JOURNAL OF APPLIED POLYMER SCIENCE VOL. I, ISSUE NO. 2, PAGES 236-239 (1959)

Effect of Spherulites on the Mechanical Properties of Nylon 66*

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INTRODUCTION

Spherulites are composite structures made up of crystalline and amorphous regions in which the crystalline regions or crystallites are arranged in an essentially radial fashion with respect to a center of growth. This characteristic arrangement results in an extinction pattern in the shape of a Maltese cross when viewed between polarizing elements.

Many partially crystalline samples of nylon have a milky appearance, and the absence of this milkiness is sometimes cited as evidence of an amorphous structure. Actually, the crystallites in nylon are too small to scatter visible light. The milkiness is due to the presence of spherulites. Optical clarity does not necessarily mean that a specimen is entirely amorphous, but only that it contains no spherulites large enough to scatter light or be seen with a microscope. To a considerable extent, per cent crystallinity and spherulitic texture can be varied independently.

Except when it is prepared as thin filaments or films and rapidly quenched from the melt, nylon 66 (polyhexamethylene adipamide) always contains spherulites. If the polymer is injection-molded into a relatively cold mold, a skin, up to 0.005 in. thick, is formed which contains no visible spherulites.

Reding and Brown[1] have discussed the effect of spherulites on the properties of polychlorotrifluoroethylene. Working with filaments 0.080 in. in diameter, they found that the samples became more brittle when treated under conditions which produced spherulites, particularly large ones.

In an earlier paper[2] we reported that spherulites do not adversely affect the toughness of nylon as measured by impact strength unless their diameter is an appreciable fraction of the thickness of the specimen. This paper will discuss in more detail the effects on certain mechanical properties due to the presence of spherulites and variations in spherulite size.

PROPERTIES OF INJECTION MOLDINGS

Test specimens were injection-molded with a 1-oz. Watson-Stillman machine from nylon 66 having a number-average molecular weight of about 17,000. The molding conditions are given in Table I.

TABLE I
Molding Conditions

Cylinder temperature	275°C.
Mold temperature	45°C.
Cylinder pressure	11,200 psi
Cycle	Open 30 sec., closed 30 sec.

Some of the specimens for the tensile stress-strain (ASTM Method D 638) and flexural modulus (ASTM Method D 790) tests were annealed in "Glycowax" S-932 at 175°C. for 30 min. to reduce molded-in stresses and point-to-point variations in crystallinity, particularly at the surfaces. This treatment did not alter the spherulite structure. Specimens for the tensile impact and brittleness temperature tests were not annealed. Other specimens were exposed to 53% R.H. at 75°C. for two weeks before testing to give them the same moisture content they would have at equilibrium with 50% R.H. at 23°C.[3]

Two polymer samples were used. One was a normal sample of polymer containing no additives. Moldings from this sample contained spherulites 25–30 μ in diameter. The other sample contained 0.25% of a nucleating agent and produced moldings with spherulites about 2 μ in diameter. The results of various physical tests on these samples are given in Table II.

* Presented at the 133rd National Meeting of the American Chemical Society, Division of Polymer Chemistry, San Francisco, California, April, 1958.

TABLE II
Mechanical Properties of Nylon Moldings vs. Spherulite Size

Property		ASTM method	Large spherulites (ave. dia. = 25–30 μ) Dry 23°C.	Large spherulites Dry 50°C.	Large spherulites Conditioned to 50% R.H., 23°C.	Small spherulites (ave. dia. = 2 μ Dry 23°C.	Small spherulites Dry 50°C.	Small spherulites Conditioned to 50% R.H., 23°C.
Flexural modulus, psi		D 790	418,000	235,000	214,000	458,000	250,000	213,000
Upper yield stress, psi		D 638	11,800	9,300	8,500	13,700	10,500	9,000
Lower yield stress, psi		D 638	8,100	7,200	6,700		7,500	6,800
Ultimate strength, psi		D 638	8,100	7,400	7,800		7,600	7,700
Ultimate elongation, %		D 638	60	190	295	25	125	280
Fraction of specimens which start to draw		D 638	5/5	5/5	5/5	0/5	5/5	5/5
Flexural creep, apparent modulus, psi (stress = 1000 psi)	0.1				178,000			155,000
	hours				± 20,000			± 10,000
	1.0				152,000			135,000
	10				127,000			116,000
	100				100,000			97,000
Fatigue endurance limit, psi[a]					3850			3750
Tensile impact strength, ft. lb./in.[3b]			177			174		
Rockwell hardness		D 785	M 79		M 59	M 88		M 60
			R 118		R 108	R 118		R 109
Brittleness temperature, °C.		D 746	−85			−60		
Density, g./cc.			1.137			1.143		
% crystallinity[c]			48			52		

[a] Axial tension and compression method run under constant maximum stress on the Sonntag Fatigue Tester.
[b] Reference 4.
[c] Reference 5.

Almost any finely divided material may act as a nucleating agent for nylon 66. Additional nuclei may be introduced during remolding. A sample of nylon 66 was molded into test bars which were then cut up and remolded several times. Each time the spherulites became smaller, as is shown in Table III.

TABLE III
Effect of Remolding on the Spherulite Size in Nylon 66

Number of times molded	Maximum spherulite diameter, μ
1	30
2	10
3	7
4	5
5	3
6	2
7	1

The flexural modulus of the bars containing small spherulites was about 10% higher than that of specimens with large spherulites when tested dry at 23°C., but this difference decreased and disappeared as the temperature or the water content was increased. The samples with small spherulites also exhibited a higher upper yield stress, a lower ultimate elongation, and a marked tendency to break at the point where most specimens neck-down and begin to cold-draw. These effects also diminished with increasing temperature or water content.

The flexural creep, fatigue endurance limit, tensile impact strength, and hardness were the same for the two samples within the limits of experimental uncertainty. However, the brittleness temperature of the polymer with large spherulites was considerably lower.

To show whether the effect on the tensile properties might be due to the presence of foreign particles, 0.9% titanium dioxide (not a powerful nucleating agent) was added. Moldings from this composition had a yield point of 12,100 psi, compared with 13,700 psi when only 0.25% of a nucleating agent was used. Therefore, nucleating agents produce a more pronounced effect than foreign particles *per se*. A comparison of Table II with Table II of Reference 2 shows that differences in per cent crystallinity can account for only about one-fifth of the differences in stiffness and yield point between sample having large and small spherulites.

EFFECT OF SPHERULITES ON THE YIELD POINT

Since variations in spherulite size seemed to have the largest and most reproducible effect on the yield point or upper yield stress of dry specimens tested at 23°C., this property was chosen for more detailed study.

The effect of the presence of visible spherulites on the relationship between the yield point of nylon 66 films and per cent crystallinity as measured by density[5] is shown in Figure 1. The films without visible spherulites were quenched from the melt in Dry Ice–heptane and then annealed at temperatures from 100°C. to 250°C. in the manner described in an earlier paper.[2] Spherulitic films were melted in a press at 290°C., transferred rapidly to a second press which was maintained at a temperature from 50°C. to 225°C., and held there for 15 minutes. This has been called "hot quenching."

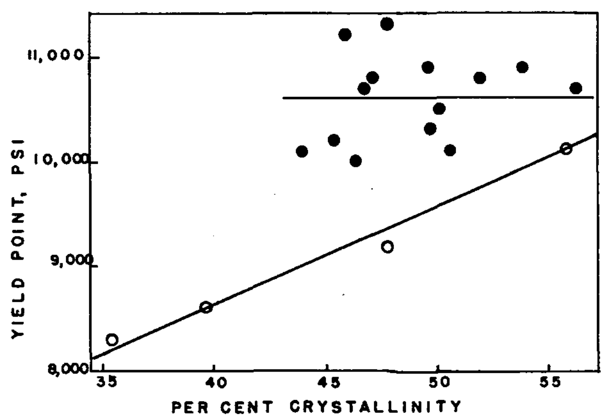

Fig. 1. The effect of visible spherulites on the yield point vs. per cent crystallinity relationship: (○) films without visible spherulites; (●) films with 30–65 μ spherulites.

The spherulites in the hot-quenched films were somewhat larger than those seen in specimens injection molded from the same polymer. They varied from about 35 μ in diameter for films quenched at 50°C. to about 65 μ in diameter for films quenched at 225°C. The most common size range was 50–60 μ. Films made from polymer containing a nucleating agent had somewhat smaller spherulites. These films were completely spherulitic. The spherulites in both films and bars impinged on each other without leaving any nonspherulitic interstices.

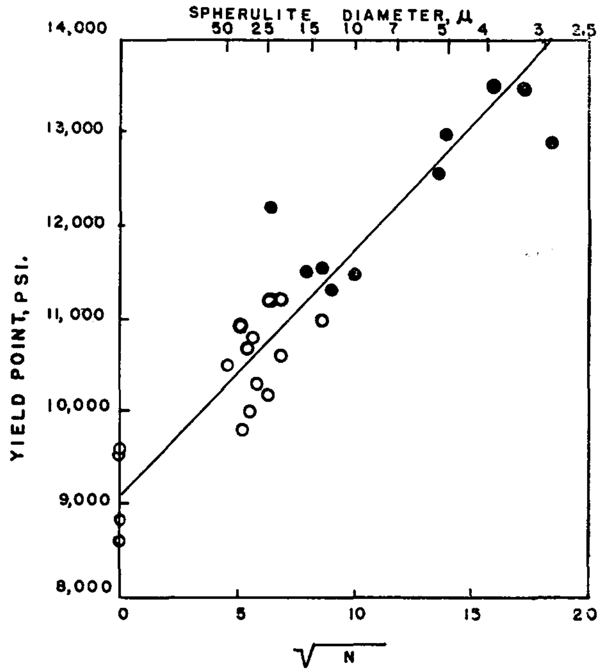

Fig. 2. Effect of spherulite size on the yield point: (○) compression-molded films; (●) injection-molded bars. N = number of spherulite boundaries per millimeter.

It is seen in Figure 1 that the yield points of spherulitic films are considerably higher than those of films without visible spherulites and are not dependent on the per cent crystallinity. The scatter is caused by variations in spherulite size.

The effect of spherulite size on the yield point is shown in Figure 2. Both films and injection moldings are included. These samples were from 45% to 52% crystalline. As the spherulite size decreases (i.e., the number of spherulites increases), the yield point increases. The yield point varies linearly with the square root of the number of spherulite boundaries per millimeter. Extrapolating this relationship to zero spherulite boundaries gives the same yield point as that of samples containing no visible spherulites. This is strong evidence that the films which had been quenched from the melt in Dry Ice–heptane and then annealed were actually nonspherulitic. Of course, the possibility remains that other procedures might produce spherulites below the limit of optical resolution.

COMPARISON OF NYLON WITH METALS

A yield point similar to that found in nylon has been observed in mild steel[6,7] and in samples of iron, molybdenum, cadmium, and zinc containing small amounts of nitrogen.[8] In these metals, the crystalline grains appear to have an effect which is similar to that of the spherulites in nylon. The yield point increases as the grain size is reduced.[9] As the temperature is raised, this effect becomes less, just as does the effect of spherulite size in nylon.[7,10] Gensamer et al.[11] state that in steel the strength indices vary linearly with the log of the aggregate size. Hall[12] applied the same relationship to the lower yield stress in steel that is used for the yield point of nylon in Figure 2. His curve extrapolated to a single crystal while ours extrapolates to nonspherulitic polymer. In each case there are no boundaries between grains or spherulites.

The mechanism by which the grain size affects the yield point and other properties in metals is thought to involve dislocations at the grain boundaries and interferences between grains which increase the stress required before plastic slip can occur.[10,13] It is not clear to what extent these ideas may be applied to high polymers. Since a spherulite boundary is a discontinuity between two patterns of oriented crystallites, some analogy with metallic grain boundaries seems possible.

In steel sheet, ductility is frequently improved by reducing the grain size, but in our work thus far on injection moldings of nylon, the opposite has been true. It is not surprising that the similarity between the two materials breaks down for larger deformations because that is where the role of the long molecular chains in nylon should be most evident.

References

1. F. P. Reding and A. Brown, *Ind. Eng. Chem.*, **46,** 1962 (1954).
2. H. W. Starkweather, Jr., G. E. Moore, J. E. Hansen, T. M. Roder, and R. E. Brooks, *J. Polymer Sci.*, **21,** 189 (1956).
3. W. B. Happoldt, A. J. Cheney, and E. M. Lacey, *SPE Journal*, **13,** 21, March, 1957.
4. C. G. Bragaw, *Modern Plastics*, **33,** 199, June, 1956.
5. H. W. Starkweather, Jr., and R. E. Moynihan, *J. Polymer Sci.*, **22,** 363 (1956).
6. R. T. Rolfe, *Steels for the User*, Philosophical Library, New York, 1956.
7. S. Timoshenko, *Strength of Materials. Part II. Advanced Theory and Problems*, 3rd Ed., Van Nostrand, Princeton, 1956.
8. H. L. Wain and A. H. Cottrell, *Proc. Phys. Soc. (London)*, **B63,** 339 (1950).
9. C. A. Edwards and L. B. Pfeil, *J. Iron Steel Inst. (London)*, **112,** 79 (1925).
10. C. H. Lorig, *Trans. Am. Soc. Metals*, **44,** 30 (1952).
11. M. Gensamer, E. B. Pearsall, W. S. Pellin, and J. R. Low, Jr., *Trans. Am. Soc. Metals*, **30,** 983 (1942).
12. E. O. Hall, *Proc. Phys. Soc. (London)*, **B64,** 747 (1951).
13. R. King and B. Chalmers, *Progress in Metal Physics*, Vol. I, Chapt. 3, *Crystal Boundaries*, Butterworth, London, 1949; R. Chalmers, *Progress in Metal Physics*, Vol. III, Chapt. 8, *Structure of Grain Boundaries*, Interscience, New York-London, 1952,

Synopsis

The presence of spherulites in nylon 66 increases the yield point and reduces the effects of variations in per cent crystallinity. Decreasing the size of the spherulites through increased nucleation results in a higher flexural modulus and yield point, a lower ultimate elongation, and a loss of ductility. These effects are markedly reduced by raising the temperature or water content. The effects of spherulite size in nylon and grain size in metals such as mild steel are compared.

Résumé

La présence de sphérulites dans le nylon 66 augmente le rendement et réduit les effets de variation du pourcentage de cristallinité. En diminuant la dimension des sphérulites par l'augmentation de la nucléation, il résulte un module de flexion et un rendement plus élevé, une moins grande élongation ultime et une perte de ductibilité. Ces effets sont remarquablement réduits par l'augmentation de la température ou par le contenu d'eau. Les effets des dimensions des sphérulites dans le nylon et les dimenstions des grains dans les métaux, tel le fer doux, ont été comparés.

Zusammenfassung

Die Gegenwart von Sphäruliten in Nylon-66 erhöht die Fliessgrenze und setzt die Wirkung einer Änderung des prozentuellen kristallinen Anteils herab. Eine Verringerung der Sphärulitgrösse durch erhöhte Keimbildung ergibt einen höheren Biegungsmodul und eine höhere Fliessgrenze, eine niedrigere Bruchdehnung und einen Verlust an Dehnbarkeit. Diese Effekte werden durch Temperaturerhöhung oder Vergrösserung des Wassergehalts merklich herabgesetzt. Die Wirkungen der Sphärulitgrösse in Nylon und der Korngrösse in Metallen, wie Flusstahl, werden verglichen.

Received April 18, 1958