

Effects of Morphology and Molecular Structure on Tensile Impact Behavior of Linear Polyethylene

R. PRITCHARD, T. DUNN, and P. KELLY, *Celanese Corporation of America, Summit, New Jersey*

Synopsis

An instrumented tensile impact test which allows a load time curve to be obtained coincident with the energy to rupture values has been applied to the examination of a series of linear polyethylene homopolymers and copolymers of varying molecular weight and thermal history. The effect of test specimen geometry was also investigated. A morphological examination of these resins indicated a strong dependence of spherulite size on molecular weight, and to a much lesser degree on molding conditions; it appeared to be independent of comonomer. The overall crystallinity, as determined by both x-ray and density methods, and crystallite perfection was increased by a slower crystallization rate, but was independent of molecular weight. The tensile impact strength (energy to rupture) was found to increase with molecular weight, and decrease on the introduction of comonomer. But the effect of thermal history gave rise to results which bore no clear-cut relation to molecular and morphological parameters. The value of the instrumented tensile impact test is shown by the fact that these apparent anomalies can now be resolved by separating the elastic and plastic portions of the deformation. An increased level and perfection of crystallinity results in higher load bearing properties accompanied by a reduction in duration of impact. It is primarily the duration, rather than the peak load, which is affected by molecular weight. The main effect produced by changing from a type L (long) tensile impact specimen to a type S (short) was to reduce considerably the duration of the plastic region while simultaneously raising the maximum elastic load; this is thought to be associated with a more localized deformation and therefore a higher rate of strain.

INTRODUCTION

Several authors have described the effects of thermal history and the corresponding differences in crystallinity on the impact resistance of polyethylene test specimens.¹⁻³ Flexural impact tests are apparently more sensitive to slight inherent differences in crystallinity than the relatively simpler tensile impact type of test. The majority of these early data were obtained from impact testing machines which measure only the energy to rupture the specimen without any indication of the degree to which the energy is absorbed in elastic and plastic deformation of the specimen. The development of an instrumented tensile impact testing apparatus⁴ has made it possible to study the mode of failure by obtaining characteristic load-time curves coincident with the impact energy necessary to rupture the specimen.

By controlling the cooling rate of the polyethylene melt, it is possible to affect the per cent crystallinity, crystallite size, and spherulite size in the molded article. Five commercially available high density polyethylenes were subjected to slow- and fast-cooling rates. The effects of morphology, molecular weight, and test specimen geometry on the tensile impact strength (energy to rupture) and the corresponding load-time curves have been investigated.

EXPERIMENTAL

Polymer Characterization

Of the polymers examined, numbers 1, 2, and 3 were homopolymers, and 4 and 5 were ethylene-butene-1 copolymers. They ranged from a nominal melt index value of 0.2 (1 and 4) to 5.0 (3 and 5).

Number-average molecular weights \bar{M}_n were calculated from vinyl infrared absorption measurements, based on the assumption of one vinyl group per molecule. Weight-average molecular weights \bar{M}_w were calculated from inherent viscosity measurements (0.1% concentration by weight in tetralin at 130°C.) employing the relationship between η_i and \bar{M}_w developed by Stacey⁵ and confirmed by Wagner.⁶

Density measurements, using the density-gradient technique, were made on specimens cut from the molded plaques. These values were used to calculate per cent crystallinity from the formula⁷

$$D_c = \frac{d_c (d - d_a)}{d(d_c - d_a)} \times 100$$

where d_c is the density of the crystalline phase (=1.005), d_a is the density of the amorphous phase (=0.84), and d is the observed density. A comparison was made with the per cent crystallinity as calculated from x-ray diffraction by the method of Aggarwal and Tilley.⁸ Similarly, a measure of the crystallite size was obtained from the x-ray diffraction line broadening, following the Scherrer equation. These results are summarized in Table I.

Microtomed sections of the plaques were examined under polarized light, and the spherulitic structures observed are shown in Figure 3. Although the plaques and knife were frozen, sections of the fast-cooled plaques of high molecular weight resins deformed during cutting and show microtome marks. This has been found to occur only with small, imperfect spherulites.⁹

Specimen Preparation

The polyethylene molding pellets were compression-molded into 6.5 × 6.5 × 0.055 in. plaques by the picture-frame technique described by Rudin and Birks.¹ All samples were molded at a platen temperature of 150°C. with a platen pressure of 1000 psi. The molten polymer and molding assembly were either slow- or fast-cooled. The fast-cooling rate was de-

fined as the removal of the entire molding assembly from the press and cooling in a room temperature press at a platen pressure of 1000 psi. The slow-cooling rate was chosen arbitrarily and consisted of the following: after molding, the molding assembly was placed in a forced-draft oven heated to 160°C. and maintained at this temperature for 1 hr. before being cooled at the rate of 30°C./hr. to room temperature.

Tensile Impact Tests

Tensile impact tests were conducted on a pendulum-type, specimen-in-base tensile impact tester. Both the apparatus and the procedure employed are fully described elsewhere.⁴ A schematic diagram of the apparatus is shown in Figure 1. The output of the quartz load cell is relayed to an oscilloscope where it is photographed as a load-time curve. The energy lost by the pendulum in rupturing the specimen and tossing the rear clamp is measured mechanically by the indicating device. In turn,

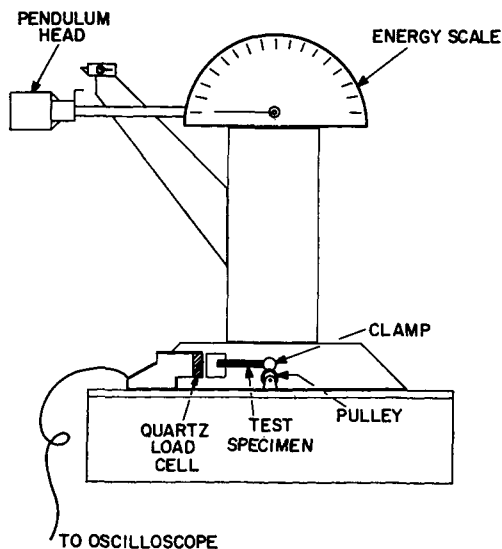


Fig. 1. Tensile impact apparatus.

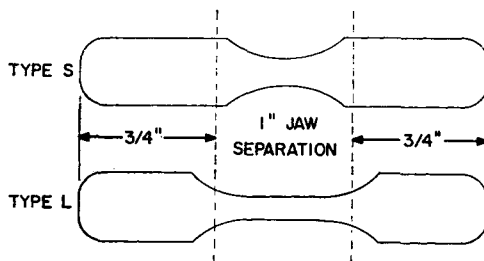


Fig. 2. Tensile impact specimens.

this scale reading is then converted to an energy to rupture value which, when divided by the minimum cross-sectional area of the specimen, is the tensile impact strength. The initial loading rate of the apparatus as depicted in Figure 1 is approximately 8100 in./min. (2 ft. free fall). The energy capacity of the tester is 5 ft.-lb.

Tests were conducted on specimens machined from the compression molded plaques. The specimen configurations are described in Figure 2 and are identical to those specified in ASTM Method D1822-61T.¹⁰ The specimen geometries are referred to as type S (short) and type L (long). The type L specimen has a relatively long geometric gage length, while the configuration of the type S specimen is such as to induce localization of the deformation incurred during impact.

RESULTS

Morphology

As indicated in Table I, \bar{M}_n remains relatively constant throughout the homopolymer series, in spite of large changes in the melt index; although there is some variation in \bar{M}_n for the copolymers, the most pronounced change for all five polymers occurs in \bar{M}_w , indicating a progressively broader molecular weight distribution.

The effect of cooling rate on the crystallinity of polyethylene specimens has been reported previously.^{1,11} A slower cooling rate gives rise to a pronounced density increase in all cases. The x-ray diffraction data are in good agreement with the per cent crystallinity calculated from density in the homopolymer series, but give higher values in the case of the co-

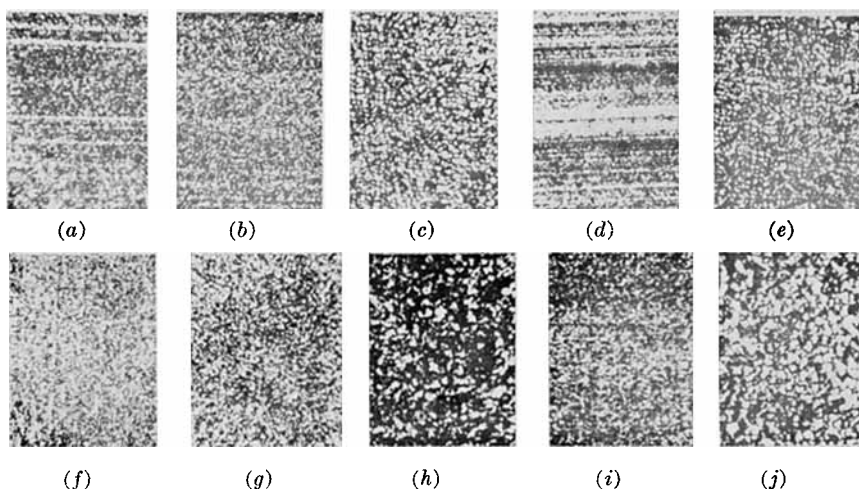


Fig. 3. Photomicrographs of (a-e) fast-cooled and (f-j) slow-cooled polyethylene samples: (a,f) $\bar{M}_w = 171,000$; (b,g) $\bar{M}_w = 137,000$; (c,h) $\bar{M}_w = 82,000$; (d,i) $\bar{M}_w = 160,000$; (e,j) $\bar{M}_w = 84,000$.

TABLE II
Tensile Impact Properties

Material designation	Type L specimen						Type S specimen								
	Region			Duration, msec.			Tensile impact, ft.-lb./in. ²			Region			Duration, msec.		
	Elastic max. load, lb.	Elastic load at failure, lb.	Plastic load at failure, lb.	Elastic region	Plastic region	Total duration	ft.-lb./in. ²	max. load, lb.	Plastic load at failure, lb.	Elastic region	Plastic region	Total duration	Elastic region	Plastic region	Total duration
Slow-cooled															
1	90	54	13	0.40	1.70	2.10	50	66	19	0.30	0.70	1.00	0.30	0.70	1.00
2	70	48	37	0.40	0.80	1.20	40	59	29	0.25	0.35	0.60	0.25	0.35	0.60
3	35	50	44	0.40	0.25	0.65	30	55	42	0.25	0.10	0.35	0.25	0.10	0.35
4	70	48	9	0.40	1.20	1.60	40	55	12	0.25	0.65	0.90	0.25	0.65	0.90
5	45	44	32	0.45	0.35	0.80	25	52	38	0.30	0.10	0.40	0.30	0.10	0.40
Fast-cooled															
1	80	48	0	0.35	2.05	2.40	45	58	0	0.35	1.20	1.55	0.35	1.20	1.55
2	70	46	0	0.35	1.75	2.10	45	59	0	0.35	1.00	1.35	0.35	1.00	1.35
3	60	45	11	0.40	1.00	1.40	35	47	20	0.25	0.35	0.60	0.25	0.35	0.60
4	70	44	0	0.30	1.85	2.15	40	51	0	0.30	1.30	1.60	0.30	1.30	1.60
5	50	37	0	0.45	1.25	1.70	30	43	16	0.30	0.30	0.60	0.30	0.30	0.60

polymers. This suggests that these techniques respond differently to the changes in polymer structure brought about by the introduction of comonomer. Although one cannot ignore the possibility that this discrepancy is due to the presence of internal voids, we interpret it as further evidence that under certain conditions comonomer units can be incorporated into, and expand, the crystal lattice.^{12,13} The use of a fixed value for the density of the polyethylene unit cell (d_c) irrespective of the amount and type of branching is then no longer justified, and caution must be exercised in relating density directly to degree of crystallinity.

Differences in crystallinity within either polymer series are slight for a given thermal treatment and apparently not affected by molecular weight within the range investigated. X-ray results confirm these observations, and in addition show no dependence of the average crystallite size on molecular weight. The crystallite size does, however, appear to be diminished in the copolymers.

The effects of cooling rate on the spherulitic structure of the samples studied is shown in Figure 3. This is relatively small compared with that due to \bar{M}_w , the polymers of lower molecular weight forming markedly larger spherulites. Similar effects using electron microscopy have recently been found by Bailey.¹⁴ No significant differences in structure between homopolymer and corresponding copolymer can be distinguished.

Tensile Impact

In this particular impact testing situation, tensile impact strength is defined as the energy required to rupture the test specimen. Within a polymer series, for either thermal treatment or specimen geometry, tensile impact strength decreases with decreasing \bar{M}_w . For a specific thermal treatment, converting to a more severe specimen geometry (L to S), decreases the tensile impact strength of all the polymers studied. The effect of cooling rate on tensile impact strength (energy to rupture), is, however, inconsistent. From a consideration of the tensile impact parameters summarized in Table II, it is apparent that tensile impact strength is affected by the load carrying capability of the material and the duration for which this load acts. It is not then surprising to find

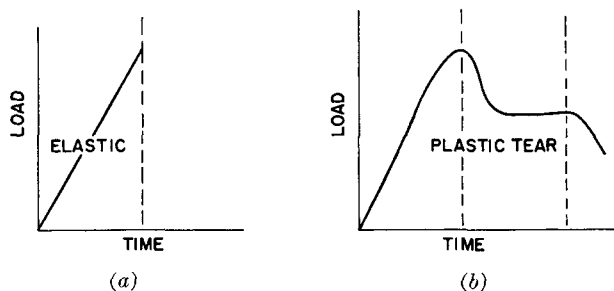


Fig. 4. Failure (a) within the elastic region and (b) in the plastic region

that materials possessing similar "energy-to-rupture" values have different characteristic load-time curves in spite of equivalent areas under the curves.

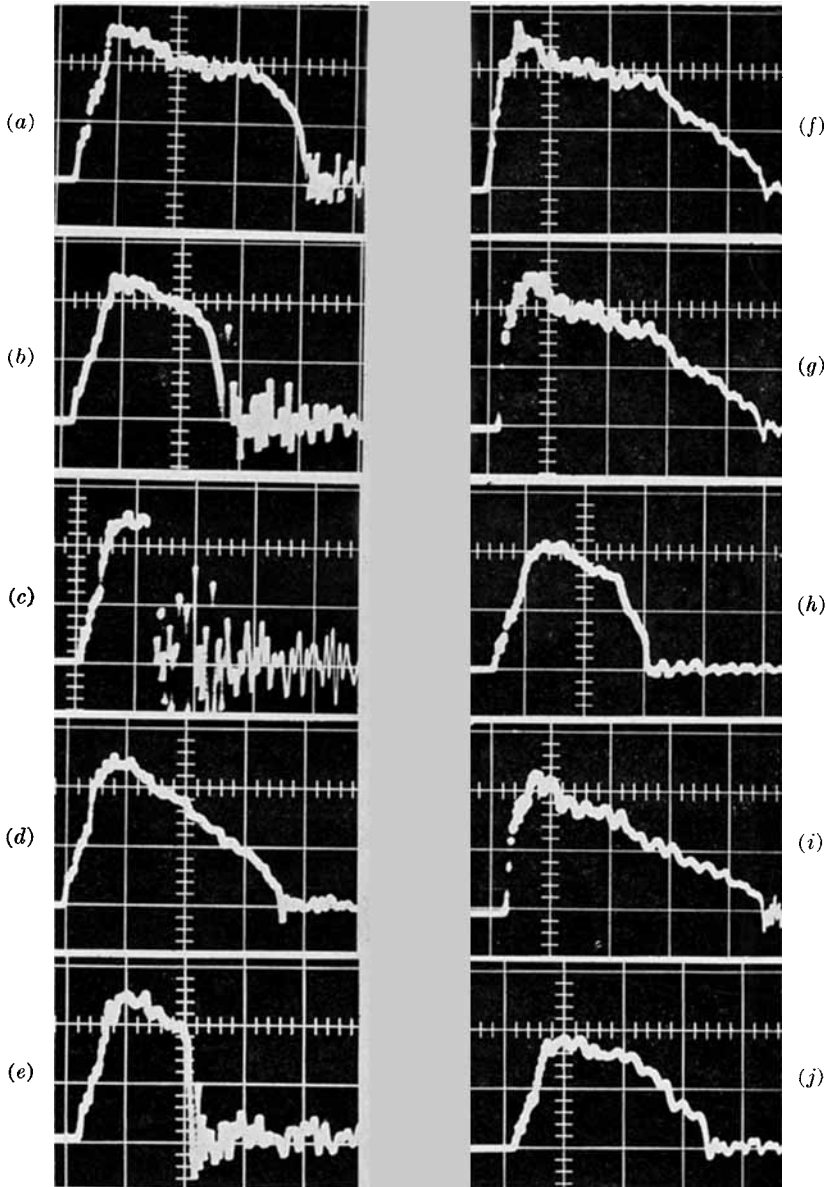


Fig. 5. Characteristic load-time tensile impact curves for type L specimens of (a-e) slow-cooled and (f-j) fast-cooled polyethylenes: (a,f) material 1; (b,g) material 2; (c,h) material 3; (d,i) material 4; (e,j) material 5. Material designations as in Tables I and II. Recording conditions: vertical, 1 cm. = 20 lb.; horizontal, 1 cm. = 0.5 msec.

Failure in a tensile impact test will occur within either of two general regions: elastic or plastic, as depicted in Figure 4.

It is generally accepted that in the plastic region, drawing, necking

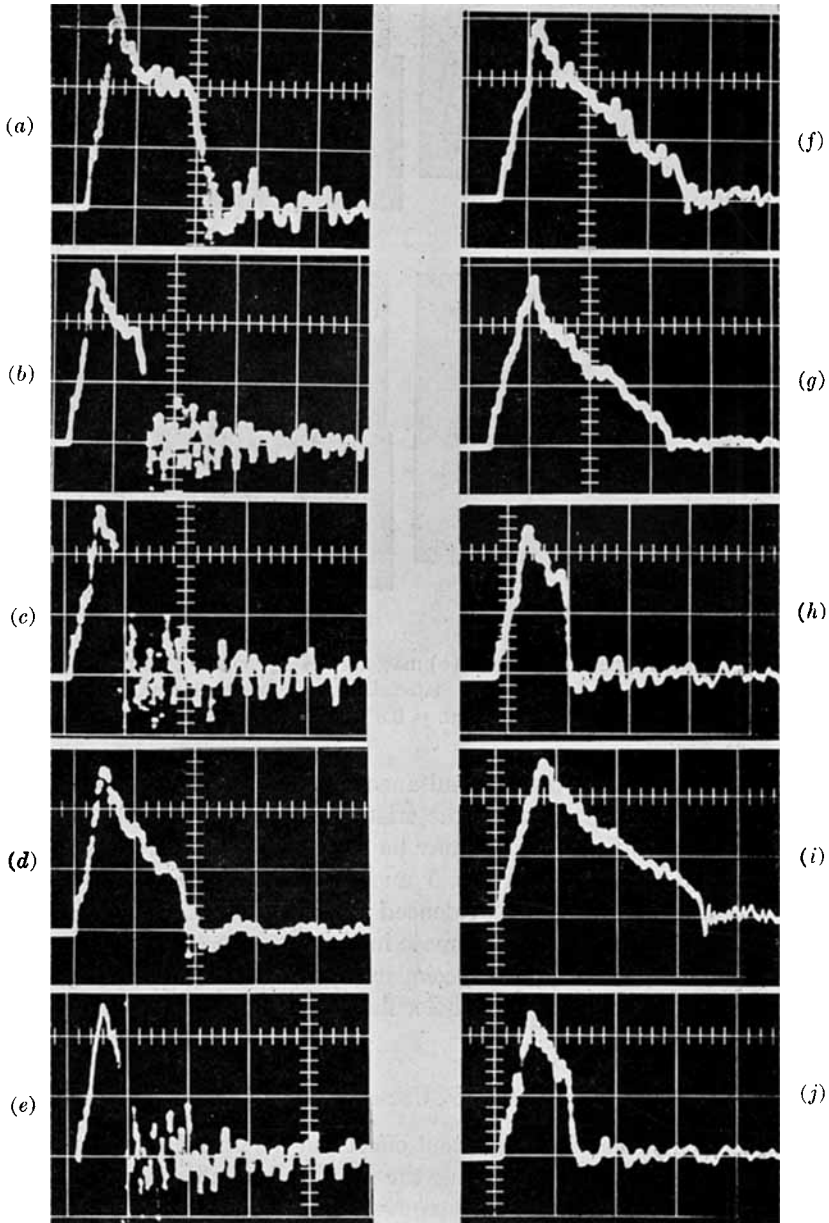


Fig. 6. Characteristic load-time tensile impact curves for type S specimens of (a-e) slow-cooled and (f-j) fast-cooled polyethylenes: (a,f) material 1; (b,g) material 2; (c,h) material 3; (d,i) material 4; (e,j) material 5. Material designations as in Tables I and II. Recording conditions: vertical, 1 cm. = 20 lb.; horizontal, 1 cm. = 0.5 msec.

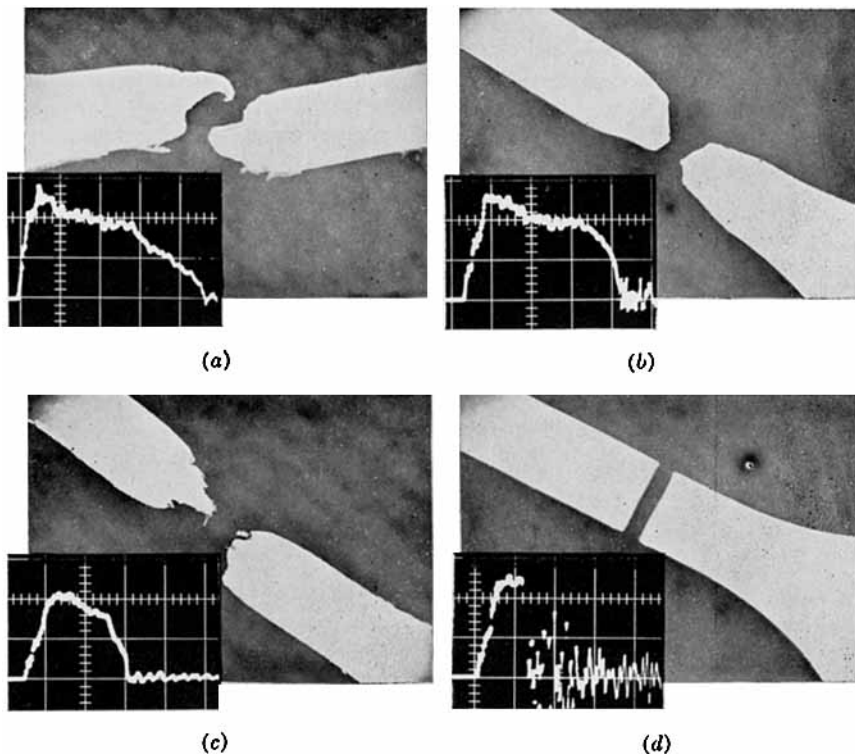


Fig. 7. Fractured type L specimen: (a) material 1, fast-cooled; (b) material 1, slow-cooled; (c) material 3, fast-cooled; (d) material 3, slow-cooled. Recording conditions: vertical, 1 cm. = 20 lb.; horizontal, 1 cm. = 0.5 msec.

down, and tearing may occur simultaneously. It is only after examining the tested specimen and its characteristic load-time curve that the predominance of a tear mechanism may be ascertained. In the actual load-time curves depicted in Figures 5 and 6 the predominance of a tear mechanism is most probably evidenced by the reduction in load (in the plastic region) with a gradual increase in the duration of impact. Photographs of the impacted type L specimens for materials 1 and 3 summarize the effects of crystallinity and molecular weight on the types of failure (Fig. 7).

DISCUSSION

As already mentioned, inconsistent effects on the tensile impact strength have been observed on increasing the overall crystallinity by a slower cooling rate. The value of the instrumented test is shown by the fact that these apparent inconsistencies disappear on considering the separate parameters involved.

In general, an increase in the amount and perfection of crystallinity leads to enhanced maximum loads in the elastic region and correspondingly

higher loads at failure, accompanied by a decrease in the duration of impact. Correspondingly, the total energy to rupture may increase or decrease. The effects of converting to a more severe specimen geometry are, in each case, similar to those found on increasing the crystallinity. Moreover, converting from a type L to type S specimen results in a reduction in the amount of drawing in the plastic region, with little effect on the amount of tear.

The molecular weight and spherulite structure are interdependent in this study, and it is not possible to separate their effects. However, the duration of impact decreases sharply with lower molecular weight and greater spherulite size.

In this paper the ambiguity of reporting one figure as a criterion of impact strength has been shown once again. The tensile impact strength of a material is affected both by the deformation incurred during the course of test, and by the force which acts during the deformation. The complex effects of morphology and molecular weights on these parameters have been demonstrated. Studies of this nature will lead to a better understanding of a material's "service" behavior.

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Résumé

On a étudié la résistance à l'impact (en tension) d'une série d'homopolymères et de copolymères de polyéthylène linéaires; l'instrument utilisé permettait d'obtenir une courbe de la tension en fraction du temps dont les valeurs coïncidaient avec l'énergie à la rupture. On a fait varier le poids moléculaire des divers polymères étudiés ainsi que leur histoire thermique. On s'est attaché également à déterminer l'effet de la forme de l'échantillon. Dans une étude morphologique de cette résine, on a trouvé que le volume des sphérulites dépendait fortement du poids moléculaire et beaucoup moins des conditions de moulage; le comonomère paraît ne jouer aucun rôle. Le taux de cristallinité (qui a été déterminé à la fois par des rayons-X et des mesures de densité) et la perfection

des cristallites, sont augmentés par une cristallisation lente mais ne dépendent pas du poids moléculaire. La résistance à l'impact en tension (énergie à la rupture) augmente avec le poids moléculaire et décroît lorsqu'on introduit un comonomère. On doit cependant remarquer que dans ces résultats l'influence du poids moléculaire et l'influence de la morphologie de l'échantillon sont considérablement marquées par l'effet de l'histoire thermique de l'échantillon. Néanmoins la valeur de l'instrument utilisé pour ces mesures permet de résoudre ces anomalies apparentes en séparant les portions élastiques et plastiques de la déformation. Lorsqu'on augmente le taux et la perfection des cristallites, on obtient un matériel qui a une plus grande résistance à la charge, ceci s'accompagne d'une réduction de la durée du choc. Le poids moléculaire affecte surtout la durée de l'application de la charge plutôt que son intensité. Lorsqu'on passe d'échantillons de type L (long) à des échantillons de type S (court) on réduit considérablement la durée de la partie plastique tandis qu'on augmente de manière simultanée la charge maximum élastique; on pense qu'il faut associer ce phénomène au fait que la déformation serait plus localisée et se produirait par conséquent à une plus grande vitesse d'élongation.

Zusammenfassung

Eine instrumentelle Zug-Stossprüfung, die eine mit den Bruchenergiewerten konsistente Belastungszeitkurve ergibt, wurde zur Untersuchung einer Reihe von linearen Polyäthylenhomopolymeren und -copolymeren verschiedenen Molekulargewichtes und thermischer Vorbehandlung herangezogen. Ausserdem wurde der Einfluss der Form der Prüfstücke untersucht. Wie aus einer morphologischen Untersuchung dieser Harze hervorgeht, ist die Sphärolithgrösse stark vom Molekulargewicht, viel weniger stark von den Formungsbedingungen und anscheinend nicht vom Comonomeren abhängig. Die mittels Röntgenbeugungs- und Dichtemessungen bestimmte Bruttokristallinität und die Vollkommenheit der Kristallite nehmen mit langsamerer Kristallisationsgeschwindigkeit zu, sind jedoch vom Molekulargewicht unabhängig. Die Zug-Stossfestigkeit (Bruchenergie) nimmt mit steigendem Molekulargewicht zu und sinkt bei der Einführung von Comonomerem. Der Einfluss der thermischen Vorbehandlung ergab allerdings keine deutliche Beziehung zu molekularen und morphologischen Parametern. Der Wert der instrumentellen Zug-Stossprüfung geht aus der Tatsache hervor, dass diese scheinbaren Anomalien jetzt durch Trennung des elastischen und des plastischen Deformationsanteils aufgeklärt werden können. Höhere und vollkommene Kristallinität führt zu höherer Belastbarkeit zugleich mit einer Abnahme der Schlagdauer. Das Molekulargewicht beeinflusst primär die Dauer und nicht die maximale Belastung. Der wesentliche Effekt beim Übergang von Zug-Stossprüfkörpern des Typs L (lang) zu solchen des Typs S (kurz) bestand in einer deutlichen Abnahme der Dauer des plastischen Bereiches bei gleichzeitiger Zunahme der maximalen elastischen Belastung. Man nimmt an, dass dies mit einer stärker lokalisierten Deformierung und daher einer höheren Dehnungsgeschwindigkeit im Zusammenhang steht.

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