An introduction to polymer physics

Wentao Hao
Hefei University of Technology

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~10 hours

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- 7.3 The plasticity and yielding of polymer
- 7.4 Fracture and strength of polymer material
- 7.5 Tensile strength
- 7.6 toughness and toughen

7.1 introduction

7.1.1 Features of mechanical properties of polymers

The most remarkable features are *high elasticity* and *viscoelasticity*

Mechanical properties of polymer are highly dependent on *temperature* and on *time-scale* of any deformation.

Viscoelsticity 粘弹性

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high elasticity – small load, large deformation

high molecular weight of polymer → flexibility → High elasticity

结构特点带来独特性能

Rubber at room temperature
Plastics at higher temperature above T_g

Due to the change of conformation, not the internal energy

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viscoelasticity

- Polymers are viscoelastic and exhibit some of the properties of both viscous liquids and elastic solids,

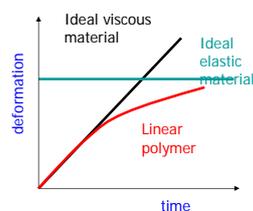- which is a result of various relaxation processes as described before.

Ideal viscous material
Ideal elastic material
Linear polymer
deformation
time

Fig. 7-1 viscoelasticity of polymer

- Under constant load, it will go *creep*
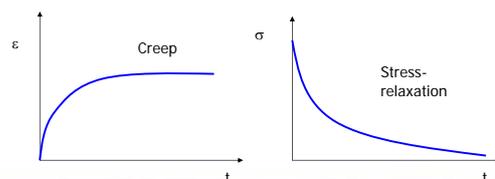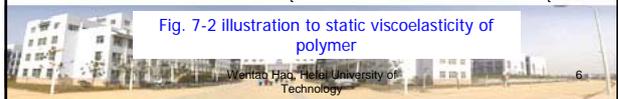- Under constant strain, it undergoes *stress-relaxation*

ε
Creep
t

σ
Stress-relaxation
t

Fig. 7-2 illustration to static viscoelasticity of polymer

Slide 7

Viscoelasticity, talking more

- Dynamic viscoelasticity
  (动态粘弹性)
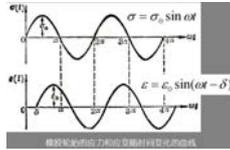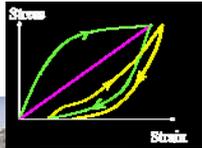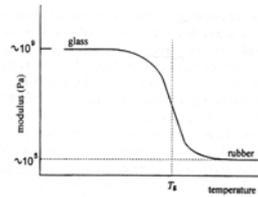 - Internal friction (内耗)
  - Hysteresis (滞后)

$$\sigma = \sigma_0 \sin \omega t$$
$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

Fig. 7-3 illustration of internal friction and hysteresis in rubber stretching

Stress / Strain

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Mechanical properties of polymer are highly dependent on *temperature* and on *the time-scale* of any deformation.

On a large time scale, such as 10000 years, linear polymer will exhibit as liquid.
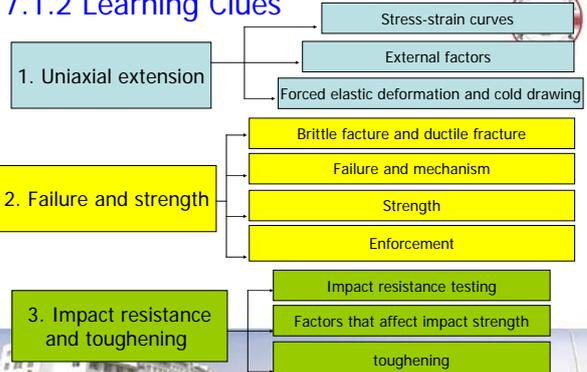
On a short time scale, such as 0.001 second, it will exhibit as a solid.

Frequency is of dramatic effects on the mechanical properties as the temperature.
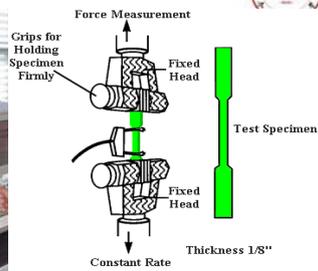
glass, rubber, modulus (Pa), temperature, T_g

Fig. 7-4 young's modulus vs. temperature

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To describe the mechanical properties, stress, strain, time and temperature must be considered.

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7.1.2 Learning Clues

1. Uniaxial extension
   - Stress-strain curves
   - External factors
   - Forced elastic deformation and cold drawing

2. Failure and strength
   - Brittle facture and ductile fracture
   - Failure and mechanism
   - Strength
   - Enforcement

3. Impact resistance and toughening
   - Impact resistance testing
   - Factors that affect impact strength
   - toughening

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7.1.3 mechanical test of polymer materials

Force Measurement

Grips for Holding Specimen Firmly

Fixed Head

Test Specimen

Fixed Head

Constant Rate of Motion

Thickness 1/8''

tensile behavior test

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Flexural strength testing

2

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impact resistance test

Scale
Starting position
End of swing
Hammer
Specimen
Anvil

Charpy impact test equipments

Slide 14
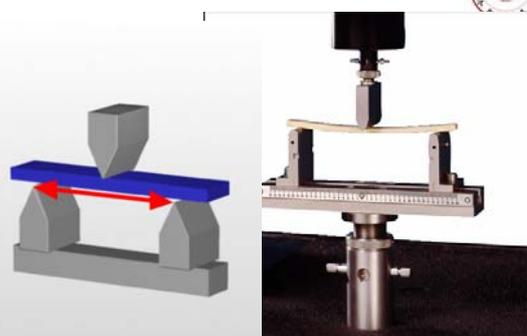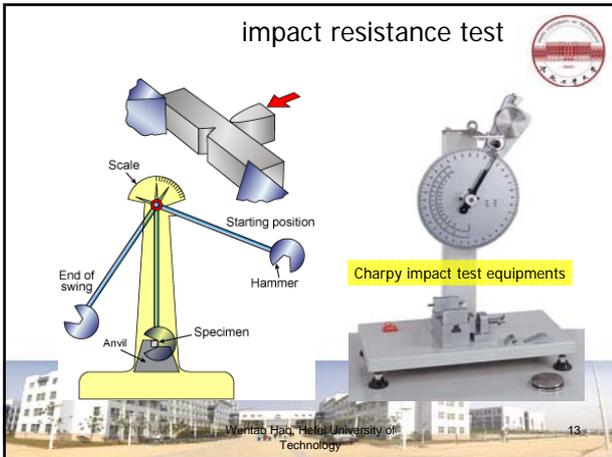
7.1.4 Elastic constants of isotropic media at small strains

- A. stress and strain
  - σ – tensile stress, $\sigma = F/A_0$,
    - the force per unit cross-sectional area;
  - ε – strain, $\varepsilon = \Delta l / l_0$,
    - the change in length divided by the original length

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- B. Modules
  - E – Young's modulus

$$E = \frac{\sigma}{\varepsilon}$$

  - G – shear modulus

$$G = \frac{\sigma}{\theta}$$

  - K – Bulk modulus

$$K = -\frac{1}{V} \cdot \frac{dV}{dp}$$

Where V is the volume of the material and p is the applied pressure.

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- C. Poisson's ratio
  - ν -- Poisson's ratio, $\nu = -\varepsilon_{perp}/\varepsilon$,
    - $\varepsilon_{perp} = \Delta a/a$, the linear strain in the direction perpendicular to the tensile stress producing the tensile strain ε

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- D. relationship between E, G and K

$$K = \frac{E}{3(1-2\nu)}$$

$$G = \frac{E}{2(1+\nu)}$$

$$K = \frac{E}{3(1-2\nu)}$$

- E. 'incompressible' elastic solid

$$K \gg E, \nu = \frac{1}{2}$$

$$G = \frac{E}{3}$$

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7.2 The stress-strain behavior of polymers

7.2.1 The stress-strain curves

Elongation at yield
STRESS
Yield stress
Engineering stress to engineering strain
STRAIN

Fig. 7-5 Typical stress-strain curve for amorphous polymer at temperature below T_g

Elastic deformation -yield-strain softening-cold drawing-strain hardening-breaking

Fig. 7-6 Typical stress-strain curve for crystalline polymer

A : elastic limit 弹性极限点

Y : Yield point 屈服点

σ_Y 屈服应力

Strainn sofening 应变软化

Stress hardening 应变硬化

Cold drawing 冷拉

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_A}{\varepsilon_A}$$

B : point of rupture断裂点

ε_A 弹性极限应变
σ_A弹性极限应力

ε_B 断裂伸长率
σ_B断裂强度

Fracture energy 断裂能

It refers to the orange area under the Stress-strain curve: Energy absorbed during the extension

$$\int \sigma d\varepsilon$$

Fig. 7-7 illustration to Young's Modulus

Fig. 7-8 Fracture energy

Information can be obtained from the stress-strain curve

* Yielding stress (Y point)
* Young's modulus (slope of OA)
* Breaking stress (B point – Y axis)
* Elongation at break (B point – X axis)
* Fracture energy (shaded area under the curve)

Fig. 7-9 Different types of stress-strain curve
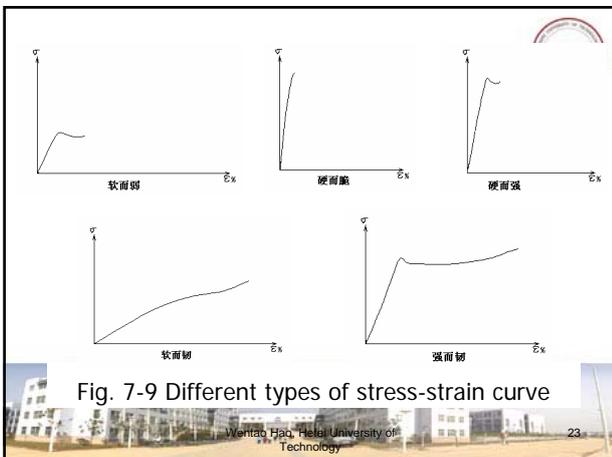
Comparison between different stress-strain curves

Type	modulus	strength	elongation	yielding	Polymer (R.T.)
Hard and brittle	High	High	Small	No	PS, PMMA, PF resins
Hard and strong	High	High	Small (5%)	Yes	Hard PVC
Hard and tough	High	High	Large	Yes, with necking and cold drawing	PA, PC, Acetyl cellulose, Cellulose nitrate
Soft and tough	Low	Low	Large (20-1000%)	Maybe	Rubber, plasticized PVC
Soft and weak	Low	Low	small	Maybe	Soft polymer gels

Attention:

- Stress-strain behavior of actual polymer material is not exactly the same as the ideal model. It may be composed of several models mentioned above.
  - Some materials may neck or yield apparently, some are not;
  - Some materials have higher fracture strength than yielding strength, the others exhibit oppositely.
- Temperature and strain rate affect the stress-strain behavior of polymer dramatically.
  - UPVC, which is usually hard and strong, might be hard and tough under very low strain rate. The elongation may be larger than 100%.

## 7.2.2 Stress-strain curves under various conditions (a) Different temperature

- Environmental temperature has huge effect on the tensile behavior of polymer materials.
- With the temperature increasing, movement of the segments is more violently and the relaxation time τ is smaller.
- Thus, the modulus and strength of the polymer decrease, accompanying with the increment of elongation
- Stress-strain curves change greatly
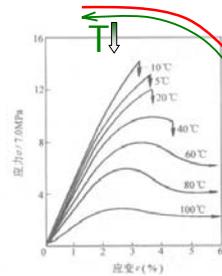
Fig. 7-10 stress-strain curves of PMMA under different temperature

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- Facture strength σ_b and yielding strength σ_y of polymer material vary with temperature, especially for the yielding strength
- With temperature increasing, the material will undergo the brittle-ductile transition
- As the temperature is below T_b, $\sigma_b < \sigma_y$, the material will fail before yielding, exhibiting to be brittle fracture
- When the temperature is above T_b, $\sigma_b > \sigma_y$, the material will yield first; after necking and cold drawing, break occurs –ductile fracture

σ_b和σ_y分别对应什么？
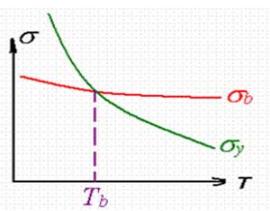
(b) Different strain rate
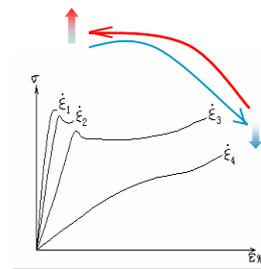
Strain rate

$$\dot{\varepsilon}_1 > \dot{\varepsilon}_2 > \dot{\varepsilon}_3 > \dot{\varepsilon}_4$$

时温等效原理：
拉伸速度快 = 时间短 = 温度低

Fig. 7-11 stress-strain curve under different strain rate
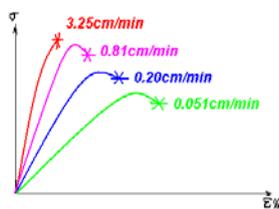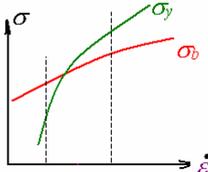

Fig. 7-12 stress-strain curve of PMMA at different strain rate

At low strain rate, the material will yield first. However, the material will break before yielding occurs at high strain rate.
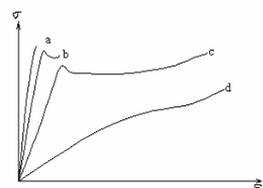
(c) Composition of Polymers

a: brittle material	Phenolic resin or Epoxy resin
b: semi-brittle material	PS, PMMA
c: ductile material	PP, PE, PC
d: rubber	Nature rubber, PIB

Fig. 7-13 stress-strain curve for different polymer
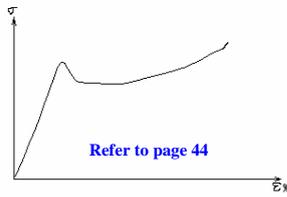
(d) Crystallization

Fig. 7-14 stress-strain curve of crystallized polymer

➤ **Strain softening** is more apparent
➤ **Re-orientation of** lamellae in the direction of the outside force
➤ **slippage** between lamellae
➤ **Formation of fibrils** from the destroyed lamellae

Refer to page 44
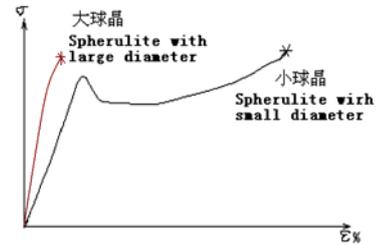

(e) Size of the Spherulites

Fig. 7-15 stress-strain curve for crystallized polymer with different crystal size

大球晶
Spherulite with large diameter
小球晶
Spherulite with small diameter

(f) Degree of Crystallization

High degree of Crystallization
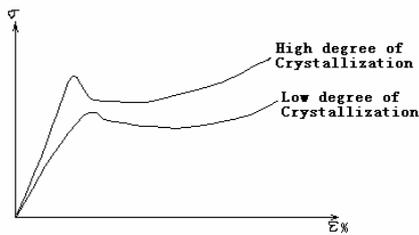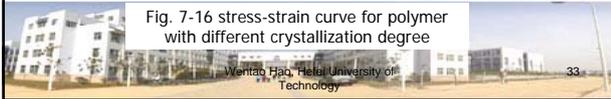Low degree of Crystallization

Fig. 7-16 stress-strain curve for polymer with different crystallization degree

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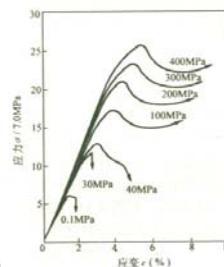
(g) Surrounding Pressure

Fig. 7-17 stress-strain behavior of PS with surrounding pressure

❑ PS is hard and brittle in normal pressure, the strength and elongation are all small
❑ However, it transfers into hard and tough material with the surrounding pressure increases
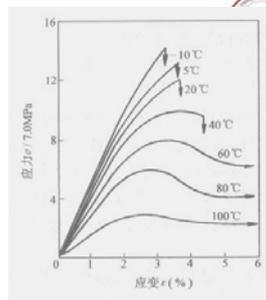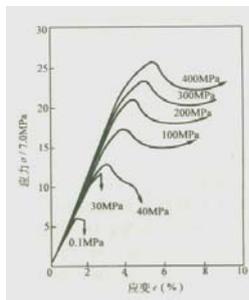

Fig. 7-18 Comparison between the two different brittle-ductile transition

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Summary to brittle-ductile transition

✦ Polymer materials can undergo brittle-ductile transition by both elevating the environmental temperature and elevating the surrounding pressure, but they are totally different.
✦ When the temperature increases, the tensile strength lowered remarkably; but the strength increases too as the pressure increases. Materials turn to be hard and tough.
✦ Such a result suggests that it is not necessary to sacrifice the strength. There must be some resolutions that the materials can be toughened with the strength being kept at a relative high level.
✦ It leads to the non-elastomer toughening.

7.2.3 forced high-elastic deformation

- It is worth to mention the physical properties of polymer materials, such as elongation, yielding and failure, at relatively low temperature
- As to the glassy amorphous polymer material, they can deform to a large degree under approximate strain rate though the segments are frozen when the temperature range is below T_g ($T_b < T < T_g$)
- It is called the *forced high-elastic deformation*
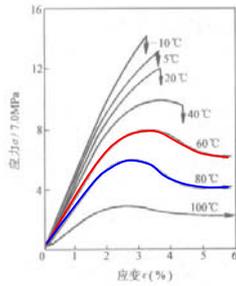
Discussions (I)

- It is very unique.
  - It is neither the same as the high-elastic deformation in rubber state nor the same as the viscosity-flow at extremely high temperature
- The nature is that segments in curled state are forced to move, being extended as in rubber state.
- The deformation can recover partly or totally when the temperature is raised up above T_g (outside force being released).

Discussions (II)

- It suggests that movement of segments can be activated under stress.
- By elevating the stress, the activation energy of segments movement in the direction of outside force is lowered.
- The relaxation time is shortened correspondingly.
- And then those segments frozen in glass state can overcome the potential barrier to move.

Discussions (III)

- The relaxation time τ is lowered with the stress σ increasing.
- The larger the σ, the lower the τ value.

$$\tau = \tau_0 \exp\left[\frac{\Delta E - a\sigma}{RT}\right]$$

ΔE – the activation energy of segments movement

a – constant

τ -- the relaxation time

7.2.4 Cold drawing of crystalline polymers

- Forced high-elastic deformation can also occur in crystalline polymers.
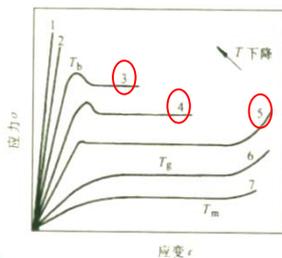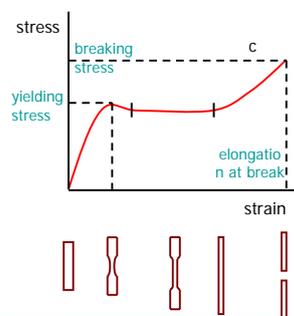- It is called the "cold drawing"

Fig. 7-19 stress-strain behavior of crystalline polymer at different temperature

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Before cold drawing, apparent yielding occurs. One or several parts on the specimen neck.

During cold drawing, necking propagates. While the deformation is enlarged persistently, the stress remains at almost the same level.

As the specimen is extended further, the stress will increase until the specimen breaks.

Fig. 7-20 stress-strain curve of crystalline polymer

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* Though the cold drawing is also a type of forced high elastic deformation, the mechanism is DIFFERIENT to that of amorphous polymers.
* In a large temperature range from T_g to nearby T_m, cold drawing can occur in crystalline polymers.
* Under stress, the original crystalline structure is destroyed, spherulites and lamellae are tear apart into smaller crystalline units.
* Molecular chains are pulled out from crystallites, and extended
* Formation of micro fibrils along the extending directions.

《高聚物的结构与性能》, p140

Fig. 7-21 Destroy of spherulites during extension

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Fig. 7-22 Destroy of lamellae during extension

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Fig. 7-23 Deconstruction of spherulites
Left: Voids appear near the edge of the spherulites inside the PU film (TEM);
Right: fibers bridges the spherulites in PP sample (SEM on the fracture surface)

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Further discussion

➢ Temperature, strain rate and molecular weight affect the cold drawing apparently.
  – If the temperature is too low or the strain rate is too high, relaxation of molecular chains is not fully developed, materials will be destroyed quickly.
  – As the temperature is too high or the strain rate is too low, chains may slide and flow, materials fail too.
  – No cold drawing
➢ Polymers with low molar mass are of shorter chains, which can not be fully extended and oriented to prevent rupture of materials. Shortly after the yielding, materials fail.

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Table 7-2 Comparison between tensile behavior of amorphous polymer and crystalline polymer

similarities		differences		
During extension	After extension	Nature	T range	Mechanism
Elastic deformation, yielding (necking) , large deformation, strain hardening	Strongly anisotropic, deformation; cannot recover at room temperature, but can recover by heating	High-elastic deformation	$T_b - T_g$	Orientation of molecular chains, no phase transition
		cold drawing	$T_g - T_m$	Including deconstruction, orientation and re-crystallization of crystallites

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7.3 The plasticity and yielding of polymer
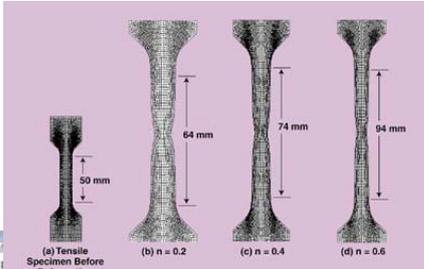
Main features of polymer yielding

① Deformation before yield point is totally recoverable
② Strain is higher than metal, about 10%-20%
③ 'Plastic flow' occurs under constant stress after yield, that is, segments oriented in the direction of outside force.
④ For most polymers, strain softening may occur under suitable conditions
⑤ Yield stress is sensitive to strain rate and temperature
⑥ Crazes and shear bands appear on the sample surface, necking occurs locally

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7.3.1 Necking and shear yield

(1) Necking: local part of the sample becomes thinner when yielding occurs

64 mm   74 mm   94 mm

50 mm

(a) Tensile Specimen Before Deformation   (b) n = 0.2   (c) n = 0.4   (d) n = 0.6

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Where —— Size: where the cross-section is smaller
Strain softening: where the stress is higher (stress concentration)

Orientation

Why —— Free volume increases
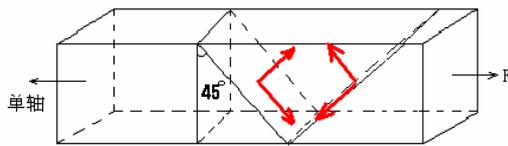
Relaxation time shortened

Without outside force $\tau = \tau_0 e^{\frac{\Delta E}{RT}}$

With outside force $\tau = \tau_0 e^{\frac{\Delta E - a\sigma}{RT}}$

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Necking

单轴   45°   F

Why necking happens?   —— $\sigma_s > \sigma_y$

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(2) mechanism and criteria of shear yield

Shear yield: before necking, the shear bands appear on the specimen surfaces with an angle of 45° to the direction of outside force.
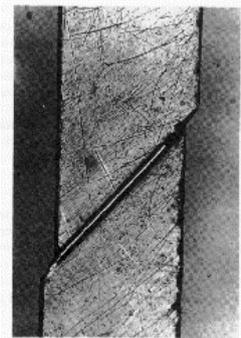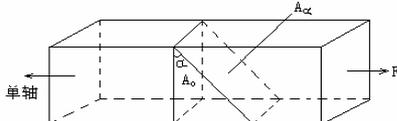

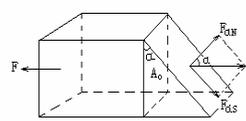**Fig. 7-26 Photograph of a deformation band in an oriented sheet of PET**

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Stress on cross section A_0, $\sigma_0 = F/A_0$

A_α A_0 单轴   F

斜截面A_α 上应力情况如何？

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斜截面A_α $A_\alpha = \dfrac{A_0}{\cos \alpha}$

受力 $\begin{cases} F_{\alpha n} = F\cos\alpha \\ F_{\alpha s} = F\sin\alpha \end{cases}$

Normal stress $\sigma_{\alpha n} = \dfrac{F\cos\alpha}{A_0/\cos\alpha} = \sigma_0 \cos^2\alpha$

Shear stress $\sigma_{\alpha s} = \dfrac{F\sin\alpha}{A_0/\cos\alpha} = \dfrac{1}{2}\sigma_0 \sin 2\alpha$

9

Discussion

Normal stress
Shear stress

α	$\sigma_{\alpha n}$	$\sigma_{\alpha s}$
α=0°	$\sigma_{\alpha n}=\sigma_0$	$\sigma_{\alpha s}=0$
α=45°	$\sigma_{\alpha n}=\sigma_0/2$	$\sigma_{\alpha s}=\sigma_0/2$
α=90°	$\sigma_{\alpha n}=0$	$\sigma_{\alpha s}=0$

Maximum shear stress occurs when α = 45°, shear band appears on the 45° surface

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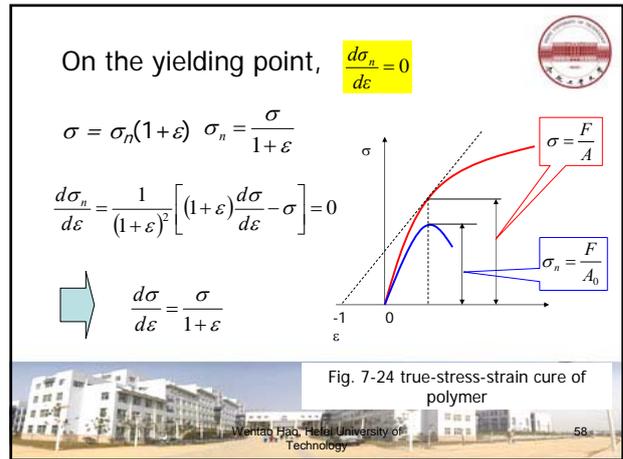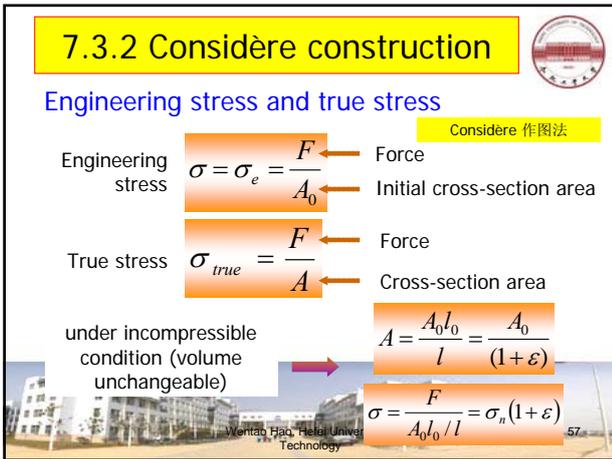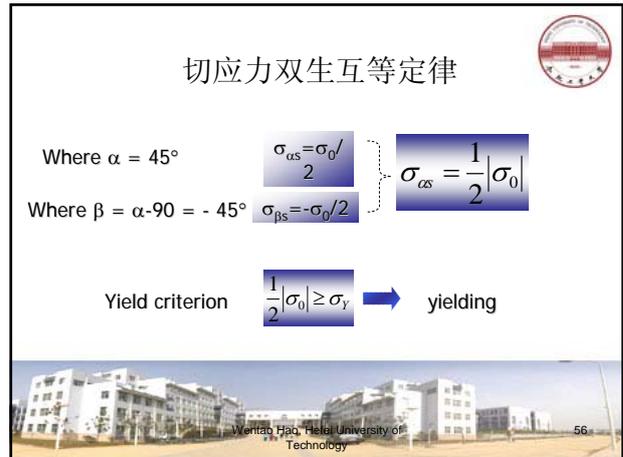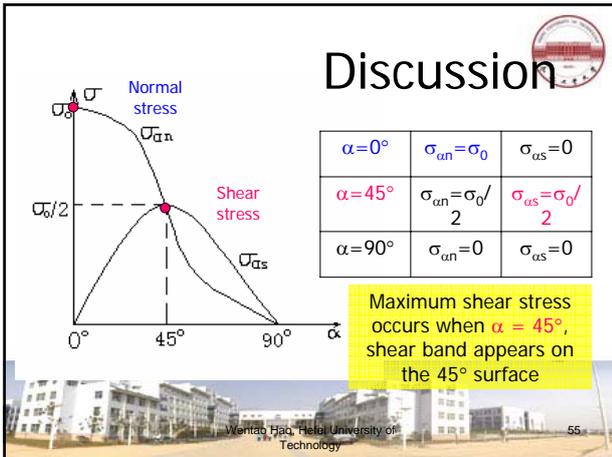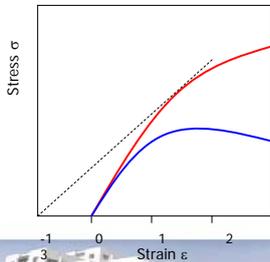## 切应力双生互等定律

Where α = 45° $\sigma_{\alpha s}=\sigma_0/2$

Where β = α-90 = - 45° $\sigma_{\beta s}=-\sigma_0/2$

$$\sigma_{\alpha s}=\frac{1}{2}|\sigma_0|$$

Yield criterion $\frac{1}{2}|\sigma_0|\geq\sigma_Y$ ⟹ yielding

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7.3.2 Considère construction

Engineering stress and true stress

Considère 作图法

Engineering stress $\sigma=\sigma_e=\dfrac{F}{A_0}$ — Force — Initial cross-section area

True stress $\sigma_{true}=\dfrac{F}{A}$ — Force — Cross-section area

under incompressible condition (volume unchangeable) $A=\dfrac{A_0 l_0}{l}=\dfrac{A_0}{(1+\varepsilon)}$

$$\sigma=\frac{F}{A_0 l_0/l}=\sigma_n(1+\varepsilon)$$

On the yielding point, $\dfrac{d\sigma_n}{d\varepsilon}=0$

$$\sigma=\sigma_n(1+\varepsilon) \quad \sigma_n=\frac{\sigma}{1+\varepsilon}$$

$$\frac{d\sigma_n}{d\varepsilon}=\frac{1}{(1+\varepsilon)^2}\left[(1+\varepsilon)\frac{d\sigma}{d\varepsilon}-\sigma\right]=0$$

⟹ $\dfrac{d\sigma}{d\varepsilon}=\dfrac{\sigma}{1+\varepsilon}$

$\sigma=\dfrac{F}{A}$

$\sigma_n=\dfrac{F}{A_0}$

Fig. 7-24 true-stress-strain cure of polymer

7.3.2 Considère construction

Fig. 7-25 different types of true-stress-strain curve of polymer

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Explanations to Fig. 7-22 (a)

- If $\frac{d\sigma}{d\varepsilon}>\frac{\sigma}{1+\varepsilon}$ at all times, no necking occurs;
- The material extends uniformly until failure.
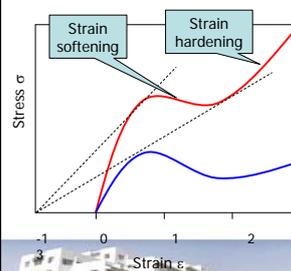- No tangent can be drawn from ε = -1.

10

Explanations to Fig. 7-22 (b)

- If $\frac{d\sigma}{d\varepsilon} = \frac{\sigma}{1+\varepsilon}$ at one point on the curve, then the material will neck and fail.

Explanations to Fig. 7-22 (c) and (d)

Strain softening

Strain hardening

- If $\frac{d\sigma}{d\varepsilon} = \frac{\sigma}{1+\varepsilon}$ at two points, then necking will followed by cold drawing.

7.3.3 Craze 银纹

- Many polymers display another type of localized yielding behavior which results in whitening of polymer material in the region of maximum deformation.
- Under a microscope, these localized regions of yielding display an increase in volume (dilatation) through formation of micro-cracks which are bridged by polymer fibrils.
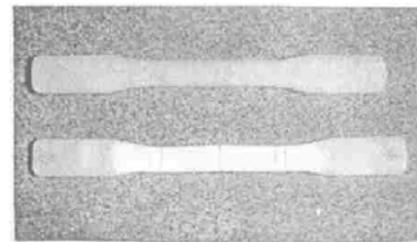
Fig. 7-27 comparison between original specimen and specimen after extension

Definition of craze

- Formation of cavities. when a polymer is under stress, which contains load-bearing fibrils spanning the gap between the surfaces of each cavity.
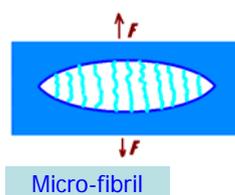

Fig. 7-28 Craze in polystyrene plate.
The arrow in the upper figure shows the direction of the main stress

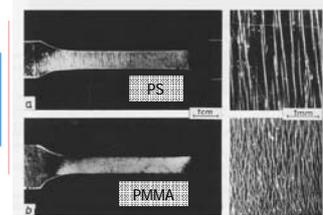## Microstructure of craze

Micro-fibril

微纤，也称为银纹质

PS

PMMA

Fig. 7-29 formation of craze before failure

Micro-fibrils is parallel to the direction of outside force; but crazes are perpendicular to the force
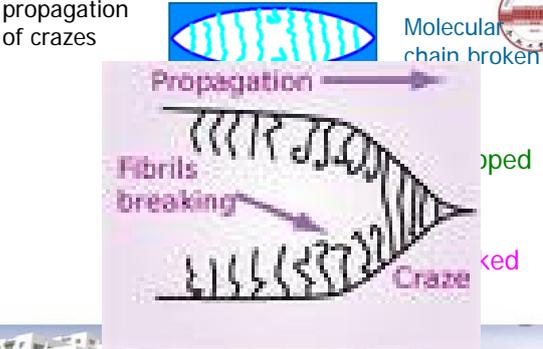
Slide 67

1. Crazes are not hollow.

2. The density is about 50% of the bulk polymer.

3. Refraction index of craze is lower than bulk polymer too, so that total reflection occurs, which results in shinning crazes.

4. Crazes will disappear after heating.

F

Slide 68
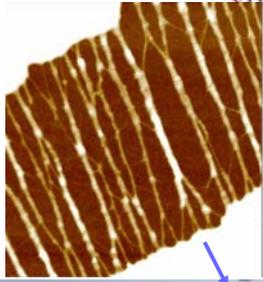
propagation of crazes

Molecular chain broken

Propagation

Fibrils breaking

Craze

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Comparison between shear yield and crazing yield

		Shear yield	Crazing yield
differences	deformation	large	Small,<10%
	Feature on curves	With apparent yielding point	No apparent yielding point
	volume	Not change	increase
	stress	Shear stress	Tensile stress
	results	Cold drawing	crack
Similarity		orientation; energy absorption; yield	

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Local plastic deformation (yield) of polymer matrix

Macro deformation of material

Tension of chains nearby the crack ends, chain broken

Plastic flow in small range
Single craze

Plastic flow in large range

More crazes

Shear bands appearing

Plastic flow in larger range
Lots of crazes
Shear bands in large range

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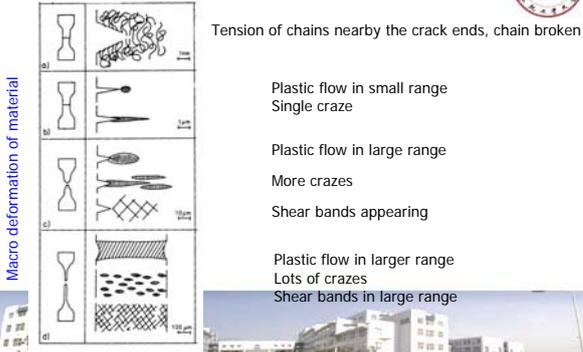
Craze, talking more

- Crazes can be induced by environmental factors, like solvents, in addition to the outside forces.
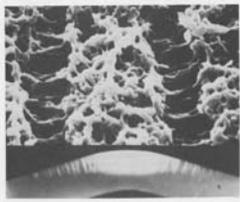
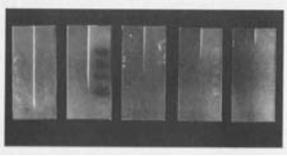Fig. 7-30 Crazes induced by bending force applied on ABS specimen

Fig. 7-31 Formation of cracks on LDPE dipped in n-propyl alcohol under bending stress

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Differences between stress craze and environmental craze

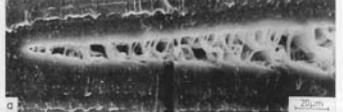Fig. 7-32 Isolated voids appear inside the environmental craze of LDPE

Fig. 7-33 Micro fibrils appear inside the stress craze of LDPE

7.4 failure and strength of polymer materials

7.4.1 brittle fracture and ductile fracture

• According to the failure features:
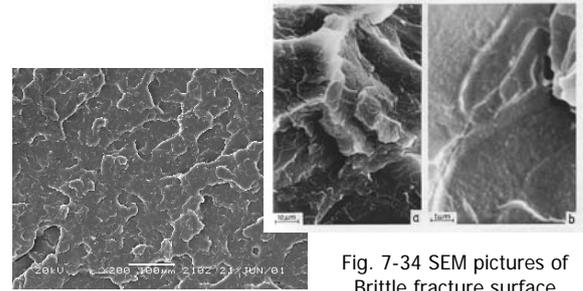 – Brittle fracture
  – Ductile fracture

Fig. 7-34 SEM pictures of Brittle fracture surface

For brittle facture, the fracture surface is usually smooth or a little bit rough; the fracture surface is normal to the extension stress; deformation is negligible
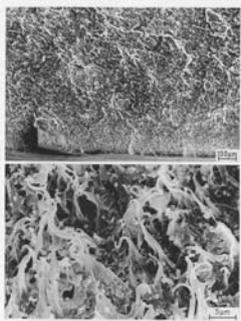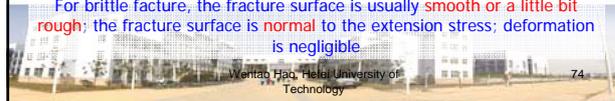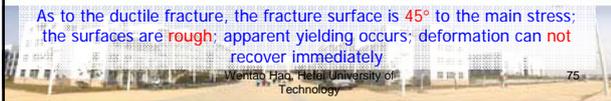

Fig. 7-35 SEM pictures of Ductile fracture

As to the ductile fracture, the fracture surface is 45° to the main stress; the surfaces are rough; apparent yielding occurs; deformation can not recover immediately
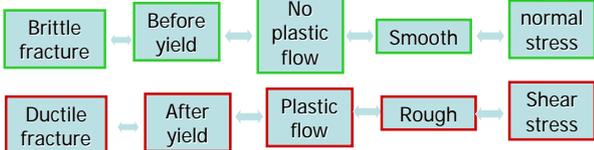

How to distinguish different type of failure?

—— the key point is before or after yield

Brittle fracture – before yield

Ductile fracture – after yield

Brittle fracture → Before yield → No plastic flow → Smooth → normal stress

Ductile fracture → After yield → Plastic flow → Rough → Shear stress

Material composition will affect the fracture, in addition to the temperature and strain rate

---

$\sigma_{nc} < \sigma_{sc}$ Materials can bear the shear stress, but can not bear the tensile stress applied, being destroyed by normal stress. No yielding.

➡ Brittle materials

$\sigma_{nc} > \sigma_{sc}$ Materials can bear the tensile stress, but can not bear the shear stress applied; yielding occurs

➡ Ductile materials

σ_{nc} Largest tensile-resistance stress, defined as the critical tensile stress

σ_{sc} Largest shear-resistance stress, defined as the critical shear stress

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Essentially, normal stress σ_n represents the tensile resistance of the materials and the tensile strength depend on the bond energy. Thus, the polymer chains usually break as the material is destroyed by σ_n
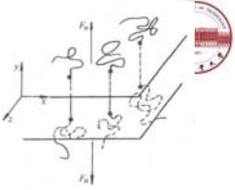
Shear stress σ_s represents the shear resistance. It depends on the cohesion energy. Slippage between polymer chains always occur during shearing.
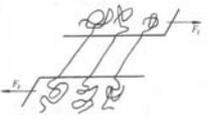
When the outside force applied on the material, distribution and variation of stress are very complicated. Fracture or yielding are competing. Occurrence of either of them is possible.

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Typical σ_{nc} and σ_{sc} of some polymer materials at room temperature

polymer	σ_{nc} / MPa	σ_{sc} / MPa
PS	40	48
SAN	56	73
PMMA	74	49
PVC	67	39
PC	87	40
PES	80	56
PEEK	120	62

PES 聚醚砜；PEEK 聚醚醚酮

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Comparing of brittle and ductile fractures

	Brittle fracture		ductile fracture	
yield	No	Yes	No	Yes
σ-ε	Linear	Non-linear	Linear	Non-linear
ε_b	small	big	small	big
Fracture energy	small	big	small	big
surface	smooth	rough	smooth	rough
Inducement	Normal stress	Shear stress	Normal stress	Shear stress

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7.4.2 fracture and mechanism

1. fracture

Induction of cracks ⟹ Crack development

Molecular motion of polymer during deformation:
- Random coils of chains extended or oriented;
- Some chains are fully extended, bearing the stress;
- Movement of segments occurs, slippage of chains

Crystallites, crosslinking or entanglements will hinder the movements of molecular chains. Some chains are bearing higher tensile stress, which will break first

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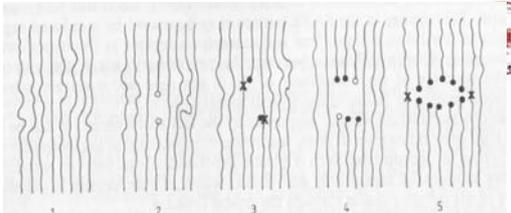
1. Some chains are bearing high stress;
2. Molecular chain breaks, free radicals formed (INDUCE)
3. Chain radicals formed
4. Chain breaks, radical reaction continues (DEVELOPMENT)
5. Repeat of reactions, cracks formed

○ — chain-end radicals；✕ — chain radicals；● — stable radicals

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- Redistribution of stresses in material occurs after the main chains break, which further leads to that:
  - stresses distribute evenly, end of fracture;
  - Or the stress distribution is worse, fracture of chains speeding up, cracks (void) developed.
- If the load is applied constantly, voids coalescence occurs, macro-cracks or defects formed.
- crack propagation results in the failure of the specimen at last

Necking Void Formation Void Coalescence

融合

Crack Propagation Failure

84
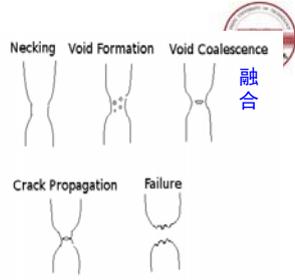
14

2. mechanism

- Material failure can be considered as chemical bonds breaking down.
- Results from other experiments indicate that the value of activation energy U during fracture is very close to the thermal degradation energy of material.
- It proves that fracture of the material is caused by the breakage of molecular chains.

$$\tau = \tau_0 \exp\left(\frac{U - \gamma\sigma}{RT}\right)$$

τ -- life span of material under load

τ_0 – material constant

U – the activation energy

γ -- structural constant

7.4.3 strength of polymer materials

1. Theoretical strength and actual strength

Theoretical strength

WHY?

Bond energy of C-C – 335~378 kJ/mol

Bond energy of single C-C – 5~6×10^{-19}J

length of C-C bond – d = 0.154 nm

$$f = \frac{W}{d} = (3 \sim 4) \times 10^{-9} N$$

$$S_0 = 20 \times 10^{-20} m^2$$

$$\sigma_{theo.} = 2 \times 10^4 \, MPa$$

actual strength

$$\sigma_{actual} = 5 \sim 55 MPa$$

Chain End, Entanglement, Interaction, Cross-linking, Defects in Lamellae, Separated Heterogeneous Matter, Void, Filler, Crystallite, Phase interfaces, Amorphous Phase Between Lamellae
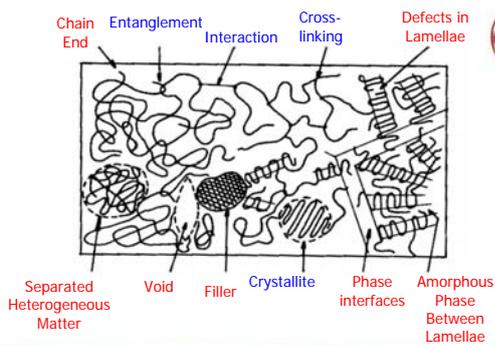
Fig. 7-36 Macro conformation of a typical polymer material

- There are many defects in polymer materials. It is why the actual strength of polymer material is much less than the theoretical strength.
- Defects – nicks on the material surface; impurities; voids; crystallites interfaces; cracks. They are small in size, but are very harmful.
  - Experiments indicate that there are many 100nm voids in glassy polymer material.
  - It is also very difficult to avoid impurities and defects during polymer manufacturing and processing.
- Stress concentration occurs around the voids, molecular chains nearby the voids will bear stress of tens or hundreds folds of the average stress.
- Failure occurs in such areas and finally propagates to the whole material.

---

2. Factors that will affect the breaking strength

I. Molecular weight
- It is a crucial factor for the strength, elasticity and toughness
- No strength for small organic molecules
- For different polymer materials, the minimum molecular weight is different too. For example, for PS, $\overline{X}_{min}$ is about 80; for PA, it is about 40
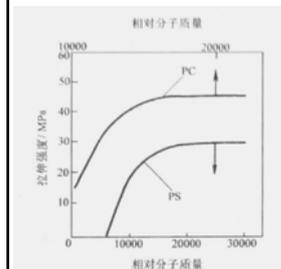

相对分子质量

PC

PS

拉伸强度/MPa

相对分子质量

With the molecular weight increasing, material strength increases gradually.

However, as the molecular weight is high enough that the interaction between chains is more than the summation of chemical bonds energy, material strength does not depend on the molecular weight any more, but relies on the bond energy.

Fig. 7-37 Dependence of tensile stress on the molecular weight

II. Crystallization

A. Crystallinity

Relationship of mechanical properties of polyethylene and crystallinity

Crystallinity (%)	65	75	85	95
Breaking strength (MPa)	14.4	18	25	40
Elongation (%)	500	300	100	20

As crystallinity increases, yielding strength, breaking strength, hardness, elasticity increase too. However, the elongation and toughness goes down. It is due to the closely packed polymer chains in crystallites. The void space is less and the interaction is stronger.

II. Crystallization

B. Size of crystallites

Evenly distributed small size spherulites are helpful in improving the material strength, elongation, modulus and ductility. They function as physical cross-linkers. However, large size spherulites will lower the elongation and ductility.
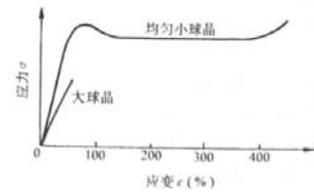

Fig. 7-38 effect of crystallite size on the tensile behavior of polymer materials

Addition of nucleating agents, quenching are all favorable to formation of smaller spherulites, which further improves the strength and ductility of materials.

Relationship between mechanical properties of PP and size of spherulites

Size of PP /μm	Tensile strength / MPa	Elongation/ %
10	30.0	500
100	22.5	25
200	12.5	25

II. Crystallization

C. Morphology of crystallites

- For the same polymer material
  - Extended chain crystallites will give rise to the largest tensile strength;
  - Materials with spherulites inside are of the smallest tensile strength;
  - Shish-kebab crystallites are in the middle position

III. crosslinking

- Crosslinking DOES affect the strength of rubbery polymer, but DOES NOT affect that of glassy polymer much.
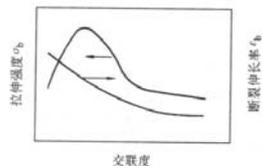

Fig. 7-39 effect of crosslinking on the tensile behavior of rubbery materials

As the crosslinking degree increases, the tensile strength of rubber material increases gradually till reaching the maximum, then decreases.

The elongation decreases continuously as the crosslinking degree increases.

Thermoset resins are of no strength if not crosslinked.

IV. orientation

- Orientation of molecular chains will enhance the mechanical property of materials along the orientation direction;
- Mechanical properties of the material in the direction perpendicular to the orientation are weaken.

7.4.4 Reinforcement of polymer material

- By filling, mixing or blending enforcing materials into the polymer matrix, mechanical properties of polymer will be improved.
- Generally useful fillers:
  - Powders (zero-dimensional)
  - Fibers (one-dimensional)
  - Sheets (two-dimensional)
- To obtain better performance, fillers must be evenly distributed, properly oriented.
- A good interface between filler and polymer is important too. Fillers shall have strong interaction with polymer material.

1. Powder fillers

- According to properties
  - Activated powder fillers
  - Inert powder fillers
- According to size
  - Micrometer-size fillers
  - Nanometer-size fillers
- Almost all the filler surfaces must be treated to enhance the interaction between fillers and the polymer material, and to prevent the aggregation of fillers.

A. Carbon blacks

rubber		Tensile strength / MPa		times
		Pure rubber	reinforced	
Non-crystalline	Silicon rubber ①	0.34	13.7	40
	SBR	1.96	19.0	10
	NBR	1.96	19.6	10
crystalline	Natural Rubber	19.0	31.4	1.6
	Chloroprene rubber	14.7	25.0	1.7
	Butyl rubber	17.6	18.6	1.1

① white carbon black reinforced

A. Carbon blacks

- Lots of active groups are on the surfaces of carbon black, which are useful in coupling polymer chains chemically or physically
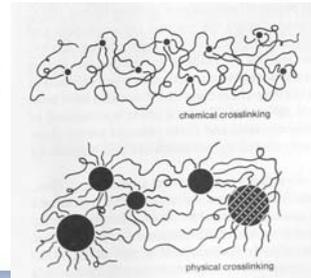 - Carboxyl groups
  - Phenol groups
  - Quinonyl groups

Fig. 7-40 illustration of physical crosslinking

A. Carbon blacks

- As one molecular chain is under stress, the stress can be passed onto the other chains by carbon black particles, stress being evenly distributed
- The whole rubber material forms a network through carbon blacks. Such a network can hold for a long period of time as the chain breaks somewhere.

B. Inert fillers

- Calcium Carbonate, Talc, Clay, metal powder and metal oxide are inert fillers
- They must be chemically modified to be active fillers
- Fatty acid, titanate, aluminate and silane coupler are generally used coupling agents
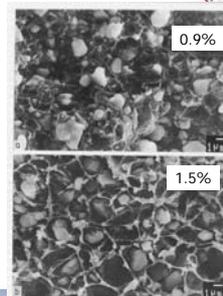

0.9%

1.5%

Fig. 7-41 SEM of HDPE filled with powder fillers treated by stearic acids

B. Inert fillers

- Inert filler can also improve the other properties of polymer material, such as conductivity, lubricating ability, higher stiffness, barrier properties
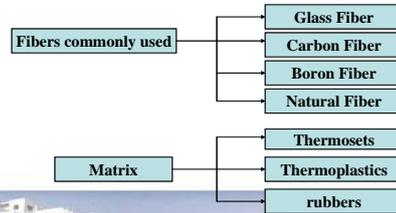
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2. Fiber reinforced material

- It is a composite combines the high strength, high modulus and size stability of fibers and low density, high ductility of resins
- The brittleness of fibers is overcame and the strength, modulus, creep-resistance, heat-resistance of plastics are also improved.

Fibers commonly used	→	Glass Fiber
	→	Carbon Fiber
	→	Boron Fiber
	→	Natural Fiber

Matrix	→	Thermosets
	→	Thermoplastics
	→	rubbers

Properties of glass fiber reinforced thermoplastics[①]					
materials	Tensile strength /10^5 Pa	Elongation /%	Impact resistance (notched)/Jm^{-1}	Young's modulus /10^9 Pa	HDT (1.86MPa)/ K
PE	225	60	78.5	0.78	321
Reinforced PE	755	3.8	236	6.19	399
PS	579	2.0	15.7	2.75	358
Reinforced PS	960	1.1	131	8.34	377
PC	618	60~166	628	2.16	405~471
Reinforced PC	1370	1.7	196~470	11.7	420~422
PA 66	686	60	54	2.75	339~359
Reinforced PA 66	2060	2.2	199	5.98~12.55	>473
POM	686	60	74.5	2.75	383
Reinforced POM	824	1.5	42	5.59	441

① glass fiber content is about 20-40%

Mechanism of fiber reinforcement

Resins can be easily deformed and undergo plastic flow. Stress can be passed from resin matrix to fibers, which are of higher strength and can bearing higher stress.
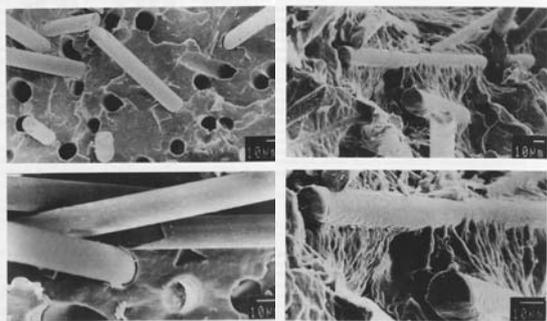

断纤维
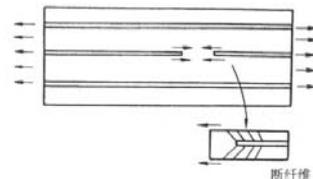
Fig. 7-42 SEM of glass fiber (30 wt%) reinforced polypropylene

Glass fiber not treated: Tensile strength 40 MPa; Impact strength 16 KJ/m²

Glass fiber treated with coupling agent: Tensile strength 87 MPa; Impact strength 34 KJ/m²

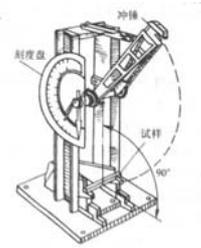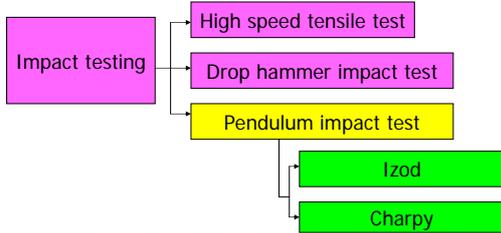## 7.5 impact resistance and toughening of polymer material

- Impact strength of polymer material is defined as energy dissipation per unit fracture area or notch width of standard specimen fractured by high speed impact.
- It represents the impact-resistance ability of polymer material, and is of technical importance
- However, it is not a material constant. The impact resistance of material depends on the testing methods and the testing conditions.

7.5.1 impact test

```
Impact testing ──┬── High speed tensile test
                 ├── Drop hammer impact test
                 └── Pendulum impact test ──┬── Izod
                                            └── Charpy
```


Charpy impact testing machine

$$I_s = \frac{A}{b \bullet d} \quad \text{KJ/m}^2$$

Where A is the dissipation energy; b is the width of the fracture plane; d is the thickness.
If the thickness of the specimen is fixed, then the I_s shall be energy dissipated per unit width of the fracture plane, KJ/m.

Area under the stress-strain curve of materials represents the energy dissipation of specimen being extended till break. It also characterizes the ductility of materials. Obviously, material with higher breaking strength σ_b and larger elongation at break ε_b is of better ductility.

$$\int \sigma d\varepsilon$$
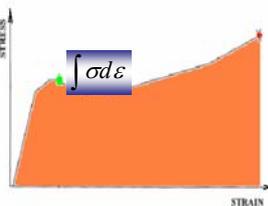
However, it is different from that of impact resistance test.

Firstly, the strain rates of the two experiments are different – strain rate of tensile test is much lower than that of impact test;

Secondly, it is volume energy dissipation in tensile test and it is fracture surface energy dissipation in impact test.

---

3 stages in impact fracture

1. Crack initiates
2. Crack propagation
3. Fracture

Some materials like UPVC is of higher energy of initiation and lower energy of propagation.
The impact strength is high as the specimen is not notched; but for the notched specimen, it will quickly fail. Crack propagation is the key stage in fracture, so that the crack propagation resistance shall be improved to toughen materials.
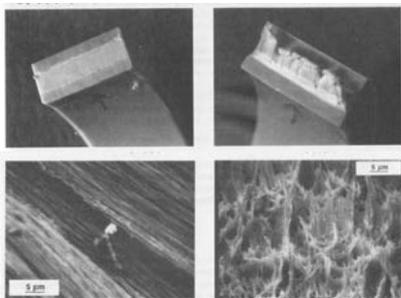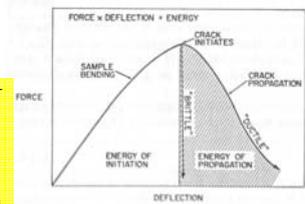

Fig. 7-43 Surfaces of brittle fracture and ductile fracture

Left: brittle fracture; right: ductile fracture

7.5.2 factors affecting the impact strength

1. Notch
   – Impact strength of specimen with preset notch is much lower than that without notch.
   – There is no crack initiation stage. Energy absorbed is consumed in crack propagation.
   – Stress concentration occurs nearby the notch. Material distortion is enlarged locally; strain rate is also speeded up; ductile-brittle transition appears; fracture is accelerated.
   – Stress concentration is more apparent as the curvature radius is smaller, so that the notch must be preset according to the testing standards strictly.

7.5.2 factors affecting the impact strength

2. **Temperature**
   – When the temperature increases, the impact strength of amorphous polymer will increase too, especially when the temperature is equal to or above Tg
   – As to the crystalline polymer, similar conclusion can be obtained.
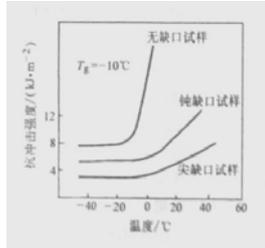   – The stress concentration is weaken as the temperature increases. The mobility of segments is also improved.

无缺口试样

$T_g = -10℃$

纯缺口试样

尖缺口试样

Fig. 7-44 Impact strength of polypropylene

7.5.2 factors affecting the impact strength

3. **Crystallization and orientation**
   – For the crystalline polymer materials, such as PE and PP, they exhibit to be ductile in tensile test as the crystallinity is about 40-60% (yielding, higher elongation etc).
   – However, the impact strength is lowered as the crystallinity is higher, because movement of segments is restricted. Deformability is poorer.
   – Materials with smaller spherulites are of better impact resistance.
   – Usually, orientation is not good to impact resistance.

7.5.2 factors affecting the impact strength

4. **Blending, copolymerization and filling**
   – The impact resistance of brittle plastics, like PS, can be improved by copolymerizing or blending with rubbers.
   – PS grafting with butadiene – high impact resistance PS (HIPS)
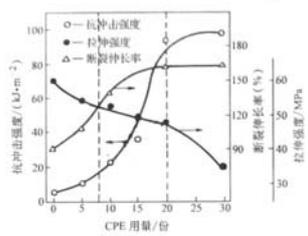   – PVC blending with CPE – ductile PVC

Fig. 7-45 mechanical properties of PVC blended with CPE

7.5.2 factors affecting the impact strength

4. **Blending, copolymerization and filling**
   – The impact strength of thermosets or brittle plastics can be improved by blending with fibers;
   – However, powder fillers usually weaken the impact resistance of brittle materials, such as PS.

7.5.3 rubber toughening

- Tiny rubber fillers evenly distributed in matrix function as stress concentrators, which can can induce the brittle-ductile transition and yield.
- Yield – craze (stress whitening) and shear bands
- Formation of craze and shear bands costs lot of energy, so that the impact strength is improved.
- Shear bands can also terminate the crazes and block the propagation of cracks.
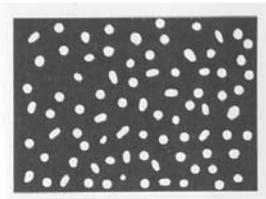

Sketch of craze initiated by rubber fillers

Fig. 7-46 Sketch of two phases of ABS White particles are dispersed rubber particles

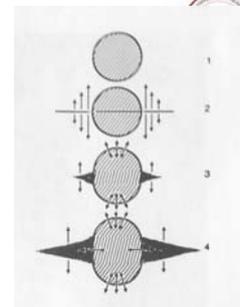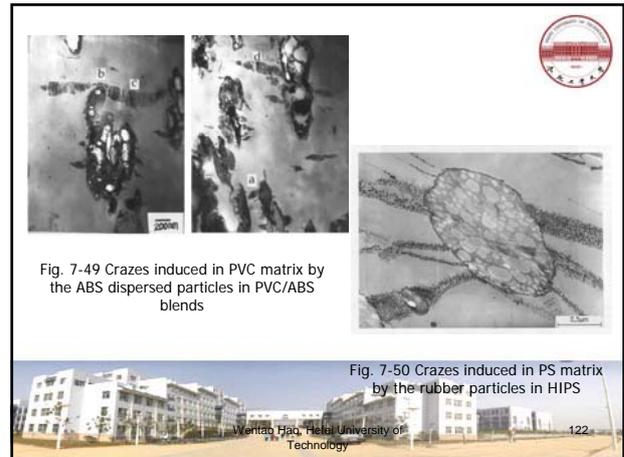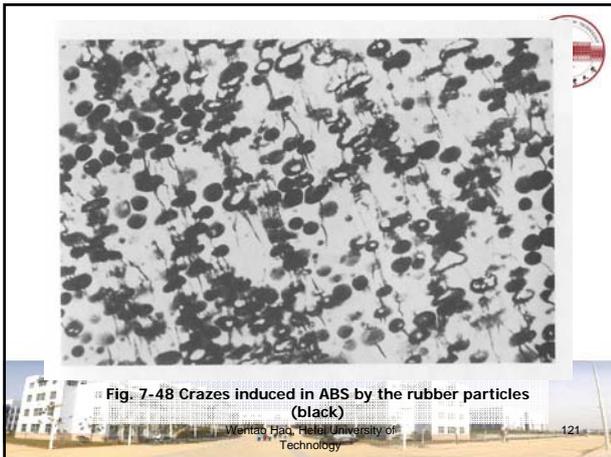Fig. 7-47 illustration to the craze initiation by rubber particles
Under stress, the rubber particles deform and induce the crazes

Fig. 7-48 Crazes induced in ABS by the rubber particles (black)

Fig. 7-49 Crazes induced in PVC matrix by the ABS dispersed particles in PVC/ABS blends

Fig. 7-50 Crazes induced in PS matrix by the rubber particles in HIPS

Drawback of rubber particle toughening

- The impact strength of materials can be improved much greatly by rubber particle toughening.
- However, the tensile strength, hardness and hot deflection temperature of materials are always lowered during rubber particle toughening, in addition to the processing fluidity.
- Research on non-elastomer toughening is underway.