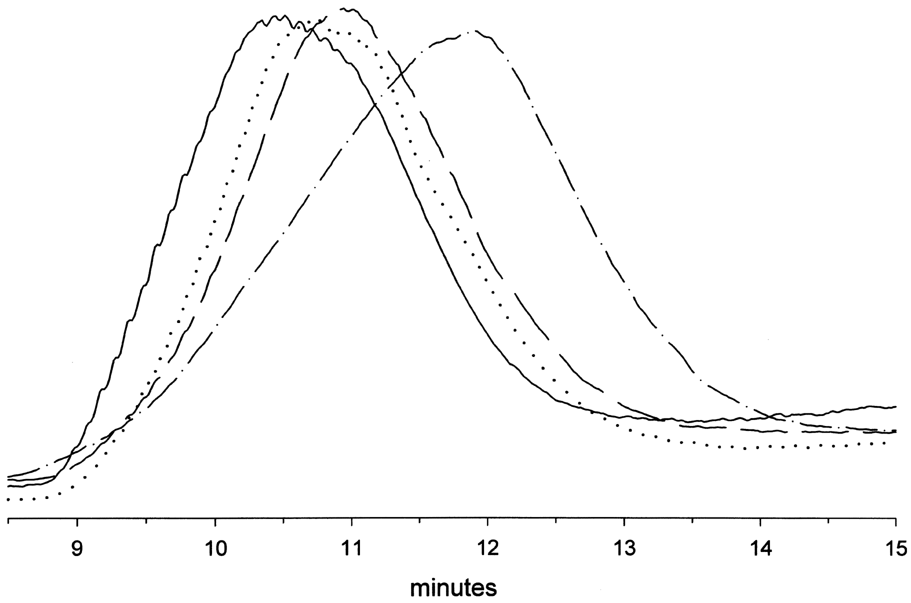

Fig. 3. HPSEC analyses of native dextran (—) and extruded dextran samples 2(· · ·), 4(– – –) and 6(– · –). See Fig. 1 for details.

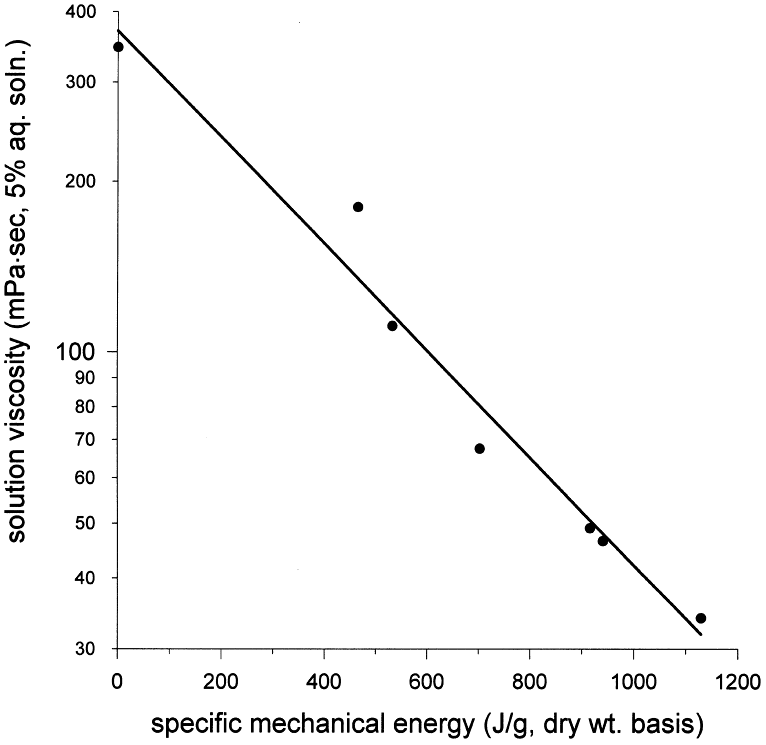

Fig. 4. Solution viscosity of 5% aqueous solutions of dextran and extruded dextrans as a function of mechanical energy input during extrusion. Viscosity was measured at a shear rate of 7.92 $s^{-1}$, at 20°C, as described in the text.

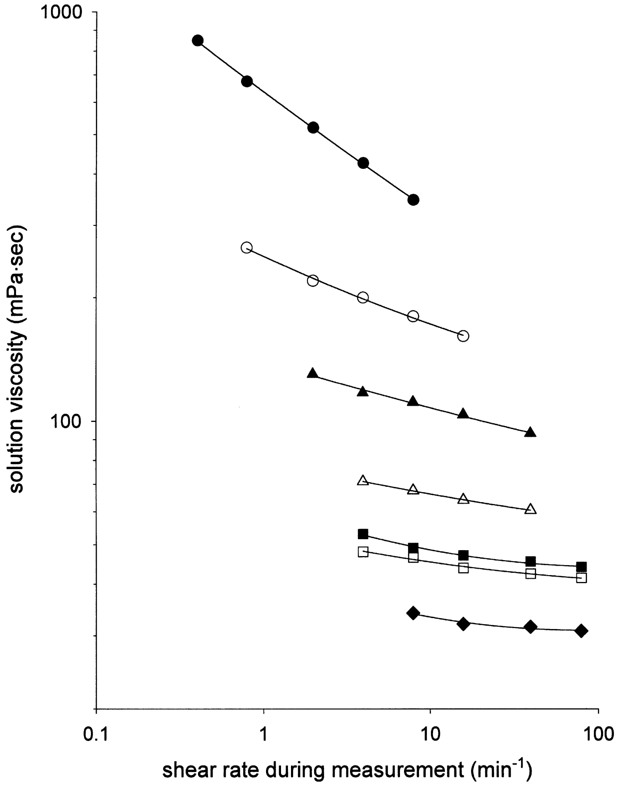

Fig. 5. Viscosity of 5% (aq) solutions as a function of shear rate during measurement for extruded dextran samples. Native dextran (●), extruded dextran samples 1(○), 2(▲), 3(△), 4(■), 5(□) and 6(◆).

This work demonstrates the feasibility of using extrusion or jet cooking for the depolymerization of dextran. For certain industrial applications this may provide a low-cost alternative to acid hydrolysis or enzymolysis. Each of the methods described here possesses certain advantages and drawbacks. Extrusion is relatively inexpensive and amenable to industrial scale-up. However, the degree of depolymerization produced in these experiments did not approach that obtainable by ultrasonication. Perhaps conditions can be found in future experiments that will lead to more extensive reductions in molecular size and viscosity. Another drawback of extrusion under the conditions described here was the production of colored byproducts, presumably from caramelization or Maillard reactions with the low levels of protein present in dextran. Our analyses indicated protein to be present in the dextran samples at the level of about 0.8% (w/w). We expect that extrusion in the presence of antioxidants or reducing agents may prevent some color formation.

Jet cooking also deserves further investigation as a useful method for the depolymerization of dextran and other polysaccharides. Although our results are preliminary, we were able to produce a material comparable to that manufactured by extrusion (Fig. 6). One notable advantage of jet cooking is that it did not result in the production of any colored or odorous by-products. This is especially advantageous in the manufacture of food ingredients. However, jet cooking requires a feedstock in relatively dilute solutions, thereby

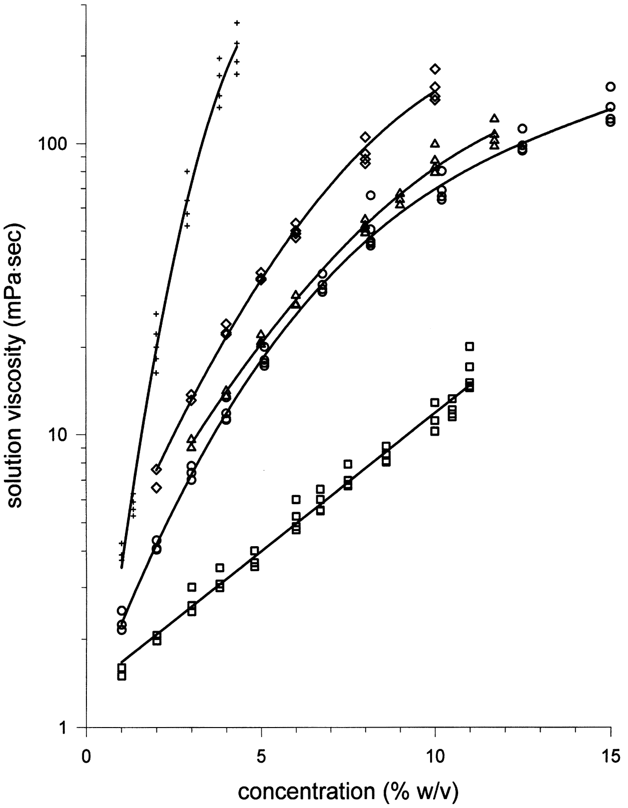

Fig. 6. Viscosity vs. concentration of dextran and depolymerized dextrans. Native dextran ( + ), dextran jet-cooked under low-pressure conditions (◇), dextran jet-cooked under high-pressure conditions (△), extruded dextran sample no. 6(○), and 1.5 MHz ultrasonicated dextran (□). Multiple symbols at each concentration represent measurements at different shear rates.

increasing the cost over extrusion, which uses solid material.

From a scientific standpoint, ultrasonication is a very interesting alternative procedure for polysaccharide treatment. Although it was studied for many years the mechanism by which it breaks polymer chains is still incompletely understood. From a practical viewpoint, it provides a product with no off-color, leads to considerable depolymerization, and no losses of material occur. On a laboratory scale, it may be the method of choice for reducing the viscosity of polysaccharide solutions. However, it is not currently amenable to scale-up to industrial processes, although improvements in sonicator design may eventually change this situation.

## 4. Conclusions

This preliminary study shows that both twin-screw extrusion and high-pressure steam jet-cooking can be used to depolymerize industrial dextran to give products with smaller molecular sizes and lower solution viscosities. Ultrasonication produced lower molecular weight fragments than either extrusion or jet cooking.

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