

Relationship Between Impact Strength and Spherulite Growth in Linear Polyethylene

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INTRODUCTION

In a series of experiments designed to develop a thermal conditioning procedure for linear polyethylene it was observed that, if a sample was cooled from 150 to 50°C. at constant rate over a period of three to twenty-four hours, a considerable loss in impact strength occurred. On the other hand, if the sample was remelted and cooled quickly, it had excellent impact strength. Grams and Gaube,¹ in their studies of Ziegler-type polyethylene, observed that slow cooling yielded a large average spherulite size, while quenched samples evidenced a smaller average spherulite size. Finally, Reding and Brown,² in a study of polychlorotrifluoroethylene, attributed the greater brittleness of the polymer slowly cooled from the melt to the larger size and greater number of spherulites. Thus, there was good reason to believe that a relationship between spherulite size and impact strength of linear polyethylene existed and that an investigation along these lines would be of interest.

EXPERIMENTAL

Ziegler-type polyethylene powders containing no additives were pelletized and injection-molded sample disks prepared. The disks were sandwiched between glass plates and the distance between the latter, 3.4 mm., kept constant by means of steel wedges. (Since all samples were clamped between glass plates during thermal treatment, air oxidation effects were essentially eliminated.) The temperatures of the samples were measured by embedding a thermocouple in a polyethylene disk surrounded by the test disks. The samples were heated by placing the glass sandwich in a temperature-programmed oven, and they were quenched by immersing the glass sandwich in ice water. In our spherulite study, thin films were prepared by pressing molten polyethylene between two sheets of electrolytic tin plate. Films of desired thickness,

5-10 microns, could be obtained by a proper choice of temperature and pressure. The tin plates were separated and the film readily removed with a few drops of mercury which amalgamated with the tin and permitted lifting of the film from the disturbed surface. The film was then placed between two glass slides and thermally treated simultaneously with the specimens used for testing embrittlement. This method is superior to that of microtoming embrittled samples, since the latter technique frequently distorts the appearance and structure of the sample. Values for average spherulite size were based on the measurement of 50 spherulites as observed with a polarizing microscope. The disks were used for impact strength measurements with a Gardner Falling Ball Impact Tester. Molecular weights were determined by light scattering.

RESULTS AND DISCUSSION

A set of experiments was carried out on a sample of Ziegler-type polyethylene having a weight-average molecular weight of 175,000, to determine the lowest temperature from which a sample could be slowly cooled to 50°C. and embrittled thereby.

TABLE I
Effect of Starting Temperature on the Impact Strength of Conditioned Ziegler-Type Polyethylene (MW = 175,000)

Conditioning		Gardner impact strength, in.-lb.
Temperature, °C.	Time, hr.	
140-50	3	16
130-50	3	11
128-50	3	>112

Table I shows that, for starting temperatures of 140 and 130°C., only 16 and 11 inch-lb. of work, respectively, were required to crack these samples, *viz.*, they were embrittled. When the starting temperature was 128°C., the sample did not crack under an impact of 112 inch-lb. Thus it was established that, in order to induce brittleness in this particular sample, it was necessary to heat it to

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130°C. This corresponded to the melting point of the polymer, a fact which was experimentally obvious since the disks became transparent on holding at this temperature.

A second set of experiments was designed to determine the highest temperature from which the sample could be quenched and still yield the brittle structure.

TABLE II

Effect of Quench Temperature on the Impact Strength of Conditioned Ziegler-Type Polyethylene (MW = 175,000)

Conditioning		Gardner impact strength, in.-lb.
Temperature, °C.	Time, hr.	
130-115	3	38
130-120	3	15
130-122	3	15
130-124	3	>112

Again the conditioning cycle was three hours for all samples. Also, all samples were cooled at constant rates from the starting temperature, 130°C., as previously established. Now, if one examines the values for Gardner impact strength shown in Table II, an abrupt change is observed in samples quenched at 124°C. Thus, the highest temperature which will yield the brittle structure is just below the freezing point of the polymer; *viz.*, at 124°C. the sample disks were transparent and at 122°C. they were opaque.

Having established the temperature range for the formation of the brittle structure, a third set of experiments was designed to determine the effect of varying the cooling rate over this range. cursory examination of the data in Table III shows that, as the rate of cooling increases, the impact strength increases and the spherulite size decreases.

TABLE III

Effect of Cooling Rate on the Embrittlement and Spherulite Size of Ziegler-Type Polyethylene (MW = 175,000)

Conditioning time, hours for cooling from 130 to 122°C.	Approximate cooling rate, °C./hr.	Gardner impact strength, in.-lb.	Average spherulite size, μ
3	2.7	13	6.8
2	4	22	5.8
1	8	44	5.2
0.750	10.7	67	4.5
0.500	16	104	4.2
0.250	32	>112	4.0
0.002	400	>112	3.5

All of the measurements shown in Table III were made on samples which were cooled down at a constant rate starting at 130°C. Although it was

necessary to heat a sample up to 130°C. in order to melt it, once melted, it did not start to freeze until cooled to about 124°C. This suggested that, once the sample was melted, it could be cooled down quickly from 130 to 124°C., and then, if slowly cooled down to 122°C., one would still find a brittle structure. This was confirmed by the results shown in Table IV.

TABLE IV

Effect of Rapid Cooling of Molten Ziegler-Type Polyethylene (MW = 175,000) on the Degree of Embrittlement

Sample	Conditioning cycle, °C.	Cooling rate, °C./hr.	Gardner impact strength, in.-lb.
1	130-122	6	34
2	130-124	720	56
	124-122	6	

Sample 2 was first cooled from 130 down to 124°C. at the rapid cooling rate of 720°C./hr.; then it was slowly cooled from 124 to 122°C. at the same rate as Sample 1, *viz.*, 6°C./hr. The small increase in impact strength observed for Sample 2 simply means that the material probably started to freeze at a temperature slightly above 124°C., and we conclude that most, if not all, of the brittle structure forms while molten polyethylene is freezing. The question then arises: Does spherulite growth also take place only in this narrow temperature range?

TABLE V

Growth of Spherulites in Ziegler-Type Polyethylene (MW = 175,000) Cooled at a Constant Rate of 3.7°C./hr.

Temperature, interval, °C.	Average spherulite size, μ
129-120	5.3 \pm 0.3
129-112	5.1 \pm 0.3
129- 53	5.2 \pm 0.3

It is seen in Table V that there is no change in average spherulite size after the sample has cooled to 120°C., *viz.*, solidified. Of course, there are no spherulites between 129 and 125°C. when the sample is still liquid. Hence, it turns out that *both* spherulite growth and embrittlement occur while the sample is freezing. This result is also in line with some nuclear magnetic resonance measurement studies made by Slichter,³ who found that crystallinity persists in Marlex 50 to within a few degrees of the melting point and that chain rotation is comparatively restricted. Certainly one would not anticipate any spherulite growth under conditions of restricted chain rotation.

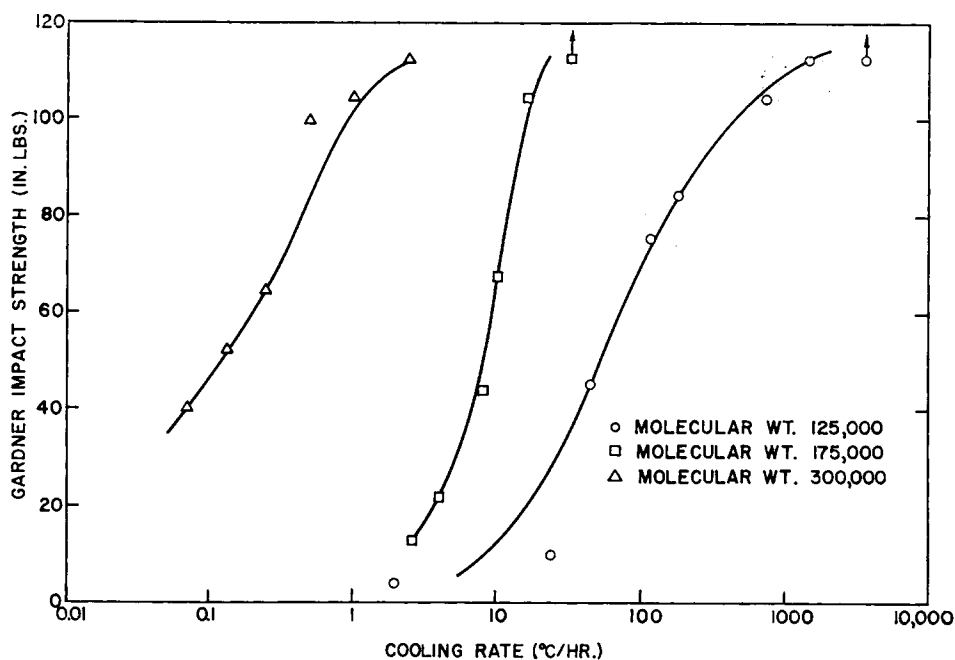


Fig. 1. Influence of cooling rate on Gardner impact strength of Ziegler-type polyethylene.

In order to round out this phase of our study, measurements similar to these were made on two other samples of Ziegler-type polyethylene having molecular weights of 125,000 and 300,000, respectively. Neither of the samples contained additives.

The influence of cooling rate on the Gardner impact strength is shown in Figure 1 for all three samples. In order to show the results for the three different molecular weights on a single graph, the cooling rate is plotted as a logarithmic function. It is to be emphasized that the conditioning cycles overlapped the freezing range of the polymers. Hence, precise control of starting and stopping temperatures was not necessary. The controlling factor was the cooling rate through the critical range which appeared to start at about 123, 124, and 126°C. for samples of weight-average molecular weight of 125,000, 175,000, and 300,000, respectively. In order to point up the sensitive relationships between molecular weight, Gardner impact strength, and thermal treatment, one can arbitrarily select a constant value for thermal embrittlement, say a Gardner impact strength of 60 in.-lb. Now, referring to Figure 1, one finds the following: a cooling rate of 0.2°/hr. for the high molecular weight material, 10°/hr. for the intermediate molecular weight material, and finally 70°/hr. for the low molecular weight material. Thus, if one wanted to limit thermal embrittlement to a value of 60, the material of molecular weight 125,000 has to be cooled through the freezing range 7 times faster than the material of molecular weight

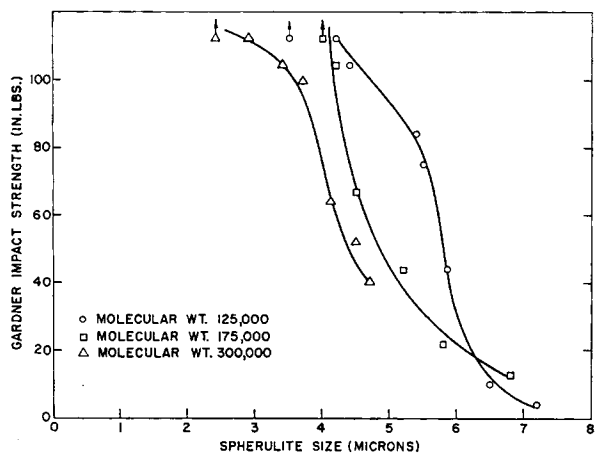


Fig. 2. Relationship between Gardner impact strength and spherulite size of Ziegler-type polyethylene.

175,000, and this latter material has to be cooled 50 times faster than a material of molecular weight 300,000. The two essential elements illustrated by this work are the following: (a) As the cooling rate decreases the impact strength decreases. (b) As the molecular weight decreases, the cooling rate through the freezing range must be considerably increased to minimize the loss of impact strength.

In Figure 2, the Gardner impact strength for each of the three samples of polyethylene is plotted against average spherulite size. It is seen that for each sample an increase in spherulite size is accompanied by a loss in impact strength. These

results lead one to the conclusion that the embrittlement observed here is a consequence of the rupture of amorphous chains strained by the formation and growth of spherulites. A similar idea was proposed by Kavafian⁴ to explain the *oxidative* embrittlement of Ziegler-type polyethylene.

At the same time, samples of a given impact strength will not have the same average spherulite size if the samples are of different molecular weights (Table VI).

For a given impact strength, the average spherulite size decreases with increasing molecular weight. Thus, it is obvious that a consideration of spherulite size alone does not fully account for embrittlement even under the conditions of these experiments.

An examination of the kinetics of spherulite growth helps to clarify this situation. Since it was established that there is no further spherulite growth below 120°C., the examination of spherulite size after various conditioning cycles is akin to

TABLE VI

Comparison of Impact Strength with Spherulite Size for Ziegler-Type Polyethylene Samples of Different Molecular Weights

Molecular weight	Spherulite size, μ	Gardner impact strength, in.-lb.
125,000	5.8	40
175,000	5.1	40
300,000	4.7	40
125,000	5.6	70
175,000	4.5	70
300,000	4.1	70
125,000	4.7	100
175,000	4.2	100
300,000	3.6	100

intermittent observation of a continuous growth process. In Figures 3, 4, and 5, spherulite size is plotted against conditioning time for the samples of weight-average molecular weights of 125,000,

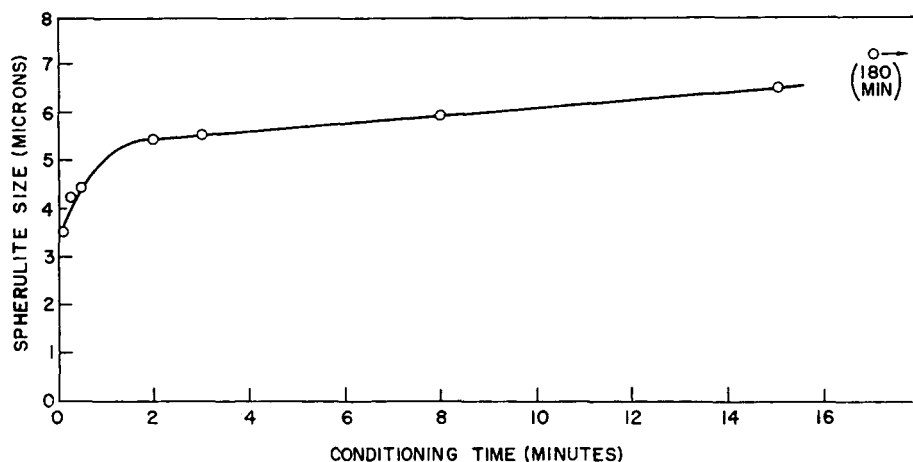


Fig. 3. Spherulite size of conditioned polyethylene: conditioning cycle, 128 to 122°C.; weight-average molecular weight, 125,000.

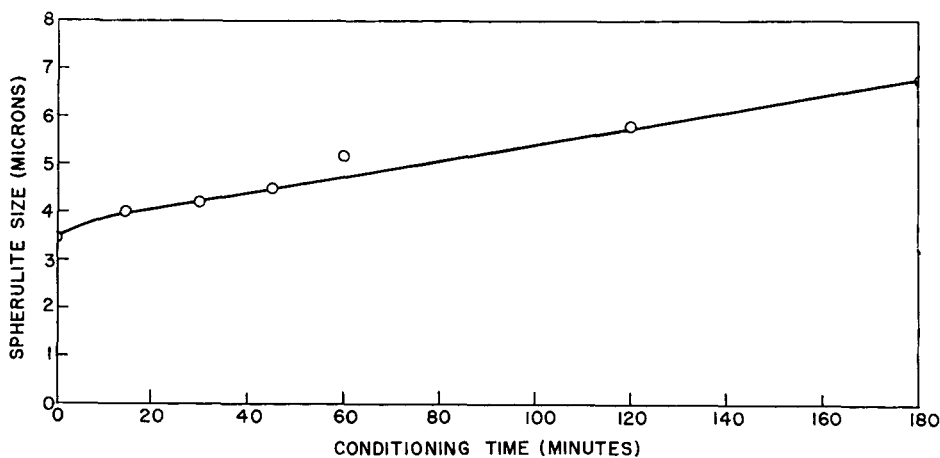


Fig. 4. Spherulite size of conditioned polyethylene: conditioning cycle, 130 to 122°C.; weight-average molecular weight, 175,000.

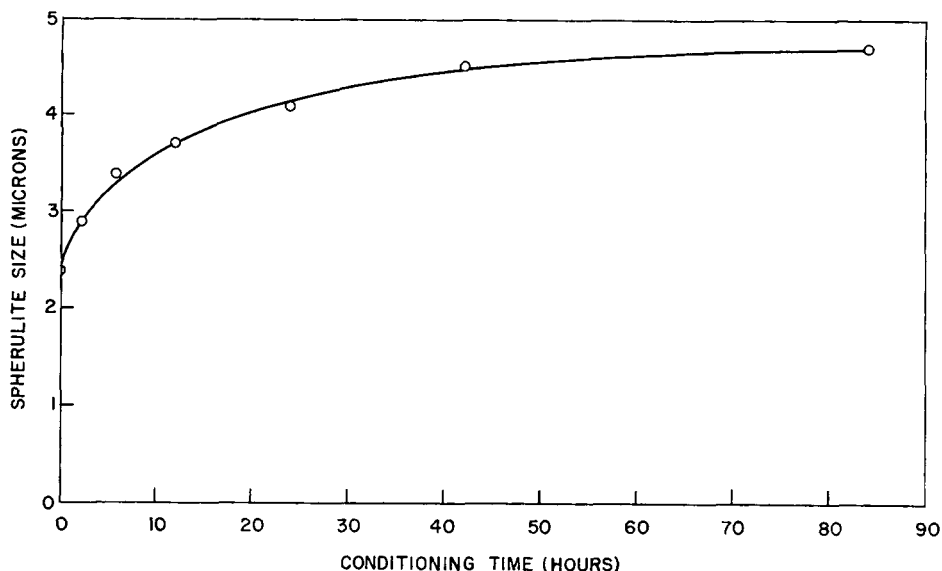


Fig. 5. Spherulite size of conditioned polyethylene: conditioning cycle, 128 to 122°C.; weight-average molecular weight, 300,000.

175,000, and 300,000, respectively. The great sensitivity of spherulite growth rate to molecular weight becomes apparent if one compares the conditioning cycle which corresponds to a particular average spherulite size for each of the molecular weights examined. For example, for an average spherulite size of 4.5 microns, conditioning cycles of 0.5 minutes, 45 minutes, and 2520 minutes are associated with the molecular weights of 125,000, 175,000, and 300,000, respectively. The evidenced decrease in growth rate with increase in molecular weight is not unexpected. A cluster of chain segments which make up a crystallite must move in a single direction if it is to participate in spherulite growth. Certainly the resistance to the movement of such a cluster will increase with increasing chain lengths of the molecules whose segments make up said cluster. At the same time, the stress on the amorphous segments of chains, most of which are participating in spherulite growth, will also increase with increasing molecular weight. This then would explain why the combination of small spherulites and high molecular weight can yield the same degree of embrittlement as the combination of large spherulites and low molecular weight.

As can be seen from Figures 3, 4, and 5, the function of spherulite size versus conditioning time is initially curved and then straightens out. It is proposed that a dual spherulite growth process occurs sequentially. As can be seen from Figure 6, the initial rate of spherulite growth is proportional to the square root of time; *viz.*, a diffusion controlled process is indicated.⁵

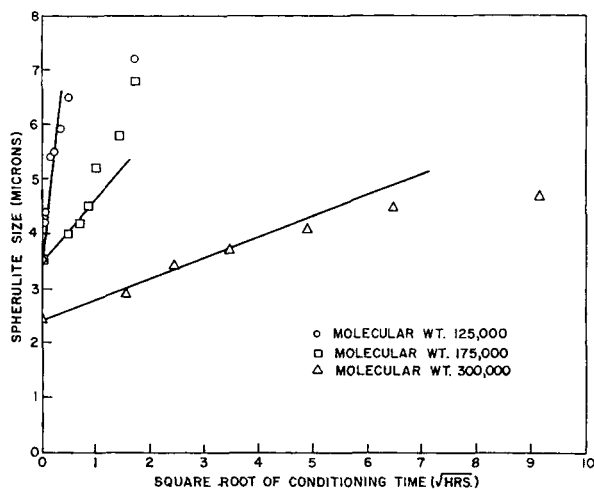


Fig. 6. Initial spherulite growth process in Ziegler-type polyethylene.

Thus, the initial rate of spherulite growth is governed by the diffusion of the latent heat of fusion away from the spherulite front. This means that spherulite formation and growth take place simultaneously with, or immediately after, crystallization. It is seen that the higher the molecular weight of the polyethylene sample, the slower the initial spherulite growth rate. This is in line with the fact that the thermal diffusivity of a liquid decreases with increasing viscosity. Thus, if the cooling rate of a process is such that only this initial spherulite growth stage occurs, one might be advised to characterize linear polyethylene by melt viscosity rather than by molecular weight. As for the second stage of growth, the process eventually

becomes linear with time in every case. This second type of growth implies a constant velocity of material transport per unit area across the spherulite boundary and could correspond to absorption of small spherulites by big spherulites. This, then, would account for the fact that, at virtually any stage in the growth process, all of the crystalline polyethylene is in the spherulite form and that spherulite size can vary independently of total crystallinity. Again, the rate of growth decreases with increasing molecular weight.

Finally, there is reason to believe that the nature of the spherulite growth characterizes the environmental stress-cracking behavior of linear polyethylene as well as its impact strength. Thus, we have demonstrated that a significant improvement in the impact strength of Ziegler-type polyethylene is realized by rapidly cooling the sample through the freezing point. A similar result had already been established by De Coste, Malm, and Wallder⁶ with respect to the environmental stress-cracking of branched polyethylene. But, at the same time, it was found that the improvement thereby achieved was temporary and disappeared after 35 days of shelf aging. This result is also in line with Slichter's³ nuclear magnetic resonance measurements, by which he found considerable chain rotation in branched polyethylene even at room temperature. The question then arises whether this effect is only temporary for a linear polyethylene. Although we have not made any environmental stress-cracking measurements, we believe that, should the increased resistance to environmental stress cracking obtained by rapid cooling be temporary for the case of linear polyethylene, we would also observe an increase in spherulite size. Spherulite sizes of rapidly cooled linear polyethylene, before and after aging at room temperature for six months, are compared in Table VII.

TABLE VII
Effect of Room Temperature Aging on Average Spherulite Size

Molecular weight of rapidly cooled sample	Average spherulite size, μ , initial	Average spherulite size, μ , after 6 months
125,000	3.5	3.6
175,000	3.5	3.4
300,000	2.4	2.7

As can be seen, the change in spherulite size is very slight, if any, and one can anticipate that the beneficial effects of rapid cooling are essentially permanent for a linear polyethylene.

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Synopsis

Samples of Ziegler-type polyethylene containing no additives were placed in a temperature-programmed oven, melted, and subsequently cooled at constant rates. Average spherulite size, based on the measurement of fifty spherulites, and impact strength by a falling ball method were determined for different cooling rates and for samples having weight-average molecular weights of 125,000, 175,000, and 300,000. It was found that both the formation of a brittle structure and the growth of spherulites occur over the relatively narrow temperature range in which the molten polymer passes from the liquid to the solid state. The rate of spherulite growth is initially proportional to the square root of time, *viz.*, diffusion controlled, but subsequently becomes linear with time. The spherulite growth rate decreases with increasing molecular weight. There is no change in spherulite size after aging six months at room temperature. The impact strength decreases with increasing average spherulite size; however, the lower the average molecular weight, the greater will be the impact strength for a given average spherulite size. The loss in impact strength is attributed to the rupture of amorphous chain strained by the formation and growth of spherulites.

Résumé

Des échantillons de polyéthylène du type Ziegler ne contenant pas d'additifs ont été placés dans un four à température contrôlée, fondus et ensuite refroidis à vitesse constante. La taille moyenne des sphérulites basée sur les mesures effectuées sur 50 sphérulites et la force d'impact par la méthode de la balle tombante ont été déterminées pour différentes vitesses de refroidissement et pour des échantillons de poids moléculaire moyen en poids de 125.000, 175.000 et 300.000. On a trouvé que la formation d'une structure cassante et la croissance des sphérulites se produisent dans le domaine relativement étroit de température lorsque le polymère fondu passe de l'état liquide à état solide. La vitesse de croissance des sphérulites est initialement proportionnelle à la racine carré du temps, c'est-à-dire régie par la diffusion et elle devient par la suite proportionnelle au temps. Il n'y a aucune variation de la taille des sphérulites après vieillissement de six mois à température de chambre. La force d'impact décroît avec l'accroissement de la taille moyenne des sphérulites; cependant au plus le poids moléculaire moyen est bas au plus grande sera la force d'impact pour une taille moyenne donnée des sphérulites. La perte de force d'impact est attribuée à la rupture de chaînes

amorphes tendues par la formation et la croissance des sphérolites.

Zusammenfassung

Proben von Polyäthylen vom Ziegler-Typus, die keine Zusätze enthielten, wurden in einen Temperatur-gesteuerten Ofen gebracht, geschmolzen und anschliessend mit konstanter Geschwindigkeit gekühlt. Die aus der Messung an 50 Sphärolithen erhaltene mittlere Sphärolithgrösse, sowie die nach einer Kugelfallmethode bestimmte Schlagfestigkeit wurden für verschiedene Abkühlungsgeschwindigkeiten für Proben mit einem Gewichtsmittelwert des Molekulargewichts von 125000, 175000 und 300000 bestimmt. Es wurde gefunden, dass sowohl die Bildung einer spröden Struktur als auch das Wachstum von Sphärolithen in dem verhältnismässig engen Temperaturbereich stattfindet, in

welchem das geschmolzene Polymere vom flüssigen in den festen Zustand übergeht. Die Wachstumsgeschwindigkeit der Sphärolithe ist anfangs der Quadratwurzel aus der Zeit proportional, also diffusionsbestimmt, wird aber dann linear mit der Zeit. Die Wachstumsgeschwindigkeit der Sphärolithe nimmt mit steigendem Molekulargewicht ab. Nach einer Alterung durch sechs Monate bei Raumtemperatur tritt keine Änderung der Sphärolithgrösse auf. Die Schlagfestigkeit nimmt mit zunehmender mittlerer Sphärolithgrösse ab; andererseits ist für eine gegebene mittlere Sphärolithgrösse die Schlagfestigkeit um so grösser, je kleiner das mittlere Molekulargewicht ist. Der Verlust an Schlagfestigkeit wird auf den Bruch von amorphen Ketten zurückgeführt, die durch die Bildung und das Wachstum von Sphärolithen überbeansprucht werden.

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