Shear Modification of Polyethylene

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Synopsis

Polymers like LDPE can be modified by applying a shearing process for an extended period. As a result the melt elasticity is reduced, as evidenced by the decrease in extrudate (die) swell at the exit of a capillary and onset of melt fracture. Melt viscosity was also slightly reduced; melt flow index (measured in short capillary) is highly increased. At the same time, melt density rises. All these parameters vary mostly for LDPE grades that exhibit the highest degree of long-chain branching. It was confirmed that the intrinsic viscosisty of the polymer samples was essentially unaffected, so that chain scission may be ruled out. Moreover, the process itself is shown to be reversible as the initial parameters were recovered by special treatment, due to heating or solvation. The mechanism of shear modification is believed to consist of disentanglement of temporary couplings between long branches. The practical utilization of this process will be pursued, as well as the scientific understanding of structuring entangled branched chains.

INTRODUCTION

Shear modification (also called shear working or shear refining) represents a special shearing history that affects some viscoelastic and optical properties of the polymer.[1-12] This process has been attributed to the disentanglement of polymeric chains in the melt, which does not cause any disruption of primary bonds. Consequently, the molecular weights and their distribution should not be altered, and the original entangled structure may be re-formed by further treatment. The polymer most amenable to shear modification exhibited long-chain branching (LCB) like low-density polyethylene (LDPE).

The main features affected by shearing were reduction in melt elasticity (due to breakup of long-range elastic structures) and improvement of optical clarity (due to the elimination of microgels). Melt viscosity of the polymer is also expected to be affected. The evidence for reversibility of the entangled structure was given by a total recovery of the original properties, through heat or solvent treatment. Shear modification may lead to improvement of melt processing and beneficial properties.

In spite of the general agreement about the shearing process and its effects, there is still a dispute among workers about whether it is exclusive to branched polymers only. Thus, Maxwell and Brockwoldt[9] verified shear modification by extruding linear polymers (HDPE) as well as branched ones (LDPE); Teh et al.[12] detected shear modification in linear LDPE. Besides, various competing mechanisms may occur during polymer processing, like chain orientation, chain scission, decoupling and recoupling of secondary bonds, and recombination of chains. The results may lead to quite different changes in the viscoelastic properties.[13] One must therefore be very cautious in the analysis of shear modification.

The whole concept of entanglement is far from being fully understood. Following the elusive works of Graesssley and others, which have been summarized in an extensive review,[14] entanglement reveals itself as an essential concept that affects polymer motion and relaxation in the melt and in concentrated solutions. Melt viscosity, modulus, and relaxation time spectrum, as well as other elastic parameters, are highly influenced by the proposed existence of temporary chain coupling (entanglements) that may be partly released by shear or thermal energy. By high dilution in good solvents, complete disentanglement is expected. In spite of the fact that disentanglement or re-entanglement are never directly visualized or measured, the concept of the intermolecular coupling called entanglement is well established in contemporary polymer science.

The role of long-chain branching in polymer flow and elasticity is also not yet clearly understood.[15] In most cases, the existence of LCB leads to reduction in the chain dimensions, which may be detected by light scattering and results in a marked decrease of intrinsic or melt viscosity at constant molecular weights. However, a competition appears between volumetric reduction and intermolecular interaction between the long branches, so that an enhancement of viscosity may also occur.[16-20] This enhancement should always appear once the size of the branches exceed those of the critical chain length for entanglement. Fujimoto et al.[20] claim that in branched polymers the main chain cannot pass through an entanglement loop and therefore the only entanglements appear between long branches, but it is believed that the slippage of these "intermeshing chain branches" may be easier than that of the main chain couplings.

Our previous studies on viscoelastic behavior of LDPE at various degrees of LCB and MWD, compared with linear HDPE, exhibit some contrasting results.[21-24] It was originally assumed that the linear chains contain a higher density of entanglement (a lower value for the subchain M_e between coupling points). This assumption explained the differences between calculated shear moduli or compliances in the melt as affected by LCB. On the other hand, the linear polymers exhibit a distinct reduction in melt flow energy of activation and shear sensitivity. In addition, most phenomena manifiested through recoverable elasticity (extrudate swell, capillary end correction, and onset of melt fracture) are definitely affected by the existence of LCB.[25] We may therefore assume that the melt elasticity may be connected with the interbranching couplings and their possible temporary rupture by appropriate shearing processes.

EXPERIMENTAL

Materials

Initial studies of shear modification were performed on three grades of LDPE provided courtesy of the Israel Petrochemical Enterprises, Ltd., Haifa. These grades were produced in an autoclave-type reactor using the ICI high-pressure process. They were fully characterized in the past[26-28] by use of a Waters GPC apparatus (Model 200) run at 130°C with TCB as a solvent. The interference of LCB has been incorporated via intrinsic viscosisty and introduced into the computer program. Typical results are shown in Table

I. Although there might be some changes in these grades from various dates of production, their typical characteristics and performance are believed to be steady. They will nevertheless be reanalyzed in the advance of this study. Two grades of a linear low-density polyethylene (LLDPE) were also studied: Union Carbide grade G-7047 and Dowlex 2042.

Shear Modification

Shearing was executed in the Brabender Plastograph at 150°C and 180°C and 60 rpm. All samples were stabilized with 0.5% antioxidant (Santanox R). Duration of shearing was 0–180 min.

Viscoelastic Measurements

Melt viscous and elastic parameters were measured by using a melt-flow-indexer and a capillary rheometer attached to an Instron Universal Tester. MFI values were performed in accordance with ASTM D1238, at 190°C, under loads of 2.16 and 5 kg. The capillary dimensions were $L = 8$ mm, $D = 2.096$ mm and $L/D = 3.8$. The capillary rheometer ran at 190°C at various shear rates. The dimensions of the capillary were $D = 0.05$ in.; $L/D = 20$ and 80. The Rabinowitsch correction was applied for the shear rates at the wall, but no end correction for shear stress was used. Recoverable elasticity was followed by measuring "extrudate (or die) swell" at the exit of the die. The diameter of the frozen extrudate was directly measured without applying any further corrections.

Melt Density

Melt density was measured by an automatic flow rate timer attached to the melt flow indexer. Conditions were 190°C and a load of 2.16 kg.

Recovery

Recovery after shear modification was performed either by heat or solvent treatment. The former consisted of an oven flushed with N_2 at 190 or 210°C for 2–3 h. In solvent treatment, the polymer was dissolved in p-xylene at 135°C and a concentration of 5%. The polymer was precipitated from the solution by use of a nonsolvent (water or MEK) and dried under vacuum at 160°C for about 30 min.

RESULTS AND DISCUSSION

Table II and Figure 1 verify the effects of shear modification at two temperatures (150 and 180°C, respectively), as evidenced by the change of the apparent extrudate swell measured at the melt flow indexer. The decrease in melt elasticity is remarkable in the case of grade E and reduces progressively with grades A and C, all grades reaching the same level at the final stage. The third grade (C) is barely affected. The linear polymer, on the other hand, exhibits a slight increase in elasticity. The initial values of extrudate swell also follow the same order (decreasing from E to C) in accordance with the influence of LCB on melt elasticity.[29] One may also note that shearing at higher temperature (180 versus 150°C) entails higher

TABLE I
Molecular Characterization Data of LDPE Samples (Ipithene, 1972)

Grade	MFI (g/10 min)	[η] (dl/g, 130°C TCB)	M_n	M_w	Dispersion $Dn = M_w/M_n$	M_z	η_o (poise; viscosity)	LBC number (n_w)	LCB parameter (g)	gM_w
100-A	0.25	1.160	21,000	320,000	15.24	2.12×10^6	540,000	57.8	0.1483	47,460
320-C	2.0	0.766	23,000	140,000	6.09	4.7×10^5	60,000	53.8	0.1560	21,860
300-E	2.0	0.975	21,100	691,000	32.80	5.11×10^6	75,000	293.3	0.0450	31,300

TABLE II
Extrudate Swell[a]

Grade	Load in MFI (kg)	Extrudate swell		Ultimate change (%)	Extrudate swell after shearing at 180°C	Ultimate change
		Original	Sheared at 150°C			
LDPE-E 300	2.16	1.679	1.379	-17.87	1.335	-20.49
	5	1.784	1.541	-13.62	1.407	-26.79
LDPE-A 100	2.16	1.455	1.360	-6.53	1.312	-9.83
	5	1.574	1.446	-8.13	1.460	-7.24
LDPE-C 320	2.16	1.369	1.332	-2.70	1.335	-2.48
	5	1.574	1.538	-2.28	1.550	-1.52
LLDPE G-704	2.16	1.088	—	—	1.235	+13.51
	5	1.145	—	—	1.322	+15.46

[a] After shearing in Brabender plastograph for 120 min at 150 and 180°C at 60 RPM. Measured at melt flow indexer at loads of 2.16 and 5 kg at $T = 190$°C.
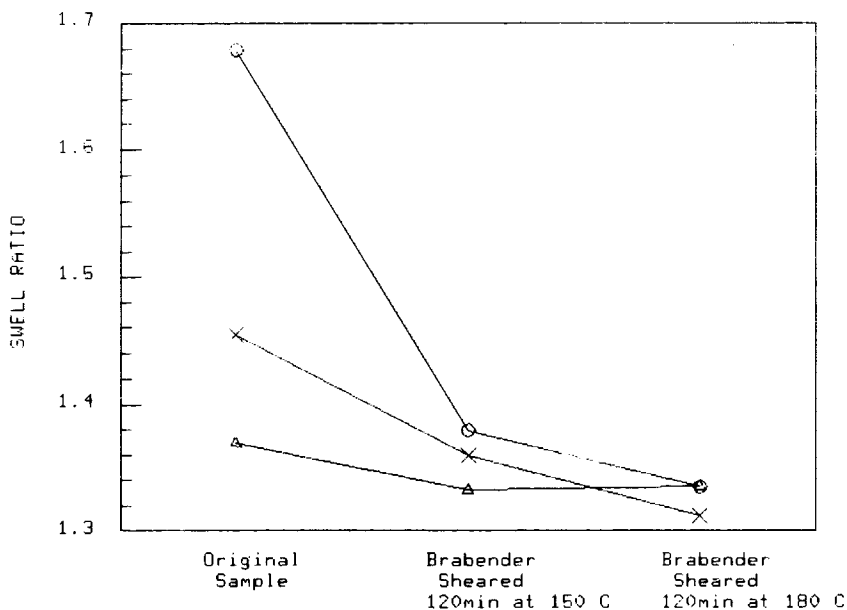
Fig. 1.   Die swell changes after shearing at 150°C and 180°C: (○) LDPE 300; (X) LDPE 100;
(△) LDPE 320.

efficiency in reduction of swell. The increase of shear modification at the
higher temperature agrees with the results of Rokudai[4] but contradicts
other works.[9,12] The difference in sensitivity to shear modification between
the four grades points out the controlling effects of LCB (and probably M_w
and MWD) on their initial swell ratio and its reduction upon shearing.

Following extrudate swell by the capillary rheometer (Table III and Figs.
2 and 3) verify much lower changes, although the order of performance
between the LDPE grades is preserved. The main reason for this discrepancy
lies in the elastic stress relaxation in longer capillaries. The progressive
decrease of extrudate swell with L/D of the capillary was shown by oth-
ers.[29,30]

Table IV verifies this effect by using two capillaries differing only in
L/D ratio. The onset of melt fracture is also slightly delayed, either by
shear modification or by measuring with longer capillaries. It may be con-
cluded that the use of short capillaries (as in the melt flow indexer in the
nonequilibrium state) leads to high sensitivity and dramatic changes when
highly branched polymers are shear modified. The exact rheologic inter-
pretation of extrudate swell, leading to the computation of steady-state
shear compliance, normal stress differences, and recoverable shear strain,
challenged many workers.[30-33] Yet, the exact performance of this measure-
ment and the effects of molecular weight, MWD, LCB, and shear conditions
are still not certain.[34]

Two grades of LLDPE, a linear version of LDPE with no long branches,
are shown unmodified by shearing (Table V). The LLDPE G-7047 actually
exhibits an increase in the swell ratio after shearing.

TABLE III
Extrudate swell[a]

Grades of LDPE (γ_{ap}/s^{-1})	300			100			320		
	Original	Sheared 120' at 180°C	Ultimate change (%)	Original	Sheared 120' at 180°C	Ultimate change (%)	Original	Sheared 120' at 180°C	Ultimate change (%)
0.57	1.150	1.080	−6.01	1.141	1.102	−3.42	1.007	1.016	+0.89
1.14	1.205	1.142	−5.22	1.181	1.126	−4.66	1.047	1.060	+1.2
2.86	1.275	1.181	−7.4	1.220	1.181	−3.20	1.142	1.141	−0.09
5.72	1.339	1.220	−8.8	1.260	1.205	−4.36	1.181	1.181	0
11.44	1.378	1.260	−8.6	1.275	1.220	−4.31	1.220	1.220	0
28.6	1.386	1.299	−6.3	1.299	1.260	−3.00	1.326	1.259	+1.8
57.2	1.401	1.339	−4.4	B.M.F.	1.275	—	1.268	1.299	+2.44
114.4	1.417	1.354	−4.4	M.F.	B.M.F.	—	1.299	1.315	+1.2
286.0	M.F.	1.370	—	—	—	—	1.388	1.322	−0.89
572.0	—	M.F.	Average: 6.39	—	—	Average: 3.83	M.F.	M.F.	Average: +0.72

[a] Affected by shear history measured in capillary rheometer.
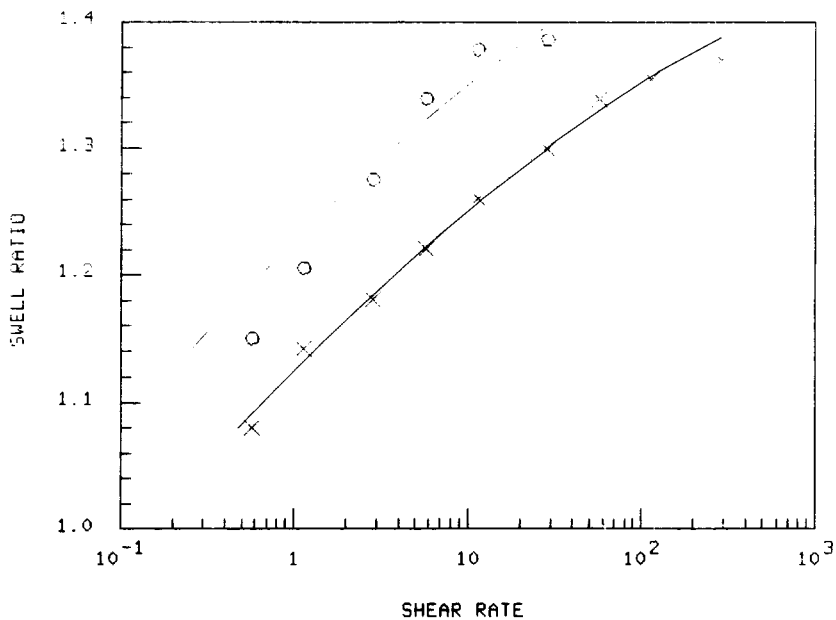MF = melt fracture; B = begin.

Fig. 2.   Swell ratio of LDPE-300 after shearing at 180°C. Capillary rheometer. (○) Original; (×) Sheared.
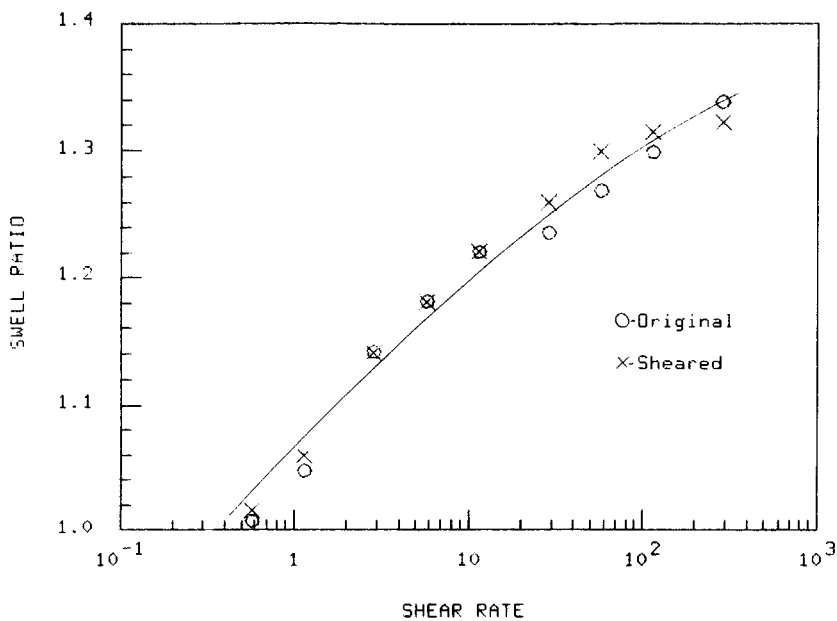

Fig. 3.   Swell ratio of LDPE-320 after shearing at 180°C. Capillary rheometer. (○) Original; (×) Sheared.

TABLE IV
Extrudate Swell[a]

$\dot{\gamma}_{ap}\,s^{-1}$	L/D = 20			L/D = 80		
	Original	Brabender sheared 120' at 180°C, 60 RPM	Ultimate change (%)	Original	Brabender sheared 120' at 180°C, 60 RPM	Ultimate change (%)
0.57	1.300	1.220	6.153	1.141	1.102	3.42
1.14	1.341	1.260	6.04	1.181	1.126	4.66
2.86	1.352	1.301	4.2	1.220	1.181	3.20
5.72	1.382	1.317	4.705	1.260	1.205	4.36
11.44	1.391	1.328	4.5	1.275	1.220	4.31
28.6	1.447	1.382	4.5	1.299	1.260	3.00
57.2	Melt fracture	1.423	—	Slight melt fracture	1.275	3.04
114.4	—	Melt fracture	—	Melt fracture	Slight melt facture	—
286.0	—	—	—	—	Melt fracture	—
572.0	—	—	—	—	—	—
			Average: 5.1			Average: 3.8

[a] Affected by L/D ratio for LDPE-100 measured in capillary rheometer at 190°C.

TABLE V
Extrudate Swell of LLDPE

LLDPE: Union Carbide G-Resin 7047 (Brabender time; 60 RPM)						Dowlex 2042 (Brabender time; 60 RPM)					
0			120' at 180°C			0			180' at 180°C		
Speed	Force	Swell	Speed	Force	Swell	Speed	Force	Swell	Speed	Force	Swell
0.05	52	1.024	0.05	60	1.063	0.05	53	1.181	0.05	47	1.181
0.1	91	1.063	0.1	86	1.102	0.1	84	1.220	0.1	77.3	1.220
0.2	155	1.102	0.2	135	1.142	0.2	138	1.260	0.2	128	1.260
0.5	300	1.181	0.5	260	1.181	0.5	260	1.299	0.5	244.5	1.299
1	469	1.260	1	407	1.299	1	397	1.388	1	375	1.299
2	678	1.165	2	574	Sharkskin	2	578	1.417	2	548	1.338
5	860	Sharkskin	5	800	Sharkskin	5		Sharkskin	5		1.417
10	890	MF	10	1020	M.F.	10	790	Sharkskin	10	790	Sharkskin

TABLE VI

Melt-Flow Index MFI after shearing in Brabender Plastograph for 120' at 150°C and 180°C, 60 RPM Measured at Melt flow Indexer at load 2.16 and 5 kg, t = 190°C, L/D = 3.8

Grade of LDPE	Load kg	Original	M.F.I sheared: 120' at 150°C	Ultimate Change %	M.F.I sheared: 120' at 180°C	Ultimate change %
300 (E)	2.16	1.947	2.86	+46.89	2.915	+49.71
	5	7.66	11.26	+46.99	11.82	+54.31
100 (A)	2.16	0.288	0.372	+29.17	0.380	+31.94
	5	1.208	1.570	+29.97	1.690	+39.90
320 (C)	2.16	1.984	2.133	+ 7.5	2.170	+ 9.37
	5	7.724	8.244	+ 6.73	8.57	+10.95
LLDPE	2.16	1.065			1.122	+ 5.35
G-7047	5	2.99			3.213	+ 7.45

Data for the effects of shear history on the melt flow index (MFI) of the three grades of LDPE and a single grade of LLDPE are shown in Table VI and Figure 4. There is a remarkable rise in MFI, which diminishes from grade E to C and further to the linear polymer, which is only slightly affected.

Measuring apparent viscosities at various shear rates in the capillary rheometer at 190°C reveals moderate changes that progressively decrease with increasing shear rates (Table VII). In general, grade E (300) verifies the highest change and C the lowest. However, at the lowest shear rates there is essentially no difference between those grades. Shear rates at the wall were corrected, and the *L/D* of the capillary was quite large (80), so
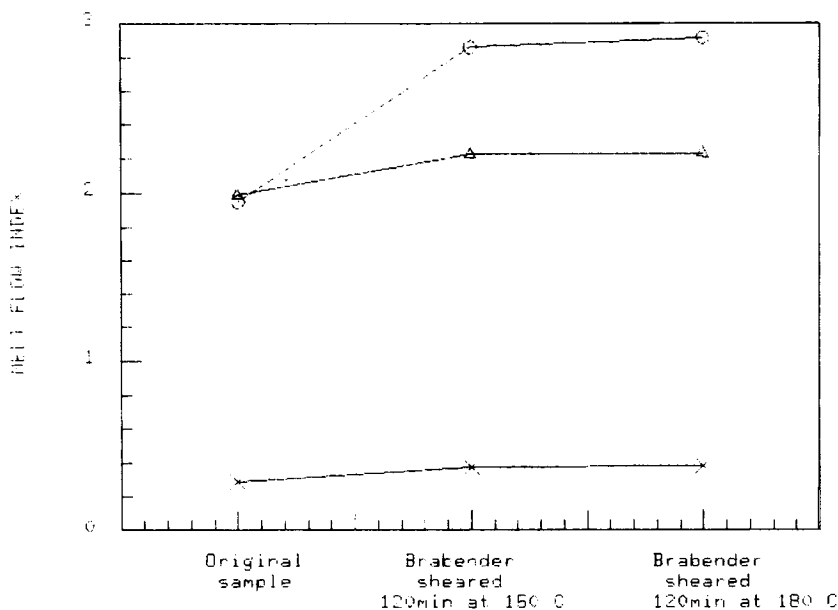

Fig. 4. MFI changes after shearing at 150°C and 180°C. Capillary rheometer. (○) LDPE 300; (×) LDPE 100; (△) LDPE 320.

TABLE VII

Apparent Melt Viscosity Apparent Viscosity (K pa s) as Affected By Shear History, Measured in Capillary Rheometer

Grade LDPE γ_{ap} sec^{-1}	- 300 - E			- 100 - A			- 320 - C		
	Original	sheared 120' at 180°C	Ultimate change %	Original	sheared 120' at 180°C	Ultimate change %	Original	sheared 120' at 180°C	Ultimate change %
1.14	4.6946	4.1115	−12.42	13.7383	11.9856	−12.81	4.4718	3.8940	−12.97
2.86	3.3801	2.9097	−13.92	8.7009	7.8345	−10.0	3.5774	3.3748	− 5.6
5.72	2.5038	2.277	−9.06	5.9533	5.4374	− 8.47	2.8747	2.7907	− 2.79
11.44	1.8465	1.708	−7.50	4.0070	3.8588	− 3.25	2.1720	2.1417	− 1.38
28.6	1.2018	1.113	−7.39	2.3470	2.2802	− 2.56	1.4054	1.4019	− 0.24
57.2	0.8450	0.784	−7.22	1.5169	1.4909	− 1.32	0.9838	0.9865	+ 0.27
114.4	0.5759	0.5503	−4.44	0.9840	0.9705	− 1.37	0.7187	0.6815	− 5.17
286.0	0.3443	0.3289	−4.47	0.5610	0.5613	+ 0.05	0.4088	0.4089	0
572.0	0.2297	0.2246	−2.22	0.3635	0.3654	+ 0.52	0.2683	0.2726	+ 1.6
$n = \dfrac{d\ln t_w}{d\ln \dot{\gamma}_w}$	0.523	0.538		0.422	0.443		0.552	0.576	

that these results are rather accurate. The significant difference between readings of MFI and apparent viscosity may be related to the elastic entrance effects that dominate the short die flow in the melt flow indexer. Additional evidence for disentanglement is exhibited in Table VII. It shows slight increases in the slopes of the flow curves before and after shearing, demonstrating the tendency toward "more Newtonian-like" flows. LLDPE suffers a slight drop in apparent viscosity due to shearing at approximately the same values as the increase in MFI. Table VIII confirms the significance of shear history in modifying the elastic responses. The critical shear stress or rate for the onset of melt fracture are effectively delayed by grades E and A but unchanged by grade C.

After describing the effects of shear modification on the viscoelastic response of polymer melts, which may be attributed to a process of disentanglement, the question of reversibility was pursued. Recovery was obtained either by heat or by solvent treatment (Table IX and Figure 5). Besides the relative changes in extrudate swell and MFI, intrinsic viscosity was also checked (in TCB at 130°C). Heat treatment is surprisingly effective, recovering the original extrudate swell and MFI (within limits). Solvent treatment has similar effectiveness, with a tendency toward higher elasticity than at the original state.[4-6,35]

Intrinsic viscosisty data reveal that shear history did not decrease the intrinsic viscosities (within experimental accuracy) and heat treatment did not apparently affect the results (except for a slight increase after solvent treatment). Future GPC studies will elucidate this picture and tell us whether chain scission or recombination occurs in the processes of shearing and recovery.

Table X provides further effects of shear modification on changes in melt density. All LDPE verify an increase in melt density after shearing at 150 and 180°C. This property is, however, recovered by heat treatment. The increase of melt density hints at an improvement of order in the melt due to partial disentanglement. It is interesting to note that even the linear grade exhibits a slight increase in melt density. As long as extrudate swell may also serve as a measure of polymer dimensions,[16,24,29] shear modification probably does decrease the hydrodynamic volume of the melt that has been partially disentangled. This explains the rise in melt-density after shearing and its eventual recovery. A competing theory[36] postulates shear modifi-

TABLE VIII
Melt Fracture Shear Stresses and Rates for Melt Fracture in LDPE, Measure in Capillary Rheometer at 190°C, L/D = 80. Shearing at 180°C for 120', 60 RPM.

Grade	Shear History	Shear stress (K pas)	Ultimate Change %	Shear rates $\dot\gamma$ sec^{-1} corrected	Ultimate Change %
300 (E)	Original	121.542	29.1	353.042	97.92
	Sheared	156.900		698.728	
100 (A)	Original	117.122	25.28	77.210	95.81
	Sheared	146.734		151.189	
320 (C)	Original	185.628	0	680.997	0
	Sheared	185.628		680.997	

TABLE IX
Recovery Recovery by Heat and Solvent Treatment.

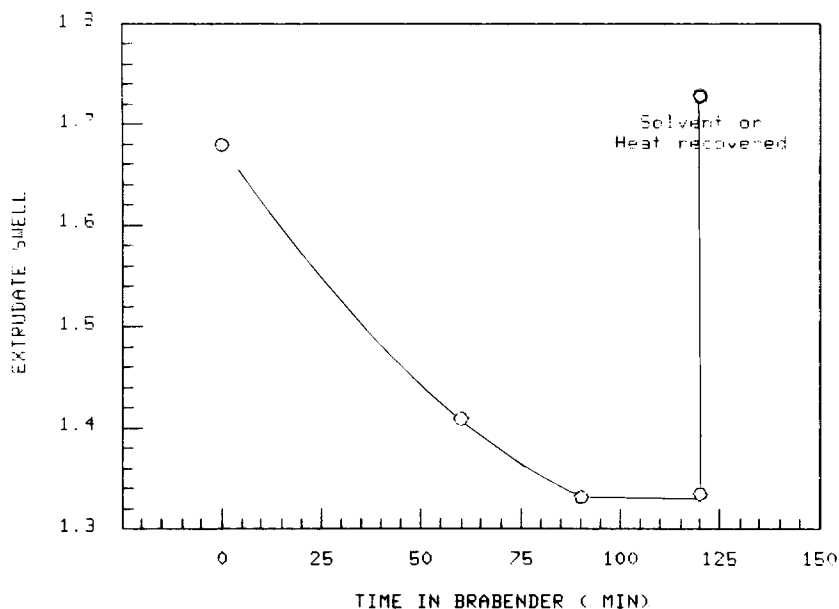| Sample	Original		Brabender Sheared		Heat Treatment		Solvent Treatment	
Load in MFI (kg)	2.16	5	2.16	5	2.16	5	2.16	5
LDPE 300								
Extrudate swell MFI gr/10 min	1.679	1.784	1.335	1.407	1.729	1.890	1.727	1.888
	1.947	7.66	2.915	11.87	2.082	7.842	1.629	6.136
Intrinsic viscosity dl/gr	0.97		0.98		0.935		1.08	
LDPE 100								
Extrudate swell	1.455	1.574	1.312	1.460	1.477	1.634	1.455	1.583
MFI gr/10 min	0.288	1.208	0.38	1.690	0.292	1.299	0.274	1.140
Intrinsic viscosity dl/gr	1.03		1.05		1.02		1.07	
LDPE 320								
Extrudate swell	1.369	1.574	1.335	1.550	1.369	1.574	1.498	1.715
MFI gr/10 min	1.984	7.724	2.170	8.57	2.099	7.892	1.581	6.41
Intrinstic viscosity dl/gr	0.84		0.87		0.83		0.85	

Fig. 5. Swell ratio of LDPE-300 after shearing stages and recovery.

cation by decreasing the size of spherical clusters in the melt, which determine the supermolecular structures.

The physical picture is not yet clear, but shear modification has a significant effect on branched polymers, and this effect is reversible, as evidence by the recovery of the original structure after special treatments.

CONCLUSIONS

Shear modification was applied by a kneading device under controlled conditions. The most branched polyethylene grade exhibits a significant decrease in melt elasticity, as measured by extrudate swell and melt fracture. At the same time, the melt flow index verifies a sharp increase. The apparent viscosity drops slightly, and melt density verifies a rise after shearing. Linear grades of LDPE are essentially unaffected.

TABLE X
Melt Density[a]

Grade Original	100 0.7074		300 0.7078		320 0.7314		LLDPE G-7047 0.7468
T (°C)	150	180	150	180	150	180	180
Sheared 120'	0.7361	0.7474	0.7493	0.7514	0.7617	0.7753	0.7564
Heat treatment	—	0.7170	—	0.7163	—	0.7469	

[a] Affected by shear history measured in the Davenport Automatic flow rate at 190.

The effectiveness of shearing increases with the increase of LCB, molecular weight, and MWD and also with a rise in time and temperature of the process.

Intrinsic viscosities are barely affected, ruling out chain scission. The initial parameters were recovered by heat or solvent treatment, indicating a reversible process.

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