Estimation of Slow Crack Growth Behavior in Polyethylene after Stepwise Isothermal Crystallization

Markus Haager,*[1] *Gerald Pinter*,[2] *Reinhold W. Lang*[1,2]

[1] Polymer Competence Center Leoben, Parkstraße 11, 8700 Leoben, Austria
E-mail: haager@pccl.at
[2] Department of Materials Science and Testing of Plastics, University of Leoben, Austria

Summary: The use of analytical methods to estimate the SCG resistance of PE pipe materials has been suggested due to the fact that the slow crack growth (SCG) behavior of polyethylene (PE) is governed by structural parameters such as molecular weight and side chains. In the research project presented here, the molecular structure of several commercially available polyethylene-high density (PE-HD) materials was analyzed using a modified stepwise isothermal segregation (SIS) technique and compared with results from fracture mechanics experiments. A good correlation between the SIS results and SCG rates was found. It turned out that the modified SIS technique is a fast and simple method and could be used to assess SCG resistance in PE.

Keywords: crack growth; differential scanning calorimetry (DSC); polyethylene (PE); side chains; stepwise isothermal segregation technique

Introduction

Polyethylene (PE) has been used successfully in pipe applications for about 40 years. Typically, a service life of 50 years is required – and even 100 years has recently been proposed. To ensure satisfactory performance, time-consuming internal pressure tests are carried out on pipe specimens. However, quicker test methods are needed to evaluate the long term behavior of new materials. Laboratory experiments and the failure of pressurized pipes in the field have identified slow crack growth (SCG) as the critical parameter that determines the life-time. As a result, several methods to estimate the life-time of PE pipes by characterizing SCG have been introduced.[1-4]

In parallel, materials science has uncovered the prime molecular and morphological parameters governing SCG and failure behavior under long-term loading conditions in pipe grade PE. The most important of these is chain structure: molecular weight and distribution, number, length

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and distribution of side chains. The structure of the macromolecules affects the fracture and SCG behavior of PE either directly or indirectly through the lamella thickness, the number of tie-molecules and the number of intercrystalline entanglements. Most recently, major efforts have been directed towards the use of analytical rather than mechanical characterization methods to evaluate the SCG resistance of PE, at least for the purpose of a quick quality-assurance technique.[5-8]

More than 20 years ago, Varga et al. proposed a new method to characterize the structure of PE by stepwise isothermal crystallization using differential scanning calorimetry (DSC).[9] Since then many research groups have used similar procedures to fractionate polymers. The technique consists of a sequenced, multiple-stage stepped thermal treatment, 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 specific crystallizable species which are responsible for the SCG resistance of PE.[2, 6, 8, 10, 11] The modified stepwise isothermal segregation (SIS) technique was introduced by Gueugnaut and Rousselot to refine the method and quantify the results of the original SIS technique. It was suggested that crystallization data be evaluated at 114 °C and 119 °C using the Avrami equation and to calculate a *drift molecular parameter*, τ, to estimate the SCG behavior of PE.[2, 8, 12]

Experimental

The studies were performed on two polyethylene-high density (PE-HD) pipe materials (PE-HD 1 & 2), and two rather brittle PE-HD blow mold grades (PE-HD 3 & 4). Relevant material properties are listed in Table 1.

Table 1. Parameters of the investigated materials (from data sheets, X_c = degree of crystallinity, M_n and M_w = number and weight average molecular mass, YM = Young's modulus, σ_Y = yield stress, SCB = number of short chain branches)

Code	X_c [%]	M_n [kg/mol]	M_w [kg/mol]	YM [N/mm²]	σ_Y [N/mm²]	Comonomer	SCB [1/1000 C]
PE-HD 1	64	16	290	1000	24	Hexene	4,0
PE-HD 2	56	15	190	700	18	Hexene	5,5
PE-HD 3	83	19	80	1650	32	Hexene	1
PE-HD 4	77	16	320	1400	30	Butene	3,2

In the research project presented here, the structure of PE was characterized using the modified SIS technique – adapted and optimized for the materials examined (Figure 1). Samples of 6 mg were weighed and sealed in aluminum-light crucibles (20 µl) prior insertion into the DSC equipment.

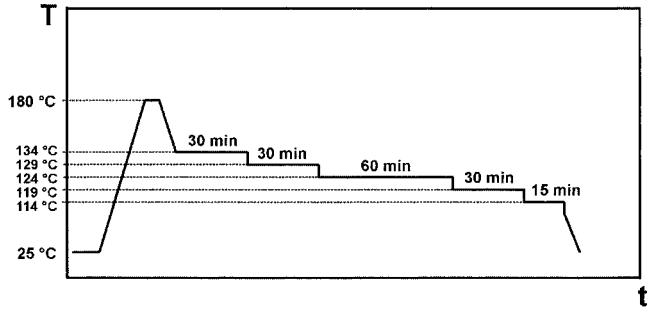


Figure 1. SIS/DSC procedure used in the project

From the recorded SIS thermograms the crystallization enthalpies, ΔH, of the 114 °C and 119 °C isothermal steps were calculated and the crystallization data were derived by signal integration with a linear baseline. Then the crystallization rate constants, k, were calculated for both temperatures with the help of the Avrami equation (Equ. 1), followed by calculation of the drift molecular parameter, τ (Equ. 2):

$$1-\chi = \exp(-k \cdot t^n) \qquad (1)$$

$$\tau = \frac{\Delta H^{119} / k^{119}}{\Delta H^{114} / k^{114}} \qquad (2)$$

where χ represents the fraction of crystallized material at time t, k is the crystallization rate constant, n the Avrami exponent and ΔH the crystallization enthalpy. τ was used to assess the SCG resistance of the materials investigated and the ranking was compared with the results from the SCG behavior tests.

SCG resistance was evaluated by using the concepts of linear elastic fracture mechanics. Under static loading conditions, SCG rates of a sharp crack in linear elastic materials can be plotted as a function of the stress intensity factor, K_I (the index I stands for pure tensile loading conditions) (Figure 2). An extended linear section is frequently revealed on a double logarithmic scale over

certain crack growth rates, indicating a power law relationship of the form:

$$\frac{da}{dt} = A \cdot K_I^m \qquad (3)$$

A and m are material constants dependent on the test conditions (temperature, environment, frequency, stress ratio, etc.). As illustrated in Figure 2, deviations from the power law may occur due to initiation processes at the beginning of the test and due to specimen breakdown at the end of the test.[3, 4, 13-15]

For the SCG experiments, specimens of the compact type (CT) (see Fig. 2) with a specimen width, W, of 40 mm were machined from 15 mm thick compression-molded sheets. Pre-cracks were made prior to the fracture mechanics experiments by pressing a fresh razor blade into the V-notch tip of the specimen at room temperature. The SCG experiments were performed at 80 °C in deionized water on a test rig which was designed and constructed at the Institute of Materials Science and Testing of Plastics (University of Leoben, A). The crack length values were measured regularly with the aid of a traveling microscope. For evaluation, the slow crack growth rates, da/dt were plotted as a function of the stress intensity factor K_I.

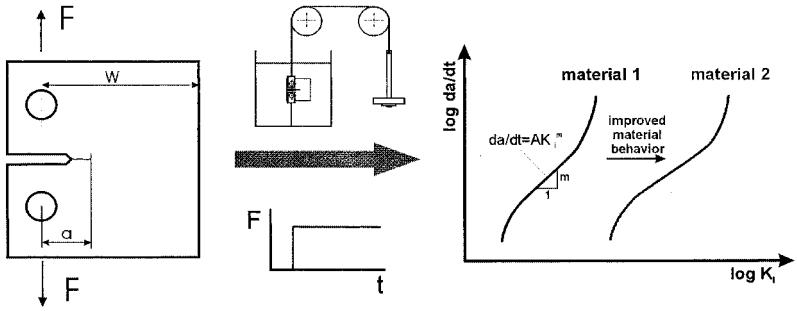


Figure 2. Schematic crack growth behavior of polymers under static loads (F = force, W = specimen width, a = crack length, t = time)

Results and Discussion

Among other things, tests with different DSC-crucibles and various sample weights were carried out before determining τ for the 4 materials. An artificial peak, superimposed on the crystallization process, was observed at the beginning of each isothermal crystallization step.

Tests with different DSC-crucibles showed that this influence can be reduced by using smaller crucibles (Figure 3).

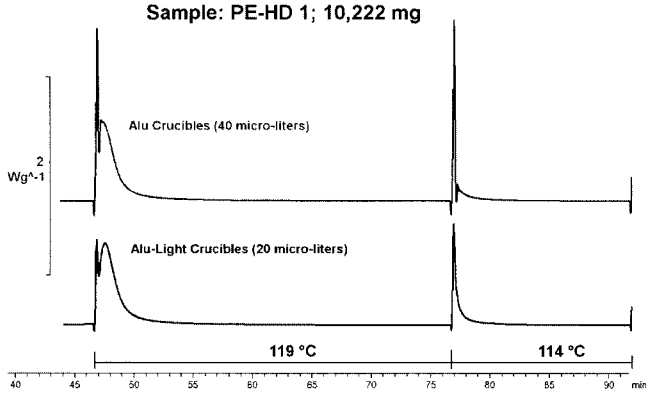


Figure 3. Isothermal crystallization at 119 °C and 114 °C of PE-HD 1 using different crucibles

The artificial peaks occur at temperature changes and are assumed to result from the finite heat transfer from the DSC to the sample. In order to obtain only the peaks from the crystallization process, the heat transfer was measured at a temperature step where no crystallization occurred (from 134 °C to 129 °C) and subtracted from the DSC signal of the isothermal crystallization step at both investigated temperatures. The outcome is a graph that contains the pure crystallization enthalpy (Figure 4, Figure 5).[16]

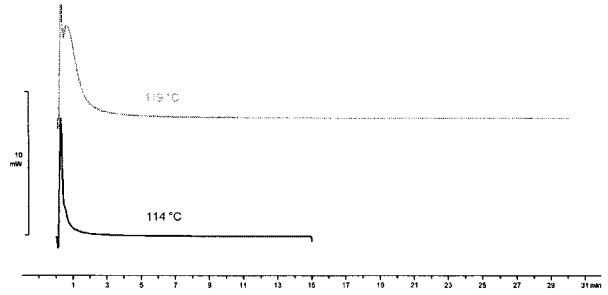


Figure 4. DSC plot of the isothermal crystallization processes of PE-HD 1 at 119 °C and 114 °C before the subtraction of the heat transfer

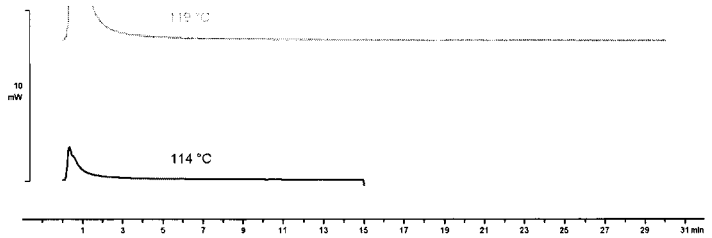


Figure 5. DSC plot of the isothermal crystallization of PE-HD 1 processes at 119 °C and 114 °C after the subtraction of the heat transfer

In addition to testing different crucibles, the influence of the sample weight on τ was studied. It turned out that τ increased considerably with the sample weight (Figure 6). This leads to the conclusion that it is vital to use the same sample size and shape in order to obtain reproducible and comparable results from the SIS measurements. For the presented research project it was decided to use a sample weight of 6 mg with an aluminum light-crucible (Figure 3), because it was observed that the artificial peak became minimal for this combination.

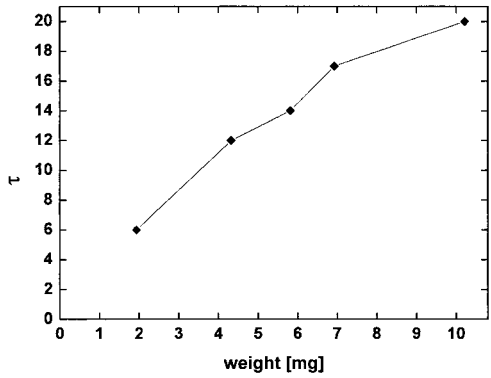
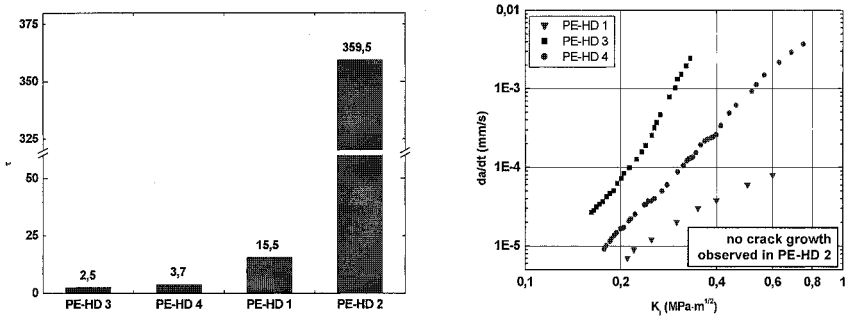


Figure 6. Dependency of τ on the sample weight

Following the preliminary tests discussed above, τ was measured for the four materials under analysis. The results are given in figure 7a and clearly show that the two pipe materials exhibit higher values of τ than the two brittle PE-HD blow mold grades. An identical ranking was obtained from the static SCG experiments conducted on CT specimens (Figure 7b). PE-HD 2 exhibits superior SCG resistance compared to the other materials, since no crack growth could be observed using the same test parameters. PE-HD 1 was second best, PE-HD 4 followed and PE-HD 3 showed the highest SCG rates. As a result it can be stated that, for the materials investigated, τ increases with increasing SCG resistance.



a b

Figure 7. Comparison of the analyzed materials: (a) drift molecular parameter, τ, (b) slow crack growth kinetics.

Conclusions

For the materials investigated, the modified SIS technique reflected the ranking established using SCG experiments. The method is a very fast and simple tool to assess SCG behavior in PE-HD, and therefore it would be thinkable to apply the modified SIS technique for quality assurance purposes.

Further investigations on a larger number of pipe materials are needed to confirm the ability of the modified SIS techniques to rank materials according to their SCG resistance as affected by side chains. In particular, the issues related to the ranking of bimodal PE-types (e.g. PE-100) vs. unimodal PE-types (e.g. PE-80) and the effects of different side chain distributions deserve further systematic investigations.[8]

In the course of this research work it became apparent that it is sometimes difficult to determine the time when the isothermal crystallization process begins. Unfortunately, the Avrami equation responds very sensitively to a shift along the time-axis and incorrect crystallization rate constants, k, are the outcome.[17] Additionally, the ability to describe the crystallization process of the SIS with the Avrami equation needs to be addressed.

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