The Effect of Molecular Weight on the Fatigue Behavior of Polystyrene

E. FODEN, D. R. MORROW, and J. A. SAUER,

Rutgers University, New Brunswick, New Jersey 08903

Synopsis

Significant improvements in the fatigue life of polystyrene can be realized by increase in molecular weight. In this investigation, samples of polystyrene of varying molecular weight were subject to alternating cycles of axial tension and compression at a test speed of 1600 rpm. One set of fatigue tests was made on samples machined from commercial whole polymer rod. A second set of samples was prepared from a PS standard having an average molecular weight of 160,000 and a narrow molecular weight distribution. A third set of samples had a high average molecular weight of 860,000. For a whole polymer, the S–log N curves tended to have the same general shape as for metals, and the endurance limit appeared to be about 1400 psi. The test results show that the average fatigue life, at any given stress amplitude, is significantly increased by increase in molecular weight. For example, the average life of the high molecular weight standard at any given stress level was found to be more than tenfold that of the low molecular weight standard.

INTRODUCTION

It is well known that, at a low molecular weight, the properties of a polymer are dependent upon its molecular weight (MW). However, it is usually considered that above some critical molecular weight value, which may be as low as 10^4, the properties tend to become independent of molecular weight.[1,2] From dilatometric studies on polystyrene fractions, Fox and Flory[3] concluded that the glass transition temperature T_g approached an asymptotic value near a MW of 30,000; and Nozaki et al.[4] noted that the temperature of narrowing of the nuclear magnetic resonance line showed similar dependence on MW as did T_g. Also Merz et al.[5] measured the storage and loss moduli of polystyrene and observed that these parameters became practically independent of MW at values greater than 10,000. In addition, a series of narrow molecular weight samples of anionic polymerized polystyrene have been recently studied in this laboratory by differential scanning calorimetry.[6] These tests showed that T_g increased noticeably with molecular weight at low values of this variable, but became almost independent of MW in the range of 50,000 to 60,000.

It is also reported that increases in MW above a certain critical value have little effect on the temperature location of relaxation mechanisms in crystalline polymers. For example, Takayanagi,[7] who studied the visco-

519

elastic properties of polymer crystal mats prepared from polyethylene fractions, and Stehling and Mandelkern,[8] who studied thin films prepared from polyethylene fractions, report that the temperature of the maxima of both the γ- and α-loss peaks are independent of molecular weight.

Despite the reported lack of dependence of T_g and other material parameters on molecular weight after a certain critical value has been reached, there are good reasons for expecting some of the mechanical properties of the polymer, such as its resistance to alternating loading, to be affected, and indeed improved, by further increases in molecular weight. Chain ends, for example, are a type of defect, and these may well be a potential source of microcracks. Secondly, intermolecular bonding should be increased with increase in MW, and as a result it may be possible to carry stress across the material more uniformly. Thirdly, higher molecular weight will allow for a greater degree of chain orientation in regions of plastic deformation near the tips of microcracks. This molecular orientation will result in a local strengthening of the material, will permit load to be transmitted despite the presence of a crack, and will ameliorate the potential stress concentrations that occur at sharp crack tips. In fact, it is well established that mechanisms of this latter type operate very effectively in materials such as polystyrene and polycarbonate and permit even fully crazed material to carry appreciable load.[9-12]

In view of the above, it is a reasonable hypothesis that increases in MW, even beyond the value at which T_g shows little change, will materially increase the fatigue life of a polymer specimen subject to alternating loading. To test this hypothesis, a research program was initiated in our laboratory. To date, rather extensive tests have been made on a typical amorphous polymer, polystyrene, and studies have begun on a typical crystalline polymer, polyethylene. The results of these tests will now be presented. An oral discussion of early test results has been given,[13] and more complete details of the apparatus and test procedures is available.[14]

A specific objective of our studies is to try to raise the rather low value of the ratio of endurance strength to ultimate strength that has been reported for many thermoplastics. For example, this ratio—for fatigue tests carried out to 10^7 cycles—is reported to be 0.19 for poly(methyl methacrylate),[15] 0.20 for cellulose acetate and polycarbonate,[15,16] 0.21 for polystyrene,[17] and 0.22 to 0.35 for various pure and filled phenolics.[18] Thus, in many homogeneous thermoplastic-type polymers, the reported endurance limit-to-ultimate strength ratio is only about 0.20. This value is less than that reported for reinforced or laminated polymers, 0.20 to 0.33,[19] for many nonferrous metals, 0.25 to 0.40,[20] and for many ferrous metals, 0.4 to 0.5.[21] Unfortunately, in most of the reported tests on polymers, the molecular weight of the specimens tested has not been given; it is conjectured that the average molecular weight values were probably in the 10^4 to 10^5 range.

APPARATUS AND TEST PROCEDURE

All fatigue tests reported herein have been carried out on a Tatnall-Krouse fatigue machine. This apparatus allows one to apply an alter-

nating axial load to two separate test specimens by means of appropriate load levers. The load levers are activated at one end by an eccentric cam arrangement driven by an electric motor. The force is transmitted to the specimen at the other end of the load lever by a set of flexure plates that insure axial loading. The stress amplitude is varied by changing the eccentricity of the cam and is determined from the measured deflection of the load lever in the center. Calibration curves are available to convert the observed deflection directly to load. The machine has a capacity of 5,000 lb, but all the tests on the polystyrene specimens were carried out with a 500-lb-capacity load lever.

The fatigue tests were carried out at zero mean stress. Hence the actual stress on the specimen varied sinusoidally from a maximum tensile value to a corresponding maximum compressive value.

If the mean stress changes during testing, an automatic load-maintaining device makes the necessary adjustments to return the mean stress to zero. There is also an automatic cut-off device on the apparatus so that when failure occurs the recording counters give the total cycles to fracture.

The machine is designed to run at 1600 rpm, and this nominal speed was found to be satisfactory for fatigue testing of polystyrene. Polystyrene has low internal friction at room temperature,[22] and hence the amount of self-heating with this material is low. Even at the speed of 1600 cycles/min, the temperature rise in the polystyrene specimens did not exceed 2°C. However, in other polymers, as shown by Shimamura et al.[23] and Ratner and Korobov,[24] self-heating effects can cause appreciable temperature rises. In fact, in polyethylene, our first test runs, which were made at a speed of 1600 rpm, caused rapid melting of the polymer.

A view of a test specimen assembled in the apparatus and ready for fatigue testing is shown in Figure 1. Various shapes of test specimens were tried and the hour-glass-shaped specimen shown in this figure was selected as being the most suitable. The specimens are assembled prior to testing in suitable metal grips and care is taken to insure axiality of loading. The specimens themselves are 3.00 in. long, 0.500 in. in diameter at the grip ends, and 0.200 in. in diameter at the reduced center section. The external radius of the reduced section was 1.500 in.

The test specimens were machined from molded rods and then polished before testing. The polystyrene specimens were smoothed with successively finer emery paper and then with a commercial polish (Noxon) until there was no evidence of surface scratches or marks to the naked eye. Before testing, the polish was removed by washing and rinsing with water.

Fatigue tests were made at various stress levels and for three different types of starting materials. One set of experiments was carried out on whole polymer of a standard commercial grade. The second and third sets of experiments were made on anionically polymerized polystyrene specimens of narrow molecular weight distribution. The low molecular weight standard had a molecular weight of 160,000 and a reported M_w/M_n value of ≤ 1.06. The higher MW standard had an average molecular weight of 860,000 and a reported M_w/M_n value of ≤ 1.15. These standards were ob-
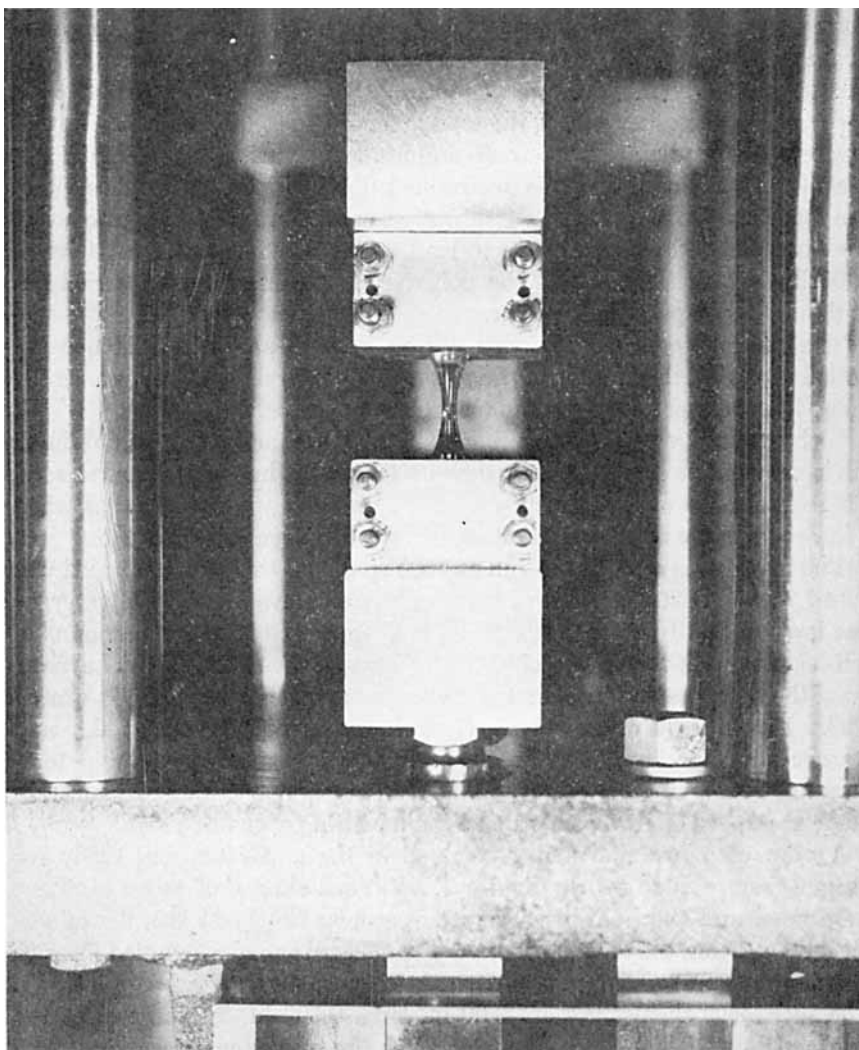
Fig. 1. Part of fatigue apparatus showing hour-glass-shaped specimen and metal specimen grips.

tained from the Pressure Chemical Co. The measured density of both fractions was 1.050 g/cc.

For all three types of polystyrene, preliminary runs were made on a Perkin Elmer differential scanning calorimeter in order to determine the glass transition temperatures. For both molecular weight standards, T_g was estimated to be about 100°C, while a value of 98°C was obtained for the whole polymer. The test runs were made at 40°C/min.

TEST RESULTS AND DISCUSSION

For the commercial-grade polystyrene, measurements of the number of alternating cycles to failure were made at four different maximum stress

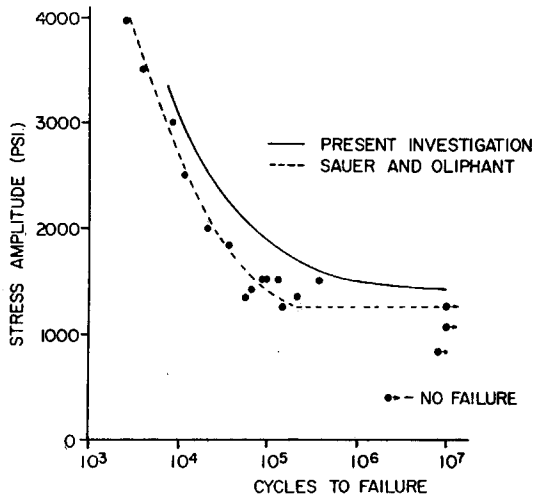levels. The stress levels selected were 3000, 2500, 2000, and 1500 psi. Seven or more specimens were tested at each stress level, and two additional specimens were tested at 1000 psi.

The test results of this first series of tests are shown in Figure 2. For each sample, the maximum stress is plotted versus the log of the number of cycles to failure. If no failure occurred prior to 10 million cycles or a little thereafter, the test was stopped. Arrows are used in this and subsequent figures to indicate specimens that did not fail. Figure 2 shows, as is usual for fatigue investigations, that considerable scatter occurs in the test data. There is also some uncertainty in the location of the endurance limit, i.e., the stress at or below which no failure will occur in 10^7 cycles. Nevertheless, the general shape of the $S-N$ curve of polystyrene is similar to that of many metals, and the endurance strength appears to be about 1400 psi.

It is of interest to compare the present data on PS with that reported by Sauer and Oliphant[16] for samples of a commercial polystyrene polymer, Lustrex LX, having an average molecular weight of 68,000. Their test results were also done in alternating tension and compression, but at 1800 rpm and on specimens having a diameter of 1 in. The comparison of the two sets of data is shown in Figure 3. The $S-N$ curves are seen to be of the same general shape, but the average fatigue lives for any given stress level and the endurance strength at 10^7 cycles are slightly higher for the specimens of the current investigation. These effects may be due to a higher average molecular weight for the current samples or to the smaller reduced area of the test specimens of this investigation.

The results of the fatigue tests carried out on the polystyrene standards of molecular weight of 160,000 are presented in Figure 4. For each of the stress levels investigated, there is some scatter of the lifetime data, but this scatter was less than that for the commercial whole polymer specimens. It appears from the results shown in Figure 4 that the data for the low

Fig. 2. Lifetime fatigue data and $S-N$ curve for polystyrene (whole polymer) under reversed tension and compression.

Fig. 3. Comparison of S–N curve of polystyrene (whole polymer) of present investigation with that obtained on polystyrene (Lustrex LX) (ref. 17) under reversed tension and compression.
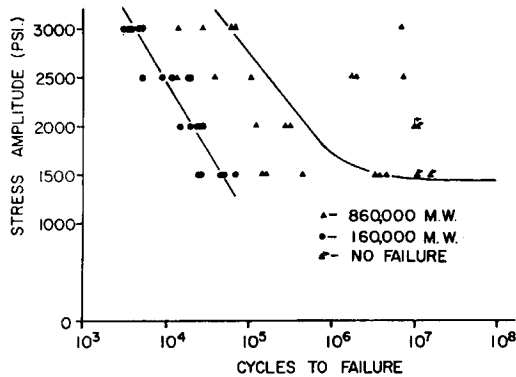

Fig. 4. Comparison of lifetime fatigue data and S–N curves of 160,000 MW polystyrene standard and 860,000 MW polystyrene standard under reversed tension and compression.

molecular weight standard can be represented by a straight line on this semilog plot. It is quite likely that this S–N curve would also level off at some lower value of applied stress, in a fashion similar to the curves of Figures 2 and 3, but test data were not taken at stress levels below 1500 psi. Hence the endurance limit for this series of test specimens is not known, but it is clearly well below 1500 psi.

The results of the third series of fatigue tests, carried out on samples prepared from the high molecular weight standard of 860,000, are also given in Figure 4. Five or more test samples were examined at each of the stress levels investigated. There is more scatter in the data for these specimens than for the lower molecular weight samples. However, despite

the scatter, the fatigue life at any given stress level of all of the samples of the 860,000 MW series, with one exception, exceeds the fatigue life of even the best samples of the 160,000 MW series. Furthermore, it is clear from the data that the average or median fatigue life has been increased by a factor of 10 or more due to the increase in molecular weight.

It is also evident that there has been a significant increase in the endurance strength, with that of the high MW sample estimated as 14,500 psi. No precise figure can be given for the percent increase because of insufficiency of test points for the lower MW sample at the lower stress levels. It is also of interest to compare the test results of Figure 4 with that of the commercial polymer shown in Figure 2. When this is done, it is noted that the commercial polymer $S-N$ curve falls between that of the low molecular weight polymer and that of the high molecular weight polymer.

In both the low and high molecular weight samples, some crazing was noted on the specimen surfaces soon after application of the load. In the high molecular weight samples, the density of crazing cracks was quite high, but the crazes appeared to stabilize and not grow to a critical crack size for rapid propagation. In the lower molecular weight samples, some larger crazes were seen, and the critical crack size for rapid propagation probably occurred earlier. It appears that the possibility of stabilizing the craze through orientation and fibril formation is not sufficiently high in the lower molecular weight samples and the stress concentration effect of crack tips is therefore much greater.

Additional tests concerning the effect of average molecular weight on the fatigue behavior of a partially crystalline polymer, polyethylene, are also underway, and the results of these studies will be presented in a later publication. For investigation of polyethylene, it is necessary to significantly reduce the test speed in order to avoid the deleterious effects of self-heating.

References

1. J. Heijboer, *Proceedings of the International Conference, Non-Cryst. Solids*, (Delft, Holland), North Holland Publishing Co., 1965, p. 232.

2. P. Lord and R. E. Wetton, *Progress in Non-Destructive Testing*, vol. 3, Heywood and Co., London, 1961, p. 85.

3. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

4. L. Nozaki, T. Kazama, and S. Okamoto, *Rep. Progr. Polym. Phys. Japan*, **X1**, 345 (1968).

5. E. H. Merz, L. E. Nielsen, and R. Buchdahl, *Ind. Eng. Chem.*, **43**, 1396 (1951).

6. R. Saba, unpublished results.

7. M. Takayanagi, in *Proc. 4th Int. Conf. on Rheology*, (Providence, R. I.) Part 1, A. L. Copley and E. H. Lees, Eds., Interscience, New York, 1965, p. 161.

8. F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).

9. J. A. Sauer, J. Marin, and C. C. Hsiao, *J. Appl. Phys.*, **20**, 507 (1949).

10. C. C. Hsiao and J. A. Sauer, *J. Appl. Phys.*, **21**, 1071 (1950).

11. C. K. Spurr and W. D. Niegisch, *J. Appl. Polym. Sci.*, **6**, 585 (1962).

12. R. P. Kambour, *J. Polym. Sci. A-2*, **4**, 349 (1966).

13. D. R. Morrow, E. Foden, and J. A. Sauer, *Bulletin APS, Series 11*, **14** (No. 3), Paper CK11, Mar. (1969).

14. E. Foden, M.S. Thesis, Rutgers University, Jan. 1969.

15. A. X. Schmidt and C. A. Marlies, *Physics of High Polymers—Theory and Practice*, McGraw-Hill, New York, 1948, p. 425.

16. G. V. Fox, *Machine Design*, Ref. Issue on Plastics, **38** (No. 14), Chap. 1, June (1966).

17. J. A. Sauer and W. J. Oliphant, *Proc. ASTM*, **49**, 1119 (1949).

18. B. J. Lazan and A. Yorgiadis, *ASTM Spec. Publ. STP No. 59*, 1944, p. 66.

19. R. B. Heywood, *Designing vs. the Fatigue of Metals*, Reinhold, New York, 1962.

20. E. R. Parker, *Materials Data Book*, McGraw-Hill, New York, 1967.

21. R. E. Reed-Hill, *Physical Metallurgical Principles* Van Nostrand, New York, 1964.

22. J. A. Sauer and D. E. Kline, *J. Polym. Sci.*, **18**, 491 (1955).

23. S. Shimamura, H. Maki, Y. Matsuda, and Y. Fujimura, *Proceeding 6th Japan Congress on Testing Materials*, Japan Soc. Co. Testing Material, Kyoto, 1963, p. 134.

24. S. B. Ratner and V. I. Korobov, *Mechanika Polimerov*, **1**, 93 (1965).