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Starch fragmentation during extrusion processing*

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This study focuses on the molecular fragmentation of starch as a result of extrusion-based thermomechanical processing. Gel permeation chromatography–light scattering and bulk intrinsic viscosity measurements were used for the macromolecular characterization. The data indicate that the extrusion processing of starch results in a reduction in its molecular weight. Such a fragmentation of the starch polymer could be attributed, at least partly, to debranching of the molecules.

(Keywords: starch; extrusion; fragmentation)

INTRODUCTION

In recent years, a variety of environmental issues relating to solid waste disposal have gained attention. The increasing fraction of solid waste attributable to commodity thermoplastics and their generally low degradability upon disposal have been a cause of growing concern[1]. Environmentally degradable thermoplastics can offer a solution to some of these problems for applications pertaining to disposal in the environment. Although a variety of biopolymers are potentially utilizable (either by themselves or in blends with synthetic polymers) towards this end, starch stands out as one of the most viable candidates owing to its low cost and availability of large feedstocks. Among the many issues that must be considered for such an application of starch, an important one is the effect of extrusion processing on starch polymer at the molecular level. Since extrusion processing of starch has been traditionally used in the food industry, a number of studies have dealt with estimating the nature and extent of extrusion-based molecular modification of starches[2–9]. These studies indicate that, under the high-shear, high-temperature conditions that exist during such processing, starches can undergo a variety of changes at the intra- and intermolecular level. One important effect, that of the fragmentation of starch, leads not only to changes in its molecular weight and the molecular-weight distribution (*MWD*), but also in the structure of the molecules, which is not surprising given the nature of starch—generally a mixture of amylose (linear or long-chain branched molecules) and amylopectin (highly branched molecules). Since the physical and mechanical properties of polymeric materials are a function of such molecular parameters, a study of this fragmentation phenomenon is of particular interest for thermoplastic applications of starch where some required levels of mechanical performance are likely to be required.

In the past, conclusions of starch fragmentation during extrusion processing have been based on bulk measurements, such as water solubility[2–6], intrinsic viscosity[4–7] and light scattering[6], as well as on size-fractionation-based measurements, namely gel permeation chromatography (g.p.c.)[3–6,8,9], with the last category yielding mainly qualitative information for reasons discussed later.

A decrease in the intrinsic viscosities of extruded whole starch samples[4–7], and their fractionated amylose and amylopectin components[4], indicates some level of reduction in their molecular weights. Quantitative assessment of the molecular-weight changes from intrinsic viscosity measurements on polymer samples is based on estimation of their viscosity-average molecular weights ($\overline{M}_v$) using the Mark–Houwink relationship:

$$[\eta] = K'(\overline{M}_v)^a$$

Unfortunately, for starches, such a calculation is possible only for the amylose component, since the Mark–Houwink parameters (K' and a) for whole starches and amylopectin are generally not available—even if they were, their general applicability could be questionable since they will very likely be dependent upon the structure of the branched components (as for dextran[10], for example) and their structure, in turn, may vary with the processing the starch undergoes. In fact, the procedure for fractionating starch into its components for detailed intrinsic viscosity measurements could itself

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effect macromolecular modifications. This could be partly responsible for measurements reported in the literature where the average intrinsic viscosities of the whole starch samples are significantly different from the weighted intrinsic viscosities of the fractionated amylose and amylopectin components[6], in contrast to the usual weighted additivity of the components' intrinsic viscosities for macromolecular mixtures[11].

Gel permeation chromatography, the most common technique for determining molecular-weight distributions of polymers, allows the fractionation of molecules according to their molecular size (the sequence of elution depends on hydrodynamic volume, not absolute mass). The hydrodynamic volume scales as the product of intrinsic viscosity, $[\eta]$, and the molecular weight of the molecule, M, for random-coiling linear and homogeneous branched polymers[12]. This leads to the universal calibration curve based on narrow molecular-weight distribution polymers. The *MWD*s of different polymer samples may then be calculated if the Mark–Houwink parameters relating $[\eta]$ to M are known. However, there are three situations where such an analysis is not applicable: (a) if the sample does not follow the universal calibration[13], (b) if intrinsic viscosity (Mark–Houwink) parameters of the polymer to be analysed are unknown, or (c) if there is a mixture of molecules of different chemical or physical structure within the same elution slice. For materials such as unfractionated starches that contain a mixture of linear and branched macromolecules (and where the branching architecture might vary with the molecular weight), determination of the effective Mark–Houwink parameter for any elution slice in a chromatographic experiment becomes an extremely difficult proposition. In such cases, the traditional g.p.c. experiment yields mainly qualitative information about changes in the *MWD*s of the starch samples. Fractionation of starch into its components would still allow the universal calibration to be applied only for the amylose (again due to availability of Mark–Houwink coefficients only for amylose). For such complex polymer systems, multidetection gel permeation chromatography is of particular use by allowing the elucidation of the absolute molecular weight of each elution slice directly, and hence the absolute molecular-weight distribution of the polymer. Such systems are based on concentration-sensitive detectors (such as differential refractive index (d.r.i.)) coupled with light scattering (l.s.) and/or differential viscometric (d.v.) detectors.

For a g.p.c.–l.s. experiment (the method used in this study), the l.s. signal (measured at an angle θ to the incident beam) from any elution slice is proportional to the excess Rayleigh ratio, R_θ:

$$R_\theta = KcM_w P(\theta) \quad (1)$$

where c is the concentration of the polymer of weight-average molecular weight M_w in that elution slice, and K is an optical constant. $P(\theta) = 1 - 2\mu^2\langle r_g^2\rangle/3! + \cdots$ is commonly termed as the structure factor (where $\mu = (4\pi/\lambda)\sin(\theta/2)$, λ being the wavelength of the incident light, and r_g the radius of gyration of the scattering polymer molecules). The concentration of the polymer in the elution slice is measured using a concentration-sensitive detector. For every elution slice, extrapolation of Kc/R_θ vs. $\sin^2(\theta/2)$ to $\theta = 0$ yields the weight-average molecular weight of the molecules in that slice.

EXPERIMENTAL

The basic material for this study was an acid-modified high-amylose starch (National Starch EK Fl. Hylon 7, approximate amylose content 70%). This material was conditioned at 50% relative humidity, and then processed in a twin-screw, co-rotating extruder (Leistriz standard model 34)[14]. Glycerine and some additional water were added to the feed to act as plasticizers. Overall, the glycerine and water contents of the material in the extruder were 13.7% and 17.7% of the total feed by mass, respectively. A small amount of low-molecular-weight processing aids were also added (< 1% of the total feed by mass). The peak temperature in the extruder was 170°C, and a screw speed of 150 r.p.m. was used during the processing, resulting in a die pressure between 55 and 88 MPa. Pellets from the extruded material were powdered, and used in the characterization studies. This material is hereafter referred to as the extruded starch.

The molecular-weight characterization was carried out on a DAWN-F (Wyatt Technology) multi-angle laser light scattering (m.a.l.l.s.) detector ($\lambda = 6328$ Å) coupled to a 150-C (Waters) gel permeation chromatography system. The chromatography was carried out using a combination of Toyo Soda 4000PWXL and 6000PWXL columns, with a guard column, at 28°C. The mobile phase was aqueous 0.5 N NaOH with a flow rate of 0.19 ml min^{-1}. The inter-detector lag was estimated using poly(ethylene oxide) standards (Toyo Soda), as described elsewhere[15]. Dextran standards (Fluka) were used for calibrating the d.r.i. detector response. The concentration of starch samples in an elution slice was then obtained from their d.r.i. responses, using a differential refractive index increment value, dn/dc, for amylose and amylopectin in the mobile phase of 0.146 (ref. 16). The g.p.c.–l.s. calculations were performed using the Astra 2.11 software (Wyatt Technology). Intrinsic viscosity of the starch samples was measured using a Ubbelohde viscometer in a water bath maintained at 25°C, with aqueous 0.5 N NaOH as the solvent. Starch concentrations of the solutions used in the intrinsic viscosity measurements were obtained by the phenol–sulfuric acid colorimetric method[17]. The starch solutions for the chromatography as well the intrinsic viscosity experiments were prepared by dissolving the samples in degassed 0.5 N NaOH and filtered with a Millipore LCR 0.5 μm filter prior to use in measurements.

RESULTS AND DISCUSSION

Figures 1a and *1b* show the d.r.i. and l.s. signals obtained from the g.p.c. experiment for the unextruded and extruded high-amylose starch. For both the samples, the elution profile obtained from the d.r.i. detector indicates molecules in significant concentrations over a large range of hydrodynamic sizes (the theoretical exclusion limit for this column set is estimated by the manufacturer to be poly(ethylene oxide) of molecular weight of 10^7). The first peak is the amylopectin component of the starch, eluting early owing to its very large size. Partially overlapping with this is the second, broad peak attributable to the amylose component. A large peak (from the processing aids and other low-molecular-weight extraneous material) was also present at the permeation volume of the columns.

The l.s. signal, on the other hand, is very different from the d.r.i. trace owing to the fact that it is proportional

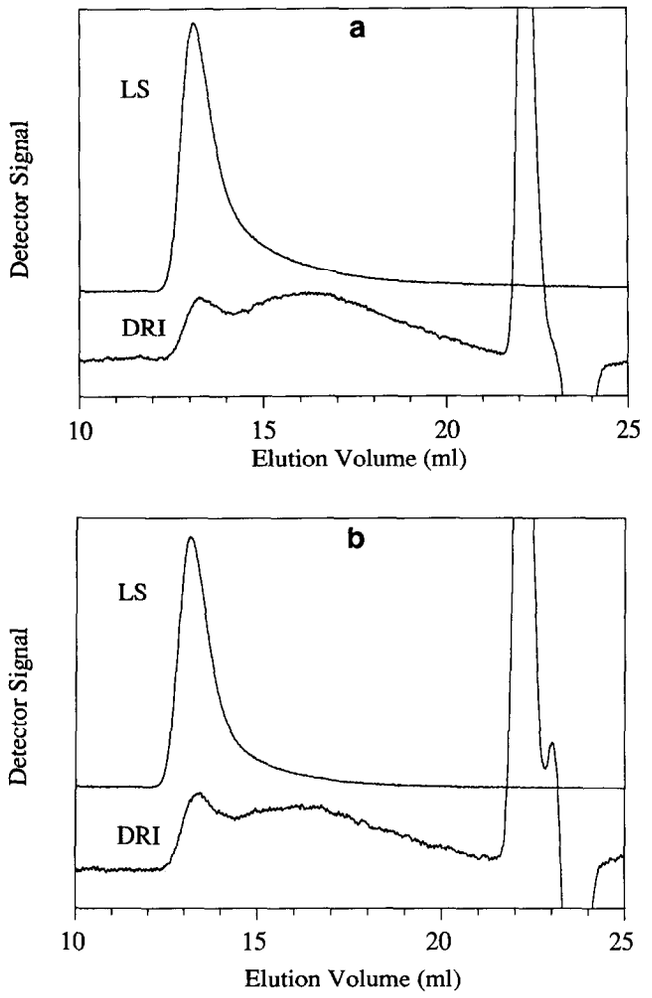

Figure 1 L.s. and d.r.i. detector signals for (a) the unextruded and (b) the extruded high-amylose starch

to the product of the concentration and the molecular weight of the polymer molecules in any elution slice. The initial sharp rise of this signal to a high value indicates that some moieties of extremely high molecular weight were excluded from the pores of the packing in the chromatographic columns. The signal intensity drops quite quickly, however, owing to the decreasing scattering contribution from the (lower-molecular-weight) materials at higher elution volumes.

Concentration (elution) profiles reported in the literature[4,6,8,9] indicate that the initial peak (attributable to amylopectin) shows significant reductions for extrusion-processed samples. Comparing the two samples in our case, the amylopectin peak shapes are not very different, and the amylose peak flattens out to some extent. The difference between our observations and those in the literature are probably due to the fact that our starting material is different from that used by the others, in that it is acid-modified prior to the thermomechanical processing. Acid attack upon starch occurs preferentially in the amorphous region of the granule[18], with cleavage of some or all of the macromolecules[19]. Amylopectin molecules in corn starch might be initially cleaved to a greater extent than the amylose molecules during acid modification[18]. Therefore, it is possible that the amylopectin molecules in the unprocessed starch used in this study had already been fragmented to some extent, and as a consequence did not undergo the same level of degradation upon extrusion processing (relative to the unextruded material) as observed by others. It should also be noted that, although the processing was carried out at a relatively high temperature, the total plasticizer fraction in the extruder was around 30%, with a part of the plasticizer being glycerine. It is not known whether glycerine and water might act differently in shielding the starch from shear forces during the extrusion processing.

Figure 2 presents the molecular weights for the two starch samples (i.e. before and after the extrusion processing) as a function of the elution volume, calculated from their d.r.i. and l.s. signals. The molecular-weight calculations were carried out only for elution volumes less than 17 ml. At higher elution volumes, the l.s. signal is quite low; given the unavoidable noise from the dust and other extraneous scatterers in the aqueous mobile phase, the l.s. signal-to-noise ratio is too low in this regime for meaningful calculations. This is illustrated by the increased scatter in the molecular-weight values for the extruded starch sample as the elution volume approaches 17 ml. As a result, it was not possible to obtain average molecular weights for the whole sample with this g.p.c.–l.s. experiment. However, the elution volume range over which the molecular-weight calculations were carried out contains the fraction of the molecules that should provide the dominant contribution to the weight-average molecular weight of the whole sample (since this high-molecular-weight fraction accounts for the majority of the l.s. signal). With this in mind, we can roughly estimate the overall weight-average molecular weights for the starch samples before and after extrusion processing to be 3.2×10^6 and 2.4×10^6, respectively.

The molecular weight vs. elution volume data indicate that, at any given elution volume, the extrusion-processed starch displays a lower molecular weight—or conversely, for a given molecular weight, the unextruded starch molecules have a higher elution volume (and therefore a smaller hydrodynamic size) than their processed counterparts. Since the two polymer samples are chemically identical, a difference in the molecular weight for the same elution volume can only be due to some

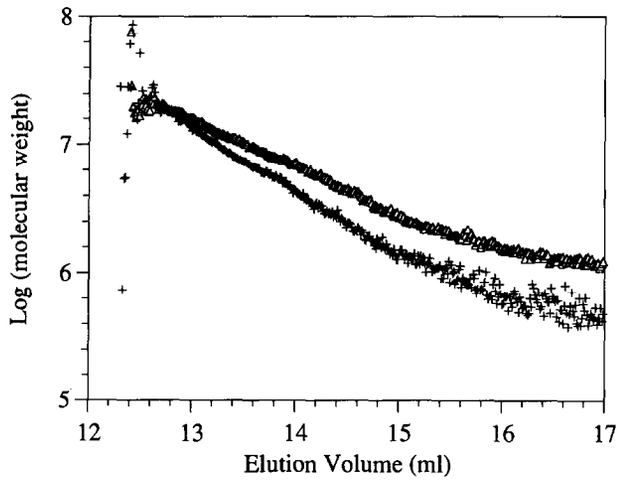

Figure 2 Molecular weight as a function of elution volume for unextruded (△) and extruded (+) high-amylose starch

differences in the architecture of the molecules (in the two samples) that elute at the same time. Amylopectin molecules are highly branched, and the amylose in high-amylose maize starches is known to have long-chain branching. In the literature, dilute-solution studies on branched macromolecules such as star polymers indicate that such molecules are more compact (and increasingly so with increasing functionality) than their linear counterparts of equivalent molecular weight[20,21]. Other work on chemically modified starches has shown that, for fractions of equal molecular weight, an increased degree of branching corresponds to a higher hydrodynamic density[22]. In our study, the observed reduction in the molecular weights at a given elution volume for the extrusion-processed starch (relative to the unextruded starch) could be similarly due to some debranching of the branched macromolecular components of the starch during the thermomechanical processing treatment. Debranching as a mechanism for fragmentation during extrusion processing has been previously reported in the literature, although the conclusions were based on observations in reductions in peak size for the amylopectin fraction during g.p.c. of starch[5]. This current study indicates that the amylose also loses branches during the extrusion processing, not surprising given the fact that the (almost) linear amylose molecules are likely to be significantly influenced by the high shear in the extruder.

The intrinsic viscosity of the unprocessed and processed samples was measured to be 108 and 95 ml g^{-1} respectively. This is only a modest reduction, but in any case intrinsic viscosity is not a very sensitive measure of the molecular properties of branched molecules. The reduction in intrinsic viscosity is consistent with the g.p.c.–l.s. data, indicating that the extrusion processing of starch leads to fragmentation of the molecules.

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