JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, 3235–3240 (1975)

Mechanical Degradation of Dilute Solutions of High Polymers in Capillary Tube Flow

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Synopsis

Experimental results on mechanical degradation in capillary tubes of polyisobutylene polymers in dilute solution are described. In laminar flow, degradation is independent of tube length, indicating that entrance effects are dominant. This shows that capillary experiments do not yield explicit information on the effect of shear stress on mechanical degradation. In turbulent flow, large entrance effects are also observed, but some degradation does take place in the fully developed flow region.

INTRODUCTION

The degradation of polymers by mechanical action is a depolymerization reaction in which the activation energy is supplied by the mechanical action on the polymer. This phenomenon has been known for some time and has been widely used in the rubber processing industry to make the raw rubber easier to work by reducing its molecular weight.

The use of high polymers as viscosity index improvers in motor oils and as drag-reducing agents in turbulently flowing liquids focused attention on the degradation of polymers in dilute solutions. Degradation reduces the effectiveness of polymer additives because of the strong dependence of effectiveness on molecular weight.

A recent paper[1] has reviewed the field very well up until 1970. Only those papers of particular pertinence to this investigation will be referred to here.

Capillary tube flows were used in this investigation to study the mechanical degradation of a number of polymers in both laminar and turbulent flow. The effects of variation in polymer molecular weight, concentration, and wall shear stress were investigated. Gel permeation chromatography (GPC) was used to observe changes in molecular weight distribution.

EXPERIMENTAL

Multiple-pass capillary flow tests were carried out at constant pressure difference in an automatic push-pull capillary rheometer shown schematically in Figure 1. The capillary diameter was 0.0208 in., and various length capillaries were used. Details of the apparatus are described by Culter.[2] Single-

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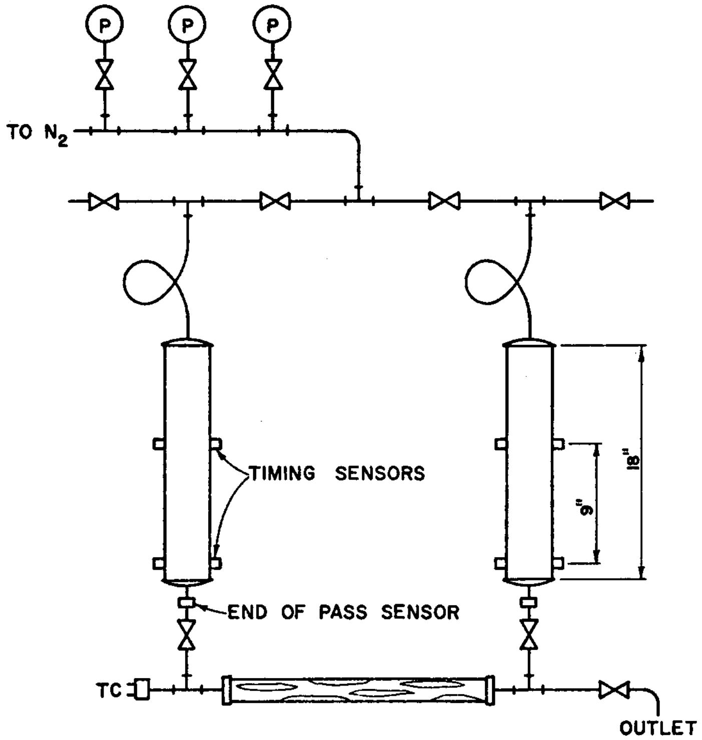

Fig. 1. Schematic of capillary degradation apparatus.

TABLE I
Undegraded Polyisobutylene Characteristics

Polymer	[η], dl/g, in tetrahydrofuran	$M_{n_0} \times 10^{-5}$	$M_{w_0} \times 10^{-5}$	$M_{z_0} \times 10^{-6}$
PIB L-200	6.83	9.94	21.8	2.93
PIB L-140	3.43	10.2	16.5	2.25
PIB L-80	1.83	3.68	7.33	1.20

pass tests were also run to estimate the elastic entrance pressure losses and the wall shear stresses by means of Bagley plots. These results then defined the initial stresses (τ_{w1}) for the multiple-pass testing.

The molecular weight distributions of fresh and degraded samples were measured by GPC using a Waters instrument which employs a differential refractometer for polymer concentration detection. The GPC solvent used in this study was tetrahydrofuran. The columns were calibrated using polystyrene standards. The results were converted to a universal calibration curve, $[\eta]M$ versus M, which was used for determining molecular weight distributions of all polymers tested. Mark-Houwink constants for the polyisobutylene polymers were estimated by the method suggested by Ambler.[3]

Values of M_n, M_w, and M_z were computed from the molecular weight distributions. Since most of the degradation takes place at the high end of the molecular weight distribution, to which M_z values are very sensitive, M_z values are reported here. Patterson et al.[4] showed that a 20% decrease in M_v

caused by degradation could cause a large decrease in drag reducing ability of a polyisobutylene solution because of the preferential degradation of the high molecular weight tail.

The polyisobutylene polymers used were obtained from Enjay Corp. Their properties are listed in Table I.

RESULTS AND DISCUSSION

Single-Pass Measurements

A series of measurements in laminary flow in 0.02-in. diameter tubes of l/d = 81, 132 and 545 were made with 0.25% L-200 in decalin. The effect of wall shear stress on the fractional reduction, M_z/M_{z_0}, is shown in Figure 2. There appears to be a threshold wall shear stress at about 1 × 10^3 dynes/cm^2. Above this apparent critical wall shear stress, degradation increases with wall shear stress. Data for a lower concentration solution of this same system (0.05%) show a lower apparent critical wall shear stress. Plotting the degradation data as a function of wall shear stress divided by concentration as suggested by Porter and Johnson[5] did not give superposition of the data for the two concentrations. A plot of degradation against wall shear rate also did not account for concentration effects.

Of particular interest is the fact that the amount of degradation is independent of tube length. This indicates that degradation occurs at the tube entrance rather than in the region of developed flow. If degradation occurred in the developed flow region, degradation would have been greater in the longer tubes which had longer residence times.

Fig. 2. Effect of wall shear stress on M_z in single-pass laminar flow.

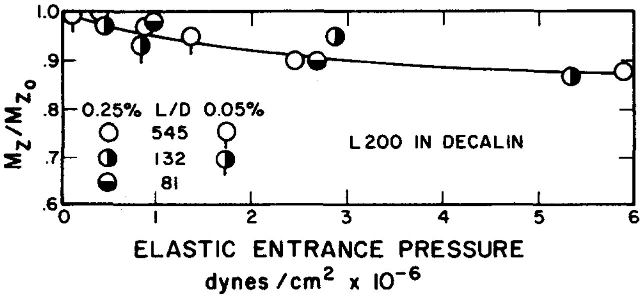

Fig. 3. Effect of elastic entrance pressure on M_z in single-pass laminar flow.

Elastic entrance pressure was determined for each point on the previous graph by means of Bagley plots. Values of M_z/M_{z0} plotted against the elastic entrance pressure give a shape (Fig. 3) similar to the results in Figure 2. Results for 0.05% L-200 in decalin also lie on the same curve, indicating that this method accounts for concentration effects with this polymer.

Multipass Measurements

The effect of number of passes on the degradation of L-200 when tested as a 0.25% solution in decalin is shown in Figure 4. The wall shear stress for the first pass was 7.5×10^3 dynes/cm^2, and pressure drop across the capillary was kept constant for subsequent passes. Once again, the l/D ratio had no effect on degradation. Similar results were obtained with 0.25% L-80 in decalin.

There are three possible sources of locally high shear stresses in the entrance region which could cause degradation of the polymer:

1. For fluids of high viscoelasticity, Metzner et al.[6] have shown that the velocity profile of a viscoelastic fluid is not blunt as it enters the tube due to the stretching flow that is developed external to the tube. In such a stretching flow, locally high stresses on entangled molecules could cause degradation. High molecular weight polymers, like L-200, would probably be subjected to more entanglement and higher stresses in the stretched flow. Using M_z/M_{z0} as a measure of degradation they do degrade more readily than lower molecular weight polymers of the same structure (L-80).

2. Another locally high stress region occurs near the entrance as the velocity profile is altered by the retarding effects of the tube wall. Culter et al.[7] explained the lack of an l/d effect on the degradation of a polystyrene polymer, which was not very viscoelastic, by attributing the degradation to the high local stresses produced in the developing boundary layer in the entrance region. This is discussed quantitatively in reference 7.

3. Williams[8] pointed out that degradation could be caused by turbulent patches which form in the entrance region and which are damped out as they travel downstream. Instantaneous shear stresses in the turbulent eddies have been shown to exceed the average local shear stress near the wall by a factor of 10 or more.[9] The existence of departures from laminar flow has been shown to occur at Reynolds numbers as low as 931.[10] Some of the multipass tests are at Reynolds numbers above 931, but the 25% L-200 solution in decalin was run at a Reynolds number of about 300 where the occurrence of tur-

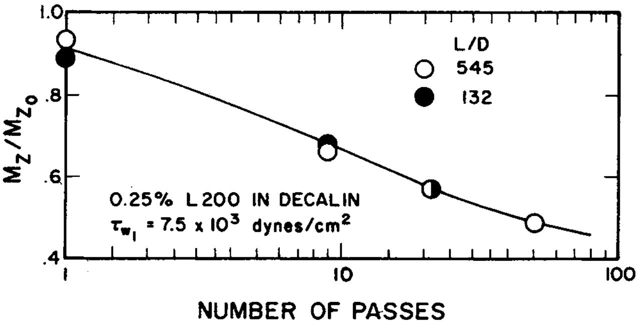

Fig. 4. Multipass Degradation in Laminar Flow.

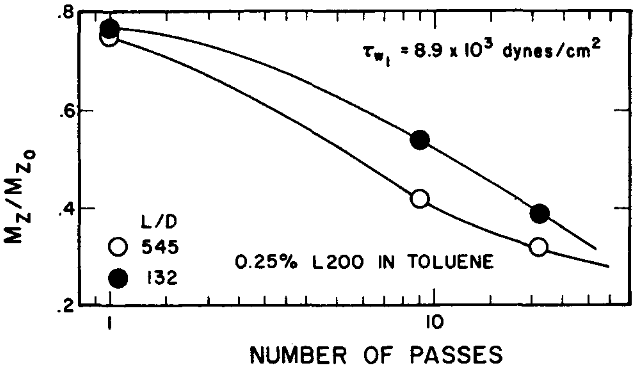

Fig. 5. Multipass degradation turbulent flow.

bulent patches is unlikely, indicating that turbulence is probably not important. This is supported by the results of Sarmasti[11] who observed no *L/D* effect at *L/D* values ranging from 25 to 800. An *l/d* of 25 is probably less than the length necessary for damping the turbulence patches.

Since many shear degrading flows for dilute polymer solutions are turbulent, measurements in the same range of wall shear stresses but in turbulent flow were made using toluene as a solvent. Results for 0.25% L-200 in toluene at an initial wall shear stress of 8.9×10^3 dynes/cm^2 are shown in Figure 5. Degradation is somewhat greater after one pass compared to the laminar data at this wall shear stress (Fig. 2). While Chang[12] has shown that degradation in turbulent flow of dilute polymer solutions in poor solvents is much more rapid than in good solvents, solvent effects are not believed to be the cause of the increased degradation as both toluene and decalin are fairly good solvents for polyisobutylene.

There is also a significant increase in the amount of degradation in the longer tube compared with the shorter at all numbers of passes, but degradation is not proportional to tube length. Apparently, while much of the degradation occurs in the entrance region in turbulent flow, additional degradation occurs in the fully developed flow region. This must be due to the high instantaneous shear stresses present in the turbulent eddies.

The importance of the entrance effects on degradation in turbulent flow can also be seen in the data of Patterson and Abernathy[13] and of Eichstadt[14] obtained on poly(ethylene oxide) solutions. The former authors noted that a disproportionate amount of degradation occurred within the first 200 diameters of their test section. They also observed that tube entrance geometry had an effect on the amount of degradation in the entrance region, with a sharp-edged tube producing more degradation than a bell mouth. Eichstadt observed more degradation in multipass pumping through a 20-foot section than for pumping through an equal length of tube in a 120-foot section.

CONCLUSIONS

1. In single-pass laminar capillary flow tests, polymer degradation occurs after a threshold wall shear stress is exceeded. The value of this threshold stress depends on solution concentration. Degradation results for dilute

polyisobutylene solutions of different concentrations do not correlate with τ_w, but do correlate with elastic entrance pressure.

2. In single-pass and multipass laminar capillary flow tests, degradation is independent of tube length, suggesting that it occurs at the tube entrance.

3. Degradation in capillary flow tests in one size tube is greater in turbulent flow (low-viscosity solvent) than in laminar flow (high-viscosity solvent) at about the same wall shear stress.

4. Degradation in turbulent capillary flow tests is dependent on tube length. Much of that degradation also occurs in the entrance region, but the high instantaneous shear stresses in the turbulent eddies apparently cause additional degradation which depends on tube length.

Symbols

l/d	length-to-diameter ratio of capillary tubes
M	molecular weight of a narrow fraction
M_n, M_w, M_z	number average, weight average, and third moment molecular weights
M_{n_0}	initial numbers average molecular weight
M_{w_0}	initial weight average molecular weight
M_{z_0}	initial third-moment molecular weight
$[\eta]$	intrinsic viscosity
τ_w	wall shear stress
τ_{w1}	wall shear stress for first pass

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Received March 6, 1975
Revised April 9, 1975