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Anomalous fracture behaviour in polyethylenes under fatigue and constant load

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The fracture behaviour of two copolymers of polyethylene were studied under fatigue and constant load. There is an anomaly because one resin was stronger under fatigue loading and the other under a constant load. The fatigue parameters that were investigated were waveform, frequency, *R*, and time under maximum and minimum stress. The fatigue failure was described in terms of the stretching of the fibril in a craze under the maximum stress and bending of the fibril under the minimum stress, whereas only fibril stretching occurs under a constant load. The damage per cycle by stretching is much less than the damage per cycle by bending the fibril. It is proposed that molecular weight has a greater influence on fatigue fracture than on fracture under a constant load.

1. Introduction

Measurements by Nishimura and Narisawa [1], Zhou *et al.* [2] and Showaib *et al.* [3], of brittle fracture in polyethylenes (PE) often show that the resistance of a resin to failure under an oscillating load (fatigue) correlates with its resistance to failure under a constant load (CL). Since the time for fatigue failure may be very short compared to the time for failure under constant load, it is very useful to obtain the ranking of resins with respect to their resistance to slow crack growth under CL by measuring their fatigue lifetime. Such a correlation between lifetimes under CL and fatigue has been demonstrated by Zhou *et al.* [2] for a series of ethylene–hexene copolymers whose lifetimes in a fatigue test varied from 30 to 800 min and whose lifetimes under CL varied from 800 to 10^6 min. However, there are examples of pairs of resins where one PE has a longer lifetime under fatigue and the other PE has a longer lifetime under a constant load. In this paper the difference in fatigue behaviour between two such resins is explored. In a previous paper by Zhou and Brown [4], the mechanism of fatigue failure in one of these resins was investigated. In this paper the details of the fatigue behaviour of the other resin will also be presented in order to understand the basis of this lack of correlation between fatigue and CL tests. Papers on fatigue by Bowman [5, 6] and Nishimura *et al.* [7] are pertinent.

2. Experimental procedure

The resin designated PE-F has better fatigue resistance and resin PE-C better resistance to slow crack growth under constant load. Both resins are used to make gas pipes. PE-F is pigmented with carbon black; it is an ethylene–butene copolymer; density = 952 kg m^{-3}, M_w = 216 000 and yield point at 42 °C = 16.9 MPa. PE-C is an orange pigmented ethylene–hexene copolymer with 4.5 butyl chains per 1000 C; M_n = 15 000, M_w = 170 000; density = 938 kg m^{-3} and yield point at 42 °C = 15.1 MPa.

Specimens were made from slow-cooled compression-moulded plaques. The geometry of the test specimen is shown in Fig. 1. The main notch was 3.5 mm deep and the two side grooves were 1 mm deep. The specimens were designed to produce practically pure plane strain fracture. The specimens were exposed to uniaxial loading using a computer-controlled servo-hydraulic Instron machine model 8501. All fatigue tests were done at 42 °C. The crack opening displacement was measured with an optical microscope with a filar eyepiece while the frequency was momentarily reduced to 0.04 Hz.

3. Results

Under a constant load, PE-C failed at 80 °C under a stress of 2.4 MPa in 30 000 min, and at 50 °C under a stress of 4.2 MPa in 200 000 min; under the

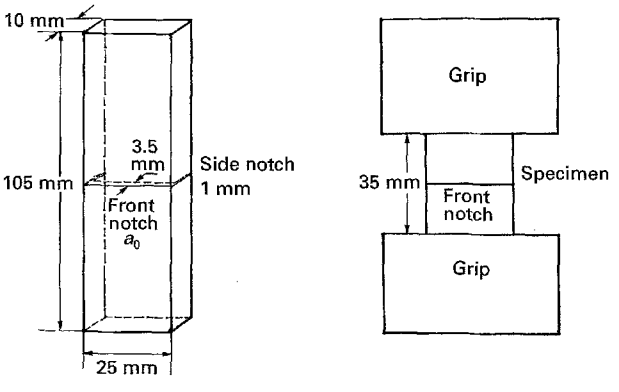

Figure 1 Specimen geometry.

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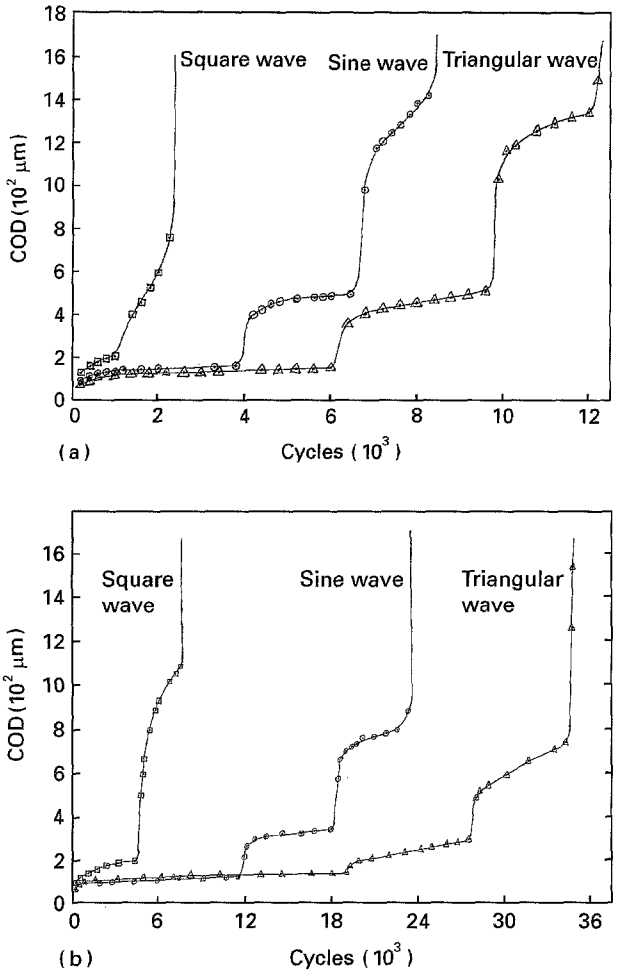

Figure 2 COD versus cycles for (a) PE-C and (b) PE-F, ± 5 MPa, 1 Hz.

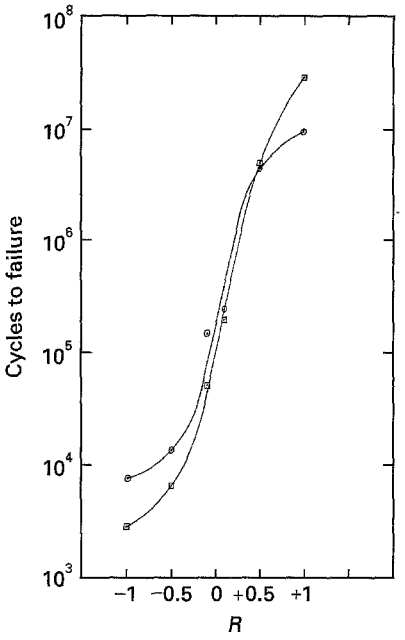

Figure 3 Cycles to failure versus R, 1 Hz. (⊙) PE-F, (⊡) PE-C.

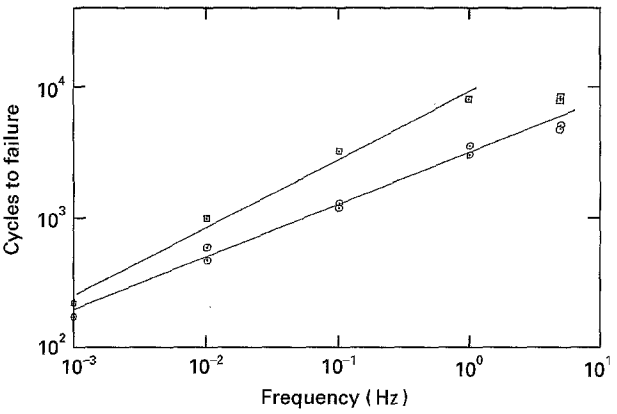

Figure 4 Cycles to failure versus frequency, ± 5 MPa. (⊡) PE-F, (⊙) PE-C.

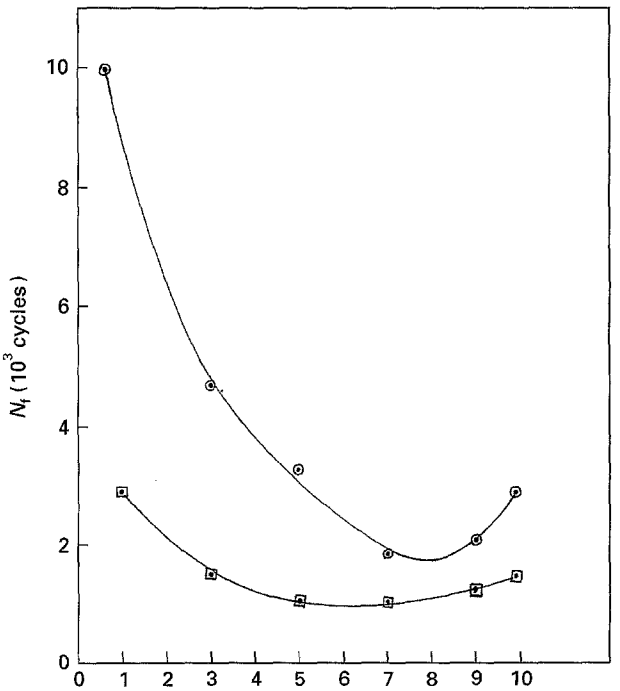

Figure 5 Cycles to failure versus time at maximum stress for square wave frequency = 0.1 Hz, ± 5MPa; t_{max} measured from 1 to 9.9 s. (⊙) PE-F, (⊡) PE-C.

corresponding conditions PE-F failed in 18 500 and 109 500 min, respectively.

Fig. 2a and b shows the crack opening displacement (COD) versus the number of cycles for each resin using three waveforms: square, sinusoidal and triangular. The effect of waveform on each resin was the same in that the cycles to failure (N_f) for PE-F was about three times N_f for PE-C for each waveform. Also, the ratios of N_f between waveforms are about the same for each resin.

Fig. 3 shows the effect of the ratio of minimum stress over maximum stress (R) for each resin. As R increases from -1 to $+1$ ($\sigma_{max.} = +5$ MPa). N_f increases in the same general way for each resin. The difference in N_f between the resins decreases to zero at $R = +0.5$. For $R = +1$, the values of N_f were calculated by converting the constant load lifetimes to cycles.

Fig. 4 shows the effect of frequency (f) at $R = -1$. For PE-F, $N_f = 8720\, f^{0.51}$ and for PE-C, $N_f = 3000\, f^{0.39}$. PE-F is more sensitive to frequency. The above equations predict that N_f would be equal for both resins at a frequency of 1.5×10^{-4} Hz.

In Fig. 5 the frequency is constant at a 10 s cycle; the waveform is square and $R = -1$. The time at maximum stress, t_{max}, was varied. Correspondingly, the time at the minimum stress varies as $10 - t_{max}$. For both resins, N_f goes to a minimum value at $t_{max} \sim 8$ s.

However, the rate of change of N_f with respect to t_{max} is greater for PE-F.

4. Discussion

In order to explain the effect of the fatigue parameters, waveform, f, R and t_{max}, it is useful to present a description of the fatigue process in polyethylene. When a notched specimen is initially loaded under plane strain conditions, a craze is formed. The fatigue resistance is indicated by the time or number of cycles at which the fibrils at the root of the notch fractures. As more fibrils fracture the crack propagates until the entire specimen fractures. For all polyethylenes the number of cycles to fracture, N_f, is related to the number of cycles to initiate fracture. Thus, the focus should be on how an individual fibril fractures, as illustrated in Fig. 6.

The most important factors that produce fibril fracture are the magnitude of the maximum load and t_{max} and the magnitude of the minimum load. When the maximum tensile load is applied, the fibril is damaged by a process of disentanglement of the molecules. When the minimum load is applied the fibril is damaged by being bent. Bending is most severe when the minimum load is compressive. The time during the bent state is not as important as the time spent in stretching the fibril.

The effect of waveform (Fig. 2) is readily explained by the fact that the time spent per cycle at the maximum stress decreases as the waveform goes from square to sinusoidal to triangular. In each case the damage done by bending is about the same, since the time spent during the bending of the fibril is not as important as the time spent during the stretching phase.

The effect of f is readily understood in Fig. 4 because the time spent per cycle under both the maximum and minimum stress is inversely related to the frequency.

The effect of R in Fig. 3 occurs because the damage by bending the fibril increases as R decreases. Every time the fibril is bent in each cycle it is damaged. Thus, the rate of disentanglement at the maximum stress is increased by the amount of prior damage produced at the minimum stress. Thus, the shape of the curves in Fig. 5 can be explained in terms of the following equation. We define the damage per cycle by $1/N_f$ and

$$\frac{1}{N_f} = \left[D_B\left(\frac{1}{f} - t_{max}\right)\right] D_s t_{max} \qquad (1)$$

where D_B is the damage rate by bending and $(1/f - t_{max})$ is the time spent at the minimum stress. D_s is the damage rate during stretching at the maximum stress. Equation 1 predicts the existence of the minimum in N_f observed in Fig. 5, but it wrongly predicts that the minimum should be at $t_{max} = 5$ s. Thus, Equation 1 is a simplification because the damage during stretching and bending are probably not linear functions of the time, and the time parameter probably does not have the same functional form for bending and stretching. The importance of Equation 1 is that it says that bending and stretching damage are interactive.

The fatigue experiments were conducted at 42 °C and a maximum stress of 5 MPa. It is interesting to determine the lifetime, t_f, under a constant load at 42 °C and 5 MPa stress. The measured lifetimes were at 80 °C, 2.4 MPa and 50 °C, 4.2 MPa. Extensive work by Brown *et al.* [8] showed that:

$$t_f = A\sigma^{-n}a^{-m}e^{Q/RT} \qquad (2)$$

where σ is stress, a is notch depth, and A, n, m and Q are material parameters. For all polyethylenes $2.6 < n < 5$; $1.3 < m < 2$ and $Q \approx 100\,000$ kJ mol^{-1}. A is the primary material parameter that denotes the big difference between polyethylenes since it can vary by a factor of 10^6 depending upon the molecular and morphological structure. Lu and Brown [9] found $n = 3.3$ and $Q = 117$ kJ mol^{-1} for PE-C. Using these same values for PE-F, the following results are obtained at 42 °C and 4.2 MPa: t_f (PE-C) $= 3.4 \times 10^5$ min and t_f (PE-F) $= 1.8 \times 10^5$ min. These failure times under a constant load when converted to cycles on the basis of a frequency of 1 Hz become N_f (PE-C) $= 2.0 \times 10^7$ cycles and N_f (PE-F) $= 1.1 \times 10^7$ cycles. These values of N_f are much larger than those under an oscillating stress and thus show that the damage per cycle inflicted on the fibril during bending is much greater than that produced by stretching. The damage during bending has a greater influence on the subsequent damage during stretching, whereas the stretching damage does not have as great an influence on the subsequent damage produced during the bending phase.

PE-C and PE-F both exhibit the same general behaviour with respect to the fatigue parameters, waveform, f, R and t_{max}. The quantitative difference in their behaviours with respect to these variables simply reflects the fact that PE-C suffers less damage with respect to the stretching process that takes place at the maximum stress and PE-F is stronger during the bending at the minimum stress.

In order to understand the difference between the two resins, it is useful to consider the difference between the fracture mechanisms during the stretching and bending of the fibril. Microscopic examinations of fibril fracture under a constant load by Brown and

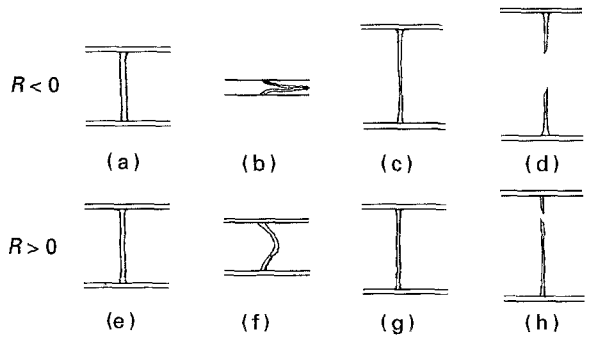

Figure 6 Sequence of failure process for a typical fibril for $R < 0$ and $R > 0$; (a) and (e) under maximum stress, (b) and (f) under minimum stress, (c) and (g) under maximum stress at a later stage. For $R < 0$ fracture occurs at centre of fibril (d). For $R > 0$ fracture occurs at end of fibril (h).

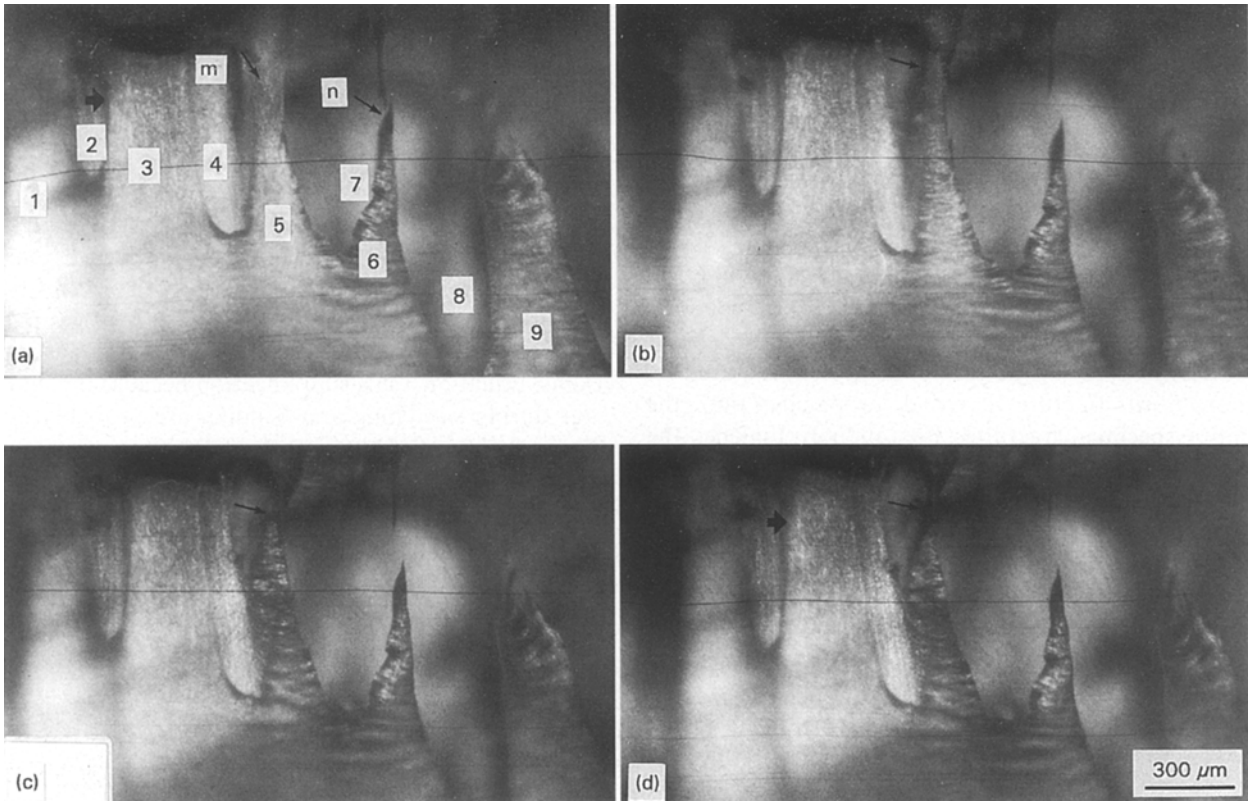

Figure 7 Successive stages in time, (a) to (d), for fibril fracture under a constant load. Note fracture by shear thinning of fibrils 5 and 7.

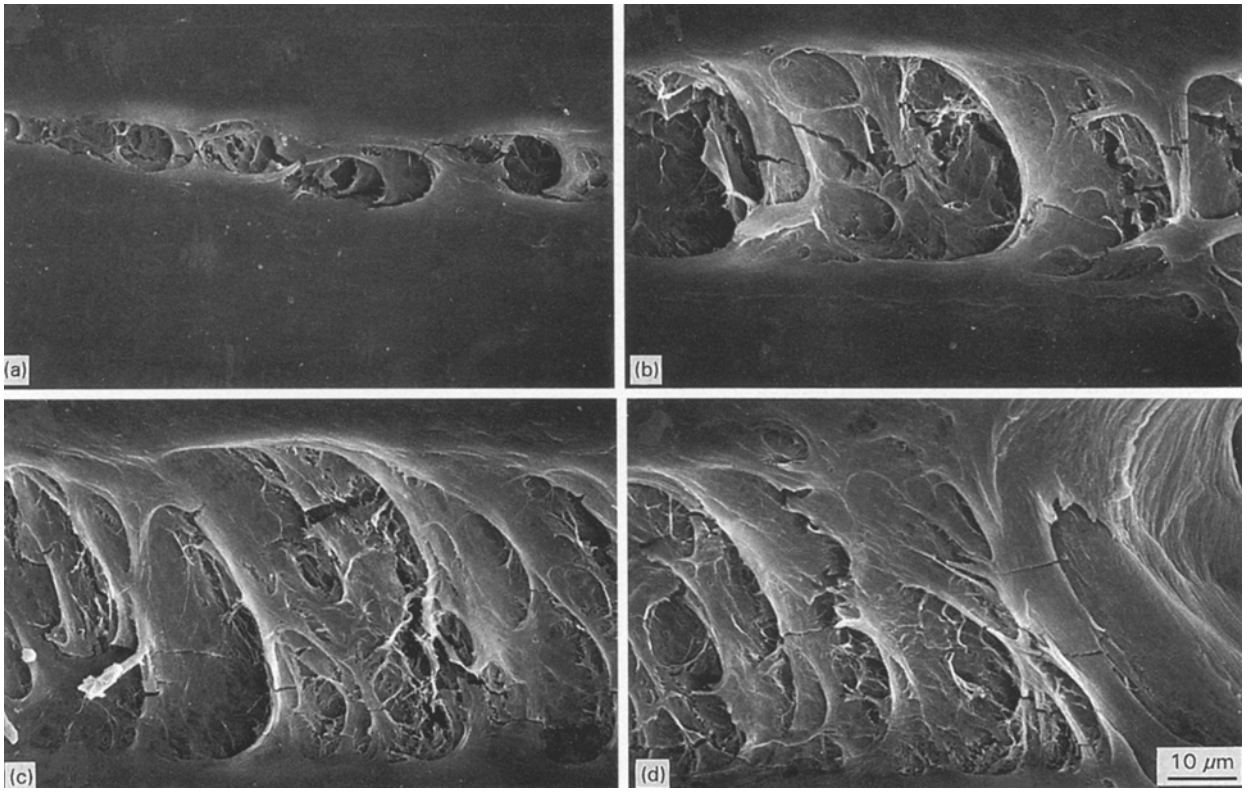

Figure 8 Successive positions in a craze produced by fatigue going from the tip (a) to near the base (d). Note the transverse fractures in the fibrils which do not occur in a constant load test.

coworkers [9, 10] has been described as a shear thinning process, as shown in Fig. 7. At the molecular level it has been described as a process of disentanglement of the molecules without the occurrence of chain scission. The damage by bending the fibril involves a high localized stress at the kink in the fibril (Fig. 6). Probably the fracture mechanism includes both chain sliding and scission. Since there is a high localized stress during bending, the fracture process is more rapid and the fracture path tends to be transverse to the length of the fibril, as shown in Fig. 8. Therefore, as the fracture propagates, all molecules in the path of the fracture

are likely to be cut during bending. It is suggested that molecular weight is a most important factor in determining the resistance to this rapid fracture process. In the case of the slow disentanglement process during stretching, the most important factor is the density of tie molecules that connect the crystals.

It is proposed (1) that PE-C is stronger under CL than PE-F because it contains more tie molecules and that these tie molecules have a higher density of short chain branches and (2) PE-F is stronger under fatigue loading because it has a higher molecular weight. Support for this proposal is based on our ongoing research, which shows that the rate of increase in fracture resistance with respect to molecular weight is greater for fatigue than under a constant load.

5. Summary

1. In polyethylenes a higher resistance to fatigue failure does not necessarily correlate with a higher resistance to failure under a constant load.
2. Fatigue failure in PE is a combination of damage by slow chain disentanglement under the maximum stress and more rapid damage by bending of fibrils at the minimum stress. The damage per cycle is much greater by bending the fibril than by stretching it.
3. Molecular weight has a greater influence on fracture by fatigue than under a constant load.

Acknowledgements

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