Effect of Free Monomer Content on the Drawing Behavior of Poly(methyl Methacrylate)

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Synopsis

Cold drawing has been used to produce oriented samples of various molecular weight grades of poly(methyl methacrylate), all of which exhibited marked strain hardening characteristics over a range of drawing temperatures. The differences between the yield and drawing behavior of the grades did not correlate with molecular weight but could instead be attributed to the plasticizing effect of additional free monomer, generated by degradation during melt processing of the polymer.

INTRODUCTION

In a number of previous publications[1,2] the influence of molecular weight and molecular weight distribution on the hydrostatic extrusion and tensile drawing behavior of polymers has been emphasized. Although the effects are most notable in crystalline polymers, especially linear polyethylene, it has been observed that the drawing of amorphous poly(ethylene terephthalate) can be affected significantly by molecular weight.[3]

Molecular weight has been found to affect the tensile drawing behavior in two respects. In the first instance, the maximum obtainable "effective" draw ratio may be reduced by increasing molecular weight. By "effective" draw we mean draw which produces increased molecular alignment and stiffness, as distinct from flow drawing where the orientation is lost because of relaxation processes during drawing. It appears that this reduction in the maximum draw ratio with increasing molecular weight can be attributed to the increasing degree of entanglement, hence the correlation is with the *weight*-average molecular weight which reflects the role of the larger molecules. Secondly, the rate of plastic deformation, especially if drawing occurs through a neck, may be increased markedly by the presence of low molecular weight polymer, giving a correlation with the *number*-average molecular weight. It is considered that such material can act as a plasticizer to expedite the plastic deformation process.

Hydrostatic extrusion studies of poly(methyl methacrylate) (PMMA) undertaken by N. Kahar in this laboratory,[4] based on commercial high molecular weight polymer (Perspex), showed that the attainable extrusion ratios were very small indeed, similar to ultrahigh molecular weight linear polyethylenes. It was therefore of interest to examine the drawing behavior of a range of materials of different chemical composition, especially with widely different molecular weight characteristics.

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EXPERIMENTAL

Materials and sample preparation. Details of the four commercially available molecular weight grades chosen for investigation are shown in Table I. Grade A was supplied in the form of 1.0-mm-thick cast sheet, while the other grades were supplied in powder or bead form and were compression molded into sheets 1.5–2.0 mm thick. Molding pressures in the region of 20 MPa were applied for 4 min at a temperature of 180°C, after which the moldings were water quenched to room temperature, mainly to facilitate a fast turn-round. Dumb-bell-shaped specimens were machined from the cast or molded sheets, using a high-speed router to minimize surface cracking. The gauge length was nominally 30 mm with a sample width of 6 mm. In order to prevent the occurrence of premature failure owing to the presence of surface cracks, which act as stress raisers, the edges and faces of the samples were polished using silicon carbide paper and Perspex polish.

Drawing procedure. The samples were drawn using a conventional Instron testing machine at a constant cross-head speed of 10 mm/min. Before mounting in the grips, the specimens were washed in warm water and detergent to remove surface grease which could act as a stress-cracking agent. The specimens were allowed to reach the oven temperature before tightening of the grips was completed, after which a further period was allowed to reach full thermal equilibrium. Samples of each grade were drawn at a range of temperatures (T_d), the temperature being monitored as constant to within ±0.5°C. Two sets of experiments were performed: (1) To compare the processing behavior, a set of samples was drawn to failure. (2) To obtain the highest possible degree of orientation, a second set of samples was drawn to extensions just below those obtained for failure in (1). The oven door was then immediately opened and the samples were cooled rapidly, while constrained, by blowing cold air.

Birefringence measurements. To quantify the degree of molecular orientation, measurements of birefringence were made directly on the drawn samples. These measurements were carried out at room temperature using a polarizing microscope with an Ehringhaus rotary compensator.

Measurement of glass transition temperature. The glass transition temperature (T_g) of the different grades was measured by differential scanning calorimetry (DSC). The determinations of T_g were carried out at a heating rate of 10°C/min using a Perkin–Elmer DSC2 machine.

Determination of monomer content. The free monomer content of the samples was assessed by measurement of the infrared absorption band at 1.625 μm corresponding to the $CH_2{=}C$ group in the methyl methacrylate monomer.

TABLE I
Type and Molecular Weights of Grades Used in the Investigation

Grade	Type	$\overline{M}_w$
A	homopolymer	2,000,000
B	homopolymer	1,800,000
C	homopolymer	550,000
D	6% w/w butyl acrylate/ methyl methacrylate copolymer	250,000

RESULTS

The results for the samples drawn to fracture are presented in Figure 1 in terms of engineering stress–strain, from which the yield stress can be seen to decrease with temperature as reported previously.[5] Sharp necks were observed to form and propagate along the specimens of all grades at low temperatures, although measurement of the samples after drawing confirmed that necking had occurred at all temperatures.   However, the fractional reduction in specimen thickness was always equal to the fractional reduction in width, indicating that drawing had taken place uniaxially.

Fracture occurred before yield for grade A at 30°C and below, and for grade D at 50°C and below.   No fracture was observed prior to yield on grades B and C, and in fact at 90°C, fracture did not occur in either grade before the limit of cross-head travel was reached.   Stress whitening was observed on all the homopolymer grades.   Although present only to a small extent for grade A, the onset of whitening was sudden and severe for grades B and C, in which it was followed very quickly by fracture.   The whitening was believed to have been caused by voiding in the material and, when severe, was accompanied by a fall in the load.

The variation of draw ratio (λ, defined as the ratio of cross-sectional areas before and after drawing) and birefringence ($|\Delta n|$) with drawing temperature is shown for grade A in Table II.   The maximum draw ratio increased with temperature and was of course higher in those samples which were cooled while constrained, as was the birefringence.   This is because of the large shrinkage in those samples which fractured, which occurred while the samples were still hot. The highest birefringences measured were in the region of 16×10^{-4}, approximately 50% higher than those obtained previously by hydrostatic extrusion.
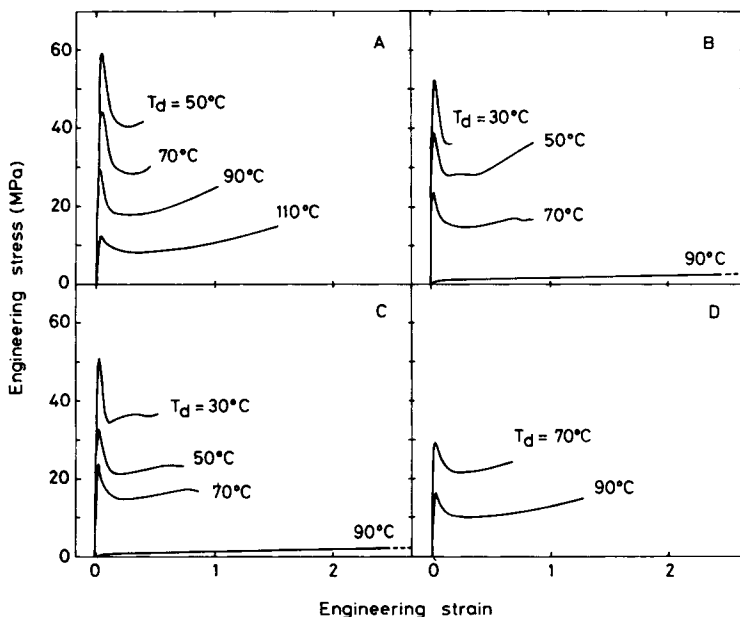

Fig. 1. Engineering stress–strain data for PMMA grades drawn to fracture at a range of temperatures.

TABLE II
Variation of Draw Ratio and Birefringence with Drawing Temperature for Grade A

T_d, °C	Fractured		Stopped and cooled while constrained	
	λ	$|\Delta n| \times 10^4$	λ	$|\Delta n| \times 10^4$
50	1.80	11.5	—	—
70	1.92	11.3	2.31	15.1
90	2.63	11.2	2.87	16.1
110	2.80	7.8	3.32	14.5

DISCUSSION

If the drawing behavior is assumed to have been homogeneous (which in fact it was not), then the data for grade A from Figure 1 can be presented in terms of true stress–strain (Fig. 2). Because of the occurrence of the neck and the change in strain rate inherent in constant cross-head speed drawing experiments, these curves are unlikely to be correct, particularly in the region of the apparent stress drop after yield where the neck is propagating. Nevertheless, at high strains, where propagation of the neck along the specimen is complete, the drawing behavior will be approximately homogeneous and the form of the curves approximately correct. The problems associated with these assumptions are considerable and will be dealt with in detail elsewhere.[6] However, it is clear that considerable strain hardening occurs after yield, a phenomenon observed on all four grades.

The engineering stress–strain behavior of the four grades is compared in Figure 3 at draw temperatures of 70 and 90°C, showing that there is no correspondence between the drawing behavior and the molecular weights of the grades. Grades A and B, while both high molecular weight homopolymers, are the most widely different, while the copolymer grade (D) exhibits intermediate behavior. It appears that at 90°C grades B and C behave as rubbery materials, while grades A and D are still below their glass transition temperatures. To investigate this, DSC determinations of T_g were performed on all grades both before and after the molding operation in which the plaques for drawing were produced. The results are shown in Table III, from which it can be seen that while T_g was in the region of 110°C for all grades before molding, melt processing caused a fall of about 20°C in the T_g of grades B and C but did not significantly affect grade D.
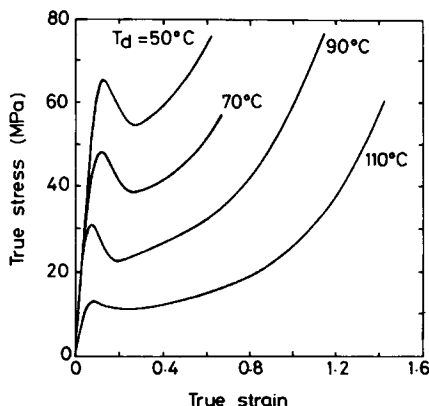

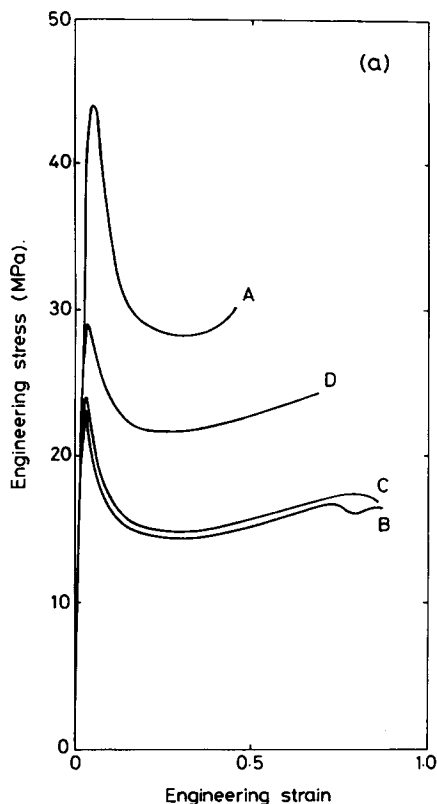Fig. 2. True stress–strain data calculated for grade A assuming homogeneous drawing.

Fig. 3. Comparison of the engineering stress–strain data for four grades of PMMA: (a) $T_d = 70°C$; (b) $T_d = 90°C$.

TABLE III

Glass Transition Temperatures of Samples before and after Melt Processing (by DSC)

Grade	T_g, °C	
	Before melt processing	After melt processing
A	110	—
B	115	92
C	108	88
D	108	104

Table IV shows the free monomer content of all the grades before and after melt processing, as determined by infrared spectroscopy. These correlate very well with the T_g data in that the free monomer content of grades B and C has been increased from less than 1% to over 5% by weight, while that of grade D is unaltered. It is therefore concluded that this additional free monomer, which is generated by degradation during melt processing, has a plasticizing effect on the polymer. This results in a lowering of T_g and hence in a reduction in the yield and flow stress of the polymer at a given temperature.

It should be noted that grade A was supplied as cast sheet and therefore was
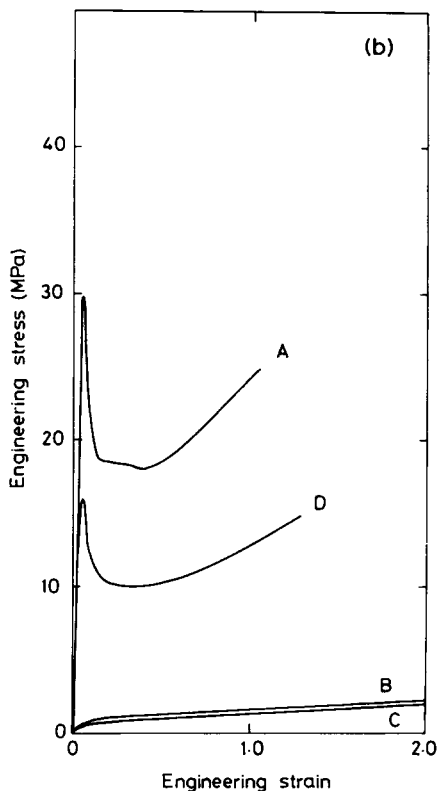
Fig. 3. (*Continued from previous page.*)

not melt processed prior to drawing. Neither the free monomer content nor T_g of grade D was changed appreciably during melt processing, because of the presence in this grade of 6% of comonomer, which confers vastly improved thermal stability compared with grades B and C. The difference in observed drawing behavior between grades A and D may be due to genuine molecular weight effects but is more likely to be a result of the presence of the comonomer.

CONCLUSIONS

Cold drawing can be used to produce oriented samples of PMMA with birefringence in the region of 16×10^{-4}, which is higher than that achieved by hydrostatic extrusion, using a range of molecular weight grades.

TABLE IV
Free Monomer Contents of Samples before and after Melt Processing

Grade	Free monomer content, % by weight	
	Before melt processing	After melt processing
A	1.4	—
B	0.9	5.1
C	0.4	7.2
D	0.5	0.5

While marked strain hardening behavior is observed from all grades below T_g, the yield and drawing behavior at a given temperature is very different for each grade. However, any molecular weight effects on the drawing behavior are completely overridden by the plasticizing effect of additional free monomer, generated during the melt processing of the polymer. Clearly this may be relevant to an understanding of the solid-phase deformation behavior of other polymers.

References

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