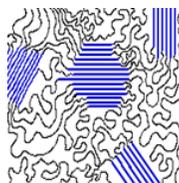


24.7: Polymer Structure and Properties

A comparison of the properties of polyethylene (both LDPE & HDPE) with the natural polymers rubber and cellulose is instructive. As noted above, synthetic HDPE macromolecules have masses ranging from 105 to 106 amu (LDPE molecules are more than a hundred times smaller). Rubber and cellulose molecules have similar mass ranges, but fewer monomer units because of the monomer's larger size. The physical properties of these three polymeric substances differ from each other, and of course from their monomers.

- HDPE is a rigid translucent solid which softens on heating above 100° C, and can be fashioned into various forms including films. It is not as easily stretched and deformed as is LDPE. HDPE is insoluble in water and most organic solvents, although some swelling may occur on immersion in the latter. HDPE is an excellent electrical insulator.
- LDPE is a soft translucent solid which deforms badly above 75° C. Films made from LDPE stretch easily and are commonly used for wrapping. LDPE is insoluble in water, but softens and swells on exposure to hydrocarbon solvents. Both LDPE and HDPE become brittle at very low temperatures (below -80° C). Ethylene, the common monomer for these polymers, is a low boiling (-104° C) gas.
- Natural (latex) rubber is an opaque, soft, easily deformable solid that becomes sticky when heated (above. 60° C), and brittle when cooled below -50° C. It swells to more than double its size in nonpolar organic solvents like toluene, eventually dissolving, but is impermeable to water. The C₅H₈ monomer isoprene is a volatile liquid (b.p. 34° C).
- Pure cellulose, in the form of cotton, is a soft flexible fiber, essentially unchanged by variations in temperature ranging from -70 to 80° C. Cotton absorbs water readily, but is unaffected by immersion in toluene or most other organic solvents. Cellulose fibers may be bent and twisted, but do not stretch much before breaking. The monomer of cellulose is the C₆H₁₂O₆ aldohexose D-glucose. Glucose is a water soluble solid melting below 150° C.



To account for the differences noted here we need to consider the nature of the aggregate macromolecular structure, or morphology, of each substance. Because polymer molecules are so large, they generally pack together in a non-uniform fashion, with ordered or crystalline-like regions mixed together with disordered or amorphous domains. In some cases the entire solid may be amorphous, composed entirely of coiled and tangled macromolecular chains. Crystallinity occurs when linear polymer chains are structurally oriented in a uniform three-dimensional matrix. In the diagram on the right, crystalline domains are colored blue.

Increased crystallinity is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent.

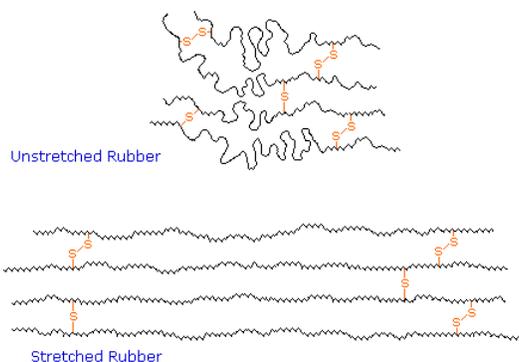
Three factors that influence the degree of crystallinity are:

- Chain length
- Chain branching
- Interchain bonding

The importance of the first two factors is nicely illustrated by the differences between LDPE and HDPE. As noted earlier, HDPE is composed of very long unbranched hydrocarbon chains. These pack together easily in crystalline domains that alternate with amorphous segments, and the resulting material, while relatively strong and stiff, retains a degree of flexibility. In contrast, LDPE is composed of smaller and more highly branched chains which do not easily adopt crystalline structures. This material is therefore softer, weaker, less dense and more easily deformed than HDPE. As a rule, mechanical properties such as ductility, tensile strength, and hardness rise and eventually level off with increasing chain length.

The nature of cellulose supports the above analysis and demonstrates the importance of the third factor (iii). To begin with, cellulose chains easily adopt a stable rod-like conformation. These molecules align themselves side by side into fibers that are stabilized by inter-chain hydrogen bonding between the three hydroxyl groups on each monomer unit. Consequently, crystallinity is high and the cellulose molecules do not move or slip relative to each other. The high concentration of hydroxyl groups also accounts for the facile absorption of water that is characteristic of cotton.

Natural rubber is a completely amorphous polymer. Unfortunately, the potentially useful properties of raw latex rubber are limited by temperature dependence; however, these properties can be modified by chemical change. The cis-double bonds in the hydrocarbon chain provide planar segments that stiffen, but do not straighten the chain. If these rigid segments are completely removed by hydrogenation (H_2 & Pt catalyst), the chains lose all constraint, and the product is a low melting paraffin-like semisolid of little value. If instead, the chains of rubber molecules are slightly cross-linked by sulfur atoms, a process called vulcanization which was discovered by Charles Goodyear in 1839, the desirable elastomeric properties of rubber are substantially improved. At 2 to 3% crosslinking a useful soft rubber, that no longer suffers stickiness and brittleness problems on heating and cooling, is obtained. At 25 to 35% crosslinking a rigid hard rubber product is formed. The following illustration shows a cross-linked section of amorphous rubber. By clicking on the diagram it will change to a display of the corresponding stretched section. The more highly-ordered chains in the stretched conformation are entropically unstable and return to their original coiled state when allowed to relax



Contributors

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