14.8 Factors that influence the mechanical properties of semicrystalline polymers

A no of factors influence the mechanical characteristics of polymeric materials.

~~eg~~. In addition, several structural/processing factors have decided influences ~~of~~ on the mechanical behaviour (i.e. strength and modulus) of polymeric materials. An increase in strength results ~~is~~ whenever any restraint is imposed on the process; eg. extensive chain entanglements or a significant degree of intermolecular bonding inhibit relative chain motions. It should be noted that even though secondary intermolecular (eg van der Waals) bonds are much weaker than the primary covalent ones, significant intermolecular forces result from the formation of large numbers of van der Waals interchain bonds. Furthermore, the modulus rises as both the secondary bond strength & chain alignment increase. As a result, polymers with polar groups will have stronger secondary bonds and a larger elastic modulus.

Effect of structural/processing factors on mechanical behavior of polymers.

- ✓ Molecular weight.
- ✓ Degree of crystallinity
- ✓ Predeformation by drawing
- ✓ Heat Treating.

Molecular wt.

The magnitude of the tensile modulus does not seem to be directly influenced by molecular weight.

TS increases with increasing molecular wt.

$$TS = TS_\infty - \frac{A}{\overline{M}_n}$$

TS_∞ is the tensile strength at infinite molecular wt.

A is a constant.

Behavior in Eqn ~~describes~~ can be explained by increased chain entaglements with rising $\overline{M}_n$.

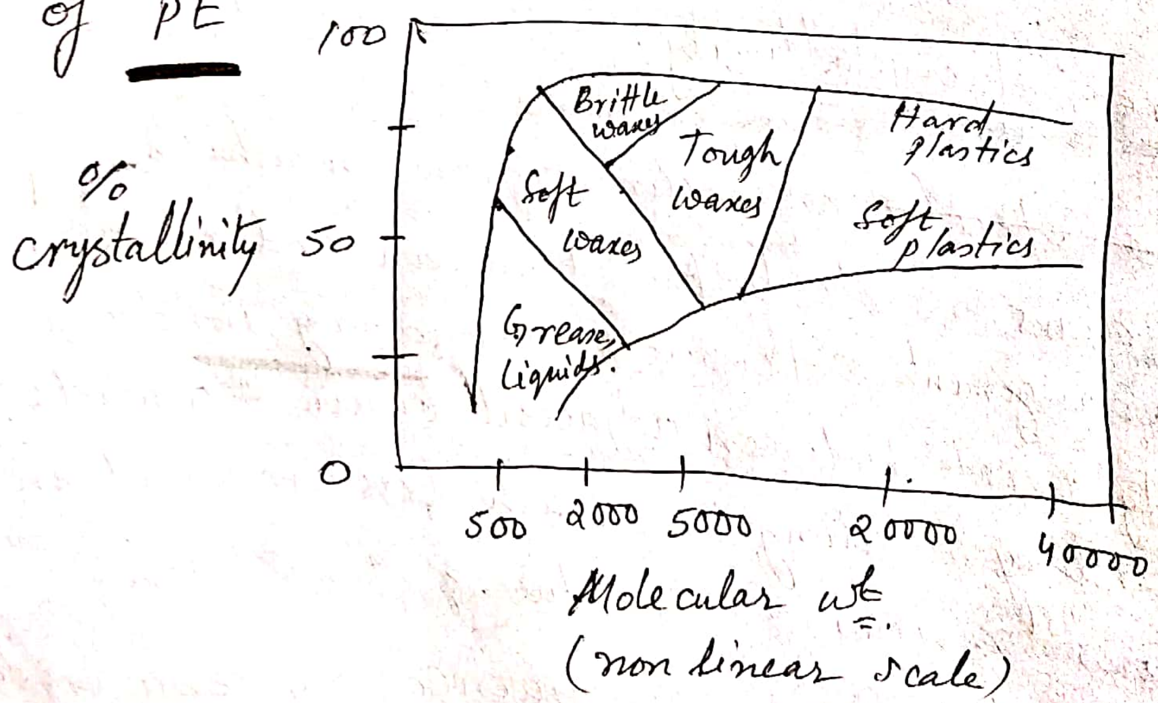
Degree of crystallinity.

For ~~a specific~~ crystalline regions in which molecular chains are closely packed in an ordered and parallel arrangement, extensive secondary bonding ordinarily exists between adjacent chain segments. This secondary bonding is much less prevalent in amorphous regions, by virtue of the chain misalignment. As a consequence, for semi-crystalline polymers, tensile modulus increases significantly with degree of crystallinity.

eg. Polyethylene — modulus increases approximately ~~with~~ an order of magnitude as the crystallinity fraction is raised from 0.3 to 0.6.

Furthermore, increasing the crystallinity of a polymer generally enhances its strength; in ~~d~~ addition, the material tends to become more brittle. The influence of chain chemistry & structure (branching, stereoisomerism, etc) on ~~dege~~ degree of crystallinity ~~et~~ shold also be taken into account.

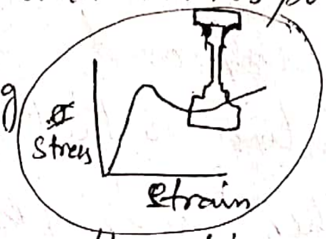
The influence of degree of crystallinity and molecular weight on the physical characteristics ~~on~~ of PE



Predeformation by drawing

~~On a Drawing — Perman~~

Mechanical strength and tensile modulus is to permanently deform the polymer in tension. This procedure is called Drawing and corresponds to the neck extension ~~procedo~~ process in fig



In terms of property alterations, drawing is the polymer analog of strain hardening in metals. During drawing of fibers & films, the molecular chains slip past one another & become highly oriented; for semicrystalline materials the chains assume conformations similiar to that represented in fig →

Degrees of strengthening and stiffening will depend on the extent of deformation (or extension) of the material. Furthermore, the properties of drawn polymers are highly anisotropic. For those materials drawn in uniaxial tension, tensile modulus and strength values are significantly greater in the direction of deformation than in other directions. Tensile modulus in the direction of drawing may be enhanced by up to approximately a factor of 3 relative to the undrawn material. At an angle of 45° from the tensile axis the modulus is a minimum; at this orientation the modulus has a value on the order of one-fifth that of the undrawn polymer.

Tensile strength parallel to the direction of orientation may be improved by a factor of at least two to five relative to that of the unoriented material. On the other hand, perpendicular to the alignment direction, tensile strength is reduced by, ~~on~~ on the order of ~~of~~ $\frac{1}{3}$rd to $\frac{1}{2}$.

For an amorphous polymer that is drawn at an elevated temperature, the oriented molecular structure is retained only when the material is quickly cooled to the ambient; this procedure gives rise to the strengthening & stiffening effects. On the other hand, if, after stretching, the polymer is held at the temperature of drawing, molecular chains relax and assume random conformations characteristics of the predeformed state; as a consequence, drawing will have no effect on the mechanical characteristics of the material.

Heat treating

Heat treating (or annealing) of semicrystalline polymers can lead to an increase in the % crystallinity, and crystallite size and perfection, as well as modifications of the spherulite structure.

For undrawn materials that are subjected to constant-time heat treatments, increasing the annealing temperature leads to the following:-

① an increase in tensile modulus.
② an increase in yield strength and
③ ~~an increase in~~ a reduction in ductility.

Note that these annealing effects are opposite to those typically observed for metallic materials — i.e. weakening, softening and enhanced ductility.

For some polymer fibers that have been drawn, the influence of annealing on the tensile modulus = decreases with increased annealing temperature due to a loss of chain orientation and strain induced crystallinity.

Deformation of Elastomers.

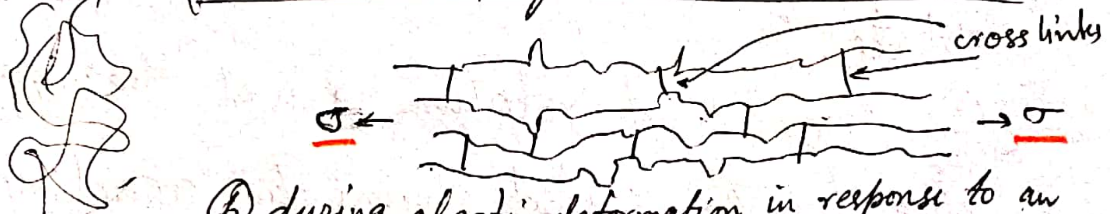
~~One of the f~~ Elastomers have the ability to be deformed to quite large deformations, and then elastically spring back to their original form. This results from crosslinks in the polymer that provide a force to restore the chains to their undeformed conformations.

Elastomeric behaviour was probably first observed in natural rubber

Typical SS characteristics = Their moduli of elasticity are quite small & furthermore, vary with strain since the ~~st~~ S S curve is non-linear.

In an unstressed state, an elastomer will be amorphous and composed of crosslinked molecular chains that are highly twisted, kinked and coiled. Elastic deformation, upon application of a tensile load is simply the partial uncoiling, untwisting, and straightening, and the resultant elongation of the chains in the stress direction. (Fig). Upon release of the stress, the chains spring back to their prestressed conformations, and the macroscopic piece returns to its original shape.

Crosslinked polymer chain molecules



~~unstress~~ (a) un stressed state

(b) during elastic deformation in response to an applied tensile stress.

Part of the driving force for elastic deformation is a TD parameter called entropy, ~~which~~ (measure of the degree of disorder within a system; entropy increases with increasing disorder).

As an elastomer is stretched and the chains straighten and become more aligned, the system becomes more ordered. From this state, the entropy increases if the chains return to their original kinked and coiled contours. Two intriguing phenomena result from this entropic effect. First, when stretched, an elastomer experiences a rise in temperature, ~~which is opposite to the behaviour found~~ Second, the modulus of elasticity increases with increasing temp., which is opposite to the behaviour in other materials.

Several criteria must be met for a polymer to be elastomeric :-

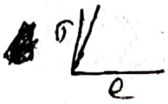
① It must not easily crystallize; elastomeric materials are ~~asf~~ amorphous, having molecular chains that are naturally coiled and kinked in the unstressed state.

② Chain bond rotations must be relatively free for the coiled chains to readily respond to an applied force.

③ For Elastomers to experience relatively large elastic deformations, the onset of plastic deformation must be delayed.

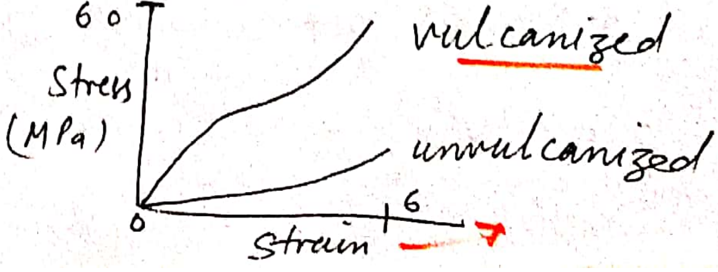
Restricting the motions of chains past one another by crosslinking accomplishes this objective. The crosslinks act as anchor points between the chains and prevent chain slippage from occurring. ; the role of cross links in the deformation process is seen in previous fig. Crosslinking in many elastomers is carried out ~~using~~ in a process called vulcanization,

Finally the elastomer must be above its Tg.

The lowest temp. at which rubber like behaviour persists for many of the common elastomers is between -50 & -90°C. Below its Tg, an elastomer becomes brittle such that its stress-strain behaviour resembles curve  .

Vulcanization :- crosslinking process in elastomers

600% elongation



Useful rubber) 1 to 5 parts by wt sulfur + 100 parts rubber. one crosslink for every 10 or 20 repeat units

Concept check