

Time-Dependent Effect of Spherulite Size on the Tensile Behavior of Polypropylene

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Synopsis

The mechanical behavior of isotactic polypropylene following primary crystallization is known to be dependent on the aging time (e.g., at room temperature). This aging time effect is believed to be related to a form of additional crystallization (sometimes called secondary crystallization). We show in the present work that the aging characteristics depend on spherulite size and that indeed the spherulite size effects reported by others very likely reflect chain rearrangements upon aging, rather than some property associated with the as-crystallized material.

INTRODUCTION

A number of authors have reported the effect of spherulite size on the mechanical properties of semicrystalline polymers. Starkweather and Brooks¹ showed that the yield point of polyethylene could be increased by decreasing the spherulite size at constant degree of crystallinity. However, concomitant changes in the lamellar microstructure were ignored in this study. Kargin² and Sogolova³ found that the yield point and tensile strength of polypropylene and isotactic polystyrene are increased by additions of crystal-nucleating agents. The increasing strength was correlated with a decreasing spherulite size in these studies. Kuhre et al.⁴ noted a similar trend of increasing strength in polypropylene with additions of nucleating agent. They concluded that a crystallinity increase associated with additions of nucleant was important in enhancing the strength. In none of these nucleation agent studies was the effect of lamellar microstructure considered. The trend of reported results thus indicates that semicrystalline polymers can be rendered somewhat harder by decreasing the spherulite size. However, it is as yet uncertain whether the causal correlation may be rather with some other parameter, say crystallinity or lamellar geometry, which parameters are in turn correlated with spherulite size. Further, it has not yet been documented whether or not the changes in tensile behavior may be associated also in some way with the strength increase which accrues with aging in these polymers.

In the present experiment, the tensile properties of polypropylene to which varying amounts of a nucleating agent were added were again studied. The crystallinity, the spherulite size, and the lamellar spacing were also

measured. Further, the effect of aging time on the strength-nucleant behavior was measured and found to be a significant factor.

EXPERIMENTAL

The material was prepared by molding polypropylylene to which sodium benzoate, the nucleating agent, had previously been added. Pellets of the polymer were prepared by extruding a mixture of molten, unstabilized Profax 6401 polypropylene, stabilizer, and varying amounts of sodium benzoate. Samples with a 0.0626 in. \times 0.125 in. gauge length were molded under pressure at 200°C and then quenched into 40°C water. Aging was done in air at room temperature.

The data reported relates to the following experimental procedures. Tensile data was obtained using an Instron tester operating at 0.2 in./min (16%/min), 0.5 in./min (40%/min), 1.0 in./min (80%/min), and 2.0 in./min. (160%/min). The spherulite size was determined from optical microscope photographs, using a linear intercept method described by Hilliard and Cahn.⁵ Small-angle scattering measurements were made using a pin-hole camera described by Statton.⁶ The wide-angle x-ray method and crystallinity interpretation are likewise as described by Statton.⁶ Density measurements were obtained using density gradient columns.

RESULTS

The effects of sodium benzoate additions on the microstructure are described in Figure 1 and Table I. These data were accumulated after

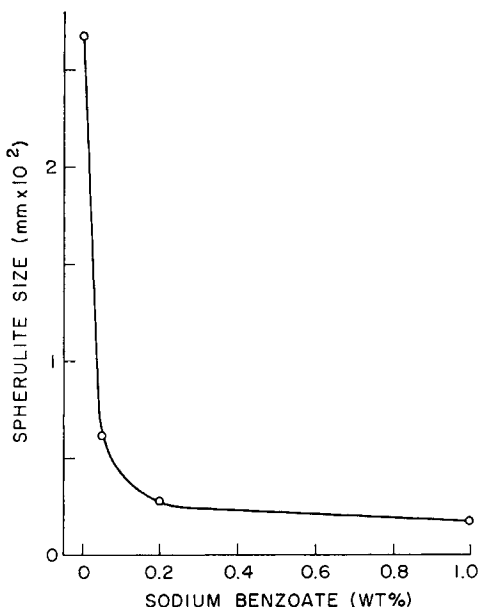


Fig. 1. Effect of nucleating agent on spherulite size.

TABLE I
Crystallinity, Long Period, and Orientation

Sodium benzoate, wt-%	Degree of crystallinity		Long period, Å	Crystallite size, Å	Orientation from 110 peak
	by density %	by x-ray, %			
0	58	53	140	166	none
0.05	58	60	150	157	none
0.2	58	60	129	151	none
1.0	70	60	154	160	none

rather lengthy storage times and are thus to be correlated with tensile data from specimens aged for long times. Figure 1 shows the relationship between sodium benzoate concentrations and spherulite diameter. A 0.05% addition of sodium benzoate effects an enormous decrease in spherulite size. Additional amounts of nucleating agent produce decrements of decreasing magnitude in spherulite size.

In contrast to the spherulite size results, the crystallinity, long period, and orientation (Table 1) show no trend with sodium benzoate content and are essentially invariant in this investigation. These data were all observed after long storage times—at which the strength varied considerably. Thus all the characterization properties except spherulite size cannot cause these variations in strength. It is not implied, however, that these properties do not change with time, but merely that their aging time dependence is not affected by crystal-nucleating agents.

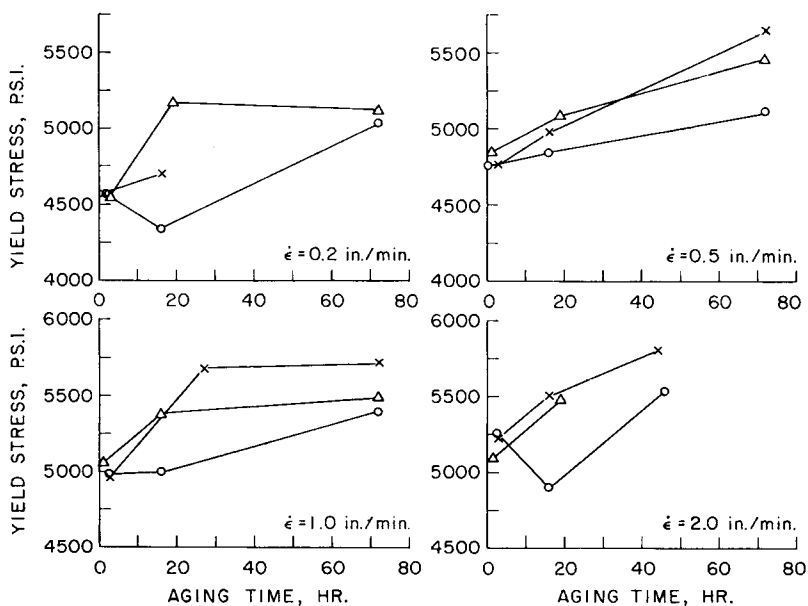


Fig. 2. Yield stress vs. aging time at four strain rate levels and three sodium benzoate concentrations: (O) 0.00% NaB; (Δ) 0.05% NaB; (\times) 1.00% NaB.

Figure 2 shows tensile strength-aging time curves for four different strain rates. At each strain rate, curves are plotted for three sodium benzoate (NaB) concentrations. The salient feature of these curves are that

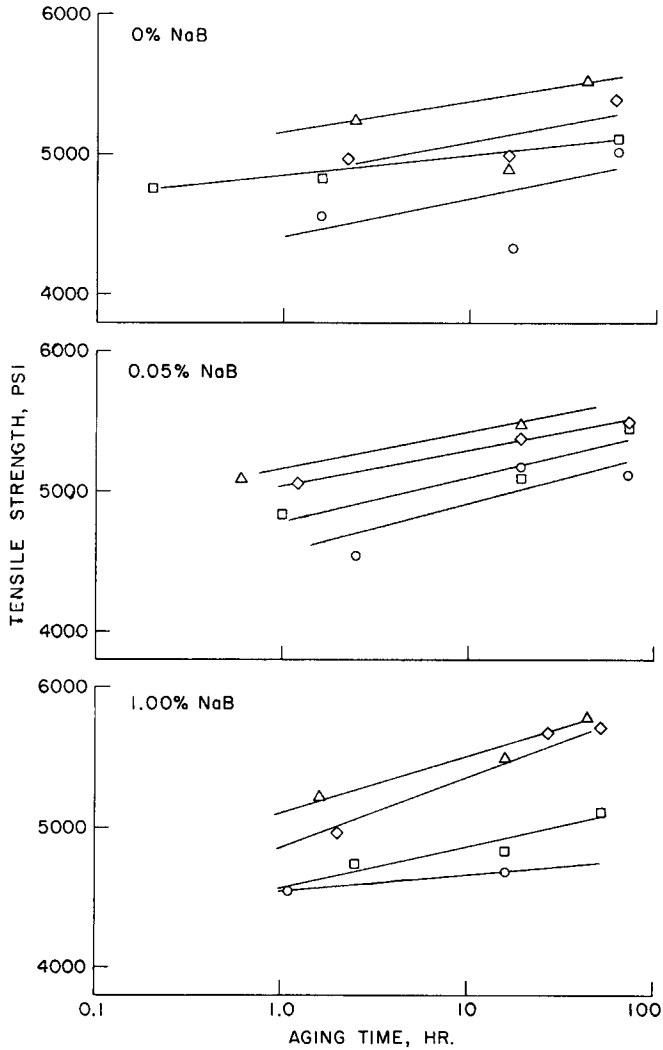


Fig. 3. Logarithmic plots of σ_y vs. t for the sodium benzoate concentrations and strain rates of Figure 2. Strain rates: (O) 0.2 in./min; (\square) 0.5 in./min; (\diamond) 1.0 in./min; (Δ) 2.0 in./min.

(a) the tensile strength increases with aging time for any given nucleant concentration and strain rate and (b) at low aging times, varying the spherulite size has no effect on the tensile strength, at a given strain rate.

TABLE II
The Effect of Sodium Benzoate and Strain Rate on Parameters K and a

Strain rate, in./min	a^a			K^a			Av
	0% NaB	0.05% NaB	1.0% NaB	0% NaB	0.05% NaB	1.0% NaB	
0.2 (16%/min)	0.0268	0.0349	— ^b	4410	4540	— ^b	4480 ± 40
0.5 (40%/min)	0.0133	0.0282	0.0267	4850	4780	4570	4730 ± 80
1.0 (80%/min)	0.0219	0.0219	0.0426	4840	5040	4860	4900 ± 60
2.0 (160%/min)	0.0182	0.0123	0.0335	5160	5170	5100	5150 ± 20
Average	0.020 ± 0.003	0.027 ± 0.004	0.034 ± 0.004	4820	4880	4770	—

^a Constants from eq. (1). NaB = Sodium benzoate.

^b Insufficient data.

It has been shown previously that aging in polypropylene progresses proportionally to log time.^{7,8} Thus, an equation relating tensile strength σ_t to room-temperature aging time t should be

$$\sigma_t = Kt^a \quad (1)$$

The exponent a is given by the slope of $\ln \sigma_t$ versus $\ln t$ lines, $\ln K$ is given by the value of $\ln \sigma_t$ at $t = 1$. A set of logarithmic curves for four strain rates at each of the three NaB concentrations is shown in Figure 3. Values of K and a have been extracted from these curves and are given in Table II.

Also given in Table II are the average values of a and K for (1) experiments at constant strain rate and (2) specimens at constant spherulite size. The following features emerge: (a*) the exponent a depends upon spherulite size but not significantly on strain rate, and (b*) the coefficient K depends upon strain rate but not on spherulite size. Result (a*) means that the portion of tensile strength which is generated by aging increases with decreasing spherulite size. The result (b*) shows that the strain rate effects upon tensile strength in polypropylene are insensitive to spherulite size.

Of the four results (a), (b), (a*), and (b*), (a) and (b*) are not new observations and are a standard part of the lore of polymer deformation. Features (b) and (a*) are, however, new and will ultimately demand explanation in terms of microstructure.

The aging observations indicate that spherulite size effects in polypropylene are not intrinsic in the same sense as are grain size effects in metals. That is, the spherulite size effect is not developed instantaneously upon formation of the spherulitic microstructure, but rather awaits additional structural rearrangements. It is not clear at present whether these rearrangements are the development of orientation in amorphous zones suggested by Gezovich and Geil,⁸ the growth of new small spherulites in the original interspherulitic zones, as observed in polyethylene and nylon 6 by Vinogradskaya et al.,⁹ or are yet another microstructural variation. The constancy of long spacing in these experiments suggests that the Gezovich and Geil orientation effect is not important in the spherulite size effect. Further careful work is necessary in order to point more firmly at the correct microstructural interpretation of the spherulite size effect.

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