JOURNAL OF MATERIALS SCIENCE **26** (1991) 1856–1860

Time–temperature–transformation diagram of polyethylene: origin of the double population of lamellae

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The factors leading to the appearance of two lamellar populations in linear polyethylene were investigated using differential scanning calorimetry and mechanical spectrometry. Two systems which underwent identical thermal treatments but which differed by their polydispersity degree show similar lamellar thickness distribution curves. It was shown that the primary factor governing the breadth of the crystallite size distribution is not the dispersity degree of the molecular weight of polyethylene. A comparison of the dynamic mechanical behaviour and the lamellar thickness distribution curves of two systems which have different sheet thicknesses indicates the existence of a single population of lamellae for the thinner specimen and two populations of crystallites for the thicker film. Thus, the appearance of a broad distribution size of crystallites depends on the existence of a distribution of the cooling rate within the sample which induces a morphological gradient because of the well known low thermal conductivity of polyethylene. In addition, based on analysis of the isothermal crystallization behaviour of linear polyethylene carried out by means of a mechanical spectrometer, a time–temperature–transformation (T.T.T diagram) was established. Thus, by drawing on physical metallurgy concepts, an original interpretation for the appearance of two populations of lamellae based on different cooling rates within the sample is found.

1. Introduction

Using calorimetric data, a model developed from the Thomson equation [1] shows bimodal lamellar thickness curves in linear polyethylene [2]. It was thus shown that this polymer exhibits two mechanical α relaxations, termed α_1 and α_2, with increasing temperature and these are related to defect diffusion within thin and thick crystalline lamellae, respectively.

According to Alamo and Mandelkern [3], the existence of two crystallite populations could be due to the melting–recrystallization phenomenon which should occur on heating. However, the real presence of a double population of crystallites was proved by means of small-angle X-ray scattering experiments carried out at room temperature [4, 5]. Moreover, Freedman *et al.* [6] have shown two characteristic sizes of crystallites in linear polyethylene using transmission electron microscopy observations performed at room temperature.

It has been suggested that in polydispersed systems, the appearance of thick lamellae results from the crystallization of the high molecular weight chains during the keeping time at the crystallization temperature range, while low molecular weight chains which are ejected into the surrounding amorphous phase only crystallize on cooling to room temperature and form the thin lamellae [7]. According to Rault *et al.* [8], the effect of chain segregation in polydispersed systems during crystallization results from chain disentanglements which preferentially occur at low supercooling.

The present work attempts to interpret differently the presence of two crystallite populations in linear polyethylene. Our interpretation is supported by the kinetic behaviour of crystallization analysed by an original method: mechanical spectrometry.

2. Experimental details

2.1. Materials

The materials used in this study were two linear polyethylenes termed A and B, which show different polydispersity degrees (7 and 12, respectively), supplied by Dr Spitz (L.M.O., CNRS, Vernaison, France) and two samples C and D whose thicknesses are about 0.5 and 0.2 mm, respectively. Samples C and D were prepared by compression moulding at 170 °C of a high molecular weight linear polyethylene, supplied by the Hoechst Company, and then quenched in water at room temperature.

Table I gives the characteristic parameters of the samples analysed.

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TABLE I: Characteristics of the analysed systems (P: polydispersity degree; d: density; X_C: crystallinity content; e: sheet thickness)

Systems	M_N	M_W	P	d	X_C (%)	e (mm)
A	1.810^4	1.210^5	7	0.954	77	1.3
B	1.310^4	1.610^5	12	0.933	70	1.3
C	6.10^5	4.10^6	6	–	40	0.5
D	6.10^5	4.10^6	6	–	42	0.2

2.2. Thermal treatments

Sheets A and B were heated in an oven to 170 °C for 30 minutes in an N_2 atmosphere and then isothermally crystallized for 24 hours at 100, 110, 120 and 130 °C and then quenched in water at room temperature.

2.3. Differential scanning calorimetry (DSC)

Melting endotherms were recorded using a Perkin Elmer DSC 1B apparatus at a heating rate of 8 °C/min. The crystallinity index (X_C) of each sample was determined through the area of the melting endothermic peak. Using a model based on the Thomson equation [1] and previously described [2], the lamellar thickness distribution curves were determined.

2.4. Dynamic mechanical spectrometry

The inverted torsion pendulum was used in this study. This set-up provides the real (G') and imaginary (G'') parts of the dynamic shear modulus and $\tan\phi = G''/G'$ as a function of temperature (for one or several fixed frequencies) or frequency (under isothermal conditions).

3. Results and discussion

3.1. Influence of polydispersity on the lamellar thickness distribution

According to some authors' assumptions [7], the presence of two populations of crystalline lamellae results from the segregation of the chain during the keeping time at crystallization temperature. In this case, the breadth of lamellar size distribution curves should depend on the polydispersity degree of the system.

Fig. 1 shows the lamellar thickness distribution curves of the two systems A and B which differ only by their polydispersity degree and which are isothermally crystallized at 100, 110, 120 and 130 °C. These distribution curves display similar patterns and each system isothermally crystallized at 120 °C and 130 °C shows two populations of crystallites: the relative amounts of thin lamellae in systems A and B are almost identical.

It can be concluded that the polydispersity degree of the system is not the primary factor governing the width of the lamellar thickness distribution curve and the appearance of two crystallite populations.

3.2. Influence of the sheet thickness on the lamellar thickness distribution

In a previous paper [2], it was shown that a morphological gradient should occur within the sample on

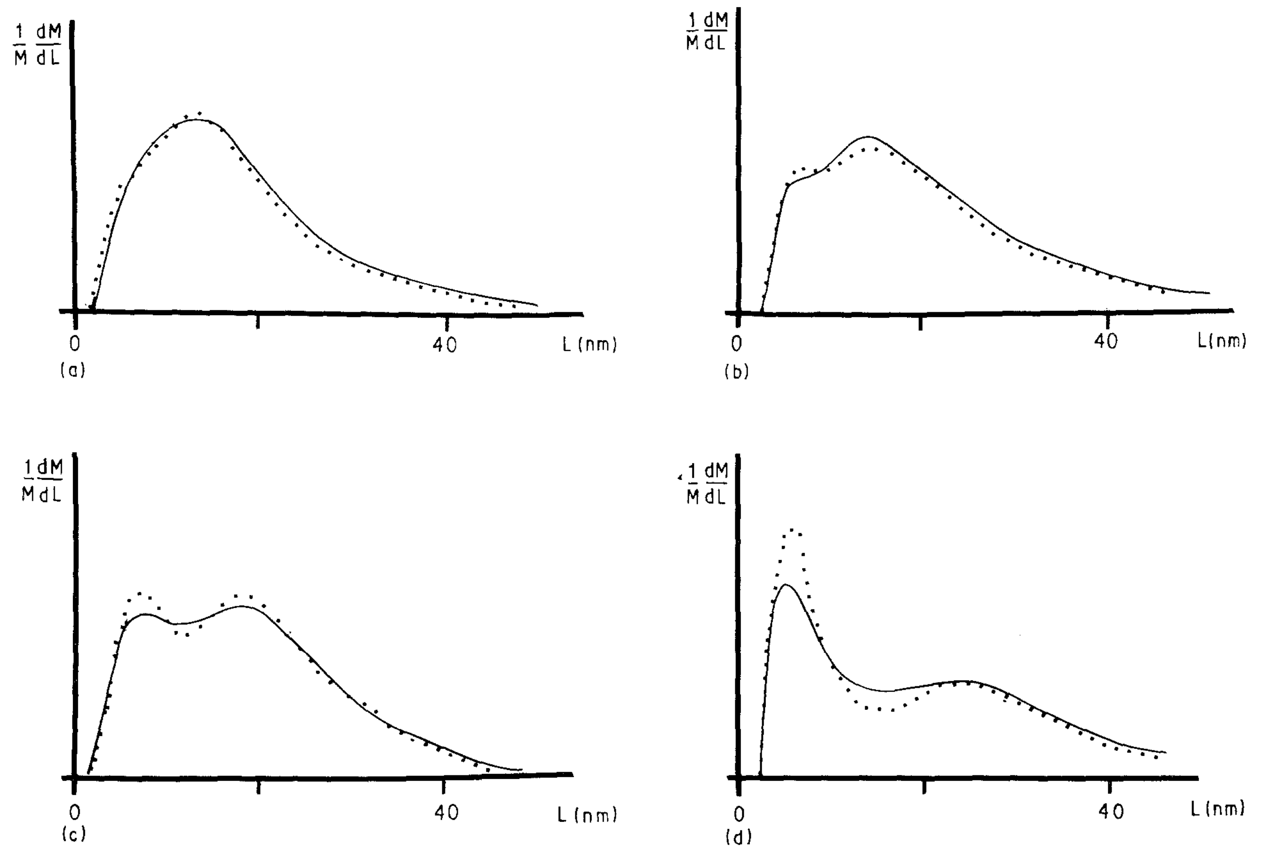

Figure 1 Lamellar thickness distribution curves of systems A (—) and B (· · ·) isothermally crystallized at: (a) 100 °C, (b) 110 °C, (c) 120 °C, (d) 130 °C.

cooling from the crystallization temperature to room temperature. Thus, a lamellar thickness distribution curve determined for a specimen drawn from the surface of a sample annealed at 130 °C exhibits a greater relative amount of thin lamellae than that of the sample core. It was suggested that the different pattern of the distribution curves displayed by the surface and core samples could be due to a thermal gradient occurring on cooling from annealing temperature to room temperature.

It follows that samples which undergo similar macroscopically thermal treatment but which are of a different thickness should have a different thermal gradient on cooling from crystallization temperature and so their microstructure should be different.

Two linear polyethylene films, systems C and D, which differ by their thicknesses, which are respectively 0.5 and 0.2 mm, were analysed by means of DSC and dynamic mechanical spectrometry. Fig. 2 shows the tan ϕ spectra at 0.1 Hz carried out in the α temperature range (from 20 to 120 °C) at a heating rate of 35 °C/h and the lamellar thickness distribution curves for both systems. Thus, the 0.2 mm thick sample shows a single α relaxation related to one population of lamellae while the sample which is twice as thick as the previous one displays two well defined α relaxations related to two populations of crystallites. These results prove the influence on sample morphology of the thermal gradient which occurs on cooling within the sample. Therefore, we can conclude that one of the primary parameters resulting in the width of the lamellar size distribution is the distribution of cooling rates within the sample.

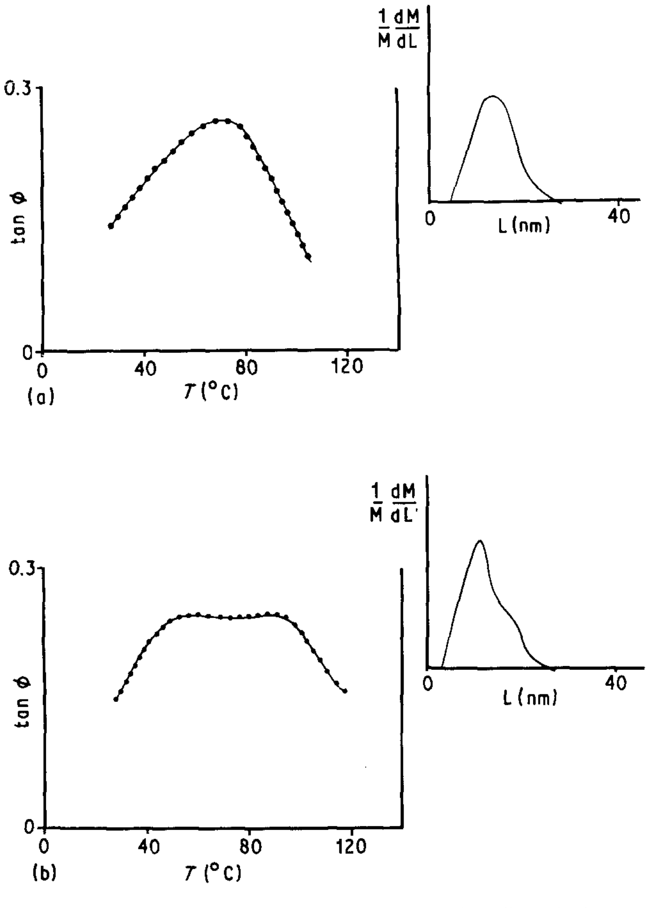

Figure 2 Isochronal spectra at 0.1 Hz and lamellar thickness distribution curves of: (a) 0.2 mm and (b) 0.5 mm thick polyethylene samples (C and D samples).

3.3. Crystallization kinetics of polyethylene; time–temperature–transformation diagram

Based on physical metallurgy concepts, we now attempt to give an original interpretation of the presence of lamellar size distributions within the sample and the presence of two populations of crystallites. Crystallization isotherms of system A were obtained using the mechanical spectrometer. The samples were heated *in situ* at a rate of 10 °C/min up to 170 °C and kept for 30 minutes at this temperature with a stream of oxygen-free dry nitrogen flowing over the sample. The isothermal crystallization temperature was reached by rapidly reducing the temperature. Thermal equilibrium at this temperature was obtained for a keeping time of 10 minutes. The evolution of tan ϕ as a function of keeping time, resulting from terms of the fraction of crystallized material, was recorded. The modulus G' is not a good probe for indicating the degree of phase transformation because stiffness also varies with the changes in size of the sample during crystallization. Moreover, in order to account for the measured parameter, tan ϕ also depends on the temperature; normalized values were used through

$$\tan\phi_N(t) = \frac{\tan\phi(t) - \tan\phi(\infty)}{\tan\phi(0) - \tan\phi(\infty)}$$

Plots of tan $\phi_N(t)$ versus time are shown in Fig. 3.

All the isotherms have a sigmoïdal shape typical of polymer crystallization behaviour. From these curves, a time–temperature–transformation diagram (TTT diagram) can be drawn (Fig. 4).

The two continuous lines give the time after which 5% and 95% variation in the normalized curves are obtained (beginning and end of crystallization, respectively). The dotted line curve shows the time needed for a 50% variation in the tan ϕ_N curve to be obtained (intermediate step of crystallization). In fact, because the nucleation and growth rates vary with temperature simultaneously, the isothermal transformation rate evolves globally. This transformation rate is related to the time required to obtain the same crystallized fraction y at various temperatures. By plotting the curves representing equal transformation, the TTT diagram can be drawn. The "C" shape of the TTT curves shows that there is a temperature range, wide in this case, where the crystallization rate is the greatest. It can be seen that crystallization begins in this temperature range for a short keeping time, probably less than 10 minutes which is the time required for thermal equilibrium. The nucleation rate increases when the temperature drops while the diffusion coefficient, which is related to the growth of crystals, decreases when the temperature is reduced. This results in an optimum temperature range of 105–120 °C. However, the parts of the TTT curves determined from the isothermal kinetics at temperatures below

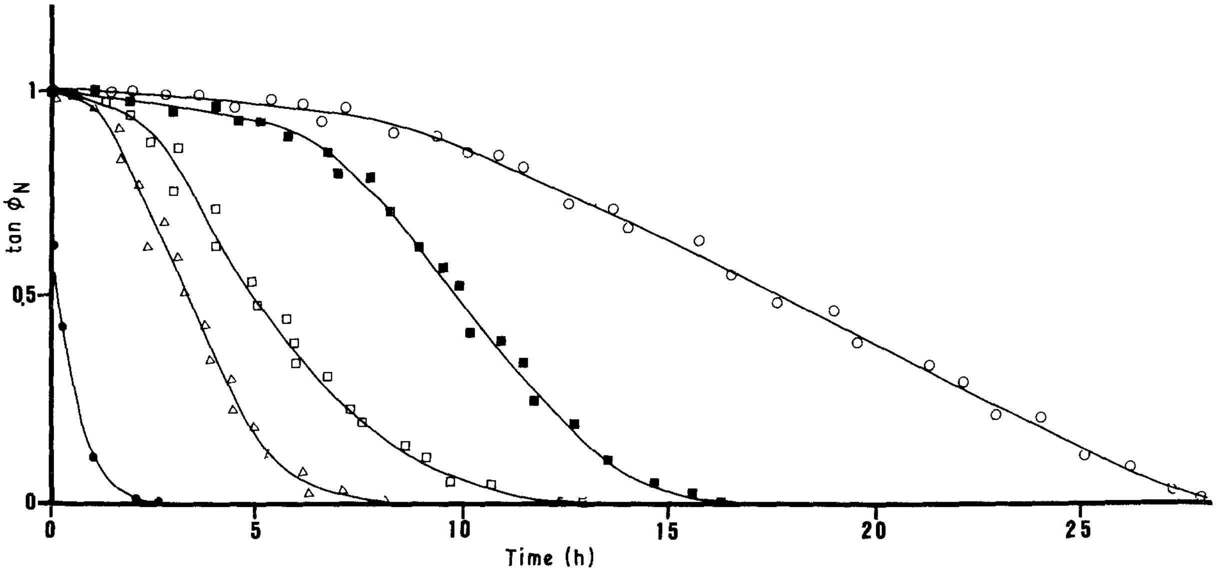

Figure 3 Plots of normalized values of tan ϕ (tan ϕ_N) versus time at different temperatures: (□) 100 °C, (●) 110 °C, (△) 120 °C, (■) 125 °C, (○) 130 °C.

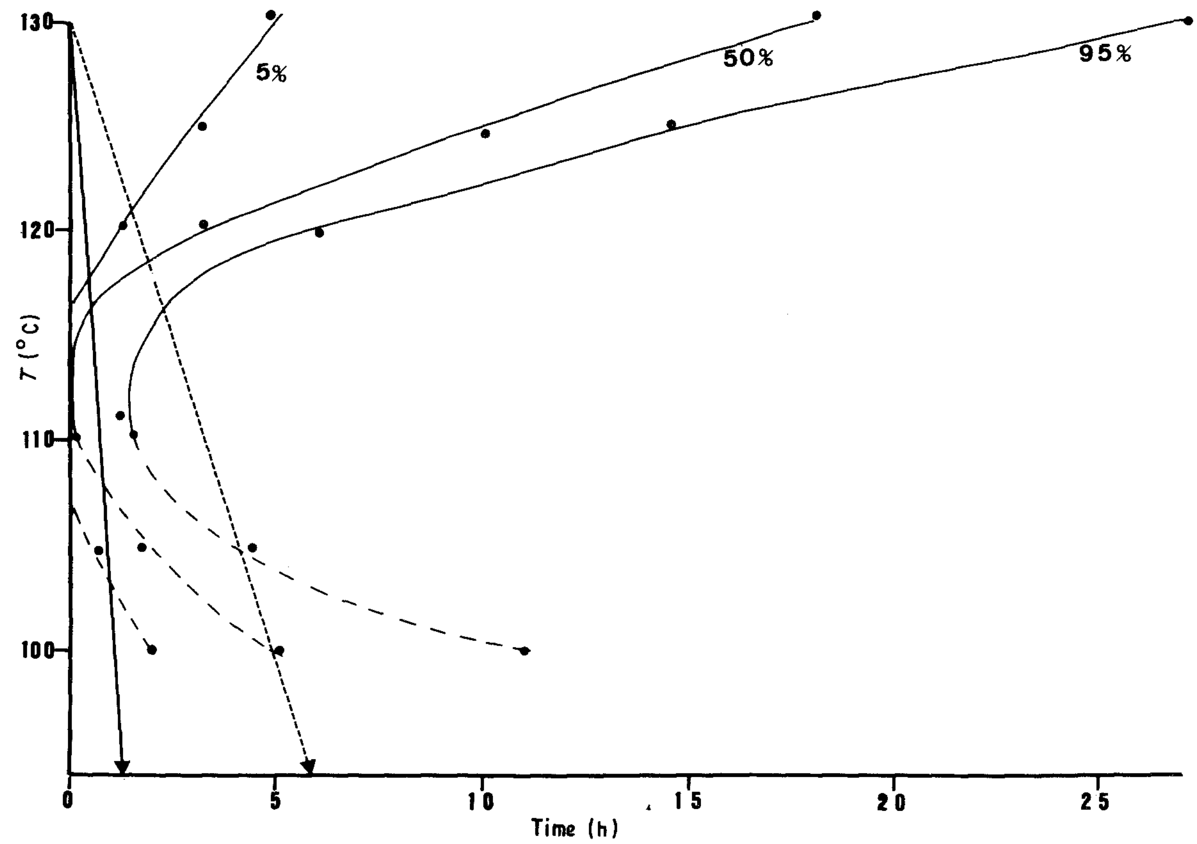

Figure 4 Time–temperature–transformation diagram. The continuous and dotted straight lines express, schematically, the cooling laws at the surface and core samples, respectively.

the crystallization "nose" do not just characterize the variation in the crystallized fraction because it was shown that the sample quenched from 170 °C to 20 °C (below the temperature range where the crystallization rate is maximum) shows a crystallinity index which is still high, about 40%. Then, as the cooling rate from 170 °C down to the isothermal crystallization temperature undergone by samples within the mechanical spectrometer is undoubtedly slower than that of samples directly quenched in water at room temperature, the initial crystallinity index of samples crystallized at temperatures below the TTT "nose" is probably higher than 40% and then isothermal variations of tan ϕ_N do not transduce only the crystallization evolution. Bearing this in mind, the presence of two populations of crystallites usually observed for polyethylene sheets of thickness up to 0.5 mm can however be interpreted from the "C" shape of the TTT diagram. For example, the thermal histories of two samples B isothermally crystallized at 100 and 130 °C and showing different patterns of distribution curves can be analysed as follows.

1. During the holding time at 170 °C, it is suggested that the previous thermal history is not completely erased; some residues of the previous crystalline organization remain because of the high viscosity of such a polymer. These residues could act as primary crystallization nuclei.
2. At the crystallization temperature of 130 °C (a temperature above the "nose" of the TTT curves), the rate of crystallization growth is higher than the nucleation rate. So, the primary nuclei, resulting from crystalline residues, grow and large lamellae are formed. On cooling from 130 °C to room temperature, the sample "crosses" the TTT curves. Thus secondary nuclei appear from the remaining uncrystallized fraction: small lamellae are formed, the quantity of which depends on the remaining uncrystallized material, i.e., the keeping time at this crystallization temperature.
3. To reach the crystallization temperature of 100 °C (a temperature below the "nose" of the TTT curves) from 170 °C, the second sample crosses the TTT curves. Few primary nuclei can grow on cooling so there is only a small quantity of crystallites formed. At the crystallization temperature of 100 °C, the nucleation rate is higher than the growth rate: new nuclei are formed and lead to the appearance of crystallites smaller than those developed on crystallization at 130 °C.

Thus, according to the description of the thermal histories undergone by samples isothermally crystallized at 100 °C and 130 °C, respectively, it is quite obvious that the sample crystallized at 130 °C shows more clearly the two populations of lamellae and the greater lamellae, experimentally observed. Moreover, the relative amounts of small lamellae should increase as the rate of crossing the TTT curves increases, i.e. as the rate of cooling from a crystallization temperature above the "nose" of the TTT curves increases. In Fig. 3, we have schematically drawn the patterns of cooling laws from 130 °C undergone by the surface and core samples, respectively. The number of large lamellae is higher for slow cooling rates, i.e. in the sample core because the TTT curves are crossed for a greater fraction of the transformed phase. However, superimposing cooling laws on the TTT diagram is not entirely justified. The determination of a transformation–continuous–cooling diagram (TCC diagram) should be better adapted to estimate the quantity of the transformed fraction as the temperature decreases. Nevertheless, by superimposing the schematic cooling laws on to the TTT diagram, the influence of cooling rate on the relative amounts of thin and thick crystallites can be qualitatively estimated. We can conclude from this study that the primary factor resulting in the appearance of a distribution of the size of crystallites is not the polydispersity degree of the polymer but the distribution of the cooling rate after thermal treatments within the sample.

The presence of two more or less well defined populations of crystallites results from the "C" shape of the time–temperature–transformation curve established from crystallization isotherms obtained by mechanical spectrometry.

Acknowledgements

The author wishes to thank Dr Vigier (GEMPPM INSA Lyon) for helpful discussions and Dr Spitz (LMO CNRS, Vernaison) for providing some of the polymers described in this study.

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Received 29 November 1989
and accepted 6 June 1990