

Influence of Morphology on the Fatigue Properties of Polypropylene

INTRODUCTION

The dynamic fatigue properties of both amorphous and semicrystalline polymers have been under active investigation for many years.¹ In spite of the relatively large body of work on semicrystalline materials, few studies concerning the effect of crystalline morphology (i.e., degree of crystallinity, spherulite size and structure, tie molecule density, etc.) have been conducted. This is particularly surprising since it is well known that crystalline morphology plays an important role in determining other mechanical properties such as yield strength and toughness.² Considering the practical importance of fatigue in determining material usefulness, we have undertaken a program in which we hope to elucidate the influence of semicrystalline morphology on fatigue. In this note we report some of our initial findings.

What little work has been done concerning the effect of morphology has focused on the degree of crystallinity (W_c). In general, the presence of crystallinity appears to improve fatigue resistance in that semicrystalline polymers exhibit lower fatigue crack propagation (FCP) rates than amorphous materials, even for comparisons using the same polymer.³ In addition, increasing W_c by about 8% for some polyethylene samples was found to result in a reduction in FCP rate,⁴ but, in the same investigation, higher cooling rates also reduced the FCP rate, even though these samples had lower percent crystallinities. The authors speculate that the latter result can be attributed to the greater number of tie molecules which are generally associated with higher cooling or crystallization rates. Although one might expect fatigue resistance to improve with decreasing spherulite size,^{5,6} to our knowledge, there has been no direct observation of this effect.

The key to investigating the influence of morphology on mechanical behavior is the ability to independently alter one microstructural parameter. This is often a formidable task. However, thermal annealing provides one with a convenient way of altering W_c without significantly changing spherulite size⁷ or tie molecule density.⁸ In this way, at least to a first approximation, we have been able to assess the influence of W_c on fatigue crack propagation in polypropylene.

EXPERIMENTAL

The polymer used in this study was Pro-fax 6523 polypropylene (PP) supplied by Himont. This material has a weight average molecular weight of approximately 400,000 g/mol, a polydispersity ratio of 6 and contains ~4% atactic material. The polypropylene was first molded at 230°C (at 20,000 psi) for a few minutes, then cooled to room temperature. The specimens were then placed in an oil bath at 190°C for 1 h and quenched into ice water. Some of the quenched samples were annealed in an oil bath at 152°C for 20.5 h.

Heats of fusion were determined using a Perkin-Elmer Differential Scanning Calorimeter (DSC-2). A heating rate of 20°/min was used to obtain the melting endotherms, and all DSC curves were analyzed and recorded using a Perkin-Elmer Thermal Analysis Data Station. Baselines defining the endothermal area were drawn from 109 to 169°C using the method of Gray.⁹ An average of at least three samples with weights of 1–1.2 mg were used to determine the heats of fusion. Percentage crystallinities were calculated using 165 J/g as the heat of fusion of 100% crystalline PP.¹⁰

To monitor spherulite size, 7 μm thick sections were cut from test pieces of bulk polymer using a LKB Ultratome III Microtome equipped with a glass knife. All sectioning was conducted at room temperature. The spherulitic structure of the specimens was viewed through crossed polarizers with an Olympus Model BHA optical microscope which was equipped with a Polaroid camera back. To further study the influence of annealing on spherulite size, sections micro-

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tomed from quenched material were annealed in a hot stage under the same conditions as described above.

All fatigue tests were performed on a MTS 810 materials testing system consisting of a MTS Model 312.21 load frame and a 3000 lb load cell. Single edge notched specimens with dimensions of $145 \times 29 \times 4$ mm thick were used in all fatigue tests. Initially, notches 10 mm long were cut into each sample with a band saw. The notch tip was then sharpened with a razor blade. Each sample was precracked with a cyclic tensile load of 1110 N at 10 Hz for 200 cycles using a haversin waveform. With all of the other test parameters kept constant, the minimum load was then increased from 0 to 71 N and the range of cyclic loading was reduced to 756 N. Prior to taking measurements, the crack tip was again sharpened with a razor blade while the sample was subjected to cyclic loading. Crack length was monitored with a Gaertner traveling microscope.

RESULTS AND DISCUSSION

Annealing of the quenched PP led to an increase in W_c of about 8% (from 46 to 54 % by weight) but no measurable change in spherulite size. In addition, annealing in the microscope hot stage under conditions identical to those used for preparation of the fatigue specimens did not affect the size of individual spherulites.

Studies on polypropylene can be complicated by the existence of several crystal forms and different overall spherulitic morphologies.^{11,12} Of particular concern for our work was the possibility that the quenched PP contained a significant amount of "smectic" material.^{13,14} To check this, we performed wide-angle X-ray diffraction measurements. There was no significant difference between the patterns for the annealed and quenched materials and no evidence for the "smectic" form was observed.

In attempting to compare the fatigue properties of quenched and annealed polypropylene, it was found to be very difficult to develop stable crack growth in either of these materials. Many different experimental conditions were tried before deciding on those used in this work. While even these conditions did not produce the amount of crack growth normally expected in a fatigue crack propagation experiment, interesting comparisons can be made between the quenched and annealed polypropylene.

Annealing the quenched PP significantly improved the fatigue properties. Representative curves illustrating sample crack length versus number of cycles can be seen in Figure 1.

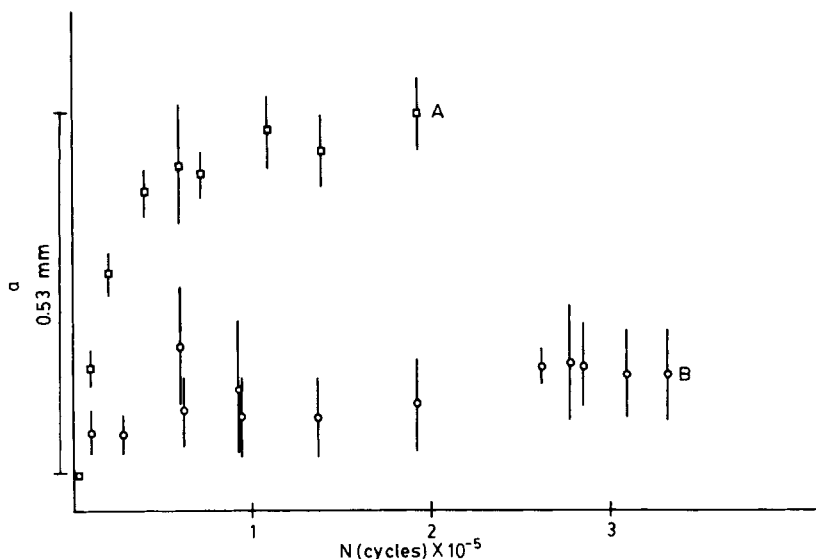


Fig. 1. Crack length (a) vs. number of cycles (n) for quenched (A) and annealed (B) polypropylene.

Similar data was obtained for additional quenched and annealed specimens. Due to variability in the precracking procedure, these curves have been normalized to the same initial crack length. On the surface, this may seem inappropriate since the stress intensity factor range (ΔK) is, in part, a function of crack length. However, the difference in total crack length is less than 3%, and, for the comparison given in Figure 1, the annealed specimen had the longer initial crack length.

The crack length of the quenched sample increases considerably in the initial part of the fatigue experiment and then levels off, reaching a limiting value at greater number of cycles. In contrast, little crack growth is observed in the annealed material over the entire range of the test. Clearly, the rate of crack growth for the quenched specimens decreases as number of cycles (or crack length) increases. In addition, since ΔK is proportional to crack length, crack growth rate decreases with increasing ΔK . While this result is contrary to observations on most polymeric materials,¹ decelerating crack growth has been observed for a number of different semicrystalline polymers.^{5,15-17} While the decreasing FCP rate cannot be explained by conventional laws of crack propagation, crack layer theory may provide a way of describing the observed results.¹⁸ Crack layer theory allows one to model the situation in which interaction of the crack with the "damaged" material preceding the crack (i.e., crazes, shear bands, etc.) strongly influences the stress field and the kinetics of damage. Using this approach, the reduction in FCP rate in PP has been attributed to blunting of the damaged zone and an increase in the "translational resistance moment."¹⁷

From scanning electron microscope observations, the damaged zones of our samples appear to be similar to those produced previously,¹⁷ and it would seem likely that a similar mechanism could explain the decelerating rate of crack growth for our samples. However, we also observed an apparent blunting of the crack tip during the fatigue experiments. As the crack tip blunts, the driving force for crack growth decreases. It is not possible at this time to say whether the crack tip blunting continued throughout the test or reached a certain stable shape.

To our knowledge, no mechanism for explaining the influence of W_c on fatigue has been suggested. In general, the comparatively better fatigue properties of semicrystalline polymers with respect to amorphous materials has been attributed to deformation and recrystallization of the crystalline microstructure.¹⁹ Since damaged zones are observed to precede controlled crack growth in polymers, by the time the crack front reaches a particular region of material, the as-formed morphology has been transformed into a different microstructure (i.e., the "damaged" material). Consequently, the rate of crack propagation will be controlled by the structure and morphology of the damaged material. The influence of the initial morphology is, in a sense, indirect since it will control conversion of the initial spherulitic structure to that of the damaged material. Provided an equivalent amount of specimen is converted to damaged material, more crystalline material must be transformed for samples of higher crystallinity. If this is indeed the case, the energy required to transform the crystal morphology preceding the crack tip would be greater for samples of higher initial crystallinity.

While annealing has clearly improved the resistance of PP to fatigue crack propagation, the same annealing procedure applied to tensile stress/strain specimens produced more brittle-like behavior.²⁰ The explanation for the observed differences is not clear at this time and further research is continuing.

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