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Course Notes of Chapter 4.3

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1. Behavior in the Solid State at Large Deformations: Plasticity vs. Fragile Rupture

Although viscoelasticity above T_g or T_m is very important for processing and the mechanical behavior of elastomers, most plastics are used in their "rigid" solid form for more or less structural applications,[1] i.e. either in their glassy or semi-crystalline state.

So far, we have stated that the elasticity of glassy or semicrystalline polymers depends mainly on van der Waals forces, because changes in conformation are not possible[2] - at least those involving a large number of bonds. The behavior at large deformations is, however, critical for the strength of an article and therefore for structural or semi-structural applications.

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[1] Elastomers are also solids, but they are not rigid.
[2] The amorphous regions of a semi-crystalline polymer show rubbery behavior, if the T_g is quite low, but the elastic modulus is dominated by the crystalline regions in this case.

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We will first deal with a special case of nonlinear viscoelasticity: the "**plastic deformation**". In fact, polymers are generally considered to be "plastic" materials, insofar as they are capable of large irreversible deformations in the glassy or semi-crystalline solid state, where they exhibit an elastic modulus on the GPa order. As indicated schematically on Slide 298, some polymers such as HDPE are indeed very ductile at ambient temperature, whereas others, such as PS, are not at all. They show a brittle behavior and tensile strain-at-break of only a few percent. This is often linked to the formation of "**crazes**". We will see that the **competition between plasticity and craze formation is highly dependent on the density of entanglements and that the brittleness is therefore intrinsic to certain types of polymers**.

This competition is also very important in practice. Provided that plasticity occurs at a relatively high stress, a significant plastic deformation leads to significant energy dissipation in the form of heat, because it is effectively irreversible. Ductile materials also show good resistance to cracking because it takes a lot of energy to advance the plastic zone that forms at the head of a crack. Ductility leads thus to a predictable behavior under stress and, even if we typically apply stresses well below the threshold of macroscopic plasticity during the fabrication of a part, high energy absorption at large deformations is often essential for safety reasons - would you prefer the glassy visor of a motorcycle helmet to be made from PS or polycarbonate (PC), for example? However, the same considerations would not necessarily come into play for other types of applications, such as a single-use cup.

2. Plasticity of Polymers: Phenomenology and Models

2.1 Particularities of Plasticity of Polymers

Metals and some ceramics are also capable of plastic deformation, but there are important differences between the behavior of ductile metals in tension and that of polymers.

In ductile metals we generally observe a well-defined elastic limit and a threshold of plasticity which depends little on the temperature and the strain rate under conditions of usual use (ambient temperature, non-ballistic strain rates). In addition, at some exceptions related to the superplasticity of shape memory metals, for example, any deformation of a metal beyond its plastic threshold is strictly irreversible and leads quickly to failure in tension.

In contrast, the distinction between elastic deformation (reversible) and plastic deformation (irreversible) is less distinct in polymers, which may show strongly non-linear viscoelastic behavior for strains much lower than the plasticity threshold, and, as we have seen, the notion of reversible deformation in a viscoelastic material depends on the time scale and temperature. Indeed, even very large plastic deformations (therefore irreversible at the time scale of the measurement) can be recovered, for example, by heating the polymer to a temperature above T_g, that is, by forcing it into the rubbery state. As we will see, this behavior is directly related to the observation of a stable plastic necking zone in ductile polymers deformed in tension.

2.2 Plastic Necking and the Role of Entanglements

During a tensile test at constant speed, a "nominal" stress ($\sigma = f/A_0$) – "nominal" strain ($\varepsilon = l - l_0/l_0$) – curve is typically obtained, where f is the measured force, l and l_0 are the instantaneous length and initial length of the sample, and A_0 is the initial cross section. Plasticity manifests itself in different ways depending on the polymer (cf. Slide 306), but it is often associated with a maximum stress, which allows us to define the threshold of plasticity σ_y by:

$$\left.\frac{d\sigma}{d\varepsilon}\right|_{\sigma_y} \equiv \left.\frac{d\sigma}{d\lambda}\right|_{\sigma_y} = 0 \qquad (1),$$

where $\lambda = 1 + \varepsilon$ (see the course on rubber elasticity).

At large deformations, the "true" stress, σ_r, is greater than σ, because the instantaneous section of the sample tends to decrease with uniaxial tensile strain. Indeed, as in the case of an elastomer, we will admit that the plastic deformation is isovolumic, i.e. that the material is incompressible. This is reasonable for large deformations because the threshold of plasticity of a rigid polymer is typically 1 to 2 orders of magnitude lower than the Young's and compressive moduli, K (a few tens of MPa compared to a few GPa). Elastic extension is therefore negligible compared to the plastic strain.

If the volume remains constant,

$$Al = A_0 l_0 \Rightarrow A = A_0 \frac{l_0}{l} = A_0 \lambda$$

so

$$\sigma_r = \frac{f}{A} = \lambda\sigma$$

and

$$\frac{d\sigma}{d\lambda} = \frac{d}{d\lambda}\left(\frac{\sigma_r}{\lambda}\right) = \frac{1}{\lambda}\frac{d\sigma_r}{d\lambda} - \frac{\sigma_r}{\lambda^2} \qquad (2).$$

At the plasticity threshold defined by Equation 1,

$$\frac{1}{\lambda}\frac{d\sigma_r}{d\lambda} - \frac{\sigma_r}{\lambda^2} = 0 \Rightarrow \frac{d\sigma_r}{d\lambda} = \frac{\sigma_r}{\lambda} \qquad (3).$$

In general, we observe that the slope of σ_r vs. λ decreases monotonically with λ at around the plasticity threshold. Thus, the nominal stress, σ, begins to decrease when λ exceeds its value at the plasticity threshold, because

$$\frac{1}{\lambda}\frac{d\sigma_r}{d\lambda} - \frac{\sigma_r}{\lambda^2} = \frac{d\sigma}{d\lambda} < 0$$

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There is therefore an instability which leads to the formation of a neck, i.e. a strong localization of the deformation, and σ reaches a maximum at σ_y followed by a sharp decrease (*yield drop*). This is valid whatever the material because it is a neck of purely geometric origin. Nevertheless, σ_r often shows an intrinsic yield drop in glassy polymers, which is related to aging effects when the sample is kept for a long time below T_g, which increases instability (Slide 306). Finally, if the intrinsic behavior $\sigma_r(\lambda)$ is known (which is not often the case) it is possible to determine the stress that corresponds to the instability from the construction of Considère (Slide 304): we look for the value of $\sigma_r(\lambda)$ where the tangent of $\sigma_r(\lambda)$ vs. λ goes through the origin.

Instability of this type often quickly leads to rupture in the metal. However, in the case of polymers, $d\sigma_r/d\lambda$ tends to increase sharply from a certain value of λ, that we will call λ_c, and $d\sigma/d\lambda$ becomes positive again, and the plastic strain propagates in the rest of the sample. **In general, there is an excellent correlation (especially in amorphous polymers) between $\boldsymbol{\lambda_c}$ and the maximum extension of the entanglement network, $\boldsymbol{\lambda_c \approx M_e/M_b}$** (Slide 305). **The plastic deformation of polymers is therefore stabilized by entanglements**. However, the existence of the rubbery plateau implies that the network of entanglements remains intact within a certain range of T above T_g. Thus, **if we deform an entangled amorphous polymer below $\boldsymbol{T_g}$, it is sufficient to heat it above $\boldsymbol{T_g}$ in the absence of stress so that the polymer returns to its undeformed state. On the other hand, if $\boldsymbol{M < 2M_e}$, the polymer becomes brittle because the plastic deformation is no longer stabilized by entanglements**.

2.3 General Yield Criteria

So far, we have only considered a single tensile test. For multiaxial stress, following the same principles as for metals and assuming that plastic deformation takes place by shearing, we often use the Von Mises criterion

$$(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 \geq 2\sigma_y^2 \qquad (4),$$

where the indices refer to the principal directions of the stress tensor,[3] and σ_y is the measured threshold in uniaxial tension (for example for $\sigma_{22} = \sigma_{33} = 0$). In metals, σ_y is approximately constant, **but in polymers $\boldsymbol{\sigma_y}$ varies appreciably with hydrostatic pressure**

$$p = -\frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \qquad (5).$$

In general, we admit a linear dependence. The more the pressure increases, the higher will be the plasticity threshold:

$$\sigma_y = \sigma_{y0} + \mu p \qquad (6).$$

[3] We choose the coordinate system so that σ_{12} etc. are zero.

An example of the effect of pressure on the tensile curves of poly(methyl methacrylate) is shown on Slide 383. It makes sense: if you increase the pressure, you reduce the space between the chains and it becomes more difficult to induce a shear in the glassy or semi-crystalline state (in contrast, in an elastomer, the local shear barriers are zero). This effect is particularly pronounced in polymers because their compression modulus, K, is about two orders of magnitude lower than for most metals.

2.4 Models for the Yield Point of Glassy Amorphous Polymers

The plasticity of polymers is strongly influenced by temperature and the strain rate (Slide 310). Any model for σ_y must therefore reflect this dependence. Indeed, plasticity can be considered as an extreme manifestation of non-linear viscoelastic behavior. However, the models presented so far about viscoelasticity are only valid for amorphous polymers at equilibrium above T_g. In order to describe the plasticity in the glassy state, we have therefore developed phenomenological *ad hoc* models that we will briefly present here.

Eyring's Model and the Importance of Secondary Relaxations

It is a simple phenomenological model (Slide 311), which describes plastic deformation in terms of molecular 'segments' (the physical nature of this "segment" is not defined) crossing over an energy barrier, ΔH (the activation enthalpy). We can think of these energy barriers as a kind of internal friction that opposes conformational changes. The presence of a stress, σ, reduces the activation enthalpy for "segments" moving in the direction of the stress. So:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 e^{-\frac{\Delta H - \sigma V^*}{kT}} \quad (7).$$

where V^* is an activation volume. For a given strain rate $\dot{\varepsilon}$

$$\frac{\sigma_y}{T} = \frac{\Delta H}{V^* T} + \frac{k}{V^*} \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \quad (8).$$

Equation 8 therefore implies that $\sigma_y = A + B \ln \dot{\varepsilon}$ at constant temperature. As shown on Slide 311, we observe this behavior for PC over a broad temperature range. We can thus estimate V^*, which is approximately 6.4 nm^3, involving a 'segment' that matches multiple PC repeating units.

In fact, **conformational relaxations involving a limited number of bonds can subsist below T_g**, even when the strain is small. These relaxations can be demonstrated by dynamic mechanical analysis (DMA), where they are manifested by peaks of *tan* δ (see our course on phenomenological viscoelasticity). In general, **the largest peak in *tan* δ, associated with T_g, is called the "α relaxation", and the other relaxations are called "secondary relaxations"**

designated to β, γ etc. in the order of their appearance when the temperature decreases below T_g.

In PC, there are no major secondary relaxations between 20 °C and its T_g of around 150 °C, the β relaxation occurs at a much lower temperature. On the other hand, PVC shows a strong β relaxation at around 50 °C and therefore two distinct plasticity regimes below and above this temperature, with a large change in V^*. **The activation of movements that correspond to secondary transitions is therefore very important for plasticity, which facilitate conformational changes that have a 'lubricating' effect**. Slide 313 shows a concrete example of how we can modify σ_y by using chemical modifications to adjust the temperature of secondary relaxation.

Argon Model (Traite des Matériaux 14, p293)

The Argon model is formally very similar to the Eyring model. It is a model based on the existence of intermolecular barriers to local shear. However, if the origin of the activation barrier is not specified in the Eyring model, in the Argon model it is attributed to the elastic deformation caused by the motion of a "segment" (the definition of "segment" remains arbitrary). Thus, the threshold of plasticity in shear becomes

$$\tau_y = \tau_0 \left[1 + \frac{16(1-\mu)}{3\pi G \beta^2 a^3} kT \ln \frac{\dot{\gamma}}{\dot{\gamma}_0}\right] \quad (9),$$

where $\dot{\gamma}$ is the shear rate, μ is the Poisson ratio, β and a are parameters and G is the shear modulus of the 'matrix' surrounding a deformed 'segment'.

Robertson's Model (Traite des Matériaux 14, p290)

In Robertson's model, the activation barrier is *intramolecular*. The bonds of a chain are assumed to be in the "*trans*" (low energy) state or in the "*cis*" (high energy) state. Without a stress, the proportion χ of *cis* bonds depends on T (remember our little calculation on Slide 69). If the applied stress, σ, is sufficiently high, $\chi(\sigma, T < T_g) = \chi(\Theta > T_g)$. We then admit that $\sigma = \eta(\Theta)\dot{\varepsilon}$ where $\eta(\Theta)$ is a viscosity which is calculated using the WLF equation.

As shown in Slide 316, the Argon model seems to be better able to describe the behavior in $T << T_g$, while Robertson's model works best as T approaches T_g. This reflects perhaps the relative importance of inter- and intramolecular barriers in these two regimes. However, these models remain essentially phenomenological, and do not explicitly take the role of, for example, secondary relaxations into account. There are many other models of this type, which more or less reproduce experimental data thanks to adjustable parameters. There also exist numerical simulations of molecular dynamics, but these are now limited by the IT resources available, therefore systems at very low volumes and at very short times can be considered, which makes their interpretation difficult.

2.5 Models for the Yield Point of Semi-Crystalline Polymers

In semi-crystalline polymers, the observed increase in σ_y with increasing lamellar thickness, *l*, is most often interpreted in terms of nucleation of dislocations and crystallographic slip within the lamellae, especially if $T > T_g$. In this case, we can neglect the contribution of amorphous regions. It follows that σ_y also increases with the degree of crystallinity, hence a much lower value for LDPE than for HDPE, for example. The role of amorphous regions is more important if $T < T_g$. Thus, σ_y of polyamide (Nylon) 6,6, whose T_g is approximately 60 °C (provided it is dry), decreases noticeably in the presence of moisture, although water molecules have no direct influence on the crystal phase.

According to Young (Traite des Matériaux 14, p298), the activation energy for the nucleation of a screw dislocation of type (hk0)[001] in a lamella of thickness l (implying slippage perpendicular to the axis of the chains) is given by

$$\Delta U^* = \frac{Gb^2 l}{2\pi}\left[\ln\frac{u^*}{r_0} - 1\right] \qquad (10),$$

with the critical width

$$u^* = \frac{Gb}{2\pi\sigma}$$

b is the Burgers vector, G is a shear modulus, and $r_0 \approx 4b$ is the radius of the core of the dislocation. It is generally accepted that a ΔU^* value of 50 to 60 kT is necessary for the nucleation of a dislocation in HDPE, which allows the calculation of $\sigma(l)$. The variation of the yield strength as a function of l predicted by Equation 10 is in qualitative agreement with experimental findings, and the orders of magnitude are correct. However, this model does not take the details of slip systems involved in the initiation of plasticity into account and only addresses the yield point. The role of amorphous regions is also ignored.

In reality, a spherulitic sample contains lamellae whose orientation is locally correlated, but random compared to the direction of macroscopic tension. In addition, the presence of folds, low symmetry of polymeric crystals, and the direction of the covalent chain bonds into the c direction severely limit the number of slippage systems contributing to plastic deformation. However, the presence of amorphous regions allows plasticity, even if the number of independent lamellar slippage systems would not be sufficient for plastic deformation in a purely polycrystalline sample. On the other hand, as in any crystalline material, the systems of activated slippage tend to orient themselves less and less favorably in relation to the tensile axis as the deformation advances.

These difficulties have given rise to a variety of so-called “self-consistent” models, based on an aggregate formed of randomly distributed crystals and entangled amorphous regions. This kind of model admits the possibility of several different slippage systems, whereby the critical stresses can be determined experimentally using oriented samples, which makes it possible to predict the evolution of the crystallographic texture of the material beyond the yield stress. Strain hardening of crystallographic origin is thus observed in simulations, in addition to entanglement effects, and we can simulate the effects of different deformation modes, for example, in uniaxial tension or in pure shear. Overall, the behavior is found to be very similar to that of an amorphous polymer, in as much as the entanglement stabilizes the large plastic strains, leading to the formation of necks with $\lambda \approx \lambda_{\text{max}}$, and the yield points are comparable to those of glassy amorphous polymers, if the degree of crystallinity is high. However, at the greatest deformations, we observe a major rearrangement of the crystal structure, with the chain axes oriented more or less parallelly to the axis of the tensile deformation, often leading to additional significant self-reinforcement which is absent in amorphous polymers.

Finally, in the case of highly pre-oriented polymers (fibers or ultra-oriented fibers, for example) the behavior is essentially brittle when they are tested in tension because sliding systems are not favorably oriented and there is often little amorphous matter, and the yield point is therefore effectively infinite. However, oriented polymers can show significant plasticity and a reduced yield point in compression (Slide 324) thanks to the formation of twinning and sliding bands. So, if the ultra-oriented fibers sometimes show exceptional properties in the direction of orientation, they are much less resistant in compression. However, if the deformation remains plastic, it is at least partly reversible thanks to the connectivity of the chains. So, unlike a glass or carbon fiber, in general, a polymer fiber does not break in compression. Indeed, organic fibers can absorb a lot of energy, hence their interest in applications such as bulletproof vests or impact resistant composites.

3. Crazing and Breakage: When a Plastic Material Behaves not 'Plastic'.

3.1 Phenomenology of Crazes

If you have a PS tensile test tube, rub its surface with your fingers and bend it slowly. You will see a lot of "**crazes**" appearing on the tensile side. They look like small cracks growing perpendicular to the tensile axis (craze means "small cracks" (*Mikrorisse* or *craquelures*). However, the fact that they manage to spread parallel to each other and perpendicular to the local tensile direction implies that **they can withstand a significant load** (compare with a real crack where the normal stress at the fracture fascia is necessarily zero).

This is clearly a very localized mode of deformation compared to a macroscopic plastic neck. An isolated craze therefore dissipates little energy, and **the formation of crazes is often associated with fragile macroscopic behavior**. They can serve as nuclei for the formation of real cracks and they provide little resistance to the propagation of a pre-existing crack. In addition, the formation of crazes implies a loss of transparency in amorphous polymers, facilitate penetration of solvents and significantly reduce stiffness.

Microscopic observations (Slides 327) show that the ability of crazes to withstand a mechanical load is due to the presence of **numerous fibrils that connect the two faces of the craze.** These fibrils, **typically around 10 nm in diameter**, and which are **separated by voids which constitute some 50% of the volume of the craze**, are **micronecks caused by localized plasticity**. Paradoxically, therefore, the formation of a craze requires high ductility, even if it leads to a macroscopic fragile behavior.

It is also observed that **the crazes occur only in tension**, i.e. never in pure shear or in compression. This makes sense, because the creation of voids is facilitated by a negative pressure and suppressed in compression. It is therefore often assumed that the formation of crazes is associated with a critical strain which depends on the pressure:

$$\varepsilon_c = A - \frac{B}{p} \Rightarrow \sigma_1 - \mu\sigma_2 - \mu\sigma_3 = C - \frac{D}{\sigma_1 + \sigma_2 + \sigma_3} \quad (11).$$

3.2 Models of Crazes

In general, it is assumed that **the nucleation of a craze is associated with a concentration of local stress** (around a hole or dust, for example). A small region of local plastic deformation appears following a deformation, but it is immediately constrained by the non-deformed material that surrounds it. A strong hydrostatic stress develops as the deformation continues, as the plastically deformed region tries to retain its volume. However, according to Equation 4, shear requires a high deviatoric stress, i.e. that $\sigma_1 \gg \sigma_2$ and σ_3 if the tension is in direction 1, for example. The strong hydrostatic stress, i.e. strong negative pressure, promotes local formation of voids. By the formation of voids, the hydrostatic stress is relaxed, and plastic deformation can continue. Thus, the voids and the ligaments that separate them are stretched in the tensile direction, and a fibrillar structure begins to appear (Slide 329).

To form a craze, this region of fibrillar deformation must propagate. The propagation mechanisms are quite controversial, with some authors talking about the nucleation of new voids in the matrix surrounding the fibrillar region, while others have proposed that the voids advance through a "meniscus instability" mechanism. However, whatever the mechanisms of propagation of the head of the craze will be, they can only be sustained if the local stress concentration remains high. To this end, it is necessary that the fibrillar regions already formed extend in the direction of the pull. **The stress at the head of the craze and its propagation speed are therefore controlled by the speed of craze expansion**, for which the mechanisms are relatively well known (Slide 330).

Surface Drawing Model

The rate of craze expansion, *v*, depends on the pressure gradient pushing the polymer from the head of the voids to the base of the fibrils (Slide 331). Let D_o* be the value of D_o, the spacing of the fibrils, which allows the fastest craze propagation for a given stress σ. The pressure at the base of the fibrils, P_2, is approximately given by

$$P_2 \approx \sigma$$

and that at the head of the voids is due to capillary forces:

$$P_2 \approx \frac{4\Gamma}{D_0}$$

where Γ is the surface energy of the polymer and we assume a radius of curvature of about $D_0/2$. The pressure gradient is therefore

$$\nabla P \approx \frac{P_2 - P_1}{D_0} = \frac{\sigma - \frac{4\Gamma}{D_0}}{D_0} \qquad (12).$$

The speed of movement of the polymer from the heads of the voids to the bases of the fibrils and, as consequence, the craze widening rate, v, depends on ∇P^n where n is an empirical constant >> 1 for most polymers (these are strong deformations here, and therefore of a very non-linear behavior). Thus, v reaches its maximum value for a given stress σ when $\nabla P(D_0)$ reaches a maximum, i.e., when

$$\frac{\mathrm{d}\nabla P}{dD_0} \approx -\frac{\sigma - \frac{4\Gamma}{D_0}}{D_0^2} + \frac{4\Gamma}{D_0^3} = 0 \Rightarrow \sigma D_0^* = 8\Gamma \qquad (13).$$

Equation 13 implies that the separation of fibrils in a craze must be inversely proportional to the stress at the surface, which has been verified by observations of crazes in PS. It also implies that the speed of expansion at a given stress

$$v^{1/n} \propto \nabla P(D_0) \propto -\frac{\sigma^2}{\Gamma} \qquad (14).$$

Therefore, for a given strain rate, the stress necessary to propagate the craze is

$$\sigma_c \propto \Gamma^{1/2}\, v^{1/2n} \qquad (15).$$

Thus, **the greater the surface energy, the greater the stress required to form a craze at a given strain rate**, which makes sense, because **the formation of voids requires the creation of new surfaces.**

Crazes and Entanglement

It is found that for the deformation of the fibrils of the crazes $\lambda \approx \lambda_{max}$, and they are therefore *a priori* stabilized by entanglement, just like macroscopic necks in case of classical plasticity. Indeed, if $M < 2M_e$, stable crazes are not observed. Nevertheless, if we admit the model of an entanglement network, where the entanglements are assumed as nodes of a network, we see (Slide 336) that the **creation of voids requires some loss of entanglements**. It is because in the presence of a network with an entanglement density N_e per unit volume, **the number of subchains crossing a unit area is $d_e N_e/2$**, where d_e is the root mean square distance between the ends of each subchain, equivalent to the separation in space of two entanglement points which are topologically linked. If the energy required to break any of these subchains is U, the energy necessary to create a unit area by splitting entangled chains becomes

$$\sigma_c \propto \Gamma^{\frac{1}{2}}\, v^{\frac{1}{n}} = \left(\gamma + \frac{d_e N_e U}{4}\right)^{1/2} v^{1/2n} \qquad (16).$$

So
$$\Gamma = \gamma + \frac{d_e N_e U}{4} \qquad (17).$$

Polymers with low entanglement density (e.g., PS, $N_e \approx 4 \times 10^{25}$ m^{-3}) form more easily crazes than high density entanglement polymers (eg. the PC, $N_e \approx 30 \times 10^{25}$ m^{-3}).

Moreover, we notice (Slide 335) that $\lambda_{craze} = 0.8\lambda_{max} > \lambda_{neck} = 0.6\lambda_{max}$ for a variety of glassy amorphous polymers deformed well below T_g, an observation that may be directly attributed to the loss of entanglements caused by the formation of a craze. This same Slide 335 also shows that **the dominant deformation mode in tension is the formation of crazes when N_e is small, and simple plastic necking when N_e is large**.

However, at temperatures just below T_g, the mobility may be high enough for the loss of entanglements which can be accommodated by forced disentanglement, instead of breaking chains. This craze formation mechanism is also favored by low strain rates and low molar masses.

Semicrystalline Polymers

At $T < T_g$, the behavior of semi-crystalline polymers is similar to that of glassy amorphous polymers, i.e. that the formation of crazes by bond scission is favored by low entanglement densities, but disentanglement is usually absent because it is blocked by the crystallization induced at large deformations. Thus, strongly entangled semicrystalline polymers like PET or PEEK hardly form crazes below T_g.

On the other hand, at $T > T_g$, the formation of voids is often observed even in highly entangled polymers due to the strong mechanical contrast between the rubbery amorphous phase and the rigid crystalline phase, which causes strong hydrostatic stresses in the amorphous phase.

The formation of voids in the amorphous phase facilitates the local plastic deformation of the lamellae. This is therefore often associated with plasticity and does not necessarily cause a brittle behavior. We therefore sometimes speak of "fibrillar deformation" rather than the formation of crazes, but the distinction between the two types of deformations is quite arbitrary.

3.3 Crazes and Rupture

The fragility of PS at room temperature is not only due to the formation of crazes. In a notched tensile test piece of PC, crazes are also observed at the crack tip depending on the test conditions, but the breaking strength remains much higher in PC than in PS. This is because the tensile strength also depends on the stability of the crazes. Brown has shown that if there is a single craze at the crack tip, the intensity factor of a critical stress in mode I (a measure of tensile strength) becomes:

$$\mathrm{K}_{Ic} \propto N_e d_e f_s (2\pi D_0)^{1/2} \qquad (18).$$

where f_s is the force required to break a chain (about 2 nN for C-C bonds). **Polymers with high entanglement density are therefore more fracture resistant in the presence of crazes, in line with experimental observations** (Slide 339). However, **if the effective value of N_e is too high, as is the case in highly crosslinked polymers, no crazes at the crack tip are observed, while the plastic deformation is also limited**, even at ambient temperature, because λ_{max} becomes very low. In fact, **thermosets are, in general, very fragile.**

Shock Reinforcement: "Rubber toughening (RT)"

We have seen that an isolated craze which forms at the head of the crack is not very dissipative because the plasticity is very localized. However, **if the formation of multiple crazes or combinations of crazes and plasticity are favored, cracking resistance can be increased, even in the most fragile polymers such as PS or PMMA**. This is the goal of ***rubber toughening***. By adding nodules of a rubber or an elastomer to the polymer we create stress concentrations all over the material when it is under tension. Numerous crazes appear at relatively low overall stresses around a crack, leading to higher energy dissipation than in the presence of a single craze. In addition, the formation of voids associated with crazes as well as in elastomer nodules promote classical plasticity by relaxing three-dimensional stresses.

As the examples on Slides 344 show, this approach is not only very effective in glassy amorphous polymers but also in rather fragile semi-crystalline polymers like PP. For this, it is necessary that the dispersion of the size and the dispersion of the elastomer nodules are well controlled and the elastomer content is not too high so as to not reduce Young's modulus excessively.

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4. Summary

- Yielding usually defined as the point where the slope of the stress-train curve becomes zero during the deformation of glassy or semicrystalline polymers. This often results in the formation of a stable neck with a draw ratio which is a materials parameter, characteristic of the entanglement network.
- σ_y decreases roughly linearly with T and decreasing deformation rate under certain conditions, in accordance with simple Eyring rate theory. However, the yield behaviour also strongly influenced by the presence of sub-T_g relaxations, in some cases providing a link between yielding and molecular structure.
- Semicrystalline polymers modelled in terms of crystallographic slip for $T > T_g$. For a constant degree of crystallinity, σ_y increases with lamellar thickness l. Thus, in general, polymers crystallized at higher temperatures have higher yield stresses.
- Crazes are crack-like defects which appear when certain polymers are tested in tension. The craze surfaces are spanned by highly drawn craze fibrils, which are load bearing. Crazing is nevertheless associated with brittle behaviour.
- Crazes form most readily in low entanglement density polymers. The formation of the craze fibrils requires loss of entanglements: the fewer entanglements there are, the less energy is consumed during fibrillation and the lower the crazing stress.
- The strength of a craze fibril and hence of the craze depends directly on the entanglement density. Low entanglement density polymers show little resistance to crack propagation and are fragile. However, although the energy dissipation due to one craze is small, and hence the toughness, it can be increased greatly by increasing the number of crazes at the crack tip. This is the basis of rubber toughening in PS and in PMMA.