Fracture of Nylon Fibres

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Even though the phenomenon of polymer fracture is well know and well studied, it is still not well understood.

If a polymer bond is put under sufficient stress, it will break. However, a polymer chain will, if possible relieve stresses by slippage or change of conformation. To reach a stress high enough to break it, the chain must have restricted movement. This is, to some extent, the case in a highly oriented system, such as a fibre.

Orientation

A polymer chain can be regarded as a one-dimensional system since its length is at least 1000 times its diameter. The polymer has very different properties along the chain as compared to across it. In a completely relaxed state, polymer chains are coiled randomly, which means that the total system will show the same properties in all directions. The chains can, however, be aligned, i.e., oriented in one direction, which means that the total system will, just as the chains, have different properties in different directions, known as anisotropy. A fibre is a highly oriented polymer system.
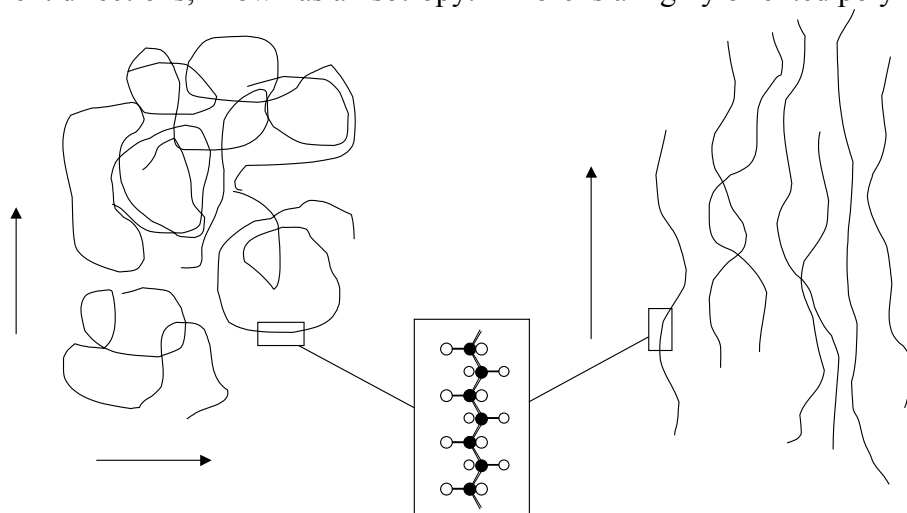

Figure 1. The left part of the figure shows randomly coiled chains. This system has the same properties in all directions. To the right are oriented chains, which gives the system different properties along and transverse to the orientation axis.

Crystallinity

In addition to orientation, a polymer can also organise in crystallites. Not all polymers can crystallise, since not all types of polymer chains can arrange themselves well enough to form crystals. Polystyrene is, for example, completely amorphous. A polymer is never 100% crystalline since it will always contain unordered parts, such as chain ends and flaws. Therefore, polymers with crystalline regions are called semi-crystalline. A polymer has to be semi-crystalline in order to be drawn into a fibre.

In an unoriented polymer the crystallites are spherulitic with the same characteristics in every direction. When the polymer is oriented, the sperulites will be deformed and rearrange in a different type of crystal called a micro-fibril. This process is called cold drawing, see Figure 2.
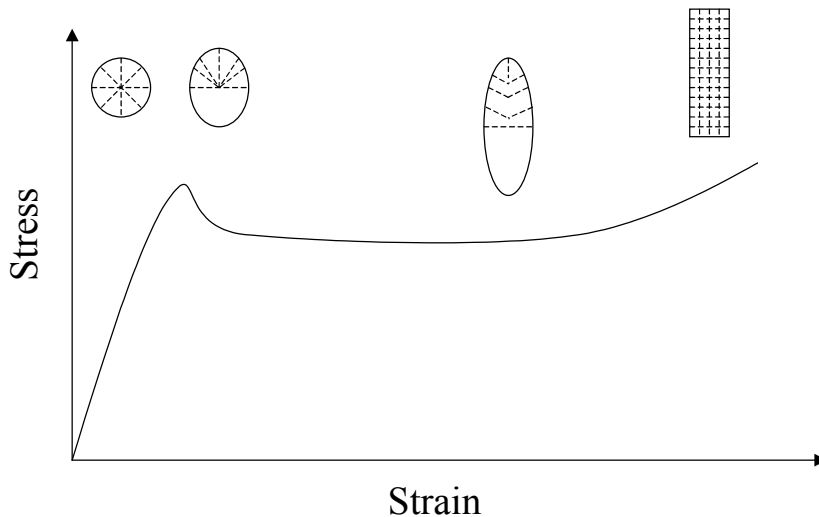
Figure 2. Stress-strain curve and reorganisation of the crystal structure for a semi-crystalline polymer during cold drawing.

Between the micro-fibrils there are amorphous parts. This part contains chain ends, closed loop chains and tie molecules. Closed loop chains starts and ends in the same crystal and will thus not help in holding the crystallites together. Tie molecules, on the other hand, start and end in different crystals and thus tie the crystallites together and are responsible for the ultimate strength of the polymer, see Figure 3.
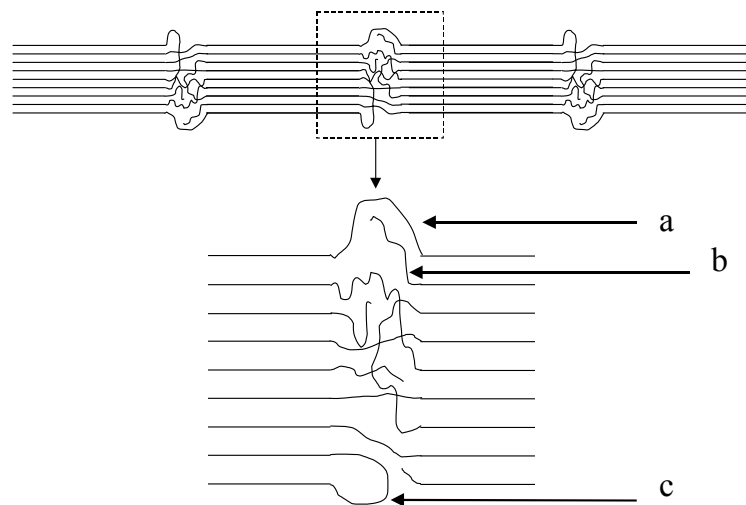

Figure 3. Crystalline and amorphous parts in a oriented system. a) Tie chain, b) chain end, c) closed loop chain.

Fracture
The tie chains will start to take the load when the system is stretched. They will then become taut and eventually, if they cannot relieve the stress in any other way, they will break. When they break they will form radicals, a very reactive molecular intermediate. The short tie chains will break first and then the slightly longer chains will start to take the load, see Figure 4.
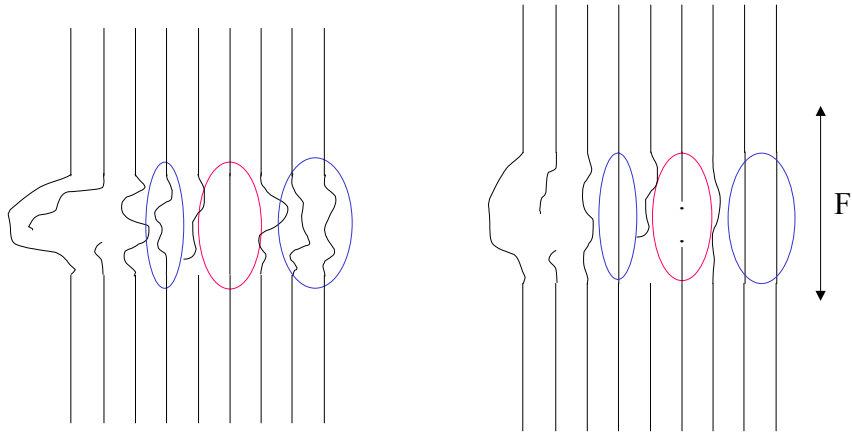
Figure 4. The taut tie chain in the middle circle breaks due to the applied force F. The slightly longer tie chains will then become taut and start to take the load.

Since there are more chains of intermediate length than short ones, see Figure 5, the polymer will get progressively stronger until so many chains have been broken that a crack will start to form. This crack will propagate and catastrophic failure will result.
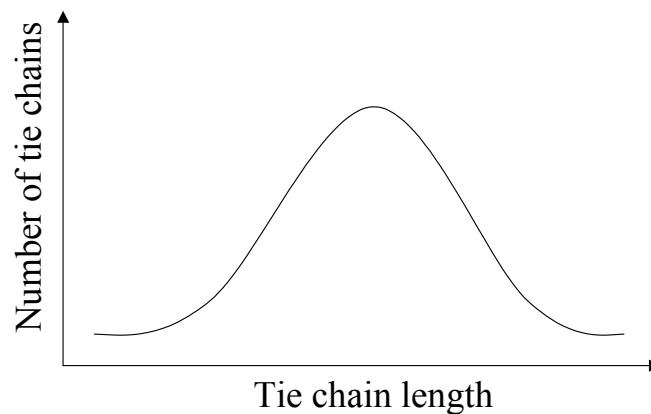

Figure 5. Distribution of the number of tie chains of different length.

Some researchers have reported that this crack will start when as few as 10% of the tie chains in a region have broken.

Measurements
When the chains are broken, radicals are formed. These are very reactive intermediates that are difficult to measure. There are, however, two measuring techniques, chemiluminescence (CL) and electron spin resonance (ESR) that have been used to study radicals formed at fracture. It is from the result of these measurements that the theory of fibre fracture has been derived. During the 1970's there were in particular two major research groups, one in Soviet Union and one in USA that worked with the ESR technique. The major findings were that radicals are not being detected until at approximately 60% of the ultimate load at failure of the fibre. Later a research group in Australia repeated the same measurements but using CL, which is known to be a more sensitive technique, and came to the same conclusion. Figure 6 shows a schematic drawing of how a CL and stress strain curve of a polyamide can look.

Figure 6. Schematic drawing of stress and CL as a function of strain of a polyamide fibre.

What was also found was that if the load is cycled the load of the previous cycle has to be surpassed in order to create new radicals, see Figure 7. This supports the theory that when stressed tie chains are broken and form radicals they are consumed and other longer chains will start to take the load.

Figure 7. Schematic drawing of CL and stress during cyclic loading of polyamide fibres.

The radicals that are formed are believed to originate from the fracture of either bond α or β in the following reaction scheme. These bonds are slightly weaker than the others due to the stabilising effect of the amide group.

References

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