Degradational effects on bisphenol A polycarbonate extruded at high shear stresses

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(*Received 4 August* 1980)

Bisphenol A polycarbonate was repeatedly extruded in a capillary rheometer at high, constant shear stresses (0.15–0.95 MPa) and at temperatures between 275 and 320°C. Changes in molecular weight and molecular weight distribution were determined. Polymer degradation occurred to a much larger extent during extrustion than under static conditions; a difference explained by viscous heating effects. The chain scission reaction had an activation energy of 113 kJ mol^{-1} for static as well as dynamic conditions, which indicates similar degradation mechanisms in both cases. The molecular scission followed non-random kinetics.

INTRODUCTION

Chain scission observed during processing has often been referred to as 'mechanical degradation', an expression widely used but unfortunately not always defined. In this study we discuss two separate effects which may appear at high shear stresses: (1) true mechanical degradation caused by rupture of macromolecules exposed to high shear forces and (2) shear heating which is the internal heat generation of fluid layers. As the result of the latter, very high temperatures may be reached at high shear rates and thermal degradation is thus greatly enhanced. Shear heating is used synonymously with viscous heating and viscous dissipation.

Kovarskaya[1] studied the changes in molecular weight of polycarbonate, which was kept in the cylinder of an injection moulding machine. He found more extensive degradation during these conditions than in a comparable test conducted in a laboratory device. No experimental details were given, but the latter case was referred to as an oxidation procedure, which would indicate that the specimen was exposed to oxygen during heating. Kovarskaya[1] concluded that the extensive degradation observed in the injection moulding machine, was the result of mechanical breakdown in combination with thermooxidative degradation. Exposure of a polycarbonate sample for less than 30 min at 250°C resulted in a significant molecular scission, which adversely affected the mechanical properties. This is contradictory to data reported by Lee[2], who observed very limited degradation of polycarbonate in the melt at 310°C. Glöckner[3] investigated the effect of recycling polycarbonate in an injection moulding machine. He measured the intrinsic viscosity of the polymer after each cycle and from this data determined the extent of chain scission. It was found that the total number of scissions per cycle increased exponentially. Glöckner[3] explained these results by two simultaneous mechanisms. One part of the degradation, which was constant for each cycle, was the result of hydrolytic chain scission. The remaining fraction, which increased exponentially with the number of cycles, was ascribed to a catalytic chain scission. Glöckner[3] suggested that products formed during the degradation acted as catalysts. The hydrolytic cleavage is catalysed by basic as well as acidic compounds, which may be formed during the polymer decomposition. The effect of moisture on the degradation of polycarbonate during injection moulding was discussed by Long and Sokol[4]. They showed that low moisture content during processing adversely affected the mechanical properties of the end product. Moisture absorption was very rapid and a maximum acceptable content of 0.03% was reached within 30 min at 24°C and 49% RH. Several methods for the detection of polycarbonate degradation were tested, but gel permeation chromatography was found to be the most satisfactory. Shea *et al.*[5] studied the effect of recycling on the properties of injection moulded polycarbonate, evaluating the extent of degradation by measuring melt flow, impact strength and molecular weight. This study also showed that moisture accelerated polymer degradation. Shea *et al.*[5] recommended measurement of melt flow for the evaluation of the moulding process as they considered this test to be much easier to perform than, for example, solution viscosity.

Polycarbonate, on exposure to heat, may react according to two principal mechanisms. When degraded in a continuously evacuated system, it rapidly crosslinks to form an insoluble gel. However, if the experiment is carried out in a sealed, evacuated vessel, chain scission occurs[6]. In a previous investigation we analysed the thermal degradation of polycarbonate in a rheometer barrel[7]. As these experiments were performed in a closed system, it was not surprising that chain scission predominated during these conditions. In the present study we have tried to elucidate the degradation reactions which occur during repetitive extrusion of polycarbonate at high shear stresses. These data may be compared with the results previously obtained under static conditions (heating in a rheometer barrel)[7]. It is also of great interest to utilize such information for the estimation of polymer degradation during processing. Earlier studies on polystyrene and polyisobutene have shown that model extrusion experiments are useful in this respect[8,9].

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0032-3861/81/060836-06$02.00

Table 1 Repetitive extrusion of polycarbonate. Data after seven extrusions

Extrusion temperature (°C)	Shear stress (τ_w, MPa)	Shear rate ($\dot{\gamma}$, s^{-1})	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_Z$	$\bar{M}_w/\bar{M}_n$
Virgin sample	–	–	13 780	30 200	49 800	2.19
320	0.15	(6350)	6800	17 600	30 600	2.59
320	0.36	4570	9200	22 000	37 500	2.39
320	0.68	12 600	9950	23 300	39 400	2.34
320	0.95	24 500	9600	23 500	39 500	2.45
305	0.15	1770	8500	21 100	36 800	2.48
305	0.36	2350	9800	22 100	35 700	2.26
305	0.68	5080	10 200	25 400	42 400	2.49
305	0.95	15 400	12 000	27 100	45 300	2.26
290	0.15	490	10 900	25 800	42 000	2.37
290	0.36	910	10 900	25 600	42 200	2.35
290	0.68	1740	11 400	26 800	44 000	2.35
290	0.95	5990	12 500	28 500	46 400	2.28
275	0.15	240	12 100	29 300	48 700	2.42
275	0.36	330	13 400	28 300	45 100	2.11
275	0.68	530	11 100	27 800	45 500	2.50
275	0.95	990	12 700	28 300	45 400	2.22

EXPERIMENTAL

Materials

A bisphenol A polycarbonate, Makrolon 2805, from Bayer AG, was used as supplied. It is heat stabilized and contains a minor amount of a mould release agent.

The methylene chloride employed for the gel permeation measurements was of analytical grade.

Extrusion

The rheological measurements were made with a Gottfert Rheometer Model HKR 2000 (Göttfert Feinwerk Technik, BmbH, Buchen, West Germany). A capillary with an L/D ratio of 60 was used, diameter 1 mm.

The polymer pellets were dried overnight at 120°C before each extrusion. Small portions of polymer were located into the heated barrel and then compacted by manual tamping. The filling procedure lasted for ~2 min and the sample was then kept in the capillary reservoir for 3 min to reach temperature equilibrium. The extrusion was carried out at high, constant shear stress (0.15, 0.36, 0.68 and 0.95 MPa) and at temperatures characteristic of injection moulding operations (275, 290, 305 and 320°C). After each cycle the extrudates were cut into pieces and reextruded. This procedure was repeated up to seven times.

G.p.c. measurements

A Waters Associates GPC Model 200 was used to obtain molecular weights and molecular weight distributions. The concept of a universal calibration proposed by Benoit *et al.* was applied[10]. Experimental details have been described previously[11].

RESULTS AND DISCUSSION

In a previous publication we reported on the thermal degradation of polycarbonate in a rheometer barrel (under static conditions)[7]. In the present study we are concerned with a related dynamic case, where the polymer is repeatedly extruded through a capillary die. These data may then be utilized for the evaluation of the effect of shear on polymer degradation. When a macromolecule is exposed to high mechanical forces chain scission may result. Polymer degradation is, therefore, likely to occur during processing at high shear stresses. A critical shear stress has to be exceeded before any effect is observed, but above this level chain scission is expected to increase with an increase in shear stress[12]. Polycarbonate was repeatedly extruded at 0.15, 0.36, 0.68 and 0.95 MPa at 275, 290, 305 and 320°C. The shear stress was kept constant within $\pm 10\%$ independent of melt temperature or number of recycles. Consequently, the polymer melt experienced the same average mechanical stress during each extrusion cycle ($n = 1$–7). However, the residence time for the material may change.

The molecular data after seven extrusions are listed in *Table 1*. A significant reduction in molecular weight was observed at all temperatures except at 275°C, where only small changes were noticed. From *Table 1* it is seen that the highest molecular weight decrease occurred at the lowest shear stress. This is contradictory to that expected from a mechanically induced reaction, and indicates that true mechanical degradation is less important than thermal degradation. This may be explained by the fact that the highest shear stresses corresponded to the shortest residence times and *vice versa*. The loading procedure, which includes the preheating period, lasted for ~5 min. As all samples were taken out at the end of each run, the total residence time was the sum of the preheating period and the extrusion time.

The changes in molecular weight as a function of the number of extrusions are given in *Tables 2* and *3*. Data obtained at the highest shear stress are listed in *Table 2*. The scission reaction is easily determined at 320°C, but at lower extrusion temperatures the low extent of degradation prevents a more careful analysis. However, at the lowest shear stress, i.e. the longest residence time, the degradation reaction could be studied in detail at all temperatures. The results are collected in *Table 3* and *Figures 1–3*. This data shows that the thermal stabilizer in the polymer compound was effective during the first extrusions. This is especially noticable at low extrusion temperatures. At 275°C a significant change in molecular

Table 2 Repetitive extrusion of polycarbonate. τ_w = 0.95 MPa

Extrusion temperature (°C)	Number of extrusions	$\bar{M}_n$	$\bar{DP}_n$	$\bar{M}_w$	$\bar{M}_Z$	$\bar{M}_w/\bar{M}_n$	$(\bar{DP}_n^0/\bar{DP}_n - 1)$
Virgin sample	0	13780	54	30200	49800	2.19	–
320	2	13200	52	28400	48600	2.15	0.04
320	3	12500	49	28600	47300	2.29	0.10
320	4	11200	44	25500	41300	2.28	0.22
320	5	10500	41	24800	40900	2.37	0.32
320	6	10000	40	23800	40000	2.38	0.35
320	7	9600	38	23500	39500	2.45	0.44
305	6	12000	47	27800	47000	2.32	0.15
305	7	12000	47	27100	45300	2.26	0.15
290	6	12900	51	28700	46200	2.22	0.06
290	7	12500	49	28500	46400	2.28	0.10
275	2	13100	52	29700	48000	2.27	0.04
275	3	14400	57	30700	49900	2.14	0
275	4	13100	52	28700	45900	2.20	0.04
275	5	12600	50	29600	48200	2.35	0.08
275	6	13300	52	29200	46700	2.19	0.04
275	7	12700	50	28300	45400	2.22	0.08

Table 3 Repetitive extrusion of polycarbonate. τ_w = 0.15 MPa

Extrusion temperature (°C)	Number of extrusions	$\bar{M}_n$	$\bar{DP}_n$	$\bar{M}_w$	$\bar{M}_Z$	$\bar{M}_w/\bar{M}_n$	$(\bar{DP}_n^0/\bar{DP}_n - 1)$
Virgin sample	0	13780	54	30200	49800	2.19	–
320	2	12700	50	28300	45800	2.23	0.08
320	3	11100	43	25800	43800	2.31	0.25
320	4	9430	37	22000	36600	2.34	0.46
320	5	9080	36	21200	35200	2.34	0.50
320	6	7950	31	19400	32900	2.44	0.74
320	7	6800	27	17600	30600	2.59	1.00
305	4	11100	44	27300	44200	2.46	0.26
305	5	10000	39	23900	40300	2.39	0.38
305	7	8500	33	21100	36800	2.48	0.64
290	4	12300	49	29500	49500	2.40	0.10
290	6	11700	46	27900	45600	2.39	0.17
290	7	10900	43	25800	42000	2.37	0.26
275	2	13800	54	31500	50200	2.25	0
275	3	12900	51	29300	47900	2.27	0.06
275	4	13300	52	28900	46100	2.17	0.04
275	5	13500	53	29900	48400	2.22	0.02
275	7	12100	48	29300	48700	2.42	0.13

weight was detected after seven cycles only. At 320°C, however, the stabilizing effect was lost after two cycles and an extensive degradation was then observed. After seven cycles $\bar{M}_n$ was half of the original value, which corresponded to an average of one scission per molecule. These results may be compared with those reported for recycling of polycarbonate in an injection moulding machine. Our data are in general agreement with the observations published by Shea *et al.* Göckner, however, reported a much higher extent of degradation. The number of scissions per molecule at 270°C were comparable with our data at 320°C. In spite of differences in experimental conditions, one may conclude that the degradation rates determined by us are much lower than those obtained in earlier investigations[13]. These discrepancies may be due in part to differences in sample origin. Polycarbonates studied in earlier work[7] were probably obtained from melt polymerization, whereas the grade reported on here was prepared by interfacial polymerization and therefore has a higher inherent thermal stability. The agreement with more recent data confirms this conclusion. It is also important to note that our sample contains a small amount of thermal stabilizer. Information about additives is not given in the cited literature.

Figures 1 and *2* show the changes in molecular weight distribution (*MWD*) observed during some of the experiments. From *Figure 1* it is obvious that a repeated extrusion at 320°C and $\tau_w = 0.15$ MPa shifts the *MWD* towards lower molecular weights. There is no sign of crosslinking which would increase the high molecular weight end of the distribution. *MWD*s, after seven cycles at various temperatures, are compared in *Figure 2*. The values are shifted towards lower molecular weights indicating significant polymer degradation. The changes at 275°C are small and the deviation from the original *MWD* after seven cycles was almost within experimental error.

The scission reaction is claimed to take place ran-

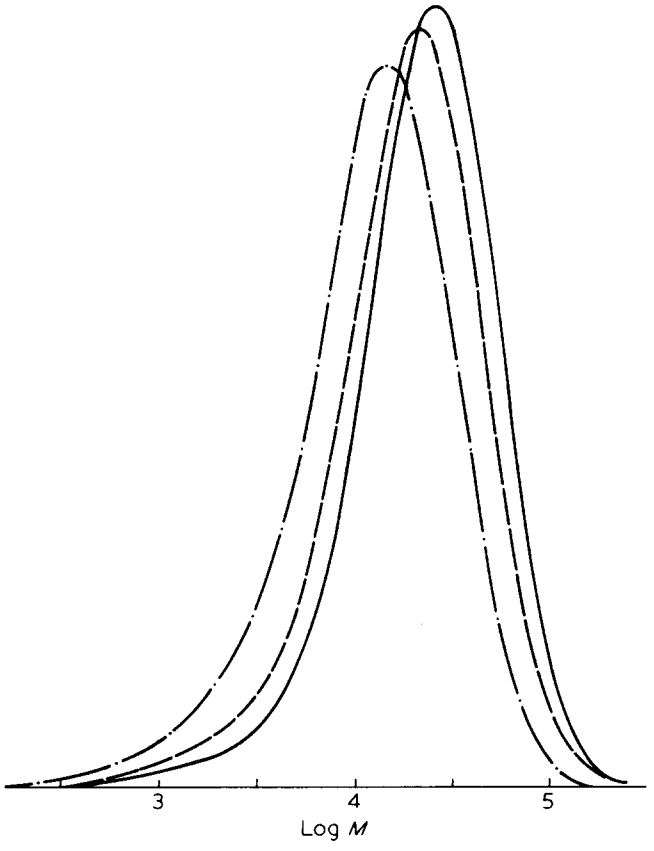

Figure 1 The molecular weight distribution after $n = 0$ (——), $n = 3$ (— — —) and $n = 7$ (— · —) extrusion at $\tau_W = 0.15$ MPa and 320°C

domly[3,6]. This means that the heterogeneity index, $\bar{M}_w/\bar{M}_n$, should approach two. As seen in *Table 1* there is a tendency towards an increase in $\bar{M}_w/\bar{M}_n$ in all experiments. This may also be observed from *Tables 2* and *3*. A small increase in polydispersity does not comply with random scission kinetics. However, the number of scissions per molecule increased linearly with the number of extrusions in all cases (cf. *Figure 3*). This is indicative of a random process, although a careful analysis of the data[13], according to a method proposed by Scott[14], showed that the molecular scission was taking place in a non-random fashion.

The number of scissions per molecule at $\tau_w = 0.15$ MPa was determined at each temperature as a function of the number of extrustions. The results are collected in *Figure 3*. After an induction period the number of scissions increased linearly. It is reasonable that the limited degradation observed during the first cycles could be due to the presence of the heat stabilizer, added to the polycarbonate. From the slopes of the straight lines in *Figure 3*, it was possible to determine degradation rates at all temperatures. These data may then be used for an Arrhenius' plot as shown in *Figure 4*. From the slope of the resulting straight line an activation energy, ΔE, of 113 kJ mol^{-1} (27 kcal mol^{-1}) was obtained. This value is similar to that calculated for the degradation reaction in the rheometer during static conditions (112 kJ mol^{-1}), which indicates similar processes in both cases[7].

The experimental results may be used to estimate the effect of shear on the extent of degradation. For this purpose, we have compared the static and dynamic

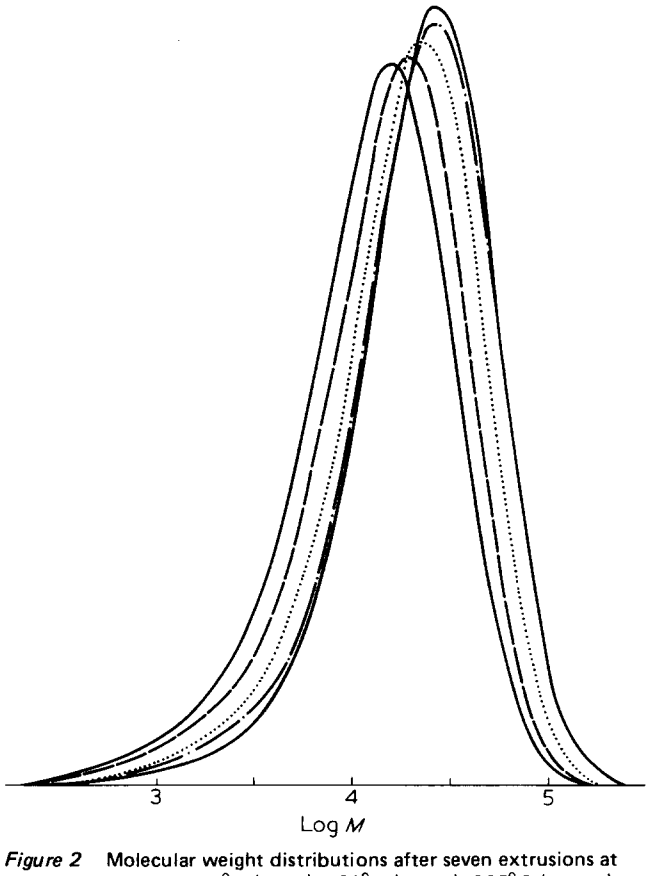

Figure 2 Molecular weight distributions after seven extrusions at $\tau_W = 0.15$ MPa and 275°C (— · —), 290°C (· · · · ·), 305°C (— — —) and 320°C (——) respectively

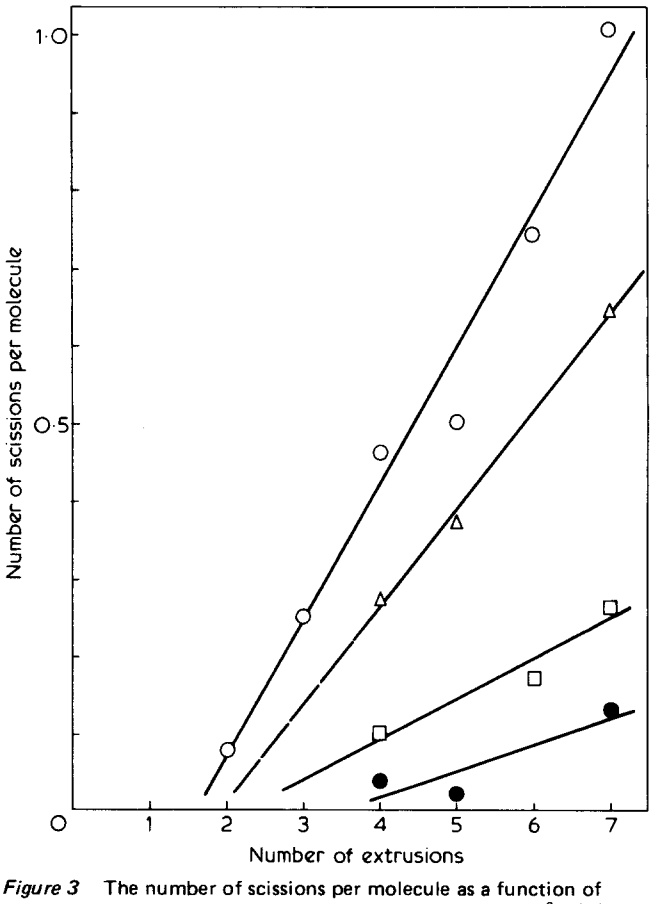

Figure 3 The number of scissions per molecule as a function of the number of extrusions. Data at $\tau_W = 0.15$ MPa and 275°C (●), 290°C (□), 305°C (△) and 320°C (○) respectively

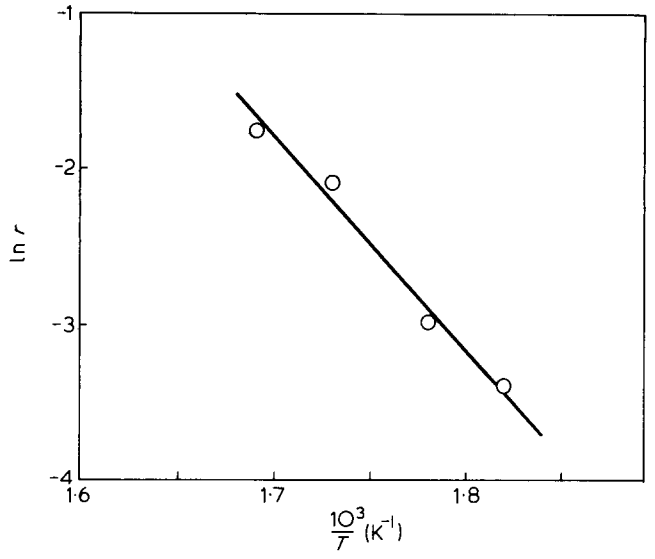

Figure 4 Arrhenius' plot for the degradation of polycarbonate during repetitive extrusion at τ_w = 0.15 MPa

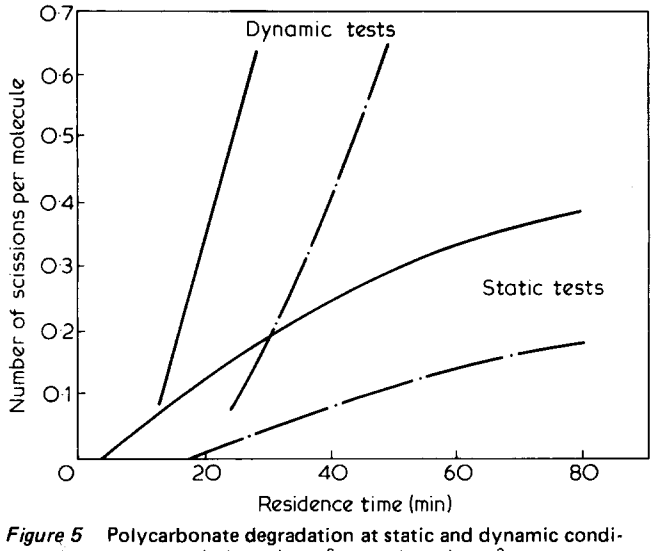

Figure 5 Polycarbonate degradation at static and dynamic conditions (τ_w = 0.15 MPa): (— · —) 305°C and (——) 320°C

experiments at 305°C and 320°C[7]. The residence times for extrusion were obtained by adding the time of preheating and extrusion. The results are shown in *Figure 5*. The dynamic data were taken at $\tau = 0.15$ MPa. It is evident that polymer degradation occurred to a much larger extent during extrusion than under static conditions.

Viscous heating occurs during extrusion of polymer melts through narrow channels[15] and, in most cases, does not affect the rheological conditions to any larger extent. However, at the high shear rates that prevail in this case, substantial temperature effects have been reported[15-18]. Approximate calculations derived from a nomogram published by Middleman[15] showed that a local temperature increase in the order of 100°C would not be surprising. Such extensive viscous heating has also been reported by others[17,18]. In spite of a fairly short residence time, the very high melt temperatures may cause significant polymer degradation. *Table 1* shows that molecular weight decreases with an increasing number of cycles. This results in a lower viscosity of the polymer melt. As shear stress is kept constant during these experiments this means that shear rate, $\dot{\gamma}$, increases with the number of

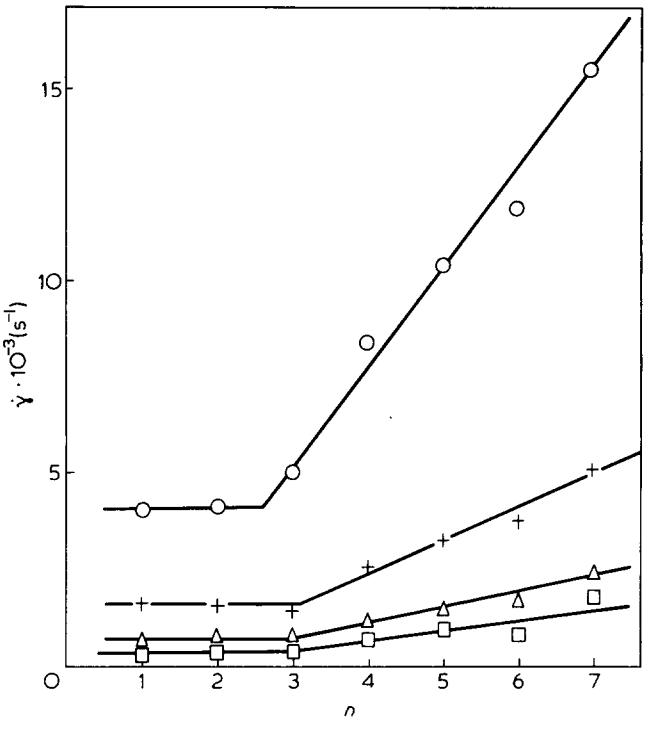

Figure 6 Shear rate, $\dot{\gamma}$, at 305°C plotted versus extrusion number, n, for a shear stress (τ_w) equal to 0.15 MPa (⊡), 0.36 MPa (△), 0.68 MPa (+), and 0.95 MPa (⊙) respectively

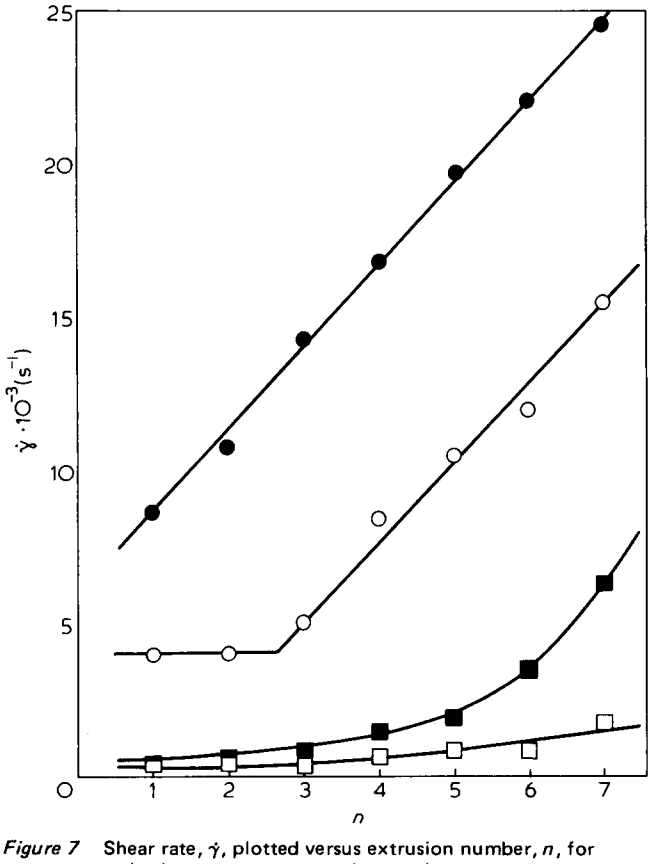

Figure 7 Shear rate, $\dot{\gamma}$, plotted versus extrusion number, n, for a shear stress (τ_w) equal to 0.15 MPa (squares) and 0.95 MPa (circles) respectively. Data at 305°C (unfilled symbols) and 320°C (filled symbols)

cycles. This is demonstrated in *Figure 6* for data obtained at 305°C. During the first cycles when no degradation occurred; there is no change in shear rate, but after the third cycle a linear increase in $\dot{\gamma}$ was observed. The change in shear rate was dramatic and at 305°C and $\tau_w = 0.95$ MPa, it doubled between the third and the fifth cycle. Similar changes were noticed at lower shear stresses. At 320°C a continuous increase in shear rate was observed, which started during the first cycle. This is in agreement with the molecular changes discussed above. At $\tau_w = 0.95$ MPa, shear rate increased linearly with the number of cycles, but at all other shear stresses, shear rate exhibited more of an exponential increase. A comparison between the results from 305°C and 320°C is shown for $\tau_w = 0.15$ MPa and $\tau_w = 0.95$ MPa respectively in *Figure 7*. At $\tau_w = 0.95$ MPa the rate of increase in shear rate is the same at the two temperatures if the initial period at the lower temperature is omitted. However, at $\tau_w = 0.15$ MPa the change in shear rate is more rapid at 320°C. It has been shown previously that viscous heating increases strongly with an increasing shear rate[16]. The large discrepancies between static and dynamic degradation as demonstrated in *Figure 5* may then be explained partly by the rapid increase in shear rate with the number of extrusions. If the effect of viscous heating could be accounted for, the shape of the dynamic curve would tend to become similar to that of the static one. The results clearly show that the set processing temperature as well as the rheological conditions have a great effect on the extent of polymer degradation.

ACKNOWLEDGEMENTS

The experimental assistance by Mrs E. Nyberg and Mr S. Noren is greatly appreciated.

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