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SUCCESSIVE SELF-NUCLEATION AND ANNEALING IN THE SOLVATED STATE OF ETHYLENE COPOLYMERS

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Successive Self-Nucleation and Annealing (SSA) in the Solvated state (STAF) is a thermal analysis technique which provides a more rapid testing alternative to temperature rising elution fractionation (TREF) for limited data analysis. Differential scanning calorimetry (DSC) is used to observe the melting behavior of the polymer after it is subjected to a series of discrete annealing steps. These annealing steps are intended to fractionate the polymer based on its short chain branching content, molecular mass, or the ‘crystallizability’. After the annealing steps are complete, the sample is cooled, and then a final melting step is performed. The resulting endotherm shows a series of peaks that correspond to each annealing step, with a decrease in short chain branching resulting in a higher peak temperature. The partial area of the highest temperature peaks above 90°C is used to calculate the fraction containing the lowest amount of short chain branching, usually assigned as the ‘homopolymer’ or ‘high density’ fraction. This method can be customized to tailor the required information for shorter run times. By eliminating some annealing steps, the shortened STAF SSA method has been shown to be able to detect and quantify minute amounts of the homopolymer fraction.

Keywords: *chemical composition distribution, crystallization, ethylene copolymer, solvated thermal analysis, successive nucleation and annealing*

Introduction

The molecular architecture of the distribution of the short chain branching (comonomer) for linear low density polyethylene LLDPE is an important parameter which determines many of the properties as it controls the crystallization and hence the final morphological structure. The Temperature Rising Elution Fractionation (TREF) method developed over the years has been used successfully in many modeling works [1–4]. To obtain good fractionation, a very slow crystallization process is required which makes the TREF technique very time consuming. Several other techniques, such as Solvated Thermal Analysis Fractionation (STAF) [5, 6], and Crystallization Analysis Fractionation (CRYSTAF) [7–9], DSC Successive Self Annealing Fractionation (SSA) [10–13], and others [14–16] have been advanced over the years to overcome the long test time.

As reported in the previous CTAS [6], NOVA Chemicals has developed an alternative technique for comonomer distribution known as Solvated Thermal Analysis Fractionation. The technique measures the crystallinity distribution rather than the comonomer distribution as ascertained in TREF and CRYSTAF. If it is true that the measured crystallinity distribution is a true reflection of the composition (comonomer) distribution, then STAF and TREF should yield essentially the same profile of distribution, provided crystalline enthalpy is equivalent to concentration. Previous studies indicated some minor differences existed between the data from TREF and STAF. This could be due to the difference in the separation/fractionation process for the TREF (from a true solution) and STAF (Solvated conditions). The enthalpy of crystalline melting in the solvated state is also a function of the composition, and hence is not a direct measurement of the concentration or amount of crystalline fraction. However, the STAF technique is simpler, and faster compared with TREF.

The first STAF technique developed [6] utilized the same crystallization program as the TREF crystallization process of 0.025°C min^{-1} giving only a saving in test time from the heating cycle. To reduce the test time further, an attempt was carried out using a higher rate of crystallization. However this resulted in subsequent fractionated profiles of crystallinity distribution as a function of dissolution temperature significantly different from the original as shown in Fig. 1.

Chemical composition distribution (CCD) analysis yields important information on the distribution of the homopolymer and copolymer distribution of the Ziegler-Natta LLDPE. In the case of single-site catalyst or mixed catalyst systems, CCD has become a critical factor in the case of dual reactor where the molecular mass distribution and chemical composi-

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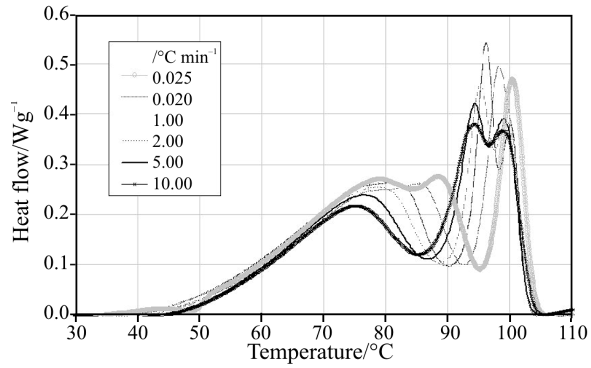

Fig. 1 Effect of crystallization rate on STAF dissolution

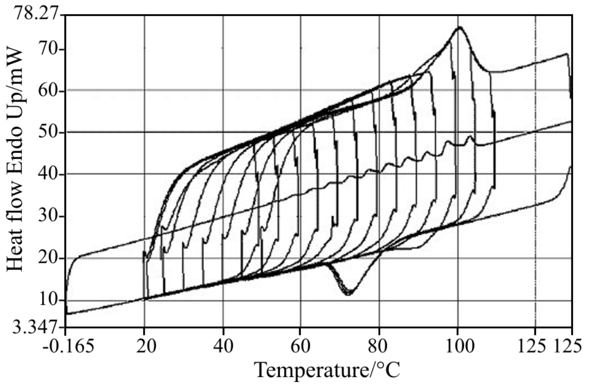

Fig. 2 DSC SSA STAF trace

tion distribution are separately controlled and tailored to give superior performance polyethylenes [17–19]. A fast and accurate method of CCD determination has become an invaluable tool in process design and product development.

In order to improve the fractionation and at the same time reduce the crystallization time, a combination of successive self-nucleation annealing technique and the solvated thermal analysis fractionation was designed and developed. We report here this new technique, which has been applied successfully to characterize quantitatively the amount of 'homopolymer' fraction in Ziegler-Natta linear low density polyethylene.

Experimental

Chemical composition distribution by TREF

Nova Chemicals TREF Analysis utilizes the following slurry pack technique. Approximately 20 mg of sample is dissolved in 12.5 mL trichlorobenzene (TCB) in a vial at 125°C for 4–5 h. Crystallization is carried out from 110 to 0°C at 0.025°C min^{-1} cooling rate. The fractionated sample is then mixed with acetone and 1.6 g Celite-545 and packed into a column. Elution is carried out with TCB at 2 mL min^{-1} flow rate from 24.5 to 110°C at a heating rate of 0.25°C min^{-1}. Concentration of the eluted solution is monitored with an IR detector. Total time required for a single run is approximately 4 days.

Chemical composition distribution by SSA STAF

Nova Chemicals novel new method of successive self-nucleation annealing in the solvated mode SSA STAF is given as follows. In the standardized test method, approximately 5 mg of sample together with 30 μL of TCB are sealed in a DSC stainless steel pan. The sample is then subjected to the thermal processing in a Pyris DSC using the program-I as outlined in Appendix 1. A typical completed DSC trace with all the heating, annealing, and cooling steps is as shown in Fig. 2.

In the SSA STAF method, the final fractionated profile obtained will be dependent on the successive annealing temperatures set in the test. Two programs are used, using 5°C-step change, one starting at 112.5°C and one starting at 110°C. A combination of these two-test programs is found to give complete detailed information on the 'homopolymer' fraction on most polyethylenes studied. Typical results for a ZN-octene-LLDPE of density = 0.91 g mL^{-1}, Melt Index = 1.0 g (10 min)$^{-1}$ are as shown in Fig. 3.

In method-1 (Fig. 3a), it can be deduced that the two peaks in the temperature range from 95 to 106°C may correspond to mainly 'homopolymer' fraction. The 103°C peak contained almost no comonomer, and the 97°C peak contained small amount of comonomer. In method-2 (Fig. 3b), it appears that a small peak in the range of 105 to 110°C may correspond to the 'true homopolymer' fraction, with the peak in the range of 98 to 105°C corresponding to a 'homopolymer' fraction containing little comonomer.

It should be noted that by the virtue of 'step annealing' process, each peak would contain a narrow range of comonomer composition, depending on the annealing temperature as well as the temperature step width. By combining the two 5°C-step programs, the final trace shows steps of 2.5°C fractionation resolutions as shown in Fig. 3c.

An SSA STAF QC method for rapid 'homopolymer' fraction determination

In the process design and product development experimentation, it is critical to be able to monitor the 'homopolymer' content. A fast turnaround time is desired. The current standard Program-I SSA STAF method has 44 steps and takes approximately four hours to finish a run. The objective of developing a

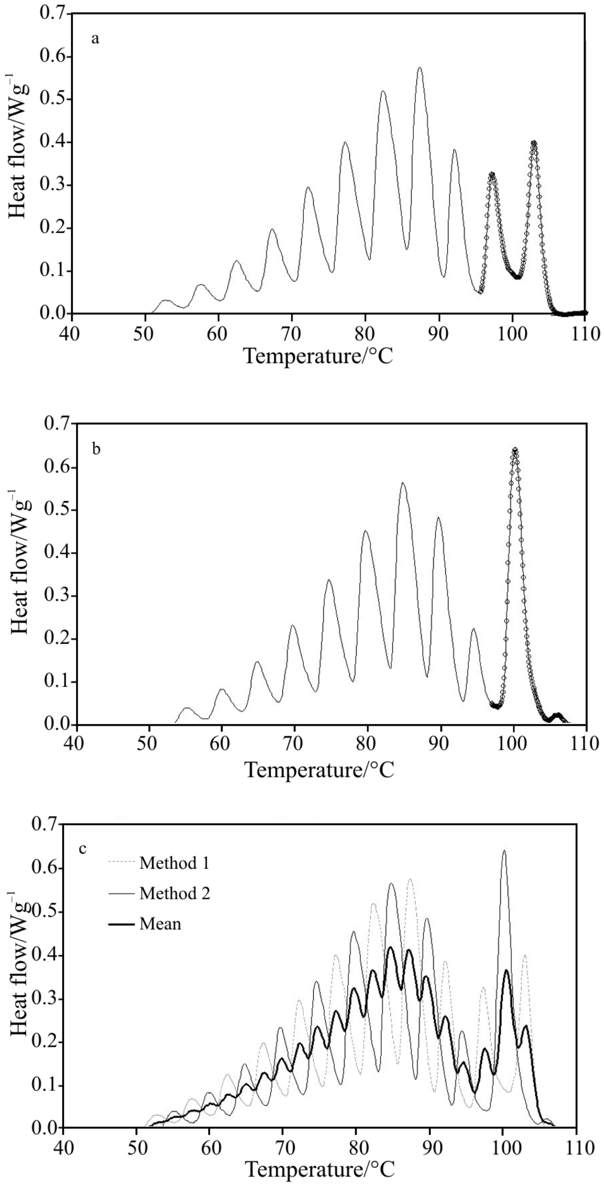

Fig. 3 a – SSA STAF method 1; b – SSA STAF method 2; c – SSA STAF-superimposed and combined traces

quality control method is to reduce that time to less than 2 h without losing significant information concerning the Short Chain Branch Distribution (SCBD), especially the high-density (HD) component (‘homopolymer’ fraction).

The method development plan was structured to modify SSA STAF conditions to yield a fast and reliable analytical method capable of detecting and monitoring the presence of very low percentages of ‘homopolymer’. For a LLDPE analysed with STAF SSA, the % of polyethylene remaining ‘un-melted’ up to 87°C (in the case of SSA method-2) and 90°C (in the case of SSA method-1) may be considered to be ‘homopolymer’ fraction.

DSC Program-II listed in Appendix 2 was first used to study the effect of shortening the time by increasing the step size for temperature range below 90°C. This gives a test time of approximately 3 h.

DSC Program-III listed in Appendix 3 was used to study the effect of ignoring the nucleation and annealing steps below the expected ‘homopolymer’ crystallization temperature in the solvated state (<88 to 90°C) using 5 nucleation/annealing temperatures. The test time was further reduced to approximately 2 h.

Materials

A total of 10 polyethylenes listed in the Table 1 below were used in this study. These samples gave a wide range of ‘homopolymer’ or HD fraction value ranging from 0 to 55%.

Results and discussion

TREF results

Figure 4 shows the overlay TREF plot for four polyethylenes containing different amounts of high density component ranging from 0 to 54%. We define here the ratio of the area of the high temperature peak

Table 1 Polyethylene density and melt index

	Density /g mL $^{-1}$	Melt Index /g (10min) $^{-1}$
Novapol LDPE	0.919	2.30
Elite Insite-LLDPE	0.916	1.00
Metallocene hexene-LLDPE	0.919	0.85
AST octene-LLDPE A	0.918	0.55
AST octene-LLDPE B	0.920	2.35
AST octene-LLDPE C	0.920	1.00
Dowlex octene-LLDPE A	0.920	1.00
Dowlex octene-LLDPE B	0.920	0.85
Sclair octene-LLDPE	0.920	0.95
Novapol hexene-LLDPE	0.918	1.00

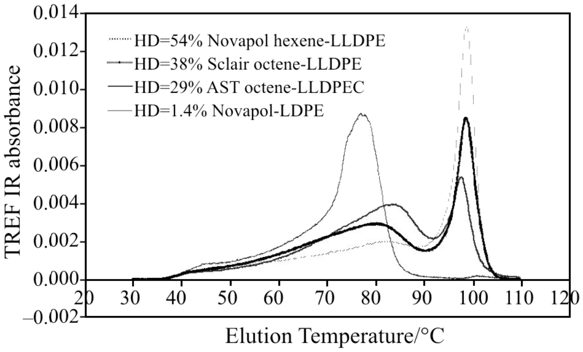

Fig. 4 Overlay plots of TREF data

above 90°C to the total area of the TREF intensity *vs.* temperature curve as a measure of the amount of high density component.

SSA STAF analysis

Figure 5 shows the comparison of the three programs, I, II, and III for sample AST LLDPE-C, where Program-I took 4 h, Program-II took 3 h, and Program-III took 2 h. There is no significant difference for the three different programs.

Figure 6a shows the dependence of % HD determined by Program-I, II, and III for the 11 samples on the % HD as determined by TREF. A correlation of 0.95 was obtained between these two methods. There was virtually no difference between Program-II and Program-III with Program-I as shown in Fig. 6b.

The overlay plots of the TREF and SSA STAF (Program-III) for 4 samples are as shown in Figs 7a to 7d. It can be seen that the two techniques yield essentially similar profile for the low temperature 'copolymer' fraction below 90°C, and very close value for the percentage fraction above 90°C.

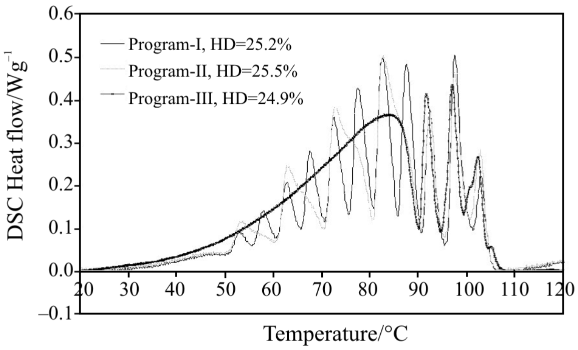

Fig. 5 Overlay plots of SSA STAF Program I, II and III method1 (Sample AST LLDPE-C, TREF measured HD=29%)

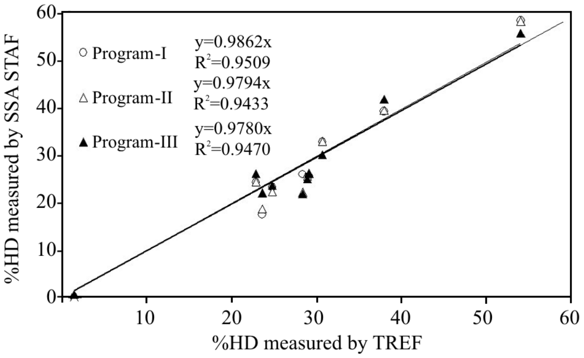

Fig. 6a %HD of TREF *vs.* % HD of SSA STAF

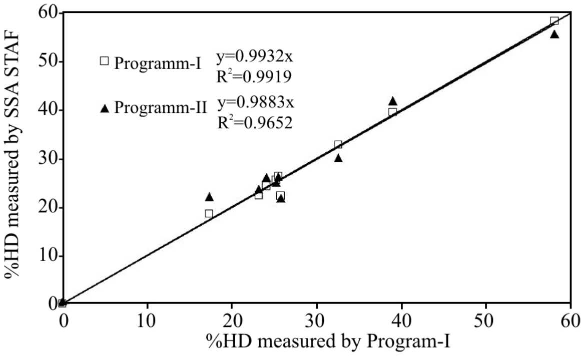

Fig. 6b %HD by Program II and III compared to Program I

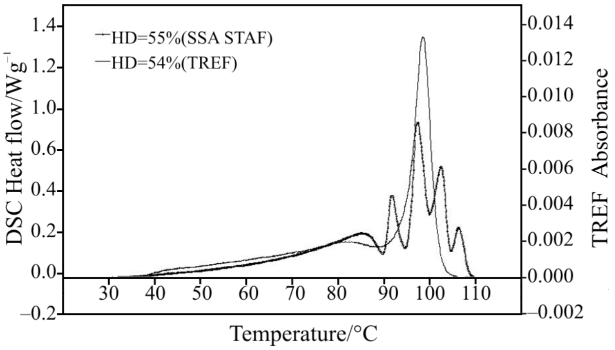

Fig. 7a Overlay plots of Novapol hexene-LLDPE

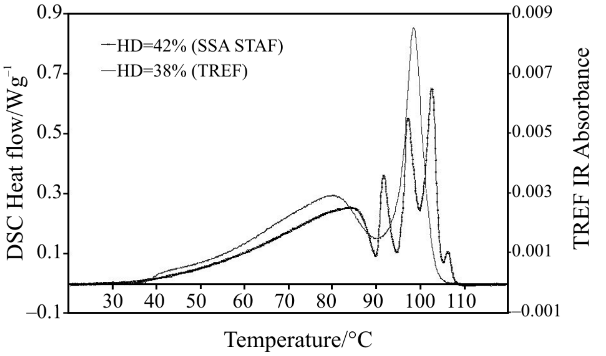

Fig. 7b Overlay plots of AST octene-LLDPE

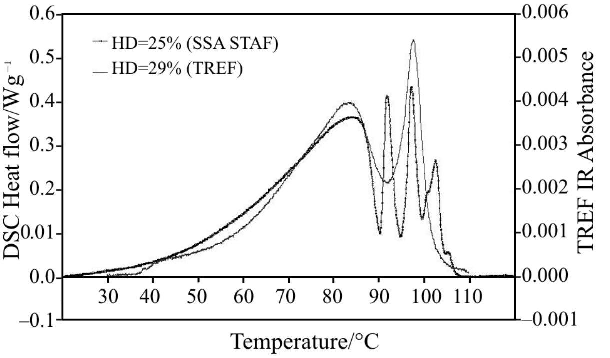

Fig. 7c Overlay plots of Sclair octene-LLDPE

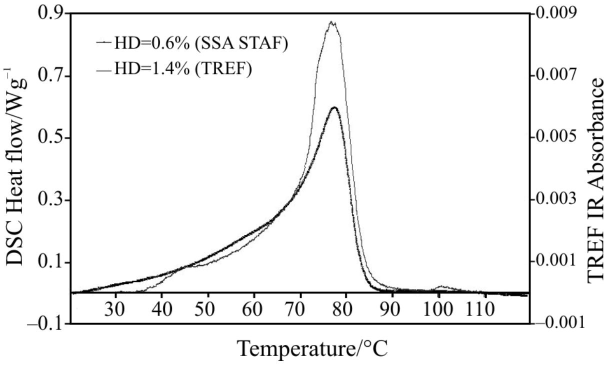

Fig. 7d Overlay plots of Novapol-LDPE

Discussion

It has been shown that the SSA STAF technique fractionated the polyethylene into a comonomer-rich fraction and a homopolymer fraction at a demarcation temperature of 90°C, similar to that exhibited in the TREF analysis.

Further it has been shown that the homopolymer fractions measured by TREF can be linearly related to that determined by the standard SSA STAF method. If the only interested parameter is the homopolymer fraction, it has further been shown that SSA STAF needs to be carried out only for the steps at temperatures above 90°C (the expected temperature demarking comonomer-rich and homopolymer fraction). This shortened the standard SSA STAF method from four hours to two hours, a critical improvement in test time required for fast analysis and turnaround results for offline reactor resins monitoring.

Conclusions

The successive self-nucleation annealing technique used in differential thermal analysis has been further improved by carrying out the process in the solvated mode. The resolution and degree of fractionation were shown to be similar to that obtained by TREF technique. The SSA STAF technique was shown to be able to provide quantitative data on the homopolymer fractions similar to the value obtained by TREF at a much shorter test time.

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Phil Edwards for supporting this work, Paul Tas for assisting in the method development and Nova Chemicals for permission to publish this work.

Appendix 1 DSC Program-I Thermal Steps for Standard SSA STAF test method –1 (4 h)

Step	Heating			Annealing time/min	Cooling		
	initial/°C	rate/°C min^{-1}	final/°C		initial/°C	final/°C	rate/°C min^{-1}
1	25	130	20	5	130	50	10
2	50	110	20	5	110	45	10
3	45	105	20	5	105	40	10
4	40	100	20	5	100	35	10
5	35	95	20	5	95	30	10
6	30	90	20	5	90	25	10
7	25	85	20	5	85	20	10
8	20	80	20	5	80	20	10
9	20	75	20	5	75	20	10
10	20	70	20	5	70	20	10
11	20	65	20	5	65	20	10
12	20	60	20	5	60	20	10
13	20	55	20	5	55	20	10
14	20	50	20	5	50	0	10
15	0	130	5				

DSC Program-I Thermal Steps for Standard SSA STAF test method –2 (4 h)

Step	Heating			Annealing time/min	Cooling		
	initial/°C	final/°C	rate/°C min^{-1}		initial/°C	final/°C	rate/°C min^{-1}
1	25	130	20	5	130	50	10
2	50	112.5	20	5	112.5	45	10
3	45	107.5	20	5	107.5	40	10
4	40	102.5	20	5	102.5	35	10
5	35	97.5	20	5	97.5	30	10
6	30	92.5	20	5	92.5	25	10
7	25	87.5	20	5	87.5	20	10
8	20	82.5	20	5	82.5	20	10
9	20	77.5	20	5	77.5	20	10
10	20	72.5	20	5	72.5	20	10
11	20	67.5	20	5	67.5	20	10
12	20	62.5	20	5	62.5	20	10
13	20	57.5	20	5	57.5	20	10
14	20	52.5	20	5	52.5	0	10
15	0	130	5				

Appendix 2 Modified DSC Program-II Thermal Steps for SSA STAF test method –1 (3 h)

Step	Heating			Annealing time/min	Cooling		
	initial/°C	final/°C	rate/°C min^{-1}		initial/°C	final/°C	rate/°C min^{-1}
1	25	130	20	5	130	50	10
2	50	110	20	5	110	45	10
3	45	105	20	5	105	40	10
4	40	100	20	5	100	35	10
5	35	95	20	5	95	30	10
6	30	90	20	5	90	25	10
7	25	80	20	5	80	20	10
8	20	70	20	5	70	20	10
9	20	60	20	5	60	20	10
10	20	50	20	5	50	20	10
11	0	130	5				

Modified DSC Program-II Thermal Steps for SSA STAF test method –2 (3 h)

Step	Heating			Annealing time/min	Cooling		
	initial/°C	final/°C	rate/°C min^{-1}		initial/°C	final/°C	rate/°C min^{-1}
1	25	130	20	5	130	50	10
2	50	112.5	20	5	112.5	45	10
3	45	107.5	20	5	107.5	40	10
4	40	102.5	20	5	102.5	35	10
5	35	97.5	20	5	97.5	30	10
6	30	92.5	20	5	92.5	25	10
7	25	87.5	20	5	87.5	20	10
8	20	77.5	20	5	77.5	20	10
9	20	67.5	20	5	67.5	20	10
10	20	57.5	20	5	57.5	20	10
11	20	47.5	20	5	47.5	0	10
12	0	130	5				

Appendix 3 Final DSC Program-III Thermal Steps for ‘Homopolymer’ fraction by SSA STAF test method (2 h)

Step	Heating			Annealing time/min	Cooling		
	initial/°C	final/°C	rate/°C min^{-1}		initial/°C	final/°C	rate/°C min^{-1}
1	25	130	20	5	130	50	10
2	50	110	20	5	110	45	10
3	45	105	20	5	105	40	10
4	40	100	20	5	100	35	10
5	35	95	20	5	95	30	10
6	30	90	20	5	90	20	10
7	20	50	20	5	50	20	10
8	0	130	5				

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