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The deformation of thin films made from extruded starch

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The deformation properties of thin starch films, approximately 2 μm thick, have been investigated. The films were made by casting from solutions of maize grits extruded at different temperatures and the strain to form shear deformation zones was measured. It was seen that the initial processing conditions of the starch affected the properties of the thin films. The deformation zones were initiated at granule remnants in films made from both unextruded maize grits and grits extruded at low temperatures. More homogeneous films were produced from maize grits extruded at higher temperatures and these films exhibited a higher strain for deformation zone formation. However, degradation was believed to be responsible for lowering this strain for films made from maize grits extruded at the highest temperatures.

INTRODUCTION

There have been few studies of mechanical properties of thin starch films. Some early studies (Wolff *et al.*, 1951; Lloyd & Kirst, 1963; Mark *et al.*, 1964; Nakamura & Tobolsky, 1967) were inspired by the possible application of thin amylose films to the safe packaging of food products. For instance, the tensile strength and strain to failure of films cast from various starches were measured and the changes effected by varying the film thickness, degree of polymerisation, amylose percentage, and plasticiser content, were noted (Wolff *et al.*, 1951). It was found that the strength and ultimate elongation were independent of film thickness, although the films were difficult to handle when thinner than 20 μm. Increasing the DP caused the strength and strain to failure of the films to increase, whereas increasing the plasticiser content resulted in a decrease in the strength but an increase in the ultimate elongation.

Techniques for measuring the strain to form deformation zones and crazes, and the strain to failure, for very thin films (< 1 μm thick) have been developed for synthetic polymers (Lauterwasser & Kramer, 1979). When thin films of glassy polymers are strained in tension they deform elastically until the yield stress, σ_y, is reached. However, beyond σ_y, rather than deform homogeneously, the films often form deformation zones (DZ) (Bowden, 1973, Donald & Kramer, 1981). These are localised regions of shear necking which are due to the polymer strain softening. They occur because the strain for further deformation, beyong the yield point, is reduced in polymers that shear soften, and so once an area yields it can then deform locally under a lower stress than the surrounding region. The deformation is concentrated in shear DZs and these grow perpendicular to the direction of applied principal stress (Bevis & Hull, 1970). The onset of deformation in the films will depend upon the yield stress of the polymer, which in turn may vary with the glass transition temperature, amount of cross-linking, molecular weight, amount of plasticiser present, and annealing time, as well as the strain rate and temperature of testing. For example, increasing the concentration of plasticiser or decreasing the molecular weight decreases the yield point. It is generally found that any

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process which restricts the motion of the polymer molecules (such as annealing leading to densification) will raise the yield stress (Bowden, 1973).

The aim of the research contained within this paper is to investigate the mechanical properties of starch films that were of the order of micrometers thick; that is, much thinner than the starch films tested by the previous authors (Wolff *et al.*, 1951; Lloyd & Kirst, 1963; Mark *et al.*, 1964; Nakamura & Tobolsky, 1967). This paper records the results from measuring the strain to form DZs in films made from maize grits. The methods used for the preparation and testing of synthetic polymers (Bowden, 1973; Lauterwasser & Kramer, 1979) were adapted for these starch-based films. The results from measuring the strain to form DZs in films made from maize grits that had been extruded at different temperatures are presented. Extrusion is a process that can subject starch granules to high temperatures and shearing forces and transform them into a viscous dough within the extruder barrel (Harper, 1981). Not only are the granules gelatinised, but the starch molecules can also be degraded, and the extent of degradation depends upon the extrusion conditions (Colonna *et al.*, 1984; Davidson *et al.*, 1984; Diosady *et al.*, 1985).

EXPERIMENTAL METHOD

The thin films were made by casting from solution. The maize grits used were 'Extra Fine Snack' grade and were obtained from Pauls Agriculture (Hull, UK). The protein content was 9·7% and the lipid content 0·8% by weight. The particle size was of the order of 500 μm. Processing of the maize grits was carried out on a Baker Perkins MPF 50D co-rotating twin screw extruder. The water content during extrusion was kept constant at 15·8% weight for weight basis as the extrusion temperature was varied. The extrusion conditions under which the samples were made are summarised in Table 1.

Table 1. Maize grit extrusion conditions

Sample	Temperature profile (°C)[a]
1	25/37/48/64/80
2	25/46/60/80/100
3	25/52/80/100/120
4	25/57/100/120/140
5	25/70/120/140/160
6	25/77/140/160/180
7	25/93/160/180/200

[a] The temperature profile records the set temperatures of the five zones along the feed port to the die (a flat plate with two 6 mm circular dies). The temperature of the final zone (underlined) is referred to as the 'extrusion temperature'. A screw speed of 250 rpm and a feed rate of 30 kg/h was used throughout.

The samples were dissolved in dimethyl sulphoxide (DMSO); each solution contained approximately 5 g of starch material per 100 ml of DMSO. The extrudates were ground with a pestle and mortar prior to dissolving in DMSO. The solutions were then placed in a water bath at 80°C for 30 min and were agitated with a magnetic stirrer. The samples were filtered through grade 4 filter paper using a Buchner funnel and side-arm flask with vacuum attachment. Glass slides, cleaned with acetone, were drawn out of the filtered solution at a constant rate of approximately 1 mm/s, to produce a thin film. The slides were placed in a vacuum oven at 80°C for 2 h to dry the films. Once the films were dry and the glass slides were at room temperature it was possible to coax the starch films gently off the slides, by first of all drawing out a rectangular shape with a scalpel in the film, and then easing the piece from one corner with a pair of tweezers. The films were attached with superglue to copper grids made of 1 mm × 1 mm squares. The superglue was 'painted' onto the grids with a pin and allowed to dry for a few seconds before the film was placed carefully onto the grid. This approach is an adaptation of that developed by Lauterwasser and Kramer (1979).

The copper grids were mounted in a specially designed straining rig that fitted under an optical microscope, enabling the samples to be viewed in both transmitted and reflected light during the experiments. Each sample of film covered 7 × 5 squares on the copper grids and these were observed at 32× magnification. The films were strained at a rate of 10^{-6}/s. Five samples of each type of film were tested and the strain to form shear DZs was recorded.

RESULTS AND DISCUSSION

The films were of the order of 2 μm thick, as was measured from optical micrographs of samples mounted edge on. They exhibited no birefringence when viewed under crossed polars before straining. Films made from the unextruded maize grits appeared to contain inhomogeneities. The films made from the maize grits extruded at lower temperatures (samples 1, 2 and 3) were also similar in appearance to these films. This contrasted with the more uniform appearance of the films made from maize grits extruded at higher temperatures. Figures 1(a) and 1(b) show the differences apparent between the two types of films. All the samples formed shear DZs perpendicular to the shear direction when strained. In the case of films from the unextruded maize grits and samples 1, 2 and 3 DZs appeared to originate at the inhomogeneities. Figure 2(a) shows a shear DZ in a more uniform film and Fig. 2(b) shows shear occurring across an inhomogeneity. All the shear DZs exhibited birefringence when viewed between crossed polars, and the extinction positions occurred

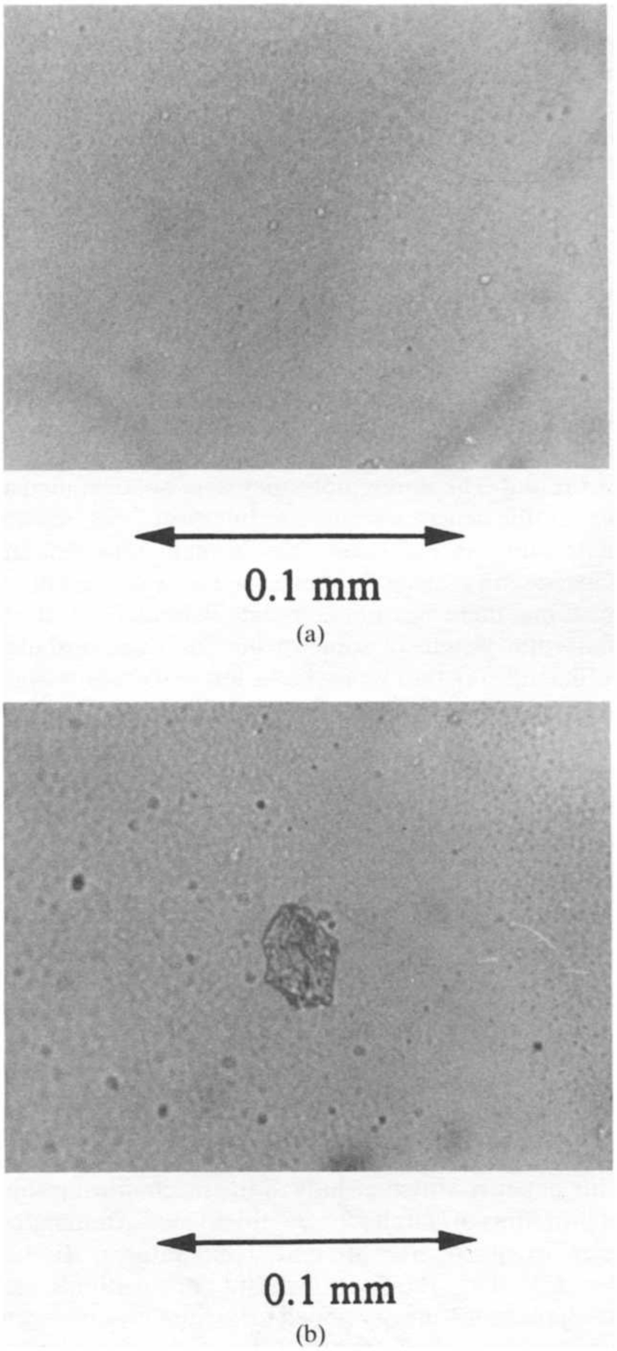

Fig. 1. Optical micrographs illustrating the difference between the more homogeneous films and the inhomogeneous films: (a) shows a homogeneous film made from a sample extruded at 180°C, and (b) shows an inhomogeneity in a film made from a sample extruded at 100°C.

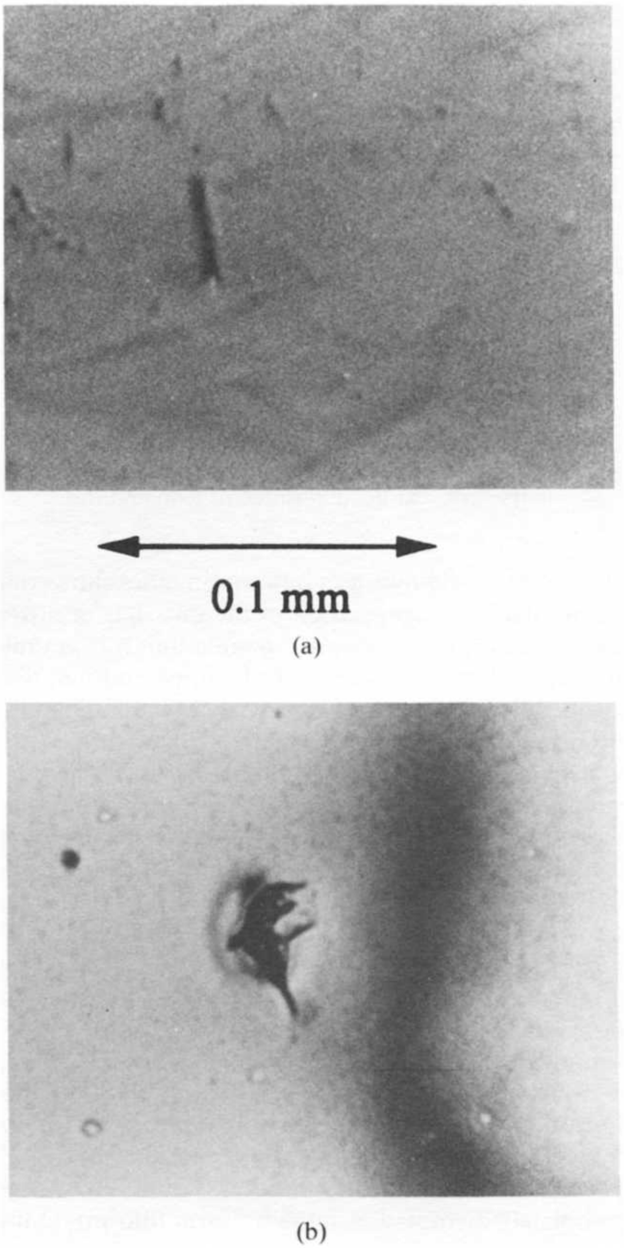

Fig. 2. Optical micrographs illustrating the difference in the shear deformation zones that occur in the two types of films: (a) shows a deformation zone in a homogeneous film made from a sample extruded at 180°C, and (b) shows a deformation zone that appears to originate at the inhomogeneity in a film made from a sample extruded at 100°C. The direction of stretching is parallel to the space bar arrow.

when the DZs were oriented perpendicular and parallel to the analyser. This is consistent with molecular orientation parallel to the major stress direction and perpendicular to the direction of growth of the DZ.

The variation of the strain at which DZs first appeared as a function of extrusion temperature are shown in Fig. 3, together with the result for unextruded material. Films made from samples extruded at 80°C and 100°C formed DZs at approximately 2% strain. This was the same, within experimental error, as the strain at which unextruded maize formed DZs. The strain to produce DZs then rose to a maximum of 4% for films made from samples extruded at a temperature of 140°C. Beyond this extrusion temperature, the strain to form DZs fell again.

The fact that films made from maize grits extruded at low temperatures and unextruded maize grits both

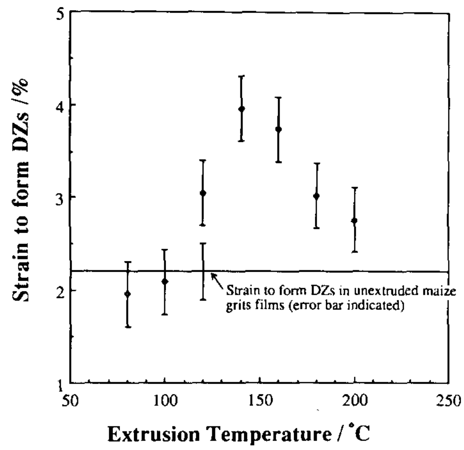

Fig. 3. Strain to form deformation zones in films made from maize grits extruded at different temperatures.

showed DZs originating at inhomogeneities shows that incomplete homogenisation of the grits has occurred for these samples. It seems probable that it is granule remnants that are observed in the films and that they act as weak links or stress concentrators. What is being observed in Fig. 1 may therefore correspond to the ghost granules reported by Doublier (1981). This idea would also explain why films made from unextruded maize and maize extruded at low temperatures exhibited similar strains to form DZs. In contrast, films made from maize grits extruded at the higher temperatures were more homogeneous in appearance and required a higher strain to fom DZs. Figures 1 and 2 showed the different appearances, before and after straining, of films made from maize extruded at 100°C and 180°C. From these it might be expected that films containing granule structure would behave in a different manner from those that did not. Films made from the maize extruded at high temperatures would be more homogeneous since the granules would have been completely disrupted. A more uniform film would not possess the stress concentrating effects of the granule remnants and so the strain to form DZs would be increased.

Evidence for granule structure surviving extrusion at low temperatures is provided from optical microscopy of the solutions from which the films were cast. Granule remnants were clearly visible in solutions of 1 and 2, and to a lesser extent in 3. They were not visible in solutions from the samples extruded at higher temperatures. Measurements of the dependent extruder variables, notably the die pressure, torque and drive power, also produced evidence that suggested that granules were not completely disrupted at low extrusion temperatures, since such properties changed rather abruptly over a narrow temperature range, as has been observed previously (Kirby *et al.*, 1988).

For films extruded at 120°C and above, no sign of granule remnants in the solutions or films was observed and there was a substantial increase in the strain at which DZ first appeared. However, for films made from samples extruded at a temperature above 140°C, the strain to form DZ falls again, despite the absence of granule remnants. The probable explanation of this lies in the fact that degradation is known to take place during high temperature extrusion (Colonna *et al.*, 1984; Davidson *et al.*, 1984; Diosady *et al.*, 1985). Degradation reduces the molecular weight of starch molecules as measured via dilute solution viscometry (Colonna *et al.*, 1984; Davidson *et al.*, 1984; Diosady *et al.*, 1985), gel permeation chromatography (Colonna *et al.*, 1984; Davidson *et al.*, 1984) and light scattering (Colonna *et al.*, 1984). These studies showed that more degradation took place as the extrusion temperature was raised. The starch molecules were not degraded as far as the sugar monomers, but were still macromolecular. And although the branch points of the amylopectin molecules were particularly susceptible to breaking, there was not complete debranching. If the molecular weight of some of the chains is degraded sufficiently far, the change in the low-molecular-weight tail of the distribution may be sufficient to affect its yield stress. Simultaneously, the loss of branch points might also be expected to cause an increase in mobility and therefore a drop in yield stress. (Branching is known to reduce mobility in synthetic polymers (Fleischer, 1985)). As debranching occurs and facilitates motion, the net effect is similar to a rise in temperature which has been shown to drop the yield stress (Bowden, 1973).) It seems likely that these effects cause the reduction in the strain to form DZs for the highest extrusion temperatures.

CONCLUSIONS

This paper recorded a study of the mechanical testing of thin films of starch (≈ 2 μm thick) made from maize grits extruded at different temperatures. It has demonstrated the applicability of methods for mechanical testing developed for synthetic polymers to bipolymers. Films prepared from the maize were strained until shear DZs were observed. Those made from the unextruded maize grits and from maize grits extruded at low temperatures contained inhomogeneities which were presumed to be granule remnants. The strain to form DZs was similar for unextruded and low extrusion temperature maize films. The shear DZs originated at the inhomogeneities, which seem likely to be acting as stress concentrators. Films made from grits extruded at higher temperatures were homogeneous and the strain to form DZs was greater in these films. However, a maximum strain to form DZs was reached for an extrusion temperature of ~ 140°C. Beyond this temperature degradation was believed to be responsible for lowering the strain to form DZs again.

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