

Modeling the Role of Stabilizing Additives During Melt Recycling of High-Density Polyethylene

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Received 4 July 2000; accepted 25 July 2000

ABSTRACT: Post-use high-density polyethylene, almost devoid of any stabilizing agents, was restabilized in various degrees and subjected to multiple extrusion cycles at different reprocessing temperatures for assessing its chemical stability. The process-induced material degradation was attributed primarily to long-chain branching caused by crosslinking. It was monitored by an increase in viscosity and evaluated on the basis of an approximate expression derived using fundamental principles of macromolecular rheology. It was determined that long-chain branching increases with temperature and the extent of processing, while decreasing with the amount of restabilizing agent added. A simple model was developed to quantitatively describe the progress of the chemical change by relating it to key material and operational variables. Besides constituting a useful method of monitoring and controlling polymer modification during processing, this model suggests ways of optimizing stabilization according to the particular processing and product requirements. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2207–2217, 2001

Key words: degradation; restabilization; processing; rheology; branching; recycling; high-density polyethylene

INTRODUCTION

The addition of stabilizing agents prevents radiation-induced and thermal degradation, sustaining polymer product quality over time. The potency of stabilizers appears to decay with usage time. Restabilization by compounding recycled plastics with fresh agent is therefore one of the major steps in polymer recycling operations.

In addition to extending polymer product lifetime, stabilizing agents are also useful in protect-

ing virgin plastics as well as recycled materials from the inevitable degradation that occurs during the relatively short-lived, yet harsh, conditions that accompany polymer processing operations. Extrusion, in particular, is one of the most damaging procedures to which a polymer can be subjected. Shear forces along with high processing temperatures lead to mechanical scission of the polymer chain that produces highly reactive macroradicals at the end of the chain fragments [R^\bullet]. These macroradicals either recombine with other chains or, more frequently, in the presence of small amounts of oxygen form peroxy radicals [ROO^\bullet] and hydroperoxides [$ROOH$]. These processes modify the average molecular weight and polymer architecture, and often render in the case

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Journal of Applied Polymer Science, Vol. 80, 2207–2217 (2001)
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of recyclates the material unsuitable for its original use.¹⁻⁶

As a rule, polymers are stabilized only for their first life, but this original stabilization is in general not sufficient to carry the material through reprocessing and a second life application. Therefore, for quality improvement and material upgrading during recycling, not only are sophisticated cleaning and separation procedures needed for the incoming stream, but also mixing with virgin material, reactive agents, compatibilizers, and/or stabilizers.³⁻⁸

Restabilization, which means addition of processing, thermal and light stabilizers in the post-used polymer, aims to minimize degradation effects during the reprocessing stage and reuse. Depending on the material, the objective is to avoid degradation of the polymer chain through side reactions such as crosslinking thus preserving the molecular weight, rheological behavior, and mechanical properties of the recyclates.²⁻⁸

During the course of processing, high-density polyethylene (HDPE) among other polymers suffers from thermal/oxidative and thermal/mechanical degradation leading to crosslinking or chain scission phenomena. The relative extent of these simultaneous yet competitive events varies, depending on the processing conditions, the availability of oxygen and, primarily, the catalyst type used for its production; classical Ziegler-type HDPE exhibits molecular-weight degradation, while Phillips HDPE leads to crosslinking up to gel formation, hence molecular weight increase.^{6,9-11} Both crosslinking and chain scission affect the molecular weight of the polymer in opposite directions and, consequently, they modify the melt flow, mechanical strength and physical characteristics of the polyolefin.¹² In practice, however, more severe problems are encountered due to crosslinking effects, since the formation of very large insoluble molecules, so-called gels, leads to inhomogeneities in the polymer melt and consequently to a deficient end product.^{6,9,13,14}

The present study attempts to assess the beneficial effects of the presence of stabilizing agents during melting, mixing, pumping, and shaping operations, where intense deformations and elevated temperatures challenge the ability of the processed polymer to remain chemically unaffected.

For this purpose, we used post-used, yellow pigmented HDPE bottle crates, almost entirely devoid of any initial stabilizing agent. This recycled material was restabilized at three different

concentrations, by adding a stabilization system. It was then subjected to melt processing in a laboratory extruder by varying the duration and temperature of the process.

Previous work on the same recycled material focused on the effects of reprocessing, heat aging, and artificial weathering on various material properties.^{6,13,14} In this article, we assess the ability of restabilization to prevent degradation under various material and operational conditions; this is accomplished by comparing the polymer rheology both before and after reprocessing, with the understanding that the extent of the chemical change is proportional to the variation in viscosity. Basic precepts of molecular rheology are used to quantify this microstructural change.

EXPERIMENTAL

Materials

The material examined consisted of granules from post-used, yellow Heineken HDPE bottle crates. The average age of these bottle crates was 9 years, and they were randomly collected from the oldest of the stock of the Hellenic Brewery SA. The crates were washed and then supplied to Mornos SA, for drying, granulation, and storage. Analysis of the homogenized crate material shows only minute residual quantities of active stabilizers, within the following range: ~200 ppm phenolic antioxidants, traces of phosphites, ~300 ppm benzotriazole-type UV absorbers, and ~500 ppm polymeric HALS.

The restabilization system used was a product of Ciba Specialty Chemicals Ltd. under the trade name Recyclossorb 550®, a blend consisting of high-molecular-weight hindered amine stabilizers (HAS) for light and long-term heat stability, antioxidants and coadditives for processing and long-term heat stability as well. The granulated stabilizer package is used mainly for restabilization of polyolefine recyclates for outside applications, such as crates, containers, waste bins from HDPE, PP, or mixed polyolefins.

A double-arm kneading mixer from Werner Company, with sigma blades and a mixing chamber of 1.50 L, was used for the dry blending of the additives with the crate material (homogenization stage).

Reprocessing Procedure

Reprocessing was accomplished at three different levels of restabilization: (1) remelting without any

addition of stabilizer, (2) remelting after restabilization with 0.2% w/w of Recyclosorb 550, and (3) remelting after restabilization with 0.4% w/w of Recyclosorb 550. For each of these degrees of restabilization, five multiple extrusion cycles were performed with a Brabender Plasti-Corder PLE 330, a single-screw laboratory extruder. The screw length was 500 mm (L) and the diameter 20 mm (D), giving an effective length-to-diameter ratio of 25 (L/D). The extruder was heated at four zones, at both the cylinder and the die. Throughout the multiple extrusion cycles, the screw rotation speed was kept at 50 rpm, yielding a throughput of ~ 0.8 kg/h.

In order to investigate the effects of reprocessing temperature on the degradation of the material, the following three different remelting temperature ranges were applied:

1. max 220°C: 190°, 200°, 210°, 220°C (temperatures of the four zones)
2. max 250°C: 220°, 230°, 240°, 250°C (temperatures of the four zones)
3. max 280°C: 250°, 260°, 270°, 280°C (temperatures of the four zones)

Melt Flow Rate and Flow Rate Ratio Measurements

Assessment of polymer degradation during reprocessing was accomplished through monitoring its rheological implications. Melt flow rate (MFR) measurements were carried out according to the procedure A of ASTM D1238 or ISO 1133, for all grades prepared and under two different weights of the ram (loads): 10.000 g and 2.160 g. In all measurements, the temperature was fixed at 190°C, whereas samples weights varied from 3 to 4 g.

Flow rate ratio (FRR), according to ASTM D1238, is defined as the dimensionless ratio of the flow rate under 190°C/10 kg over the flow rate at condition 190°C/2.16 kg; it appears to represent the shear thinning capacity of the fluid under stress conditions of dissimilar severity. The FRR values were determined after the first, third, and fifth remelting cycles, at the three different remelting temperatures, and for the three different levels of restabilization. Table I presents the MFR and FRR values for nonrestabilized and restabilized HDPE.

DISCUSSION

The above variation of MFR signifies a systematic increase of the polymer viscosity with the degree

of processing. This increase is attributable to limited chemical degradation, which causes an effective reorganization of the molecular architecture of the processed material. This degradation is worsened by increasing the temperature and the degree of processing, and may be tempered by the presence of stabilization agents.

Conversion of MFR Measurements to Viscosity Values

Rheological information and the existing knowledge of the effect of macromolecular architecture on the flow properties of polymers are used for an approximate quantitative analysis of the chemical degradation. In the absence of a rheometer, an MFR device has been used to evaluate the incremental viscosity increase after processing. MFR is a widely used empirical index used to assess polymer rheology; it is defined as the polymer mass extruded from a device of known geometry, under the pressure generated from the imposition of a prescribed external load, f , at a given temperature, T . MFR values collected under two different force loads— f and f' —are converted to viscosity estimates, by an approximate conversion scheme presented in the Appendix. It is assumed that the non-Newtonian viscosity, η , of the polyethylene melts in our study is subject to the power law expression.¹⁵:

$$\eta = m/\dot{\gamma}^{1-n} \quad (1)$$

where $\dot{\gamma}$ is the shear strain rate, a measure of the deformation intensity. The material constants m and n may then be evaluated by the following expressions:

$$m = \left(\frac{fd}{\pi \ell D^2} \right) \left[\frac{75 \pi \rho d^3}{(3 + 1/n) \text{MFR}} \right]^n \quad (2)$$

$$\begin{aligned} n &= \ln \left(\frac{f}{f'} \right) / \ln \left(\frac{W}{W'} \right) = \ln \left(\frac{f}{f'} \right) / \ln \left(\frac{\text{MFR}}{\text{MFR}'} \right) \\ &= \ln \left(\frac{f}{f'} \right) / \ln(\text{FRR}) \quad (3) \end{aligned}$$

The MFR and FRR data presented in Table I were used in conjunction with eqs. (2) and (3) to extract the pertinent rheological parameters. n was shown to decrease slightly with the temperature and the extent of processing and increases with the level of restabilization. By contrast, m dem-

Table I Melt Flow Rate and Flow Rate Ratio Data Versus Reprocessing Conditions of the Recycled HDPE

A. Original Nonrestabilized and Unreprocessed HDPE			
MFR _{10 kg} (g/10 min)	60.05		
MFR _{2.16 kg} (g/10 min)	7.5		
FRR _(10/2.16)	8.006667		
B. Nonrestabilized HDPE			
Reprocessing Extrusion at 220°C			
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	58.05	55.975	53.775
MFR _{2.16 kg} (g/10 min)	7.15	6.65	5.85
FRR _(10/2.16)	8.118881	8.417293	9.192308
Reprocessing Extrusion at 250°C			
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	57.9	54.625	51.425
MFR _{2.16 kg} (g/10 min)	6.85	6.2	5.25
FRR _(10/2.16)	8.452555	8.810484	9.795238
Reprocessing Extrusion at 280°C			
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	56.375	52.925	49.85
MFR _{2.16 kg} (g/10 min)	6.05	4.9	3.9
FRR _(10/2.16)	9.318182	10.80102	12.78205
C. Restabilized HDPE With 0.2% Recyclosorb 550®			
Reprocessing Extrusion at 220°C			
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	58.725	56.4	55.05
MFR _{2.16 kg} (g/10 min)	7.3	6.8	6.4
FRR _(10/2.16)	8.04452	8.29412	8.60156
Reprocessing Extrusion at 250°C			
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	58.25	56.4	54.275
MFR _{2.16 kg} (g/10 min)	6.95	6.4	5.8
FRR _(10/2.16)	8.38129	8.8125	9.35776

Table I *Continued*

	Reprocessing Extrusion at 280°C		
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	57.65	55.425	53.875
MFR _{2.16 kg} (g/10 min)	6.15	5.85	5.1
FRR _(10/2.16)	9.37398	9.47436	10.5637

D. Restabilized HDPE With 0.4% Recyclossorb 550®			
	Reprocessing Extrusion at 220°C		
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	59.375	58.1	57.265
MFR _{2.16 kg} (g/10 min)	7.5	7.15	6.9
FRR _(10/2.16)	7.91667	8.12587	8.29928

	Reprocessing Extrusion at 250°C		
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	58.975	57.35	55.75
MFR _{2.16 kg} (g/10 min)	7.05	6.7	6.5
FRR _(10/2.16)	8.36525	8.5597	8.57692

	Reprocessing Extrusion at 280°C		
	1st Cycle	3rd Cycle	5th Cycle
MFR _{10 kg} (g/10 min)	58.55	56.575	55.4
MFR _{2.16 kg} (g/10 min)	6.45	6.2	5.8
FRR _(10/2.16)	9.07752	9.125	9.55172

MFR, melt flow rate; FRR, flow rate ratio; HDPE, high-density polyethylene.

onstrates the exact opposite variation. For the purpose of maintaining a simplicity in the analysis and in view of the small n variation, n was kept constant and equal to the value in the pre-processed, nonrestabilized state at 220°C, i.e., $n = 0.737$. Then, the m values were extracted for each of the material and processing conditions tested. These m values, along with the viscosity value at a low rate of $\dot{\gamma} = 0.1 \text{ s}^{-1}$ are listed in Table II.

Deciphering Changes in Molecular Architecture by Analyzing Viscosity Estimates

It is to be expected that the intense shear and temperature fields within the extruder impose

severe strain to the ability of the processed polyethylene molecules to remain intact. A number of those chains break up through scission, and these fragments are recombined through crosslinking with their neighbors to form new molecules. Some of those newly created units maintain (more or less) the linear chain architecture of their precursors while other ones assume branched configurations.¹¹ A plausible, if oversimplified, scenario to explain the observed net viscosity increase is that linear-to-linear chain transformations do not cause any major shift in the weight average molecular weight of the linear chain component; whereas there are always several unreacted fragments, some of the reacted fragments have joined initial chains to form even longer linear mole-

Table II Values of Parameters m , Viscosity Values at a Low Rate of $\dot{\gamma} = 0, 1 \text{ sec}^{-1}$ and Degree of Process Induced Branching (x -values) Versus Reprocessing Conditions of the Recycled HDPE

A. Original Nonrestabilized, and Unreprocessed HDPE			
m (MPa/sec ^{0.7367})	2.55		
η (MPa sec)	4.67		
Degree of branching (x)	0.0		
B. Nonrestabilized HDPE			
Reprocessing Extrusion at 220°C			
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.61	2.68	2.76
η (MPa sec)	4.78	4.92	5.0
Degree of branching (x)	0.0142	0.0306	0.0495
Reprocessing Extrusion at 250°C			
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.61	2.73	2.85
η (MPa sec)	4.79	5.0	5.23
Degree of branching (x)	0.0153	0.0420	0.0718
Reprocessing Extrusion at 280°C			
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.67	2.79	2.92
η (MPa sec)	4.89	5.12	5.35
Degree of branching (x)	0.0273	0.0573	0.0881
C. Restabilized HDPE With 0.2% Recyclosorb 550®			
Reprocessing Extrusion at 220°C			
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.59	2.67	2.71
η (MPa sec)	4.74	4.89	4.98
Degree of branching (x)	0.0092	0.0271	0.0383
Reprocessing Extrusion at 250°C			
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.60	2.67	2.74
η (MPa sec)	4.77	4.89	5.03
Degree of branching (x)	0.0127	0.0271	0.045

Table II Continued

	Reprocessing Extrusion at 280°C		
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.62	2.70	2.76
η (MPa sec)	4.81	4.95	5.06
Degree of branching (x)	0.0172	0.035	0.0486

D. Restabilized HDPE With 0.4% Recyclossorb 550®			
	Reprocessing Extrusion at 220°C		
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.57	2.61	2.64
η (MPa sec)	4.71	4.78	4.83
Degree of branching (x)	0.004	0.014	0.020

	Reprocessing Extrusion at 250°C		
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.58	2.63	2.69
η (MPa sec)	4.73	4.83	4.93
Degree of branching (x)	0.007	0.02	0.032

	Reprocessing Extrusion at 280°C		
	1st Cycle	3rd Cycle	5th Cycle
m (MPa/sec ^{0.7367})	2.59	2.66	2.70
η (MPa sec)	4.75	4.88	4.95
Degree of branching (x)	0.010	0.026	0.035

HDPE, high-density polyethylene.

cules. Most of the reacted linear fragments end up as parts of larger branched polymers. In an ever further simplification concerning the branching mechanism, it is assumed that a small fraction, x , of the initial linear chains, of average molecular weight M_{L1} , after breaking in the middle, crosslinks with the (easier to find due to higher concentration) unbroken chains to form three-arm stars of molecular weight $M_{B2} \approx 3M_{L1}/2$. Consequently, the final, postprocessed, melt is a "blend" of linear with slightly branched chains of weight average molecular weight, M_2 :

$$M_2 = (1 - x)M_{L2} + xM_{B2} \approx (1 - x)M_{L1} + 3xM_{L1}/2 \quad (4)$$

where subscripts L and B signify a linear or a branched molecule, respectively, while 1 and 2 stand for the preprocessed and postprocessed material, respectively.

An alternative expression for M_2 may be constructed in connection with its impact on the fluidity. Based on fundamental precepts of molecular rheology of the entangled state, and assuming nothing concerning molecular size variation, the change in viscosity between the preprocessed and final state of the linear component is related to the corresponding molecular weight change as follows¹⁶:

$$\eta_{L2}/\eta_{L1} \approx (M_{L2}/M_{L1})^{3.5} \quad (5)$$

The effect of branching on the viscosity (η_B) of a branched polymer melt of molecular weight M_B and functionality f (i.e., number of major branches emanating from a central point; $f = 3$ in our case), is even more dramatic, described by an exponential variation¹⁷:

$$\ln(\eta_B/\eta_{CB}) \approx \alpha(2M_B/fM_C - 1) \quad (6)$$

where M_C is the molecular weight at the onset of entanglements (a material constant depending on the molecular rigidity; for PE, it is roughly equal to 4000) and η_{CB} the melt viscosity at $M_B = M_C$; α is a proportionality constant of order unity.

Starting from this last expression and supposing that the chemical change does not affect the functionality of the branched structures, but only their size, one may construct a comparative relationship equivalent to eq. (5), applicable to star-like molecules:

$$\frac{\ln \eta_2 - \ln \eta_{CB}}{\ln \eta_1 - \ln \eta_{CB}} = \frac{M_{B2} - 0.5fM_C}{M_{B1} - 0.5fM_C} \quad (7)$$

Here, as well as in most practical melt applications, η_B and M_B are orders of magnitude higher than η_{CB} and M_C ; consequently, one may approximate

$$\ln(\eta_{B2})/\ln(\eta_{B1}) \approx M_{B2}/M_{B1} \quad (8)$$

From the suggestion that the processed melt of evolving microstructure is actually a blend of mostly linear chains with an ever increasing portion of 3-arm stars [eqs. (5) and (8)] and the phenomenological observation that, as a rule, the viscosity of blends is subject to the logarithmic

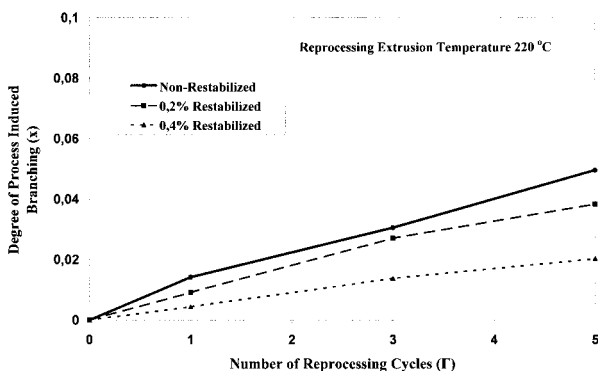


Figure 1 Effect of the extent of reprocessing on induced branching at an extrusion temperature of 220°C.

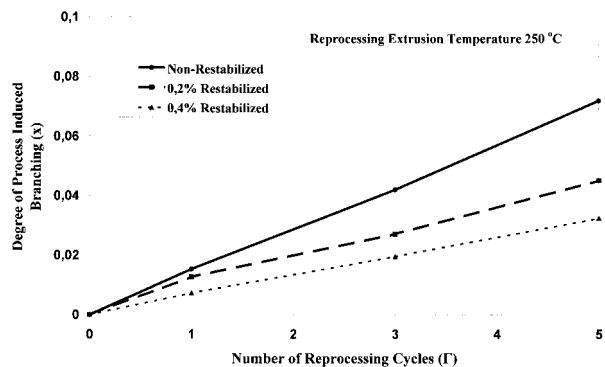


Figure 2 Effect of the extent of reprocessing on induced branching at an extrusion temperature of 250°C.

additivity, an alternative expression for M_2 may be constructed^{18,19}:

$$M_2 \approx (1 - x)M_{L1}(\eta_{L2}/\eta_{L1})^{1/3.5} + xM_{L1}\ln(\eta_{B2})/\ln(\eta_{B1}) \quad (9)$$

What this expression actually says is that the evolving rheology of the melt under degradation resembles that of a linear or a branched polymer melt in proportion to the participation of the corresponding linear or branched component. A useful, albeit very approximate, relationship connecting the rheological change to the degree of process-induced branching may therefore be constructed by comparing eqs. (4) and (9):

$$x = \frac{(\eta_2/\eta_1)^{1/3.5} - 1}{(\eta_2/\eta_1)^{1/3.5} - (\ln \eta_2/\ln \eta_1) + 0.5} \quad (10)$$

The above analysis concerning the evolving microstructure is applied to the rheology measurements of the previous section. η_1 and η_2 are correspondingly the viscosity values at the low shear rate of 0.1 s^{-1} before and after processing, presented in Table II. Also listed are the x values calculated from eq. (10) for the various reprocessing and restabilization conditions.

Phenomenology of Polymer Modification and Model Development

The degrees of conversion, x , evaluated above are plotted for each processing temperature in Figures 1–3, where it is seen that degradation increases practically in linear proportion to the extent of processing, and decreases with the concentration of the restabilization agent added. Furthermore, and not surprisingly, cross-compar-

ison of the degradation curves generated under nonisothermal processing experiments but under identical degree of restabilization shows higher levels of induced branching with any increase in the processing temperature.

The ensuing attempt to quantitatively model the progress of the chemical change and to relate it to key material and operational variables is based on the following observations:

1. The temperature (T) variation of x follows the Arrhenius law, $x \sim e^{-\Delta H/RT}$, where ΔH represents the activation energy of the branching reaction or any of the controlling precursor chemical steps, and R is the gas constant (8.3 J/mol K). A simple regression analysis of the x values collected in nonisothermal conditions but under the same extent of processing and restabilization yields $\Delta H \approx 22.14$ kJ/mol.
2. As illustrated in Figures 1–3, x increases (almost) linearly with the degree of processing. This is represented by the number of extrusion cycles employed and symbolized by Γ , which is in essence the amount of cumulative straining work imparted on the material.
3. Finally, degradation, x , decreases with the concentration of restabilization agent, c , in a linear fashion, up to a critical concentration $c_0 \approx 0.68\%$, where, at least in theory, degradation is eliminated.

Implementation of the above observations into equation form results in the following composite variable, appropriate for the description of the degradation progression:

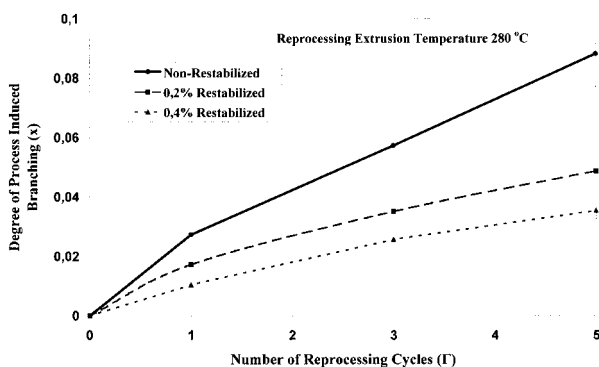


Figure 3 Effect of the extent of reprocessing on induced branching at an extrusion temperature of 280°C.

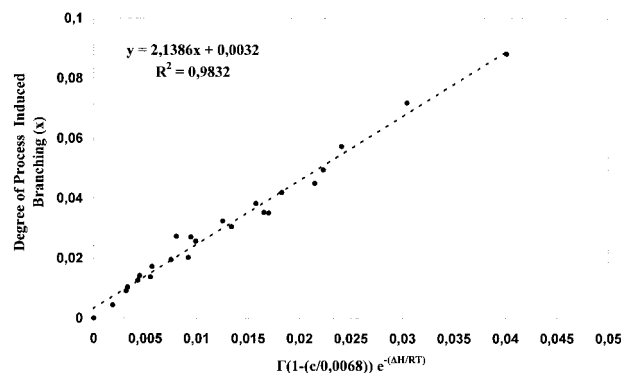


Figure 4 Generalized depiction of dependence of process-induced branching of recycled high-density polyethylene (HDPE) on temperature, restabilization level, and extent of reprocessing: $\Delta H \approx 22.14$ kJ/mol.

$$x = \text{function of } \{\Gamma[1 - (c/c_0)]e^{-\Delta H/RT}\} \quad (11)$$

All our experimental x data (except for three obviously erratic points) renormalized according to the aforementioned logic, are plotted in Figure 4, which demonstrates the remarkable capacity of our model in merging all data into one curve and reaffirms that degradation is actually a linear function of the new founded variable with a proportionality constant roughly equal to 2.14:

$$x \approx 2.14\Gamma[1 - (c/c_0)]e^{-\Delta H/RT} \quad (12)$$

It is worth stipulating that the experimental strategy followed and the analytical model built here are useful (after appropriate adaptations) for the more general purpose of characterizing and quantifying a series of process-induced structural modifications of chemical or mechanical origin (chain scission, limited crosslinking). A derivative benefit may also be the development of more precise ways of preventing or enhancing these phenomena according to our needs and to predict the necessary quantity of stabilizers for a given process to achieve a certain degree of processing stabilization.

CONCLUSIONS

Post-used high-density polyethylene, almost entirely devoid of residual stabilizing agents, was restabilized in various degrees and subjected to successive reprocessing cycles in a single screw extruder, under a series of processing temperatures. The process-induced material degradation,

attributed primarily to chain branching, was monitored by an increase in viscosity and evaluated quantitatively from MFR measurements on the basis of an approximate expression derived in this study by using fundamental precepts of macromolecular rheology. A simple model was built to obtain a quantitative description of the progress of the chemical change by relating it to key material and operational variables, such as temperature, extent of processing, and amount of restabilizing agent added.

Most of the tools developed and implemented in the present study have utility that transcends polymer recycling. They present useful methods of monitoring polymer modification during processing or reactive extrusion of even virgin polymers, and suggest judicious ways of controlling operating conditions or optimizing stabilization according to the particular processing and product requirements.

APPENDIX: METHOD OF CONVERTING MELT FLOW RATE MEASUREMENTS TO APPROXIMATE VISCOSITY VALUES

In order to develop an approximate method of converting MFR values into viscosity, one first has to consider the non-Newtonian flow onto the pertinent geometry of the MFR device outlet. For a cylindrical die of length ℓ and diameter d , and for a "power law fluid" ($\eta = m\dot{\gamma}^{n-1}$), the volumetric flow rate, Q , is related to basic operational and material characteristics as follows:

$$Q = \frac{\pi d^3}{8(1/n + 3)} \left(\frac{\Delta P d}{4m\ell} \right)^{1/n} \quad (\text{A.1})$$

The shear stress exerted on the walls of the die is

$$\sigma_w \equiv \eta_w \dot{\gamma}_w = \Delta P d/4\ell \quad (\text{A.2})$$

where ΔP is the end-to-end pressure drop, while w as a subscript stands for wall.

The shear rate at the same location is

$$\left(\frac{d\gamma}{dt} \right)_w = \frac{32Q}{\pi d^3} \left(\frac{3}{4} + \frac{d \ln Q}{4d \ln \sigma_w} \right) = \frac{8Q}{\pi d^3} \left(3 + \frac{1}{n} \right) \quad (\text{A.3})$$

From the definition of the MFR (in g/10 min)

$$\text{MFR} = 600\rho Q = 600W \quad (\text{A.4})$$

where W is the MFR (in g/s) and ρ the density (in g/cm³).

By stipulating that most pressure drop takes place within the narrow outlet die of the MFR device, and by ignoring the drop that occurs in the superimposed cylindrical feeding tank of diameter D and variable length ($L(t) = L(0) - Qt/\pi D^2$) controlled by the piston, which moves under a force f , then:

$$\Delta P/\ell \approx f/\pi\ell D^2 \quad (\text{A.5})$$

Appropriate combination of all the above information results in

$$\eta_w = \frac{f\rho d^4}{32\ell D^2 W(3 + 1/n)} \quad (\text{A.6})$$

and

$$\left(\frac{d\gamma}{dt} \right)_w = \frac{8W}{\pi\rho d^3} \left(3 + \frac{1}{n} \right) \quad (\text{A.7})$$

Finally, by comparing the experimental results generated by a second force load, f' , of considerably different magnitude, eqs. (2) and (3) may be derived.

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