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MECHANICAL PERFORMANCE OF POLYMERS

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Polymers are shaped in their fluid state and used in their solid state. And polymers are rich not only in their huge variety in chemical composition but even more because of the large number of different structures they form. The intrinsic anisotropy, given the long one dimensional flexible chains that constitute polymers, is characterized by the difference in bond strength of the primary, usually covalent, bonds along the chain and the secondary, usually Van der Waals or hydrogen, bonds between chains. A (thermoplastic) polymer differs from its monomer, or oligomer, by its length that forms physical entanglements. The entangled network orients in flow and retracts (on two time scales: inside its tube formed by the presence of its neighbours that holds the target chain, Rouse relaxation, and by relaxing the tube itself, disengagement). The chain dangles at its ends (contour length fluctuations) and escapes from its neighbours, while neighbours tend to escape as well (convective constraint release). It is a match, a game with winners and losers, and part of the dynamics is slowed down and finally frozen in by cooling. It is for this reason that quantitative rheology, the science of non-Newtonian fluid mechanics, is important to predict, for example, frozen-in molecular orientation that reflects the anisotropy remaining in the product formed induced by flow during making of the product.

In the fluid state, the secondary bonds loose strength and degenerate to a background viscosity to the moving chains, with friction coefficient ζ usually thought concentrated in beads that, connected by springs, constitute an idealized chain. After averaging, fluid rheology concentrates on how smooth, but dynamic, entangled ropes move in flow. Sometimes the ropes are branched, making snake type escape motion much more complex. Displacements are large.

In the solid state, displacements are limited and all properties are determined by the secondary bonds by which chains interact. But polymers are not as solid as thought on first sight and even in the solid state they are fluids, albeit with a huge viscosity. Even without applying stress, local motion of chain parts is possible, allowing the chains to slowly reach a situation more close to local equilibrium, which was not reach because chain kinetics considerably slow down when passing the glass transition upon cooling, or when crystals appear freezing in the entanglement structure. This process of physical ageing has been studied for a long time. But there is more. Of course temperature, but much more interesting and drastic also stress decreases the viscosity that results from the secondary bonds. As a consequence, yielding is rate dependent and can be considered as stress induced melting, or a stress induced passing of T_g. The material flows and upon increasing the deformation, the entangled network is stretched and oriented. In solid state rheology, the network is rather boring, Neo-Hookean is sufficient, but the viscosity between the chains forming the network is complex and rich. Even the network modulus depends somewhat on network density, but more upon the distance to T_g. Upon releasing the stress, the viscosity immediately increases a number of decades and the apparent solid is reformed. More fun is that the history of physical ageing, the local increase in viscosity by a local increase in density by local better packing of chains, can be completely removed by flow: a process called mechanical rejuvenation. It can be understood considering that local segmental flow removes local segmental densification.

Interesting is that overall mechanical performance of polymers is completely determined by (i) the value of the stress at yield, (ii) the mechanical rejuvenation that follows upon segmental flow and results in macroscopic strain softening, and (iii) the network stretch that results in macroscopic strain hardening. Solid state rheology focuses on a quantitative prediction of how the viscosity of the secondary bonds depend on temperature, stress, strain rate, and the intrinsic state of the material represented by its age and the counter process which is rejuvenation upon local flow. Fun is that ageing kinetics is not only accelerated by temperature, but also by stress itself, since both increase the local segmental mobility. This all makes not only the interpretation of a simple tensile test somewhat more complex that thought on first sight, but also allows quantitative prediction of the complete processing history in the present state of the polymer, but also how this state develops in time. Interesting moreover is that all kinetic parameters are determined by the segmental mobility only, changing the secondary interactions between the chains, and therefore do not depend on molecular weight(distribution) of the polymer and consequently have to be determined only once. Without performing any mechanical test, the long term failure behavior of

polymers under static or dynamic loading can be quantitatively predicted once the processing history is known.
Conclusion: Fluid rheologists are happy, since at high temperatures, or in the presence of solvents, they can simplify the secondary interactions between chains to a local friction coefficient experienced upon relative motion of passing chains, and can focus their attention completely on the behavior of smooth entangled ropes that move like snakes in a non-affine way within an imposed flow. Solid rheologist are happy, since for them the network contribution is just that of a spring, with a somewhat strange spring modulus, experiencing an affine motion, and can focus their attention on how ageing kinetics, temperature, stress and deformation rate determine the viscosity, which is the result of the secondary interactions. Both rheologists, however, meet when we want to predict the mechanical performance of semi-crystalline polymers. In these polymers, details of segmental orientation of the entangled chains in flow determine not only the stress during flow, but also nucleate crystallization, enhancing its rate tremendously, but moreover direct the anisotropy of the crystals formed. As a consequence, the presence of a tiny bit of high molecular tail in the molecular weight distribution of a polymer can make a completely different product with completely different mechanical performance. It remains to be seen whether fluid and solid state rheologists stay happy, facing this challenge. In any way, they need each other and have to rely on each other skills. We are probably facing an era of great cooperation.