Detection of Divergences in Polyethylene Resins Fabrication by Means of the Modified Stepwise Isothermal Segregation Technique

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Received 20 November 1997; accepted 18 December 1998

ABSTRACT: The selective crystallization behavior of a series of commercial mediumand high-density polyethylene resins has been studied by means of an original modified procedure of the stepwise isothermal segregation technique using differential scanning calorimetry. The technique consists of a sequenced multiple-stage stepwise thermal treatment of the materials allowing separation of the macromolecules with respect to their length-to-branching content and distribution. It is assumed that such a separation process gives an image of the proportion of specific crystallizable species, which are in turn responsible for slow crack growth resistance of the resins under study. A drift molecular parameter is calculated from a combination of the crystallization data at 119°C and 114°C. This molecular parameter is capable of revealing some divergences regarding the fabrication of a commercial polyethylene resin within a decade. Such divergences are well correlated with premature brittle failures under hydrostatic pressure testing of a series of correctly extruded pipes. Furthermore the drift molecular parameter allows a ranking of different medium- to high-density polyethylene resinsthe lower this parameter the better the slow crack growth resistance of the materials. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2103-2112, 1999

Key words: modified SIS technique; PE molecules separation; drift molecular parameter; fabrication divergences; PE materials ranking

INTRODUCTION

Recent research in the field of polyethylene (PE) characterization have clearly shed light on the influence on slow crack growth (SCG) of both molecular weights and comonomer branching distributions which rule the pipe's wall crystalline microstructure and govern mainly the molecular disentanglement process responsible for the long-term brittle failures of PE pipes.¹⁻³ Ishikawa et al.,² then Scholten et al.,^{4,5} postulate about the comono-

mer distribution dependence of the results of pipes' hydrostatic pressure resistance experiments.

Specific populations of macromolecules—the medium to the longest ones—would be responsible for the improvement of SCG resistance; the longer these chains and the higher their degree of comonomer branching, the better the hydrostatic pressure resistance.

The increase of both the content of the tie molecules (which participate in several crystalline parts) and the entanglements density would be the governing process for such improvement,⁶ this concept being at the origin of the development of the so-called third generation high-performance PE resins.

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Journal of Applied Polymer Science, Vol. 73, 2103-2112 (1999)

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The increasing complexity of the chemical structures of the PE resins used on the gas distribution networks since the 1960s and 1970s requires adaptation and development of characterization methods capable of detecting possible divergences in PE manufacturing that could be responsible for premature field failures.

The fractionation technique has been proved to be a good but highly expensive and/or time consuming candidate regarding the characterization of the chemical structure of macromolecules in terms of branching distribution vs. chain length.^{4,5,7–9} Therefore, reliable but less expensive methods were successfully developed ca. 1990. Kamiya et al.¹⁰ developed the stepwise isothermal segregation (SIS) technique which permits the separation of the macromolecules with respect to their crystallizability.

From this method—based on differential scanning calorimetry (DSC)—a clear qualitative differentiation of several current PE materials could be achieved. From this method, additional results were obtained by Scholten and Rijpkema⁵ that prove the accuracy of the technique in revealing some variations with time of the resin of old excavated high-density (HD) and medium-density (MD) PE pipes. Moreover, Constantin et al.¹¹ proposed an encouraging correlation between the SIS method and the temperature rising elution fractionation (TREF) technique.

To be able to reveal slight variations in the chemical structure of PE quantitatively, a modified version of the SIS technique was proposed in 1995.¹² This development responds to some anomalies revealed on several 1992 batches of medium-density PE pipes displaying premature brittle failures under the classic 80°C/4 MPa/1000 h hydrostatic pressure test, although passing the 80°C/4.6 MPa/165 h experiments. On the basis of the modified SIS method, the data generated on five different batches of PE pipes extruded from an MDPE commercial resin (from 1987 to 1992) reveal a sharp transition in the material ca. 1991–1992,¹² which confirms the qualitative trends obtained by Scholten et al.^{4,5,13} on a similar material.

Thus, given these encouraging results, the modified DSC-SIS method has been refined in terms of data processing, in order to be applied to the different PE materials currently used on the gas distribution networks. A so-called "drift" molecular parameter is calculated from the DSC crystallization data on the basis of a classic Avrami approach.

TECHNIQUE AND EQUIPMENT

Methodology

The SIS method consists of a sequenced heatingcooling-heating treatment of the material to distinguish the macromolecular species with regard to their respective crystallizabilities.^{5,10} To adapt to the PE studied, the "modified" SIS version differs on both experimental and data analysis levels.

On the experimental level, first the temperature range was extended from -10° C to 170° C to improve peak integration. Secondly, an isothermal step at 114°C was added to account for a wider range of crystallizable molecules. Then the duration of each thermal sequence was adapted and optimized to ensure the best reliability along with the most reduced experiment duration.

The modified DSC-SIS thermal program used is described in Figure 1. On the data analysis level, to go over the qualitative treatment made generally by comparing the second-melting DSC traces,^{2,5,10} a processing of the data concerning the isothermal crystallization thermograms is made, which permits calculation of both the crystallization enthalpies and the kinetic parameters.

Analyzing the crystallization steps instead of the second-melting trace makes it possible to access the intrinsic crystallizabilities of the molecular species after total annihilation of the fabrication-induced thermomechanical history. Moreover, such treatment gives the most reliable results given the complex thermal history generated by the second melting of the material (recrystallization/remelting—"disturbing" phenomena) which is clearly dependent on the heating rate chosen.¹²

Experimental Setup

A DSC with an integrated cooling unit (Model DSC30, Mettler-Toledo, CH-8606) (Greifensee, Switzerland) calibrated with Indium (melting point 156.6°C and melting enthalpy 28.45 J/g) was used for the thermal characterization of the PE materials.

To ensure good consistency of the results, first a complementary checking calibration procedure was systematically made by means of standard hot-bench substances within the range 60-250 °C, as shown in Figure 2(a). This procedure permitted a better than 99.8% accuracy on the temperature of the isothermal steps and better than 98% on



Figure 1 Modified stepwise isothermal segregation (DSC-SIS) methodology and related DSC thermograms.

the enthalpies. Secondly, blank thermograms were made and substracted to the samples DSC traces for each crystallization step, to account for possible divergences with time of the thermoanalyzer. Typical blank thermograms are shown in Figure 2(b). The calibration/checking procedure was repeated after a series of about 12 to 24 samples.

Data Processing

The 6-step DSC-SIS thermograms (see Fig. 1) were evaluated by means of the control/processing unit of the thermoanalyzer (Model TC11, Mettler-Toledo, Switzerland) interfaced with a personal computer (Model 486, Compaq Computer Corporation, Houston, Texas, USA). The crystallization data were derived from both the 114°Cand the 119°C-isothermal steps from signals integration with a linear baseline and after blank substraction. The crystallization enthalpy referred to as ΔH_c^{Ti} , and the times for 25%, 33%, 50%, 66%, and 75% of crystalline transformation, referred to as t_{χ}^{Ti} , for the crystallization temperature Ti, were then evaluated, as shown in Figure 3(a,b). The 124°C-isothermal step was not treated because of the absence of exothermal signal at this temperature for the materials under study (see Fig. 1).

The crystallization kinetic parameters referred to as k^{Ti} and n^{Ti} (for each crystallization step) were then calculated from these data on the basis of the Avrami expression:^{14,15}

$$1 - \chi = \exp(-k \cdot t^n) \tag{1}$$

where χ represents the fraction of crystallized material at time t for the temperature Ti. The kinetic parameters at each crystallization step



Figure 2 (a) Calibration checking procedure of the calorimeter by means of standard substances. The full lines correspond to the perfect correlation of the theoretical and the measured values. (b) Blank isothermal DSC traces at 119°C (a) and 114°C (b).

were obtained from the double-Log expression of equation 1 as follows:¹²

$$LogLog(1/1 - \chi) = Log(k) + n \cdot Log(t)$$
 (2)

Samples Studied

Modified SIS experiments were performed on several commercial materials—both MDPE and HDPE—supplied by Borealis (Finland), Fina(Belgium), and Solvay (Belgium) within 12 years and referred to as PE 3, PE 6, PE 8, and PE 12. All the materials were commercially compounded with normal package additives, including carbon black (approximately 2.3% wt). Technical data regarding the materials studied are given in Table I. Samples were taken from 63 mm and 110 mm (external diameter) pipes midwall (wall thickness = external diameter/11) to avoid extrusion-induced disturbances (e.g., chain scission) near the pipe surfaces



Figure 3 (a) Determination of the 119°C-isothermal step crystallization parameters $\Delta H_{\rm c}^{119}$ and t_{χ}^{119} . (b) Determination of the 114°C-isothermal step crystallization parameters $\Delta H_{\rm c}^{114}$ and t_{χ}^{114} .

and to ensure comparison of intrinsic crystallizability of the materials.

Four hundred micrometer-thick slices were extracted from pipe midwalls by means of a microtome (Model Polycut S, Reichert-Jung, Germany) from which 10 mg \pm 1 mg discs were punched. For each pipe, a series of 6 to 12 test samples were used. Generally, stacking three discs per test sample was necessary to achieve the desired test weight.

RESULTS AND DISCUSSION

Experimental Crystallization Behavior of MDPE

The treatment of the Avrami plots at 119°C and 114°C for the PE 3 ethylene-butene copolymer leads to the following comments.

The Avrami exponents remain constant from one pipe to another, between 2.32 and 2.53. These values are consistent with those found in the literature^{15,16} for such copolymer. The Avrami plot at 114°C leads to more scattered values of n that are spread between 1.8 and 2.2. The origin of such low n values was explained elsewhere.¹² Figure 4 shows the evolution of the Avrami rate constants with the year of pipe fabrication for the two isothermal steps.

 k^{119} seems to decrease slightly from 1987 to 1990–1991 and then more drastically from 1990– 1991 to 1992 whereas k^{114} increases from the oldest pipe (TGI) to the newest ones (CAV and DRI). Noteworthy is that k^{114} is about 50 to 60 times greater than k^{119} , meaning a far slower crystallization kinetic at 119°C compared with 114°C. In addition, the crystallization enthalpy at

PE No.	Density (g/cm ³)	Weight Averaged, Molecular Weight, $\bar{M}_w~(\mathrm{g/mol})$	Number Averaged, Molecular Weight, \bar{M}_n (g/mol)	Comonomer Type	Branching Content (/1000 C)	Melt Flow Index 190°C/5 kg (g/10 min)
PE 3	0.949	167,000	17,800	Butene	7	0.70
PE 6	0.940	136,000	16,800	Hexene	6	0.90
PE 8	0.950	149,000	13,700	Butene	6.5	0.85
PE 12	0.956	170,000	11,900	Butene	9	0.45

Table I Technical Data (Mean Values) of the Materials Under Study

PE, polyethylene.

119°C remains steady from 1987 to 1990–1991 and then increases for the 1991 and 1992 batches, whereas the crystallization enthalpy at 114°C behaves inversely, as shown earlier.¹²

The trends obtained reveal significant differences in the crystallization characteristics after 1990-1991 because no extrusion-induced disturbances could be put in light on these pipes from the first melting phase, as proved earlier¹² and as expected because the thermomechanical histories of the materials were annihilated during the first melting phase. In addition, Table II shows that the dynamic crystallization phase leads to similar values of both the crystallization temperature and the dynamic crystallization enthalpy, meaning a similar behavior from 114°C to the ambient temperature whatever the pipe lot. Thus, crystallizability differences in the seven materials are revealed in the range of 124–114°C, which can be viewed qualitatively during the second melting (see Fig. 1). Moreover, the data confirm a sharp transition ca. 1991, which could be at the origin of the aforementioned poor mechanical behavior of the pipes after this date. The tendencies of both enthalpies and Avrami rate constants have been explained in terms of a chain length-to-branch content compromise.¹²

The relatively poor SCG resistance of the newest batches (CAV and DRI) could be attributed on the one hand to a lower proportion of the 114°Ccrystallizable species (lower enthalpies) along with a lower branch content (higher rate constants), and on the other hand to a higher proportion of the 119°C-crystallizable molecules (higher enthalpies) along with a higher branch content (lower rate constants). These considerations correlate with qualitative data obtained by Scholten et al.^{4,5} who have shed light on a similar transition in 1991 regarding this material, although they have worked on the 123°C-and 118°C-isothermal steps.

Working on the second melting SIS thermogram Scholten et al.^{4,5} show a progressive shift of the melting temperatures toward the highest ones, along with the progressive disappearance of the low-temperature component. In addition, Brown et al.³ have proved the mechanical improving effect of the medium-range crystallization temperatures (meaning the medium-range crystallizable species) on the lifetime of ethylene-octene copolymers; the more bimodal the crystallization temperature distribution (i.e., the biggest the fraction of medium-to-low temperatures with respect to the highest ones), the better the lifetime. Moreover Scholten and Smeltink¹³ have pinpointed that for the socalled first- and second-generation polyethylene



Figure 4 Avrami rate constants for the 119°C- and the 114°C-crystallization step for the seven batches of ø 63 mm PE 3 pipes.

PE 3 TGI (1987) TMY (1989) TOV (1990) TOC (1	991) CAV (1992)
Dynamic crystallization 96.4 ± 0.9 96.9 ± 0.6 95.8 ± 1.3 96.9 ± 0.6	$= 0.5 \qquad 97.2 \pm 0.6$
Dynamic crystallization 147.6 ± 3.9 140.1 ± 5.0 143.6 ± 6.5 148.6 ± 6.5 enthalpy (J/g) 147.6 ± 3.9 140.1 ± 5.0 143.6 ± 6.5 148.6 ± 6.5	± 3.5 140.9 ± 8.3

Table II Dynamic Crystallization Parameters T_c^d and ΔH_c^d for Five Batches of \emptyset 63 mm PE 3 Pipes (Peak Integration Between 114°C and 30°C, Linear Baseline)

PE, polyethylene.

resins, the higher the comonomer content on the medium to the longest molecules, the better the SCG resistance under hydrostatic pressure testing.

All these trends and considerations suggest proposing a unique dimensionless parameter, referred to as "drift molecular parameter," that would link the crystallization parameters aforementioned and whose value could give an image of the SCG resistance of the PE under study.

Drift Molecular Parameter

The expression proposed for the drift molecular parameter accounts for the respective influences of both the 114°C- and 119°C-molecular species in terms of quantities and kinetics:

$$\tau = \begin{pmatrix} \frac{\Delta H_c^{119}}{\Delta H_c^{\text{Tot}}} \\ \frac{\Delta H_c^{114}}{\Delta H_c^{\text{Tot}}} \end{pmatrix} \cdot \begin{pmatrix} \frac{1}{k^{119}} \\ \frac{1}{k^{114}} \end{pmatrix}$$
(3)

where ΔH_c^{Tot} represents the total crystallization enthalpy for both isothermal steps and dynamic phase between 114°C and 30°C. Equation 3 can be rewritten more simply as:

$$\tau = \frac{\frac{\Delta H_c^{119}}{k^{119}}}{\frac{\Delta H_c^{114}}{k^{114}}}$$
(4)

From this simplified expression of τ it is thus possible to evaluate the bimodality level of the distribution (crystallization enthalpies), taking into account the influence of the comonomer branches (rate constants).

The accuracy regarding the calculation of the drift molecular parameter τ depends on the accu-

racy regarding the evaluation of the parameters ΔH_c^{Ti} and k^{Ti} from the isothermal steps.

Thus $\frac{\Delta \tau}{\tau}$ was evaluated from $\frac{\delta k^{T_i}}{k^{T_i}}$ and $\frac{\delta (\Delta H_c^{T_i})}{\Delta H_c^{T_i}}$ both calculated from the standard deviations on the mean values for each individual series of 6 to 12 samples.

This was performed on a series of six 63 mm pipe batches from a unique PE resin from 1987 to 1992. The mean value of $\frac{\Delta \tau}{\tau}$ was found to be about 30-35%. The origin of such a poor accuracy could be searched on three levels: 1. the normal heterogeneity of the MDPE under study which would be difficult to eliminate anyway; 2. the errors regarding the calculation of the components of the drift parameter. One possible way to reduce these errors-while keeping the same number of test samples per series-would be to consider more t_{χ}^{Ti} , data in the calculation of k^{Ti} ; and 3. a disturbing crystallization phenomenon from 124°C to 119°C and from 119°C to 114°C that could be due to a nonsufficiently high cooling rate from step to step that could create a nonequilibrium state of the DSC signal. This phenomenon would be more emphasized by the existence of an electrical disturbing signal visible on the blank curves [see Fig. 2(b)]. This problem is revealed by the nonsystematic appearance of an exothermic shoulder in the 119°C-isothermal peak which modifies the peak integration of the exothermic crystallization trace and consequently modifies the Avrami parameters calculation.

To get a better understanding of the problem met on several PE samples, a PE 3 specimen sample was tested with three additional isothermal steps at 122°C, 121°C, and 120°C followed by the normal step at 119°C. The existence of DSC exothermic signals at these temperatures indicate simply that crystallization occurs below 124°C. Peaks integration gives an enthalpy of about 20 to 30 J/g for the three additional steps.

		Drift Molecular Parameter,	τ
PE	First Cycle	Second Cycle	Third Cycle
PE 3 (1983) (Ø 160 mm pipes) PE 6 (1988) (Ø 110 mm pipes)	$\begin{array}{c} 150.1 \pm 52.5 \\ 66.8 \pm 23.4 \end{array}$	$\begin{array}{c} 83.1 \pm 29.1 \\ 59.4 \pm 20.8 \end{array}$	$\begin{array}{c} 141.3 \pm 49.5 \\ 104.9 \pm 36.7 \end{array}$

Table III	Values of the Dr	ift Molecular	Parameter	Calculated	l from	Triplicate	SIS (Cycl	les
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PE, polyethylene.

With these modifications, the disturbing exothermal shoulder disappears but the enthalpy of the 119°C step is reduced to \approx 50% of the original value obtained in normal modified SIS conditions. Actually, we have to make the assumption that the overall signal at 119°C represents most surely the crystallizability behavior of the 123–119°C molecular species, that would correspond to the 20–30 nm lamellae thickness in the solid body,¹⁷ meaning the medium to the highest molecular weights.

Consequently, in some particular cases, peak integration of the 119°C step should be refined by a correct choice of the baseline lowest limit in the range 0-1.5 min, suggested by the blank curve shape [see Figure 2(b)].

Another way to eliminate the peak shoulder in the 119°C signal was tested by adding to the normal procedure only one additional isothermal step at 119.5°C during 10 sec. This procedure gave a nonsystematic result regarding the disappearance of the shoulder and consequently it was not used anymore.

In addition, the reproducibility on the determination of τ has been tested on duplicate and trip-



Figure 5 Evolution of the drift molecular parameter with the year of pipe fabrication for eight batches of PE 3 pipes (Ø 63 mm and Ø 160 mm).

licate runs on two different copolymers referred to as PE 3 and PE 6. As shown in Table III, the values obtained for the parameter τ determined during a single experiment appear similar from either a first, a second, or a third SIS cycle, given the experimental accuracy of about 35% aforementioned.

Considering that cycle 2 (respectively 3) erases the former crystallization history generated under cycle 1 (respectively 2) and that the DSC material is free from any mechanical-induced disturbances from one cycle to another, τ could be considered an intrinsic parameter with an accuracy of $\approx 35\%$.

Divergences in PE Fabrication

The modified SIS procedure was applied first on a series of PE 3 pipes (diameter, 63 mm) for which the drift molecular parameter was calculated. In addition, a 160 mm pipe was also used to enlarge the range of fabrication period. Figure 5 shows that τ remains approximately constant from 1983 until 1990. A transition period appears ca. 1991 when τ increases drastically until 1992. These results confirm the trends



Figure 6 Evolution of the drift molecular parameter for different MDPE and HDPE batches within a 12-year period.



Figure 7 Correlation of the SCG resistance with the molecular parameter τ .

obtained on the basis of the less refined treatment, as presented formerly.¹² Then a sharp transition in the crystallization behavior of this material ca.1991 is clearly demonstrated. Such a transition is accompanied by systematic premature brittle failures of the 1992 pipes under hydrostatic pressure test conditions at 80°C/4 MPa, independently of the pipe diameter and/or the pipe manufacturer.

Thus the increasing of τ can reasonably be correlated with an alteration of the SCG resistance of this material. These results suggest a fix of an upper limit (meaning a critical value) for the drift molecular parameter. This limit, referred to as threshold of fabrication drift in Figure 5, can be fixed around 160–170 taking into account the accuracy of the results. To check the validity of such procedure on other PE materials, the parameter τ

was calculated for different commercial MDPE and HDPE materials.

Ranking of the PE Materials According to the Drift Molecular Parameter

Figure 6 presents the results obtained on three MDPE and one HDPE in superimposition with the data of Figure 5 (from which uncertainty bars have been removed). Given the aforementioned accuracy on τ , it seems that the materials can be ranked according to the respective values of τ vs. the fabrication year. Except for the PE 3 material, no sharp increase of the drift molecular parameter is recorded for the other materials, which have been proved to pass the checking procedures during this period of time, on the basis of hydrostatic pressure testing in particular. The fluctuations of

the mean values of τ with the year of fabrication possibly could be attributed to the fact that only one batch is tested (except for 1991 and 1992), but it could also be attributed to real quality fluctuations of the materials. This hypothesis remains to be addressed more clearly.

Nevertheless, noteworthy is that the ranking of the mean values of τ is well correlated with the SCG resistance ranking (hydrostatic pressure testing, cone test, etc.) of the corresponding materials in the increasing order PE 3–PE 8, PE 6, PE 12, the latter being a high-performance HDPE, as shown in Figure 7. Moreover the 80°C/4 MPa-hydrostatic pressure testing permits ranking of the PE 3 material batches with respect to their τ values.

Thus, the lower the value of τ the better the SCG resistance of these materials. Consequently, the threshold of fabrication drift defined herein is a good indicator for the detection of fabrication divergences of the PE 3 material batches.

CONCLUSION

The modified SIS procedure described herein is well suited to the quantitative study of the crystallization behavior of so-called second- and thirdgeneration medium-to-high density polyethylene resins displaying different SCG resistances.

The calculation of a drift molecular parameter combining the crystallization parameters for two representative isothermal steps permits on the one hand to detect very accurately some divergences regarding fabrication of a commercial resin within a decade and, on the other hand, to rank currently used PE materials.

The drift molecular parameter is well correlated with the SCG behavior under 80°C/4 MPa hydrostatic pressure conditions, in particular; the lower this parameter the better the SCG resistance. The trends obtained will be refined with more extensive data in progress now and confronted to full-notch creep experiments on prenotched rods.^{18,19}

Thus, the methodology presented herein seems to be a serious candidate for the evaluation of the mechanical properties of the PE materials, based on an intrinsic molecular parameter.

REFERENCES

1. Lustiger, A.; Markham, R. L. Polymer 1983, 24, 1647.

- Ishikawa, N.; Shumisu, T.; Shimamura, Y.; Goto, Y.; Omori, K.; Misaka, N. 10th International Fuel Gas Pipes Symposium, New Orleans, LA, October 27–29, 1987.
- Brown, N.; Lu, X.; Huang, Y.; Harrison, I. P.; Ishikawa, N. Plast Rubber Compos Process Appl 1992, 17, 255.
- Scholten, F. L.; Wikkerink, J. B. W. European Gas Research Group, Expert Group on Plastic Pipes, Internal Report, 1992.
- Scholten, F. L.; Rijpkema, H. J. M. 8th Plastics Pipes Conference, Eindhoven, The Netherlands, September 21–24, 1992.
- Brown, N.; Lu, X. Fundamental Mechanisms of Failure in Polyethylene Gas Pipes; GRI's Annual Report No. 93/0277, Gas Research Institute, Chicago, Illinois, 1993.
- Pidgeon, M. G.; Rudin, A. J Appl Polym Sci 1994, 51, 303.
- Cooper, A. R. Determination of Molecular Weights in Chemical Analysis; Wiley Interscience: New York, 1990; Vol. 103.
- 9. Monrabal, B. J Appl Polym Sci 1994, 52, 491.
- Kamiya, T.; Ishikawa, N.; Kambe, S.; Ikegami, I.; Nishibu, H.; Hattori, T. Proc. Annual Technical Conf. (ANTEC), Soc Plast Eng 1990, p. 871.
- Constantin, D.; Roussel, D.; Szalamacha, T. Polymer Processing Society European Regional Meeting, Strasbourg, France, August 29–31, 1994.
- Gueugnaut, D.; Rousselot, D. 9th Plastics Pipes Conference, Edinburgh, UK, September 18-21, 1995.
- Scholten, F. L.; Smeltink, M. 9th Plastics Pipes Conference, Edinburgh, UK, September 18-21, 1995.
- Turi, E. A. Thermal Characterization of Polymeric Materials; Academic Press, Inc., Orlando, FL, 1981.
- Ozawa, T.; Thermal Analysis: Comparative Studies on Materials; Kambe, H., Garn, P. D., Eds.; Halsted: New York, 1974; p. 155.
- Gupta, A. K.; Rama, S. K.; Deopura, B. L. J Appl Polym Sci 1984, 51, 231.
- Gueugnaut, D.; Rousselot, D. Polymer Processing Society European Regional Meeting, Stuttgart, Germany, September 26–28, 1995.
- Nishio, N.; Iimura, S. Full-Notch Creep Test Method for Life Prediction and Quality Evaluation for Polyethylene Pipes; Technical Report; Tokyo Gas Co. Ltd., R & D Institute: Tokyo, Japan, 1984; Vol. 29, pp. 25–37.
- Ouâkka, A.; Dang Van, K.; Gueugnaut, D.; Blouet, P. 10th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge, UK, April 7-11, 1997.