

The Study of Cracking and Fracturing of Spherulitic Isotactic Polypropylene

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Introduction

This article deals with the cracking of isotactic polypropylene due to a spherulization mechanism and the effect of various amounts of spherulization on the fracturing and physical properties of that polymer.

In previous unpublished experiments it was noted by the author that isotactic polypropylene, when melted and subsequently crystallized at 125°C. under silicone oil, sometimes showed cracks between spherulite boundaries. Padden and Keith¹ have observed a similar type of cracking in polypropylene. In order to determine the exact mechanism of this cracking and its possible effect on the physical properties of polypropylene, the spherulizing process leading to cracking was studied dynamically.

Experimental

The Dynamic Observation of Spherulization

Films, two mils thick, of isotactic polypropylene were mounted in silicone oil between two cover glasses. The specimen was melted in a thermostatically controlled bath of silicone oil at 200°C. for one-half hour. Next, the specimen was quickly placed onto a heating stage mounted on a polarizing microscope. Photomicrographs were taken on 35 mm. film at 30 sec. intervals throughout the crystallization period. It was found that the observation and the photographing of the crystallization process could be better made with the use of the first-order red retardation plate which aided in characterizing the spherulites and especially in increasing the visibility of the nonbirefringent background. Because of the motions which take place in the growth of spherulites, a relatively fast shutter speed was needed ($1/2$ sec.); this necessitated the use of a high intensity light source and high speed film. The original photomicrographs were taken in color on high speed Ektachrome.

Dynamic Growth of Spherulites

Figure 1 illustrates the spherulitic growth process taken at 30 sec. intervals. Figure 1a shows the budding spherulites 1 min. after being placed on the crystallization stage. These young spherulites appeared as spheres which showed an unusually low order of retardation. (A quantitative estimate of retardation cannot be made from the black and white photomicrographs shown in this article; however, in the original color photomicrographs and even more so by visual observation, the order of retardation was quite evident.) The phenomena of weakly birefringent young spherulites was noted by Jenckel and Klein² in their studies on polyurethane.

Figure 1b shows growth at 1.5 min. By this time the retardation of the spherulites had increased. Figure 1c shows growth at 2 min., Figure 1d at 2.5 min., Figure 1e at 3 min., Figure 1f at 3.5 min., and Figure 1g at 4 min. At 4 min. the film in the field of the slide is completely saturated with spherulites.

Figure 1h shows the film at 4.5 min.; this figure shows that between 4 and $4\frac{1}{2}$ min. cracks have appeared between spherulite boundaries.

The reason for the appearance of cracks is believed to be related to the considerable contraction that is present in the formation of spherulites. Bunn³ states that this contraction may be of the order of 10%. The cracks appear to be similar to the type shown by Padden and Keith around polypropylene spherulites,¹ but different from those shown by van Schooten,⁴ who showed cracking of polypropylene sheets by oxidative aging in air at 135°C. Van Schooten's work shows cracks occurring principally through spherulite radii. In the present work, the mechanism cannot be principally oxidative since all operations have been carried out under silicone oil. Upon close examination of the photographs in van Schooten's work, many cracks may also be seen along the spherulite boundaries in addition to the radial cracks.

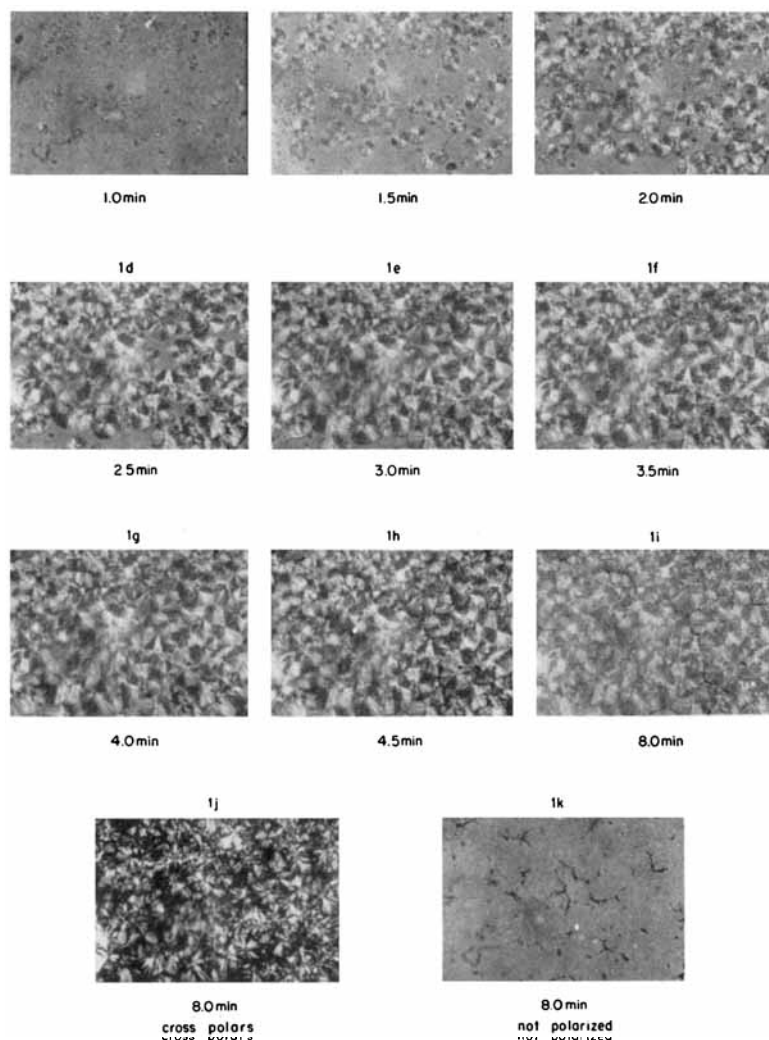


Fig. 1. Dynamic observations of polypropylene spherulization at 125°C. (Cross polars and first-order red plate except when noted): (a) 1 min., (b) 1.5 min., (c) 2 min., (d) 2.5 min., (e) 3 min., (f) 3.5 min., (g) 4 min., (h) 4.5 min., (i) 8 min., (j) 8 min. cross polars, (k) 8 min. not polarized.

It is also interesting to note the fine lines circling the spherulite centers. It is presumed that the boundaries of these spherulites, in cracking, allow strains to be released and thus allow the spherulites to dome up. This sudden doming probably pops the cover glass up and breaks the continuity of the silicone oil film. The oil, due to capillary effects, would tend to gather around the top of the dome and the cover glass; the edge of the oil around the center of this spherulite would appear as a circle around the dome. It is believed that doming to some degree is present even if cracks do not appear. Photographs of domed spherulites have appeared often in the literature.

If these spherulites are indeed domed, then it is

obvious that the thickness at the center of the spherulite is greater than that at the circumference. This thinner area near the circumference should therefore be weaker than at the thicker center. The effect of these weaker spots on fracture will be discussed later.

Figure 1*i* shows the film after 8 min. of crystallization; the cracking has not increased. However, some of the circles around the center of the spherulite have become less intense, perhaps due to a redistribution of silicone oil. Figure 1*j* shows the sample after 8 min. of crystallization, taken between crossed polars without the first-order red retardation plate. In this case the cracks are not visible which indicates an advantage of using the

first-order red retardation plate in cracking studies. Figure 1*k* was photographed without polarizers and the cracks appear clearly.

Effect of Spherulites on Physical Properties

It is obvious that if the internal cracking phenomena occurred to any large extent the polymer would literally fall apart. This type of behavior has actually been described by Padden and Keith,¹ where the individual spherulites "could be separated, one from another, with the fingers like pieces of a jigsaw puzzle." However, in the course of the present experiments, in the majority of cases, cracking was either very minor or did not occur at all. The cracking phenomena of completely spherulitic films at temperatures other than 125°C. was also rare. Cracking was never observed in partially spherulitic films.

Obviously, since cracking occurs rarely, the case of a polymer with extremely poor physical properties due to internal cracking would seldom be encountered. Because of its more common presence, the effect of partially spherulitic or completely spherulitic noncracked polymer on physical properties is probably more important. Thus a study of noncracked partially spherulitic and nonspherulitic films would be of more practical interest than a study of cracked films. Of particular interest would be the effect of the degree of spherulization on the physical properties of these noncracked polymers. A series of varying degrees of spherulization was chosen for these experiments: non-spherulitic (quenched), partially spherulitic (2 min. of crystallization), completely spherulitic (10 min. of crystallization), original nontreated film.

The method of preparation of the above films paralleled that used for those prepared on the hot stage in the cracking experiments. Two mil films were again mounted in silicone oil between two cover glasses and melted in a silicone oil bath for one-half hour. After melting, they were crystallized in a silicone crystallization bath at 125°C.; one sample was crystallized for 2 min.; another sample was crystallized for 10 min. After the required time, the crystallized samples were quenched in acetone at -70°C. As a control, the other sample was melted in the identical manner to the crystallized sample but was quenched immediately to prevent crystallization. After quenching, the samples were removed from between the cover glasses, cut into dumbbells, and measured for width, thickness, and birefringence.

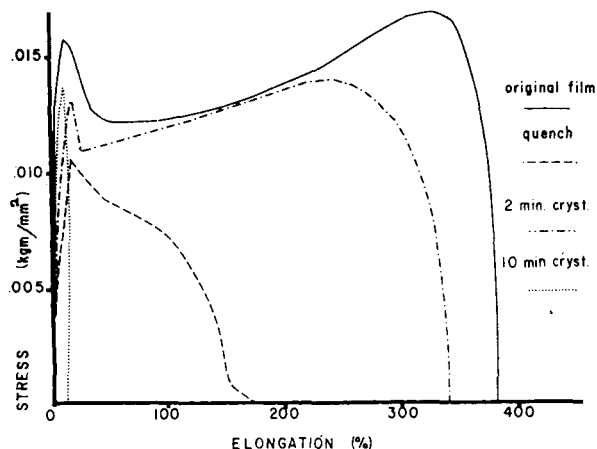


Fig. 2. Effect of spherulization on tensile properties.

The specimens were next mounted in an Instron tensile tester and elongated at an extension rate of 100% per minute; the stresses were normalized to cross-sectional area. The resulting stress-strain curves are shown in Figure 2. As can be seen from this figure, the yield point and the stiffness to yield appear to increase with an increase of spherulization, the exception being the original sample. This generally agrees with the work of Starkweather and Brooks,⁵ who found similar results with nylon. The original sample, that which had not gone through any treatments, can be seen to have a high strength and to neck very well. The sample crystallized for 2 min. necks quite well, but not as much as the original sample. The quenched sample is quite weak and necks very poorly. The sample crystallized for 10 min., although initially very strong, is extremely brittle and does not appear to neck at all.

After being broken in the stress-strain tests, the necked portions of the samples were measured for birefringence and compared to the birefringence before stretching. These values may be seen in Table I. The untreated film shows birefringence

TABLE I
Birefringence of Crystallized Polypropylene Film

	Birefringence
Untreated film	0.00121
Untreated film stretched	0.0245
Quenched film	0
Quenched film stretched	0.00577
Crystallized 2 min.	Spherulites and 0
Crystallized 2 min. stretched	0.0136
Crystallized 10 min.	Spherulites
Crystallized 10 min. stretched	Spherulites

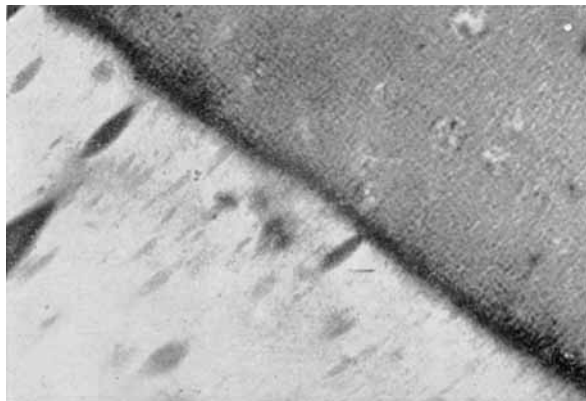


Fig. 3a. Transition lines between necked and unnecked portions of the films (cross polars and first-order red plate).



Fig. 3b. Area of drawn film further away from the neck.

caused by the manufacturing process; no spherulites were visible. On stretching this sample to break in its oriented direction its birefringence increased approximately twentyfold. The quenched sample showed zero birefringence originally; upon stretching to break, it became only moderately birefringent; no spherulites were visible. The sample crystallized for 2 min. showed spherulites in a nonbirefringent matrix, and on stretching showed a substantial birefringence. The sample crystallized for 10 min. was completely spherulitic before straining and after straining, no distortion or change could be seen in the nonfractured areas; also, no necking was apparent.

The mechanism of the distortion of spherulites in the partially spherulitic film (crystallized 2 min.) through the neck was most interesting. The necked area of this sample was photographed between crossed polars and the first-order retardation plate (Fig. 3a). In this figure the stretching direction is shown from the upper right to the lower left with the unnecked portion at the upper right. Before reaching the necking point, the spherulites lie apparently undisturbed. Beyond the necking point, the spherulites begin to be drawn out into ellipsoidal figures.

The drawing out of small spherulites into streak-like material has been illustrated by Bryant⁶ and Keith and Padden⁷ on polyethylene, Jenckel and Klein² on polyurethane, Starkweather et al.⁸ and Langkammer and Catlin⁹ on nylon.

In Figure 3a a very interesting single spherulite can be seen, apparently not drawn out at all, embedded beyond the necked area showing that occasionally a spherulite will not be drawn out. In an

area further away from the necking point, the spherulites can be seen to be drawn out further into lines (Fig. 3b).

Considering the stress-strain curves, the birefringence data, and the visual observations made of the noncompletely spherulitic films, it may be concluded that the tensile and drawing properties are probably quite dependent upon the crystallinity of the sample. The untreated original sample shows superior tensile properties and a very large increase of birefringence on stretching, probably due to its high initial crystallinity. The quenched sample shows very poor physical properties and shows a much lower increase in birefringence on stretching, probably due to its lower crystallinity. The sample crystallized for 2 min. shows quite good physical properties and can be drawn to a high birefringence. As can be seen from Table I, this sample has no initial birefringence in its matrix; however, the matrix is probably more crystalline than that of the amorphous sample.

The completely spherulitic film (10 min. of crystallization) will be considered separately. The birefringence of this film was not measurable since it was completely spherulitic before and after stretching. The stress-strain behavior showed very brittle breaks with no necking (Fig 2). A study of the fracture of this film was most interesting. Figure 4 shows a portion of the broken film where both fragments were jigsawed together. As was the case in the mechanism of cracking during spherulization, the fracture due to stress was generally along the outside border of the spherulite, analogous to the breaking of metals at crystal boundaries. Keith and Padden⁷ have

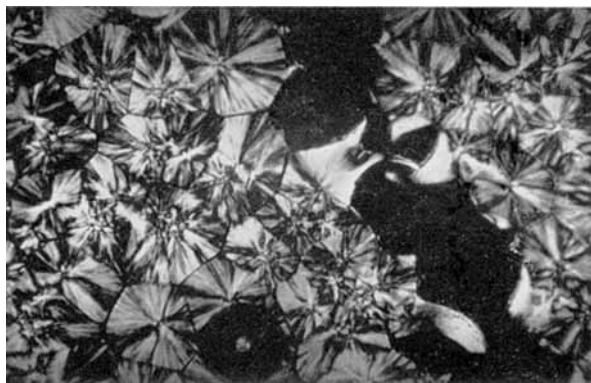


Fig. 4. Fracture of a completely spherulitic film (broken 100% per minute extension).

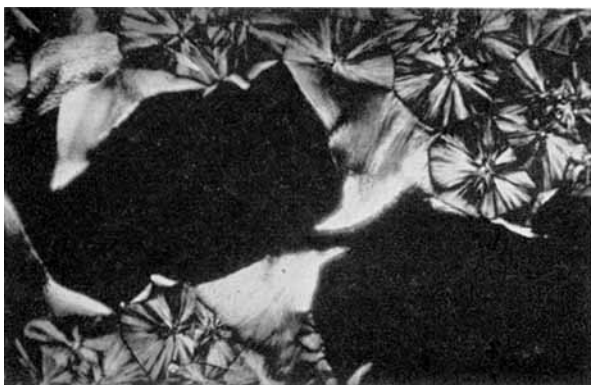


Fig. 5. Fracture of a completely spherulitic film (broken 20% per minute extension).



Fig. 6. Fracture of a completely spherulitic film (broken at high rate of speed).

observed this type of fracture in polyethylene spherulites which were of fine texture; coarse spherulites yielded breaks which showed irregular paths regardless of spherulite boundaries. The weakening of polypropylene spherulite boundaries due to oxidative mechanisms was predicted by Kefavian.¹⁰

The rupture along spherulite boundaries of isotactic polypropylene noted in the present work is different from the type found in other polymers. Reding and Brown¹¹ found that in polychlorotrifluoroethylene, the spherulites break along the radius. Leeuwerik¹² found that for Teflon the fissures appeared to originate at the nucleating centers and do not pass through the main boundaries. Reding and Walter¹³ have found that stressed polyethylene tends to develop radial cracks within the spherulites.

The effect of the rate of extension upon the nature of fracture in completely spherulitic films was next investigated. It may be seen in Figure 4 that the material drawn out of spherulites at 100% per minute showed positive birefringence and, as noted previously by Keith and Padden,⁷ fibrilous structure. When the strain rate was decreased to 20% per minute on another sample of completely spherulitic noncracked film, the amount of material drawn out of the spherulite increased (Fig. 5). Another film, broken very quickly by snapping by hand, showed a very clean break with very little material drawn out of the spherulite (Fig. 6). The effect of rate of elongation on spherulites has been studied by Starkweather et al.,⁸ who found that for partially spherulitic nylon films, spherulites have a small effect on the physical properties; however, at higher speeds the impact strength is reduced.

Discussion

As seen from the data, spherulization, in one way or another, greatly influences the properties of the films.

If spherulization is complete, in some cases the stress generated by the contracting mechanism is enough to cause cracks. However, the appearance of cracks in fully spherulitic films is relatively rare; the reasons for crack formation in one case and not another is not understood. This unpredictable cracking behavior may be due to an unknown experimental variable or to sample variation. Absorbed oxygen may be a factor in cracking since van Schooten⁴ has shown the severe effects that oxidative aging can have on polypropylene and Kefavian¹⁰ on polyethylene. Rysavy and Balaban¹⁴ have shown that the catalyst used in polymerization can affect the degradation rate of isotactic polypropylene especially in the presence of oxygen.

In the case of complete spherulization and the absence of internal cracking, it is obvious from the externally fractured films (Figs. 3, 4, and 5) that

the boundaries of spherulites are weak spots since fracture occurred through the boundaries. The reason for the boundary weak spot in a film may be that the boundary is the thinnest part of a dome, which is another possible reason for boundary failure faults between spherulites. Also, the possibility exists of the higher molecular weight chains crystallizing into the spherulite initially leaving the lower molecular chains for spherulite formation at a later time. This mechanism (analogous to zone refining) would form a spherulite whose chains, in the vicinity of the boundary, would be of a lower molecular weight than those chains crystallized near the center. Although stress-strain behavior of completely spherulitic films indicates brittleness with no flow, microscopic examination of the fracture shows that in some cases some material has been drawn out of the spherulite. From the limited amount of data it appears that the amount of material drawn out of spherulites seems to be an inverse function of the drawing rate.

Keith and Padden⁷ have shown that the tendency of spherulitic films to be drawn out rather than crack is proportional to coarseness; i.e., a finer texture spherulitic film would tend to be drawn out rather than crack. In these investigations it has been shown that the size of the spherulites grown under identical conditions also influences whether spherulites will crack or be drawn out; completely spherulitic films crack while smaller spherulites in incompletely spherulitic films tend to be drawn out.

The superior tensile properties of the film crystallized for 2 min. over the sample quenched is probably not due to the presence of spherulites in the 2-min. crystallized sample, but rather due to the higher crystallinity of its nonbirefringent matrix. The quenched sample, which is probably quite noncrystalline, will draw to a very limited birefringence. This lack of drawability, together with poor tensile properties, indicates the importance of crystallinity on physical properties in such a polymer. The original film which, like the quenched sample contained no spherulites but had a higher crystallinity, showed a large increase in birefringence on drawing and superior tensile properties.

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Synopsis

Isotactic polypropylene was melted and crystallized at 125°C. Crystallization was observed dynamically on a microscopic heating stage. Spherulites, when first formed, appear to have a lower order of birefringence than after some growth. Between 4–4.5 min. of crystallization cracking occurs between spherulitic boundaries. In a parallel experiment samples crystallized at 125°C. were quenched after different degrees of spherulization. The effect of degree of spherulization on stress-strain properties was studied and the necks and fractures of the samples studied. The completely spherulitic samples broke abruptly at spherulitic boundaries without necking. The rate of elongation affected the nature of the fracture of completely spherulitic samples. At low rates of elongation the spherulites have a tendency to "pull out" at the fracture. At high rates of elongation the spherulites break more sharply at their boundaries.

Résumé

Le polypropylène isotactique a été fondu et cristallisé à 125°C. La cristallisation a été observée dynamiquement au moyen d'un dispositif microscopique chauffant. Les sphérolites une fois formés semblent avoir un ordre de biréfringence inférieur à celui observé après croissance. La séparation des limites des sphérolites se produit après 4 à 4.5 min. de cristallisation. Dans une expérience parallèle, la cristallisation d'échantillons à 125°C a été arrêtée brutalement à différents degrés de sphérolation. L'influence du degré de sphérolation sur les propriétés de tension-élongation a été étudiée de même que l'étirage et les fractures des échantillons. Les échantillons entièrement sphérolitiques subissent une rupture abrupte aux limites des sphérolites sans plissement. La vitesse d'élongation affecte la nature de la fracture des échantillons entièrement sphérolitiques. A faible vitesse d'élongation les sphérolites ont tendance à être étirées aux fractures. A vitesse d'élongation élevée les sphérolites subissent une rupture plus nette à leurs bords.

Zusammenfassung

Isotaktisches Polypropylen wurde bei 125°C geschmolzen und kristallisieren gelassen. Die Kristallisation wurde dynamisch auf einem Mikroskopheiztisch beobachtet. Unmittelbar nach der Bildung scheinen die Sphärolithe einen geringeren Grad an Doppelbrechung zu besitzen als nach einem gewissen Wachstum. Bei einer Kristallisationsdauer von 4–4,5 Minuten tritt Rissbildung zwischen den Sphärolithgrenzflächen auf. In einem Parallelversuch wurden bei 125°C kristallisierte Proben nach verschieden weit fortgeschrittener Sphärolithbildung abgeschreckt. Der Einfluss des Ausmasses der Sphärolithbildung auf das Spannungs-

Dehnungsverhalten wurde untersucht und die Einschnürungen und Bruchstellen der Proben studiert. Die völlig sphärolithischen Proben ergaben an den Sphärolithgrenzen sofort Bruch ohne vorherige Einschnürung. Die Dehnungsgeschwindigkeit hatte, bei völlig sphärolithischen Proben, einen gewissen Einfluss auf die Natur des Bruches. Bei kleiner Dehnungsgeschwindigkeit haben die Sphärolithe beim Bruch eine Tendenz zum "Herausziehen." Bei hoher Dehnungsgeschwindigkeit findet ein schärferer Bruch der Sphärolithe an ihren Grenzflächen statt.

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