JOURNAL OF APPLIED POLYMER SCIENCE VOL. 16 (1972)

NOTES

Interrupted Stress–Strain Experiments of Nylon 6

INTRODUCTION

The ability of most polymers to exhibit yield behavior and cold drawing is well known even though the extent of the phenomena is dependent upon polymer type and experimental temperature.[1] If the stress–strain curve is interrupted in the cold-drawing region, Vincent has shown that a new yield peak will form in one case but not another.[2] It is just this aspect that is focused on here—interrupted stress–strain tests. In some cases the experiment was stopped at the yield peak and allowed to stress relax. This same technique was also done in other parts of the stress–strain curve. Other times the sample was unloaded completely and then pulled again.

EXPERIMENTAL

The material was Allied Chemical Company's caprolactam nylon 6 film, 1 mil in thickness. The sample size was 1 in. wide and 2 in. between clamps. All testing was done on a standard Instron testing machine. The cross-head and chart speeds were both 2 in./min, giving a strain rate of 100%/min. The stress relaxation was done by elongating the sample to the length desired and then stopping the downward travel of the crossbar. The unloading experiments were done by reversing the downward travel of the crossbar without stopping at all. The film was not treated in any way prior to use, therefore it contained an equilibrium amount of moisture. However, the room was thermostated at 72°F and 50% R.H., so all testing was done at constant temperature and humidity.

RESULTS

The original stress–strain curve of nylon 6 is that of a typically cold-drawing material (Fig. 1). There is a well-defined yield point followed by the relatively constant stress region during which the sample is necking down. After all the material between the clamps has necked down, there is a sharp, almost linear rise up to the breaking point. With minor variations, this is the type of curve one obtains from an uninterrupted tensile experiment on the Instron testing machine. However, when the experiment is interrupted, major variations occur the nature of which depend upon the point at which the experiment is stopped.

In Figure 2, the sample was elongated up to the yield point and then held constant. The sample "stress relaxes" spontaneously, very sharply at first and then much more gradually as an asymptotic function would. When the sample was elongated again, the yield peak that formed was of greater height than the original. Even the shape was different. There was a pointed peak superimposed on the original shape. The rest of the stress–strain curve followed the usual pattern. There was a cold-drawing region followed by the upward turn to the breaking point.

Figure 3 shows a sample that was handled only slightly differently. The sample was elongated up to the yield peak and then stopped, allowed to stress relax, and pulled again. As before, the yield peak is higher than it otherwise would have been. In the middle of the cold-drawing region, the elongation was again held constant. Once more the sample stress relaxed. When the sample was elongated again, another yield peak formed lower than the first but above the cold-drawing region. The elongation was stopped and allowed to stress relax toward the end also and pulled again. Even in this region another yield peak developed. After this yielding, the stress level rose sharply to the ultimate extension.

This series shows that not only can a higher-than-original yield peak be formed, but also yield peaks can be developed in the cold-drawing region and in the upper portion of the stress–strain curve as well. These phenomena have not been shown before.

Another sample was allowed to stress relax three times in the cold-drawing region, as can be seen in Figure 4. Each time the experiment was continued, a new yield peak developed. It was always smaller than the original but clearly defined above the normal cold-drawing stress level. More yield peaks were observed in the upper portion of the stress–strain curve as well. It seems there is no limit to the number of yield peaks that can be developed in any portion of the curve. The yielding behavior of nylon is obviously not a one-time event, but can be generated as often as desired provided there is still undrawn material left in the sample and it has been allowed to stress relax.

All the samples up to this point had been allowed to stress relax at the peak of the yield point. Figure 5 shows the results of allowing the sample to form the initial yield peak

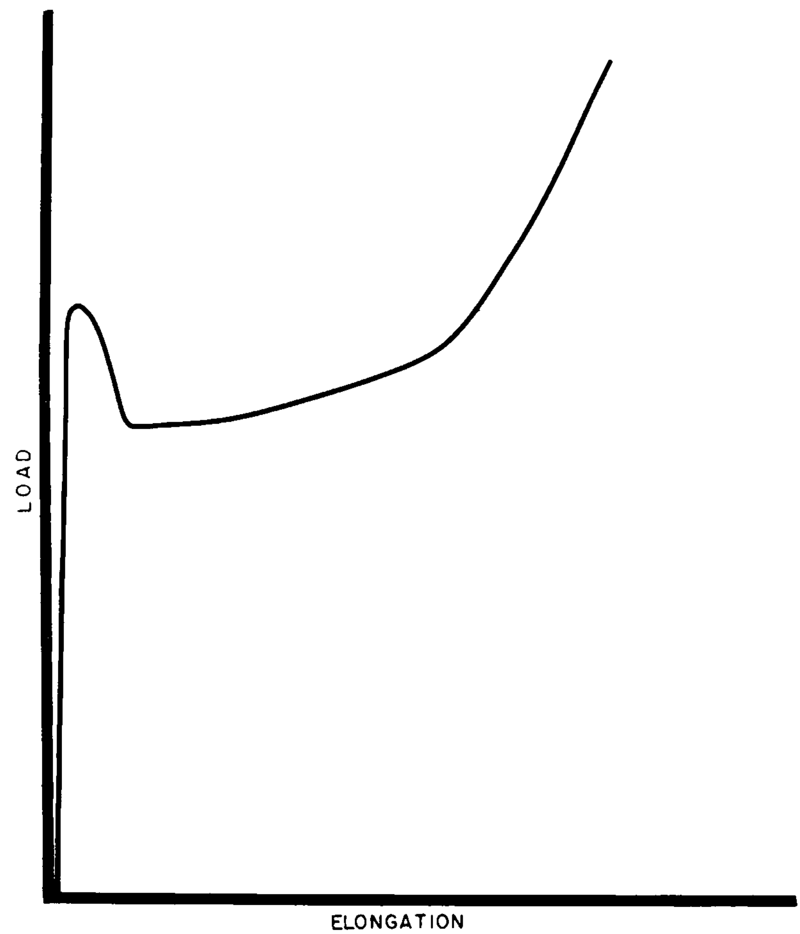

Fig. 1. Original stress–strain curve of nylon 6.

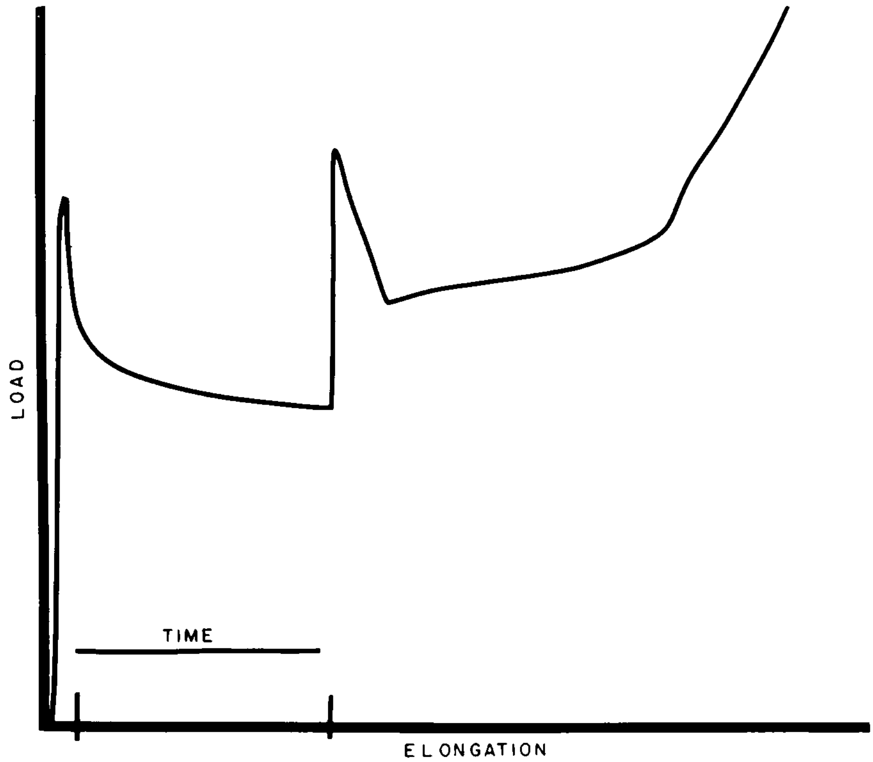

Fig. 2. Stress–strain curve interrupted at yield point, allowed to stress relax and pulled again.

first and then interrupting the experiment in the cold-drawing region. The sample was allowed to stress relax four times in the cold-drawing region, and each time a new yield peak formed when the sample was pulled again. The yield peaks were also formed in the upper portion of the curve as well. This shows that the sample can be pulled in the usual fashion to form the original yield peak and still develop a number of yield peaks afterward. It is true, however, that each of the successive yield peaks formed is always smaller than either the original normal one or the new one formed by stress relaxing at the original yield point. In Figure 6 we see a sample that has nine yield peaks after the original, all of which are within the cold-drawing region.

A slight variation was done in Figure 7. The sample was allowed to form the original yield peak and then allowed to stress relax the first time at the onset of cold drawing. This sample was allowed to stress relax for only seconds and pulled again. Each time the sample was allowed to relax for only seconds right after the yield peak formed. First, it can be seen that there are many yield peaks in what would normally be the cold-drawing region. Also, the height of the new yield peaks is smaller than had been formed in the other experiments. This means that the height of the new yield peaks is also related to a certain extent to the time allowed for stress relaxation. It may very well be that the longer the sample is allowed to stress relax, the higher the new yield peak will be.

These results permit one to draw certain conclusions concerning the cold drawing of nylon:

1. The "yielding" of the sample does not necessarily have to be limited to a single occurrence. It is limited to a single event if the sample is pulled continuously without interruption.

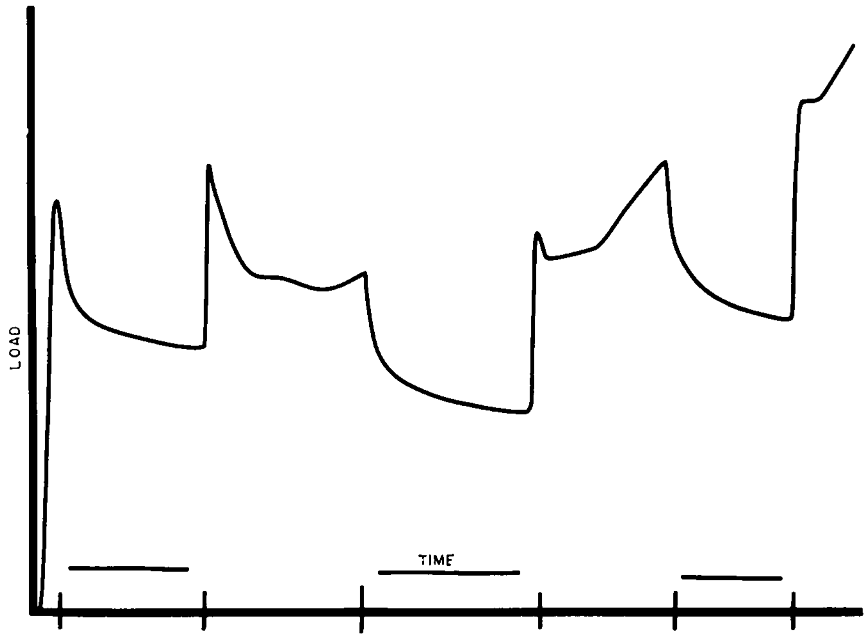

Fig. 3. Stress–strain curve interrupted at yield point, in cold-drawing region and in linear portion.

2. Allowing the sample to stress relax at the maximum of the original yield point will produce a new yield peak that is of greater intensity than the original.

3. Yield peaks can be formed in the cold-drawing region as well as in the final portions of the stress–strain curve.

4. The longer the sample is allowed to stress relax, the higher the new yield peak will be, within certain limits.

Some interpretation of what is transpiring at the molecular level is also possible at this time. The initial yielding of the polymer involves a breakdown of structure of some kind. It is not known, through, whether it is really at the molecular level or of a higher, gross structure sort. However, one thing is clear, the breakdown is not permanent or completely irreversible. Part of the original structure can be recovered through the stress relaxation process. The only condition under which the breakdown gives the impression of being complete or permanent is if the sample is pulled continuously. And here it is misleading only because of the stress concentration at the necking zone which causes the neck to propagate. It is clear that if for some reason the original neck did not propagate once formed, a new yield peak would develop along with a new necking region. This must mean that the structure breakdown is actually going on during the cold-drawing stage at the shoulder of the neck.

Evidence for the somewhat reversibility of the yielding process comes from the experiments in which the sample was elongated up to the yield peak and then held at constant length. After the sample was allowed to stress relax at the maximum of the yield peak and pulled again, it was found that the new yield peak was much higher than the original would have been. This combination of events seems to represent a contradiction in what is occurring. First of all, for the sample to stress relax means the sample must continue to orient itself in its direction of pull to relieve the stress. Logically then, it would seem reasonable for the original structure to be breaking down more. However, to obtain a higher-than-original yield peak, it would seem to be a prerequisite for the sample to return

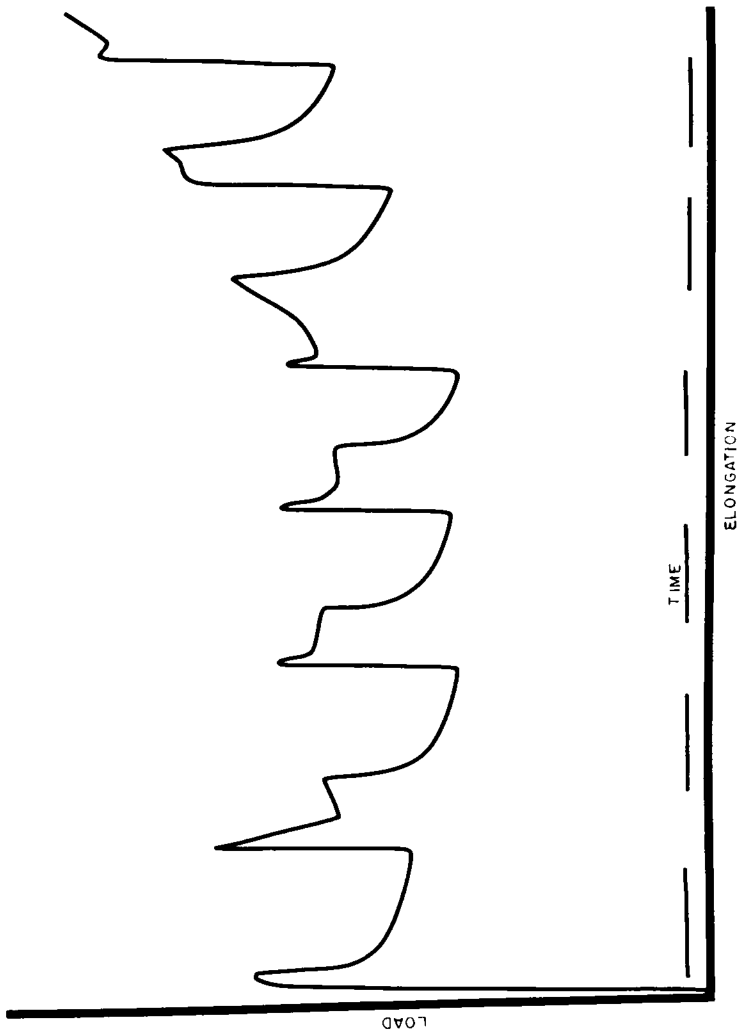

Fig. 4. Stress-strain curve interrupted at yield point and at 5 subsequent points.

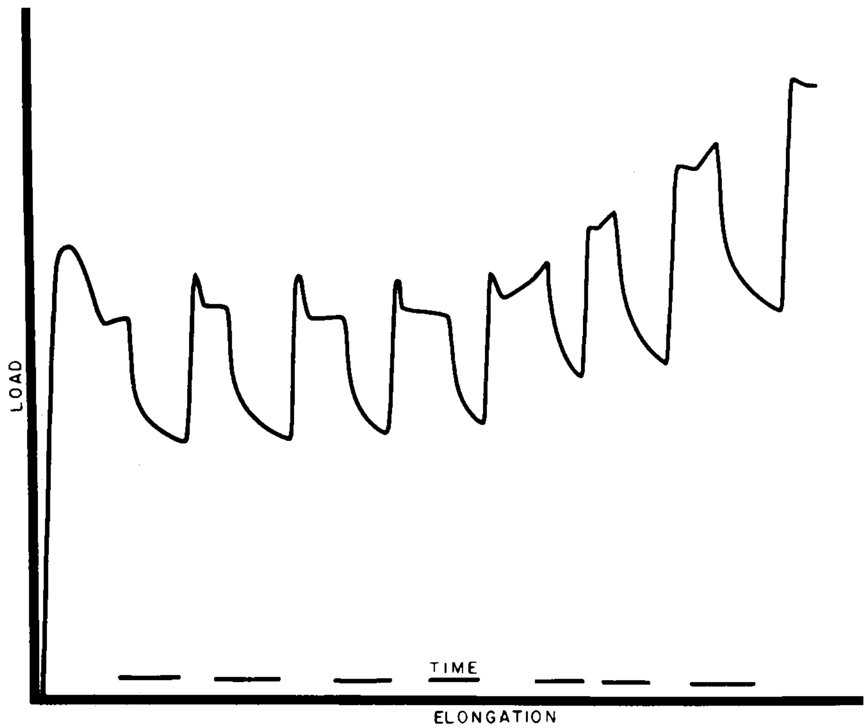

Fig. 5. Stress–strain curve interrupted 7 times in cold-drawing region.

to its original structure in a more stable or lower energy state. If the new state after stress relaxation were not more rigid, how can one account for the higher yield peak?

It is conceivable, however, that pulling the sample up to the top of the original yield peak and holding does not completely break down the original "set" but imparts mobility to it. Now, even though the sample is stress relaxing, which means the structure is rearranging to relieve the stress, the structure being formed during this stress relaxation period is a more rigid one than the original. It is also possible that analysis at this point should not involve a great deal of molecular motion but perhaps a very small amount of chain mobility coupled with "domain" or section mobility.

It has also been found that merely interrupting the stress–strain experiment is not sufficient to observe these phenomena. The sample must be allowed to stress relax at the original yield peak to observe the new higher yield peak. If the sample is not allowed to stress relax, the effect is not observed.

CONCLUSIONS

It is rather difficult to offer a definitive interpretation of what is going on during cold drawing, much less during interrupted cold-drawing experiments. Although we would have liked to add to the understanding of cold drawing, the present study must be taken more in the light of observations which, in conjunction with other observations, may lead to satisfactory explanations.

It is our intention to examine the structure of the polymer closely for distinguishing features which may have arisen as a result of these experiments. In addition, other polymers will be studied to see if what is reported here is specific in nature to nylon 6 or rather a general tendency of polymers under stress.

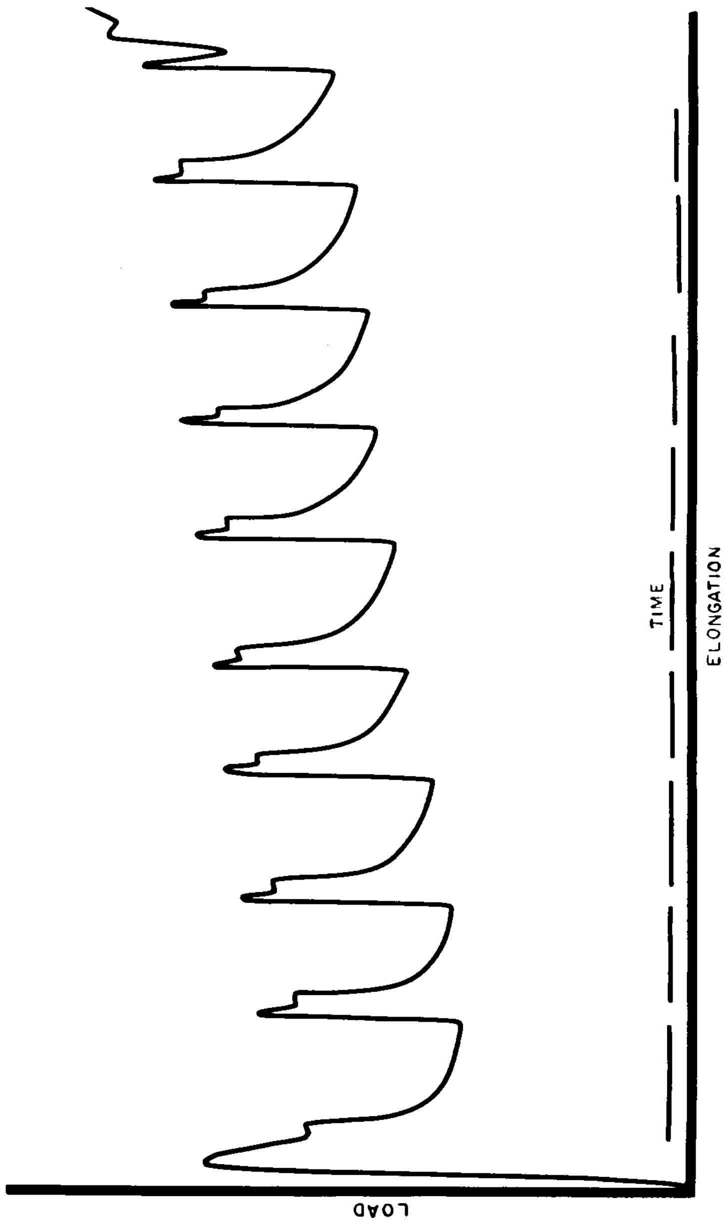

Fig. 6. Stress-strain curve interrupted 9 times in cold-drawing region.

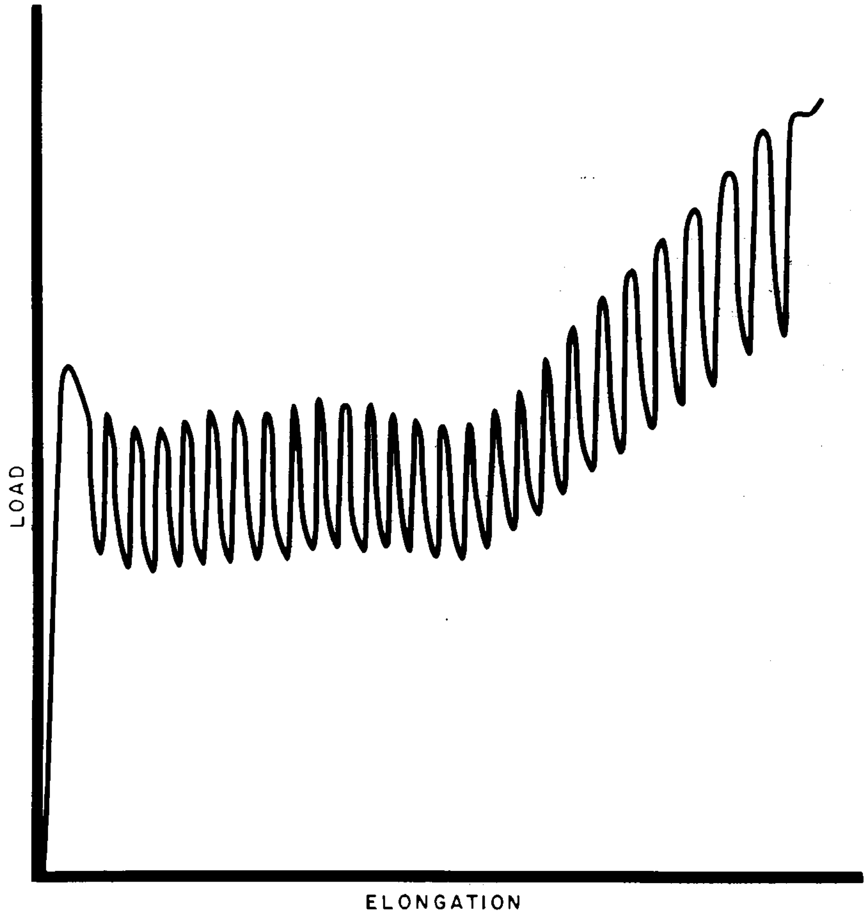

Fig. 7. Stress–strain curve of sample allowed to stress relax briefly (few seconds) 26 times after original yield point.

The author is most appreciative of the many helpful discussions with Prof. R. D. Andrews, Stevens Institute of Technology.

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Received October 28, 1971
Revised December 29, 1971