Additional Yield Peaks of Methylated Polyamide: Effect of Chain Length

INTRODUCTION

It has been described for some polymers exhibiting plastic deformation that if the tensile test is interrupted in the cold-drawing region, an additional peak appears on the stress–strain curve.[1–3] This means that the tensile test continues only after an increased stress has been applied, compared with the uninterrupted test. In rheological models plastic deformation is represented by Saint Venant's element of mechanical friction. The stress increment mentioned above may then be compared with the difference between the friction force at rest (static friction) and the friction of motion (kinetic friction). Up to now no definitive physical interpretation of this phenomenon has been proposed, neither has there been any unambiguous specification of the conditions of its occurrence. Vincent[1] found for unplastisized poly(vinyl chloride) that an additional peak appears if the test piece was allowed to relax; no peak appeared, however, if the sample was unloaded to zero. A detailed experimental study of nylon 66 fibers showed[2] that if the test was interrupted by a certain interval of relaxation and then continued again, not only was an additional peak formed, but the whole stress–strain curve was shifted toward higher stresses. The ultimate values of stress and strain were not distinctly affected, however. Additional yield peaks have also been observed[3] with nylon 6 after each interruption of the test by stress relaxations in the cold-drawing region. In this case the mechanism of the phenomenon is seen in a certain reversibility of the structural transformation at the shoulder of the neck.

EXPERIMENTAL

The starting material used in our investigation was copolymer of 12-dodecane lactam (1 mole) with N-methyl-12-dodecane lactam (2 moles) (sample 1). The polymer was linear and contained only amino groups as endgroups.[4] The number-average molecular weight of the sample was 8420. The presence of N-methyl lactam units gives rise to increased solubility and allows one to prepare a film for mechanical measurements by casting from a solution in chloroform. The decrease in crystallinity due to methylation may also explain the considerable decrease in the main transition temperature[5] with respect to the usual crystalline polyamides: $T_\alpha(100\ \text{Hz}) \sim -10°\text{C}$. Chains of sample 1 were linked to form an extended molecule[4] by a reaction with hexamethylene diisocyanate; in this molecule the block of sample 1 and the respective low molecular weight link (sample 2) were repeated several times. The number-average molecular weight of sample 2 was 64,000, which corresponds to 7.4 starting blocks in one chain.

Mechanical measurements of the two samples were performed with a table Instron apparatus at room temperature (25°C) and at a test rate 2 cm/min. The test pieces were cut out from films 30–150 μm thick and were in the form of strips with an initial width of ca. 5 mm and a working length of 1 cm. The repeatedly tested fragments of test pieces had the same working length.

RESULTS

Stress–strain patterns of samples 1 and 2 are plotted in Figure 1. Both samples had a distinct yield point, but drawing occurred rather homogeneously, without formation of a pronounced neck. Within the cold-drawing region, a hysteresis loop (until complete unloading of the test pieces) was performed with constant strain rate; after that, the strain was increasing till break. The curve of sample 1 continued after interruption in the original direction as if there were no interruption at all. On the other hand, on the curve of sample 2, secondary yield peaks were observed after interruption of the test and reloading. Moreover, ultimate tensile strength and strain-at-break values were higher for sample 2 with a higher molecular weight than sample 1. The interrupted tensile test was repeatedly performed also on fragments of test pieces of sample 2 (Fig. 2). In this case, too, secondary yield peaks appeared on the curves after interruption of the test. The tests were repeated on several test pieces with similar results.

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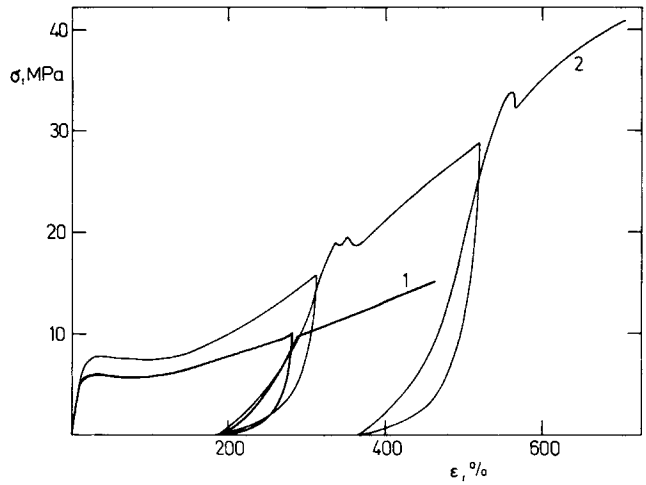

Fig. 1. Records of interrupted tensile tests of samples with various chain lengths interrupted by a hysteresis loop: 1, MW 8,400; 2, MW 64,000.

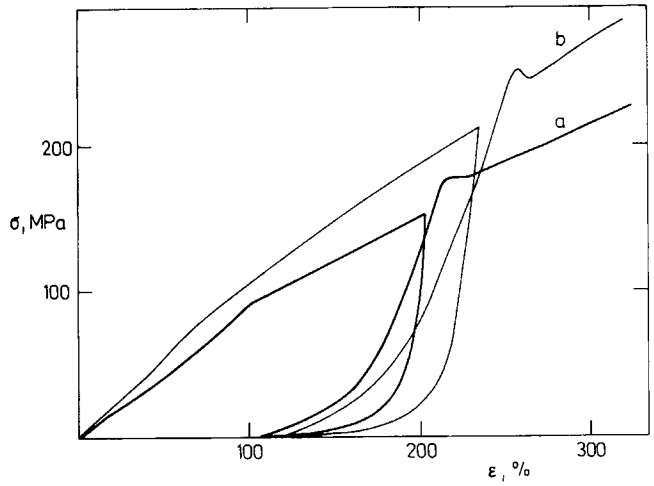

Fig. 2. Records of interrupted tensile tests repeated on fragments of sample 2 5 min after break: (a) tensile test repeated for a second time; (b) tensile test repeated for a third time.

The above results allow to infer that the occurrence of secondary yield peaks need not necessarily be related to the mechanism of neck formation and propagation. With drawn test pieces (Fig. 2), although the primary yield peak was not observed, additional peaks appeared after the test had been interrupted. Secondly, secondary peaks were observed with sample 2 but not with sample 1, which had a much lower molecular weight. This suggests a connection between the effect of "static friction" and physical interactions between adjacent molecules.

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