

Reprocessing and Shear Modification of Polyethylene

ARIE RAM and SHIMON GETZ, *Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel*

Synopsis

Reprocessing of used polyethylene serves as a promising solution to a severe ecological and economical problem. This material, however, has frequently been exposed outdoors and demonstrates poor workability and inferior mechanical properties. In this study, we attempt to explore ways for the improvement of flow and product performance by intensive shear processing. When shearing reclaimed polyethylene (LDPE) containing some degree of crosslinking and oxidation, either by repetitive injection molding, extrusion or roll milling, the fluidity of the recycled polymer is gradually increased, frequently with rising ductility of the product and a decrease in melt elasticity. As a result, a practical way of reclaiming poor-flowing, partially gelled polymer has been found. Additionally, the recycled material can be blended with virgin polyethylene, preferably of the linear low density type. Virgin polyethylene by itself, however, demonstrated an opposite response to intensive shear. There was a drop in fluidity, a rise in melt elasticity, and usually a decrease in ductility. All this is believed to result from the degradation processes that may consist of initiation of microgels and recombination of polymer chains by free radicals, as shown by an actual increase in intrinsic viscosity and in the higher modes of molecular weight averages. It was noted that the controlling mechanism of shear modification of virgin polymer differs from that occurring with a partially crosslinked structure. Results of the shear modification of both virgin and reclaimed polyethylene, by continuous kneading in a Brabender Plastograph, indicate mainly a chain scission mechanism. In all cases the melt viscosity dropped together with the ductility of the final product.

INTRODUCTION

Recycling of used plastics is becoming an important solution to an ecological nuisance, and may also serve as a viable approach to recovery of waste material. Yet the road to success is hampered by various technical and economical obstacles. When dealing with a mixture of plastics (mainly from domestic wastes), the deterioration of mechanical properties due to incompatibility and effects of foreign matter may nullify their usefulness. Attempts to improve the main mechanical properties of such polymer blends have been successful to some extent.^{1,2}

Recycling of uncontaminated used plastics, i.e., based on a single generic family, is therefore more practical. The major source for recovery is low-density polyethylene (LDPE) found in agricultural and industrial uses, as well as in commercial packaging. This material, when properly sorted and treated, can substitute for virgin PE in various useful products. However, the physical properties of such recovered polymers are usually inferior to those of virgin grades. Films of LDPE that have been used as covers for greenhouses, and similar horticulture structures experience some degree of oxidation and crosslinking as a result of their exposure to the environ-

ment. This may cause difficulty in reprocessing due to a remarkable increase in melt viscosity. It will also degrade the mechanical properties, seen as a decrease in ductility and toughness, and end up with poor product appearance.

In this work, we tried to improve both the workability and the ductility of recycled LDPE by utilizing intensive-shear processing methods similar to the mastication process in the rubber industry. Initial results are very encouraging, but the interference of various reversible and irreversible effects, such as shear-modification (disentanglement), chains scission, gel breaking, and chain recombination by free-radical oxidation and crosslinking, lead to the conclusion that further basic study is needed.

EXPERIMENTAL

Materials. The recycled LDPE, originated from Ipethene type A, a product of Israel Petrochemical Enterprises, Ltd., that has been utilized as a 4-mil film in greenhouses and treated by washing, densifying, and repelletizing. The recovery of the material was carried out by various fabricators which introduced special equipment for treatment of used polyethylene films. Typical properties of virgin and reclaimed LDPE are shown in Table I.

Characterization. Molecular weight averages and distribution were obtained using a GPC apparatus (Waters 200) operating at 130°C with TCB solutions. The use of a universal calibration system and the interference of long-chain branching were described elsewhere.^{3,4}

The melt flow index was measured at four different loads (1.2, 2.16, 5, and 10 kg) on a Davenport MFI apparatus. Data in Table I refer to the conventional load of 2.16 kg, as outlined in ASTM D-1238.

Intrinsic viscosity was measured in TCB solution at 130°C (also used for MWD determination).

The gel content was directly measured by extracting the soluble fraction (sol) with boiling xylene, filtering, and weighing the residue.

The accuracy of this method is rather poor at low gel concentration. Carbonyl numbers were obtained using an IR spectrophotometer (Perkin-Elmer). The content was determined by the size of the peak at 5.85 μm .

TABLE I
Properties of LDPE Virgin and Recycled Grades

Property	Units	Virgin A	Recycled		
			B	C	D
MFI	g/10 min	0.27	0.09	0.04	0.07
IV	dL/g	1.02			
\bar{M}_w	$\times 10^{-4}$	24.0			
\bar{M}_n	$\times 10^{-4}$	2.9			
D_n		8.2			
Gel	%	0	9.5	4.5	
Carbonyl	%	0	0.015	0.05	
Tensile strength	kg/cm ²	157	150	110	120
Elongation	%	460	64	35	272
Modulus	kg/cm ² $\times 10^{-3}$	185		2.25	

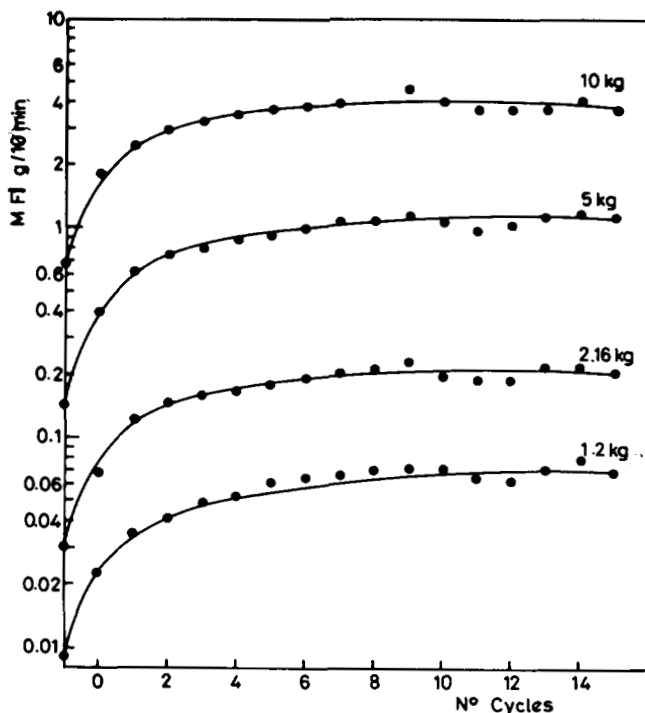


Fig. 1. Effect of injection molding on MFI of reclaimed LDPE.

Specimen Preparation. Specimens for mechanical property determination were prepared either by compression molding, on a 100-ton press, produce of Moore, Ltd., or by injection molding on a Arburg 221E/150P machine. The latter procedure introduces chain orientation which markedly reduces ultimate elongation. The conditions were as follows: Compression molding: force, 20 tons; temperature, 180°C; cooling time, 15 min; mold dimensions, 160 × 160 × 3 mm. Injection molding: melt temperatures, 200/210/220°C; injection pressure, 600 kg/cm² and a 6-s hold at 280 kg/cm²; flow time, 3 s; cooling time, 35 s at room temp. The mold was specially designed for standard tensile and impact test dumbbells and bars.

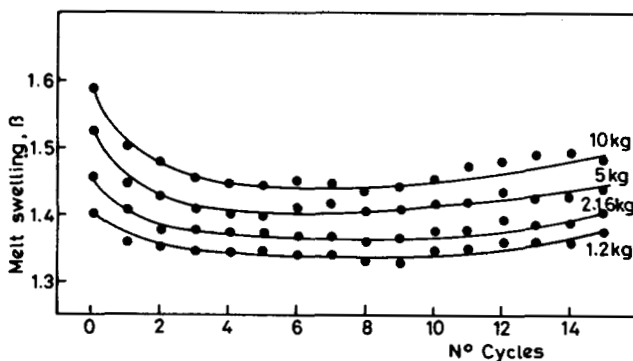


Fig. 2. Effect of injection molding on melt swell of reclaimed LDPE.

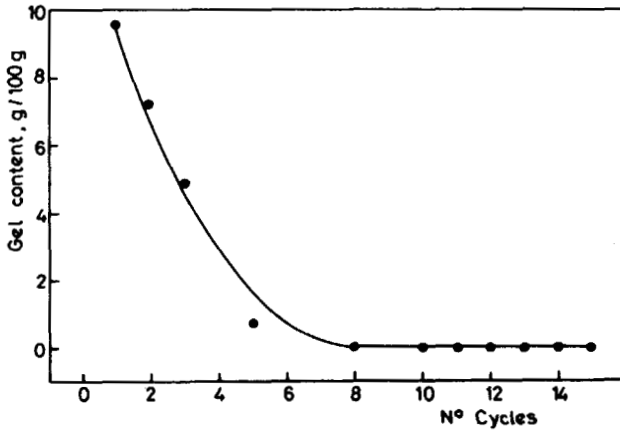


Fig. 3. Effect of injection molding on gel contents in reclaimed polyethylene.

Determination of Mechanical Properties. Mechanical properties were determined in an Instron machine using a crosshead speed of 10 cm/min for tensile strength and ultimate elongation, and 1 cm/min for modulus determination. Dimensions of dumbbells were $3 \times 12.5 \times 80$ mm.

Rheological Measurements. The changes in the rheological behaviour were followed by using the MFI apparatus at the four load levels mentioned above. It provided us with apparent fluidity (inverse viscosity) and extrudate swell (the ratio between the diameter of extrudate and that of the capillary).

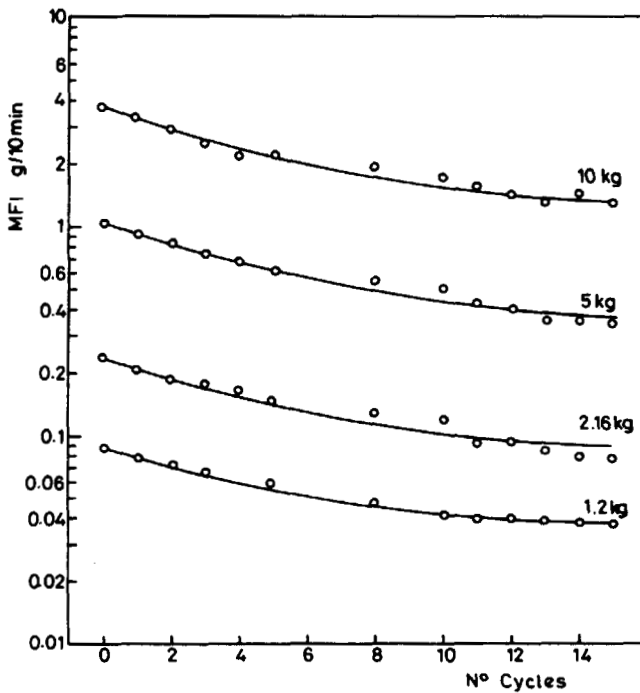


Fig. 4. Effect of injection molding on MFI of virgin LDPE.

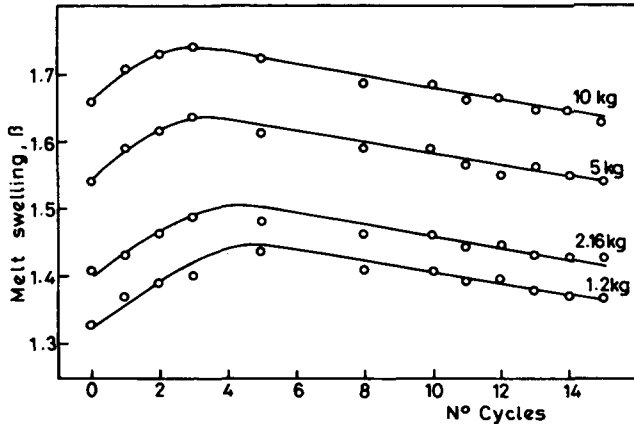


Fig. 5. Effect of injection molding on melt swell of virgin LDPE.

The significance of the latter as a criterion for melt elasticity and its relation to normal stress and shear compliance of branched polyethylene have been discussed elsewhere.⁵

Processing and Shear Modification. Melt processing and shearing were performed using four different methods:

A. Injection molding, under conditions as outlined in the previous paragraph. After each injection molding cycle, the bars were granulated for a total of 15 cycles.

B. Extrusion was done on a 20 mm single-screw Thoret extruder ($L/D = 14$), at a die temperature of 180°C. The material was granulated before reprocessing the batch.

C. Roll milling was utilized as a continuous shearing process for periods up to 18 min using a Berstoff two-roll mill. The conditions were as follows: Temperature of the front roll, 160–170°C; of the rear roll, 150–160°C. Speed of the front roll, 15 rpm and the rear roll, 7 rpm.

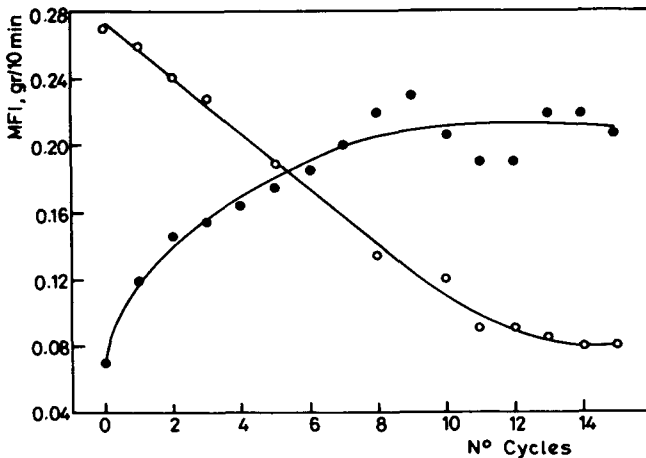


Fig. 6. Comparative history of fluidity after cycles of injection molding.

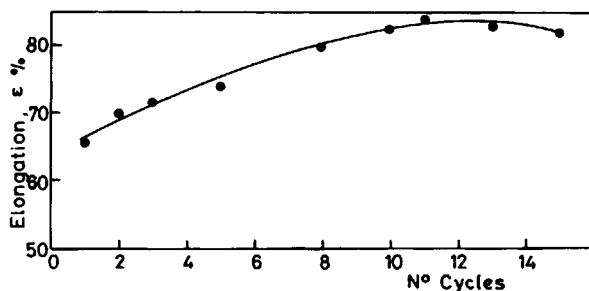


Fig. 7. Effect of injection molding on elongation of reclaimed LDPE.

D. Kneading was performed using a Brabender plastograph set for continuous shearing at 60 rpm and 180°C for periods of 15, 30, 60, and 120 min.

RESULTS AND DISCUSSION

Table I shows the properties of reclaimed LDPE as compared with the original virgin polymer. The major deterioration of properties in the reclaim is represented by a significant decrease in fluidity (as determined by extremely low values for MFI) and ultimate elongation, mainly associated with the existence of gel.

Figure 1 exhibits the effect on the MFI of shearing reclaimed polyethylene, type B, with 15 cycles of injection molding. The measurements were made at four levels of loading. The reclaimed material was received in two forms: (1) as originally received; (2) after pelletizing. There is a definite improvement in fluidity after 8–10 cycles, levelling off with further cycling. The use of the multiple-point MFI system verifies this clear tendency. Extrudate swelling shows a reduction to a minimum around 8–10 cycles of injection, which is shown in Figure 2. The main cause of the decrease of both melt viscosity and elasticity may be attributed to the apparent breakdown of the existing gel fraction during intensive shearing, as directly shown in Figure 3.

TABLE II
Characterization of LDPE Type A after Several Injection Cycles

Property	Properties after injection cycles				
	0	1	5	10	15
MFI (g/10 min)	0.24	0.21	0.15	0.12	0.06
$[\eta]$ (dL/g)	1.02		1.10	1.22	1.21
$\bar{M}_w (\times 10^{-4})$	24	29	32		
$\bar{M}_n (\times 10^{-4})$	2.9	3.7	2.5		
D_n	8.2	7.8	12.7		
$\bar{M}_z (\times 10^{-4})$	270	270	420		
$\bar{M}_{z+1} (\times 10^{-4})$	610	700	920		
Gel (%)	0			0	
Carbonyl (%)	0			0	

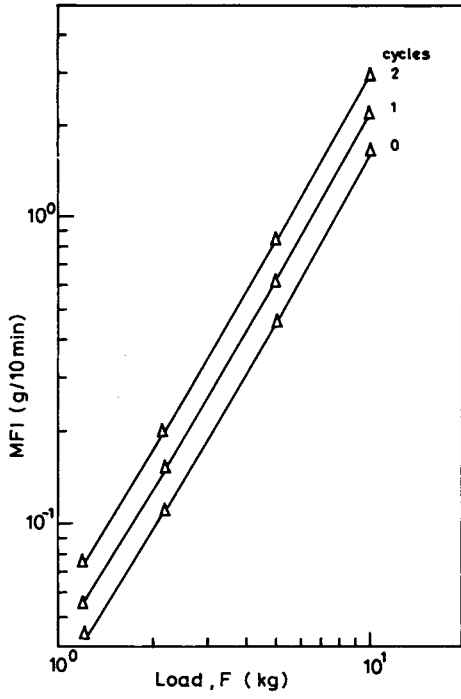


Fig. 8. Effect of extrusion on fluidity of reclaimed LDPE.

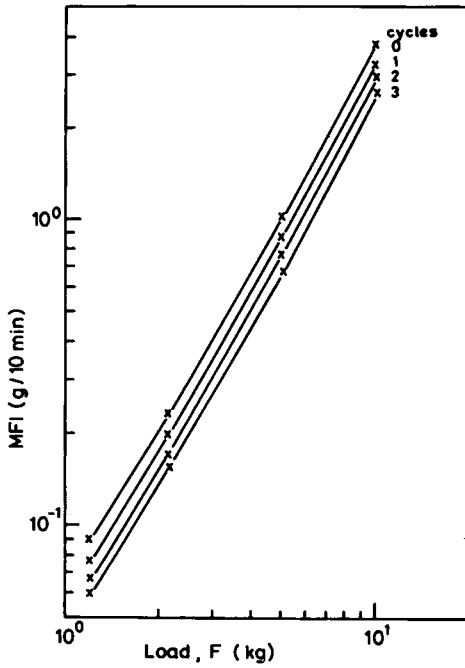


Fig. 9. Fluidity curves of virgin LDPE, after cycles of extrusion.

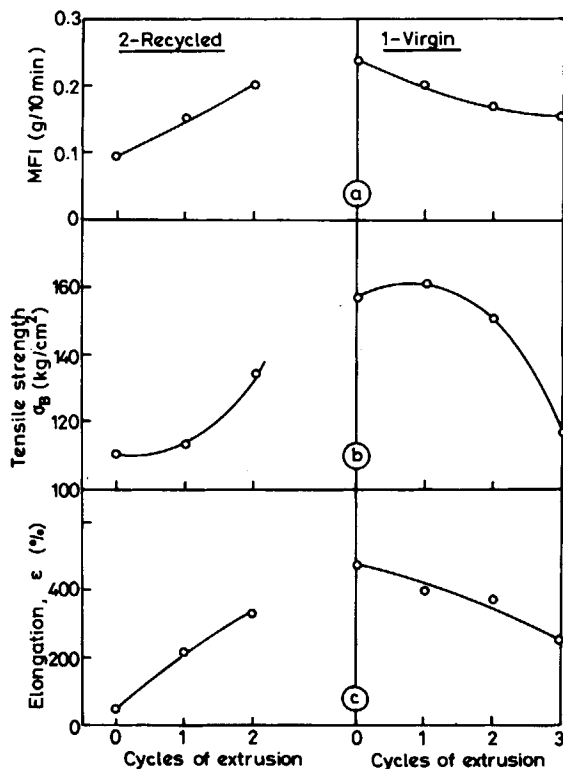


Fig. 10. Effect of extrusion on fluidity and mechanical properties of virgin and reclaimed LDPE.

Reprocessing of virgin polymer, type A, however, resulted in changes in the opposite direction: decrease in MFI and initial increase up to a maximum in extrudate swell—as shown in Figures 4 and 5, respectively. The contradictory response to shearing between virgin and recycled LDPE is shown in Figure 6 after replotting the standard MFI data.

Along with the improvement in the flow of recycled polyethylene during shearing, the ductility is also moderately increased as demonstrated in Figure 7, which refers to the changes in ultimate elongation. At the same time there is also a slight decrease in tensile strength. The results lead to the obvious conclusion that two different phenomena occur during reprocessing. The reclaimed polymer, partly crosslinked, was masticated so that the gel gradually broke down, resulting in an enhancement of fluidity and ductility together with some decrease in melt elasticity. This type of shear modification is definitely advantageous in an attempt to reutilize scrap polymer. Shearing of a virgin polymer, however, leads to degradation by thermal and mechanical effects, resulting in free-radical chain recombination and a microgel structure, which is still soluble. The new structure entails an increase in melt and solution viscosity, elasticity and molecular-weight averages (the higher modes), as shown in Table II. Direct measurement of melt viscosity on a cone-and-plate (Ferranti Shirley) rheometer also indicated an increase in the apparent viscosity after several cycles of in-

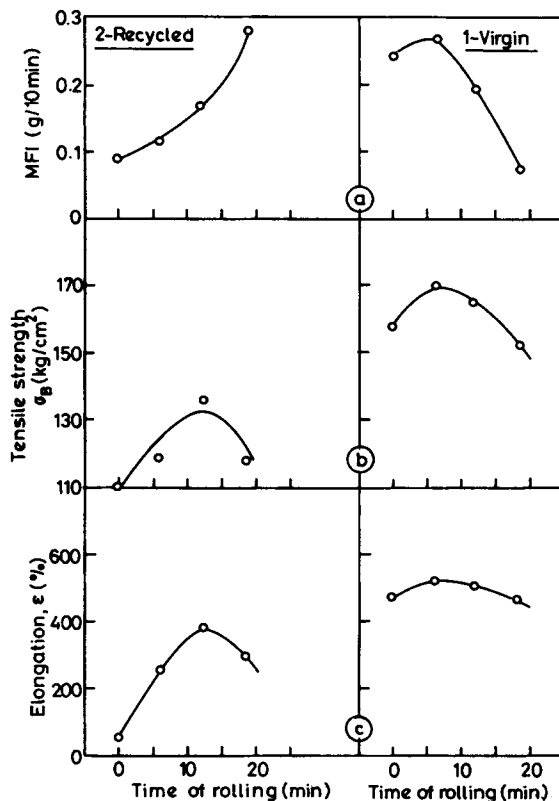


Fig. 11. Effect of rolling between mills on fluidity and mechanical properties of virgin and reclaimed LDPE.

jection molding. The mechanical properties change accordingly to give an increase in tensile strength but only a slight change in ultimate elongation. The latter normally increases upon increasing \bar{M}_w but diminishes with the appearance of gel.

Extrusion represents a more direct and logical mode of intensive shearing, but the lower expected shear rates (around 180 s^{-1}) and the short residence time again call for repetitive cycles. It is interesting to note, however, that the response to shear is very similar to that described before. The MFI of the recycled polyethylene (type C) exhibits a steady increase with the duration of shearing, as shown in Figure 8. The results are described by straight parallel lines on log-log paper, indicating the existence of an apparent power-law fluidity, and a simple shift in the MFI values with subsequent shear cycles. Figure 9 shows change in the opposite direction with shear modification of virgin polyethylene. As summarized in Figure 10, the contradiction in mechanical properties and fluidity is really striking.

The use of the roll mill provides us with a continuous shearing device, which is actually widely utilized in the rubber industry for mastication. Figure 11 shows the appropriate changes in mechanical properties as well as in fluidity of recycled (type C) vs. virgin grades. The effects of shear history on the melt viscosity are similar to those in the previous processes.

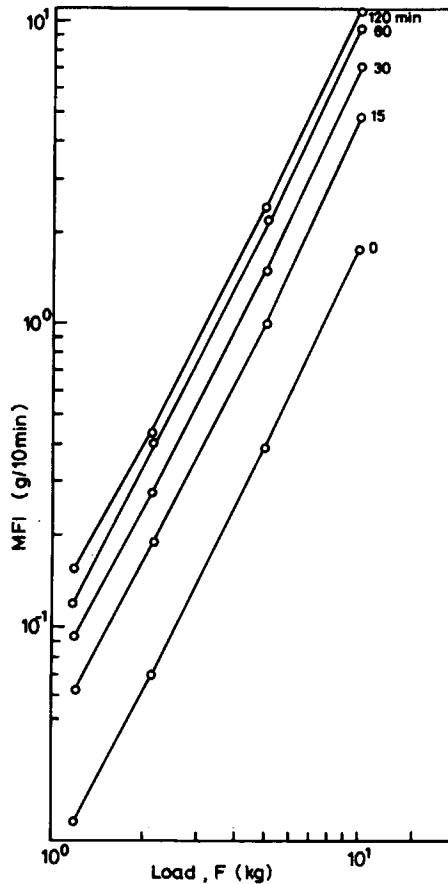


Fig. 12. Fluidity curves of reclaimed LDPE after periods of kneading.

The mechanical properties, however, respond in an erratic way. There appears to be additional chain scission following oxidation due to exposure to the atmosphere of the hot melt shearing on the roll mill.

The Brabender Plastograph, while not representing an industrial processing machine, provides a thorough and continuous shear history which enables systematic study of modification or degradation processes. Kneading in a 30 cm³ chamber confirms a distinct increase of MFI (at various loads) when recycled polyethylene (type D) was handled, mainly in the initial 30 min, as shown in Figure 12. Similar behavior, but to a lesser extent, occurs upon shearing virgin polyethylene, but this increase is partly hampered by using antioxidant (0.5% Ianox) in order to control chain scission (see Fig. 13). The increase in MFI of unstabilized polyethylene indicates the prevailing degradation under continuous shearing at the Brabender. The relative shear modification of recycled virgin PE, with and without extra antioxidant stabilization, is exhibited in Figure 14 while Figure 15 describes the relative decrease in elasticity (melt swell) of these samples. We tried to compare the continuous shearing history at the brabender where dissipated heat is accumulated to the intermittent process of injection molding,

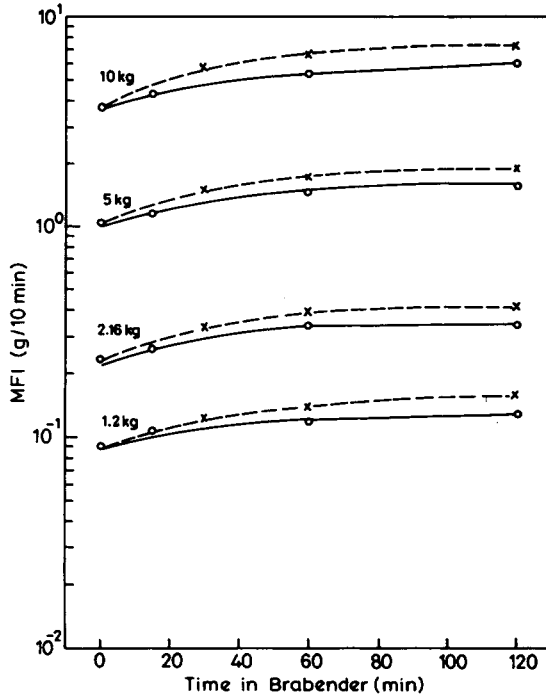


Fig. 13. Fluidity curves of virgin LDPE after periods of kneading. (x) IPE 100; (o) IPE 100+AO.

under similar strain conditions. The approximate values for strain in the injection molding process is obtained by the equation $\gamma = n \times 2.5 \times 1140$ where n = number of cycles, 2.5 s is taken for flow time, and $\dot{\gamma} = 1140 \text{ s}^{-1}$ (the calculated maximum shear rate at the gate wall). The approximation of strain under the kneading conditions of the Brabender at 60 rpm (maximum shear rate taken as 5.8 s^{-1}) is taken as $\gamma = 5.8t$ where t = time(s).

Figures 16 and 17 describe the difference in shear modification efficiency for those two processes for recycled polymers, as verified by melt flow and

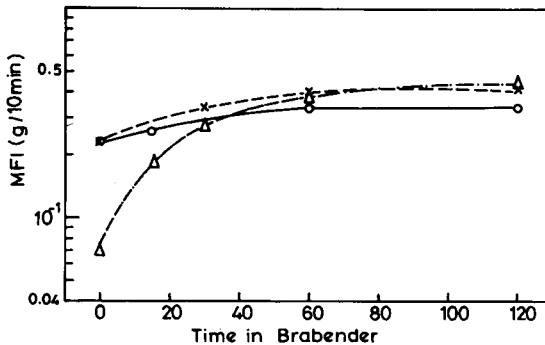


Fig. 14. Comparative NFI history of virgin, stabilized, and reclaimed LDPE samples: (o) IPE 100 + AO; (x) IPE 100; (Δ) reclaimed LPDE.

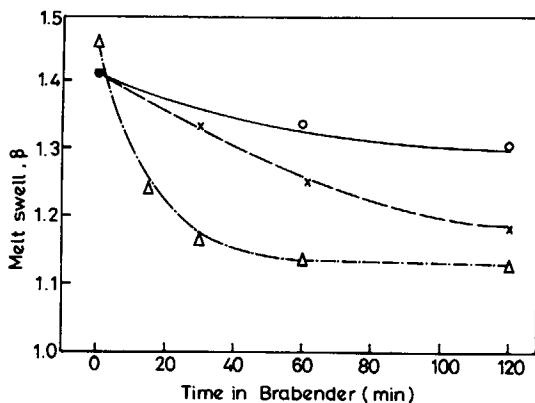


Fig. 15. Comparative swell history of virgin, stabilized, and reclaimed LDPE samples. Symbols same as Fig. 14.

elasticity behavior. In the latter, effects of relaxation between injection cycles may also be critical. One should remember, however, that the calculated values for strain are very rough, as the geometry of the rotating blades in the Brabender cell prevents any exact calculation. It is hard to anticipate a closer similarity between those two processes in any way. Through its continuous kneading and mixing under shear conditions, the Brabender succeeds in breaking the existing gels and even lead to chain scission of originally virgin polymers. On the other hand, the short periods of intensively shearing virgin polymers during the injection cycles, lead to the onset of crosslinking and recombination of the chains. Summarizing the effects of continuous kneading in the Brabender (Fig. 18), it seems that chain scission controls the behavior of virgin polymers, while it is superimposed on breakage of the gel in case of recycled PE. The relative contribution of each has yet to be determined, but the decrease in elongation and tensile strength as well as the continuous increase in fluidity for both polymer grades leads to no other conclusion. Thus, although some effects of shear modification, possibly due to temporary disentanglement of the intermingling chains under prevailing shear conditions, are desirable, as claimed by some,^{6,7} irreversible degradation from chain scission such as occurred in this study is obviously undesirable. The major advantage of

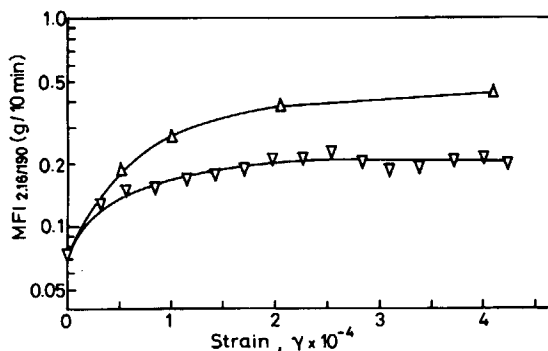


Fig. 16. MFI after accumulated strain history in injection and kneading: (▽) Injection; (Δ) Brabender.

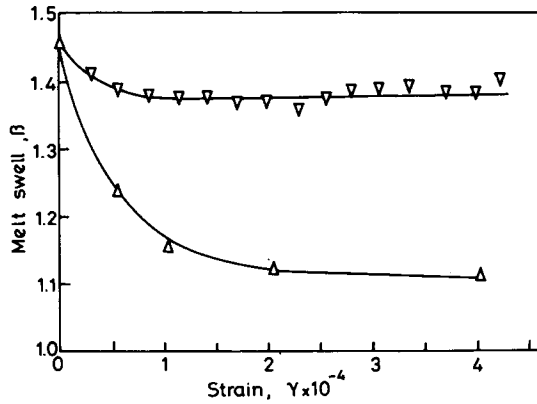


Fig. 17. Melt swell after accumulated strain history in injection and kneading. (∇) Injection; (\triangle) Brabender.

shear modification is claimed to be a reduction in melt elasticity, without any significant effect on molecular character or mechanical properties, while the original polymer structure can always be recovered under appropriate conditions. This is apparently not happening under our conditions in the Brabender.

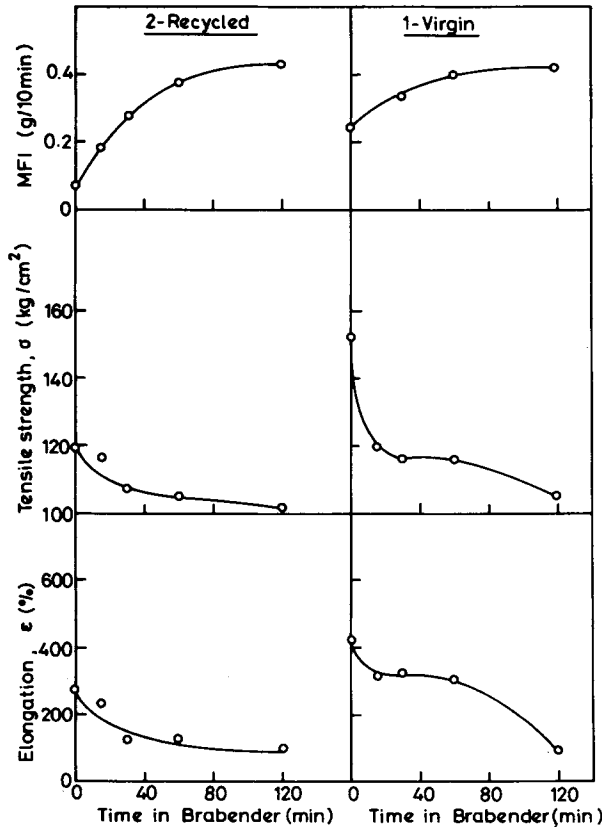


Fig. 18. Summary of flow and mechanical properties of reclaimed and virgin LDPE after periods of continuous kneading.

TABLE III
Mechanical Properties of Blends

Material	Elongation (%)	Tensile strength (kg/cm ²)	Modulus (kg/cm ²)
Recycled LDPE (D)	270	119	1,788
LLDPE (L)	580	200	3,075
D + 10% L	340	133	2,300
D + 20% L	421	151	2,300
LDPE (A)	422	152	1,850
D + 20% A	312	143	3,250

The response of virgin LDPE to reprocessing was studied by Sandromonghegh and Scott.⁸ They also found a decrease in MFI with duration of shear but were able to detect the formation of gel and an increase in tensile strength and elongation. Others^{9,10} found a reduction of MFI upon reprocessing of PP, and HDPE, but have conflicting results as to the effects on the mechanical properties.

An additional attempt to enhance the mechanical properties of recycled polymers was undertaken, by blending with virgin grades of either LDPE or LLDPE (Unifos-8001, Union Carbide). Details are given in Table III. While blending with 20% LDPE (type A) improved elongation, strength, and stiffness of the recycled material, the use of the linear type of low-density polyethylene contributed more to the improvement of ductility and strength. A two-stage process of controlled shearing followed by some blending with a premium type of polyethylene may improve the mechanical properties and workability of recycled polyethylene.

CONCLUSIONS

This study demonstrates some practical approaches for the improvement in flow and ductility of recycled LDPE samples. The method depends on the shear modification of the partly crosslinked polymer under controlled conditions. After repetitive processing cycles of injection molding, extrusion or roll milling, there is an increase of the melt-flow index (fluidity), decrease in elasticity (extrudate-swell), and increase of the elongation at break for the recycled polymer. Under same conditions, virgin polymer shows quite a contrary performance. The MFI drops and swell increases, while elongation is essentially not affected.

It is interesting to note that both virgin and recycled materials exhibit a decrease not only in melt viscosity and elasticity but also in tensile strength and elongation in a continuous kneading process. This indicates the existence of degradation via chain scission. It seems that blending with virgin LLDPE and LDPE offers another useful method for the successful reclaim of used polyethylenes.

The authors wish to thank the National Council for Research and Development and the Israel Ministry of Absorption, for their financial aid and encouragement. The cooperation of Dr. H. Alcalay, from Ripal, Ltd., is highly appreciated.

References

1. A. Ram, M. Narkis, and J. Kost, *Poly. Eng. Sci.*, **17**, 274 (1977).
2. D. R. Paul, C. E. Vinson, and C. E. Locke, *Polym. Eng. Sci.* **12**, 157 (1972).
3. J. Miltz and A. Ram, *Polymer*, **12**, 685 (1971).
4. A. Ram and J. Miltz, *J. Appl. Polym. Sci.*, **15**, 2639 (1971).
5. A. Ram, *Polym. Eng. Sci.*, **17**, 793 (1977).
6. B. Maxwell and A. Brockmoldt, *J. Rheol.*, **25**, 55 (1981).
7. M. Rokudai, *J. Appl. Polym. Sci.*, **23**, 463 (1979).
8. C. Sandramonghegh and G. Scott, *Eur. Polym. J.*, **16**, 1037 (1980).
9. M. Bezaie and S. Zaidi, *Kunststoffe*, **4**, 64, 171 (1974).
10. D. Williams and M. Bevis, *J. Mater. Sci.*, **15**, 2834 (1980).

Received August 12, 1983

Accepted February 24, 1984